CARBIDE FORMATION IN A NICKEL-BASED SUPERALLOY DURING ELECTRON BEAM SOLID FREEFORM FABRICATION

by

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ABSTRACT

The Electron Beam Solid Freeform Fabrication process involves the use of an electron beam to make near-net-shape metal parts without the need for tooling. Material in wire form is fed into a melt pool maintained on the surface of the part by the electron beam and a positioning system causes the deposition to occur in a line-by-line, layer-by-layer fashion. Solidification occurs at a high rate, forming a fine dendritic microstructure and fine dispersion of primary carbides. This structure is believed to be optimal for the manufacture and safe use of certain nickel-base superalloy parts, notably turbine disks. The growth of carbide particles from the liquid during EBSFF processing of Alloy 718 has been modeled assuming diffusion control and isolated spherical carbides. The driving force for growth is assumed to increase in a linear manner throughout the temperature range of carbide precipitation. The model predicts the maximum carbide size as a function of EBSFF operating parameters and the alloy niobium and carbon levels. For the material and conditions used experimentally in this work, the model predicts a maximum diameter of approximately 1.0 μm. The maximum carbide size will become an important determining factor for turbine disk performance when oxide and nitride inclusions have been eliminated through improved melt practices. To illustrate this, the low-cycle fatigue life as a function of carbide size for a standard specimen geometry was calculated.

Extraction replica transmission electron microscopy of EBSFF samples identified carbides in the 300-600 nm range, consistent with a population having the predicted maximum size. Another dispersion of carbides larger than 3 μm was also observed in the EBSFF samples. These are believed to be original carbides that survived the EBSFF thermal cycle without completely dissolving. More thorough dissolution can probably be obtained with EBSFF process modifications. Control material from a conventional vacuum arc remelted ingot with similar composition was also examined and plate-like carbides up to 40 μm in length were noted. This is an indication of the enormous potential of the EBSFF process to refine the carbide morphology and size distribution without the need for a reduction in carbon content.

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>2</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>3</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>4</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>6</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>7</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>9</td>
</tr>
<tr>
<td>ELECTRON BEAM SOLID FREEFORM FABRICATION</td>
<td>15</td>
</tr>
<tr>
<td>LITERATURE SURVEY: CARBON AND CARBIDES IN ALLOY 718</td>
<td>23</td>
</tr>
<tr>
<td>MODEL</td>
<td>37</td>
</tr>
<tr>
<td>I. Electron Beam-Material Interaction during EBSFF of Alloy 718</td>
<td>37</td>
</tr>
<tr>
<td>II. Heat Transfer during EBSFF of Alloy 718</td>
<td>40</td>
</tr>
<tr>
<td>III. Thermodynamics of Solidification of Alloy 718</td>
<td>46</td>
</tr>
<tr>
<td>IV. Growth of Carbide Particles</td>
<td>53</td>
</tr>
<tr>
<td>V. Effect of Carbide Size on Fatigue Behavior</td>
<td>60</td>
</tr>
<tr>
<td>EXPERIMENTAL VERIFICATION</td>
<td>64</td>
</tr>
<tr>
<td>I. Production of EBSFF-718 Specimens</td>
<td>64</td>
</tr>
<tr>
<td>II. Sample Characterization</td>
<td>67</td>
</tr>
<tr>
<td>DISCUSSION</td>
<td>80</td>
</tr>
<tr>
<td>CONCLUSIONS</td>
<td>84</td>
</tr>
<tr>
<td>FUTURE WORK</td>
<td>85</td>
</tr>
<tr>
<td>APPENDIX A: CHEMICAL ANALYSES</td>
<td>88</td>
</tr>
<tr>
<td>APPENDIX B: ACRONYMS</td>
<td>89</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>90</td>
</tr>
<tr>
<td>BIOGRAPHICAL NOTE</td>
<td>94</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

1. Conceptual drawing of EBSFF process 15
2. EBSFF of annular parts 16
3. Range of allowable processing power as a function of beam energy for pure iron 18
4. Stringer of nitride inclusions in as-received Alloy 718 wire 22
5. Effect of inclusion size on low-cycle fatigue life 26
6. Charpy impact energy as a function of carbon content 27
7. Stress rupture life and ductility for Alloy 718 with standard and low carbon content 29
8. Rank of the elements according to sublimation enthalpy 31
9. Creep crack growth rate as a function of carbide stringer orientation 32
10. Corrosion resistance in 5% FeCl$_3$ + 10% NaCl at 50 °C for 24 hours 33
11. Effect of carbon content on machinability of cast + HIP Alloy 718 34
12. Calculated thermal history of material behind the beam 44
13. Cooling rate vs. temperature for material behind the beam 46
14. Pseudo-binary phase diagram for Alloy 718 solidification 47
15. Liquidus surface for Ni-Nb-C ternary system within the Ni-NbC-Ni$_3$Nb composition triangle 48
16. Liquidus surface for Alloy 718 pseudo-ternary system within γ-NbC-Laves composition triangle 49
17. DTA cooling curve for EBSFF Alloy 718 50
18. Expanded view of the γ-rich corner of the Alloy 718 pseudo-ternary diagram 51
19. Solidification path for alloy with starting composition 5.14 wt% Nb, 0.037 wt% C 53
20. Plot of carbide growth trajectory for Alloy 718 59
21. Log-log plot of the maximum carbide size vs. cooling rate 60
22. Effect of carbide size on fatigue life 62
23. Low-cycle fatigue life vs. cooling rate, based on the carbide size 63
24. Experimental electron beam solid freeform fabrication apparatus 65
25. Tunnels of porosity in initial EBSFF samples 67
26. EBSFF/substrate boundary 69
27. Agglomerated inclusion in EBSFF material 70
28. EDS maps of an agglomerated inclusion similar to the one depicted in Figure 27 70
29. Optical micrograph of VAR-718 72
30. Optical micrograph of EBSFF-718 73
31. STEM brightfield image of extraction replica 77
32. Ni and Nb EDS maps for the same region shown in Figure 31 77
33. Laves phase 78
34. Intermediate-sized carbide 78
35. Second field viewed in STEM 79
36. Ni and Nb EDS maps for the same region shown in Figure 35 79
LIST OF TABLES

1. Nominal Composition of Alloy 718	23
2. Creep Properties of Alloy 718 at Two Carbon Levels	28
3. Electron-Material Interaction Parameters for Alloy 718	39
4. Physical Properties of Alloy 718 at 538 °C	44
5. Input Parameters for Growth Model	58
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INTRODUCTION

Aircraft engine turbine disks are required to withstand some of the most hostile conditions conceivable for a mechanical component. These disks operate at rotational speeds which can exceed 150,000 rpm\(^1\), and this results in substantial stresses caused by inertial loading from the blades attached to the rim. Furthermore, the rim is in contact with hot combustion gases and can attain temperatures as high as 750 °C.\(^2\) The only materials currently known that are capable of attaining reasonable service life in this application are the nickel-based superalloys. These alloys consist of a nickel-rich fcc matrix hardened by a fine dispersion of intermetallic precipitates. Some of the more popular turbine disk alloys are: Astroloy, Alloy 718, IN-100, and René 95.

In most high-performance engine designs, the disks are locally stressed above yield in some places during high-load conditions such as take-off. These infrequent plastic strain excursions induce low-cycle fatigue, and the resistance to fracture under these conditions is generally the life-determining consideration in this application. Low-cycle fatigue performance generally has a strong dependence on microstructural features, such as grain size, precipitate volume fraction and size, and particularly the morphology and distribution of non-metallic inclusions. These structural variables are highly sensitive to the processing history of the material.

Superalloy turbine disks are currently made via one of two processing routes: casting/forging (ingot metallurgy) or powder metallurgy. In the ingot metallurgy approach, an initial charge of scrap with some virgin metal is Vacuum Induction Melted (VIM) and cast into long, small-diameter ingots called electrodes. These are remelted by Vacuum Arc Remelting (VAR) or Electro-Slag Remelting (ESR) into a water-cooled copper mold to form an ingot of larger diameter. The ingot is subsequently homogenized at temperatures near the melting point to reduce microsegregation to an acceptable level. The ingot then undergoes a succession of open-die forging operations to further homogenize the structure.
and reduce the grain size. The exact nature and order of these processes is usually proprietary, but often includes upsetting between flat dies as well as an incremental transverse pressing operation called cogging. The resulting billet is then cut into appropriately sized slices called mults and each of these is closed-die forged through a succession of dies to obtain the final shape.

The powder metallurgy route also begins with VIM, but the melt is converted into a fine powder by one of several atomization techniques. The most common of these is inert gas atomization, in which a stream of molten metal is divided into fine droplets through the action of multiple inert gas jets. After manufacture, the powder is graded to ensure a narrow size distribution and to eliminate any large contaminant particles. The powder is then encased in a sacrificial steel can and consolidated by either Hot Isostatic Pressing (HIP) or hot compaction followed by hot extrusion. This results in a fully dense billet that is then sectioned into mults and forged to final dimensions as described above.

Unfortunately, fundamental technical and economic limitations of both conventional processing methods prevent disk performance from being improved much beyond present levels. A major problem with cast/wrought material is the extensive segregation that occurs in the highly alloyed grades used for disks. The slow solidification rates result in a very coarse dendritic microstructure, with large compositional differences between the dendrite cores and interdendritic spaces. The ingot must be homogenized at very high temperatures for long times to reduce the composition gradients to acceptable levels. Even when acceptable chemical homogeneity is attained, the coarse grain structure requires very large forces and high temperatures to achieve acceptable deformation rates during ingot conversion to billet. Furthermore, density-driven convective flows can give rise to macrosegregation, called “freckles” in these alloys. Discrete areas lean in solute called “white spots” can occur if exposed dendrites in the pipe cavity of the electrode fall into the melt pool and become entrapped in the solid before completely dissolving. All of these problems increase in severity with ingot size, leading to an acknowledged maximum
diameter of approximately 20 in. for the most difficult grades. Since a large amount of reduction is required to achieve a reasonably small and uniform grain size, this limits the size of the disks that can ultimately be produced from the ingots.

An additional problem is the number and size of non-metallic inclusions found in the ingot. Large inclusions have a very detrimental effect on the low-cycle fatigue life if they are located near the surface in highly stressed areas. This problem is compounded by the fact that some that are large enough to cause premature failure are still too small to be detected by presently available non-destructive inspection techniques. The inclusions found in these alloys are typically oxides, nitrides, and carbides, as well as a small amount of borides and sulfides. The main source of oxides is degradation of the refractory lining of the VIM crucible and tundish. These are called exogenous inclusions and can be quite large. They are removed primarily by filtration and flotation in the tundish during VIM casting, but experience indicates that these measures are not entirely effective. Inclusions can also be indigenous; these form when oxygen, nitrogen, and carbon dissolved in the metal combine with reactive alloying elements in the liquid pool during remelting. In the case of oxygen and nitrogen, the majority of precipitation occurs well above the liquidus. The solubility of carbides in the liquid is somewhat higher and these generally precipitate during solidification.

Segregation of the hardening alloying elements during solidification is not a problem with powder processing; the relatively high cooling rate experienced by the powder produces a dendritic microstructure several orders of magnitude finer than in ingot solidification. This microstructure would produce ideal properties for a turbine disk. Unfortunately, it is not possible to retain this excellent microstructural quality through the consolidation step. While the powder is being heated to the high temperatures necessary for consolidation, surface-active elements such as carbon diffuse to the powder free surfaces and form carbides. These carbides, combined with oxides usually present at the powder surface, form a network outlining the prior particle boundaries in the consolidated material.
This nearly continuous web of non-metallic inclusions can be very detrimental to properties such as toughness and low-cycle fatigue. Furthermore, the powder process is not immune to inclusions of the more familiar discrete type; these are introduced from the refractory lining in the crucible before atomization and can also arise from contaminant particles introduced during powder handling before the consolidation operation.

In most cases, the conventional processing routes can be used to produce acceptable turbine disks, but careful precautions and additional operations are required to address the fundamental shortcomings. For example, the highest quality material presently attainable commercially by ingot metallurgy has an ESR step inserted between VIM and VAR. In this triple-melting technique, the ESR operation reduces oxide inclusions and "white spot" segregation to acceptable levels, and the final VAR remelt reduces gaseous impurities and minimizes the incidence of freckles. This makeshift solution is serving the present needs of the turbine industry, but substantial improvement in the future will require a revolutionary advance. Within the realm of ingot metallurgy, the next step in cleanliness is Electron Beam Cold Hearth Remelting (EBCHR). In this process, the molten metal is contained in a water-cooled copper hearth so that there is no contact with refractories. A long residence time in the hearth enables pre-existing oxides and nitrides to be eliminated by flotation. The benefits of EBCHR have been demonstrated in numerous laboratory trials, but it has yet to achieve widespread industrial application due to excessive cost.

The key to achieving the highest possible quality in powder metallurgy parts is the elimination of all sources of contamination at every processing step. This begins with the construction of the melting crucible and especially the atomization nozzle. All components contacting the liquid metal are made of specialty refractories to reduce degradation to very low levels. After the powder is produced, extremely meticulous precautions must be taken in handling it. The powder must not come into contact with any organic material of any kind. Even rubber O-ring seals in powder-conveying ducts have been found to be sources of contamination.1 The powder should be maintained in vacuum or inert gas at all times.
following its manufacture. This will keep the oxide surface layer to a minimum, reducing the prior-particle boundary network of oxides in the consolidated product. Processes have even been developed in which the powder is exposed to acid mixtures to remove the oxide layer. The powder is generally sieved just before encapsulation to limit the size of any contaminant particles to less than the powder size. Obviously, this provides an incentive to make the powder as small as possible to begin with, but there are severe cost penalties for doing this and it can actually be detrimental since the oxide layer becomes proportionally larger at the smaller powder sizes. Collectively, the additional labor and capital cost resulting from the need for such extreme precautions can make powder metallurgy parts cost as much as four times higher than comparable cast/wrought parts.4

Some costly steps are shared by both the ingot and powder metallurgy processing routes. The output of each of these primary processes is a billet of simple cylindrical or square cross-section, which must be then converted into the complex shape of the turbine disk. Forging therefore requires a number of blows, each with a different pair of dies. The initial dies have simple depressions, whereas the final dies must reflect all of the intricacies of the part itself. Dies for forging the superalloys are made from either tool steels or refractory metals, depending on the temperature range and forging technique. These materials are very hard at room temperature, which results in low machining productivity, long lead times, and high labor cost. This large outlay for tooling constitutes a fixed cost that can only be recouped through amortization over long production runs. The situation is made worse by die wear, which can cause production delays and impose costs associated with remachining. This multi-step forging process incurs other costs as well. Material is lost at every step, leading to overall material utilization rates that can be as low as 10%. Each forging step requires reheating of the part and incurs additional energy and handling costs. Some amount of costly machining of the final part is generally required as well, to remove flash and to form certain topographical features which are difficult to obtain by forging.
It is clear from the foregoing that an entirely new process for making turbine disks is needed to address the shortcomings of the existing production methods. In particular, what is needed is a process that has the capability to guarantee a low inclusion size, while simultaneously achieving a level of segregation control that can permit the production of ingots larger in diameter than is presently possible. In addition, the process should have a reduced reliance on hard tooling to shorten lead times and allow flexibility in lot size. Ideally, this would result in a lower production cost as well, but it should be noted that a somewhat higher production cost can be recouped in lower operating cost over the life cycle of the disk if the process provides design advantages that reduce the weight and/or increase the reliability of the disk.

