CHARACTERIZATION OF OXIDE BIFILMS AND NONMETALLIC INCLUSIONS IN INVESTMENT CAST SUPERALLOY IN100

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2014
To my family
ACKNOWLEDGMENTS

Thank you to my advisor Gerhard Fuchs for giving me the opportunity and needed guidance to be a part of this research endeavor. I am confident that there is a still a place for metallurgy in the modern world, and there will continue to be for the foreseeable future. I feel that I have found a pleasant niche in aerospace materials, and I owe this to my experiences in graduate school. I know that I would not soon be beginning my career with Pratt & Whitney’s structural alloys research and development team if not for this. Thank you for sharing the depth of your knowledge during our time working together.

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Sample chemistry report of cast IN100

XRI of bottom filled, vacuum cast, and turbulated PT blades

XRI of bottom filled, argon cast, and conventionally gated PT blades

XRI of bottom filled, vacuum cast, and conventionally gated PT blades

XRI of top filled, vacuum cast, and turbulated PT blades

XRI of top filled, argon cast, and conventionally gated PT blades

XRI of top filled, vacuum cast, and conventionally gated PT blades

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<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>APB</td>
<td>Anti-Phase Boundary</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing Materials</td>
</tr>
<tr>
<td>BF-TEM</td>
<td>Bright Field Transmission Electron Microscopy</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscatter Electron</td>
</tr>
<tr>
<td>CI</td>
<td>Confidence Interval</td>
</tr>
<tr>
<td>CPS</td>
<td>Counts per Second</td>
</tr>
<tr>
<td>DS</td>
<td>Directionally Solidified</td>
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<tr>
<td>EDM</td>
<td>Electrical Discharge Machining</td>
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<tr>
<td>EDS</td>
<td>Energy Dispersive X-Ray Spectroscopy</td>
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<tr>
<td>FCC</td>
<td>Face-Centered Cubic</td>
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<tr>
<td>FPI</td>
<td>Fluorescent Penetrant Inspection</td>
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<td>FIB</td>
<td>Focused Ion Beam</td>
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<tr>
<td>HCF</td>
<td>High Cycle Fatigue</td>
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<tr>
<td>HR-TEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
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<tr>
<td>HTAL</td>
<td>High Temperature Materials Lab</td>
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<tr>
<td>HIP</td>
<td>Hot Isostatic Press</td>
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<tr>
<td>HRC</td>
<td>Howmet Research Center</td>
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<tr>
<td>LIMS</td>
<td>Liquid Metallorganic Ion Source</td>
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<tr>
<td>MAIC</td>
<td>Major Analytical and Instrumentation Center</td>
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<tr>
<td>NDI</td>
<td>Non-Destructive Inspection</td>
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<tr>
<td>NMI</td>
<td>Non-Metallic Inclusion</td>
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<tr>
<td>PSB</td>
<td>Persistent Slip Band</td>
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<td>PT</td>
<td>Power Turbine</td>
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<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>PIT</td>
<td>Process Improvement Team</td>
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<tr>
<td>RMS</td>
<td>Root Mean Square</td>
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<tr>
<td>SAM</td>
<td>Scanning Auger Microprobe</td>
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<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>STEM</td>
<td>Science, Technology, Engineering, or Math</td>
</tr>
<tr>
<td>SEI</td>
<td>Secondary Election Imaging</td>
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<tr>
<td>SC</td>
<td>Single Crystal</td>
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<tr>
<td>TMF</td>
<td>Thermo-Mechanical Fatigue</td>
</tr>
<tr>
<td>TCP</td>
<td>Topologically Close-Packed</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-High Vacuum</td>
</tr>
<tr>
<td>UF</td>
<td>University of Florida</td>
</tr>
<tr>
<td>VIM</td>
<td>Vacuum Induction Melting</td>
</tr>
<tr>
<td>XRI</td>
<td>X-Ray Radiographic Imaging</td>
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<tr>
<td>Z</td>
<td>Atomic Weight</td>
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CHARACTERIZATION OF OXIDE BIFILMS AND NONMETALLIC INCLUSIONS IN INVESTMENT CAST SUPERALLOY IN100

By
Max A. Kaplan
May 2014

Chair: Gerhard Fuchs
Major: Materials Science and Engineering

Oxide bifilms are a proposed casting inclusion reported to have been observed in vacuum investment cast polycrystalline Ni-base superalloys. This investigation seeks to determine if current superalloy casting methods can result in the formation of oxide bifilms, and subsequently if it is possible to observe and characterize this phenomenon. The effect of casting atmosphere, turbulence, filtering, HIP, and heat treatment have been investigated to identify the critical parameters that may result in bifilm formation in Ni-based superalloy IN100. Bifilms have been reported to impact mechanical behavior and fracture characteristics of cast superalloys, therefore tensile and fatigue testing was used in an effort to identify the effects of each casting and processing parameter on bifilm formation. Characterization of mechanical test specimens sought to identify the role of bifilms in the fracture mechanics of the conditions utilized, as well as the prevalence of bifilm formation and the chemical composition(s) of oxide bifilms. The characterization methods used were SEM, EDS, SAM, AES, STEM, BF-TEM, and HR-TEM. Tensile and fatigue test data did not indicate an influence of bifilms on the mechanical behavior of IN100, however there was a considerable impact due to the formation of Ti oxycarbide inclusions. Statistical analysis confirmed that vacuum and
argon cast material under conditions expected to cause abundant bifilm formation exhibit no measurable debit to mechanical properties as compared to conditions anticipated to prevent/remediate bifilms. Bifilms were not identified during metallographic characterization or fractographic analysis of mechanical test specimens. In-situ ultrahigh vacuum Auger fractography also did not indicate the presence of bifilms in the fracture behavior of IN100 in any processing condition. However, a sulfur-enriched monolayer has been identified on the surface of dendritic casting porosity, as characterized by Auger analysis. Metallographic and fractographic analysis identified Ti oxycarbide inclusions in the case of air cast alloys. These inclusion structures were found to consist of fine blocky external M(Ti, Mo)C carbide enveloping an internal core of ultra-fine polycrystalline alumina. Given the results of this study, the superalloys casting industry is expected to be exposed to minimal risk of component degradation due to the presence of oxide bifilms.
CHAPTER 1
INTRODUCTION

Machining Ni-based superalloys can be onerous and costly. In addition, most superalloy components for aerospace applications, such as blades and vanes, possess complicated external, and in some cases internal, geometries. For these reasons, many superalloy components are investment cast to near net shape in order to minimize machining and finishing operations. Investment cast superalloys can be polycrystalline, directionally solidified columnar grained, or single crystal components. In the most advanced aerospace applications, polycrystalline investment cast superalloys have been losing popularity to either single crystal components with higher temperature capability or powder metallurgy Ni-based alloys with higher strength capabilities that can utilize superplastic isothermal forging. However, investment cast polycrystalline Ni-based superalloys are still often used in many legacy engines or smaller, less advanced, aircraft engines.

There are several issues that can manifest during the investment casting process, one of which is the formation of nonmetallic inclusions. Superalloys are extremely reactive with many gaseous species at high temperatures, particularly oxygen and nitrogen. For this reason casting vendors are constantly trying to minimize the oxidation of molten superalloys, which will generally lead to the formation of oxide dross inclusions and other species of nonmetallic inclusions. Inclusions are typically embrittling and undesirable, which is why beginning around the 1950’s aerospace superalloy vendors began switching to using vacuum metallurgy on the production scale [1]. This included a shift to vacuum induction melting and vacuum investment casting.
Such a shift in industrial practices has allowed for substantial improvement in usable material properties.

Aerospace applications often demand that considerable conservatism be built into design systems, as catastrophic failure would likely result in the loss of life/lives. In direct opposition to this is the constant desire in aerospace to reduce weight to improve thrust to weight ratios and fuel burn efficiency. The desired reduction in weight is particularly true for rotating parts, as weight savings in these components can often have a substantial cascading effect. For example, reducing blade thickness allows for a reduction in disk size, which allows for a smaller shaft diameter, and so on. These seemingly contradictory motivations are what gives rise to the requirement for exceptional material quality that is generally associated with aerospace materials. Many critical components must be designed such that failure in service is extremely unlikely, therefore aerospace parts are often designed to the minimum properties of a material plus an additional factor of safety based on statistical analysis of mechanical tests. Therefore, removal of low strength outliers, and a reduction in data scatter, dramatically improves the usable design strength of superalloy components. Improving design strength allows for the use of smaller, thinner, and/or lighter parts, which in turn increases engine efficiency. This is the primary reason for the popularization and sustained use of vacuum metallurgy in these material systems. Such technology has allowed for significant improvements in material quality and cleanliness through minimization of inclusions and precise control of alloy chemistry.

One particular type of inclusion that has been gaining attention recently is the oxide bifilm. This is a phenomenon that has been primarily investigated in Al-based
alloy systems, however recent publications have reported observations, as well as predictions, of bifilms in polycrystalline investment cast Ni-based superalloy systems [2-6]. Bifilms are of particular interest because of at least two turbine fractures resulting in catastrophic engine failures, one of which lead to a fatal aircraft crash. Some have attributed these engine failures to be (at least in part) due to the presence of bifilms in polycrystalline investment cast Ni-base superalloys [3]. Furthermore, the presence of bifilms have been theorized to persist in vacuum cast superalloys, suggesting that current industry standard casting procedures are not sufficiently preventing the formation of such detrimental inclusions [2-6].

Bifilm formation is theoretically possible whenever a molten metal capable of forming a solid and continuous oxide is exposed to turbulence [4, 7]. The molten metal reacts with its casting atmosphere and forms an approximately 20 nm thick oxide skin, which due to surface perturbations of the fluid, can cause the oxide to fold and become entrained into the melt [4, 7]. Since bifilms are created by casting turbulence, one suggested method of bifilm prevention is to bottom fill investment castings. Reports suggest that a properly designed bottom-gated casting could eliminate turbulence while filling a mold cavity, therefore preventing bifilm creation by preventing entrainment [5]. Current industry practice is to top fill vacuum investment cast superalloys, which is an inherently turbulent process. Therefore there is significant interest in assessing the tangible benefits, if any, to bottom filling.

Unfortunately, there are some unavoidable monetary drawbacks to bottom filling. The most obvious is having to dramatically alter casting procedures throughout nearly every investment casting vendor, which would be very costly and time consuming. In
addition, bottom filled casting designs necessitate the use of exceptionally large gating systems in order to completely fill a cluster mold [5]. This creates a large amount of waste material, which must then be scrapped and recycled. This represents an inherent cost to bottom filled molds, therefore if the investment casting industry is to be expected to substantially alter its mold filling procedures, significant improvements to material properties must be demonstrated.

In addition to the issues associated with bottom filling, much of the casting community remains unconvinced that bifilms are indeed a serious concern regarding alloy cleanliness. Much of the research published to date has been largely unsuccessful in characterizing oxide bifilms in detail. Most often it is casting parameters theorized to affect bifilm formation which are frequently evaluated comparative to conventional casting practices, and disparities in mechanical test data are then explained by the presence or absence of bifilms [2, 3, 5, 8-14]. These conclusions are frequently drawn without direct observation of bifilms, though some studies have attempted to quantify alloy bifilm content indirectly [15-18]. In addition, fractographic analysis of mechanical test specimens may in many cases conclude that bifilms are affecting fracture behavior, but this is often done by observation of features that are theorized to be due to bifilms and then determining their presence by inference [3, 4, 6, 7, 9, 10, 19, 20]. In current literature, actual characterization of bifilms is sparse and often not greatly detailed, and clearly more thorough characterization is needed.

This study seeks to identify critical casting and processing parameters that either promote or inhibit bifilm formation in polycrystalline investment cast Ni-based superalloys. The alloy chosen for study is IN100, a commonly investment cast, high
temperature, and high strength alloy that is frequently used for aerospace applications. The specific processing variables evaluated include the effects of casting turbulence, casting atmosphere, gating filters, heat treatment, and HIPing. In addition, the statistically significant effects of these processes on the mechanical properties of cast materials are investigated. Namely, ultimate tensile strength, yield strength, ductility, and high cycle fatigue life are examined. Finally, this study seeks to thoroughly characterize the fracture behavior of IN100 in each of these processing states, while attempting to identify the role, if any, played by the presence of bifilms on fracture mechanics. This novel approach utilizes characterization techniques with the spatial resolution or surface sensitivity to be capable of clearly detecting bifilm inclusions. In addition, fracture behavior in the absence of bifilms is characterized as extensively and conclusively as possible to provide alternate explanations for material behavior.
CHAPTER 2
BACKGROUND

Superalloy Historical Context

Much of the drive to develop high temperature materials has been fueled by the aerospace industry from the 1940’s and on. Beginning during World War II, there was immense interest in development of viable and improved gas turbine engines to serve as the power plant for the next generation of military aircraft. However, such high temperature materials had only begun to be developed, as the previous generation of heat resistant steels and carbide strengthened alloys could not sufficiently operate in the necessary high temperature, high stress, and corrosive environments [21]. From this need, the class of materials that came to be known as superalloys was developed. Development of materials such as Pratt & Whitney’s Waspaloy was a watershed moment in the development of the next generation gas turbine engines like the J48 [22]. The creation of Waspaloy happened to coincide with the development of adequate industrial vacuum pumps, born from the Manhattan Project out of the need for vacuum processing uranium. Air processing Waspaloy had previously created excessive rejected parts and poor forgeability, but the later implementation of vacuum processing allowed for the production of this new class of alloys with sufficient cleanliness and therefore forgeability [23]. Since then, there has been a constant push for high temperature and high strength capabilities in nickel superalloys that continues today.

Superalloy Strengthening

Ni-based superalloys possess the unusual ability to endure load-bearing operations at high homologous temperatures, even while in unforgiving environments for long spans of time. They owe much of the ability to be used in such applications to
γ/γʹ precipitation strengthening. The γ phase is the continuous nickel-rich FCC matrix phase that is generally solid solution strengthened with refractory elements such as W, Nb, Cr, Mo, Ta, Re, etc. The γʹ phase is the discontinuous ordered L1₂ intermetallic precipitate phase Ni₃(Al,Ti). Fortunately, this precipitate phase remains stable and coherent with the γ matrix up to very high homologous temperatures, which is a rare metallurgical phenomenon. In addition, γʹ is present in varying precipitate sizes simultaneously. There exists the large micro-scale primary γʹ, and smaller nano-scale secondary γʹ that resides in continuous γ-channels. This creates a bimodal distribution of precipitates that substantially improves material performance. Ni-base superalloys can utilize a wide range of γʹ volume fractions, usually from about 20-70 vol% [24, 25], depending on the intended application.

The presence of γʹ substantially affects the deformation behavior of superalloys by altering dislocation movement. Dislocations in the FCC matrix phase γ have been shown to dissociate into Shockley partials as follows [25]:

$$\frac{a}{2}(110)(\overline{1}1\overline{1}) \rightarrow \frac{a}{6}(211)(\overline{1}1\overline{1}) + \frac{a}{6}(12\overline{1})(\overline{1}1\overline{1})$$

(2-1)

These Shockley partials are separated by an intrinsic stacking fault. Stacking fault spacing, \(d\), is inversely proportional to stacking fault energy, \(\gamma_{SF}\), which is dependent on alloy composition.

When a glissile dislocation approaches the coherent γ/γʹ interface, there are multiple energy barriers that must be overcome for dislocation motion to continue into the precipitate. The active slip system in γʹ is not the same as that in γ, and depends on temperature. At low temperatures, the active slip plane in γʹ is the {111} plane and equivalent to γ, however the slip directions are not equal. At elevated temperatures the
active slip plane in γ’ changes to {001} and therefore cross slip must occur [25]. In
addition, in order for any dislocation to travel through the γ’ precipitate, it must form a
superdislocation comprised of two superpartials bounding an anti-phase boundary
(APB). The formation of an APB presents a substantial energy barrier because,
depending on the active crystallographic plane, it necessitates the formation of Al-Al
and/or Ni-Ni bonds. This is highly energetically unfavorable for the ordered L12 crystal,
and therefore APB formation energy is relatively high [25]. APB energy is also a function
of chemistry, and alloying additions such as Ti, Nb, and Ta will increase APB energy.
For these reasons, the presence of the γ’ precipitate creates substantial impediments to
dislocation motion that actually increase with temperature (due to the necessity for
cross-slip as well as the introduction of complex planar defects such as Kear-Wilsdorf
locks). Such retardation of dislocation motion is the primary source of precipitation
strengthening in Ni-based superalloys.

In addition to precipitation strengthening, Ni-base superalloys also utilize
substantial hardening from solid solution strengthening of the γ phase. Maximum solid
solution strengthening occurs from distortion of the FCC lattice due to addition of
incompatible solute elements (i.e. do not abide by the Hume-Rothery rules). For this
reason, refractory metal additions such as W, Mo, Nb, Ta, and Re provide substantial
solid solution strengthening, but alloy content of each must be kept low to prevent the
formation of embrittling topologically close-packed (TCP) phases such as σ, μ, P phase,
R phase, or Laves phase [25, 26].

An additional method of strengthening superalloys, particularly polycrystalline
cast or wrought alloys, is the presence of carbide and/or boride strengthening. Carbides
and borides of varying chemistry can form, and the carbide or boride structure depends on the alloy composition and thermal history of the material. Common carbides and borides include: primary cubic MC carbides that have homogeneously nucleated, FCC $M_{23}C_6$ carbides that nucleate heterogeneously on grain boundaries during heat treatment, homogeneously nucleated FCC $M_6C$ carbides, or tetragonal $M_3B_2$ borides precipitating on grain boundaries [26]. Much of the grain boundary strengthening imparted by carbides and borides is essential in improving creep properties, as the carbide or boride effectively pins the boundary to inhibit grain boundary sliding [26].

### Vacuum Induction Melting

Superalloys are most commonly vacuum processed while in the liquid state due to their extreme reactivity with gaseous species such as O and N. In general, superalloys are melted by vacuum induction melting (VIM) prior to investment casting, in a process where the charge is melted, tapped, and cast without breaking vacuum [27]. There are a number of advantages to VIM. One obvious benefit is reducing the extent to which the melt reacts with its environment by limiting the total available O and N content, as total pressure in practice is typically reduced to less than 10 mTorr. Additionally, VIM allows for very precise control of alloy chemistry. VIM is also inherently conducive to removal of detrimental high vapor pressure impurities such as Pb and Bi, as these species will evaporate and are then removed by the vacuum system [28, 29]. VIM also allows for effective degassing and removal of H and O by substantially reducing the solubility of both [30]. In addition, O tends to be removed from the melt when O in solution with the melt reacts with available C in the alloy during what is known in industry as the “carbon boil” [27-29]. This occurs when C and O in solution with the melt react to form CO, which then precipitates, and is subsequently removed.
from the melt by the vacuum system as it bubbles off. The major drawback to VIM processing is cost, as vacuum melting is inherently more expensive than air melting. Control of alloy content is critical during VIM, and “pickup” of alloy additions from previous melts can pose a significant problem if not actively managed. In addition, reaction with refractory furnace linings is a constant concern, especially during processes such as VIM which attempt to minimize melt reactions [27].

**VIM Operation**

Figures 2-1 and 2-2 should be referenced for familiarization with VIM crucibles and VIM furnaces. The induction melting crucible is a steel casing containing refractory bricks and a crucible lining. Between the casing and the refractory are induction heating coils and water chilled cooling coils. The induction coils repeatedly flux a magnetic field to create a current in the charge placed inside the crucible, which generates resistive heating to melt the charge. The crucible is kept cool by the water-chilled copper cooling coils wrapping the crucible between the refractory bricks and steel case. Crucible liners inevitably reduce from repeated use and are deoxidized, or “stripped”, by successive melts. For this reason, liners must be replaced when eroded [26, 27, 29]. Lining material is what makes contact with the molten alloy, and is selected based on the charge to be melted, but typically includes Al₂O₃, CaO, ZrO₂, or MgO [30]. The induction crucible is contained in a large vacuum chamber with a charge lock that can be opened to lower in the charge material to be melted.

Most VIM furnaces today are double chamber furnaces, with a separate chamber for pouring and casting [28, 30]. In order to cast, molten metal is poured into a tundish to transfer the alloy from the melting chamber to the casting chamber. The tundish is essentially a refractory lined steel tray that often includes dams and filters to remove
dross [28, 29]. Dross is the mass of oxidation products that forms on the surface of molten alloys. Filters incorporated into a tundish can have a significant effect on reducing inclusion content of an alloy. The effectiveness of filters depend on casting conditions, cleanliness of feed stock, alloy content, and filter geometry (i.e. pore size, thickness, etc.) [29].

**Setting Chemistry with VIM**

The material added to the furnace to be melted via VIM is categorically referred to as virgin (never previously vacuum melted), reactive, and revert/scrap. Virgin material may contain substantial dissolved O and N content, so for this reason virgin material is typically melted and degassed prior to the addition of reactive elements. This helps prevent reactive alloy additions from forming undesirable oxides, nitrides, oxycarbides, carbonitrides, etc. with the gaseous species in solution with the virgin material [29]. Revert/scrap generally refers to excess material generated during other stages of the superalloy component fabrication cycle. This can include anything from gating material to machining chips, and essentially refers to recyclable superalloy material [28]. It is also significant to note that revert and scrap can be reclaimed for use from different alloys than the intended heat that is being made, so long as the alloying elements in the recycled material are compatible (also present in the alloy designations of the heat) and accounted for when calculating the total material balance for heat production. The precise amount and composition of each type of material added must be balanced to result in a final chemistry that is within the target chemistry, and must also take into account pickup/loss during melting [27, 28]. While the charge is molten and all additions have been made, a small portion may be ladled off to check chemistry prior to pouring the heat into a mold [28].
Dross Formation During VIM

Although melting is conducted under vacuum environments, sufficient residual air can be present to form dross on the surface of the melt. This is partially formed from melt reactions with the chamber atmosphere, and partially formed from erosion of the crucible lining. Dross formation from reaction of a melt with its chamber atmosphere is relatively straightforward, however forming dross from a mold/metal reaction can be a little more complex. As an example, consider a crucible lining comprised of magnesia. Deoxidation would occur as follows [29]:

\[
2 \text{Al (melt)} + 3 \text{MgO (crucible)} \rightarrow \text{Al}_2\text{O}_3 \text{(melt)} + 3 \text{Mg (melt)}
\] (2-2)

Since the superalloy contains significant aluminum content, which is sufficiently reactive with oxygen to reduce the magnesia liner, alumina dross can be generated in this manner. The product of crucible erosion can also be gaseous, as is the case with carbon, which can also be a very active alloying element at high temperature. Using a magnesia liner as an example again, another possible mold/metal interaction that may occur (depending on carbon content, oxygen dissolved in the melt, temperature, etc.) is as follows [29]:

\[
\text{C (melt)} + \text{MgO (crucible)} \rightarrow \text{Mg (melt)} + \text{CO (gas)}
\] (2-3)

Of course there many possible mold/metal or metal/atmosphere reactions that can occur. In fact, it is common for multiple and/or complex oxide structures to form, so it is relevant to note that there may be multiple reactive species acting simultaneously [31]. Fortunately, much of the dross created is in the form of a variety of low density oxides, which will generally float to the surface of VIM melts [28, 29]. The main exception to this is HfO₂, which is roughly as dense as the melt and typically does not float to the melt surface. However, most dross can be skimmed from the melt, and is
often removed at various stages of the VIM process. For example, runners/launders and tundishes will often have a system of baffles, dams, and weirs to skim dross that has separated from the molten alloy [28, 29, 32]. An example of this can be seen in Figure 2-3. Remaining dross can often be removed by the use of a ceramic filter, such as a reticulated ceramic foam filter [28, 29, 33, 34]. These filters can be added to the tundish for removal of dross prior to casting, and an example of this can be seen in Figure 2-3.

**Investment Casting**

Investment casting is quite literally an ancient method of producing cast metal parts that has been in use since the Bronze Age, and principally the same method is still widely utilized in industry today [32]. Of course, there have been substantial improvements in the process since that era. The renewed popularity of investment cast parts was primarily developed from the thrust to cast early superalloys beginning in the 1940’s. Superalloys are notoriously difficult to machine, and in an effort to minimize machining, investment casting offered a method of creating near-net shape parts. Many of the benefits that can be achieved with investment casting also include: control of grain structure (i.e. polycrystalline, directionally solidified, or single crystal), use of ceramic cores for casting integrated cooling passages, relatively lower cost for the intended application, and the ability to cast with very reactive alloy additions (ex. Y, Hf, Al, Ti, etc.) [32, 33, 35].

**Investment Casting Procedure**

The subject of interest for this dissertation is polycrystalline alloys, therefore investment casting procedures discussed will pertain to this class of alloys. See Figures 2-4 and 2-5 for illustrations of the investment casting process. Investment casting begins with a wax pattern of the finished product, produced by injection of the wax into a
master mold. If internal cooling is to be utilized, a ceramic core is added to the mold prior to wax injection. Several wax patterns are then arranged into a cluster mold and dipped in a fine ceramic slurry, which typically contains an ultrafine silica binder [33]. The first coating applied is the material that will make contact with the molten alloy, and is often referred to as the facecoat. For this layer, a nucleating agent such as cobalt aluminate is often used for polycrystalline alloys to refine grain structure [32, 33]. Next, stucco is applied to the cluster mold to build up the mold wall and add strength and thermal resistance to the shell [32, 33, 35]. Shell materials can vary, and may be comprised of alumina, silica, zircon, or aluminosilicate depending on necessary mold strength, casting temperature, and the alloy to be cast [33]. Successive layers of the shell are built using alternating dips in ceramic slurry and application of refractory stucco. The stucco applied will become coarser with each layer in order to impart more strength into the shell [33, 35].

After the shell molding is complete, the wax pattern is burned out in a furnace. The green shell is then fired and allowed to cure. Next, each shell is inspected, mold fiber insulation is applied where/if necessary, and the mold is ready for casting [32, 33, 35]. The cluster mold is loaded into a preheat furnace and preheated to the desired mold temperature. The mold is then transferred into the casting chamber of a double chamber VIM furnace and kept in a vacuum environment for pouring [32, 33, 35]. The opposite chamber is the VIM portion for melting charges, as was previously discussed. It should be noted that in practice casting vendors do not typically melt a combination of virgin/reactive/revert feed stock to set chemistry for investment casting. It is standard practice to instead purchase master alloy of certified chemistry from a vendor, and to
use this as the charge to be melted by VIM for investment casting. However, master alloy has been manufactured via VIM by the process previously discussed.