A number of processes have been developed over the past decade with the goal of reducing reliance on part-specific tooling and machining, and it is logical to consider their applicability to the present problem. The most prominent of these Solid Freeform Fabrication (SFF) techniques are: Three-dimensional Printing (3DP), Selective Laser Sintering (SLS), and spray forming. All of these processes have certain advantages and disadvantages, and each is superior to the others for certain types of fabrication problems. For example, 3DP and SLS are capable of very high dimensional accuracy for net-shape manufacturing, but productivity suffers due to the need for powder spreading and leveling between each layer. It seems unlikely that these processes can be scaled up to economically produce large parts such as turbine disks. Moreover, complete melting of the powder generally does not occur in these processes, and they are therefore subject to many of the same defects that are encountered in conventional powder metallurgy. On the other hand, spray forming has no such inherent quality limitations since the part is formed directly from semi-solid droplets and there is no need for powder handling. High deposition rates can be attained, and large parts can be produced economically; however, there is little control over drop placement and only simple shapes can be created.
ELECTRON BEAM SOLID FREEFORM FABRICATION

There exists an approach that provides a combination of capabilities uniquely suited to the task of quickly fabricating large components to near-net-shape. In this process, called Electron Beam Solid Freeform Fabrication (EBSFF), parts are built up in a layer-by-layer fashion as in other SFF techniques. However, the similarity ends there; the addition of the metal comprising each layer is accomplished by feeding wire into a melt pool maintained on the surface of the previous layer by an electron beam (shown conceptually in Figure 1). A positioning system permits controlled motion of the melt pool relative to the part, and hence the location where the deposition is taking place. Successive beads of deposited metal are placed adjacent to each other to form a layer. After a layer is deposited, the part is lowered relative to the wire feeder and beam: focus position so that another layer can be deposited on

Figure 1. Conceptual drawing of EBSFF process
the surface of the previous one. This process is repeated with suitable variations in each layer's geometry until the desired shape is formed. Parts can be built up on a flat surface by horizontal translation relative to the electron beam, or annular parts can be fashioned by deposition onto a rotating cylindrical substrate (Figure 2). The latter variation is likely to be used for producing turbine disks and other parts with some degree of axial symmetry. A multiple-axis positioning system would allow the part to be re-oriented to produce features on virtually any of its surfaces. Prudent choice of the substrate and orientation allows internal channels to be created. Of course, as with all manufacturing techniques, there are limitations to the geometrical constructions that can be formed.

Dimensional control in EBSFF is better than in spray forming, but not as good as in 3DP or SLS. The spatial resolution is limited to a distance approximately equal to the diameter of the feedstock wire. Since relatively large wires can and should be used to economically produce large components such as turbine disks, dimensional accuracy will be low. Furthermore, the as-produced surface finish is unacceptable for most purposes.
since there is usually some waviness arising from the one-dimensional nature of the deposition process. These factors dictate that EBSFF be followed by a final forging and/or machining operation for turbine disk production. It is important to note that forging will only require a single die set since the as-produced disk will be very close to the final shape and will have a fine, uniform starting grain size. Since extensive deformation of the part is not necessary, forging can be performed on a relatively small press, greatly reducing the capital outlay required. Furthermore, the low forces will result in long die life.

The energy deposition behavior of electron beams is very different from that of other high energy density heat sources, such as lasers and plasma arcs. These are referred to as surface sources since they deposit all of their thermal energy within tens of nanometers of the surface in metallic materials. On the other hand, high velocity electrons penetrate some distance into the target material, losing their energy gradually through multiple collisions with the material's component atoms. Thus, a volume of material directly beneath the beam impingement point is heated instantaneously without the need for conduction from the surface. The depth of electron penetration increases with the accelerating potential (beam energy) and decreases with average atomic number and density of the material.

Davé has shown that this volumetric heating feature has the potential to make the EBSFF process very economical when compared with processes using surface heat sources. In essence, the subsurface energy deposition allows more heat input for a given surface temperature. Vaporization and radiation are strongly increasing functions of the temperature at the surface, so these energy loss mechanisms will decrease in relative importance as the beam energy is increased. Conduction losses also increase at the higher beam energies because of the larger volume being heated, but there is nonetheless a net gain of power available for melting. This widening processing space (Figure 3) translates into an increase in the maximum attainable deposition rate. Note that Figure 3 is drawn with one atmosphere as the highest tolerable vaporization pressure; this value is arbitrary, and the
practical limiting vaporization level will actually be determined by the detrimental effects of the vapor on electron beam generation and propagation.

Assuming that high-energy beams are used so that vaporization is kept to a minimum, the productivity (deposition rate) attainable in the process is expected to be limited by heat transfer from the part. After the thermal energy is used for deposition, it must be removed from the part as quickly as possible. If the bulk temperature of the part becomes too high, it may lose its shape or its fine solidification microstructure may coarsen. Active cooling of one or more of the part’s surfaces will be necessary to limit this temperature rise. Since low-energy electron beams require a high vacuum for beam propagation, cooling is generally accomplished with a water-cooled copper chill in contact with the surface of the part opposite that on which deposition is taking place. Fortunately, high-energy beams are capable of propagating in an atmosphere, and this means that the part can be immersed in a bath of suitable fluid to minimize the overall temperature rise in the part.

Unfortunately, the need for part cooling to increase productivity exacerbates another

![Diagram](image-url)

**Figure 3.** Range of allowable processing power as a function of beam energy for pure iron. The beam radius and travel velocity are taken to be 0.35 cm and 5 cm/s, respectively. 5
problem: cracking caused by surface tensile residual stress in the part. Temperature gradients are produced in the part as a consequence of the localized heat input required for deposition. Differential thermal contraction due to uneven cooling after processing leads to the residual stress. It is cumulative with every layer added so that the material's ultimate strength is eventually exceeded at the surface and cracking occurs. This effectively limits the maximum size of the part that can be produced. Careful control of the post-processing cooling conditions may mitigate this problem, but a better solution is possible due to a unique feature of electron and other high-energy-density beams. If designed for the purpose, the beams can be produced in the form of pulses of sub-microsecond duration. The ensuing rapid local thermal expansion leads to shock wave propagation throughout the part. Localized plastic deformation occurs at the shock front as it passes through the part. This greatly reduces the elastic stresses and leaves the surface in a state of compressive residual stress. If the surface of the part is shock-treated periodically during processing and during cooling, the residual stress can be maintained at a level below that which will cause cracking. Since deformation occurs only at the shock front at any given time, there is very little macroscopic dimensional change associated with the treatment.

The economics of EBSFF are of great interest for comparison to conventional processing and to other SFF methods. For low-energy EBSFF, the electron beam generation equipment is not expensive, but a high vacuum system with a chamber large enough to contain the part is also required. This costly accessory can be dispensed with for high-energy beams, which are capable of passing through gases at normal atmospheric pressure without significant attenuation. Only a relatively economical inert gas enclosure is needed. On the other hand, the electron accelerator itself increases in cost as the beam energy increases, and heavy radiation shielding is also required to protect personnel and other equipment from the hard x-rays produced. Nevertheless, a laser of comparable power output will likely be even more expensive, if one can be obtained at all. Moreover, recent
advances in electrical insulation technology may result in substantial decreases in the cost of intermediate-energy (0.5-1.5 MeV) electron accelerators in the near future.\textsuperscript{6}

In terms of operating cost, few high energy density heat sources are better than electron beams. The overall energy efficiency of electron beam generation can be upwards of 50%, while a typical value for high-power lasers would be about 1%. Furthermore, much of the laser’s power can be absorbed by the vapor cloud above the target surface or reflected away by the surface itself. In contrast, electrons penetrate the vapor cloud with negligible attenuation and backscattering from the surface is minimal, especially for high-energy beams. For nickel-based alloys, backscattering losses decrease from about 20% to less than 10% as beam energy is increased from 0.1 MeV to 4.0 MeV. Electron beam generation units are also relatively maintenance-free, with few moving parts or crucial adjustments. The only component requiring regular replacement is the filament. It is usually a tungsten wire or foil that is heated so as to produce electrons by thermionic emission. The tungsten oxidizes and evaporates over time, and the filament eventually fails from thermal stresses. It is generally located at the top of the electron beam generating column and in most designs, it is fairly easy to change. In contrast, most lasers have many optical components such as lenses and mirrors that require constant labor-intensive re-alignment and cleaning for peak efficiency. Due to imperfect transmissive or reflective properties, these components heat up during continuous operation and eventually wear out. They are often made from exotic materials such as ZnSe and can be very expensive to replace.

The EBSFF process offers several important microstructural quality advantages over conventional processing methods. The improvements over the ingot processing route mostly arise from the fact that only a small volume of metal solidifies at any one time. This leads to a higher local solidification rate and a finer and more uniform microstructure. This fine microsegregation is easily eliminated by a very economical homogenization treatment due to the short diffusion distances involved. Properties are also expected to be more homogeneous since the extent of macro-segregation is limited to less than the size of the
bead cross-section. Freckling does not occur as there is not enough time to form jets of interdendritic liquid. While powder production also subjects the material to rapid solidification at rates similar to those in EBSFF, the powder's excellent microstructure cannot be used to full advantage due to the problems caused by consolidation. On the other hand, the EBSFF process produces a fully dense part from the liquid in one step. From the standpoint of microstructural quality, the process can be viewed as combining the best features of both ingot and powder metallurgy: rapid solidification without the difficulties caused by consolidation.

There are some additional quality benefits of EBSFF that are not directly related to the high solidification rates. For example, the use of wire as feedstock should greatly reduce the incidence of very large non-metallic inclusions. The process of drawing the wire down to a very small diameter will cause breakage at any location where a large inclusion is present. An analysis of the deformation taking place in the drawing process can be used to calculate the largest inclusion that is capable of passing through the die without causing the wire to rupture. The maximum inclusion size can be determined with a high degree of certainty in this way and can then be used as a design parameter for EBSFF parts that are subjected to low-cycle fatigue. This can be viewed as a new kind of diagnostic test that can take the place of the non-destructive tests currently used to detect non-metallic inclusions. However, this screening procedure will be far more effective than any NDT methods currently in use since it should be able to detect much smaller inclusions at lower incidence levels. It is also proactive; if an inclusion is detected, only a small amount of raw material need be scrapped, as opposed to a whole billet or even a completed part. Even if a reasonably large inclusion is able to survive the drawing process without causing breakage of the wire, it will probably be fractured into many smaller inclusions by the high forces involved. These will be distributed into stringers in the wire (Figure 4) and ideally would be scattered throughout the melt pool during EBSFF, greatly reducing the potency of the inclusion as a fatigue initiation site.
Figure 4. Stringer of nitride inclusions in as-received Alloy 718 wire.
Unetched longitudinal section, 1088x.
LITERATURE SURVEY: CARBON AND CARBIDES IN ALLOY 718

Alloy 718 is one of the most frequently specified alloys for aircraft engine turbine disks. The primary reason for this popularity is its high strength at intermediate temperatures (up to approximately 650 °C). Alloy 718 is strengthened by fine precipitates of γ', an intermetallic phase with the formula Ni₃Nb. This is in contrast to most other superalloys which are strengthened by an Ni₃(Al, Ti) phase called γ'. The γ' phase is a more potent strengthenener than γ', but unfortunately it is only metastable; above about 650 °C, it begins to dissolve and re-precipitate as a stable form of Ni₃Nb called δ. The δ primarily appears as a coarse grain boundary phase and so does not appreciably strengthen the matrix. The kinetics of precipitation of γ' are several orders of magnitude slower than for γ', so that relatively long heat treatments of several hours are required to develop full strength. However, the sluggish precipitation is a major advantage from the standpoint of weldability; welds do not have time to fully harden during cooling and therefore are not susceptible to strain-age cracking. This is why Alloy 718 is specified for so many other engine parts such as shafts and diffuser cases. Another positive attribute is the low content of expensive alloying elements, as shown in Table 1. In particular, the absence of cobalt and the high iron level make the alloy very economical when compared to rival γ'–strengthened alloys.

| Table 1. Nominal Composition of Alloy 718⁸ |
| Ni  | Cr  | Fe  | Nb  | Mo  | Ti  | Al  | Si  | C   |
| 53.0| 18.6| 18.5| 5.0 | 3.1 | 0.9 | 0.4 | 0.3 | 0.04 |

The carbides present in Alloy 718 are predominantly NbC, with some Ti substituting for the Nb. They form during solidification, often heterogeneously nucleating on pre-existing TiN particles, which have the same crystal structure. This is in contrast to the
carbides in many other superalloys and the stainless steels which form via solid-state reactions. Several investigations have shown that the carbide size is inversely related to the local solidification rate.\textsuperscript{9} The slow cooling conditions in the center of a 20-inch VAR ingot can lead to very large carbides, which generally exhibit an unfavorable sheet-like morphology as well. Very little modification of the carbides is possible through heat treatment, although some coarsening has been reported at temperatures of 1150 °C and above.\textsuperscript{10} Severe plastic deformation can fracture the carbides into small pieces and spread them out in the direction of deformation, producing the stringers often seen in wrought product. Neither of these morphology changes are favorable from the standpoint of properties, so that the carbide distribution produced by solidification is the best that can be expected in the final part.