When casting, a molten head of metal is maintained at the top of the casting (referred to as a hot top) to ensure adequate feeding and minimize risk of macro-shrinkage defects. After the alloy has solidified the cluster is removed from the casting chamber, and the shell is removed by “knockout” whereby the mold is mechanically fractured by impact and removed from the cast part. Gating is cut off and the part is grit blasted to remove residual mold material. The casting then undergoes finishing procedures such as final machining operations [33, 35]. Next, the part is inspected to customer specifications, and generally undergoes visual inspection, dimensional inspection, fluorescent penetrant inspection (FPI) to check for external defects, x-ray radiographic imaging (XRI) to check for internal defects, macro-etching for grain inspection, and ultrasonic inspection to measure wall thickness [35].

**Post-solidification Thermal Treatment**

Following casting, some Ni-based superalloys may be given a hot isostatic press (HIP) cycle. HIP is a method of exposing a component to simultaneous elevated temperature and hydrostatic pressure by means of a gaseous medium (typically argon or helium) [36]. A schematic representation of a HIP vessel can be reviewed in Figure 2-6. The purpose of HIP is to fully densify a material. In the case of investment cast material, this is accomplished by closing porosity inherent to casting (i.e. dendritic microshrinkage porosity). For some alloys and conditions, the benefits of HIP includes a reduction in mechanical test data scatter (particularly stress rupture life), and an improvement in fatigue strength at elevated temperatures [32, 33]. HIP temperatures are selected to be above the γ’ solvus, but below the incipient melting temperature. For
most superalloys, HIP temperatures are in the range of 1200°C to 1220°C, typical pressures are about 103 MPa, and typical treatment time is about four hours [33]. It should be noted that cooling rates following a HIP cycle are significantly slower than cooling rates that can be achieved with forced gas quenching, air cooling, etc. This is because material cannot be rapidly removed from the insulated HIP vessel or quenched in situ. As a result of the slow quench rates, the γ’ structure that forms following HIP is generally very coarse.

Following casting or HIP, Ni-based superalloys are usually given heat treatment(s), which can vary greatly depending on the alloy and the intended application. One classification of heat treatment often given to cast polycrystalline Ni-based alloys is the solution heat treatment. Due to the inherently slow cooling rates following investment casting, the γ’ that develops in the as-cast condition is often coarse and segregated [32, 37, 38]. In order to create a finer and more uniform γ’ microstructure, a solution heat treatment can be utilized. This involves a hold for a specified time above the γ’ solvus temperature, followed by quenching with a specified quench rate. The hold above the γ’ solvus (solvus temperature varies significantly by alloy and processing) allows for solutionization of the γ’ to prepare for re-precipitation. γ’ solvus temperatures can vary from 1080°C for IN939 to 1308°C for PWA1484 [32, 39]. Note that this temperature range does not include γ” strengthened alloys such as IN718, which possesses a γ’ solvus temperature as low as 915°C [32]. Since γ” does not occur in IN100 (and therefore is not relevant to this work), γ” strengthening will not be considered for further discussion. The γ’ solvus temperature range for IN100 is
1205°C to 1225°C [32]. Heat treatment hold times can vary depending on severity of segregation and target mechanical properties [33].

Quenching has significant influence on the morphology and size of re-precipitated γ’ that is formed post-solution, and varies depending on alloy chemistry and quench rate [32, 37, 38]. In practice, most polycrystalline cast alloys that have not been HIPed are actually given a subsolvus “partial solution” heat treatment, whereas directionally solidified (DS) and single crystal (SC) cast alloys are given a full supersolvus heat treatment. The primary purpose of a subsolvus heat treatment is to prevent grain coarsening in polycrystalline alloys, which obviously is not an issue for DS and SC alloys. Partial solutionization ensures that sufficient residual γ’ particles are retained to prevent grain boundary migration [38]. The residual precipitate often includes large and irregular γ’ and/or eutectic γ’. This is possible since the solution temperature of eutectic γ’ is greater than the solution temperature of primary γ’. Typical “partial solution” heat treatment temperatures for polycrystalline superalloys range from about 955°C for IN713 to 1080°C for IN100 [32]. Theoretically, rapid quenching from the solution temperature would produce a γ matrix that is homogenous with solutionized primary γ’ (in addition to large irregular unsolutioned γ’, such as eutectic γ’), however in practice this is not the case. Rapid quenching from the solution temperature generates a fine homogenous dispersion of primary γ’ precipitates, which is desired for optimal mechanical properties [38]. Complete suppression of γ’ precipitation following solutionization is difficult and generally undesirable.

Following the partial solution heat treatment, an ageing heat treatment is often utilized for polycrystalline superalloys. This processing sets the primary γ’ precipitate
size and morphology, which is critical for coherency with the matrix, mechanical properties, and microstructural stability [37, 38, 40]. The fine and homogeneously dispersed γ′ precipitates that are formed from the partial solution quenching stage coarsen upon ageing. The precipitates consume local γ′ forming elements in solid solution with the γ matrix to create the primary γ′ structure. Primary γ′ size can vary substantially between alloys, heat treatments, and processing, but is very roughly 0.3 μm to 3 μm [41]. Simultaneous to this process is the formation of secondary γ′. This is the further precipitation occurring in the continuous γ matrix, referred to as “γ channels”, of fine and homogeneously distributed nanometer-scale γ′ [38]. This creates the beneficial bimodal γ′ structure that was previously discussed. Many alloys (particularly DS and SC alloys) will utilize further ageing heat treatment(s) to develop the secondary γ′ precipitate structure and/or carbide structures, however this is not the case for cast polycrystalline IN100 and therefore these heat treatments will not be discussed.

**Trace Sulfur Impurities**

Nonmetallic trace impurities, namely P and S, have been known to be detrimental to a wide variety of mechanical properties in Ni-based alloys. At intermediate temperatures (about 400°C to 800°C), S has been shown to partition to grain boundaries and create a significant intergranular weakening effect, resulting in reduced ductility, creep strength, and stress rupture life [38, 41-44]. At high temperatures (about 1000°C and above), S has been shown to partition to oxidizing surfaces [45-48]. The effect of trace S content on oxidation behavior has been of particular interest in many superalloy investigations. Removal of S from the alloy by hydrogen annealing, reducing alloy contents of about 10 ppm to approximately 35 ppb, has yielded impressive beneficial effects to scale adhesion and oxidation resistance by
dramatically reducing oxide spallation [46, 48]. Bulk sulfur removal from an alloy through conventional processing methods is difficult as it does not readily volatilize during VIM. However, lime slags have been shown to be effective in desulfurization, and can be employed during alloy manufacture [27]. Sulfur gettering elements such as Zr, Mg, and rare earth elements such as Y can be utilized as minor alloying additions to bind with dissolved sulfur and form less detrimental sulfides [41, 48].

**Typical Casting Defects**

A wide variety of casting defects are possible in investment cast superalloys. Casting defects are often detrimental to a variety of properties, such as formability, fatigue life, stress rupture life, and ductility, and can therefore hinder optimization of component designs [23, 32, 33, 49]. Some casting defects can preclude safe use of a component, or be the cause for rejection of parts. The ultimate goal of investment casting is to produce parts of a given geometry with optimal and reproducible properties, each within a given tolerance. Therefore, most casting defects need to be prevented, or at least minimized. Generally, the debit to material properties due to casting defects scales with the size of the defect. Fortunately, larger defects are also often easier to detect [33]. Casting defects relevant to this dissertation will be discussed herein.

**Casting Porosity**

Casting porosity can be broadly discussed in three categories: entrapped gas porosity, macroshrinkage porosity, and microshrinkage porosity. Entrapped gas porosity is fairly straightforward, consisting of undissolved gasses such as O₂, N₂, and H₂, which either remain out of solution during solidification, or precipitate during solidification [32]. This entrapped gas will tend to form spherical voids, which are roughly two to three
times larger than microshrinkage pores. Fortunately, entrapped gas porosity is a very rare phenomenon, since degassing while melting and maintenance of adequate vacuum environments during VIM and casting will prevent the entrapment and formation of undissolved gas pores [32].

Macroshrinkage porosity is also fairly straightforward conceptually, though in practice it can often be a significant obstacle for the casting engineer. Principally, macroshrinkage is a direct result of the 2-6% volumetric contraction face-centered cubic (FCC) metals experience upon solidification and cooling [50]. Macroshrinkage, often just called “shrink”, results from the volumetric contraction of the last metal to solidify, and can create large surface-connected or internal cavities. An example of this type of severe shrink (encountered during the research of this dissertation) can be seen in Figure 2-7. It should be noted that macroshrinkage is not always surface-connected, and in some instances must be detected by XRI when the macroshrinkage is internal. Additionally, in parts of sufficient cross-sectional area, severe macroshrinkage can also create a phenomenon known as “pipe shrinkage” [51]. This occurs when the centerline of a cast part or billet, which is typically the last metal to solidify, contracts radially outward and forms an oriented channel of macroporosity running down the length of the part, hence the name pipe shrinkage. It also follows that macroshrinkage issues will trend with increasing cross-sectional area, and tends to occur in thicker sections of a casting [32]. Avoiding macroshrinkage primarily requires proper casting design. Specifically, a casting must utilize proper gating configuration to ensure that shrinkage regions are confined to the gating section [32, 33]. This ensures that shrink does not persist into the cast component, and requires that there is adequate feeding of the
casting. "Feeding" refers to maintaining a head of liquid metal in the gating section that can fill gaps in the mold cavity and macroshrinkage as they develop. Adequate pour volume and maintenance of a hot top can also help with ensuring proper feeding. The process of producing sound castings requires substantial knowledge of the solidification behavior of the alloy, as well as the thermal behavior of the molten metal and mold shell [32, 33]. Solidification modeling can often be an indispensable tool in designing castings that avoid macroshrinkage.

Microshrinkage casting porosity (often referred to a microporosity) is unavoidable, and will form in any dendritically solidified material [33]. Microporosity can vary greatly in size, but is generally in the range of 1-100 μm in diameter. Dendritic porosity tends to be more abundant in heavily segregated parts, such as components with large cross-sectional area or high volume fractions of γ’ [35]. This is unsurprising, as the cause for microshrinkage porosity is due to dendritic segregation, and therefore the cause for these phenomena is fundamental to the nature of dendritic solidification. An alloy in the process of dendritic solidification can be viewed as displaying three distinct regions: a solid region, a “mushy zone”, and a liquid region. These regions are fairly intuitive, as the solid region is the section of the solidifying metal that is 100% solid (sub-solidus), the liquid region is the section of the solidifying metal that is 100% liquid (super-liquidus), and the “mushy zone” is the term used for the semi-solid region between these boundaries (ΔT between liquidus and solidus). The primary dendrite arms are oriented perpendicular to the solidification front, and secondary dendrite arms are parallel to the solidification front [52]. As the dendrites grow and impinge on each other, small gaps are formed between the secondary dendrite arms since it is not likely
for dendrites to perfectly fit together. In addition, cooling dendrites will experience thermal contraction and pull away from each other. Molten metal from the liquid region does flow into the mushy zone and fill the space between dendrites, however 100% filling is never achieved due to the tortuous flow path between the secondary dendrite arms and thermal contraction of the dendrites [32]. The pore that forms in the interdendritic region is dendrite shaped, as it is simply the exposed surface of a dendrite. This allows for easy identification during metallographic and fractographic analysis. As an example, Figure 2-8 illustrates locations of microporosity forming in a solidifying alloy.

There are several factors that impact the size and abundance of microshrinkage porosity. Perhaps the most important of these factors is solidification time, as this is the most readily controlled. Essentially, more rapid solidification necessitates higher thermal gradients which produces smaller dendrites [32], which is obvious when considering that rapid solidification also produces a finer grain structure. Smaller dendrites exhibit smaller unfilled interdendritic spaces, and therefore smaller micro-pores are formed. As stated previously, the impact of casting defects scales with size, so finer dispersed pores are preferred. It is interesting to note that short solidification time itself promotes incomplete filling of the mushy zone as it will promote liquid freezing prior to complete filling being achieved. However, short solidification times inherently necessitate larger thermal gradients, which reduces dendrite size, and this reduction in dendrite size has a greater impact on microporosity formation than solidification time. Models have been developed to predict the propensity for IN100 to form microporosity under a given set of
conditions. One such model, developed by J. Lecomte-Beckers, utilizes a microporosity index $\Delta P^*$ that describes the tendency of microporosity formation in IN100 [53]:

$$\Delta P^* = \frac{24\pi \nu \beta' \eta t^3}{\rho_1 g} (\Delta T / G)^2 R'$$  \hspace{1cm} (2-4)

Where $\nu$ is interdendritic liquid viscosity, $\beta'$ is solidification shrinkage, $\eta$ is the number of dendrite channels per unit area, $t$ is dendrite tortuosity, $\rho_1$ is interdendritic liquid density, $g$ is the gravitational constant, $\Delta T$ is the solidification range, $R'$ is the average solidification rate, and $G$ is the thermal gradient. Many of these variables are chemistry dependent, and it was determined experimentally that Al, Ti, and Co increased the propensity for microporosity formation, whereas Cr decreased the likelihood of forming pores [53].

**Non-metallic Inclusions**

There are many opportunities for non-metallic inclusions (NMIs) to be introduced into an alloy, which includes alloy manufacture, remelting, and casting. It is necessary that NMIs be kept to a minimum, as it is well known that NMIs have a significant impact on material properties, particularly low temperature fatigue in superalloys [49, 54]. In a broad sense, NMIs can be primarily separated into two categories: ceramic inclusions and dross inclusions. The source of ceramic inclusions is straightforward, and is the entrapment of any refractory ceramic used when processing molten alloys [33]. One example could be mold inclusions originating from debris from the investment casting mold that may have spalled or fractured during casting. This could also include fractured or spalled ceramic core debris in the case of alloys cast with internal cooling passages. Essentially, whenever a molten alloy comes in contact with a brittle refractory ceramic, there is potential for the generation of ceramic inclusions. However, with good casting
practice, careful selection of refractory materials, and accurate non-destructive inspection (NDI), ceramic inclusions can be mostly avoided.

Dross formation has been discussed in detail in the section "Dross formation during VIM". Dross formation occurs from two major sources: mold/metal interactions whereby molten metal deoxidizes a refractory ceramic it is in contact with and subsequently reacts with the generated oxygen in solution, and metal/atmosphere reactions whereby molten metal oxidizes or nitrides via interaction with residual gases in the melting or casting chamber. Dross inclusions occur when either dross entrapment is not successfully prevented, and/or dross is not effectively filtered from the melt. Dross inclusions can vary in chemistry and often depend on crucible materials used, however Al, Mg, Zr, Hf, and Si containing inclusions are the most common. Although modern vacuum metallurgy substantially reduces the likelihood of dross inclusion formation, because of inherent deficiencies in vacuum levels on the production scale and the extreme reactivity of Ni-based superalloys, dross inclusion formation is still possible.

Oxide Bifilms

One newly proposed casting inclusion, known as oxide bifilms, has recently been reported in a few polycrystalline investment cast Ni-based superalloy samples [3, 6]. The presence of oxide bifilms in Ni-superalloy systems are of particular interest because at least two turbine fractures have been attributed to, at least in part, the presence of bifilms in cast superalloy components [3]. Both fractures resulted in engine failures, and one engine failure resulted in a fatal aircraft crash. However, even though there have been dire conclusions related to the presence of bifilms in Ni-based superalloys, the majority of bifilm research has pertained to air cast Al alloys. Suggestions of bifilms persisting in vacuum cast superalloys was not published until 2004, and any
observation of possible bifilms is superalloys also was not published until 2004 [5, 6]. In contrast, bifilm theories in air cast Al systems began building momentum in the early 1980’s. For this reason, much of the theories pertaining to bifilms have been developed by study of Al alloys. However, many of these theories have since been applied to other alloy systems mostly unchanged. Many of the bifilm theories discussed herein have been developed for explanation of behaviors seen in Al alloys, but have also been applied to cast polycrystalline Ni-based superalloys with essentially no modification.

**Bifilm Formation**

Bifilm formation is theoretically possible whenever a molten metal capable of forming a solid and continuous oxide is exposed to turbulence. The molten metal reacts with its casting atmosphere and forms an approximately 20 nm thick oxide skin [2, 4]. For example, in the case of aluminum alloys this would be a nano-scale layer of alumina overtop of the melt pool. This oxide skin can fold and become entrained into the melt due to surface perturbations of the fluid and turbulence during liquid processing [2, 4, 7, 16, 55]. This is shown schematically in Figure 2-9. The event of molten metal splashing is how thin pockets of unbound oxide inclusions are generated. Bifilms can then either become entrapped in the solidifying metal, or be further folded due to turbulence to form a structure that is more crumpled in appearance [4, 7]. An example of what has been identified as a tangled bifilm structure observed metallographically is shown in Figure 2-10. It is important to note that although bifilms are reported to be nanometers thin, they are theorized to possess a total surface area on the order of millimeters [4, 6]. The formation of bifilms is also stated to persist in vacuum systems, as it has also been reported that the formation of this folded oxide skin is possible with vacuum cast
components, and that residual oxygen in the melting and casting chambers is sufficient for bifilm formation [2-6].

Bifilms are described as a doubled-over oxide, which creates an unbound oxide-oxide interface and forms a casting inclusion that behaves as a preexisting crack [2, 4, 7, 56, 57]. The distinction that bifilms are formed from a folded thin oxide film is extremely significant. This is one of the major distinctions between a bifilm and a traditional dross inclusion. Also, due to the unique morphology of the bifilm, they are stated to exhibit a variety of unusual behaviors that are acutely distinct from that of traditional dross inclusions. This is partially attributable to the idea that bifilms are orders of magnitude thinner in cross-section than dross inclusions, but are very large in surface area and maintain an abrupt and continuous unbound interface. This unique morphology is also often stated to be the reason why the pervasiveness of bifilms can be frequently overlooked, even though bifilms may have strong impacts on material properties [2, 4, 7].

**Bifilm Porosity**

Bifilms are theorized to play a major role in the formation of dendritic casting porosity [2-5, 7, 9-11, 17, 19, 55, 58, 59]. This type of casting porosity is created during solidification after the bifilm is entrained into the melt. As dendrites grow the oxide bifilm is wedged between the impinging dendrites, blocking fluid flow in the mushy zone. As the alloy cools and contracts, the bifilm theoretically unfolds and fills the space between dendrite arms, creating casting porosity [4, 7, 58]. This process can be exacerbated if gas content from the casting environment has been trapped between the layers of the bifilm during the entrainment process [4, 7, 58]. This process of bifilm-assisted dendritic porosity formation is shown schematically in Figure 2-11. More conventional
explanations of microporosity have previously been outlined in the “Casting Porosity” section. However, bifilm theories assert that these more traditional mechanisms for imperfect fluid feeding in the mushy zone fail to account for the presence of bifilms, and are therefore incomplete.

Bifilms are also theorized to play a major role in the formation of entrapped gas porosity [4, 7, 16, 17, 55, 57, 58], though these theories can often seem unusual and counterintuitive. Also shown schematically in Figure 2-11 is the theory of bifilm unfurling, by which a bifilm that has become crumpled due to turbulence can unfold while a casting is still molten. During unfurling, it is expected that hydrogen content in solution with the melt will diffuse to the hollow space interior to the bifilm and precipitate to form H₂ gas [4]. This precipitation is expected to facilitate bifilm unfurling. Should gas precipitation continue beyond this stage of unfurling, it is further asserted that bifilms are capable of “inflation”, creating the spherical pores often associated with entrapped gas porosity [4, 7, 57].

**Bifilm Embrittlement of Intermetallic Precipitates**

Bifilms have been theorized to be a preferred nucleation site for brittle intermetallic precipitates in alloys, with the most common examples being silicides in Al-based alloys [4, 19, 57, 60, 61], carbides in Ni superalloys [3, 4, 6], and graphite in cast iron [4, 62]. Observation of the presence of fractured precipitates in the microstructure or fractographic examinations of mechanical test specimens is often interpreted as evidence for this type of heterogeneous nucleation having occurred. The tortuous morphology of bifilms is also suggested to be a mechanism by which intermetallic precipitates are embrittled. This theory suggests that folds in the bifilm from previous furling and unfurling will behave as preexisting cracks in the precipitates. A nucleating
precipitate is expected to form around these folds, but effectively be left with sharp surface cracks penetrating into the particle. This process is illustrated schematically in Figure 2-12.

**Effect of Bifilms on Mechanical Properties**

Bifilms are described as a doubled-over oxide, creating an unbound oxide-oxide interface, which is a casting inclusion that behaves as a preexisting crack. Clearly the presence of preexisting cracks are undesirable for mechanical properties. Bifilms have been reported to degrade the mechanical properties of Ni-base superalloys and numerous other alloy systems [3-5, 8-12, 15, 16, 20, 55, 57, 61, 63-65]. These reports include reductions in: tensile strength, bend strength, fatigue life, impact strength, creep strength, secondary phase strength, grain boundary strength, ductility, corrosion resistance, stress corrosion cracking resistance, and thermo-mechanical fatigue (TMF) resistance. This also coincides with a reported increase in casting defects and casting quality issues that contribute to scatter in mechanical test data, such as: porosity, hot tearing, and inclusions. In addition, there have been reported predictions of astounding increases in mechanical properties if bifilms can be successfully avoided [2-4, 57, 66], with some publications suggesting that complete prevention of bifilms can yield metals possessing theoretical fracture strengths [57, 66]. Given that bifilms have a strongly negative impact on tensile and fatigue properties, within current literature the presence of bifilms is often determined by identifying debits to mechanical properties, and correlating such reductions to casting conditions that would be favorable for biffilm formation [2, 4, 8-13, 15, 63, 67]. Conversely, processing parameters that are expected to prevent or remediate the effect of bifilms are often correlated to improvements in mechanical test data. However, the material systems in which such analysis has been
done is limited, and much of the current research pertains to air cast Al-based systems. Since bifilms have been reportedly observed in polycrystalline investment cast Ni-based superalloy systems, but similar mechanical testing studies have not been performed, it is imperative to determine if such debits and/or improvements to mechanical test data can be observed in a Ni-based alloy system.

**Bifilm Prevention and Remediation**

There has been significant interest in methods of bifilm prevention and/or bifilm remediation. One suggested method of bifilm prevention, particularly in Ni-base superalloy turbine blades, is to bottom fill investment castings [5]. Reports suggest that a properly designed bottom-gated casting would eliminate turbulence during casting, therefore preventing bifilm creation by preventing entrainment [2]. Conceptually this is simple, suggesting that preventing perturbations of the melt surface would therefore prevent generation of any new bifilms. An example of top fill and bottom fill turbine blade casting designs are given in Figure 2-13.

One suggested method for reducing the impact bifilms have on mechanical properties is through the utilization of HIP [4, 8-10]. Reports from studies of Al alloys suggest that the use of HIP can cause perforations in the oxide structure, allowing for metallic bonding through the oxide fractures, and can reduce the effect of bifilms on properties. This process is sometimes referred to as bifilm “healing”. A schematic representation of this is shown in Figure 2-14. These publications also report improvements in room temperature fatigue life, tensile ductility, and tensile strength from the utilization of HIP, and attribute these improvements in properties to the remediation of bifilms. The necessary characterization to support these claims, however, is quite limited.
New and Thickened Bifilms

Bifilms are often distinguished categorically as being either “new” or “old” bifilms [3, 4, 6, 8-10, 20]. New bifilms are described as the alumina films that are present immediately following turbulent casting [4, 7, 20]. The number of entrained new bifilms is theorized to be additive, and accumulates with each stage of molten metal processing [4, 6, 7]. Old bifilms are described as being an oxide film which had been previously introduced to the alloys system and subsequently thickened [3, 4, 6, 20]. New bifilms have been stated to exhibit a thickness of only about 20 nm [2, 4, 7], whereas thickened bifilms have been characterized as being as much as three orders of magnitude greater in thickness [3, 6]. The old films are stated to originate from the growth of “new” alumina films [3, 4, 6, 20]. Such growth can occur from the thickening of new bifilms that have been entrained at any stage during liquid metal processing. Oxide film growth is usually attributed to exposure of the alloy to elevated temperatures following the casting of ingots [6]. During such exposure at temperature, new bifilms are theorized to consume oxygen in solution with the alloy, generating bulk oxide growth and therefore thickening the bifilm. Thickening is also in some cases theorized to coincide with a conversion of the oxide structure from alumina to an Al$_2$O$_3$MgO spinel [4, 20]. It should be noted that superalloys only contain trace amounts of O and Mg, so this type of thickening and conversion is unlikely (see “Deficiencies in Bifilm Theories”). The new alumina bifilms can therefore function as a type of precursor for the formation of “old” thicker spinel bifilms.

Bifilm Characterization

New bifilms are difficult to characterize due to their geometry and volume fraction, therefore when bifilms are observed in the literature it is most often thickened.
bifilms that are being characterized [3, 6]. Characterization of new bifilms is rarely reported, and the depth to which they are characterized is very limited, with only a few examples in the literature [4, 59]. Since bifilms have a strongly negative impact on tensile and fatigue properties, bifilms are often located by fractographic analysis of mechanical test specimens [3, 4, 6, 9, 10, 19, 20]. The existence of the thin alumina films is frequently determined by inference. For example, planar surfaces seen during fractographic analysis can in many cases be identified as the result of cracking along the bilayer of oxide, effectively splitting the oxide bifilm (or in a sense propagating the preexisting crack) [3, 4, 6, 9, 10, 20]. This is a common method seen in the literature for identifying the presence of new bifilms during fractographic analysis, and examples are shown in Figure 2-15. A wide variety of cracking observed during microstructural analysis is also frequently attributed to a similar mechanism of bifilm splitting [2-4, 6, 8-10, 19]. However, sufficient evidence to support these conclusions is currently very limited [19, 68]. Furthermore, quantitative characterization, beyond the observation of “thickened bifilms” that have identified through fractographic analysis, is also limited [3, 6]. In most current literature, locations theorized to exhibit new bifilms such as porosity, cleavage planes, grain boundaries, dendrite arms, etc. are observed fractographically and simply assumed to be due to the presence of a bifilm [4, 9, 10, 17, 19, 20, 58]. Somehow, characterization of new bifilms typically does not extend beyond this. Therefore, it is imperative to identify such locations that may exhibit the presence of an oxide film and extensively characterize them. Furthermore, it is not possible to assert that thickened bifilms have in some way formed from a new bifilm precursor without first obtaining thorough characterization of the new bifilms.
Deficiencies in Bifilm Theories

The first and most surprising inadequacy that can be seen while reviewing bifilm literature is the stunning lack of direct observation and characterization of new bifilms in studies attempting to investigate the effects and behaviors of bifilms. Many behaviors and phenomena that are thought to be due to the presence of bifilms are observed (ex. reduced pressure test porosity, fractographic features, and mechanical data discrepancies), however the new bifilms are virtually never observed directly. In fact, their presence is simply assumed due to their expected behaviors by inference. Many studies point to the low volume fraction of bifilms and extremely thin cross section in an effort to explain why direct observation is difficult compared to other types of inclusions [3, 4, 56, 57]. One study has suggested that a reason for the lack of observation of bifilms is that transmission electron microscopy (TEM) sample preparation would be expected to destroy the bifilm [4]. Another study includes a table describing the structure and morphology of bifilms, but states in the table description “in absence of definitive experimental results these data are speculative” [69]. Other publications go so far as to describe bifilms as “invisible” or “invisible macro defects”, suggesting that castings typically contain random crack-like defects that have been simply overlooked because they are essentially unobservable [2, 3, 56, 57]. However, in the modern era of nano-materials it seems unreasonable to suggest that an oxide film might be unobservable, regardless of how thin it may be. This surprising lack of characterization is one of the foremost reasons for why the research of this dissertation is so necessary.

There are also some aspects of bifilm theories that appear very perplexing. For example, there are many descriptions of the oxide films folding, furling, crumpling, unfurling, and even inflating. Yet, this type of flexible behavior seems entirely
counterintuitive for what, in essence, is a brittle ceramic film. Another example would be the idea of bifilm thickening in Ni-based superalloys to create “old bifilms”. The assumption is that sufficient dissolved oxygen persists in the alloy (even after degassing during VIM) to create bulk oxide growth in the bifilm during heat treatment [3, 6], which seems very unlikely considering that a degassed VIM-melted superalloy will possess O content of at most 10 ppm, and will typically contain much less [29]. In addition, a growing alumina film in superalloys would require the local depletion of aluminum content in the alloy, creating a depletion region of γ’ as is seen in the oxidation of superalloys [70, 71]. However, such a γ’ depletion region has never been observed in “thickened bifilms”. The assertion of bifilm thickening also does not address the fact that similar structures being identified as thickened bifilms can be observed in as-cast components, but are identified as dross inclusions.

Bifilm theories also often seem superfluous, as more conventional explanations adequately address material behavior without considering bifilms. For example, the role of bifilms in porosity generation seems unnecessary, as dendritic casting porosity and entrapped gas porosity would mechanistically be capable of forming with or without the oxide film. More specifically, precipitation of hydrogen gas causing bubbles in a molten Al alloy is precisely the process by which entrapped gas porosity is thought to form [72, 73], and the addition of an inflating oxide bubble seems both outlandish and unnecessary in explaining this phenomenon. Additionally, this requires that material responses to HIP cycles be reconciled with bifilm theories. The current explanation that bifilms must be fracturing and perforating to allow metal bonding across the oxide interface also seems unlikely and unnecessary to explain the effects of HIP.
Furthermore, the residual perforated bifilm should still be observable in a microstructure, but so far this has never been conclusively identified in the literature. Another serious deficiency in the role of bifilms in forming casting porosity is the fact that materials that have no capability to form solid and continuous oxides still display casting porosity. So-called “plastic crystals” such as succinonitrile and pivalic acid, which closely mimic the dendritic solidification of FCC crystals, also display clear evidence of casting porosity [74, 75]. Even when such polymeric materials (which have no ability to form solid and continuous oxides) are processed to be of ultra-high purity and are solidified under vacuum, these dendritic solidification structures will still display dendritic casting porosity that is similar to what is seen in Ni-based alloys.

Lastly, the role of bifilms in mechanical behavior of materials is not adequately supported. Although the presence of preexisting cracks would indeed be expected to be highly detrimental, without direct observation of bifilms in the fracture mechanisms of these materials there simply is not enough to support the argument of bifilms acting as preexisting cracks. Observing discrepancies in mechanical properties in conditions expected to generate varying amounts of bifilms may point to bifilms being an acting variable, however this is far from conclusive. Additionally, some bifilm researchers have gone so far as to postulate that total removal of bifilms in metallic materials could result in materials that approach theoretical fracture strength [2-4, 57]. These types of broad and extreme assertions inevitably cast doubt on other aspects of bifilm theories and their effect on mechanical behavior.
Figure 2-1. Schematic of vacuum induction melting crucible

[Reprinted with permission from ASM International, 2008, "Vacuum Induction Melting," Casting, 15(Melting and Remelting), pp. 116-123, Fig. 2]
Figure 2-2. Schematic of a top-opening, double-chamber VIM furnace

[Reprinted with permission from ASM International, 2008, "Vacuum Induction Melting," Casting, 15(Melting and Remelting), pp. 116-123, Fig. 3]
Figure 2-3. Schematic of vacuum induction melting (VIM) processing of superalloys

[Reprinted with permission from Maurer, G. E., 1989, "Primary and Secondary Melt Processing–Superalloys," Superalloys, Supercomposites, and Superceramics, J. K. Tien, and T. Caulfield, eds., p. 68, Fig. 17]
Figure 2-4. Schematic of the steps in the shell investment casting process

[Reprinted with permission from Horton, R. A., 2008, "Investment Casting," Casting, 15(Expendable Mold Casting Processes with Expendable Patterns), pp. 646-661, Fig. 2]
Figure 2-5. Industrial investment casting showing A) Automated dipping of investment casting mold and B) cutaway view of shell mold for an air-cooled gas turbine blade

[Reprinted with permission from Donachie, M. J., and Donachie, S., 2002, "Investment Casting," Superalloys : A Technical Guide, p. 84 Fig. 5.3]
Figure 2-6. Schematic of a HIP apparatus using an external yoke for closure

[Reprinted with permission from Gessinger, G. H., 1984, "Powder Consolidation Methods," Powder Metallurgy of Superalloys, p. 70 Fig. 3.8]

Figure 2-7. Examples of severe macroshrinkage porosity in polycrystalline investment cast IN100
Figure 2-8. An SEM micrograph of dendrites, illustrating locations between secondary dendrite arms where microporosity is located

[Reprinted with permission from Bouse, G. K., and Mihalisin, J. R., 1989, "Metallurgy of Investment Cast Superalloy Components," Superalloys, Supercomposites, and Superceramics, J. K. Tien, and T. Caulfield, eds., p. 129, Fig. 18]
Figure 2-9. Schematic representation of bifilm behavior. Bifilm formation creating preexisting crack from A to B, and creation of bubbles C and D

[Reprinted with permission from Campbell, J., 2006, "Entrainment Defects," Mater. Sci. Tech., 22(2), p. 128, Fig. 1]

Figure 2-10. Tangled bifilm seen on polished surface

[Reprinted with permission from Campbell, J., 2006, "Entrainment Defects," Mater. Sci. Tech., 22(2), p. 129, Fig. 4]
Figure 2-11. Schematic representations of bifilm assisted casting porosity formation illustrating A) Simply folded bifilm B) Tangled convoluted bifilm C) Overinflation of a bifilm resulting in spherical pore and D) The over-inflation of a bifilm late in solidification resulting in an interdendritic pore

[Reprinted with permission from Campbell, J., 2006, "Entrainment Defects," Mater. Sci. Tech., 22(2), p. 133, Fig. 8]
Figure 2-12. A schematic illustration of the growth of an Al-Si eutectic into a melt containing a population of oxide bifilms, showing the incorporation of transverse cracks into Si particles

[Reprinted with permission from Campbell, J., 2011, "The Origin of Griffith Cracks," Met. Trans. B, 42(6), p. 1095, Fig. 5]
Figure 2-13. Filling system design showing A) Bottom-filled system with ceramic foam filter for casting blades and B) Top-filled for casting blades

Figure 2-14. Schematic of porosity/bifilm healing during HIP and subsequent fracture during tensile testing

Figure 2-15. Fractographic surface facets interpreted as indicating the presence of new bifilms in Al-based alloys for samples A) Loaded in fatigue and B) loaded in tension

[Part A reprinted with permission from Nyahumwa, C., Green, N. R., and Campbell, J., 2001, "Influence of Casting Technique and Hot Isostatic Pressing on the Fatigue of an Al-7Si-Mg Alloy," Met. Trans. A, 32(2), p. 352, Fig. 8]

[Part B reprinted with permission from Campbell, J., 2006, "Entrainment Defects," Mater. Sci. Tech., 22(2), p. 136, Fig. 12b]
CHAPTER 3
EXPERIMENTAL PROCEDURE

The following is a description of the materials, methods, tools, and procedures utilized for the investigation discussed herein.

Materials

This research effort was a collaborative effort with the Alcoa Howmet Research Center in Whitehall, MI. Howmet is an exotic metals casting producer, and a major supplier for aerospace and industrial gas turbine firms. The intent of the investigation was to determine if current commonly used superalloys investment casting procedures generate significant risk of potential oxide bifilm inclusion formation. In addition, comparisons between current industry standard practices and those proposed in published research investigating bifilms were evaluated to determine if a measurable and significant difference between materials produced by these means could be observed. Conclusions were made based on evaluation of polycrystalline Ni-based investment cast superalloy material received from Howmet Research Center (HRC). This evaluation includes: Room temperature tensile properties, room temperature fatigue properties, microstructural characterization of mechanical test specimens, fractographic analysis of mechanical test specimens, and surface analysis of Auger pin samples. Room temperature mechanical testing was selected for two primary reasons. First is to minimize the formation of fracture surface oxides, which may be conflated with bifilms. Second is that this testing condition is expected to be the most sensitive to the presence of embrittling inclusions [49, 76, 77]. Observed comparative differences between material conditions were used to ultimately assess the superalloys investment casting industry’s exposure to risk due to the presence of oxide bifilms.
The first alloy selected for preliminary study was the commonly used polycrystalline cast Ni-based superalloy B1900. This alloy is commonly used in gas turbine aircraft engines for blading applications when higher temperature capabilities of DS or SC alloys are not needed. The nominal composition of this alloy can be reviewed in Table 3-1. This material was investment cast at the Alcoa Howmet Research Center in Whitehall, MI. B1900 was cast into 5 cylindrical bars using typical vacuum investment casting procedures (see Chapter 2). Cylindrical bars were approximately 9 cm in length and 1.25 cm in diameter. Casting procedure included a top filling method that produces turbulence during mold filling. No filters were used in order to retain all oxide inclusions that may have formed during melting and casting. The cast bars were machined by Howmet into threaded tensile specimens according to ASTM E 8 standards, and were tested by Howmet in the as-cast condition. The tested material and tensile data was supplied by Howmet to the University of Florida in a preliminary attempt to replicate the results reported in 2004 by Rashid et al. [6]. This report indicated the presence of oxide bifilms in vacuum cast polycrystalline Ni-base superalloy following fractographic examination by SEM.

The alloy chosen for more intensive primary investigation was the commonly used polycrystalline cast Ni-based superalloy IN100. This alloy is also commonly used in gas turbine aircraft engines for blading applications when higher temperature capabilities of DS or SC alloys are not needed. The nominal composition of this alloy can be reviewed in Table 3-2. This material was investment cast at the Alcoa Howmet Research Center in Whitehall, MI. In total, IN100 was used to cast 128 bars and 115 blades, and was cast with varying casting conditions. The cast bars utilized a “carrot
bar” design, instead of cylindrical bars, to improve mold filling and reduce hot tearing and macroshrinkage. This design can be reviewed in Figure 3-1. Two blade designs were utilized in this study. Initial blade castings were made with a proprietary “generic blade” design used internal to Howmet for research material, referred to as Process Improvement Team (PIT) blades. PIT blades possessed a root to blade tip length of 10.16 cm and a blade width of 5.08 cm. Due to castability and shrinkage issues, this was later changed to a smaller proprietary design based on a variant of a commonly produced high pressure turbine blade design. These power turbine (PT) blades possessed a root to blade tip length of 7.93 cm, a maximum blade width of 3.32 cm at the base, and a minimum blade width of 2.15 cm at the tip. An image of these blades can be reviewed in Figure 3-2. In total, 46 PIT blades and 69 PT blades were cast. However, only 14 PIT blades were received from Howmet. The remaining PIT blades were scrapped due to casting issues. All PT blades were received.

A master heat that contained 70% virgin raw materials were melted by VIM and investment cast into cluster molds. Each mold contained bar samples to be machined into mechanical test specimens, and turbine blades to be used for microstructural characterization. Vacuum casting was conducted using standard VIM and investment casting procedures (see Chapter 2). Melting and casting atmospheres were carefully controlled and maintained at total pressures of less than 15 mTorr. Argon casting was conducted by first achieving vacuum conditions, and then backfilling the melting and casting chamber with Ar to a total pressure of 10 Torr. The introduction of Ar permitted the vacuum to be “broken” without introducing significant oxygen or nitrogen content. This allowed for evaluation of effects from the reduction in oxygen and nitrogen content.
as compared to the effects of reduced nominal pressures. Air casting was achieved by casting in atmospheric air. For each casting environment, samples were either top filled or bottom filled. Top filled samples utilized a gating design which would allow the molten metal to turbulently fill the mold cavity from the top down. Bottom filled samples were gated to fill the mold cavity from the bottom up to minimize turbulence. In addition, some vacuum cast samples employed turbulent gating, where Howmet proprietary turbulators were installed in the gating of the cluster mold to induce additional turbulence. A Howmet proprietary extruded ceramic filter was utilized for some air cast samples. A complete sample matrix can be reviewed in Figure 3-5. Following casting, all samples were inspected by FPI and XRI at HRC. HRC provided a chemistry report for each cluster mold cast, and an example chemistry analysis can be reviewed in Appendix A.

IN100 Heat Treatment

It is important to note that the main goal of this research effort was not maximization of mechanical properties. The primary focus was the effect of casting and processing conditions on oxide bifilms and nonmetallic inclusions. For this reason, heat treatment and HIP conditions were kept constant to minimize variables, and utilized industry standard procedures. The purpose for HIP and heat treatment have been previously described (see Chapter 2). A partial solution heat treatment was utilized (i.e. not fully solutionized), as is typically the case for cast IN100. HIP and heat treatment schedules can be reviewed in Table 3-4. Samples were tested in the as-cast, heat treated, and HIP and heat treated conditions. Sample conditions for both bars and blades can be reviewed in Figure 3-5. It should be noted that samples that were HIPed and heat treated were first HIPed and then subsequently heat treated. Heat treatment
following HIP was not modified, again in an effort to minimize variables. HIP and heat treatment were performed at HRC.

**Mechanical Testing**

A major component of this study was the analysis of the mechanical behavior, namely tensile and fatigue, and the material response to processing parameters. This was done in an effort to examine variation in mechanical test data that may suggest behavior due to bifilms, similar to results seen in current bifilm literature.

**B1900 Tensile Testing**

B1900 tensile bars were tested in an effort to replicate fractographic and microstructural results reporting the presence of oxide bifilms in polycrystalline investment cast superalloys. Cast cylindrical bars were machined by Howmet. Tensile specimens were machined according to internal Howmet standards equivalent to ASTM E 8. Sample geometry can be reviewed in Figure 3-3. Tensile samples were tested in the as-cast condition at room temperature. B1900 tensile samples were tested at HRC. Three tensile samples were pulled in tension at room temperature to failure. One additional tensile sample was pulled to 3% strain at room temperature, then discontinued and removed for examination. One final tensile sample was pulled to 1% strain at room temperature, then discontinued and removed for examination. All tested tensile samples were then sent to the University of Florida (UF) for analysis. Fracture surfaces from each tensile bar pulled to failure were removed and mounted for fractographic analysis. The opposite half of each tensile bar pulled to failure was cross-sectioned along the gauge length, then mounted and polished for metallographic analysis, allowing for a transverse examination of the microstructure near the fracture
surface. The interrupted tensile samples were cross-sectioned along the gauge length and prepared similarly for metallographic analysis of the transverse microstructure.

**IN100 Tensile Testing**

IN100 tensile bars were tested in an effort to evaluate the effect of casting and processing parameters on the potential formation of oxide bifilms and subsequent tensile behavior. Carrot bar castings were machined into mechanical test specimens by Howmet according to internal Howmet standards equivalent to ASTM E 8. Sample geometry can be reviewed in Figure 3-3. The number of tensile bars tested in each condition can be reviewed in Figure 3-5. Room temperature tensile tests were conducted at HRC. Tensile samples were pulled to failure at room temperature, and 0.2% yield stress, ultimate tensile stress, and elongation were measured. All tested tensile samples and associated tensile data were then sent to UF for analysis. Fracture surfaces from each tensile bar pulled to failure were removed and mounted for fractographic analysis. The opposite half of each tensile bar was cross-sectioned along the gauge length, then mounted and polished for metallographic analysis, allowing for a transverse examination of the microstructure near the fracture surface.

**IN100 Fatigue Analysis**

IN100 fatigue bars were tested in an effort to evaluate the effect of casting and processing parameters on the potential formation of oxide bifilms and the subsequent effect on fatigue life. Carrot bar castings were machined by low stress grinding into threaded high cycle fatigue (HCF) samples with a maximum surface finish of 0.2 μm root mean square (RMS). HCF sample machining was performed by Element Materials Technology (formerly MAR-TEST) in Cincinnati, OH. Carrot bar castings were machined into HCF samples according to a modified version of internal Howmet fatigue sample
standards that do not have an ASTM equivalent. Fatigue sample geometry can be reviewed in Figure 3-4. The number of fatigue bars tested in each condition can be reviewed in Figure 3-5. Machined fatigue bars were then sent to UF. Room temperature fatigue testing was conducted at the University of Florida High Temperature Materials Lab (HTAL) using a servo-hydraulic driven Instron load frame with a Satec 8800 series controller.

All HCF samples were subjected to stress-controlled HCF testing at room temperature until failure, and the number of cycles to failure was recorded. Room temperature HCF with a tension-tension loading condition was selected since this condition was anticipated to be the most sensitive to the presence of inclusions [49, 54, 76]. Loading conditions can be reviewed in Table 3-5. An R-ratio of 0.1 was selected as this type of tension-tension loading condition was expected to be the least defect-tolerant [49]. \( \sigma_{\text{max}} \) was selected based on tensile results, such that:

\[
\sigma_{\text{max}} \approx 0.9 \times \bar{\sigma}_{\text{yield}}
\]  

\( \sigma_{\text{min}} \) was selected to achieve R=0.1. Fracture surfaces from each bar fatigued to failure were removed and mounted for fractographic analysis.

**Statistical Analysis**

Relevant statistical analysis was generated for tensile and fatigue data pools using Microsoft Excel and Minitab 15. Aggregate tensile and fatigue properties are shown in column charts generated by Excel displaying mean properties and error bars that are representative of sample set maxima and minima. Further statistical analysis via Minitab 15 included generation of probability plots by assembling data pools of a measured mechanical property. A substantial amount of information on how to use
Minitab and its statistical tools can be gained by reading the tutorials included in the software package. For this study, the data pool of measured material samples would be segregated categorically to compare selected processing conditions against a given material property in an effort to determine if these populations of data could be considered statistically distinct. For example, a probability plot would be generated of the fatigue life of samples across the data pools of vacuum cast, argon cast, and air cast samples. From probability plots, a number of powerful statistical analyses can be performed. P-values were used in testing for normality, i.e. fit to normal distribution. Lower p-values, typically < 0.005, indicate poor fit to a normal distribution. Therefore, low p-values can indicate the presence of an unconstrained acting variable, with a level of confidence that corresponds to the p-value threshold chosen. Another test for normality, the Anderson–Darling test, is also given as the AD value. The AD value can indicate deviation from normality, and the threshold value will vary depending on sample size and confidence level, but generally a lower AD value indicates better fit to a normal distribution [78]. Standard deviation for the data set is also generated, which can be useful in gauging scatter in data and generating confidence intervals. Each probability plot also generates a confidence band for the plotted data on the basis of a 95% confidence interval (CI), which is extremely useful in determining if populations of data can be considered statistically significant on a 95% CI. This allowed for a quantitative method of determining if mechanical behavior observed can be considered distinct between populations of data. An example probability plot that utilizes these statistical methods can be reviewed in Figure 3-6.
Sample Preparation and Characterization

A major component of this study was the characterization of materials and test specimens received from HRC and specimens tested at UF HTAL. Metallographic, fractographic, and Auger pin samples were analyzed using the characterization tools available at the UF Major Analytical and Instrumentation Center (MAIC).

Metallography

Metallographic specimens were prepared from the halves of fractured tensile bars pulled to failure, as well as the two interrupted B1900 tensile tests. These bars were sectioned longitudinally, allowing for a cross-sectional analysis of the microstructure near the fracture surface. At least one longitudinal samples was taken from each tensile test condition (see Figure 3-5). Samples for inclusion analysis, taken from threaded portion of test specimens, were taken by sectioning an approximately 1 cm thick sample from the threaded end of a test bar. This was to allow for analysis of the inclusion structure in material that could be assumed to be unstrained. All samples were sectioned using an Allied TechCut 4 low speed diamond wafering saw equipped with a high concentration diamond metal bond wafering blade.

Following sectioning, all samples were cleaned ultrasonically for 15 mins in acetone, followed by another 15 mins of ultrasonic cleaning in methanol. All metallographic specimens were mounted in a two-part epoxy resin, Buehler EpoxiCure, a room temperature curing epoxy. Samples were allowed to cure overnight. Grinding and polishing was performed on a LECO Vari/Pol VP-55 polishing wheel utilizing standard metallographic preparation techniques. Silicon carbide grinding paper with a grit rating of 120 grit was used to plane samples. This was followed by grinding with progressively finer silicon carbide grinding paper with grit ratings of: 240, 320, 400, 600,
and 800. Following this colloidal alumina slurries consisting of alumina suspended in water was applied to Buehler microcloth polishing cloths. Each slurry was assigned its own cloth to avoid grit contamination. Progressively finer colloidal alumina was used with particle sizes of: 25 μm, 14.5 μm, 5 μm, 3 μm, 1 μm, 0.3 μm and 0.05 μm. Following polishing, samples were rinsed with water and sample surfaces were cleaned with a cotton ball soaked in soapy water. The soaps used were Alconox and Sparkleen. The samples were rinsed again and dried under pressurized air.

Samples prepared for metallographic analysis were swab etched with γ′ etchant where indicated. The γ′ etchant utilized was Pratt & Whitney #17 (100 mL H₂O + 100 mL HCl + 100 mL HNO₃ + 3 g MoO₃). This etchant preferentially attacks the γ′ precipitate phase, leaving the residual gamma channels and former location of precipitates visible upon metallographic inspection. Samples were analyzed in the unetched condition where indicated. Unetched samples were preferable for carbide and inclusion analysis. Samples prepared for further analysis of inclusions were deep etched. The deep etchant solution consisted of 70 mL HCl + 30 mL H₂O₂. Immediately after the deep etching solution was made, the sample was submerged in the bubbling etchant for 90 seconds, then removed and submerged in water. Example microstructures of samples prepared by γ′ etching, no etching, and deep etching can be reviewed in Figure 3-7.

**Fractography**

Fracture surfaces were removed from tensile and fatigue specimens. Fractographic specimens were taken by perpendicularly sectioning the end of a fractured bar such that an approximately 1 cm thick sample was removed. At least one sample was taken from each material condition for both tensile and fatigue tests (see Figure 3-5). All samples were sectioned using an Allied TechCut 4 low speed diamond
wafering saw equipped with a high concentration diamond metal bond wafering blade. Following sectioning, all samples were cleaned ultrasonically for 15 mins in acetone, followed by another 15 mins of ultrasonic cleaning in methanol. Samples were dried under pressurized air, and mounted on aluminum SEM stubs using conductive double-sided carbon adhesive SEM tape.

**Scanning Electron Microscopy**

SEM characterization was performed on fractography samples and metallographically prepared specimens. A conductive path between metallographic samples and the sample holder must exist in order to be examined by SEM. Since the epoxy mounts were non-conducting, some samples were electrically grounded by providing a conductive pathway to the sample holder by using either colloidal graphite paint (graphite in an isopropanol suspension), or conductive double-sided SEM adhesive tape. Other samples were sputter coated with an approximately 20 nm thick conductive carbon coating. This is useful when attempting to examine microstructure near the sample edge, as is the case when analyzing microstructure just below the tensile fracture surface. For this reason, most tensile samples analyzed were carbon coated prior to SEM examination.

The instruments utilized were a JEOL 6400 and FEI XL-40. Both instruments were equipped with secondary election imaging (SEI), backscatter electron (BSE) imaging, and energy dispersive x-ray spectroscopy (EDS) capabilities. The majority of SEM imaging was performed using SEI mode. This was preferable for general microstructure and fractographic examination such as imaging of carbide structures, γ’ structures, inclusion structures, persistent slip bands (PSBs), porosity, and fractographic surface features. BSE was utilized in specific cases where either sensitive topographical
contrast or atomic weight (Z) contrast was necessary. Z-contrast was particularly useful in identifying oxycarbide inclusion structures and some MC carbide structures.

EDS was utilized to generate qualitative and semi-quantitative chemistry data. The EDS techniques utilized includes spot analysis, line scanning, and elemental mapping. Spot analysis was useful in determining chemical information regarding site-specific microstructural features. Spot analysis was capable of generating EDS spectra and a semi-quantitative analysis of EDS spectra to give the approximate atomic composition of the location analyzed. This was primarily useful in analyzing the chemical content of carbide and oxycarbide structures. Carbon coated samples were typically analyzed qualitatively, as the carbon coating distorted quantitative results. Line scans yielded information about relative atomic content in a site-specific line designated in a microstructure. This was particularly useful in analyzing interfaces, such as phase layers observed in an oxycarbide inclusion. Elemental mapping was primarily utilized to show the location of detectible elements in a field of view, which was useful in determining the location of MC carbides detected during fatigue sample fractography.