Historically, carbides have been viewed as microstructural features rather than inclusions since their maximum size is limited to that permitted by growth processes during solidification. Although they are generally present at much lower volume fraction, oxides and nitrides are a more serious concern since they are free to agglomerate while suspended in the liquid and so can be virtually unlimited in size. Nonetheless, the carbides can and do have a negative impact on a variety of technologically important properties. Furthermore, they are effectively inert with respect to solid-state treatments, so that most workers in the field have been content to simply document their effects on various properties. Few have considered the possibility that a more holistic processing approach might provide a way to influence development of the carbides at the outset so as to modify their morphology and size distribution, rendering them harmless. Only very unsophisticated attempts have so far been made in this direction, such as reducing the overall carbon content to extremely low levels. Aside from requiring the use of costly virgin raw materials, this simplistic approach has several significant drawbacks which will be discussed in detail later. The large body of literature dealing with such low-carbon variants of Alloy 718 is nevertheless a valuable resource for assessing the effect of carbides on a variety of properties. The following
review of this literature should serve to point out some of the possible benefits of refining the carbide size independent of alloy carbon level.

The most obvious detrimental effect of carbides arises because their formation consumes some niobium and titanium, and these atoms are then not available to participate in the precipitation hardening reactions. This would be expected to reduce the volume fraction of $\gamma'$ and $\gamma$ present in the alloy after heat treatment. The amount of hardener taken out of circulation is fairly small, though, and there is little noticeable effect on the tensile yield or ultimate strength of Alloy 718. This is fortunate since the primary design requirement for turbine disks is low-temperature strength at the bore to carry the inertial loads from the rim of the spinning disk and the attached blades.

Once the strength condition has been satisfied, the life-limiting property becomes low-cycle fatigue (LCF) and a large number of investigations in this area have implicated carbides as potential initiation sites.\textsuperscript{11,12} This is not surprising since the carbides are hard, non-metallic particles comparable to oxides and nitrides and they behave similarly when embedded in a relatively compliant metal matrix: any overall tensile stresses applied to the part tend to be concentrated at the particle/matrix interface. For inclusions close to the surface under low-cycle fatigue loading conditions, cracking or debonding from the matrix usually occurs within the first few stress cycles. Carbides can even be fractured prior to service during deformation processing or machining.\textsuperscript{13} In any event, the result is a crack with length of the order of the particle diameter and the remaining life of the part is spent propagating the crack to failure. Since the crack growth rate is a strongly increasing function of the crack length, forcing initiation to occur at smaller inclusions can increase the lifetime of the part substantially, as shown in Figure 5. Of course, initiation is facilitated even more by clusters and stringers of inclusions, especially if they are oriented normal to the surface of the part.

Even in conventional ingot processing, advances in melting techniques such as filtration have reduced the average size of oxide and nitride inclusions to the point where LCF
initiation frequently occurs at carbide particles or perhaps even grain boundaries. There is still a finite possibility that a large cluster or stringer of inclusions may be present and designing against this possibility incurs considerable weight and cost penalties. However, if the very large inclusions could be eliminated, the most potent crack initiation sites would be carbides and small oxides/nitrides. Carbides are far more plentiful in the material than the ceramic inclusions, and their average size is also somewhat larger. Therefore, any action taken to reduce the size of the carbides and/or improve their morphology would greatly inhibit crack initiation. On the other hand, carbides do not appear to accelerate the propagation of fatigue cracks. One study noted that carbides and nitrides up to 20 μm in diameter observed on LCF fracture surfaces had no effect on the striation spacing in their immediate vicinity.

The influence of carbides on mechanical properties is not limited to low-cycle fatigue. They can also serve as low-resistance pathways for fracture in monotonic loading, causing a reduction in toughness and ductility. Hirano et al found that material from a low-carbon heat of Alloy 718 absorbed much more energy during Charpy impact testing than material with standard chemistry. Although no deeper understanding was sought, the investigators clearly believed that this was due to the elimination of carbides, rather than from reduction of atomic carbon either in the bulk or at the grain boundaries. These workers also noted that tensile ductility as measured by reduction in area was improved in the low-carbon
material and this was independently corroborated by Banik et al.\textsuperscript{18} and Jackman et al.\textsuperscript{19} This latter work also included Charpy and fracture toughness testing at three carbon levels. The Charpy impact energy steadily decreases with carbon content, as shown in Figure 6. The only investigation into the mechanism for this behavior was performed by Mills and co-workers,\textsuperscript{20} who used fractographic observations to establish that carbides and nitrides nucleate dimples early in the fracture process.

![Figure 6. Charpy impact energy as a function of carbon content\textsuperscript{19}](image)

The highly-stressed but relatively cool core of the disk requires high strength, toughness and fatigue resistance to withstand the very large stresses applied to it. On the other hand, the rim is only subjected to relatively moderate stresses from the rotational forces exerted by the blades, but it is directly exposed to hot combustion products and so must have good creep resistance. As with the low-temperature properties, it is expected that carbides will have detrimental effects on high-temperature deformation and fracture in Alloy 718. However, a great deal of controversy is evident in the literature regarding changes in creep properties as a function of carbon content. Early studies by Stroup and Pugliese indicated that stress rupture life and elongation were sharply diminished in very low carbon material and this was the consensus opinion for many years.\textsuperscript{21}

The issue was re-opened some time later when Moyer presented results showing a lack of any detrimental effects on stress rupture properties even when carbon was lowered to
Table 2. Creep Properties of Alloy 718 at Two Carbon Levels

A. Stress-rupture Properties at 1200 °F and 100 ksi

<table>
<thead>
<tr>
<th>wt% C</th>
<th>Processing</th>
<th>Life (hrs.)</th>
<th>% Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.008</td>
<td>Standard</td>
<td>282.7</td>
<td>21.3</td>
</tr>
<tr>
<td>0.027</td>
<td>Standard</td>
<td>329.8</td>
<td>30.2</td>
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<tr>
<td>0.008</td>
<td>Mini-grain</td>
<td>66.7</td>
<td>33.0</td>
</tr>
<tr>
<td>0.027</td>
<td>Mini-grain</td>
<td>88.3</td>
<td>31.5</td>
</tr>
</tbody>
</table>

B. Creep Properties at 1100 °F and 120 ksi—Standard Processing

<table>
<thead>
<tr>
<th>wt %C</th>
<th>% Creep after 25 hours</th>
<th>% Creep after 870 hours</th>
<th>Life at 0.2% Creep</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.008</td>
<td>0.052</td>
<td>1.034</td>
<td>319.2</td>
</tr>
<tr>
<td>0.027</td>
<td>0.074</td>
<td>0.890</td>
<td>235.9</td>
</tr>
</tbody>
</table>

C. Creep Properties at 1100 °F and 120 ksi—Mini-grain Processing

<table>
<thead>
<tr>
<th>wt %C</th>
<th>% Creep after 25 hours</th>
<th>Life at 0.2% Creep</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.008</td>
<td>0.105</td>
<td>74.7</td>
</tr>
<tr>
<td>0.027</td>
<td>0.094</td>
<td>76.2</td>
</tr>
</tbody>
</table>

0.003 wt%. He attributed the prior workers' results to the primitive melt practices in use at that time, specifically the lack of an intentional magnesium addition. Workers from the same laboratory examined this issue seven years later and reached the same conclusion, but some of their own published data seems to make the very point that they are trying to downplay (Table 2). In their defense, the trend is not conspicuous, amounting to only about 15-20% improvement in stress rupture life for the higher carbon level. Creep life in the standard condition (supersolvus forging) supports the authors' contention, but even here the intermediate measurements reveal unusual behavior: the higher-carbon material creeps at a faster rate initially, but the creep rate it ultimately attains is obviously much lower than for the lower carbon material. No significant variation in creep life with carbon content is seen for mini-grain material.
Another group of researchers addressed this topic independently at about the same time but their testing produced quite different results. As shown in Figure 7, stress rupture life and ductility were both substantially degraded in the material with 0.006 wt% C vs. that with 0.033 wt% C.\textsuperscript{18} The other workers responded three years later with a study substantiating their earlier assertion that low carbon levels do not degrade creep performance. This time, their data was more convincing; full plots of creep strain vs. time were provided, and these showed slightly lower creep rates for the low-carbon material. It should be noted that the low-carbon material in this study actually had 0.010 wt% C, somewhat higher than in any previous work. In fact, carbides were actually observed in this material, although there was much less stringering than in the control heat, which had 0.027 wt% C.\textsuperscript{23} As part of a broad survey of properties, Schirra and Viens noted strikingly lower stress-rupture life for 0.05 wt% C vs. 0.007 wt% C. Stress-rupture ductility is slightly higher for the high-carbon material, though. As with the previous investigation, carbides were observed even in the low-carbon material.\textsuperscript{24}

![Graph showing stress rupture life and ductility for Alloy 718 with standard (0.033 wt%) and low (0.006 wt%) carbon content.](image)

**Figure 7.** Stress rupture life and ductility for Alloy 718 with standard (0.033 wt%) and low (0.006 wt%) carbon content\textsuperscript{18}

It is the opinion of the present author that some of the widespread disagreement in this area is caused by failure to distinguish between the compositional effect of carbon additions and the effect on primary carbide size/morphology. Like other interstitial elements,
carbon's size mismatch with the atoms of the matrix causes it to segregate to the grain boundaries. Once there, it is expected to act as a very powerful grain boundary strengthener on the basis of the strength of bonds formed with the matrix elements and between carbon atoms. In the ideal solution approximation, the bond energy is roughly equal to the enthalpy of sublimation. When the elements are ranked according to this criteria, carbon is found to be the most powerful grain boundary strengthener available (Figure 8). The regular solution model provides improved accuracy, but does not substantially change the ranking of the elements. This strengthening of grain boundaries should have a beneficial effect on the creep and stress-rupture properties, as well as fracture toughness and some forms of stress-corrosion cracking.

Improvements in creep and stress-rupture properties with increasing carbon content have been observed experimentally for a surprisingly wide variety of nickel alloys, ranging from simple corrosion-resistant alloys\textsuperscript{25} to the most advanced precipitation-hardened superalloys.\textsuperscript{26} In fact, before the advent of single-crystal turbine blades, carbon was frequently added to polycrystalline blade alloys for the express purpose of reducing creep by inhibiting grain boundary sliding. However, it is important to recognize that subtle changes in chemistry or processing can interfere with either the segregation of carbon to the grain boundaries or with its strengthening effect. Other interstitial elements may be more surface active and can successfully compete with carbon for some of the grain boundary sites. This reduces coverage and hence cohesiveness to a greater (sulfur) or lesser (boron, phosphorus) degree. Variations in bulk alloy chemistry may also have an effect on the propensity to form lower carbides (such as $M_6\text{C}$ and $M_{23}\text{C}_6$) at the grain boundaries, where they may be either helpful or harmful, depending on morphology.\textsuperscript{27} These poorly understood interactions may obscure carbon's beneficial effect on grain boundary cohesion.
Figure 8. Rank of the elements according to sublimation enthalpy. This plot can be used to determine the effect of a segregating element on grain boundary cohesion (adapted from Seah). 

In contrast, primary carbides seem to unequivocally degrade creep performance in Alloy 718. Figure 9 shows creep crack growth results for samples with three different distributions of carbides: two with stringers oriented parallel and perpendicular to the crack propagation direction, and a third with a fine and homogeneous carbide distribution. The stringer-containing specimens clearly exhibit much higher crack growth rates, with the parallel orientation being the most deleterious. Through careful optical and SEM observations, these workers were also able to determine the mechanism for the acceleration of creep crack growth caused by the carbides. The crack growth was found to be discontinuous, with microcracks periodically forming ahead of the main crack. The
Figure 9. Creep crack growth rate as a function of carbide stringer orientation. In another investigation, cast material with a coarse carbide distribution was found to perform poorly in notched stress-rupture testing. The carbon content for this “problem” material was approximately the same as that for several other reference heats (0.05-0.06 wt%). For some of the “problem” specimens, stress-rupture testing was interrupted and cross-sections of the cracks were prepared metallographically. Carbides slightly behind the crack tip were observed to be almost completely oxidized. The cracks were filled with a glassy phase, presumably a product of the carbide oxidation, and it was theorized that this phase might embrittle the grain boundary ahead of the crack. Moreover during oxidation, the carbides appeared to swell to several times their initial volume. This further aids crack propagation by providing a local crack-opening force superimposed on the overall load.
Even non-mechanical properties are not immune to the deleterious effects of carbides. This was demonstrated by Hirano et al for pitting corrosion using an immersion test in 5% FeCl₃ + 10% NaCl solution.¹⁷ As shown in Figure 10, the results vary substantially with heat treatment, but in general, the weight loss due to pitting is two to three times higher for commercial Alloy 718 than for low-carbon Alloy 718. Other immersion tests designed to induce general corrosion and intergranular attack did not show any variation in corrosion rate with carbon content. The mechanism for enhanced pitting was not explored in the study, but presumably the carbides act as cathodic regions, accelerating dissolution of nearby anodic regions in the matrix. A reduction in carbide size might lead to a more uniform potential distribution over the part surface and hence less pitting, but the phenomena involved are complicated and it is difficult to make predictions with any confidence. Nonetheless, any improvements in this area would be very beneficial to the reliability of disks in aircraft that are routinely deployed in salt spray environments.

![Graph showing corrosion rate](image.png)

**Figure 10.** Corrosion resistance in 5% FeCl₃ + 10% NaCl at 50 °C for 24 hours (adapted from Hirano et al¹⁷)

Coarse carbides are also unfavorable from a fabrication standpoint. They can interfere with the efficient removal of material by machining, a major problem in light of the fact that
some gas turbine engine parts are produced by machining away 80% or more of the material from the initial stock. WC-Co tool materials are generally used to machine Alloy 718, and the (Nb, Ti)C carbides have hardness that approaches that of WC. The large carbides are likely to span more than one depth of cut and therefore some of them must be fractured by the tool. The ensuing impact and sharp exposed edges of the carbide cause rapid tool wear. To get reasonable tool life, the machining speed must be reduced, negatively impacting machining productivity. The machinability of Alloy 718 has been shown by Schirra and Viens\textsuperscript{24} to increase with decreasing carbon content (Figure 11).

Here, the machinability rating is the productivity obtained relative to a reference alloy, SAE 1020 free-machining steel. These workers also performed metallographic analyses indicating that the improvement arose primarily from a reduction in the number of carbides and in the maximum carbide size. Smaller carbides require less energy to fracture and may be removed by other mechanisms such as pull-out, as well as causing less abrasive wear to

![Graph showing the effect of carbon content on machinability of cast + HIP Alloy 718](image)

Figure 11. Effect of carbon content on machinability of cast + HIP Alloy 718 (plotted from the data of Schirra and Viens\textsuperscript{24})
the tool. Large carbides have also been found to cause “mottling,” a macroscopically visible pattern of blemishes on the machined surface.\textsuperscript{31}

Alloy 718 is frequently specified for complex welded assemblies because of its excellent resistance to strain-age cracking. However, the alloy is still vulnerable to heat-affected zone cracking, especially if the base metal contains large carbides. The mechanism for this is incipient melting of the carbides and infiltration of the grain boundaries by the ensuing liquid. Stresses arising from thermal contraction of the weld deposit and base metal then pull the grain boundary apart.\textsuperscript{32} If the amount of liquid in any one area of the grain boundary is small, the carbon and any other melting point depressants can diffuse away quickly. This allows the boundary to solidify before experiencing high stresses during cooling. Smaller carbides are therefore much less likely to produce microfissures.