A wide variety of instrument conditions were utilized. Beam size was routinely adjusted depending on imaging mode and EDS signal. EDS signal was gauged by counts per second (CPS) displayed by the detector. Aperture size was occasionally adjusted depending on depth of field concerns, resolution needed, and EDS signal. Working distance for the JEOL 6400 was typically kept at 15 mm, especially during EDS analysis, however this working distance was sometimes increased due to depth of field concerns for fractographic analysis. Working distance for the FEI XL-40 was typically kept to 10 mm, especially during EDS analysis, however this working distance was also
sometimes increased due to depth of field concerns. Accelerating voltage was adjusted between 5 KeV to 20 KeV for the JEOL 6400 and between 5 KeV to 30 KeV for the FEI XL-40 depending on surface sensitivity needed, EDS signal strength, and necessary resolution. Sample rotation and tilt were frequently utilized during fractographic analysis, especially to maximize signal reaching the EDS detector.

**Auger Analysis**

Cast blades were machined by electrical discharge machining (EDM) by Advanced Manufacturing Techniques, Inc. in Clifton Park, New York to remove several small Auger pin samples from each blade. Auger pins were machined from the root of at least one cast blade in each sample condition (see Figure 3-5). Auger pins could only be removed from the root of PT blades, as this was the only location thick enough for extraction. However, Auger pins were removed from the root, mid-airfoil, and blade tip sections for PIT blades. The Auger pins were cylindrical notched samples 20.3 mm in length and 3.18 mm in diameter. A blunt notch was machined 11.4 mm from the top of the sample, and to a depth of 0.51 mm. A schematic illustration of Auger pin geometry can be reviewed in Figure 3-8. It was determined that a small notch needed to be ground into the sample surface 3.2 mm from the shorter end of the Auger pin. This notch was precisely ground so that the set screw of the sample holder would rest in the notch, and this was necessary to prevent the set screw from slipping during in-situ sample fracture. Set screw notch grinding was accomplished using a handheld rotary engraving tool equipped with a grinding wheel attachment. Prior to analysis, each Auger pin was ultrasonically cleaned in methanol for 15 mins three times, refreshing the methanol bath for each ultrasonic cleaning. This was to ensure that no residue from machining or handling remain on the sample surface, as analysis must be conducted in
ultra-high vacuum (UHV) conditions. Any residual oils from handling would not permit the extremely high vacuum levels that were necessary.

Each Auger pin was loaded into a copper sample holder, which was then loaded into the carousel-style stage of a PHI 660 scanning Auger microprobe (SAM). The carousel system allowed for multiple samples to be pumped to ultra-high vacuum levels prior to in-situ fracture. These high vacuum levels were accomplished through multiple means. Vacuum levels on the order of magnitude of $10^{-8}$ Torr were initially achieved by evacuating the sample chamber using an ion pump. This would require loading samples first into an exchange chamber that was evacuated by a turbomolecular pump, then loading the sample into the chamber and allowing the chamber to be evacuated by the ion pump overnight. Once nominal pressures in the range of $10^{-8}$ Torr were achieved, a sublimation pump was utilized to reduce pressures into the sub-nTorr range. This requires resistive heating of a titanium filament, which is housed in the same chamber as the ion pump. Upon resistive heating, Ti ions were sputtered in a line of sight process and deposited onto available free surface, primarily within the ion pump chamber. The presence of fresh Ti ions would then getter remaining O and N, forming TiO and TiN, thereby reducing total pressure into the $10^{-10}$ Torr range.

It was deemed necessary that in-situ fracture occurred in ultra-high vacuum conditions of less than 0.5 nTorr such that fracture surface oxide monolayer formation times would be long enough to permit ample time for examination. This conclusion was reached based on the results of prior kinetic studies of nickel oxidation in which it was determined that a monolayer of NiO forms in about 1 second at nominal pressures of $10^{-6}$ Torr [79]. Given that NiO under such conditions will follow Langmuirian adsorption
kinetics [80], a simple relationship utilizing the Langmuir exposure parameter can be created such that:

\[ 1L \approx 10^{-6} \text{Torr} \times \text{sec} \]  

(3-2)

This indicates that each order of magnitude of reduction in nominal chamber pressure corresponds to one order of magnitude increase in reaction time for formation of an oxide monolayer. This indicates that if 10^{-10} Torr vacuum levels can be achieved, an exposure time of 10,000 seconds (2.77 hrs) would be necessary for formation of a NiO monolayer, theoretically providing ample time for surface analysis of a newly fractured sample surface. For the purposes of this calculation, reaction kinetics were assumed to be equivalent to pure nickel, though in the case of a Ni-base superalloy more complex competing chemisorption would be present.

Samples were fractured in-situ by moving the sample holder containing the sample to be analyzed into a set of copper jaws contained in the sample chamber. Once mechanically secured in place, the auger pin was fractured by an actuating hammer, exposing a fresh fracture surface for Auger electron spectroscopy (AES) analysis. Samples were immediately analyzed to minimize gettering, and analysis was terminated once an appreciable O signal was generated due to such gettering. This typically occurred after a couple hours of analysis time, as had been predicted. SAM analysis included secondary electron imaging, generation of AES spectra, elemental mapping by AES, and elemental AES depth profiling. Auger data was analyzed using the RBD Instruments PHI AugerMap and AugerScan software packages. Elemental depth profiling was performed using a rastering Ar ion beam to mill the sample surface. The ion beam raster area was adjusted to set mill rates of material removal, and was
adjusted to meet the desired material removal rate. Sputter time was recorded while
depth profiling and compared to mill rates of a Ta₂O₅ standard of known thickness using
identical conditions. This allowed for estimations of sputter depth with time, and
therefore estimations of elemental content as a function of depth.

**Transmission Electron Microscopy**

To further elucidate the structure of oxycarbide inclusions, some oxycarbide
inclusions observed metallographically were removed via focused ion beam (FIB) lift-out
for TEM analysis. Metallographically prepared samples had to be carefully removed
from epoxy mounts via mechanical fracture, then cleaned and mounted on an aluminum
SEM stub. FIB was performed with an FEI Strata DB 235 dual beam FIB/SEM equipped
with a liquid metallorganic ion source (LIMS) for protective Pt layer deposition. Samples
were prepared using standard FIB lift-out procedures. A layer of protective Pt is first
deposited on the feature of interest, in this case across an oxycarbide inclusion. That
region is then micromachined from the sample surface using a Ga ion beam, and
attached by Pt welding to an Omniprobe micromanipulator. The sample is then
transferred to a Cu TEM sample grid, Pt welded to the sample grid, and cut from the
micromanipulator. The sample is then thinned to a maximum of 100 nm thickness and
removed for TEM analysis.

TEM analysis was performed using a JEOL 2010F high resolution TEM (HR-
TEM). This instrument was equipped with scanning transmission electron microscopy
(STEM) and EDS capabilities. Bright field TEM (BF-TEM) was performed for general
microstructure characterization and location of sites of interest. STEM/EDS was
performed to generate EDS line scans across oxycarbide inclusion structures. HR-TEM
imaging was performed to analyze the bonding and grain boundary structure of
interfaces within an oxycarbide inclusion, namely matrix/TaC, TaC/Al₂O₃, and Al₂O₃/Al₂O₃ interfaces.
Table 3-1. Composition of polycrystalline B1900 in weight percent

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<th>Nominal</th>
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<td>Boron</td>
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Adapted from ASM International [81]

Table 3-2. Composition of polycrystalline IN100 in weight percent

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Adapted from Furrer et al. [82]
Figure 3-1. Carrot bar dimensional schematic
Figure 3-2. Image of a typical PIT blade (left) and PT blade (right)
Figure 3-3. Schematic drawing of tensile sample design. Proprietary information redacted
Figure 3-4. Schematic drawing of fatigue sample design. Proprietary information redacted.
<table>
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<tr>
<th>Environment</th>
<th>Filtration</th>
<th>Fill Condition</th>
<th>Gating</th>
<th>Processing</th>
<th>Heat Treatment</th>
<th>Tensile Bars (#)</th>
<th>Fatigue Bars (#)</th>
<th>Blades (#)</th>
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<td></td>
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<td>Heat Treat</td>
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Figure 3-5. Complete IN100 sample matrix

Table 3-3. IN100 HIP and heat treatment schedules

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<td>2200°F, 15 KSI, 4hrs</td>
</tr>
<tr>
<td>Partial solution heat</td>
<td>1975°F in vacuum, hold 4hrs; gas fan cool to 1600°F, hold</td>
</tr>
<tr>
<td>treatment</td>
<td>12hrs; air cool to room temperature</td>
</tr>
</tbody>
</table>

Table 3-4. IN100 HCF test conditions

<table>
<thead>
<tr>
<th>Variable</th>
<th>Set Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{\text{max}}$</td>
<td>690 MPa</td>
</tr>
<tr>
<td>$\sigma_{\text{min}}$</td>
<td>69 MPa</td>
</tr>
<tr>
<td>$\Delta \sigma$</td>
<td>621 MPa</td>
</tr>
<tr>
<td>R-ratio</td>
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</tr>
<tr>
<td>Waveform</td>
<td>Triangular</td>
</tr>
<tr>
<td>Frequency</td>
<td>15Hz</td>
</tr>
</tbody>
</table>
Figure 3-6. Probability plot of fatigue life between vacuum, argon, and air cast samples. The lack of overlap in 95% CI for air cast indicates that it is statistically distinct from argon or vacuum cast samples.
Figure 3-7. Examples of IN100 metallography examined by SEM showing A) Unetched microstructure for carbide examination B) γ' etched microstructure C) Unetched microstructure for oxycarbide inclusion examination and D) Deep etched microstructure for oxycarbide inclusion examination

Figure 3-8. Schematic illustration of Auger pin geometry. All units in inches.Courtesy of Eric Lambers
CHAPTER 4
RESULTS: TENSILE TESTING

As a preliminary examination, five B1900 bars were cast using typical industrial superalloys casting procedures. This process involves vacuum investment casting utilizing top filled molds. All B1900 tensile samples were tested in the as cast condition at room temperature. Three bars were pulled to failure, one was pulled to 3% strain, and another tensile bar was pulled to 1% strain. These tensile bars were then analyzed via SEM fractography and metallography as a first check for the presence of bifilms, utilizing investigation techniques similar to current bifilm literature. This analysis will be discussed first, however, the majority of room temperature tensile testing was performed on IN100 test bars utilizing a variety of casting conditions and post-casting processing. For a full IN100 sample matrix, see Figure 3-5. It should be noted that tensile testing was not performed to compare material to publications on the tensile strength of B1900 or IN100. Tensile testing was performed to determine if trends in tensile strength related to oxide bifilms are observable, and to generate metallographic and fractographic samples to determine any effects of oxide bifilms on the fracture mechanics of these materials.

**B1900 Tensile Testing**

Fractographic analysis of tensile samples pulled to failure was conducted using SEM. The fracture surface of B1900 tensile bars exhibited some locations of dendritic casting porosity (Figure 4-1). However, the observed dendrites did not show any evidence of oxide inclusions or oxide films. EDS analysis indicates that the dendritic casting porosity exhibited a chemical composition similar to the nominal alloy composition, with the exception of carbon due to the relative inaccuracy of light element
quantification by EDS. In addition to this, cleavage planes also did not exhibit any evidence of oxide films (Figure 4-2). EDS analysis indicates that the cleavage planes analyzed exhibited a chemical composition similar to the nominal alloy composition, again with the exception of carbon.

No evidence of new or old oxide bifilms was found to be present in the fracture surfaces analyzed. There were no detectable nonmetallic inclusions. However, a substantial amount of microvoid formation was apparent in the fractography of each sample (Figure 4-3). These microvoids did not show clear evidence of oxide defects. Instead, the microvoids appear to have formed in the presence of carbides that had fractured due to elongation from the tensile load applied. EDS analysis confirms that the carbide cracking observed occurs in MC carbides, rich in Ta, Mo, and Ti (Figure 4-4). Each of these alloying additions are known to be strong primary MC carbide forming elements [26]. The carbide composition observed is similar to typical literature reports [83, 84]. It is expected that the Ni, Cr, and Al signals detected by EDS are originating from nearby matrix material due to spatial resolution limitations. If these elements are removed from the calculation, a composition very close to the stoichiometric metal to carbon atomic ratio of 1:1 is observed.

The microstructures seen in tensile bar samples pulled to failure were analyzed by SEM and secondary electron imaging. There were no detectable nonmetallic inclusions in the gauge length cross-section of these samples. Dendritic casting porosity was observed in these samples (Figure 4-5). Sample porosity was randomly distributed throughout the gauge length, and there did not appear to be an increased population of porosity near the fracture surface. The dendritic casting porosity did not exhibit evidence
of new bifilms. EDS indicates that the dendritic casting porosity possessed a chemical composition similar to the nominal alloy composition, in agreement with EDS data taken during fractographic analysis.

The metallography of the tensile bars pulled to failure clearly showed an abundance of carbide cracking near the fracture surface (Figure 4-6). There was also a substantial amount of secondary cracking observed near the fracture surface. This secondary cracking almost exclusively occurred in the presence of clusters of fractured carbides, and the secondary crack paths observed closely corresponded to such clusters. There was no indication of oxide films present along this cracking. Significantly less carbide cracking was observed in locations further from the fracture surface. A limited amount of carbide cracking could be located in the sample pulled to 3% elongation and interrupted. Furthermore, a very limited amount (one instance) of carbide cracking was located in the sample pulled to 1% elongation and interrupted. Examples of each are shown in Figure 4-7. Some current reports state that such carbide cracking may be due to the nucleation of carbides on bifilms. However, there was no clear indication that these carbides had nucleated on oxide films, or that such carbide cracking was related to the splitting of bifilms.

**IN100 Tensile Testing**

As stated previously, the vast majority of tensile testing was performed on IN100 samples that were cast while altering a variety of casting conditions and post-casting treatments (see Figure 3-5). Samples were tested at room temperature and UTS, YS, and elongation were measured. Additionally, metallography of cross-sectional samples and fracture surfaces of tensile samples were analyzed and compared to the measured tensile data. The total pool of tensile data was repeatedly separated between conditions.
expected to yield varying results based on predicted bifilm behavior, and statistical analysis of this data allowed for objective determination of material response trends.

**Casting Atmosphere Effects**

Vacuum cast, air cast, and argon cast samples were compared to evaluate if there is a measurable impact on tensile behavior due to casting environment. Average UTS, YS, and tensile elongation results between casting atmospheres and fill conditions are shown in Figures 4-8 through 4-10. There did appear to be an influence of casting atmosphere on UTS, as indicated by statistical analysis displayed in Figure 4-11. A low p-value, large AD value, and apparent bimodal distribution in air cast UTS are shown. There was a similar effect of casting atmosphere on tensile elongation, as shown in Figure 4-12. Interestingly, there was not a statistically distinct reduction in cumulative mean UTS or elongation for air cast samples. These results indicate the presence of an uncontrolled variable influencing the air cast data set population, causing deviation from normality. These deviations are due to the sample data in the low strength and low ductility portion of the distributions, which would most likely be caused by the presence of large NMIs. Due to this population of low strength samples, there was also a reduction in minimum UTS for air cast samples (Figure 4-8) and substantial reduction in minimum ductility for air cast samples (Figure 4-10). There did not appear to be an effect of casting environment on YS (Figure 4-9).

The presence of large Ti oxycarbide inclusions in samples in the low strength regime of air cast samples was confirmed by fractographic and metallographic analysis, and examples of each can be seen in Figure 4-13. It should be noted that the inclusions observed are not true oxycarbides, however historically oxycarbide, carbonitride, etc. inclusion stringers have been referred to by this nomenclature. Therefore, although
these inclusions are a heterogeneous structure of discrete oxide and carbide phases, the term oxycarbide is also used in this dissertation. These inclusion structures were observed in low strength air cast material, and occurred in both top and bottom filled samples. Fracture surfaces of low strength air cast samples exhibited very large (approx. 100 μm to 1mm) oxycarbide inclusions. These fracture surfaces exhibited many regions that were brittle in appearance. However, high strength and high ductility air cast material, as well as all vacuum cast and argon cast samples, exhibited fractographic features much more similar to that seen in B1900 samples, as shown in Figures 4-14 and 4-15. In these cases, fracture of M(Ti, Mo)C carbides was associated with microvoid formation, which ultimately led to ductile tensile fracture following the classic mechanism of microvoid coalescence. High strength air cast material, as well as vacuum cast and argon cast material, also exhibited microstructural features similar to those seen in B1900 samples (Figures 4-14 and 4-15). In these cases, there is significant near-surface fractured MC carbides and evidence of secondary cracks closely following clusters of fractured MC carbides. These results indicate that although casting environment did have a noticeable impact on the tensile behavior of IN100, this was due to the formation of large Ti oxycarbide inclusions and did not appear to be related to bifilms.

**Casting Turbulence Effects**

Top filled and bottom filled samples were compared to evaluate if there is a measurable impact on tensile behavior due to casting turbulence. Average UTS, YS, and tensile elongation results between casting atmospheres and fill conditions are shown in Figures 4-8 through 4-10. When comparing the UTS of top filled vacuum and argon cast material to bottom filled, there was no measurable difference between these
data set populations. The statistical analysis shown in Figure 4-16 indicated good fit to normality (i.e. high p-value, low AD value). The overlapping scatter bands show that it is not possible to consider these populations of data as statistically distinct, therefore there is no measurable difference in UTS of these samples. Tensile elongation of top filled samples as compared to bottom filled is shown in Figure 4-17. There was again good fit to normality and no measurable difference in tensile elongation in top filled samples as compared to bottom filled. There also did not appear to be an effect on YS due to turbulence. Bifilm theories suggest that the introduction of turbulence during top filling of Ni-based superalloys results in formation of embrittling bifilms [2-6], however there was no measurable impact on UTS or elongation.

In order to further examine the effects of casting turbulence, the most turbulent samples were compared to the least turbulent. The most turbulent samples were those that were top filled and had a gating system that utilized turbulators installed in the gating. The least turbulent samples were those that utilized conventional gating (i.e. no turbulators) and were bottom filled. All of these samples were vacuum or argon cast. Average UTS and YS results between turbulence levels are shown in Figure 4-18. Statistical analysis of UTS data sets is shown in Figure 4-19 and indicated good fit to normality. The overlapping scatter bands show that it is not possible to consider these populations of data to be statistically distinct. This indicates that there is no measurable difference in UTS for the most turbulent samples as compared to the least turbulent. Average elongation results between the most and least turbulent samples is shown in Figure 4-20, and statistical analysis of these data sets is shown in Figure 4-21. Again, there was no measurable difference in tensile elongation between the most turbulently
and least turbulently cast samples. This further supports the argument that among samples cast in vacuum and inert environments, there appears to be no measurable effect on tensile strength or ductility due to casting turbulence. This strongly contradicts a wide body of published bifilm literature.

**Filtering Effects**

Filtered and unfiltered air cast samples were compared to evaluate if there is a measurable impact on tensile behavior due to the use of an extruded ceramic filter. It was anticipated that filtering would have the greatest effect on air cast samples, as there would be a greater likelihood in removing dross inclusions if more total dross were to be present in the melt. Therefore, the effects of filtering was only tested in air cast conditions. Average UTS and YS results between filtering conditions are shown in Figure 4-22. Average elongation results between filtering conditions is shown in Figure 4-23. Unfortunately, this was a limited data set (see Figure 3-5), and a full and thorough statistical analysis was not possible. Reviewing mean properties indicates that there is a mean shift in UTS, with an improvement in UTS through use of filtering. There also appears to be an improvement in minimum UTS through use of a filter. Elongation results indicate an improvement in mean tensile elongation and minimum elongation through use of a filter. However, since the data set is limited, these benefits of filtering are qualitative.

**HIP Effects**

HIP and heat treated samples were compared to heat treated samples in an effort to evaluate the effect of HIP on tensile properties. Average UTS results between HIP and no HIP samples are shown in Figure 4-24. Here a reduction in minimum UTS was observed for HIPed samples. Statistical analysis of UTS is shown in Figure 4-25.
and indicated good fit to normality. The overlapping scatter bands show that it is not possible to consider these populations of data to be statistically distinct, and indicates that there is no measurable difference in mean UTS for vacuum or argon cast HIP and heat treated samples as compared to vacuum or argon cast no HIP and heat treated samples. There was, however, a strong impact on YS due to HIP. Average YS results between HIP and no HIP samples are shown in Figure 4-26, and statistical analysis of YS data sets for argon and vacuum cast samples is shown in Figure 4-27. Statistical analysis indicated good fit to normality, and also showed that YS for HIP samples is distinct from YS of no HIP samples. YS for samples that had been HIPed was considerably reduced, with a mean YS reduction of 71.8 MPa. There was also a strong impact on tensile elongation due to HIP. Average elongation results between HIP and no HIP samples are shown in Figure 4-28, and statistical analysis of elongation data sets for argon and vacuum cast samples is shown in Figure 4-29. Statistical analysis indicated good fit to normality, and also showed that tensile elongation for HIP samples is distinct from elongation of no HIP samples. Elongation for samples that had been HIPed was substantially increased, with a mean increase of 3.2% elongation.

Although it is expected that remediation of bifilms via HIP would increase ductility, such a reduction in yield strength would not be anticipated. Upon further investigation, it was shown that this is actually evidence of softening due to precipitate coarsening as opposed to an influence from bifilms. This effect can be seen metallographically in Figure 4-30. This is likely due to inadequate γ’ solutioning during post-HIP heat treatment. See Chapter 8 for discussion.
It should also be reiterated that the objective of this study was not to maximize properties or optimize post-casting processing, but to observe any possible impacts of oxide bifilms. There was no measurable or observable impact on tensile behavior that can be directly attributed to bifilms. Furthermore, the effect of HIP on the morphology of oxide inclusions was not similar to what has been predicted by relevant literature pertaining to bifilms [8-10]. The size and morphology of Ti oxycarbide inclusions observed metallographically was not impacted by the utilization of HIP and heat treatment cycles (see Chapter 7 for additional analysis). Furthermore, the appearance of oxycarbide inclusions on fracture surfaces of low strength air cast tensile samples also was not effected by HIP. It should be noted that the oxycarbide observed fractographically in Figure 4-13a was observed in a HIP and heat treated air cast sample, whereas the oxycarbide observed fractographically in Figure 4-31 was observed in an air cast sample in the as cast condition. Neither of these inclusions exhibit a continuous oxide film. Furthermore, the oxycarbide inclusion in the as cast sample shown in Figure 4-31 exhibits multiple scales of discontinuity, exhibiting gaps and voids in the oxide structure on both the micro and nano-scale. This conflicts strongly with published bifilm research [9, 10], since it appears that discontinuities in the oxide structure exist prior to HIP treatments, and in fact the inclusion structure is invariant to utilization of HIP. Additionally, oxide inclusions were not observed to be continuous films in the fractography of any sample condition.
Figure 4-1. Dendritic casting porosity in B1900 tensile sample pulled to failure examined fractographically for bifilms

Table 4-1. Semi-quant EDS analysis of spot indicated in Figure 4-1

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Ta</th>
<th>Mo</th>
<th>Ti</th>
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<td>8.97</td>
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<td>7.82</td>
<td>51.37</td>
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<tr>
<td>Weight %</td>
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<td>-----</td>
<td>5.14</td>
<td>2.30</td>
<td>4.65</td>
<td>1.10</td>
<td>7.62</td>
<td>9.79</td>
<td>64.05</td>
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</table>
Figure 4-2. Cleavage plane in B1900 tensile sample pulled to failure examined fractographically for bifilms

Table 4-2. Semi-quant EDS analysis of spot indicated in Figure 4-2

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<th>Ti</th>
<th>Cr</th>
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<th>Ni</th>
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<td>1.15</td>
<td>7.15</td>
<td>10.78</td>
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Figure 4-3. Microvoid formation examined fractographically showing A) Examined microvoid B) High magnification view of carbide cracking and C) Cluster of fractured carbides
Figure 4-4. Cluster of carbide cracking in microvoid shown in Figure 4-3a examined by EDS analysis

Table 4-3. Semi-quant EDS analysis of spot indicated in Figure 4-4

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<th>Ti</th>
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<td>13.31</td>
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<tr>
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Table 4-4. Semi-quant EDS analysis of spot in Figure 4-4, matrix signal omitted

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<td>Weight %</td>
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Figure 4-5. Dendritic casting porosity examined metallographically for bifilms

Table 4-5. Semi-quant EDS analysis of spot indicated in Figure 4-5

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<th>Ta</th>
<th>Mo</th>
<th>Ti</th>
<th>Cr</th>
<th>Co</th>
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<tbody>
<tr>
<td>Atomic %</td>
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<td>-----</td>
<td>8.97</td>
<td>0.60</td>
<td>2.28</td>
<td>1.08</td>
<td>6.90</td>
<td>7.82</td>
<td>51.37</td>
</tr>
<tr>
<td>Weight %</td>
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<td>-----</td>
<td>5.14</td>
<td>2.30</td>
<td>4.65</td>
<td>1.10</td>
<td>7.62</td>
<td>9.79</td>
<td>64.05</td>
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</table>
Figure 4-6. Microstructural carbide cracking in B1900 tensile sample pulled to failure showing A) Fracture surface connected secondary cracking following fractured carbide clusters and B) Clusters of near fracture surface carbide cracking.

Figure 4-7. Carbide cracking located metallographically in B1900 tensile sample pulled to A) 3% strain and B) 1% strain.
Figure 4-8. Mean IN100 UTS across fill conditions and casting atmospheres. Error bars representative of data set range

Figure 4-9. Mean IN100 YS across fill conditions and casting atmospheres. Error bars representative of data set range
Figure 4-10. Mean IN100 elongation across fill conditions and casting atmospheres. Error bars representative of data set range.