In light of the technological importance of the carbide distribution in this alloy, it is surprising that only one previous attempt has been made to model the formation of primary carbides. Nastac \textit{et al}\textsuperscript{33,34} have developed a very ambitious model that embodies essentially all of the solidification-related phenomena occurring during VAR and ESR of Alloy 718, including carbide formation. A finite element heat transfer model is first used to determine the thermal history at all points within the ingot, which is then used as input data for stochastic models that yield the columnar grain structure and the distribution of NbC and Laves. The carbide formation model assumes a known number density of nuclei all begin growing at the equilibrium liquidus temperature. Each is assumed to be at the center of a spherical volume element and growth is limited by diffusion of carbon from the liquid. Interference between volume elements is neglected so that the element’s outer surface is maintained at the bulk liquid composition. The interface velocity can then be calculated.

In general, the model of Nastac and co-workers seems to be focused on the details of computation at the expense of fully capturing the underlying phenomena. In particular, the thermodynamics of carbide formation seem to have been oversimplified; the carbide start temperature is taken to be the alloy liquidus, even though it is known to be somewhat
lower. The number density of carbide nuclei, a required input parameter, can only be determined through quantitative metallography. The model also does not consider cooling rates higher than about 15 °C/s since it is primarily concerned with ESR and VAR of large ingots. Furthermore, the use of finite elements and stochastic variables introduces unnecessary complexity. Clearly, a new model is required that can account for the high cooling rates present in EBSFF. As will be shown in the next section, suitable assumptions can produce an entirely deterministic model requiring a minimum of numerical computation.
MODEL

I. Electron-Material Interaction during EBSFF of Alloy 718

In general, electrons impinging on the surface of a solid will travel some distance into it, interacting with many of the component atoms. Each of these collisions will involve a transfer of energy from the electron to the atom. In the vast majority of cases, the thermal vibrational energy of the atom will be increased as a result of the impact, and the electron will continue on into the material with a slightly lower kinetic energy. If a sufficiently high energy (high accelerating voltage) is imparted to a large number of electrons (high current) and these are made to strike a material in a small area, the rapid rise in thermal energy can cause melting at that location. This effect is put to use in the EBSFF process to accomplish controlled, selective deposition of metal.

However, it is important to remember that each electron-atom interchange can have other possible outcomes. In some cases, the electrons undergo a nearly elastic collision with an atomic nucleus and are reflected back toward their source with very little loss in energy. The reflected electrons may lose some energy to interactions with other atoms after this, but many escape from the material altogether. These are called backscattered electrons and they can constitute a major energy loss term. The fraction of incoming beam power that is carried away by the backscattered electrons decreases with accelerating voltage and increases with the target material’s density and average atomic number. However, the electron scattering process is a stochastic one, and the backscattering losses must either be determined empirically or obtained from Monte Carlo computational models. Unfortunately, no work of this kind dealing with Alloy 718 has been reported in the open literature. However, Davé has performed the necessary Monte Carlo simulations to determine the backscattered energy fraction as a function of beam energy for 304 stainless steel. This alloy has similar density and average atomic number to Alloy 718, and its
backscattering behavior, given in Table 3, will be used in subsequent calculations as a close approximation of that of Alloy 718.

As mentioned above, the kinetic energy of non-backscattered incoming electrons is lost gradually, through multiple collisions with the atoms of the target material. This results in heat being deposited some distance below the surface where the beam strikes. The depth of penetration of the electrons increases with accelerating voltage. Since the same electron scattering processes which produce backscattering are operative here, Monte Carlo methods must again be used to determine the electron energy deposition profile. In this case, electron-electron interactions must be taken into account as well as electron-nucleus interactions. Davé has performed the necessary calculations for a variety of metals including Alloy 718 using the TIGER/ETS Monte Carlo codes developed by Halblieb et al.\textsuperscript{35} The output of the calculations is the average energy loss per unit of path length experienced by an incident electron, \( \frac{dE}{dR} \). This quantity is also referred to as the stopping power and is itself a function of the electron energy. The average mass per unit area of material that can be penetrated by an electron with incident energy \( E_0 \) is then:

\[
R(E_0) = \int_{0}^{E_0} \frac{1}{\left( \frac{dE}{dR} \right)^{-1}} dE
\]

This distance is called the electron range and can be converted into more conventional units of length by dividing by the material's density. These quantities are listed in Table 3 for Alloy 718 at a variety of beam energies. Also tabulated is \( \kappa \), a dimensionless quantity characterizing the electron energy dependence for a given material:

\[
\kappa = \frac{E_0}{R \left( \frac{dE}{dR} \right)_{E_0}}
\]
Table 3. Electron-Material Interaction Parameters for Alloy 718

<table>
<thead>
<tr>
<th>Incident Electron Energy, MeV</th>
<th>Backscattered Energy Fraction</th>
<th>Stopping Power, MeV-cm²/g</th>
<th>Range, g/cm²</th>
<th>Range, cm, assuming ρ = 8.2 g/cm³</th>
<th>κ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.169</td>
<td>2.8190</td>
<td>0.0216</td>
<td>0.0026</td>
<td>1.6396</td>
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<tr>
<td>0.2</td>
<td>0.158</td>
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<tr>
<td>0.4</td>
<td>0.145</td>
<td>1.5450</td>
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<tr>
<td>0.7</td>
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<tr>
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<tr>
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<td>0.078</td>
<td>1.5880</td>
<td>2.6530</td>
<td>0.3235</td>
<td>0.9495</td>
</tr>
</tbody>
</table>

Interpolated from the above data:

| 0.12                          | 0.167                         | 2.51                       | 0.030        | 0.0035                            | 1.615 |

To simplify the application of the electron absorption data to the present problem, the energy deposition is assumed to occur with axial symmetry and be constant to a depth κR beneath the surface. A radial Gaussian distribution is assumed for the beam shape and the effective beam radius r_b is arbitrarily defined as the 1/e power point. A known beam radius can therefore be used to obtain the distribution parameter, σ, of the Gaussian from

\[ r_b = \sqrt{2}\sigma \]

A maximum volumetric strength (energy density) can then be defined for the heat source:

\[ A_0 = \frac{P_A}{\kappa \pi r_b^2 R} \]

where \( P_A \) is the power absorbed by the workpiece (beam power net of backscattering losses). \( A_0 \) can be used as a normalization factor for the Gaussian distribution to produce a complete source term:

\[ \Theta(r', x') = A_0 \cdot \exp\left(-\frac{r'^2}{r_b^2}\right) \text{ for the range } 0 \leq x' \leq \kappa R \]
This expression is in cylindrical coordinates with $x'$ being the depth coordinate and $r'$ the transverse radial coordinate. In cartesian coordinates with $y'$ and $z'$ parallel to the material surface:

$$\Theta(x', y', z') = A_0 \cdot \exp\left(\frac{-y'^2 + z'^2}{r_{B}^2}\right)$$

for $0 \leq x' \leq kR$

The experimental work in this investigation uses an accelerating voltage of 120 kV at a beam current of 3.4 mA, producing 408 W of power in the beam. However, the data in Table 3 indicate that 16.7% of this power is carried away by backscattered electrons, for a total absorbed power $P_a$ of just 340 W. The average electron range $R$ at this beam energy is 0.0035 cm and $\kappa$ is 1.615. This means that a shallow layer below the surface will be heated very intensely by this low-energy beam. The peak source intensity $A_0$ is therefore rather high at $1.32 \times 10^7$ W/cm³ for a beam radius $r_{a}$ of 0.015 in.

II. Heat Transfer during EBSFF of Alloy 718

After the energy has been deposited and a small volume has been heated to very high temperatures, the heat will begin to diffuse throughout the workpiece according to the Fourier law of conduction. The temperature field resulting from a moving volumetric source in a thick plate has been determined by Davé.\textsuperscript{37} His model draws heavily upon previous work in this area, most notably Rosenthal's solution for a moving point source,\textsuperscript{38} and Eagar and Tsai's solution for a distributed surface source.\textsuperscript{39} Several key assumptions are shared with these models: the effects of phase changes and material addition are ignored, and the relevant physical properties are assumed constant with respect to temperature. The Green's function for a point source is multiplied by the volumetric source function obtained above and is integrated over space and time to obtain the temperature field. Davé performed the integration on a simplified Green's function in which the horizontal coordinates were set to zero, yielding temperature information only as a function
of depth below the center of beam impingement. This approach was suitable for determining power input requirements and melt depth, but the thermal history of points behind the beam is required for metallurgical investigations such as the present one.

The full Green’s function given by Davé is again presented here:

\[
g = \frac{1}{8[\alpha \pi (t-t')]^2} \cdot \exp \left\{ \frac{-[(y-V_0(t-t')-y')^2-(z-z')^2]}{4\alpha(t-t')} \right\} \cdot \left\{ \exp \left[ \frac{-(x-x')^2}{4\alpha(t-t')} \right] + \exp \left[ \frac{-(x+x')^2}{4\alpha(t-t')} \right] \right\}
\]

where \( \alpha \) is the thermal diffusivity, and \( V_0 \) is the travel speed (assumed parallel to the y-axis). \((x, y, z)\) is the point of interest at time \( t \) and \((x', y', z')\) is the center of the point of impingement of the beam. Note that the Green’s function is written for a coordinate system moving with the beam, so that the material can be considered as a fluid flowing past a stationary beam. The temperature field established after long times will be unvarying in this coordinate system and is thus referred to as pseudo-steady state. Since we are only interested in the limiting case in which material becomes molten and then solidifies at the slowest possible rate, we can confine our analysis to the centerline of the beam’s travel at the surface: \( x = z = 0 \). The Green’s function is now:

\[
g = \frac{1}{4[\alpha \pi (t-t')]^2} \cdot \exp \left\{ \frac{-[(y-V_0(t-t')-y')^2-(z')^2]}{4\alpha(t-t')} \right\} \cdot \exp \left[ \frac{-(x')^2}{4\alpha(t-t')} \right]
\]

To obtain the expression for temperature, the Green’s function is multiplied by the temperature rise caused by the source term \( \Theta \) and integrated:

\[
T = \iiint \iiint \frac{\Theta(x', y', z')}{\rho C_p} \cdot g \cdot dx'dy'dz'dt
\]

where \( \rho \) and \( C_p \) are the density and heat capacity of the material, assumed constant with temperature. The expressions for the source term and Green’s function can now be
non-dimensionalized and substituted. Non-dimensionalization will proceed according to the
scheme used by Davé:

\[ \gamma \equiv \frac{y}{r_B}, \quad \gamma' \equiv \frac{y'}{r_B}, \quad \eta' \equiv \frac{z'}{r_B} \]

transverse coordinates normalized by the beam radius

\[ \zeta \equiv \frac{x}{R}, \quad \zeta' \equiv \frac{x'}{R} \]

depth coordinate normalized by the electron range

\[ \tau \equiv \frac{R^2}{4\alpha} \]

characteristic time for thermal conduction based on range

\[ \psi \equiv \frac{t}{\tau}, \quad \psi' \equiv \frac{t - t'}{\tau} \]

time normalized by the characteristic time

\[ \phi \equiv \frac{r_B}{R} \]

beam aspect ratio

It will also be convenient to define a parameter comparing the relative magnitude of heat
transport by motion of the material and by conduction. By analogy to fluid systems where
heat transfer has both a convective and conductive component, this quantity is called the
Peclet number:

\[ Pe \equiv \frac{2r_B V_0}{\alpha} \]

With these substitutions, the expression becomes:

\[ T(\gamma, \psi) = \frac{P_\lambda}{\alpha \kappa C_p R} \int_0^\psi \int_0^\psi \int_0^\infty \int_0^\infty \frac{1}{2\pi[\pi \psi']^2} \exp[-\gamma'^2 - \eta'^2] \cdot \exp \left[-\frac{\phi^2}{\psi'} \left((\gamma - \gamma')^2 + \eta'^2\right) - \frac{Pe}{4} (\gamma' - \gamma) \right]\cdot \left[ \frac{\psi'}{2}\right] \cdot d\zeta' d\gamma' d\eta' d\psi' \]

Separating into component integrals containing only one space variable each:

\[ T(\gamma, \psi) = \frac{P_\lambda}{4\pi \alpha \kappa C_p R} \int_0^\psi \frac{Q_1 \cdot Q_2 \cdot Q_3}{[\pi \psi']^2} \cdot \exp \left[-\left(\frac{Pe}{4}\right)^2 \frac{\psi'}{(2\phi)^2}\right] d\psi' \]
\[ Q_1 = \int_{-\infty}^{\infty} \exp \left[ -\eta'^2 \left( 1 + \frac{\phi'^2}{\psi'} \right) \right] \cdot d\eta' = \frac{\pi \psi'}{\sqrt{\psi' + \phi'^2}} \]

\[ Q_2 = \int_{0}^{\kappa} \exp \left[ -\frac{\zeta'^2}{\psi'} \right] \cdot d\zeta' = \sqrt{\pi \psi'} \cdot \text{erf} \left[ \frac{\kappa}{\sqrt{\psi'}} \right] \]

\[ Q_3 = \int_{-\infty}^{\infty} \exp \left[ -\gamma'^2 - \frac{\phi^3}{\psi'} (\gamma - \gamma')^2 - \frac{Pe}{4} (\gamma' - \gamma) \right] \cdot d\gamma' = \]

\[ \frac{\pi \psi'}{\sqrt{\psi' + \phi^2}} \cdot \exp \left[ -\frac{\phi^3 \gamma^2 + \left( \frac{Pe}{4} \right) \psi' \gamma + \left( \frac{Pe^2}{8} \right) \psi'}{\psi' + \phi^2} \right] \]

The final integral is:

\[ T(\gamma, \psi) = \frac{P_s}{4\pi \alpha \kappa \rho C_p R} \int_{\gamma_0}^{\gamma} \frac{1}{(\psi' + \phi^3)} \cdot \text{erf} \left[ \frac{\kappa}{\sqrt{\psi'}} \right] \cdot \exp \left[ -\left( \frac{Pe}{8} \right) \frac{\psi'}{\phi^2} \right] \cdot \exp \left[ -\frac{\phi^3 \gamma^2 + \left( \frac{Pe}{4} \right) \psi' \gamma + \left( \frac{Pe^2}{8} \right) \psi'}{\psi' + \phi^2} \right] \cdot d\psi' \]

After some manipulation of the exponentiated terms,

\[ T(\gamma, \psi) = \frac{P_s}{4\pi \alpha \kappa \rho C_p R} \int_{\gamma_0}^{\gamma} \frac{1}{(\psi' + \phi^3)} \cdot \text{erf} \left[ \frac{\kappa}{\sqrt{\psi'}} \right] \cdot \exp \left[ -\frac{\phi^3 \gamma^2 + \left( \frac{Pe}{4} \right) \psi' \gamma - \left( \frac{Pe}{8} \right) \frac{\psi'^3}{\phi^2} \right] \cdot \frac{1}{\psi' + \phi^2} \right] \cdot d\psi' \]

This integral does not have a closed-form solution, but it can be very closely approximated through numerical methods. The temperature as a function of distance behind the beam is found by evaluating the expression for progressively higher values of the y-coordinate. Since the material is moving at constant velocity relative to the beam, this distance scale can easily be converted to time, giving the thermal history of material behind the beam. If this calculation is performed for a travel speed of 1.0 in./s and an ambient
temperature of 25 °C, the thermal history shown in Figure 12 is obtained. The physical properties for Alloy 718 listed in Table 4 were also used in this calculation.