Figure 4-11. Probability plot of UTS for all vacuum, argon, and air cast samples. Scatter bands representative of 95% CI.
Figure 4-12. Probability plot of elongation for all vacuum, argon, and air cast samples. Scatter bands representative of 95% CI.
Figure 4-13. Representative low strength air cast HIP and heat treated tensile sample with 676 MPa UTS, 655 MPa YS, and 1.7% elongation. A) SEM fractography of large NMI B) EDS spectrum of carbide region indicated in A showing enrichment in C, Ti and Mo C) EDS spectrum of oxide region indicated in A showing enrichment in Al and O and D) SEM metallography of Ti oxycarbide inclusion in same sample

Table 4-6. Semi-quant EDS analysis of spots indicated in Figure 4-13D

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<th>V</th>
<th>Cr</th>
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<td>----</td>
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<td>1.98</td>
<td>2.71</td>
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Figure 4-14. Representative vacuum cast sample with 869 MPa UTS, 772 MPa YS, and 7.1% elongation. A) SEM fractography of fractured carbide cluster associated with microvoid formation B) EDS spectrum of fractured carbide region indicated in A and C) SEM metallography of same sample, γ’ etched, and showing secondary cracking that follows near-surface clusters of fractured carbides
Figure 4-15. Representative high strength air cast sample with 923 MPa UTS, 729 MPa YS, and 9.5% elongation. A) SEM fractography of fractured carbide cluster associated with microvoid formation B) EDS spectrum of fractured carbide region indicated in A and C) SEM metallography of same sample, unetched, and showing secondary cracking that follows near-surface clusters of fractured carbides.
Figure 4-16. Probability plot of UTS for vacuum cast or argon cast top filled samples and vacuum or argon cast bottom filled samples. Scatter bands representative of 95% CI.

Figure 4-17. Probability plot of elongation for vacuum or argon cast top filled samples and vacuum or argon cast bottom filled samples. Scatter bands representative of 95% CI.
Figure 4-18. Mean UTS and YS for gating with turbulators and conventionally gated vacuum or argon cast samples. Error bars representative of data set range.

Figure 4-19. Probability plot of UTS for most turbulent and least turbulent vacuum or argon cast samples. Scatter bands representative of 95% CI.
Figure 4-20. Mean tensile elongation for most turbulent and least turbulent vacuum or argon cast samples. Error bars representative of data set range.

Figure 4-21. Probability plot of tensile elongation for most turbulent and least turbulent vacuum or argon cast samples. Scatter bands representative of 95% CI.
Figure 4-22. Mean UTS and YS for air cast filtered and unfiltered samples. Error bars representative of data set range.

Figure 4-23. Mean tensile elongation for air cast filtered and unfiltered samples. Error bars representative of data set range.
Figure 4-24. Mean UTS for HIP and heat treated and no HIP heat treated samples. Error bars representative of data set range.

Figure 4-25. Probability plot of UTS for vacuum or argon cast HIP and heat treated and no HIP heat treated samples. Scatter bands representative of 95% CI.
Figure 4-26. Mean YS for HIP and heat treated and no HIP heat treated samples. Error bars representative of data set range.

Figure 4-27. Probability plot of YS for vacuum or argon cast HIP and heat treated and no HIP heat treated samples. Scatter bands representative of 95% CI.
Figure 4-28. Mean tensile elongation for HIP and heat treated and no HIP heat treated samples. Error bars representative of data set range.

Figure 4-29. Probability plot of tensile elongation for vacuum or argon cast HIP and heat treated and no HIP heat treated samples. Scatter bands representative of 95% CI.
Figure 4-30. Vacuum cast sample SEM metallography, γ’ etched with Pratt & Whitney #17 A) Typical no HIP heat treated microstructure showing primary γ’ B) Typical no HIP heat treated microstructure showing secondary γ’ C) Typical HIP and heat treated microstructure showing primary γ’ and D) Typical HIP and heat treated microstructure showing secondary γ’
Figure 4-31. NMI in air cast tensile sample tested in the as cast condition A) SEM fractography showing inclusion discontinuity B) Location for EDS analysis C) Micro-scale oxide discontinuities D) Nano-scale oxide discontinuities

Table 4-7. Semi-quant EDS analysis of spots indicated in Figure 4-31B

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<th>Spectrum (at%)</th>
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<th>Ti</th>
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<td>2.45</td>
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CHAPTER 5
RESULTS: FATIGUE TESTING

All fatigue testing was performed using IN100 samples that were cast while varying a variety of casting conditions and post-casting treatments (see Figure 3-5). Samples were fatigued to failure at room temperature and cycles to failure were recorded. Fatigue conditions were held constant for each sample (see Chapter 3 for procedure). Additionally, fracture surfaces of fatigue samples were analyzed and compared to the measured fatigue life. The total pool of fatigue data was repeatedly separated between conditions expected to yield varying results based on predicted bifilm behavior, and statistical analysis of this data allowed for objective determination of material response trends. It should be noted that fatigue testing was not performed to compare fatigue life to current literature reports on the fatigue strength of IN100. Fatigue testing was performed to attempt to identify fatigue life trends that could be related to the effects of oxide bifilms, and to generate fracture surfaces for analysis to determine any possible influences on fracture mechanics due to oxide bifilms.

Casting Atmosphere Effects

Vacuum cast, air cast, and argon cast samples were compared to evaluate if there is a measurable impact on fatigue behavior due to casting environment. Average fatigue life between casting atmospheres and fill conditions is shown in Figure 5-1. There did appear to be a significant influence of casting atmosphere on fatigue life. A significant reduction in mean fatigue life is observable, and a very substantial reduction in minimum fatigue life was also clear. This was further indicated by statistical analysis displayed in Figure 5-2. The clear lack of overlap in the scatter band of air cast samples, as compared to vacuum and argon cast, indicates that this is a statistically distinct
population with a reduced mean fatigue life. Mean air cast fatigue life was approximately
60,000 cycles less than mean vacuum or argon cast fatigue life. Interestingly, all data
sets, including air cast samples, exhibited good fit to normality (i.e. low AD value and
high p-value). This varies from tensile results, where a bimodal distribution was visible
in air cast sample UTS and elongation. This behavior corresponded to the presence or
absence of large inclusions, but air cast tensile samples did not have a statistically
significant reduction in cumulative mean UTS and elongation. In the case of fatigue, the
data set population does exhibit a statistically significant reduction in mean fatigue life.
Although low fatigue life air cast samples did experience a reduction in cycles to failure
due to the presence of NMI's, air cast HCF samples did not exhibit a bimodal response.

**Turbulence Effects**

Top filled and bottom filled samples were compared to evaluate if there is a
measurable impact on fatigue behavior due to casting turbulence. Average fatigue life
results between casting atmospheres and fill conditions is shown in 5-1. When
comparing the fatigue life of top filled vacuum cast and conventionally gated material to
bottom filled vacuum cast and conventionally gated material, there was no measurable
difference between these data set populations. The statistical analysis shown in Figure
5-3 indicated good fit to normality. The overlapping scatter bands show that it is not
possible to consider these populations of data as statistically distinct, therefore there is
no measurable difference in fatigue life of these samples.

As a further examination of the effects of casting turbulence, the most turbulent
samples were compared to the least turbulent. The most turbulent samples were those
that were top filled and had a gating system that utilized turbulators installed in the
gating. The least turbulent samples were those that utilized conventional gating (i.e. no
turbulators) and were bottom filled. It should be noted that comparisons are made between samples that were vacuum cast. Average fatigue life results between turbulence levels are shown in Figure 5-4. Statistical analysis of fatigue life data sets is shown in Figure 5-5 and indicated good fit to normality. The overlapping scatter bands show that it is not possible to consider these populations of data to be statistically distinct. This indicates that there is no measurable difference in fatigue life for the most turbulent samples as compared to the least turbulent.

**Filtering Effects**

Filtered and unfiltered air cast samples were compared to evaluate if there is a measurable impact on fatigue behavior due to the use of an extruded ceramic filter. It was anticipated that filtering would have the greatest effect on air cast samples, as there would be a greater likelihood in removing dross inclusions if more total dross were to be present. Average fatigue life results between filtering conditions are shown in Figure 5-6. Unfortunately, this was a limited data set (see Figure 3-5), and a full and thorough statistical analysis was not possible. Reviewing mean properties indicates that there is a slight mean shift and change in minimum fatigue life, however these changes are relatively minor. Reviewing mean fatigue life does not strongly indicate an effect from filtering, however this data set was also limited.

**HIP Effects**

Samples in the HIP and heat treated condition were compared to samples in the heat treated condition in order to evaluate if there is a measurable impact on fatigue behavior due to utilization of HIP. Average fatigue life results between casting atmospheres and HIP conditions is shown in Figure 5-7. When comparing the fatigue life of vacuum cast material in the HIP and heat treat condition to vacuum cast materials
in the heat treated condition, there was no measurable difference between these data set populations. The statistical analysis shown in Figure 5-8 indicated good fit to normality. The overlapping scatter bands show that it is not possible to consider these populations of data as statistically distinct, therefore there is no measurable difference in fatigue life of these samples. The elimination of porosity by HIP was anticipated to have an effect on fatigue life, but interestingly it did not. This may indicate that porosity formed in no HIP samples was smaller than the critical pore size that could cause an overall reduction in observed fatigue life.

**Initiation Mechanisms**

Fatigue initiation mechanisms were determined by SEM fractography, and found that fatigue initiation can vary substantially between certain specific sample conditions. Comparisons can be made between the fatigue life of a given sample and its fatigue crack initiation behavior. The fractography for each distinct type of fatigue crack initiation mechanism is described herein.

**Vacuum or Argon Cast**

The SEM fractography between vacuum and argon cast samples was indistinguishable, as the initiation mechanisms were similar for samples cast in each condition. The initiation mechanisms for these samples can be considered in two primary categories: Samples with HIP and samples without HIP. Samples with HIP exhibited fatigue crack initiation via persistent slip band (PSB) formation in the presence of surface-connected or near-surface M(Ti, Mo)C carbides, and an example of this is shown in Figure 5-9. In this example abundant PSB formation, deformation bands, and ratchet lines are observable in the vicinity of surface-connected carbides. The composition of carbides is confirmed by EDS. The number of carbides present at an
initiation site varied from one to several. Carbide size ranged from about 25 μm to 100 μm. Most HIP samples only exhibited one initiation site, however some samples exhibited 2-4 initiation sites. An example of multiple initiation sites is also shown in Figure 5-9.

Samples without HIP exhibited 3 types of initiation sites: PSB formation on surface-connected or near-surface M(Ti, Mo)C carbides, PSB formation on near-surface dendritic casting porosity, or PSB formation on both porosity and MC carbides. An example of each initiation mechanism is shown in Figures 5-10 through 5-12. In these examples abundant PSB formation, deformation bands, and ratchet lines are observable in the vicinity of surface-connected or near-surface MC carbides and dendritic casting pores. The composition of carbides is confirmed by EDS. The number of carbides or pores present at an initiation site varied from one to several. Carbide and pore sizes were typically within the range of approximately 25 μm to 100 μm. Samples without HIP typically exhibited only one fatigue crack initiation site. Overall, the fatigue initiation behavior was very similar in samples with and without HIP, with the exception of the presence of porosity in some of the no HIP samples. It should also be explicitly stated that some samples that had not been HIPed still did not exhibit casting porosity at the fatigue crack initiation site.

Analysis of both fracture surfaces from the same fatigue bar (referred to as side A and side B in Figure 5-13), reveals mechanistically how fatigue initiation occurs in room temperature IN100. In this example the sample is a bottom filled, vacuum cast, turbulently gated, HIPed and heat treated HCF sample. Opposite faces of the fractographic surfaces generated by fatigue failure show mirror image surface-
connected MC carbides at the initiation sites, as can be seen in Figure 5-13. EDS elemental mapping is very effective in revealing that the entire surface-connected “flat region” bounded by slip bands in both sides A and B is the initiating carbide. This indicates that the fatigue crack initiation event is not occurring at the matrix/carbide interface (or possibly bifilm/carbide interface), but instead occurs from the creation of a through-crack of the MC carbide. It is this through-cracking of the carbide that then propagates and ultimately leads to fatigue failure.

It should be noted that there was no observable difference in fatigue fractography between samples cast with varying turbulence levels. Among vacuum cast samples, the fractography of fatigue samples cast with high levels of turbulence (i.e. with turbulators and top filled) was indistinguishable from fatigue samples cast with low levels of turbulence (i.e. conventionally gated and bottom filled). There was no observed impact on fractography due to the presence, absence, or remediation of bifilms. This result conflicts with current bifilm literature.

**Air Cast**

Fatigue crack initiation in air cast samples was typically quite distinct from vacuum or argon cast samples. Generally, fatigue crack initiation occurred from PSB formation on very large surface-connected Ti oxycarbide inclusions. NMI size ranged from approximately 100 μm up to as large as approximately 1.5 mm. Representative SEM fractography showing an initiating inclusion and PSB formation at the inclusion interface in an air cast sample tested in the as cast condition is shown in Figure 5-14. It should be noted that the inclusions observed are not true oxycarbides, however historically oxycarbide, carbonitride, etc. inclusion stringers have been referred to by this nomenclature. Therefore, although these inclusions are a heterogeneous structure
of discrete oxide and carbide phases, the term oxycarbide is also used in this
dissertation.

The size of the initiating inclusions seems to correlate well with the reduction in
fatigue life for air cast samples. This is an unsurprising result, and it has been well
documented that fatigue life decreases with increasing flaw/inclusion size [85]. The
large range in initiating inclusion size also likely explains the wide relative scatter (i.e.
wide range in fatigue life) seen in air cast fatigue samples. Additionally, there was a
noticeable correlation between fractography and fatigue life. The samples in the high
fatigue life regime were more likely to exhibit no oxycarbide inclusions at all. In absence
of the oxycarbide inclusions, fatigue crack initiation occurred on near-surface or surface-
connected M(Ti, Mo)C carbides. More details are described in the next section “Fatigue
Life Effects on Fractography”. Air cast samples only exhibited one initiation site per
sample, and the initiating inclusion was generally much larger than initiating carbides or
pores in vacuum or argon cast samples. The initiation site relative to the fatigue crack
propagation region observed on fracture surfaces of air cast samples was typically
larger than those observed in vacuum and argon cast samples, and exhibited less
defined deformation bands and ratchet lines. This is likely due to formation of a larger
initiating crack, which requires less propagation to reach the critical crack length
required for overload to occur.

Similar to results observed in tensile samples, the structure of oxycarbide
inclusions observed in fatigue crack initiation sites of air cast fatigue bar fracture
surfaces did not exhibit a change in morphology from the use of HIP. Oxide structures
observed in these inclusions were again patchy and discontinuous for samples in the as
cast condition, as well as samples in the heat treated and samples in the HIP and heat treated conditions. The oxide structure was again found overtop very large M(Ti, Mo)C carbides. Representative fractography of Ti oxycarbide inclusions located at the fatigue crack initiation sites in as cast, heat treated, and HIP and heat treated samples are shown in Figures 5-14 through 5-17. There was no evidence of a change in inclusion structure, inclusion thickening, or evidence of bulk oxide growth. This conflicts with current reports pertaining to the response of bifilms to HIP and heat treatment cycles. It should also be noted that there were still inclusions observed in air cast samples that had been filtered, and there was not a strong correlation between fractographic features and filtering.

**Fatigue Life Effects on Fractography**

In the case of vacuum and argon cast samples, there was no noticeable trend between fatigue life and fractography. Interestingly, the shortest fatigue life vacuum or argon cast sample (79,236 cycles to failure) and the longest fatigue life sample (180,913 cycles to failure) both exhibited fatigue crack initiation at near-surface or surface-connected MC carbides. SEM fractography of the initiation sites for these samples is shown in Figures 5-18 and 5-19. Carbide composition was verified by EDS. There was no apparent trend between the presence of porosity at the fatigue initiation site and fatigue life. There was no evidence of oxide bifilms exhibiting an effect on sample fractography, and therefore there was no evidence for bifilms affecting fatigue life.

There was a noticeable trend between fractography and fatigue life in the case of air cast samples. There was a tendency for fatigue life to be shorter as initiating inclusion size becomes larger, which is not surprising. Furthermore, air cast samples in
the high fatigue life regime were more likely to not exhibit initiation at oxycarbide inclusions at all. Representative initiation sites are shown for the shortest fatigue life sample (16,202 cycles to failure) and the longest fatigue life air cast sample (108,971 cycles to failure) in figures 5-20 and 5-21. In the case of the shortest fatigue life sample, the initiating inclusion was extremely large and surface-connected, measuring approximately 1.5 mm across. The region of the fracture surface containing the NMI is very apparent when viewed via backscatter detection. Oxycarbide inclusion composition was also verified by EDS. In the case of the longest fatigue life air cast sample, fractography actually appeared very similar to that seen in vacuum or argon cast samples, with the primary initiation site exhibiting PSB formation in the vicinity of a near-surface MC carbide. There were also observable secondary initiating carbides with PSB formation. The primary initiating carbide measures only approximately 25 μm across, agreeing with the general trend that fatigue life correlated with initiating particle size. Carbide composition was confirmed by EDS.

These results suggest that the fatigue conditions utilized will preferentially initiate fatigue cracks at surface-connected or near-surface inclusions, carbides, or pores. Since fatigue life was found to decrease with increasing the size of the initiation site microstructural features, it seems likely that fatigue was occurring at the “most preferable” surface feature present in a given test bar. The propensity for fatigue initiation seems to be related to initiator size and orientation. The possible fatigue initiators varied with processing, with Ti oxycarbide inclusions being available for crack initiation in air cast samples and pores being available for crack initiation in no HIP samples. Overall, distribution of fatigue initiators appeared to be a randomized process,
with the fatigue crack initiation event “seeking” the most prone available location for surface initiation. Even though this was the case, none of the investigated samples indicated that the presence of bifilms was creating a preferential location for fatigue crack initiation, or that there was any type of preexisting crack due to bifilms.
Figure 5-1. Mean fatigue life results from varying casting atmospheres and fill conditions. Error bars representative of data set range.

Figure 5-2. Probability plot of fatigue life for all vacuum, argon, and air cast samples. Scatter bands representative of 95% CI.
Figure 5-3. Probability plot of fatigue life for top fill and bottom fill vacuum cast samples. Scatter bands representative of 95% CI

Figure 5-4. Mean fatigue life across casting atmospheres and gating conditions. Mean fatigue life for gating with turbulators and conventionally gated vacuum cast samples. Error bars representative of data set range
Figure 5-5. Probability plot of fatigue life for most turbulent and least turbulent vacuum cast samples. Scatter bands representative of 95% CI

Figure 5-6. Mean fatigue life from varying casting atmospheres and filtering conditions. Mean air cast fatigue life for unfiltered castings and samples utilizing a ceramic filter. Scatter bars representative of data set range.
Figure 5-7. Mean fatigue life from varying casting atmospheres and HIP conditions. Scatter bars representative of data set range

Figure 5-8. Probability plot of fatigue life for vacuum cast samples in the HIP and heat treat condition and heat treated condition. Scatter bands representative of 95% CI
Initiation site 1

Initiation site 2

D/O

E/O
Figure 5-9. Fatigue initiation sites in top fill, vacuum cast, and HIP sample A) Low magnification SEM image of multiple initiation sites B) Fatigue initiation site 1 C) Fatigue initiation site 2 D) EDS spectrum from location shown in B and E) EDS spectrum from location shown in C
Figure 5-10. Fatigue initiation site in bottom fill, argon cast, and no HIP sample A) SEM image of initiation site showing PSB formation on carbides B) EDS spectrum of carbide indicated in A and C) EDS spectrum of carbide indicated in A

Figure 5-11. Fatigue initiation site in bottom fill, vacuum cast, and no HIP sample showing PSB formation on dendritic casting porosity
Figure 5-12. Fatigue initiation site from top fill, turbulently cast, and no HIP sample A) SEM image of initiation site showing PSB formation on carbides and dendritic casting porosity B) EDS spectrum of location indicated in A C) EDS spectrum of location indicated in A D) EDS spectrum of location indicated in A E) EDS spectrum of location indicated in A and F) EDS spectrum of location indicated in A
Figure 5-13. Both fractographic surfaces, sides A and B, taken from the same bottom filled, vacuum cast, turbulently gated, HIPed and heat treated HCF bar A) Side A EDS mapping and B) Side B EDS mapping
Figure 5-14. Fatigue initiation site in air cast sample tested in the as cast condition showing A) BSE image of initiation site and B) SEI of PSB formation on oxycarbide/matrix interface
Figure 5-15. Fatigue crack initiating oxycarbide inclusion located in air cast sample tested in the as cast condition showing A) SEI of discontinuous oxide structure B) EDS spectrum from oxide region and C) EDS spectrum from M(Ti, Mo)C carbide region.
Figure 5-16. Fatigue initiation site in air cast heat treated sample showing A) BSE image of initiation site B) PSB formation on oxycarbide/matrix interface C) SEI of discontinuous oxide structure D) EDS spectrum from carbide region and E) EDS spectrum from oxide region.
Figure 5-17. Fatigue initiation site in air cast HIP and heat treated sample showing A) BSE image of initiation site B) PSB formation on oxycarbide/matrix interface C) SEI of discontinuous oxide structure D) EDS spectrum from carbide region and E) EDS spectrum from oxide region
Figure 5-18. Fatigue crack initiation site in longest fatigue life sample, 180,913 cycles to failure. Argon cast, top fill, and no HIP.
Figure 5-19. Fatigue crack initiation site in the shortest fatigue life vacuum or argon cast sample, 79,236 cycles to failure. Vacuum cast, top fill, and no HIP
Figure 5-20. Fatigue crack initiation site in longest fatigue life air cast sample, 108,971 cycles to failure. HIPed heat treated and filtered.
Figure 5-21. Fatigue crack initiation site in shortest fatigue life air cast sample, 16,202 cycles to failure. Filtered and tested as cast. BSE image showing strong Z-contrast with initiating NMI.
CHAPTER 6
RESULTS: AUGER ANALYSIS

In the literature describing bifilms, fracture surfaces are frequently characterized via SEM/EDS in an effort to identify bifilms during fractographic analysis. This technique allows for adequate analysis of the “thickened bifilms”, however the surface sensitivity of SEM/EDS analysis is inadequate for the characterization of “new bifilms”. Generally, fractographic features that appear to exhibit bifilms are imaged via SEM, and a bifilm is simply assumed to be present (see Chapter 2 for literature review). In fact, such fractographic features have never been investigated by characterization methods with adequate surface sensitivity for analysis of thin oxide films such as Auger electron spectroscopy, x-ray photoelectron spectroscopy, secondary ion mass spectrometry, etc. In this study, these fractographic features, such as cleavage planes, microvoids, fractured carbides, non-metallic inclusions, and dendritic casting porosity were investigated by in situ scanning Auger microprobe fractography of Auger pin samples (see Chapter 3 for procedure details). Each of these fracture locations have been stated to form due to the presence of bifilms [2-7, 9-11, 17, 19, 55, 57-59, 64], and existing publications include examples of these fractographic features said to exhibit bifilms [4, 19, 57, 64]. Auger analysis is an ideal technique for investigation of these features, as it allows for extremely surface sensitive (< 1 nm) chemical characterization following in situ fractography, unambiguous detection of monolayer films, and accurate depth profiling of chemical composition.

Fractographic analysis was conducted by fracturing up to 7 Auger pins extracted from every blade casting condition (refer to Figure 3-5 for a list of casting conditions). Each of these blade conditions were evaluated for the presence of bifilms and oxide
inclusions. Sample fracture occurred under ultrahigh vacuum conditions, with nominal pressures of less than 0.5 nTorr. Analysis was conducted for approximately 3 hours per sample. Slow gettering of residual oxygen does occur, even in ultrahigh vacuum conditions. Once evidence of gettering became apparent, analysis was terminated. Gettering is observable by the development of a detectable oxygen peak in AES spectra taken from control regions of fractographic surfaces (i.e. regions not containing oxides or inclusions). Control regions were analyzed immediately following fracture to serve as a baseline, and consistently exhibited no measurable oxygen peak. This allowed for objective determination of whether a detected oxygen peak was due to gettering or the presence of an oxide film.

**Cleavage Planes**

Cleavage planes from each blade condition were characterized in an effort to determine if such fractographic features had formed due to bifilm splitting. In all of the Auger pins fractured and all of the cleavage planes analyzed in each pin, none exhibited AES spectra indicative of an oxide film. In fact, all cleavage planes investigated generated AES data that is indistinguishable from matrix material. This is true for samples in all casting conditions, even for air cast and top filled samples which are reported to be ideal conditions for bifilm formation. This result is highly significant and indicates that fractographic features such as those shown in many publications pertaining to bifilms, very likely cannot be considered to be due to bifilm splitting. These features are more than likely formed due to the classic theory of crack propagation along a favorable crystallographic, textural, or carbide cluster orientation, and are actually unrelated to the presence of an oxide film. A side-by-side comparison in Figure 6-1 shows a given cleavage plane examined by the in situ Auger fractography method,
and is compared to a similar feature reported in a publication stating that this type of fractographic feature is caused by bifilms. However, the corresponding AES spectrum does not indicate an oxide film. Additionally, representative fractography and AES spectra from vacuum, argon, and air cast samples are shown in Figures 6-1 and 6-2.

**Microvoids and Fractured Carbides**

Significant microvoid formation was observed in fractured Auger pins, similar to tensile fractography observed via SEM. Also similar to tensile fractography, microvoid formation was observed to be due to fractured MC carbides. Some publications have theorized that MC carbide brittleness may be due to nucleation on bifilms [3, 4, 6], and SAM/AES allowed for reliable investigation of this claim. In all of the Auger pins fractured and all of the microvoids analyzed in each pin, no fractured carbides exhibited AES spectra indicative of an oxide film. Every fractured carbide characterized yielded an AES signal with substantial C, Ti, and Mo peaks, but did not indicate the presence of an oxide or yield observable O or Al peaks. Quantified AES spectra generally yielded carbon content close to ideal stoichiometry of approximately 50 at% C. Some Ni was still detectable in locations where fractured carbides were analyzed, likely due to the limited spatial resolution of SAM/AES and relatively small size of the carbides. Figures 6-3 through 6-5 show representative fractured carbides in microvoids for vacuum, argon, and air cast samples.

The absence of an oxide film is true for samples in all casting conditions, even air cast and top filled samples. This result indicates that even in conditions where abundant bifilm formation is predicted, fractured carbides observed in fracture surface microvoids cannot be considered to be due to bifilm embrittlement. It is well known that carbide
precipitates possess limited ductility, and it seems more than likely that carbide nucleation on bifilms is not the correct mechanism to explain carbide brittleness.

Dendritic Porosity

In the case of no HIP samples, dendritic porosity was visible on the fracture surface of Auger pins. Some publications have claimed that bifilms are a primary source of casting porosity, and have stated that the surface of dendritic casting pores exhibit oxide films [2-5, 7, 9-11, 17, 19, 55, 58, 59]. However, this assertion has never been confirmed, and SAM/AES fractography allowed for reliable investigation of dendritic porosity surface composition. In all of the Auger pins fractured and all of the dendritic pores analyzed in each pin, no pores exhibited AES spectra indicative of an oxide film. Surprisingly, there was a ubiquitous sulfur-rich layer identified on the surface of casting porosity. Every dendritic casting pore analyzed exhibited an AES spectrum with a distinct sulfur peak. An example of this is shown in Figure 6-6. The reasons for formation of a sulfur-rich layer are not certain, and require substantial further investigation.

Compositional mapping of sulfur indicated that the sulfur layer is also continuous, and covers the entire pore surface. This is shown in Figure 6-7B. Furthermore, every pore mapped for sulfur content in this way also shows a continuous sulfur layer covering the pore surface. Auger depth profiling shown in Figure 6-7D indicated that the sulfur-rich layer is extremely thin, and is approximately a monolayer. Precise measurement of thickness is not possible by this method of depth profiling, however sputter times for depth profiling can be approximately compared to milling rates of a Ta$_2$O$_5$ standard of known thickness. The sputter conditions used produced a milling rate of 2.5 nm/min on a Ta$_2$O$_5$ standard, and the sulfur rich layer was removed in approximately 1 min of
sputter time. This indicates an approximate thickness of 2-3 nm, however this assumes that Ta$_2$O$_5$ possesses equal milling rates to IN100, which is not necessarily true. Furthermore, this also assumes perfectly uniform material removal, which is also not true. Due to spatial resolution limitations, and material removal non-uniformity, it is likely that a sulfur-enriched monolayer is the actual morphology of the observed structure. Post-sputter AES spectra were similar to spectra obtained from base metal. The cause of this sulfur layer is uncertain, although it is clear that oxide films are absent from the surface of dendritic casting pores in all materials analyzed. These results indicate that the dendritic porosity formed in all of the conditions considered was not due to the presence of bifilms. It can be concluded that observed porosity was due to dendritic shrinkage and limited interdendritic flow of molten fluid in the semisolid mushy zone during solidification.

**Oxycarbide Inclusions**

In some air cast samples, Ti oxycarbide inclusions could be observed on the fracture surface of some Auger pins. It should be noted that the inclusions observed are not true oxycarbides, however historically oxycarbide, carbonitride, etc. inclusion stringers have been referred to by this nomenclature. Therefore, although these inclusions are a heterogeneous structure of discrete oxide and carbide phases, the term oxycarbide is also used in this dissertation. The appearance and morphology of these inclusions was very similar to tensile and fatigue SEM fractography results. Discontinuous oxide structures were identified overlaying very large M(Ti, Mo)C carbides. Furthermore, these types of large inclusions were the only instance in which any form of oxide structure could be identified in a fractured Auger pin. SAM imaging was relatively poor in resolution capabilities comparative to SEM, so for clarity an SEM
image of an oxycarbide inclusion identified in a post-analysis fractured Auger pin is shown in Figure 6-8. SEM and SAM imaging indicates that the oxide is patchy and discontinuous as opposed to a continuous film, as seen if Figures 6-8 and 6-9A. AES spectra indicate that there are distinct oxide-rich and carbide-rich locations, as seen in Figures 6-9C and 6-9D. Due to spatial resolution limitations there is some signal blending between these locations whereby oxide regions exhibit some carbide signal and carbide regions exhibit some oxide signal. However, considering the surface sensitivity of AES, these results do indicate that this structure is heterogeneous, and exhibits distinct oxide and carbide phases.

Depth profiling of oxycarbide inclusions was performed to determine if the inclusion structure observed during fractography is layered similarly to inclusion structures identified in metallographically prepared samples (see Chapter 7). This form of surface sensitive depth profiling would also allow for detection of phases that may be in the morphology of a thin interfacial film, which could have been previously undetected. Additionally, the thickness of each phase can be estimated by this technique. A representative depth profile is shown in Figure 6-9E. It can be seen that the inclusion structure exhibits 3 distinct phases, which are layered as follows: Al₂O₃ / M(Ti, Mo)C carbide / Ni-matrix. Precise measurement of thickness is not possible by this method of depth profiling, however sputter times for depth profiling this inclusion can be approximately compared to milling rates of a Ta₂O₅ standard of known thickness. The ion beam conditions used produced a milling rate of 52 nm/min using a Ta₂O₅ standard. The alumina layer was removed in approximately 7.75 mins of sputter time, and the carbide layer was removed in approximately 12.5 mins of sputter time.
This indicates that the alumina layer is approximately 400 nm in thickness, and the MC carbide layer is approximately 650 nm in thickness. These results agree with other characterization methods used in the study of oxycarbide inclusions in this dissertation.

The type of oxycarbide characterized is very similar in morphology to other inclusions identified in Ni superalloys that have been reported to be thickened bifilms \[3, 6\]. However, in absence of any substantial evidence of the thin, or “new”, bifilm it is not possible to state that these oxycarbide inclusions have formed from thickening of a new bifilm precursor. Furthermore, the oxides identified in this study were found to be one to two orders of magnitude thicker than the predicted thickness of an oxide bifilm. The oxides observed were also not similar in morphology to an oxide bifilm, and were not observed to be continuous films. Morphology of these oxides was also unaffected by exposure to HIP and/or heat treatment. Given these observations, it is more likely that the oxides observed in these non-metallic inclusions are actually dross inclusions, consisting of solid alumina, as opposed to an unbound bilayer of oxide films. As will be discussed (see Chapters 7 and 8), it is also likely that the presence of dross inclusions has created favorable conditions for abundant MC carbide nucleation.
Figure 6-1. In situ Auger fractography of cleavage plane similar to surface feature identified in previous study as an unraveled bifilm A) SAM image of cleavage plane in top fill, vacuum cast, HIP and heat treat sample B) SEM image of surface feature identified as a bifilm C) SAM image of location in A rotated 30° and D) AES spectrum of cleavage plane in C

[Part B reprinted with permission from Dispinar et al., 2011, "Porosity, Hydrogen and Bifilm Content in Al Alloy Castings," Mater. Sci. Eng. A, 528(10-11), p. 3862, Fig. 4]
Figure 6-2. In situ fractography of cleavage planes in representative samples A) Bottom filled, argon cast, and as cast sample B) Top filled, air cast, and as cast sample C) AES spectrum of location indicated in A and D) AES spectrum of location indicated in B
Figure 6-3. In situ fractography of microvoid formation on fractured MC carbide in vacuum cast, bottom filled, turbulently cast, HIP and heat treated sample A) SAM image of location analyzed and B) AES spectrum and compositional quantification of location indicated in A
Figure 6-4. In situ fractography of microvoid formation on fractured MC carbide in argon cast, bottom filled, and as cast sample A) SAM image of location analyzed and B) AES spectrum and compositional quantification of location indicated in A.
Figure 6-5. In situ fractography of microvoid formation on fractured MC carbide in air cast, top filled, and as cast sample A) SAM image of location analyzed and B) AES spectrum and compositional quantification of location indicated in A.
Figure 6-6. In situ fractography of dendritic casting porosity in top filled, air cast, as cast sample A) SAM image of location analyzed and B) AES spectrum of location indicated in A.
Figure 6-7. In situ fractography of dendritic casting porosity in bottom filled, vacuum cast (with turbulators), and heat treated sample A) SAM image of location analyzed B) AES mapping of sulfur content in location shown in A C) Pre-sputter AES spectrum of location indicated in A D) Elemental depth profile of location indicated in A. Sputter conditions used produced a mill rate of 2.5nm/min on a Ta$_2$O$_5$ standard E) Post-sputter AES spectrum of location indicated in A
Figure 6-8. SEM image of oxycarbide inclusion identified in fractured Auger pin extracted from air cast, top filled, HIP and heat treated sample showing heterogeneous inclusion structure.
Figure 6-9. In situ fractography of oxycarbide inclusion in air cast, top filled, HIP and heat treat sample A) SAM image of inclusion before depth profiling B) SAM image of inclusion post-sputter C) AES spectrum of region indicated in A D) AES spectrum of region indicated in A E) Elemental depth profile of oxide region analyzed in D. Sputter conditions used produced a mill rate of 52 nm/min on a Ta₂O₅ standard and F) AES spectrum of region indicated in B.
CHAPTER 7
RESULTS: OXYCARBIDE CHARACTERIZATION

Ti oxycarbide inclusions can be observed in superalloys that have been exposed to excessive amounts of oxygen during liquid processing [31]. In this study Ti oxycarbide NMIs were observed in the fractography of some air castings, as well as stringer inclusions in the microstructural analysis of some air castings. Oxycarbide inclusion clusters were not observed in all air castings, and their presence in fracture surfaces and microstructures appeared to be the result of random probabilistic events. However, the morphology of these inclusion structures did appear to be strikingly similar to inclusions in current literature reported to be due to thickened bifilms [2-4]. A side-by-side comparison can be seen in Figure 7-1. It should be noted that the inclusions observed are not true oxycarbides, however historically oxycarbide, carbonitride, etc. inclusion stringers have been referred to by this nomenclature. Therefore, although these inclusions are a heterogeneous structure of discrete oxide and carbide phases, the term oxycarbide is also used in this dissertation.

When observed metallographically, such inclusions frequently exhibited the appearance of being a tangled cluster of stringer inclusions. In current literature, tangled clusters of inclusion stringers have been identified as thickened, or “old”, bifilms [2-4]. This operates based on the assumption that such clusters of inclusions are forming from bulk oxide growth of the “new” bifilm precursors, with thickening occurring during exposure to elevated temperatures (see Chapter 2). Although, it should be noted that such inclusions are not necessarily identified as oxycarbides, but are often reported to be thickened oxide bifilms. For several reasons, it seems unlikely that this could be the case for inclusions identified in this study. One primary reason is that inclusion
structures that appeared similar to “thickened bifilms” were observable in as-cast alloys. As-cast alloys would provide nearly no time for bulk thickening of internal oxides, aside from cool-down time following casting, so it seems highly unlikely that such inclusions could be due to bulk oxide thickening. Additionally, inclusion structures appeared unchanged between as-cast alloys and alloys that had been HIPed and heat treated. However, since the inclusion structures observed metallographically in this study appear very similar in morphology to such inclusions identified as thickened bifilms, it was decided that further characterization would be necessary to determine if evidence of a thickened bifilm could be identified.

**SEM Metallography**

Samples where oxycarbide inclusions had been identified during metallographic analysis have been selected for further study. It was immediately noted that backscatter imaging showed strong contrast with the inclusion structures, as seen in Figure 7-2. This is undoubtedly atomic number contrast, showing that the inclusion cluster is rich in lower atomic number elements as compared to the surrounding matrix. To elucidate this structure, EDS line-scanning was performed, as seen in Figure 7-3. It is also interesting to note that when analyzed metallographically, the alumina phase appears dark in secondary electron imaging. This was unexpected, since when viewed fractographically the alumina phase typically appears bright and will charge under the electron beam.

Previous EDS spot analysis has shown that this type of structure is rich in Ti, Mo, C, Al, and O and was identified as M(Ti, Mo)C carbide and alumina (also see Chapters 5 and 6). The current analysis confirmed these results. These phases, identified as TiC (with some substitutional solubility for Mo) and Al₂O₃, create the following layered structure: Ni-matrix/TiC/Al₂O₃/TiC/Ni-matrix. This structure is very intriguing, as bifilms
are theorized to be a nucleation site for MC carbides. In this case, an alumina inclusion does appear to be acting as a nucleant for MC carbides. Therefore, this type of inclusion structure required further investigation.

**Deep Etching**

In some cases, Ti oxycarbide inclusion stringers appear metallographically to be a layered structure of M(Ti, Mo)C carbide, and in other cases only a stringy morphology of MC carbide is observable. Therefore, some air cast samples displaying these stringy NMIIs were deep etched in order to elucidate the 3-dimensional structure of the oxycarbide inclusions. Deep etching revealed that the Ti oxycarbide stringer inclusions only appear stringy and layered when metallographically polished. The deep etched inclusions actually consisted of clusters of very fine blocky M(Ti, Mo)C carbides (confirmed by EDS in Figure 7-8) as shown in Figure 7-4. This indicates that the subsurface morphology of stringer inclusions is actually a collection of micron scale carbides, measured to be approximately 1 μm or less in diameter.

Samples prepared for deep etching had to first be metallographically polished in order to locate oxycarbide inclusion clusters. In some locations of the deep etched inclusion, the previously polished surface could still be observed. It was noted that the previously polished surfaces appeared to exhibit the presence of an internal alumina core, as shown in Figure 7-5. However, the structure that had been subsurface prior to deep etching did not exhibit alumina in any location. In fact, a morphology of fine blocky carbides was the only structure revealed in such subsurface inclusion clusters. Considering that deep etching did not reveal an alumina structure, and that alumina was only visible in portions of the inclusion structure that had been polished into, it seems apparent that the alumina is actually completely internal to the oxycarbide inclusion.
This would indicate that the M(Ti, Mo)C carbide is enveloping an internal alumina phase.

In an effort to pinpoint the location(s) of the internal alumina core, EDS mapping was utilized and can be seen in Figure 7-6. Elemental maps revealed that the inclusion structure is rich in carbide-forming elements Ti, Mo, and C, and also indicated that the inclusion structure is mostly devoid of Ni. However, EDS mapping also revealed that the inclusion structure is rich in aluminum, which would not be possible if the inclusion consisted only of blocky carbides. This also indicates that there is some internal alumina structure to the inclusion, indicated because signal generation is occurring in subsurface material up to 1 μm in sample depth. However, due to surface sensitivity and spatial resolution limitations, EDS mapping was not capable of indicating precise locations of internal alumina with acceptable resolution. The likely reason why the internal alumina could not be resolved is because the appearance of the internal alumina film was strongly influenced by accelerating voltage used. Low accelerating voltages could not be used for mapping, since these conditions did not produce adequate CPS for reasonable signal generation. However, as seen in Figure 7-7, the internal alumina film is only visible while utilizing lower accelerating voltages, likely due to changes in surface sensitivity and spatial resolution. Unfortunately, a 30 KeV accelerating voltage had to be used in order to generate an elemental map in a reasonable span of time. EDS spot analysis was also used in an effort to characterize the internal alumina film, and can be seen in Figure 7-8. EDS spectra and semi-quantitative analysis both indicate an enrichment of Al and O at the location of the internal alumina film, but are again limited
by spatial resolution. Use of a larger EDS detector would likely enable adequate EDS mapping while using reduced accelerating voltages.

**TEM Analysis**

To further elucidate the structure of the internal alumina in the Ti oxycarbide inclusions, and determine if the internal alumina could be a bifilm, an oxycarbide inclusion observed in an air cast sample prepared for metallography was removed via FIB lift-out. This would allow for TEM examination of a cross section of the inclusion structure, which was deemed necessary due to the spatial resolution limitations of SEM.

**FIB Removal**

An air cast IN100 sample was prepared metallographically, and an oxycarbide stringer location was selected for FIB lift-out. The precise location chosen for examination can be seen in Figure 7-9. Ion beam imaging yielded strong contrast between the MC carbide phase and internal alumina phase, clearly indicating the location of each. It is interesting to note that the oxycarbide inclusion seen in Figure 7-9 was observed in an air cast IN100 sample in the HIP and heat treated condition, whereas the oxycarbide inclusion seen in Figures 7-2 and 7-3 was observed in an as-cast air cast IN100 sample. This shows that the oxycarbide inclusions did not appear to be affected by HIP and heat treatment cycles, which indicates that the NMIs were invariant to exposure to elevated temperatures.

**STEM Analysis**

A STEM image of the sample removed by FIB lift-out can be seen in Figure 7-10, showing a profile view of the Ti oxycarbide inclusion. EDS analysis of the location can also be reviewed in Figure 7-10. An EDS line-scan of the sample yields results that are in agreement with Auger depth profiling (see Chapter 6), indicating that the layered
structure (in this case viewed in profile, orthogonal to the plane of metallographic imaging) is Ni-matrix, an outer inclusion layer of TiC, and internal alumina. The sum spectrum shown indicates the presence of magnesium. The presence of Mg in an inclusion is often indicative that there had been a mold/metal interaction, with the molten superalloy stripping (deoxidizing) Mg content from the melt crucible resulting in trace Mg content [32]. In this case, trace Mg content in the alloy likely originates from a mold/metal interaction occurring during master alloy manufacture.

**BF-TEM and HR-TEM Analysis**

A BF-TEM image of the sample removed by FIB lift-out can be seen in Figure 7-11, showing several internal boundaries. These boundaries are shown by HR-TEM to be grain boundaries in Figure 7-12. These results indicate that the Ti oxycarbide inclusion is comprised of very fine external M(Ti, Mo)C carbides and fine polycrystalline (< 100 nm grains) internal alumina. It also should be noted that there is not an indication of pre-existing cracks due to bifilms at these interfaces. In fact, every interface investigated by HR-TEM was clearly bound and exhibited a visible grain boundary. This result strongly contradicts the notion that this inclusion structure can behave as a pre-existing crack. The internal alumina did exhibit a visible void in Figure 7-11, though it is unclear if this is from thinning during sample preparation. However, the discontinuous nature of the alumina has been previously noted during fractographic analysis (see Chapters 5 and 6).

Much of the internal alumina core appears to be multiple grains in width. As seen in Figure 7-11, the internal alumina is typically 1-3 grains across in this sample, depending on location. However, it is important to note that some locations of this sample clearly contain a single grain spanning the width of the internal alumina
structure. An example of this is shown in Figure 7-13. This indicates that the internal alumina was not formed from a bilayer of alumina films that have been sintered together, which seems to rule out the possibility that it had formed from an oxide bilayer behaving as a precursor. A more likely explanation is that the internal alumina had actually formed during molten processing as a bound polycrystalline dross inclusion, not an unbound bilayer.
Figure 7-1. Nonmetallic inclusions showing A) Thickened bifilm prepared metallographically B) SEM metallography of Ti oxycarbide inclusion cluster in air cast, top filled, as-cast IN100 tensile sample C) Fatigue crack initiating from an old bifilm in sand cast aluminum alloy and D) SEM fractography of Ti oxycarbide inclusion in air cast, top filled, HIP and heat treated IN100 fatigue sample

[Part A reprinted with permission from Campbell, 2006, "Entrainment Defects," Mater. Sci. Tech., 22(2), p. 129, Fig. 4]  
[Part C reprinted with permission from Wang et al., 2006, "Oxide Films, Pores and the Fatigue Lives of Cast Aluminum Alloys," Met. Trans. B, 37(6), p. 888, Fig. 1a]
Figure 7-2. BSE imaging of inclusion cluster shown in Figure 7-1b exhibiting strong Z-contrast
Figure 7-3. SEM metallography of layered structure in Ti oxycarbide inclusion in air cast, top filled, as-cast tensile sample. EDS line-scan location and data shown.
Figure 7-4. SEM imaging of deep etched Ti oxycarbide inclusion clusters in air cast, top filled, as-cast IN100 tensile sample revealing a fine blocky morphology
Figure 7-5. SEM imaging of deep etched Ti oxycarbide inclusion in air cast IN100 with previously polished surface and internal alumina film visible.
Figure 7-6. EDS mapping of deep etched oxycarbide inclusion showing A) Field of view B) Carbon C) Molybdenum D) Titanium E) Aluminum and F) Nickel
Figure 7-7. SEM imaging of deep etched oxycarbide inclusion imaged with accelerating voltage equal to A) 5 KeV B) 15 KeV C) 20 KeV D) 30 KeV
Figure 7-8. EDS spot analysis of deep etched oxycarbide inclusion showing A) Field of view B) MC carbide EDS spectrum and C) Internal alumina EDS spectrum

Table 7-1. Semi-quant EDS analysis of spots indicated in Figure 7-8

<table>
<thead>
<tr>
<th>Spectrum (at%)</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Mo</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Co</th>
<th>Ni</th>
</tr>
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<tr>
<td>B</td>
<td>68.56</td>
<td>---</td>
<td>1.08</td>
<td>7.11</td>
<td>17.64</td>
<td>1.04</td>
<td>0.80</td>
<td>0.80</td>
<td>2.97</td>
</tr>
<tr>
<td>C</td>
<td>42.87</td>
<td>26.43</td>
<td>4.2</td>
<td>5.03</td>
<td>13.31</td>
<td>---</td>
<td>1.23</td>
<td>1.37</td>
<td>5.57</td>
</tr>
</tbody>
</table>
Figure 7-9. Stringy Ti oxycarbide inclusion chosen for FIB lift-out A) Ion beam imaging of inclusion showing good contrast between internal alumina and TiC layers and B) Ion beam imaging showing the exact region selected for FIB lift-out
Figure 7-10. Analysis of layered oxycarbide inclusion showing A) STEM image showing inclusion structure and line-scan location B) EDS line-scan indicating the layering in the inclusion structure and location of each phase and C) EDS sum spectrum generated from line-scan location indicated
Figure 7-11. BF-TEM imaging of sample extracted from oxycarbide inclusion
Figure 7-12. HR-TEM imaging of locations indicated in Figure 7-11 showing A) Alumina/alumina boundary B) Alumina triple point C) Alumina TiC boundary and D) TiC/matrix boundary
Figure 7-13. BF-TEM analysis of internal interfaces in oxycarbide inclusion showing a region of internal alumina that is a single grain between TiC layers.
CHAPTER 8
DISCUSSION

The Ni-based superalloy IN100 has been mechanically tested and characterized in a wide variety of sample conditions in an effort to identify the significance of oxide bifilms in the behavior of this material. Following extensive analysis, it was not possible to directly characterize oxide bifilms, and it was also not possible to observe the effect of oxide bifilms on the mechanical behavior of IN100. It was not possible to identify oxide bifilms as a mechanism for sample fracture in any testing method used. It is proposed that oxide bifilms are not a prevalent phenomenon in the microstructure or have any effect on the mechanical behavior of IN100. In the absence of oxide bifilms, explanations for observed material behaviors are given herein. Additionally, the significance of the results generated and conflicts with existing reports will be discussed.

Casting Atmosphere

Casting atmosphere was found to have a substantial impact on the mechanical behavior of IN100, and significantly affected tensile elongation, ultimate tensile strength, and fatigue life. The important variable between the casting atmospheres used was the relative amount of oxygen present in the melting and casting chambers. In the case of vacuum casting, nominal vacuum levels were maintained at $< 15$ mTorr. Through the analysis of this study, it can be determined that this was adequate in preventing the formation of undesirable inclusions. In the case of argon casting, the vacuum was “broken” by introducing argon to nominal pressures of 10 Torr. The introduction of argon and subsequent increase in nominal pressures did not have an apparent effect on the formation of dross inclusions. Air casting, however, was found to promote the formation
of deleterious oxycarbide inclusions. The relationship between oxygen content and inclusion formation is not surprising, and has been thoroughly studied during the early introduction of vacuum metallurgy to Ni-based superalloys during the 1940’s and 1950’s. However, the significant observation in this study is that the increase in oxygen content and subsequent reduction in properties was related to the formation of typical nonmetallic inclusions but not oxide bifilms.

**Tensile Response**

The tensile behavior in vacuum cast, argon cast, and some high-strength air cast samples was dominated by the formation of microvoids in the vicinity of fractured M(Ti, Mo)C carbides. Tensile behavior between vacuum and argon cast samples did not change significantly, and were indistinguishable from each other. Tensile fracture in low-strength vacuum and argon samples were not mechanistically distinct from tensile fracture in high-strength vacuum and argon cast samples. No vacuum or argon cast tensile samples exhibited any evidence of tensile behavior being an inclusion dominated material response. Furthermore, Auger analysis indicates that the fractographic features observed do not exhibit oxide films of any thickness (further discussion is included in the “Fracture Mechanisms” section). There are some reports that have suggested that the presence of bifilms in vacuum processed Ni-based superalloys can limit material ductility [3, 6]. Given the results of this study, however, it is proposed that such reports may have actually been examining Ni-based superalloy that was processed using inadequate vacuum systems and/or casting practices. As will be further discussed in the “Oxycarbide Inclusions” section, the type of inclusions observed in a “vacuum investment cast superalloy” [6] are remarkably similar to the inclusions identified in the fractography of air cast superalloy in the contents of this dissertation. In the 2004 study
of Rashid et al., inclusions identified in the investment cast superalloy were stated to be thickened bifilms. However, given the results presented in this study it seems more likely that this was actually a misidentified oxycarbide inclusion. In the case of vacuum/inert processed IN100 in this research, no such inclusions were observed.

Tensile fracture behavior in low-strength air cast samples, however, was dominated by the presence of large oxycarbide inclusions acting as stress concentrators. These inclusions created an apparent bimodal distribution in air cast UTS and tensile elongation data. The bimodal mechanical response indicates that the presence of inclusions created a disruptive shift in tensile behavior, as opposed to a single continuous response in properties. This disruptive behavior at first seems to indicate a binary material response. This involves a substantial reduction in UTS and elongation occurring if NMIs are present, and behavior typical to vacuum/inert processed material if inclusions are not present. Interestingly, UTS and elongation were not perfectly accurate in predicting the presence/absence of inclusions in fractography of some tensile samples, and some high-strength tensile samples still exhibited the presence of large (approximately 500 μm) inclusions. This indicates that there may not be a simple binary material response to the presence/absence of inclusions, and that other variables such as inclusion size, orientation, morphology, number, density, and/or location in the tensile bar may also be influencing behavior. The utilization of 3-dimensionally resolved characterization techniques with large sample volumes, such as x-ray tomography, may be useful in future studies to determine the critical variables for inclusion structure as a predictor of tensile embrittlement.
Fatigue Response

Fatigue crack initiation in vacuum cast, argon cast, and high fatigue life air cast samples was dominated by the presence of near-surface porosity and/or the formation of through-cracking in the bulk of surface-connected or near-surface M(Ti, Mo)C carbide(s). Persistent slip band formation was evident in the vicinity of these features, and fractography indicated crack growth occurring radially outward from these locations. No vacuum or argon cast fatigue samples exhibited any evidence of fatigue behavior being an inclusion dominated material response. There have been some studies suggesting that fatigue life of vacuum cast superalloys is dominated by the presence of bifilms. Given the results of this work, it is suggested that the use of bifilms to explain fatigue behavior in Ni-based superalloys is not correct. For example, one study of “Bifilm Defects in Ni-based Alloy Castings” [3] suggests that thermo-mechanical fatigue failure is only possible in the presence of a bifilm. The authors further assert that fatigue crack initiation in superalloys is generally a bifilm controlled process, with the bifilm behaving as a preexisting crack. There was a lack of supporting evidence presented by Campbell et al. to validate this claim, and a lack of any observation in this study that IN100 fatigue is a bifilm-dominated process. It is likely that although the authors may have expected fatigue in superalloys to be bifilm related, this claim is essentially unsubstantiated, whereas the results of this study has provided compelling evidence to indicate that fatigue in superalloys is not bifilm related.