Table 4. Physical Properties of Alloy 718 at 538 °C

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity</td>
<td>19.6 W/m°C</td>
</tr>
<tr>
<td>Density</td>
<td>8040 kg/m³</td>
</tr>
<tr>
<td>Heat Capacity</td>
<td>560 J/kg°C</td>
</tr>
<tr>
<td>Thermal Diffusivity (calculated from the above data)</td>
<td>2.53 x 10⁻⁶ m²/s</td>
</tr>
</tbody>
</table>

![Graph](image)

Figure 12. Calculated thermal history of material behind the beam

To determine the cooling rate, the expression for temperature is first differentiated with respect to $\gamma$.
\[
\frac{dT}{d\gamma} = \frac{P_a}{4\pi\alpha\kappa r C_r R} \int_0^\gamma \frac{1}{(\psi' + \phi')^2} \cdot \text{erf}\left[\frac{-\phi' \gamma + \left(\frac{P_e}{4}\right) \psi' \gamma - \left(\frac{P_e}{8}\right) \psi'^2}{\psi' + \phi'}\right] \cdot d\psi' \cdot d\gamma
\]

\[
= \frac{P_a}{4\pi\alpha\kappa r C_r R} \int_0^\psi -2\phi' \gamma + \left(\frac{P_e}{4}\right) \psi' \cdot \text{erf}\left[\frac{-\phi' \gamma + \left(\frac{P_e}{4}\right) \psi' \gamma - \left(\frac{P_e}{8}\right) \psi'^2}{\psi' + \phi'}\right] \cdot d\psi' \cdot d\gamma
\]

\gamma \text{ and } t \text{ are related through the travel velocity: } \gamma = \frac{V_0 t}{r} \text{ and } \frac{d\gamma}{dt} = \frac{V_0}{r}

\[
\frac{dT}{dt} = \frac{dT}{d\gamma} \cdot \frac{d\gamma}{dt} = \frac{V_0}{r} \frac{P_a}{4\pi\alpha\kappa r C_r R} \int_0^\gamma -2\phi' \gamma + \left(\frac{P_e}{4}\right) \psi' \cdot \text{erf}\left[\frac{-\phi' \gamma + \left(\frac{P_e}{4}\right) \psi' \gamma - \left(\frac{P_e}{8}\right) \psi'^2}{\psi' + \phi'}\right] \cdot d\psi'
\]

As was the case for the temperature, this integral does not have an analytical solution and must be evaluated numerically. Once this is done for a number of values of \(\gamma\), the results can be combined with those of the \(T\) vs. \(\gamma\) calculations to give a plot of cooling rate vs. temperature (Figure 13). This representation is convenient since we are seeking the cooling rate over a specific temperature range (between the liquidus and solidus) rather than at a specific time. It can be seen from Figure 13 that the cooling rate during solidification is approximately 7670 °C/s.
III. Thermodynamics of Solidification of Alloy 718

Alloy 718 is among the most complex of commercial alloys with nine alloying elements present in significant amounts. Obviously, phase relationships encompassing all of these species are beyond the present capability for experimental verification. However, it was recognized early on that the solidification behavior is largely determined by the concentration of only a few key constituents. Eiselstein, the alloy’s inventor, proposed that all of the constituent elements except niobium be grouped together and considered as a single component. The main features of the solidification behavior could then be explained using a binary phase diagram, with the \( \gamma \) solid solution of substitutional elements and the topologically close-packed Laves phase (M\(_2\)Nb) forming a eutectic in the composition range of interest (Figure 14). Small variations in the concentration of most of the grouped elements were found not to have a significant effect on the phase boundaries, but silicon
was noted to promote Laves phase formation. The grouping of minor elements with nickel to form a generic \( \gamma \) component is a common feature of all subsequent thermodynamic models of this alloy as well.

![Pseudo-binary phase diagram for Alloy 718 solidification](image)

Figure 14. Pseudo-binary phase diagram for Alloy 718 solidification

As the alloy was more thoroughly investigated, an important secondary reaction was observed to occur during solidification: the formation of carbides. While oxides and nitrides generally begin to precipitate at temperatures well above the liquidus in this alloy, carbide formation does not begin until some primary \( \gamma \) phase has already formed.

Furthermore, carbon is generally present in the commercial alloy in far greater amounts than the other interstitials (0.01-0.1 wt% vs. <0.01 wt% for phosphorus and <100 ppm for oxygen, nitrogen, and boron). Thus carbon has a profound effect on the solidification behavior, and a more complex phase diagram is required. Radhakrishnan and Thompson\(^{42}\) have proposed a so-called pseudo-ternary diagram with \( \gamma \), Nb, and C as the components. They have further speculated that the diagram is very similar to that of the Ni-Nb-C system. While this system has not been extensively studied, a previous investigation had succeeded
in establishing an approximate liquidus projection in the area of interest, shown in Figure 15.

![Liquidus surface for Ni-Nb-C ternary system within the Ni-NbC-Ni₃Nb composition triangle](image)

Figure 15. Liquidus surface for Ni-Nb-C ternary system within the Ni-NbC-Ni₃Nb composition triangle

Two factors hinder the use of the Ni-Nb-C system as the basis for a pseudo-ternary model for the solidification of Alloy 718. One problem arises from the fact that no Laves phase (Ni₂Nb) is present on the Ni-Nb-C diagram, whereas it appears almost universally in as-solidified Alloy 718. It can only be assumed that the other elements present in Alloy 718 cause the formation of Laves phase in place of the Ni₃Nb that forms during freezing of nickel-rich Ni-Nb-C liquid. The other issue is that the true nature of the reaction occurring at e₃ in the diagrams is not definitively known. It is represented in Figure 15 as a ternary eutectic or class I four-phase equilibrium, described by the following reaction: L → Ni + NbC + Ni₃Nb in the Ni-Nb-C system, or L → γ + NbC + Laves in Alloy 718. However, a class II reaction, L + γ + NbC → L + γ + Laves, could also occur at this point (Figure 16). Radnakrishnan and Thompson favored the ternary eutectic interpretation based on their examination of Vincent’s SEM micrographs of Alloy 718. However, recent experimental...
work by DuPont et al revealed very little intermixing of the NbC and Laves phase in as-solidified Ni-Fe-Cr-Nb-Si-C alloys. This would seem to indicate that the reactions take place at different times during solidification, as they would under the class II formulation.

Figure 16. Liquidus surface for Alloy 718 pseudo-ternary system within $\gamma$-NbC-Laves composition triangle, showing a Class II reaction at $e_3$.

The solidification path for alloys within the primary $\gamma$ phase field will depend upon the ratio of the carbon and niobium contents. For high C/Nb, the alloy will first form $\gamma$ and subsequently follow a curved path away from the $\gamma$ corner toward the line of two-fold saturation between the liquid and $\gamma$ and NbC (line between $e_1$ and $e_3$). Upon reaching it, the solidification path progresses down the line of two-fold saturation towards $e_3$, all the while precipitating $\gamma$ and NbC from the melt in a "eutectic-like" fashion. At $e_3$, the solidification path begins to follow the line of two-fold saturation between $\gamma$ and Laves phase; when all carbon has been rejected from the liquid at $e_2$, it solidifies into binary eutectic $\gamma$-Laves. It should be noted that very high C/Nb ratios will cause solidification to conclude on the line of two-fold saturation between $\gamma$ and NbC, without the liquid composition ever reaching $e_3$.

For low C/Nb, $\gamma$ will again be formed first from the melt, but the solidification path will miss the $e_1-e_3$ line and will instead intersect the $e_3-e_2$ line directly. $\gamma$-Laves eutectic-like solidification will then take place along the $e_3-e_2$ line as above, concluding with the terminal binary eutectic at $e_2$. At some intermediate C/Nb ratio, the solidification path will hit point
e_3 directly and only a tiny amount of NbC will be formed during the class II reaction before solidification proceeds along e_3-e_2.

For the present discussion, only compositions which form significant amounts of NbC on solidification are of concern. Moreover, since all of the formation of NbC phase occurs prior to the class II reaction at e_3, the details of Laves phase formation along the e_3-e_2 line can safely be ignored. The segment of the e_1-e_3 line between the intersection of the primary solidification path and the class II reaction is of interest here as it is the region of carbide precipitation. The endpoints of this segment in temperature-composition space must be determined for use as the input values to the growth model. The temperatures of these two points are most easily determined by Differential Thermal Analysis (DTA) for the composition of interest. Cooling data should be used, preferably at a high cooling rate to more closely match the solidification conditions prevailing during EBSFF. A DTA curve taken on cooling for the EBSFF Alloy 718 material used in this investigation is shown in Figure 17. The temperature difference between the sample and reference is plotted as a

Figure 17. DTA cooling curve for EBSFF Alloy 718
solid line, while the dashed line is the derivative of this function with respect to time.

Taking each reaction to begin at the first deviation from the local baseline, we find

\[ T_{L \rightarrow (\gamma + NbC)} = 1263 \, ^{\circ}C \] \text{ and } \[ T_{(L + NbC) \rightarrow (\gamma + Laves)} = 1176 \, ^{\circ}C \].

This is in fairly good agreement with the results of Knorovsky et al., who found that the \( L \rightarrow \gamma + NbC \) reaction began at 1252 \(^{\circ}C\) and \((L + NbC) \rightarrow (\gamma + Laves)\) was initiated at 1198 \(^{\circ}C\). Note that these are averages obtained from DTA runs on four different heats of Alloy 718.

Through careful quantitative metallography on a number of experimental alloys, DuPont et al. have established the liquidus projection in the \( \gamma \)-rich corner of the pseudo-ternary diagram for a simplified alloy system (Ni, Fe, Cr, Si, Nb, and C only). This diagram is shown in Figure 18. The class II reaction was found to occur at 23.1 wt% Nb and 0.04 wt% C, with the line of two-fold saturation between \( \gamma \) and NbC taken to be linear with C-axis intercept \( a = 1.13 \) wt% C and slope \( b = -0.047 \) wt% C per wt% Nb. The locations of the lines denoting the reactions are expected to be relatively insensitive to minor compositional changes so that this diagram can be taken to be valid for Alloy 718 as well.

![Figure 18. Expanded view of the \( \gamma \)-rich corner of the Alloy 718 pseudo-ternary diagram](image)
In contrast, the primary solidification path is unique to each alloy composition and must be calculated according to the procedure given by DuPont et al.\textsuperscript{50} Niobium is assumed to exhibit negligible back-diffusion into the solid during solidification, while the opposite extreme (infinitely fast diffusion through the solid) is assumed for carbon. Partitioning of niobium during primary solidification is therefore governed by the Scheil equation, whereas the equilibrium lever rule can be used for carbon.

\[
f_l = \frac{C_{0,C} - k_c C_{l,C}}{(1 - k_c) C_{l,C}}
\]

\[
f_l = \left( \frac{C_{l,Nb}}{C_{0,Nb}} \right)^{\frac{1}{k_{Nb}-1}}
\]

The distribution coefficients for Alloy 718 have been determined experimentally\textsuperscript{49} to be \(k_c = 0.21\) and \(k_{Nb} = 0.45\). Equating the two expressions for the fraction liquid and solving for \(C_{l,Nb}\) gives:

\[
C_{l,Nb} = C_{0,Nb} \left( \frac{C_{0,C} - k_c C_{l,C}}{(1 - k_c) C_{l,C}} \right)^{k_{Nb}-1}
\]

This is the equation for the primary solidification path. Figure 19 shows a plot of the path for the specific alloy composition of interest here (\(C_{0,Nb} = 5.14\) wt\% and \(C_{0,C} = 0.037\) wt\%). The point of intersection with the line of two-fold separation is found by solving the two equations simultaneously:

\[
\frac{C_{l,C} - a}{b} = C_{0,Nb} \left( \frac{C_{0,C} - k_c C_{l,C}}{(1 - k_c) C_{l,C}} \right)^{k_{Nb}-1} \quad \text{and} \quad C_{l,C} = a + bC_{l,Nb}
\]

For our alloy composition, the resulting coordinates for the start of carbide formation are \(C_{l,Nb} = 21.13\) wt\% and \(C_{l,C} = 0.1368\) wt\%. All of the necessary thermodynamic data for the growth model is now available.
Figure 19. Solidification path for a starting composition of 5.14 wt% Nb, 0.037 wt% C

IV. Growth of Carbide Particles

As the alloy is rapidly cooled from above the liquidus, γ will form and partitioning of Nb and C into the liquid will occur as described above. When the liquid composition reaches the line of two-fold saturation, NbC will begin to precipitate from the melt along with more γ. At high carbon concentration, a lamellar eutectic-like structure will be formed. However, this structure is not observed for the low carbon concentrations present in commercial alloys, and a divorced eutectic appears to be formed instead. Therefore, in this discussion, the NbC will be considered to nucleate as discrete particles from the melt. For simplicity, the NbC will also be assumed to be pure and stoichiometric. After the initial particles are formed, the liquid composition moves down the eutectic-like trough and other particles are nucleated. The original precipitates will still continue to grow during this period, hence it is reasonable to presume that they will ultimately become the largest present
in the material. The maximum size of the carbides can therefore be assumed only to depend on the kinetics of growth and not on nucleation.

The cooling rates attained by the EBSFF process, while high compared to most solidification processes, are assumed to be low enough that the chemical kinetics of growth are not affected. This means that local equilibrium will exist at the carbide/liquid interface and bulk diffusion of carbon and niobium through the melt will be the factor limiting growth. A further assumption is possible since carbon is present in the alloy in far more dilute concentration than niobium (0.18 at.% vs. 3.21 at.%) and they are both required in roughly the same proportions for NbC formation. This means that the carbon required for growth will have to be transported over much greater distances. Mass transport of niobium can then be taken to be very fast relative to carbon, and it is assumed to be readily available at the interface at all times during growth. This simplifies the problem to that of a single component element diffusing to the surface of a growing particle. This problem has been thoroughly treated in the literature for the case of solid/solid reactions taking place isothermally in binary alloy systems. The approach taken here will be along the same lines, but will deviate in some places as a result of the continuous cooling occurring in EBSFF and the solid/liquid, pseudo-ternary nature of the reaction being examined.

In order to form a volume increment \(dV\) of an NbC precipitate, a number \(dn\) of solute (carbon) atoms in addition to those already present will have to arrive at the interface. Assuming spherical particles,

\[
V = \frac{4}{3} \pi r^3, \quad dV = 4\pi r^2 dr, \quad \text{and}
\]

\[
dn = \frac{\left(C_{NbC}^i - C_L^i\right)}{M_C} \rho_{NbC} dV = 4\pi r^2 \frac{\left(C_{NbC}^i - C_L^i\right)}{M_C} \rho_{NbC} dr
\]

where \(C_L^i\) is the concentration (weight fraction) of carbon at the interface in equilibrium with phase \(y\), \(M_C\) is the atomic weight of carbon, and \(\rho_{NbC}\) is the density of NbC. Assuming that NbC is a stoichiometric compound, there will not be a composition variation within the
particle and the $i$ superscript can be dropped. However, the liquid composition in
equilibrium with NbC varies significantly during the course of growth. This can most
easily be observed on one of the orthogonal-axis versions (Figures 18 and 19) of the
pseudo-ternary liquidus projection: once the liquid composition has entered the $\gamma$-NbC
eutectic-like trough, further cooling results in an approximately linear change in carbon
concentration. This path is undoubtedly not very linear with respect to temperature, but this
approximation will nonetheless be made in the interest of simplicity. The slope $m$ of the
liquidus with respect to carbon concentration can then be considered constant. With a
cooling rate $\chi$ that is likewise assumed to be linear through the temperature range of
interest, the concentration variation will also be a linear function of time:

$$C_L = C_L^0 - (m \cdot \chi)t.$$  

$C_L^0$ is the carbon concentration at the start of growth, given by the
point at which the solidification path strikes the line of two-fold saturation on the liquidus
projection. With these modifications, the number of solute atoms required for an
infinitesimal increase in particle radius is:

$$\frac{dn}{dr} = 4\pi r^2 \left( \frac{C_{NbC} - (C_L^0 - m\chi t)}{M_C} \right) \rho_{NbC}$$

Since $n$ is a function of both $r$ and $t$, and $r$ is also a function of $t$,

$$\frac{dn}{dt} = \frac{\partial n}{\partial r} \frac{dr}{dt} + \frac{\partial n}{\partial t} \frac{dt}{dt} = 4\pi r^2 \rho_{NbC} \left( \frac{C_{NbC} - C_L^0 + m\chi t}{M_C} \right) \frac{dr}{dt} + 4\pi r^3 \rho_{NbC} \frac{m\chi}{M_C}$$

The excess carbon required at the interface can only be supplied by diffusion, and the
flux of atoms is then given by Fick's laws in spherical coordinates. The maximum
supersaturation is just 0.00865, and this is assumed to be small enough that the effect of
the particle's growth on the diffusion field can be ignored. Then, for a time interval $dt$, the
magnitudes of the two fluxes can be equated,

$$4\pi r^2 \frac{C_{NbC} - C_L^0 + m\chi t}{M_C} \rho_{NbC} \frac{dr}{dt} + 4\pi r^3 \rho_{NbC} \frac{m\chi}{M_C} = 4\pi R^2 \left( \frac{dD_L C'_L}{dR} \right)$$

55
where $R$ is the radial coordinate with origin at the center of the particle, $D_L$ is the diffusion coefficient of carbon in the liquid and $C'_L$ is the concentration of carbon in the liquid in mol./m$^3$ as a function of $R$.

$C'_L$ will now be converted to weight fraction $C_L$ according to the relation $C'_L = \frac{\rho_L}{M_L} C_L$,

where $\rho_L$ is the density of the liquid. Also, the diffusion coefficient and the density of each phase will be taken to be constant with respect to both temperature and composition.

$$4\pi r^2 \frac{(C_{nbC} - C^0_L + m\chi t)}{M_C} \rho_{nbC} \frac{dr}{dt} + \frac{4}{3} \pi r^3 \rho_{nbC} \frac{m\chi}{M_C} = 4\pi R^2 \frac{\rho_L}{M_C} D_L \left( \frac{dC_L}{dR} \right)_R$$

The flux balance equation can now be rearranged and integrated with respect to $R$ and $C$:

$$\int \frac{dR}{R^2} = \int \frac{\rho_L}{\rho_{nbC}} \frac{D_L dC_L}{r^2 \left( \frac{dr}{dt} \right) (C_{nbC} - C^0_L + m\chi t) + \frac{1}{3} r^3 m\chi}$$

The integration is carried out over the entire diffusive field, from the particle surface to an infinite distance into the liquid. The value for the bulk concentration in the liquid, $C^\infty_L$, can be expected to decrease during cooling as the growing carbides serve as sinks for the carbon that is in supersaturated liquid solution. However, this time dependence cannot be easily determined. It is very likely to be subject to significant variation from point to point in the liquid, depending on the degree of interference from the diffusion fields of other nearby carbides. As we are interested in the local conditions leading to the largest possible carbide, we will assume that there is no interference from other carbides, with growth occurring in liquid that has not been depleted in solute from its initial value, $C^0_L$. The integration can now take place with limits $R = r$, $C = C^0_L - m\chi t$ and $R = \infty$, $C = C^0_L$ to give:

$$\frac{1}{r} = \frac{\rho_L}{\rho_{nbC}} \frac{D_L \left( C^0_L - (C^0_L - m\chi t) \right)}{r^2 \left( \frac{dr}{dt} \right) (C_{nbC} - C^0_L + m\chi t) + \frac{1}{3} r^3 m\chi}$$
This equation can be rearranged to yield the interface velocity:

\[
\frac{dr}{dt} = \frac{\rho_L D_L m \chi t - \frac{1}{3} r^2 m \chi}{\rho_{NbC} \left( C_{NbC} - C_L^0 + m \chi t \right)}
\]

This differential equation can also be solved to obtain the precipitate radius as a function of time. It is a first order differential equation that can be made linear through a change of variable.

\[
\frac{dr}{dt} + \frac{m \chi r}{3 \left( C_{NbC} - C_L^0 + m \chi t \right)} = \frac{\rho_L D_L m \chi t r^{-1}}{\rho_{NbC} \left( C_{NbC} - C_L^0 + m \chi t \right)}
\]

With \( z = r^2 \) and \( r \frac{dz}{dt} = \frac{1}{2} \frac{dz}{dt} \), the equation is linearized:

\[
\frac{dz}{dt} + \frac{2 m \chi z}{3 \left( C_{NbC} - C_L^0 + m \chi t \right)} = \frac{2 \rho_L D_L m \chi t}{\rho_{NbC} \left( C_{NbC} - C_L^0 + m \chi t \right)}
\]

The integrating factor is:

\[
e^\left( \int \frac{2A}{3 \left( C_{NbC} - C_L^0 + m \chi t \right)} dt \right) = e^{\ln \left( C_{NbC} - C_L^0 + m \chi t \right)^{\frac{2}{3}}} = \left( C_{NbC} - C_L^0 + m \chi t \right)^{\frac{2}{3}}
\]

Multiplying both sides by the integrating factor gives

\[
\left( C_{NbC} - C_L^0 + m \chi t \right)^{\frac{2}{3}} dz + \frac{2 m \chi}{3 \left( C_{NbC} - C_L^0 + m \chi t \right)} z dt = \frac{2 \rho_L D_L m \chi t}{\rho_{NbC} \left( C_{NbC} - C_L^0 + m \chi t \right)^{\frac{2}{3}}} dt
\]

The left side constitutes an integrable combination equal to \( z \left( C_{NbC} - C_L^0 + m \chi t \right)^{\frac{2}{3}} \)

Substituting for \( z \) and integrating the right side produces:

\[
r^2 \left( C_{NbC} - C_L^0 + m \chi t \right)^{\frac{2}{3}} = \frac{2}{5} \frac{\rho_L D_L}{\rho_{NbC} m \chi} \left( C_{NbC} - C_L^0 + m \chi t \right)^{\frac{2}{3}} \left[ 3 m \chi t - \frac{9}{2} \left( C_{NbC} - C_L^0 \right) \right] + C
\]

The initial condition is \( r = 0, t = 0 \) so that

\[
C = \frac{9}{5} \frac{\rho_L D_L}{\rho_{NbC} m \chi} \left( C_{NbC} - C_L^0 \right)^{\frac{5}{3}}
\]
After substituting, the complete growth law is obtained:

\[
r = \frac{3}{5} \frac{\rho_L D_L}{\rho_{NbC} m \chi} \left[ 2m \chi t - 3\left(C_{NbC} - C_L^0\right) + \frac{3\left(C_{NbC} - C_L^0\right)^5}{\left(C_{NbC} - C_L^0 + m \chi t\right)^3} \right]
\]

This expression shows the familiar \( \sqrt{Dt} \) dependence encountered in isothermal growth, but it is modified by a term with cube-root dependence that reflects the variation in thermodynamic driving force over time. This relation is plotted in Figure 20 for the experimental composition using the data shown in Table 5. The liquid density given here is extrapolated from the published results of a numerical model developed in the interest of predicting freckling behavior. The density of stoichiometric NbC at 1200 °C was calculated from experimentally determined values for the density at room temperature and the linear thermal expansion coefficient. The diffusion coefficient given in Table 5 is that used by Nastac and co-workers in their carbide formation model, but this value should be taken as a very rough estimate. No data on the diffusivity of carbon in molten nickel alloys is available, and there is a great deal of disagreement between the results for the similar but more thoroughly investigated iron-carbon system.

<table>
<thead>
<tr>
<th>Table 5. Input Parameters for Growth Model</th>
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<tbody>
<tr>
<td>Liquid density, ( \rho_L )</td>
</tr>
<tr>
<td>Carbide density, ( \rho_{NbC} )</td>
</tr>
<tr>
<td>Diffusion coefficient, ( D_L )</td>
</tr>
<tr>
<td>Cooling rate, ( \chi )</td>
</tr>
<tr>
<td>Carbon content of carbide, ( C_{NbC} )</td>
</tr>
<tr>
<td>Initial carbon content of liquid, ( C_L^0 )</td>
</tr>
<tr>
<td>Slope of liquidus, ( m )</td>
</tr>
<tr>
<td>Carbide formation temperature range, ( S )</td>
</tr>
</tbody>
</table>
Figure 20 is somewhat misleading since the time available for growth is not really an independent variable. It is limited to the amount of time spent in the temperature range of carbide formation after nucleation. We are concerned only with the largest possible particles, so we will consider only those that nucleate at the earliest possible time. The time available for the growth of these particles is then known definitively: $t_{\text{max}} = \frac{S}{\chi}$, where $S$ is the temperature range over which carbide formation occurs for the particular alloy composition we are dealing with. This leads to an expression for the size of the maximum carbide particle as a function of cooling rate:

$$r_{\text{max}} = \sqrt[5]{\frac{3 \rho L D_L}{5 \rho_{NbC} m \chi} \left[ 2mS - 3(C_{NbC} - C_L^0) + \frac{3(C_{NbC} - C_L^0)^{5/3}}{(C_{NbC} - C_L^0 + mS)^{2/3}} \right]}$$

This relation is most conveniently visualized in the form of a log-log plot:
Figure 21. Log-log plot of the maximum carbide size vs. cooling rate

It can be seen in Figure 21 that the model predicts the largest carbides to be just under 1 μm in diameter for the EBSFF conditions of interest (a cooling rate of -7670 °C/s).

V. Effect of Carbide Size on Fatigue Behavior

The empirical relationship for crack growth rate in low cycle fatigue for many metals is found to be:

\[
\frac{da}{dN} = C \cdot \Delta \epsilon_p^\gamma \cdot a^\beta
\]

where \( a \) is the crack length, \( N \) is the number of cycles, and \( \Delta \epsilon_p \) is the plastic strain increment. \( C \), \( \gamma \), and \( \beta \) are constants dependent upon the material and testing conditions. No completely satisfactory theoretical basis has yet been proposed for this equation, but it can be thought of as a differential form of the widely accepted Coffin-Manson relation.\(^{56}\)
For most low-cycle fatigue situations, the overall state of plastic strain in the part does not vary significantly with crack length over the majority of the fatigue life. It can therefore be grouped with the constant $C$ to form a new constant called $\alpha$:

$$\frac{da}{dN} = \alpha a^\beta$$

Two distinct regimes of fatigue crack propagation have been observed in low cycle fatigue testing of Alloy 718.\(^5\)\(^7\) In the initial phase, the crack propagates along \{111\} slip planes within grains, producing a faceted fracture appearance. When the crack reaches a certain length, it stops following the slip planes and the fracture surface takes on a more conventional striated appearance. The true reason for this transition is not known, but it is probably related to the number of grains encompassed by the crack tip plastic zone. In any event, the change in crack propagation mechanism causes a corresponding change in the coefficient $\alpha$ and exponent $\beta$ of the relation for crack growth rate:

when $a \leq a_{\text{transition}}$\(\begin{align*}
    \alpha_{\text{faceted}} &= 3.5 \times 10^{-5} \\
    \beta_{\text{faceted}} &= 1.0
\end{align*}\)\hspace{1cm} when $a > a_{\text{transition}}$\(\begin{align*}
    \alpha_{\text{striated}} &= 3.5 \times 10^{-4} \\
    \beta_{\text{striated}} &= 2.0
\end{align*}\)

Note that these parameters are intended for use with crack length given in mm and are dependent upon the test conditions and part geometry. The number of cycles to failure can be found by performing the integration in each regime and summing:

$$N_f = N_{\text{faceted}} + N_{\text{striated}} = \frac{1}{\alpha_{\text{faceted}}} \ln \frac{a_{\text{transition}}}{a_{\text{initial}}} + \frac{1}{\alpha_{\text{striated}}} \left( \frac{1}{a_{\text{transition}}} - \frac{1}{a_{\text{critical}}} \right)$$

Non-metallic inclusions present at the surface are known to fracture or debond from the matrix in only a few stress cycles, producing a crack of dimensions comparable to those of the particle itself. Therefore, the initial crack length can be assumed equal to the diameter of the largest particle present at the surface. If variables associated with the low-cycle fatigue conditions are held constant, this relation can now be used to assess the fatigue life improvement to be gained from processing changes which affect the size of the non-metallic inclusions. Denda et al have done this for their specific low cycle fatigue testing
conditions, resulting in the plot shown in Figure 22.\textsuperscript{57} Their testing was done on smooth cylindrical specimens with a diameter of 6.35 mm machined from forged and direct-aged Alloy 718. Testing was done with a sinusoidal wave form with a stress ratio of 0 (tensile only), a maximum stress of 1180 MPa (5 MPa above the yield stress) and a frequency of 5 Hz. For this particular case, the critical crack length for fast fracture is approximately 1600 \( \mu m \). The faceted-striated transition was observed to occur when the crack had grown to between 100 and 150 \( \mu m \) and Denda \textit{et al} chose the lower end of this range to produce the curve in Figure 22.