Fatigue behavior in low fatigue life air cast samples, however, was dominated by the presence of oxycarbide inclusions acting as stress concentrators and brittle crack initiators. This is not a surprising result, as it has been shown in previous work that room temperature fatigue life of Ni-based alloys decreases with increasing inclusion size [49,
54, 86]. Additionally, it is well documented that a large proportion of a high cycle fatigue sample’s lifetime is in the crack initiation regime, with relative time initiating a fatigue crack being inversely proportional to overall fatigue life [87]. If a large and brittle stress concentrator is present in the material, it is unsurprising that fatigue life would be reduced, likely by reducing the time for fatigue crack initiation to occur.

Interestingly, air cast samples did not exhibit a bimodal distribution in fatigue life. Unlike tensile elongation and UTS, which both did exhibit bimodal distributions, fatigue life showed a continuous reduction in fatigue life that was proportional to inclusion size. The shortest fatigue life air cast samples exhibited the largest inclusions, intermediate fatigue life samples exhibited smaller inclusions, and the longest fatigue life air cast samples exhibited no oxycarbide inclusions. This indicates that fatigue behavior testing was sensitive to the presence of inclusions, and that the primary factor in determining the fatigue life of inclusion-containing samples was inclusion size. It is important to clarify that since room temperature fatigue behavior was sensitive to the inclusion content of IN100, it would follow that room temperature fatigue behavior would also be sensitive to bifilm content. However, this was not determined to be the case. This will be discussed further in the “Casting Turbulence” section below.

**Casting Turbulence**

**Material Response**

 Casting turbulence was not found to have a substantial impact on any of the examined material behaviors. There was no trend observed in tensile elongation, yield stress, UTS, or fatigue life as a function of casting turbulence in vacuum processed IN100. Furthermore, there was no correlation between fractography or microstructures with casting turbulence in vacuum processed IN100. Room temperature fatigue testing
was shown to be sensitive to inclusion size, with fatigue life being inversely proportional to inclusion size. However, there was no measurable trend between turbulence and fatigue life. There are only two possible explanations for this behavior. Either there were no bifilms present in any of the samples tested, or bifilms were not an active mechanism in the fatigue behavior of vacuum processed IN100. In either case, it is clear that there was no observed risk of fatigue failure due to the presence of bifilms. This is very contradictory to existing research, which states that bifilms can form in turbulently vacuum investment cast Ni-based superalloys, and that the presence of bifilms are highly detrimental to fatigue life [2, 3, 6]. 

Room temperature tensile fracture was also shown to be affected by the presence of inclusions, though the relationship was less clear than in the case of room temperature high cycle fatigue. Since tensile properties also showed no relationship with casting turbulence, it can be stated that either bifilms were not present in the tensile materials tested, or bifilms had no impact on tensile fracture. This must be the case as bifilms have been described as being extremely detrimental to tensile properties of superalloys [2-6], and bifilms are reportedly formed due to casting turbulence [2, 4, 7, 16, 55], but there was no observable effect on tensile properties due to turbulence in this study. Additionally, Auger analysis did not indicate the presence of nanometer thickness oxide films on the fracture surface of samples cast in any condition regardless of turbulence. Further, all of the samples exhibited very similar fractographic surface features. Considering these results, it is clear that there is no observed risk of tensile failure due to the presence of bifilms. This is also contradictory to previous reports, which conclude that bifilms are detrimental to tensile properties [2-6].
Existing Technologies

It should be stated that the effects of casting turbulence on air processed IN100 have not been extensively investigated in this study (see Figure 3-5). The interest of the current investigation centered on the effects of casting turbulence on vacuum processed IN100, since IN100 is vacuum processed when cast in industry. Air casting was investigated primarily as an attempt to force bifilm formation if not observed in vacuum processed alloys. However, the reduction of turbulence and/or use of bottom filling systems have been shown to produce some measurable improvements in certain air cast alloys. Additionally, bottom filling is by no means a new technology, and has been a mature process for the production of steel ingots since at least as early as 1920 [88]. The reduction of turbulence and bottom filling while teeming steel during ingot production by the open hearth process improved surface quality by reducing the likelihood of the formation of oxide “scabs” on the surface of the ingot. It has been shown that the surface quality of some grades of steel can be improved by bottom filling during open hearth processing [89, 90], however bottom filling has also been noted to increase cost and increase the likelihood of the formation of nonmetallic inclusions in certain steel alloys [90]. The source of the additional inclusions is reportedly due to increased contact with refractory materials from the necessarily longer gating and runner systems used during bottom filling. This allows for more opportunity for ceramic inclusions from fractured refractories and/or more opportunity for metal/refractory reactions (i.e. stripping, erosion, deoxidizing, etc.) to occur due to the increased contact of the molten metal with the refractory. In the case of certain air cast alloys, bottom filling has been reported to reduce entrapped gas porosity and the incorporation of dross inclusions [91-93].
Cost

There are numerous impediments to implementation of bottom filled casting designs in industrial vacuum investment casting of Ni-based superalloys. The primary barrier is cost, which can be broadly considered categorically as inherent cost, transitional cost, and opportunity cost. The inherent cost refers to the fact that bottom filled casting designs are inherently more expensive than castings that utilize a top filled design. This is due to the fact that very large gating and runner systems must be employed to ensure adequate mold filling (see Figure 2-13). Simple hydrostatic relationships dictate that the fluid height in the gating system must be at least equal to the mold height, and reducing gating height would cause incomplete mold filling. Additionally, in order to provide molten metal feeding, in practice the gating height would need to be considerably greater than the mold height. Furthermore, there exists a minimum gating diameter as dictated by the fluidity of the melt and necessary mold filling times, so the gating and runner diameter cannot be simply reduced to reduce waste. The necessarily large gating and runner sections represents an inherent inefficiency of bottom filled casting designs, which decreases productive efficiency by increasing material waste. This decrease in casting efficiency, by increasing scrap generation, represents a considerable cost to the casting industry.

The transitional cost refers to the fact that casting procedures would need to be changed, which requires retooling, redesign of molds, structural changes to casting equipment, rewriting procedural documents such as standard operating procedures, retraining of engineers and technicians, etc. This broad change in casting practices represents a very large cost to the superalloys investment casting industry. The opportunity cost refers to the fact that process optimization will be time consuming. This
is due to the fact that the new casting procedures will inevitably need time for iterative improvement, and will therefore be operating at decreased productivity until the processes have been optimized. This reduction in total output represents a cost in that, for a given span of time, a casting vendor will be producing fewer parts, at higher cost, than would be the case if casting practices were unaltered. Clearly, given all the additional costs mentioned, it would be necessary to demonstrate a considerable improvement in properties, reliability, rejection rate, etc. to justify the additional cost of bottom filled casting designs. However, as has been discussed in this chapter, there was no observed benefit to bottom filling. Given that this is the case, it does not seem advisable that expensive precautions be taken to avoid bifilm formation in vacuum investment cast superalloys.

**Casting Issues**

In addition to the cost of bottom filling, it was determined during this investigation that current components cannot be bottom filled by simply inverting the blade orientation in the mold design. Appendices B and C address issues encountered when casting power turbine blades, observing casting defects as indicated by the nondestructive inspection techniques XRI and FPI. Component designs were unchanged between the top and bottom filled castings, with the primary differences being a 180° rotation in blade orientation of the mold design and an increase in mold fill height. It was determined that the bottom filled castings were much more prone to the formation of casting defects, and were particularly prone to hot tearing. Casting defects were indicated by XRI and FPI in 50% (9 of 18) of bottom filled blades, which appeared to be primarily due to hot tearing. No casting defects (0 of 18) were indicated by XRI in top filled blades, and 5.6% (1 of 18) of top filled blades indicated casting defects by FPI.
This blade exhibited a round indication in the attachment section of the blade (see Figure C-12). Given the location and morphology of the FPI indication in this blade, it probably is not due to hot tearing and is more likely due to macroshrinkage.

Many of the bottom filled blades showed typical indications of hot tearing, whereas none of the top filled blades exhibited hot tearing. In general, hot tearing occurs when a solidifying component is subjected to thermal contraction, but is constrained due to friction with the mold wall [33]. Grain boundaries possess extremely limited strength at very high temperatures, and such frictional forces can be sufficient to induce intergranular tearing. Components are particularly susceptible to hot tearing in locations of abrupt geometrical change, which is due to mismatch in contraction rate of the thin and thick parts and the geometrical transition behaving as a stress concentrator. This effect was observed in this study where hot tearing typically occurred at the transition between the attachment platform and blade length (often at the trailing edge). The likely cause for increased susceptibility to hot tearing in bottom filled blades is simply gravitational effects. The heaviest section of the blade is of course the attachment. While the cast part is solidifying and contracting, in the case of a bottom filled mold (blade tip facing up) the weight of the attachment would be assisting in opening hot tears by imposing a tensile stress relative to the crack (see Figures 2-13 and C-1 as visual aids). In the case of a top filled mold (blade tip facing down), the weight of the attachment would be compressive relative to a hot tear, therefore assisting in prevention of crack formation. Additionally, having the bulk of the last metal to solidify at the top of the casting may act as a hot top, which would also assist in preventing hot tearing. The susceptibility to hot tearing of an inverted casting design is one among
many possible stumbling blocks for the superalloys casting industry in implementing bottom filled molds, and further emphasizes that precautions related to avoiding bifilm formation do not appear to be needed, since there is no demonstrable improvements in properties.

**Hot Isostatic Pressing**

There was an observable effect on material behavior and microstructures due to utilization of HIP, however it was determined that these effects more than likely were not due to the effect of HIP on oxide bifilms. Current publications suggest that utilization of HIP can improve mean UTS, minimum UTS, mean elongation, minimum elongation, minimum room temperature fatigue life, and mean room temperature fatigue life of aluminum alloy A206-T71 [9, 10]. These results are attributed to “healing” of thin alumina bifilms. The results of this study do not agree with these conclusions.

In the case of tensile properties, substantial softening was observed in HIPed samples. This was clearly due to over-coarsening of γ’ following the necessarily slow cooling rates following HIP. Although both minimum and mean elongation was increased, this was due to softening and not due to the effect of bifilm healing, and also coincided with a substantial decrease in yield strength. There also was no increase in minimum or mean UTS. Rather, there was an observed decrease in minimum UTS, further indicating that tensile behavior was not strongly influenced by a potential effect of HIP on bifilms. Aside from over-coarsening γ’, HIP had the obvious microstructural effect of eliminating dendritic casting porosity. However, the porosity elimination is more than likely due to the classic mechanism of densification, which is analogous to diffusion bonding facilitated by plastic deformation and creep [36, 94]. Explanation of porosity closure via bifilm fracturing and “healing” is therefore an unnecessary and incorrect
explanation for pore closure during HIP in this alloy system. This is certainly the case given that Auger samples indicated conclusively that the surface of dendritic casting pores exhibited no oxide films. This indicates that dendritic porosity in IN100 was not bifilm-assisted, and that the effects of HIP on porosity where not related to oxide bifilms.

In the case of room temperature fatigue life, there was no conclusive difference in mean fatigue life or minimum fatigue life due to use of HIP. The HIP cycle did eliminate porosity as a mechanism for fatigue crack initiation, although surprisingly this did not translate into an improvement in fatigue life or a reduction in data scatter. This indicates that although porosity is a possible mechanism for room temperature fatigue crack initiation, it is not necessarily dominant as compared to initiation on primary MC carbides. This may be due to porosity remaining smaller than a critical pore size that would cause fatigue life to be reduced.

Removal of porosity via HIP has been shown to reduce scatter and improve fatigue life in polycrystalline cast Ni-based superalloys, however this is true at elevated temperatures [32, 33, 35, 41]. Room temperature fatigue tends to be more dominated by inclusions or carbides [49, 54, 86], which is why room temperature fatigue was selected for study. Additionally, HIP removal or porosity has been shown to increase stress rupture life [33, 41]. Clearly there are applications for HIP in this alloy system, however the purpose of this study was strictly to investigate the effect of HIP on oxide bifilms. In addition, the microstructure of HIPed samples was not optimized. Investment cast IN100 typically is not HIPed, so a standard HIP cycle for a non-hafnium bearing polycrystalline alloy was utilized, but the industry standard IN100 partial solution heat treatment was still used post-HIP in an effort to minimize process variables. While it
may be possible to develop a post-HIP solution heat treatment to optimize microstructure, the purpose of this investigation was not to optimize heat treatments. It is possible that if microstructure optimization were pursued, there may be some measurable benefit to use of HIP, however it is clear from the results of this study that such benefits would be due to microstructural improvements and not an influence from oxide bifilm remediation.

**Fracture Behavior**

Numerous tensile and fatigue fracture mechanisms were observed in this study. Fracture mechanisms and relevant fractographic features are discussed and contrasted with current literature pertaining to bifilms.

**Carbide Cracking**

Tensile fracture mechanisms among vacuum cast, argon cast, and high strength air cast samples were very apparent following fractographic and metallographical analysis. These samples appeared to follow classic microvoid coalescence behavior, with microvoid formation occurring in the vicinity of fractured M(Ti, Mo)C carbides. Secondary cracking was also observed to closely follow fractured MC carbides, and there was an observable abundance of fractured MC carbides in the microstructure of material near the fracture surface. Literature pertaining to bifilms suggests that this process is actually due to heterogeneous carbide nucleation on the surface of bifilms [3, 4, 6]. However, in situ Auger analysis of fractured pins shows conclusively that there is no observable oxide film on the surface of fractured carbides, as would be expected in the case of bifilm-assisted nucleation (see Figure 2-12 indicating the theorized location of the bifilm). Auger analysis also did not indicate the presence of oxide films on the surface of microvoids. Furthermore, the fractured carbides and microvoids observed via
Auger fractography were indistinguishable from the morphology and composition of fractured carbides observed in microvoids formed in tensile samples. It is suggested that bifilms were not related to the formation of carbide cracks and subsequent microvoids in any sample condition of IN100 examined. Microvoid coalescence as a mechanism for ductile fracture is a well understood and documented process [95]. Supplementing this model of ductile fracture with the presence of bifilms is likely both unnecessary and incorrect.

This study has also shown that fatigue initiation on MC carbides is likely not related to carbide nucleation on bifilms. If fatigue initiation were occurring due to carbide nucleation on bifilms, it would be expected that fatigue initiation would occur at the carbide/matrix interface. This is anticipated since the carbide would be nucleating on one face of the bifilm, but possess an unbound interface (essentially preexisting crack) between the carbide and matrix. However, it was shown that fatigue initiation was actually occurring due to through-cracking of the carbide. This type of through-cracking has also been theorized to be related to nucleation on bifilms (again see Figure 2-12), but this is unlikely. Unfortunately, it is not currently possible to test fatigue in situ in an Auger microprobe. However, given that Auger pins do not exhibit oxide films on the surface of fractured carbides, as previously mentioned, carbide embrittlement is likely not due to nucleation on bifilms. Without any observable presence of bifilms on the surface of fractured carbides, it is proposed that bifilm-related carbide embrittlement is an incorrect mechanism for explaining carbide brittleness. However, it should be stated that oxide inclusions (not necessarily bifilms) have been shown, in certain cases, to be
an effective carbide nucleant [96-100]. This is discussed further in the “Non-metallic Inclusions” section.

**Cleavage Planes**

Some bifilm publications suggest that cleavage planes and other similar fractographic features are related to the presence of bifilms [4, 13, 55]. However, Auger analysis has provided compelling evidence that in the case of cast Ni-based superalloys this is not the case. In situ Auger fractography did not indicate the presence of an oxide film in any sample condition, even samples predicted to be the most favorable for bifilm formation (i.e. top filled and air cast). Therefore, it is not possible to locate fractographic features that may appear to be related to bifilms and simply assume that it is due to bifilms, or that it is somehow indicative of the presence of bifilms. In the absence of bifilms, cleavage planes are therefore formed from the well understood process of crack propagation along a favorable crystallographic orientation, textural orientation, and/or between favorable microstructural features [101]. Considering that secondary cracking was found to closely follow fractured MC carbides, it is likely that cleavage planes observed fractographically are simply the result of the crack path occurring between carbide particles, and is not evidence of bifilm splitting.

**Dendritic Porosity**

Porosity was observed to act as a fatigue crack initiation mechanism, with PSBs forming in the vicinity of near-surface casting porosity. This was determined to be an equivalently dominant fatigue crack initiation mechanism as MC carbide fracture. Porosity was also observed in the fractography of tensile samples, however secondary cracking was not observed to closely follow dendritic casting pores. Some research theorizes that dendritic casting porosity is formed due to the presence of oxide bifilms.
Auger fractography has provided compelling evidence that this is not the case, and the surface of dendritic casting pores of every sample condition investigated do not exhibit oxide films. This indicates that casting porosity identified in cast Ni-based superalloys cannot be assumed to be due to the presence of bifilms, and that bifilm related dendritic porosity is not a real mechanism for the formation of dendritic casting porosity in IN100. In reality, porosity must be occurring due to the well-established mechanism of dendritic microshrinkage and incomplete molten metal feeding into the mushy zone during solidification [32, 53].

Dendritic casting porosity analyzed via Auger fractography did exhibit a sulfur-rich monolayer. This sulfur enriched layer was ubiquitous and continuous, and was found to cover the entire surface of every dendritic casting pore analyzed. This result was both interesting and unexpected. There are a number of possible explanations for the formation of this sulfur layer. One possibility is that sulfur is being strongly rejected from the dendrite upon solidification, and ultimately the last material to solidify in the interdendritic region and dendrite surface is sulfur-rich. It is well known that sulfur is a very strong melting point suppressant in the case of Ni-based alloys, and can be observed in regions of incipient melting [102]. This would imply that sulfur possess a very low partition ratio, indicating strong partitioning to the liquid phase. The shortcomings of such a theory, however, is that this implies the monolayer film is a segregation effect. This means that the sulfur content would also be concentrated in eutectic regions of the microstructure. It is possible for sulfur to also enrich dendrite surfaces if strong sulfur rejection from the dendrite were occurring. However, to identify a ubiquitous continuous monolayer film of sulfur with such an abrupt concentration
profile (see Figure 6-7) does not seem likely. This would require that segregation is giving rise to a concentration of sulfur of about 30 at% at the dendrite surface, which drops approximately to the ppm level in the immediate subsurface material. An easy method of testing if dendritic segregation is an active mechanism would be to intentionally cast material with excessive entrapped gas porosity. Following Auger fractography these pores could be analyzed for sulfur content. If sulfur is not indicated, it would be clear that the sulfur enrichment is unique to only dendritic porosity.

Another possible explanation for the formation of the sulfur-rich layer could be the volatilization of sulfur from the bulk material following casting. This suggests that sulfur would be sublimating from the dendrite surface, or evaporating from the liquid in the mushy zone, and subsequently coats the interior surface of the dendritic pore in a process similar to physical vapor deposition. This explanation fits the observed structure well, in that this deposition process could produce a continuous monolayer sulfur film. Additionally, it is expected that the interdendritic regions of the microstructure would be enriched in sulfur due to rejection from the solid phase upon solidification, as was described earlier in this section. The primary shortcoming of this theory is that sulfur does not (in molten Ni) volatilize as readily as may be expected. It has been empirically determined that some trace impurities such as Se, Cu, Te, Pb, and Bi will be readily volatilized and removed from the melt during VIM [32]. Other trace impurities such as As, Sn, Sb, and S are not readily removed during VIM [32], indicating that sulfur is not a high vapor pressure impurity. This is true for sulfur vapor above molten Ni alloy (the original study was on 80Ni-20Cr [103]), however it is possible that this is not necessarily true for sulfur sublimation over solid Ni. There may exist a temperature window during
cooling in which sulfur sublimation could be occurring. Of course, substantial thermodynamic modeling would be necessary to determine if this is possible.

A third, and by far most likely, explanation for the formation of a sulfur-rich layer would be due to diffusional segregation while cooling after casting. At high temperatures, it has been shown that sulfur strongly diffuses to free surfaces and oxidizing interfaces [45-48, 104-109]. It is very likely that sulfur is diffusing to the pore surface simply because it is an available free surface. It is important to note that, in the case of as cast material, the only elevated temperature experienced by the casting was during cooling following pouring. At intermediate temperatures, in some cases, sulfur has been shown to diffuse to grain boundaries preferentially [43, 110-112]. This indicates that the formation of a sulfur-enriched monolayer is occurring following casting, but in the temperature window during cool-down in the range of approximately 600-900°C. It is worth noting that sulfur is not a rapidly diffusing interstitial element, and has been shown to diffuse substitutionally in Ni lattice sites [43]. Subsequently, the diffusion rate of sulfur in Ni is similar to self-diffusion rates of Ni in Ni. Additionally, sulfur levels in this alloy are in the < 10 ppm range (See Appendix A). It may seem possible that the temperature window provided only from cool-down following casting does not allow for a realistic amount of time for adequate bulk diffusion of sulfur to form a sulfur-enriched layer. However, Auger analysis by L. A. Harris has shown that upon heating a nickel sample with sulfur content of < 10 ppm in an Auger microprobe to 600-900°C, a strongly sulfur-enriched surface layer develops in approximately 1-2 mins. This indicates that the sulfur content of IN100 investigated in this study, the diffusion rates of sulfur, and the time the cast materials had been in the 600-900°C temperature window
were all likely sufficient for formation of a sulfur-enriched monolayer. One method of investigating this possible explanation would be to generate cooling curves of cast components, then combine this information with thermodynamic modeling of the diffusional behavior of sulfur in Ni-based alloys. This approach could indicate if diffusion, within the determined time constraints, is a reasonable explanation for the sulfur enrichment at pore surfaces. It is also important to note that this mechanism of sulfur surface enrichment may be working in tandem with dendritic segregation, as there may be local enrichment of sulfur content in the microstructure of material in the vicinity of the dendritic casting pore.

**Oxycarbide Inclusions**

This study has sought to thoroughly characterize both new and thickened oxide bifilms using methods comparable to applicable literature, as well as utilization of techniques capable of greater spatial resolution, surface sensitivity, and more in-depth analysis. These results are compared to current research pertaining to bifilms in an effort to more accurately describe a phenomenon that has previously been subjectively evaluated. Ti oxycarbide inclusions were observed and characterized, and while they do not share most of the characteristics of thickened bifilms, they do share some remote similarities such as morphology and material embrittlement. For these reasons, Ti oxycarbide inclusions were extensively characterized by SEM, TEM, and Auger microprobe.

**SEM Metallography and Fractography**

SEM investigation was useful in analyzing the morphology and chemistry of oxycarbide inclusions. The analyzed inclusions were notably similar to inclusions identified in bifilm literature as thickened bifilms [3, 6]. SEM metallographic analysis
revealed that in some cases oxycarbide inclusions appeared to be a layered structure, consisting of outer layers of TiC and an inner layer of alumina. Bifilms have been theorized to be a nucleation site for MC carbides [3, 4, 6], and in some cases the internal alumina did appear to be film-like in morphology. However, there were several aspects of the oxycarbide inclusion that were distinctly dissimilar from the theorized behavior of bifilms. The internal alumina phase was more than one order of magnitude thicker than published thicknesses of an oxide bifilm [2, 4]. Additionally, SEM metallography and fractography indicated that the morphology and size of the oxycarbide was not modified by exposure to high temperature and HIP cycles. The inclusion did not exhibit considerable thickening following heat treatment. The inclusion structures identified in as cast material were indistinguishable from inclusion structures identified in HIP and heat treated material. Fractographic analysis indicated that inclusions in both of these sample conditions were discontinuous, and exhibited micro and nano discontinuities in the oxide phase. This indicates that the inclusions identified did not exhibit a perforated structure due to HIP, and the oxide phase never existed as a continuous unbroken film. These observations do not agree with current theories published on the subject of bifilm response to HIP [9, 10]. It should also be noted that if bifilm thickening were an accurate description of the formation mechanism of this type of inclusion, a depletion of aluminum local to the oxide film would be expected. This is because the thickening alumina would necessarily be consuming Al in solid solution with the alloy. SEM and TEM EDS line-scans, as well as Auger depth profiling, indicated the opposite. Al content in the matrix material near the inclusion was found to be constant. It is also important to note that formation of an alumina dross inclusion in an
air cast heat of IN100 would be anticipated. Brief review of Ellingham diagrams [113] indicates that alumina formation would be the most thermodynamically favorable oxide to form in the IN100 alloy system. Magnesia formation would theoretically create a greater reduction in free energy of the system. Since trace Mg does exist in this material (likely from crucible liner deoxidation during master alloy production), some Mg content can in some cases be detectable in the oxide phase (see Figure 7-10C).

Finally, given the lack of observation of thin bifilms during the extent of this investigation, it is not possible to assert that the inclusion structures identified are due to bifilm thickening. In order to convincingly state that some observable inclusions characterized in this and other studies are due to bifilms, the thin bifilm precursor must first be identified and characterized. In this work, however, compelling evidence has been presented to indicate that thin bifilms do not exist in IN100. Given this result, it would also strongly indicate that observed inclusions are not due to bifilm thickening.

The conflicting results in this study, compared to the literature, indicate that the inclusions analyzed do not behave similarly to the theorized behaviors of bifilms, and therefore were not formed due to the presence of bifilms. As a more likely explanation, it is proposed that the observed inclusions were caused by more typical alumina dross inclusions and not oxide bifilms. This makes intuitive sense, as substantially more alumina dross formation occurs in air cast material, and oxycarbide inclusions were only identified in IN100 that had been air cast. Although it may at first seem to be a minor distinction, there is a profound difference in expected behaviors between dross inclusions and bifilms. As has been discussed previously (see Chapter 2), there is some literature predicting behaviors in oxide bifilms that would not be anticipated in the case
of dross inclusions. However, as will be discussed, it is likely that the alumina dross inclusions were behaving as a heterogeneous nucleation site for abundant nucleation of MC carbides.