![Graph showing the effect of carbide size on fatigue life](image)

\textbf{Figure 22. Effect of carbide size on fatigue life (adapted from Denda \textit{et al}°)}

The results of the previous model for maximum carbide size can be combined with the model for fatigue crack propagation behavior to determine a conservative low-cycle fatigue life for EBSFF parts. The maximum carbide size as a function of cooling rate can be taken as the initial crack size in the fatigue crack growth law to produce the plot shown in Figure
23. The cooling rate can be controlled through changes in the EBSFF process variables (primarily beam energy, current and travel velocity), which means that the LCF life can be controlled within a certain range. Of course, this assumes that the danger from large oxide and nitride inclusions has been eliminated through chemistry or melt process changes.

![Graph](image)

Figure 23. Low-cycle fatigue life vs. cooling rate, based on the carbide size
EXPERIMENTAL VERIFICATION

I. Production of EBSFF-718 Specimens

A prototype Electron Beam Solid Freeform Fabrication incremental caster has been constructed to perform preliminary investigations into the feasibility of manufacturing large parts using this technique. Because of safety and capital cost issues, the high energy electron beams (>1 MeV) which are the real focus of this investigation are very unattractive for research purposes. The testbed has therefore been assembled around a low-energy (<150 keV) electron gun and vacuum working chamber from a commercial electron beam welder, a Hamilton-Standard model W-2. The modifications to the stock piece of equipment were extensive, including the addition of high-accuracy x- and y-axis part positioning tables, a vacuum-capable wire feeder with x, y, and z-axis positioning capability, and an active cooling system for the part. Vacuum feedthroughs for these components were installed in the chamber wall, and many of the machine’s original systems were repaired or upgraded as required. Computer control of the part positioning tables, wire feeder z-axis positioner, beam on/off, and wire-feeder on/off was implemented. National Instruments LabView® software was used to integrate the many computer-controlled elements into a coherent user interface. A sketch of the in-chamber working elements of the prototype is shown in Figure 24.

As with all experimental equipment, the current implementation of the EBSFF caster has some limitations. Fully automatic part production is currently restricted by the hardware to maximum dimensions of 12" x 12" x 1" (l x w x h), but taller parts can be made with difficulty through periodic manual re-configuration of the positioning table supports. Expansion of the build envelope can be accomplished relatively easily through the addition of a vertical part positioner and a larger part mounting plate for the carriage of the x-y positioning table. This is not deemed necessary at this point in the development of the
process, but may become useful in the future. The wire feeder is designed to accept 0.035 in. diameter wire in 25 or 30 lb. spools. This is a standard size and quantity, which greatly facilitates wire procurement, but does not permit consideration of the wire size as a process variable. The wire feed rate is limited to a maximum of 100 in./min. The practical maximum travel velocity of the part positioning tables depends primarily on the mass of the part, but speeds of 1.0 in/s are easily obtainable for small sample parts. At present, the control software has only been developed to perform deposition in rectangular areas, since simple shapes are preferable for metallographic and mechanical property investigations. Control software designed for rapid prototyping processes should be readily adaptable to EBSFF when it becomes necessary to evaluate the ability of the process to produce more complex geometries.

Figure 24. Experimental electron beam solid freeform fabrication apparatus

The following sequence of operations is required to accomplish deposition of a part. The substrate, usually a flat plate made of the same material that will be deposited onto it, is securely clamped to a water-cooled plate mounted on the carriage of the x-y table. The vacuum chamber is closed and allowed to pump down to a vacuum of at least 2 x 10^4 torr.
The electron beam is focused to a point on the part surface prior to deposition and the
deflection coils are used to produce a slightly elliptical pattern somewhat larger than the
wire diameter in the transverse direction. The position of the wire feed head is then adjusted
so that the impingement point of the beam and wire coincide at the desired starting location
on the part. While the wire feeder is equipped with straightening rolls, some lateral
curvature often persists from the coil set of the horizontally-mounted spool, especially with
hard alloys. This must be accounted for so that the previously-deposited adjacent beads will
not deflect the wire before it reaches the pool. The wire feed rate is not under computer
control and is set manually at this point. The software is then directed to deposit the
required length and number of adjacent beads to produce the desired part dimensions.
During deposition of a bead, the wire is fed in the same direction as the part is moving, so
that it enters the trailing edge of the pool. When one layer is finished, the software directs
the wire feeder z-axis positioner to increment by the layer thickness, and another layer is
deposited on top of the previous one. This process is iterated until the part reaches the
required height.

A number of deposits of Alloy 718 up to approximately 0.25 in. thick have been made
successfully using this equipment. The substrate for deposition in each case was a 0.25 in.
 thick Alloy 718 plate which had been sandblasted to remove any oxide scale or other
contamination from the surface. Initial parts were made with each bead being deposited
directly on top of a bead from the previous layer. This produced extremely smooth and
vertical side walls, but ‘tunnels’ of porosity were found between the beads (Figure 25). This condition would be unacceptable in production parts, and the pores also entrapped
abrasive during metallography, making it difficult to obtain a scratch-free surface.
Therefore, later deposits were made with beads being deposited between the beads of the
previous layer, producing sound metal but also tapering side walls. A taper was also
designed into the front and back walls to prevent bulges of material from forming at the
beginning and end of each deposited line. All of the sample parts exhibit a relatively smooth top surface that is only slightly ridged in the direction of deposition.

![Figure 25. Tunnels of porosity in initial EBSFF samples](image)

Transverse section, unetched, 54.4x

II. Sample Characterization

A sample for metallographic analysis was deposited by offsetting the beads in each layer as described above. The travel speed was 1.0 in./s and wire feed rate was 50 in./s. The beam current was 3.4 mA at an accelerating voltage of 120 kV, making for a gross power output of 408 W. The beam was scanned at a frequency of 60 Hz in an elliptical pattern with major and minor axes of 0.045 in. and 0.015 in., respectively. The line pitch was 0.040 in. and the z-axis of the wire feeder was incremented by 0.012 in. per layer. After fabrication, the part was unclamped from the chill plate and was reduced to a more
manageable size using a Hypertherm Powermax 350 plasma cutter. These cuts were made at least 0.5 in. from the deposit so that it would not be within the heat-affected zone produced by the plasma. A Buehler Samplmet 2 abrasive cutter fitted with a resin/rubber-bonded alumina wheel was used in further sectioning of the deposit. Metallographic sections were made in three orthogonal directions: longitudinal-horizontal, longitudinal-vertical, and transverse. The longitudinal-vertical and transverse specimens were mounted in carbon-filled Bakelite (Buehler Konductomet I) using a Buehler Simplimet 3 automatic mounting press, while the longitudinal-horizontal specimen was large enough to be left unmounted.

Metallographic sample preparation was performed using manual techniques. If necessary, the samples were made flat on a 45 μm metal-bonded diamond grinding disc and subsequently ground with a 15 μm diamond disc. Flowing water was used as the coolant in both steps. Rough grinding was continued on Ultra-Plan, a stainless steel mesh surface, charged with a water-based 45 μm diamond slurry. A 9 μm diamond slurry, also water-based, was used on an Ultra-Pad cloth for the final grinding step. Polishing commenced with water-based 3 μm and 1 μm diamond slurries on Texmet 2000 and Texmet 1000, respectively. Final polishing was performed with weighted samples for approximately 30 minutes in a Buehler Vibromet I vibratory polisher on Microcloth charged with a 0.05 μm gamma alumina/distilled water slurry. The samples were ultrasonically cleaned in a solution of Ultramet I detergent in distilled water for at least 30 minutes between each step.

The light optical microscope was used to examine the samples in the unetched condition. A portion of the substrate plate is also visible in the transverse and longitudinal vertical sections and there is a striking difference between the appearance of these two materials. The baseplate material has a high density of light gray or pinkish second-phase particles which are believed to be carbides. The majority range in size from approximately 5-20 μm, with a small number of larger particles. There is also a far less abundant phase
which is gold in color and angular in shape, and this is most likely titanium nitride. The nitrides are often in contact with carbides, if not completely enveloped by them.

By comparison, the EBSFF material appears almost completely featureless, with only an occasional carbide or nitride visible. Figure 26 is a low-magnification micrograph of the boundary between the substrate and EBSFF deposit which clearly illustrates the disparity.

![Approximate location of boundary](image)

Figure 26. EBSFF/substrate boundary, unetched, 54.4x
EBSFF material is on the right

The few particles present are at the low end of the size range observed in the substrate. Very large dark gray particles were also visible optically in the EBSFF material, although they were extremely infrequent, with an approximate number density of only 3-4 particles/cm² of polished surface. They were often perfectly circular and had a number of
nitrides around their periphery, giving a "sunburst" appearance (Figure 27). Energy Dispersive X-ray Spectroscopy indicated that the dark core is alumina and confirmed that the outer particles are titanium nitrides (Figure 28).

Figure 27. Agglomerated inclusion in EBSFF material Unetched, 1088x

Figure 28. EDS maps of an agglomerated inclusion similar to the one depicted in Figure 27
It is important to note that there are significant differences in chemistry between the EBSFF deposit and the substrate plate. The most relevant of these is the higher carbon level in the substrate (0.047 wt% vs. 0.037 wt%), which partially explains its higher carbide volume fraction. The substrate plate has also had a processing history substantially different from that of the EBSFF material. Since being ESR remelted into an ingot, it was homogenized, upset, cogged into billet, and rolled to final dimensions. To provide a better comparison to EBSFF material, a small piece of an as-cast Alloy 718 VAR ingot was procured from a primary producer. The piece was in the form of a pie-shaped section from a transverse slice through the ingot. Chemical analysis revealed that the VAR material had composition fairly close to that of the EBSFF deposit, with particularly fortuitous correspondence in the carbon content (0.038 wt% vs. 0.037 wt%). This was corroborated by DTA testing which revealed a great deal of similarity between the on-heating curves for these two materials. Therefore, it will be assumed that differences in the microstructure of these two product forms can be attributed solely to the solidification processing each has been subjected to.

A bandsaw was used to extract a portion of the VAR material near the outer edge of the sector of provided material. This piece was then sectioned with the abrasive wheel into specimens containing transverse, axial-radial, and axial-tangential faces relative to the original ingot. These samples were prepared metallographically using the methods described above for EBSFF samples. A light gray phase was visible at high volume fraction on the etched surface of the VAR material in all three orientations. This phase was much coarser than that observed in either the EBSFF or substrate material. It also often exhibited an irregular morphology consisting of long curved sections tapering to a point at the edges. Some nitrides could also be seen but not as many as in the EBSFF and baseplate material.

A variety of etchants were found to reveal the solidification structure in the EBSFF and VAR samples. Both are dendritic, but the scale of the microstructure is vastly different; the
dendrites in VAR material could be seen with the naked eye if it was etched deeply enough, while those in the EBSFF material were only clearly resolvable at magnifications of 400x and above (Figures 29 and 30). With most etchants, the Nb-depleted dendrite cores appear white, while the Nb-rich interdendritic regions are darkened. In the VAR material, the carbides were almost always found to be in the interdendritic spaces rather than within the dendrites. Etching of the VAR material also reveals another phase, which is similar to the carbides in size and placement. It is believed to be Laves phase and can be easily differentiated from the carbides at this scale since it is somewhat more blocky and has a lumpy, partially dissolved appearance. Thin plates of δ phase (needles in a two-dimensional section) can usually be seen emanating from the Laves phase. Like the majority of carbides, this phase is too small to be viewed optically in EBSFF material.

Figure 29. Optical micrograph of VAR-718, 435x
Etched in 600 mg K$_2$S$_2$O$_5$/30 ml HCl/70 ml H$_2$O for 2 minutes
On the other hand, the Scanning Electron Microscope (SEM) has more than adequate resolution to observe the sub-micron precipitates present in the EBSFF material. Indeed, both carbides and Laves phase are clearly visible on a deeply etched sample. However, there is a problem in discriminating between the two; the rapid solidification results in both having a similar blocky appearance, and there is not enough time during cooling for any telltale δ needles to form around the Laves phase. Unfortunately, secondary electron mode does not provide very much atomic number contrast, and backscattered electron mode does not have adequate resolution to detect the precipitates. EDS analysis cannot be used to differentiate the phases since both phases contain Nb and there is too much matrix interference to positively detect the presence or absence of nickel in the precipitate.

One possible method for differentiating the carbides from the Laves phase is tint etching. This technique uses reagents that selectively deposit a thin film of reaction product
on specific phases in the alloy. The film is produced on either cathodic or anodic phases depending on the exact nature of the reagent. Carbides (and other non-metallic inclusions) are expected to be highly cathodic in most electrolytes and should be colored differently from the matrix. Colors cannot be seen in the SEM, of course, but the reaction films should exhibit both topological and material contrast with the uncoated material. Unfortunately, a suitable tint etchant could not be found, although three formulations from the literature were tested. One of these, potassium metabisulfite in hydrochloric acid, did not have sufficient specificity for carbides, coloring the slightly cathodic Laves phase as well. Another, alkaline potassium permanganate, was too discriminating, coloring some carbides but not others. A third etchant, a mixture of selenic and hydrochloric acids, could not be made to work at all, possibly due to the presence of highly cathodic filler in the conductive mounting medium.