**Auger Analysis**

Auger SAM/AES analysis was very useful in indicating the size and morphology of oxycarbide inclusions. SAM imaging was capable of indicating that oxycarbides located in fractured Auger pins exhibited a heterogeneous morphology, with a patchy alumina phase found overtop of a very large M(Ti, Mo)C carbide phase. AES spectra were capable of showing a strong enrichment of Al and O in the oxide phase, and a strong enrichment of Ti and C in the carbide phase, but unfortunately did not possess the spatial resolution to definitively show the heterogeneity of this structure. However, given the extreme surface sensitivity of AES, this result still does indicate the discontinuous nature of the alumina phase. If the alumina phase were to exist as a continuous film that also possesses thick and thin regions, even in the thin regions theoretically covering the carbide phase in a continuous film, much more pronounced Al and O signals would be anticipated. This would be true even if the “thin” regions were a monolayer film, since the sample depth at which Auger electrons are generated is only approximately 10 Å. Considering the surface sensitivity of this analysis technique, if a continuous monolayer oxide phase were covering the entire inclusion structure the AES signal generated would indicate only the presence of alumina. This result supports the idea that the oxide film viewed fractographically is not evidence of bifilm splitting, since if this were the case a continuous oxide phase would be anticipated in the inclusion structure.
Auger depth profiling was useful in indicating that there are no thin interfacial phases present, and that the layered structure is as it appears to be: Al₂O₃/TiC/Matrix. Depth profiling also was capable of estimating thicknesses of each phase. The oxide phase was estimated to be about 400 nm in thickness, approximately 20-400x the size of reported thicknesses of bifilms [2, 4]. This further supports the conclusion that the oxide phase observed in oxycarbide inclusions is not evidence of a bifilm, and likely has not formed due to the presence of bifilms. It is again asserted that this oxide structure is likely from the formation of alumina dross inclusions, as these inclusions would be similar in size to those observed in the results of this dissertation [33].

**Deep Etching**

Deep etching yielded the surprising result that oxycarbide inclusions are actually comprised of very fine blocky external MC carbides that are less than 100 μm in size. This indicates that the inclusions only appear stringy when metallographically polished. Furthermore, it was determined that the alumina layer observed in metallographically prepared samples is actually completely internal to the outer layer of M(Ti, Mo)C carbide. Although SEM examination was limited by spatial resolution and surface sensitivity, it was still capable of confirming the presence of an internal aluminum and oxygen rich structure. The presence of abundant and very fine MC carbides suggests that these carbides nucleated much more rapidly than is typical in a cast structure. Their presence on the surface of the internal alumina also suggests that these carbides have nucleated heterogeneously. Although this agrees with some prevailing theories on bifilms [3, 4, 6], this does not necessarily indicate that the internal alumina is a bifilm, since many similar behaviors would be anticipated from any alumina inclusion.
MC carbide nucleation on alumina inclusions in superalloy systems has been documented in other studies [96-98], as well as MC carbide nucleation on alumina inclusions in IN100 [99, 100]. In these studies typical morphologies of MC carbides (blocky, ~20μm) have been observed containing alumina “cores” that vary in shape from film-like to spherical. The prevailing theory among these reports is that small oxide and nitride particles in the melt behave as heterogeneous nucleation sites for the precipitation of MC carbides. As the melt cools, MC carbides begin to nucleate just below the liquidus temperature of the alloy. Following nucleation, the carbide grows and envelops the alumina core. This is mechanistically similar to the bifilm-assisted carbide nucleation theories that have been proposed, however it is important to make the distinction that the nucleating inclusion does not need to be a bifilm. Mechanistically, any alumina inclusion would be capable of triggering this behavior.

Oxycarbides in superalloys of the size and morphology seen in this study have not been commonly observed in the literature. However, it is possible that these inclusions have formed in a manner similar to the alumina-core-containing carbide structures discussed. Given the morphology of the external TiC, it is being proposed that this structure is caused by rapid and abundant heterogeneous MC carbide nucleation on the surface of the alumina dross inclusion. This creates the fine blocky structure that is observed, analogous to the formation of a chill-zone grain structure observed on the surface of cast ingots. Of course, further investigation is necessary to determine if this is an accurate explanation.

**TEM Analysis**

Utilizing the spatial resolution of STEM and EDS analysis via TEM, it was possible to clearly observe the layered phases in oxycarbide inclusions. The structure
consisted of external TiC layers and internal Al₂O₃. BF-TEM imaging indicated that the TiC and alumina phases were polycrystalline, with both consisting of ultrafine grains ranging from approximately 70 nm to 300 nm. HR-TEM revealed that each of these interphase interfaces are bound. None of these interfaces appeared to exhibit preexisting cracks. Some voids could be observed, however it is unclear if these voids formed while sample thinning during sample preparation. Some locations of the internal alumina were shown to be monocrystalline, indicating that this structure could not have formed from a bilayer alumina film. Although there are some similarities in this structure as would be expected in a bifilm, considering the lack of preexisting cracks or unbound oxide-oxide interface, this structure does not appear to be a bifilm. It is proposed that the alumina core observed is a polycrystalline alumina inclusion, with the morphology of a single oxide layer that is dense and bound, as opposed to an unbound bilayer. Considering that this type of inclusion was only observed in air cast alloys, it is also likely that the alumina core is a dross inclusion.

These results strongly indicate that a larger sampling volume will be necessary to determine the structure of the internal alumina. Additionally, 3-dimensional analysis of the alumina is imperative in order to determine the morphology of this inclusion. It is possible that although the alumina core appears film-like when polished metallographically, or viewed in a 2-dimensional cross section via TEM, it may not actually possess this type of structure 3-dimensionally. Just as the bulk structure of the carbide phase in oxycarbide inclusions was not anticipated, it is difficult to anticipate the morphology of the alumina core without 3-dimensional characterization. Previous research has indicated that alumina inclusions in nickel alloys can possess a wide
variety of morphologies including: Dendritic, faceted, plate-like, spherical, and stringy clusters [114].

Final Thoughts

After review of the overall results presented in this study, there is little doubt that oxide bifilms as described in bifilm literature are not present in IN100, regardless of how favorable conditions may be for the formation of such a casting defect. Considering the lack of any indication that bifilms exist in this material, it is further hypothesized that bifilms may not occur in any cast superalloy system. In many instances throughout the course of this work it was shown that fundamental underpinnings of bifilm theories were either unnecessary, a misinterpretation of results, or incorrect mechanisms for explaining physical phenomena. A significant lack of results in bifilm literature showing tangible evidence of the existence of bifilms continues to persist. Given the deep disagreement between the results found in this study and those postulated in bifilm literature, the broader existence of bifilms in any material system now seems questionable. Without substantial hard evidence for the existence and behavior of bifilms, there does not seem to be sufficient cause to apply bifilm theories to cast superalloys. The responsibility must lay with proponents of bifilm theories to present compelling and conclusive data to suggest that such theories are valid and applicable before such mechanisms can even be considered for broad adoption.
CHAPTER 9
CONCLUSIONS

Closing Remarks

The current investigation has sought to provide substantive understanding of whether oxide bifilms form in investment cast superalloys. Direct evidence of bifilms in vacuum, argon, and air processed IN100 was not observed. Following the mechanical analysis and in-depth characterization presented in this study, it has been determined that bifilms do not form in IN100 processed under both typical and atypical conditions. The findings of this study strongly conflict with a limited number of previous reports pertaining to oxide bifilms. Therefore, further study into other facets of bifilm theories, utilizing appropriate characterization techniques and objective analysis methods, is recommended.

Conclusions

Results in vacuum investment cast B1900 tensile samples were not similar to the 2004 study by Rashid et al. on vacuum cast superalloys. Oxide bifilms were not identified by SEM/EDS. However, air casting IN100 introduced risk of oxycarbide inclusion formation. Inclusion formation created bimodal tensile behavior for UTS and elongation data. Tensile fracture in air cast IN100 was influenced by embrittling Ti oxycarbide inclusions, particularly in low strength and low ductility samples. Oxycarbide inclusions analyzed fractographically exhibited macro, micro, and nano discontinuities. The oxide phase was not observed to be a continuous film. Air cast IN100 mean fatigue life was reduced by approximately 45.8% (59,950 cycles) as compared to vacuum cast. Fatigue crack initiation in air cast IN100 was due to persistent slip band formation in the presence of surface-connected or near-surface MC carbides, dendritic casting porosity,
and/or Ti oxycarbides. Fatigue fracture was not related to the presence of oxide bifilms. Fatigue crack initiation was sensitive to defect size. Shorter fatigue life air cast samples exhibited larger non-metallic inclusions. The fracture surfaces of longer fatigue life air cast samples did not exhibit non-metallic inclusions.

Tensile fracture in vacuum and argon cast IN100 was due to typical microvoid coalescence and not influenced by oxide bifilms. Fatigue crack initiation in vacuum or argon cast IN100 was due to persistent slip band formation in the vicinity of surface-connected or near-surface MC carbides and/or dendritic casting porosity. Fatigue fracture was not related to the presence of oxide bifilms. Fatigue crack initiation on MC carbides occurred due to creation of a through-crack of the MC carbide.

Room temperature tensile and high cycle fatigue properties of vacuum and argon processed IN100 was not detectibly influenced by casting turbulence. XRI and FPI indicated that 50% of bottom filled blades exhibited evidence of hot tearing. XRI and FPI did not indicate hot tearing in top filled blades. Utilization of HIP softened IN100 by creating over-coarsened γ’ precipitates. This reduced mean YS by 71.8MPa and increased mean tensile elongation from 6.4% to 9.6%. HIP did not measurably increase UTS or fatigue life. Ti oxycarbide morphologies were invariant to HIP and heat treatment cycles.

Cleavage planes, fractured carbides, dendritic porosity, and oxycarbide inclusion stringers are not evidence of the presence of bifilms. These structures were determined to have formed in the absence of oxide bifilms. Dendritic casting pore surfaces exhibited a ubiquitous and continuous sulfur-enriched surface monolayer. Ti oxycarbide inclusions consist of internal alumina enveloped 3-dimensionally by fine blocky M(Ti,
Mo)C carbide. It is suggested that the internal alumina core is due to formation of dross inclusions. Ti oxycarbide inclusions are layered as follows: Ni-matrix/MC carbide/alumina/MC carbide/Ni-matrix. The internal alumina is polycrystalline. Some regions of the internal alumina are a single grain in width. Each interface in oxycarbide inclusions exhibits a grain boundary and appears bound with no pre-existing cracks.

**Future Work**

Given the results of this study, application of the analysis methods utilized should be brought into other domains of bifilm theories. Namely, similar analysis techniques should be applied to cast aluminum alloys. The FIB/TEM analysis method could be applied to analysis of silicides in cast aluminum alloys, as these precipitates have been theorized to nucleate on the surface of bifilms [4, 19, 57, 60, 61]. A wide variety of brittle intermetallic precipitates have been theorized to form on the surface of bifilms, and HR-TEM would be critical tool for identifying unbound interfaces in such structures. The in situ Auger analysis methods presented in this dissertation should also be applied to aluminum alloys. By utilizing SAM/AES, fractographic features often associated with bifilms in aluminum alloys can be objectively and conclusively evaluated.

More in depth analysis of air cast material could be useful in further analyzing any possible benefits to mechanical properties from reduction of casting turbulence in air cast systems. The material chosen should be one that can often be air processed or vacuum processed, such as some bearing steel alloys. If trends in mechanical properties, such as fatigue life, were to develop from the study of air cast material, the alloy could then be subsequently vacuum processed and then analyzed to determine if such trends in properties with casting turbulence persist. This would determine if bottom
filling can produce measurable benefits to air cast alloys, and if these trends continue to be true when the alloy is vacuum processed.

Further analysis of the nano-scale sulfur layer on the surface of dendritic casting pores could yield useful information on the behavior of sulfur in cast alloy systems. This would include thermodynamic modeling of the stability of sulfur in the solid and liquid phases of IN100 during each stage of solidification. Additionally, Auger analysis of cast IN100 containing entrapped gas porosity would be capable of determining if the generation of a sulfur-rich layer is related fundamentally to dendritic segregation and rejection of sulfur from the solid phase during solidification.

A further method of analyzing the segregation behavior of sulfur and other trace metalloid impurities could be performed by planar solidification of single crystal Ni-based superalloys. Previous studies have utilized planar solidification as a method of developing partition ratios of alloying elements, determining the tendency of alloy additions to segregate to the solid or liquid phases during solidification [115]. This would essentially use similar techniques to evaluate the partitioning behavior of trace impurities. In order to do this, a Ni superalloy bar would be initially solidified using the Bridgman method. If high thermal gradients and slow solidification rates are utilized, a planar solidification front can be achieved [32, 115-118]. The cast bar would be partially solidified by a planar front, and then interrupted and rapidly quenched to complete solidification. Samples from the planar solidified end of the bar and the quenched end of the bar could then be removed and analyzed by glow discharge mass spectrometry. This method would allow for very accurate and quantitative measure of trace impurity content, and partition ratios of trace impurities could be established. It has been shown
that planar solidification of Si wafers substantially reduces the content of some impurities such as phosphorus via strong segregation to the liquid phase ahead of the solidification front [119]. It may also be possible that similar effects can be observed in Ni-based superalloys as well. If there is significant removal of trace impurities, it could be beneficial to determine if this imparts any improvements on mechanical properties or oxidation behavior, since it has been shown that trace impurity content can have strong impacts on stress rupture life [41, 112] and oxide spallation [46, 47].

Additional analysis of oxycarbide inclusions in IN100 would be invaluable. This type of inclusion was observed to have at least some similarities to current bifilm theories, namely the nucleation of MC carbides on an alumina core. However, more investigation is necessary to determine if the alumina core found in these inclusions exhibits other similarities to bifilms. 3-dimensional characterization of the alumina core would be extremely valuable in determining if the internal alumina possess a film-like morphology. A useful technique in pursuing this would be serial sectioning via FIB, which has been performed in previous studies at UF [120]. This method would allow for serial sectioning and reconstruction of 3-dimensional models of the alumina cores found in several oxycarbide inclusions.

An additional method of 3-dimensional characterization of inclusions would be X-ray tomography. This method could give further insight into the 3-dimensional morphology of oxycarbide inclusions, and would be capable of analyzing relatively large sample volumes. This could also assist in elucidating other factors that generate the relationship between oxycarbide inclusions and their impact on tensile properties.
Possible factors include inclusion size, orientation, morphology, number, density, and/or location in the tensile bar.

Analysis of oxycarbide inclusions in other alloy systems containing varying carbide forming elements would also be useful in understanding oxycarbide formation. For example, it could be determined if air cast B1900 would nucleate Ta carbide on an alumina core instead of TiC. Since B1900 contains significant Ta content (see Table 3-1), and it has been documented that Ta is generally a stronger MC carbide former than Ti [26, 96], it would be useful to investigate how this change in chemistry affects the oxycarbide structure. This could be further extended to an alloy such as B1900+Hf, as it has been documented that Hf is generally a stronger MC former than Ta [26, 96], and also has a significantly greater partition ratio to the liquid phase during solidification due to strong rejection from dendrite cores [115].

Analysis of oxycarbide inclusions formed in the environment of a sessile drop furnace could be useful in further understanding the heterogeneous nucleation of MC carbides on alumina formed from liquid/atmosphere interactions. Air melting in this type of environment would allow for the formation of external alumina dross on the surface of the melt. With the presence of a controlled alumina dross, the solidified button can then be sectioned to examine the presence of heterogeneously nucleated MC carbides as compared to homogeneously nucleated MC carbides. Critical parameters for oxycarbide formation such as alloy and casting chamber oxygen content could be experimentally determined.

Conclusive analysis of the theory of bifilm thickening could be performed using isotopic oxygen as a tracer gas during casting. The use of isotopic tracer analysis in
combination with SIMS characterization has proven to be a powerful method of gaining fundamental understanding of oxidation behavior in superalloy systems [121-125]. This technique would be applied to cast alloy systems by melting and casting superalloy in a VIM system that has been backfilled to a pressure of 1 atm with a blend (by pressure) of 80% Ar and 20% $^{18}$O$_2$. This would replicate the roughly 20% oxygen contained in atmospheric air without introducing other variables such as N content. If IN100 were used, it would be expected to form oxycarbide inclusions under these conditions, similar to the inclusions observed in the results of this dissertation. Following casting, the superalloy could then be prepared metallographically and analyzed for inclusion content. The primary distinction is that using isotopic oxygen during casting as a tracer gas allows for the determination of the oxygen source consumed during an oxidation event. This would be possible using SIMS to characterize the inclusions, since SIMS is readily capable of resolving locations that are rich in the isotopic tracer gas as compared to locations where atmospheric oxygen ions are detected. If the inclusions exhibit a heterogeneous oxide structure where SIMS detects regions with high $^{18}$O$^-$ signal and other regions with high $^{16}$O$^-$ signal, this would be an indication of bifilm thickening as it suggests that bulk oxide thickening has occurred through consumption of atmospheric oxygen in solution with the alloy. If the inclusion consists of a homogeneous oxide structure rich in only the isotopic oxygen, this must indicate that the oxide phase is a typical dross inclusion.
## APPENDIX A
### SAMPLE CHEMISTRY REPORT

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<table>
<thead>
<tr>
<th>Vendor</th>
<th>Howmet Dover Alloy</th>
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<table>
<thead>
<tr>
<th>Customer</th>
<th>Customer Part ID Base Spec</th>
<th>Rev</th>
<th>Amend</th>
<th>Eng</th>
<th>Class</th>
<th>Test</th>
<th>Reason</th>
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<tbody>
<tr>
<td>PRATT &amp; WHITNEY AIRCRAFT</td>
<td>PVM650</td>
<td>AF</td>
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### Chemistry Specifications

<table>
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<tr>
<th>Element</th>
<th>Result</th>
<th>Units</th>
<th>Min</th>
<th>Max</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum (Al)</td>
<td>5.64</td>
<td>%</td>
<td>5.00</td>
<td>6.00</td>
<td>XRF</td>
</tr>
<tr>
<td>Bismuth (Bi)</td>
<td>&lt;0.1</td>
<td>ppm</td>
<td>0.3</td>
<td>ICPMS</td>
<td></td>
</tr>
<tr>
<td>Boron (B)</td>
<td>0.02</td>
<td>%</td>
<td>0.1</td>
<td>0.02</td>
<td>SSAM</td>
</tr>
<tr>
<td>Carbon (C)</td>
<td>0.16</td>
<td>%</td>
<td>0.15</td>
<td>0.20</td>
<td>Combustion</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>8.57</td>
<td>%</td>
<td>8.00</td>
<td>11.00</td>
<td>XRF</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>14.05</td>
<td>%</td>
<td>13.00</td>
<td>17.00</td>
<td>XRF</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.03</td>
<td>%</td>
<td>0.30</td>
<td>SSAM</td>
<td></td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>&lt;1</td>
<td>ppm</td>
<td>5</td>
<td>ICPMS</td>
<td></td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>13</td>
<td>ppm</td>
<td>RPT</td>
<td>RPT</td>
<td>SSAM</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>&lt;0.01</td>
<td>%</td>
<td>0.20</td>
<td>SSAM</td>
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<tr>
<td>Molybdenum (Mo)</td>
<td>2.93</td>
<td>%</td>
<td>2.00</td>
<td>4.00</td>
<td>XRF</td>
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<tr>
<td>Phosphorus (P)</td>
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<td>%</td>
<td>0.015</td>
<td>ICP</td>
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<tr>
<td>Selenium (Se)</td>
<td>&lt;1</td>
<td>ppm</td>
<td>1</td>
<td>ICPMS</td>
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</tr>
<tr>
<td>Silicon (Si)</td>
<td>&lt;0.01</td>
<td>%</td>
<td>0.20</td>
<td>SSAM</td>
<td></td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>&lt;1</td>
<td>ppm</td>
<td>RPT</td>
<td>RPT</td>
<td>ICPMS</td>
</tr>
<tr>
<td>Sulfur (S)</td>
<td>&lt;0.001</td>
<td>%</td>
<td>0.015</td>
<td>Combustion</td>
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<tr>
<td>Tellurium (Te)</td>
<td>&lt;0.2</td>
<td>ppm</td>
<td>0.5</td>
<td>ICPMS</td>
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<tr>
<td>Thallium (Tl)</td>
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<td>ppm</td>
<td>0.6</td>
<td>ICPMS</td>
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<tr>
<td>Titanium (Ti)</td>
<td>4.62</td>
<td>%</td>
<td>4.50</td>
<td>5.00</td>
<td>XRF</td>
</tr>
<tr>
<td>Vanadium (V)</td>
<td>0.78</td>
<td>%</td>
<td>0.70</td>
<td>1.20</td>
<td>XRF</td>
</tr>
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<td>Zirconium (Zr)</td>
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<td>%</td>
<td>0.03</td>
<td>0.09</td>
<td>SSAM</td>
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<tr>
<td>Al + Ti</td>
<td>10.25</td>
<td>%</td>
<td>10.00</td>
<td>11.00</td>
<td>Calculation</td>
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<tr>
<td>PHACOMP</td>
<td>2.36</td>
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**Remarks**

SAMPLE FROM TAPERED BAR SECTION - NOT GATING STUB

**Approved By**

Eric Hagen, Chemical Analyst
Reported Results Meet All Specification Requirements

**Date Approved**

5/5/2012

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Figure A-1. Sample chemistry report of cast IN100
APPENDIX B
POWER TURBINE X-RAY RADIOGRAPHY

X-ray radiography was utilized as a nondestructive method of identifying casting irregularities. XRI between top filled and bottom filled vacuum or argon cast power turbine blades is presented in this appendix. X-ray images have been identified according to filling method, and indications of shrinkage, cracking, or other structural irregularities are marked. Casting irregularities were identified in 5 out of 6 bottom filled molds (9 out of 18 bottom filled blades) and none of the top filled blades. Bottom filled blades were found to be more prone to hot tearing.
Figure B-1. XRI of bottom filled, vacuum cast, and turbulated PT blades
Figure B-2. XRI of bottom filled, argon cast, and conventionally gated PT blades
Figure B-3. XRI of bottom filled, vacuum cast, and conventionally gated PT blades
Figure B-4. XRI of top filled, vacuum cast, and turbulated PT blades
Figure B-5. XRI of top filled, argon cast, and conventionally gated PT blades
Figure B-6. XRI of top filled, vacuum cast, and conventionally gated PT blades
Visual inspection aided by the use of a fluorescent penetrant dye was utilized as a nondestructive method of identifying casting irregularities. Visual inspection between top filled and bottom filled vacuum or argon cast power turbine blades is presented in this appendix. Images have been identified according to filling method, and indications of shrinkage, cracking, or other structural irregularities are marked in grease pencil. Casting irregularities were identified in 9 out of 18 bottom filled blades and 5 out of 6 bottom filled molds. Casting irregularities were identified in 1 out of 18 top filled blades and 1 out of 6 top filled molds. This blade exhibited a round indication in the attachment section of the blade (see Figure C-12). Given the location and morphology of the FPI indication in this blade, it probably is not due to hot tearing and is more likely due to macroshrinkage. FPI indications not contained in the blade (i.e. in the gating section) are not considered. Bottom filled blades were found to be more prone to hot tearing.
Figure C-1. Visual inspection of bottom filled, vacuum cast, and turbulated PT blades
Figure C-2. Visual inspection of bottom filled, vacuum cast, and turbulated PT blades
Figure C-3. Visual inspection of bottom filled, argon cast, and conventionally gated PT blades
Figure C-4. Visual inspection of bottom filled, argon cast, and conventionally gated PT blades
Figure C-5. Visual inspection of bottom filled, vacuum cast, and conventionally gated PT blades
Figure C-6. Visual inspection of bottom filled, vacuum cast, and conventionally gated PT blades.
Figure C-7. Visual inspection of top filled, vacuum cast, and turbulated PT blades
Figure C-8. Visual inspection of top filled, vacuum cast, and turbulated PT blades
Figure C-9. Visual inspection of top filled, argon cast, and conventionally gated PT blades
Figure C-10. Visual inspection of top filled, argon cast, and conventionally gated PT blades
Figure C-11. Visual inspection of top filled, vacuum cast, and conventionally gated PT blades
Figure C-12. Visual inspection of top filled, vacuum cast, and conventionally gated PT blades
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Max Kaplan was born in Elizabeth New Jersey in 1988. He grew up in Cranford, New Jersey for most of his childhood. He attended public schools in Cranford, Hillside Avenue Elementary School and Cranford high school. During that time he was involved in a number of athletic and musical activities, and frequently changed his interests. In high school he spent much of his free hours working part time. In fall of 2006 he began attending Lehigh University in Bethlehem, Pennsylvania. He initially entered uncertain of the engineering subgroup he wanted to study, but within his first year developed his interests in materials engineering. In 2007 he met Marina Moser, who has been his copilot ever since.

In the fall of 2010 Max began his doctoral program at the University of Florida as a Graduate Student Fellow, studying high temperature materials under Dr. Gerhard Fuchs. His research was a collaborative effort, working alongside a team of engineers at the Alcoa Howmet Research Center in Whitehall, Michigan. In the fall of 2012 Max received the International Symposium on Superalloys Scholarship in support of his research on nickel-based superalloys. In the spring of 2013 Max received the South East Alliance for Graduate Education and the Professoriate award in support of his endeavors as a minority student earning a doctorate in a science, technology, engineering, or math (STEM) field. In the summer of 2013 Max interned in the structural alloys group at Pratt and Whitney in East Hartford, Connecticut. Following this internship he accepted a position, upon graduation from his doctoral program at UF, as a senior engineer in the materials division of Pratt and Whitney. Also in the summer of 2013, Max accomplished his greatest achievement, and was engaged to his college girlfriend and best friend Marina Moser. In the fall of 2013 Max received the “Best
Paper” award at The Minerals, Metals, and Materials Liquid Metal Processing and Casting conference in Austin, Texas. Now, following graduation, Max is beginning his career in the materials division of Pratt and Whitney in East Hartford, Connecticut.