An even more advanced sample preparation technique is clearly required to distinguish the carbides and Laves phase. Scanning Auger electron spectroscopy/microscopy can accurately determine phase composition, but does not have sufficient lateral resolution to observe particles in the 1 μm size range. On the other hand, Transmission Electron Microscopy (TEM) would definitely provide the necessary information. However, this characterization method requires a specimen thin enough for electron transparency (less than about 100 μm), and producing such a specimen from the bulk material is a time-consuming task requiring specialized equipment and a skilled operator. However, another method commonly used to prepare samples for TEM observation was found to be far more convenient. It is called extraction replication, and produces a sample nearly ideal for the present purpose: the second phase particles are embedded in an electron transparent film so that they can be imaged or analyzed via EDS without any interference from the matrix.

The making of extraction replicas does not require any equipment beyond what is normally present in the metallographic laboratory, although some special skills are required. A specimen is metallographically prepared through at least the rough polishing
stage and is given a light etch. The etchant is carefully selected to dissolve the matrix but leave any second phases intact. The time of this etch should be limited so that the second phase particles are merely in heavy relief above the surface and are not etched completely out. Next, a thin layer of carbon is deposited on the surface via a carbon arc. The specimen is then etched again, this time more heavily than before. This completely frees the particles from the matrix, so that there is no longer a mechanical connection between the carbon film and the specimen. After the film is removed, it can be viewed in either the TEM or SEM.

Extraction replicas were prepared from two of the EBSFF specimens (transverse and longitudinal horizontal) using the methodology of Vincent, the only published study providing experimental details of extraction replica preparation specifically for Alloy 718. The initial etch was performed electrolytically at 5 V in a solution of 15% sulfuric acid, 64% phosphoric acid, and 21% distilled water for 10 s. At this point, an additional etch was performed in 5% hydrofluoric acid, 10% glycerol, 85% distilled water at 2 V for 10 s. Vincent recommends this step to remove any oxide film produced by the pre-etch. The carbon film was then deposited on the two specimens in a commercial coating device. The film was then scored into squares approximately 2 mm on a side using a razor blade. The stripping etch was 10% hydrochloric acid in methanol at 4 V. The specimens were then plunged into distilled water at a slight angle so that the surface tension of the water could be used to pull the film away from the specimen. Several pieces of the film even smaller than the scored squares broke away from each specimen and remained floating on the surface of the water. They were captured on standard 3 mm diameter copper TEM specimen grids. The grids had been previously cleaned in 10% sodium hydroxide solution so that they would be wet more easily by the water. The grids, now containing the films, were allowed to dry thoroughly before further handling.

One of the carbon film fragments was viewed in a Vacuum Generators HB603 250 kV Scanning Transmission Electron Microscope (STEM) equipped with a Link Analytical EDS system. A brightfield image of the first region observed appears in Figure 31. A large
number of particles are visible, but EDS analysis showed that the vast majority of these contained some nickel as well as niobium (Figure 32), revealing them to be Laves phase rather than carbides. Some of these particles of Laves phase were slightly electron transparent, consistent with a thin plate morphology (Figure 33). To locate carbide particles for closer scrutiny, x-ray maps for nickel (K) and niobium (K, L) were made and compared. Indications on the niobium maps without a corresponding indication on the nickel map were deemed to be carbides. A small number of carbides were found in this way, consistent with the low volume fractions seen in the feedstock wire and VAR ingot. Some were larger than 3 µm in diameter and were presumed to be the anomalously large carbides seen occasionally in EBSFF material under the light optical microscope. There were also some extremely tiny particles (~50 nm diameter) with no nickel signature that were arrayed in a neat line. Closer inspection revealed these to be borides. Finally, a few particles were in the size range of interest (500 nm to 1 µm) and one of these is shown in Figure 34. A second field was also examined (Figure 35) and this one contained only a few carbides of moderate size (approximately 300 nm).
Figure 31. STEM brightfield image of extraction replica

Figure 32. Ni and Nb EDS maps for the same region shown in Figure 31
Figure 33. Laves phase

Figure 34. Intermediate-sized carbide
Figure 35. Second field viewed in STEM

Figure 36. Ni and Nb EDS maps for the same region shown in Figure 35
DISCUSSION

A substantial decrease in the volume fraction of carbides visible optically in EBSFF Alloy 718 vs. VAR material of similar composition was observed. While it is possible that some of the "missing" carbon could be retained in solid solution, the cooling rate is probably not high enough for this to account for a significant amount of the shortfall. Instead, the carbon is believed to be present in the form of carbide precipitates too small to be visible in the optical microscope (about 1 μm or less). The carbides in this alloy form during solidification by nucleation and growth from the liquid. They are not significantly altered by any subsequent solid-state process, so that the cooling rate during solidification is the chief determining factor of their size. Cooling rates during solidification are much higher in the EBSFF process \(10^3\text{-}10^4^\circ\text{C/s}\) than in any bulk casting process \(10^0\text{-}10^2^\circ\text{C/s}\).

A model for the carbide growth under the conditions present during EBSFF processing was developed from first principles. The model examines the growth of isolated spherical particles with long-range diffusion of carbon in the liquid being the rate-controlling process. The growth occurs under an increasing driving force since the liquid around an isolated particle becomes more supercooled as the temperature is decreased. If nucleation is assumed to occur immediately upon entering the carbide-containing three-phase field in the pseudo-ternary diagram, the model will predict the maximum carbide size expected in the material. This maximum size is of interest in forecasting the low-cycle fatigue initiation behavior in the absence of pre-existing non-metallic inclusions.

In the interest of confirming the validity of the growth model, an experimental determination of the size distribution of carbides present in EBSFF material was also undertaken. A bimodal distribution was observed, with the smaller population in the mid-to-high sub-micron range, and the larger population being approximately 3 to 5 μm. Based on these results, it was concluded that the smaller carbides formed during solidification,
while the larger population constituted carbides present in the feedstock wire that were incompletely dissolved during EBSFF processing. Incomplete dissolution is most likely the result of the presence of low-temperature regions in the melt pool due to the elliptical scanning pattern of the electron beam. This problem may be addressed by using special-purpose electron optics to obtain a circular beam spot with uniform intensity throughout. A different scanning pattern or frequency might also provide a satisfactory solution.

The difficulties inherent in detecting and viewing a sub-micron minority phase led to a very small statistical sample size for the smaller carbide population. The few that were observed were substantially smaller than the maximum size predicted by the growth model. This is reasonable in light of the fact that the vast majority of carbide particles will require some amount of undercooling for nucleation and will therefore not reach full size in the limited time available for growth. The low aspect ratio of the small carbides validates the assumption of spherical particles used in the model, although close inspection reveals that they are slightly faceted (Figure 34).

Both theory and experimental evidence suggest that the EBSFF process has the potential to eliminate carbide inclusions as low-cycle fatigue initiation sites. Unfortunately, this will not benefit turbine disk designers until the large oxide and nitride inclusions that are presently the major source of scatter in the LCF lives of turbine disks can also be eliminated. Some vacuum refining does occur in the process, as evidenced by the lower oxygen (22 ppm vs. 56 ppm) and nitrogen (50 ppm vs. 54 ppm) levels in the chemical analysis for the EBSFF material vs. the feedstock wire. However, there is still a substantial volume fraction of inclusions remaining after EBSFF. There is also reason to believe that the drawing process used in the manufacture of feedstock wire could break inclusions into smaller pieces. However, a refinement of the inclusion size distribution by this mechanism was not noted. In fact, the current implementation of the process seems to collect oxides and nitrides into large agglomerations which are likely to be very deleterious to the fatigue properties. Once more, the elliptical scanning pattern used in the current implementation of
the EBSFF process is believed to be the cause of this undesirable behavior. A vortical flow may be set up that causes the low-density inclusions to collect in the center of the ellipse where they are free to coalesce into a single large mass. Again, a beam spot of uniform intensity might prevent this from occurring. Another approach may be to use the inclusion collection effect to good advantage by sweeping the inclusions to the end of a deposited bead, where they could easily be removed by machining.

The ability of EBSFF to improve the size distribution and morphology of carbides in Alloy 718 independent of carbon content is unprecedented. This has important implications for alloy design, since it may provide an opportunity to increase carbon to levels that previously would have been forbidden due to an unacceptable carbide size and morphology. It has already been shown that one of the possible benefits of such a compositional change might be an improvement in creep resistance. Furthermore, if carbides could be made small and numerous enough, they could also serve as strengthening particles, as is currently done in cobalt-base alloys. These two effects could be used together to extend the usable temperature range of Alloy 718 above the current γ” solvus of about 650 °C. A dispersion of fine carbides might also be used for grain boundary pinning in wrought product. In present practice, grain growth is prevented by precipitating δ-phase during the final forging operation. Since the δ-solvus is only about 950 °C, final forging is limited to temperatures lower than this. A stable grain size at higher temperatures would bring the economy of lower forging pressures, as well as freeing the Nb in the δ to participate in γ” formation during subsequent aging treatments. There is also the possibility of greatly reduced segregation. If the carbon level can be made high enough, Laves phase formation during solidification can be completely suppressed. Combined with the fine dendrite arm spacing present in EBSFF material, this could completely eliminate the need for any kind of homogenization treatment. Lastly, higher allowable carbon levels would lead to a reduction in raw material cost through greater utilization of scrap metal. None of
these beneficial effects of chemistry modification would be possible without independent control of carbide morphology.
CONCLUSIONS

1) The EBSFF process can be used to produce superalloy components to near-net-shape. This capability has been demonstrated for simple shapes made from Alloy 718.

2) EBSFF processing causes a substantial decrease in the size of primary carbides when compared to bulk solidification processes. The carbide morphology also shifts from an irregular flat shape to approximately spherical.

3) The decrease in carbide size is consistent with the decrease in the time available for growth at the faster cooling rates encountered in EBSFF processing.

4) The refinement of carbide size and morphology produces an improvement in most mechanical properties. Of primary importance for turbine disk application is the increase in low-cycle fatigue initiation life that accompanies a decrease in the maximum carbide size.

5) For the investigated EBSFF conditions, some carbides are not completely dissolved in the melt pool and remain as a population of relatively large particles at low volume fraction in the finished part.

6) The current implementation of the EBSFF process causes oxides and nitrides present in the raw material to agglomerate into large, deleterious lumps. The mechanism is believed to be density-driven separation in vortices set up by the elliptical scan pattern of the electron beam.
FUTURE WORK

This thesis has presented a tantalizing glimpse of the possibilities for microstructural manipulation using EBSFF. However, a great deal of work is still required to validate the conclusions and assess the potential of the process. Firstly, more thorough experimental confirmation of the carbide growth model is needed. At present, this is hampered by an inability to easily differentiate between the Laves phase and carbide phase. This problem would be most elegantly solved by concocting an etchant that could dissolve the Laves phase as well as the matrix. Only the carbides would then remain on an extraction replica or etched surface, allowing the size distribution to be rapidly characterized by STEM or SEM analysis. Another possibility would be a brief homogenization treatment to eliminate the Laves phase, but it is not known whether appreciable coarsening of the carbides would also occur. A final option would be laborious element mapping of many fields in the STEM on extraction replicas made by the procedure described in the text.

It would also be prudent to verify that the expected LCF life improvement actually occurs. Since the model for LCF life is based on a standard specimen geometry, experimental results can be directly compared with it. However, the EBSFF process variables should first be modified to eliminate the anomalously large carbides and the agglomerated oxide/nitride inclusions seen in material produced with the present parameters. Switching to a beam spot with more uniform intensity throughout the melt pool may accomplish this. On the other hand, the possibility of sweeping the agglomerations to the edges of the part should be investigated as a purification technique. A different scan frequency may allow the agglomerations to be maintained indefinitely in the melt pool instead of dropping out of it and becoming entrapped in the solidifying metal. Other strategies for inclusion control should also be pursued, such as the use of the wire drawing process to remove large inclusions before they are even able to enter the melt pool. At
present, nothing is known about this exciting possibility, although the analytical tools required to assess its feasibility probably already exist within the wire drawing industry.

A thorough battery of mechanical tests should also be performed to determine whether other properties may be inadvertently improved or degraded. The creep performance and tensile strength would be of particular interest, as these may be enhanced by a fine dispersion of carbides. Fabricability evaluations of the EBSFF material should also be performed, as the welding, machining and forging behavior are all expected to be substantially different from conventionally produced material.

Electron Beam Solid Freeform Fabrication is a relatively new process, and the feasibility of using it to make turbine disks or any other type of part has yet to be determined. The present work has done little to demonstrate the near-net-shape capability of the process. In fact, the tunnel porosity observed in some of the initial trials raises serious questions about the ability to produce shapes with vertical walls. This could be a major problem since many commercial parts fall into this category. On the other hand, an optimal bead placement scheme may be found that alleviates the problem. In any event, it is clear that additional work is needed in this area. Similarly, the effectiveness of shock processing in mitigating surface tensile residual stresses will also need to be assessed. Most likely, this will done by treating EBSFF specimens of a standard geometry at an external laser-based facility, and measuring the residual stresses relative to untreated control specimens.

An initial investigation into alloy design for EBSFF turbine disk materials should also be undertaken. The possibility of creating alloys that are completely free of Laves phase should be investigated, although this may be difficult in light of the non-standard (high-carbon) feedstock material required. Powder-cored wire or pre-placed powder beds may be necessary for exploratory work in this area. Again, other properties will have to be investigated to make sure that they are not degraded by the chemistry change.

A potential benefit of EBSFF which should not be ignored is the capability to fabricate parts with graded microstructure and/or composition. This is the ultimate materials solution
to the problem of the turbine disk's diverse property requirements. A fine-grained microstructure is needed at the bore for high strength, while coarse grains would provide better creep resistance at the rim. A limited microstructural grading capability already exists in the present implementation, since heat input and travel speed can be varied over a substantial range while deposition is occurring. This capability can be utilized to produce a demonstration part in the very near future and the extent of the property variation can be assessed. Compositional grading holds out even more promise; the core of the disk could be made from a \( \gamma' \)-strengthened alloy such as Alloy 718, and the composition could be gradually changed so as to replace Nb with Al and Ti as the disk is built. Again, the primary impediment to research in this area is the lack of suitable feedstock material. A dual-wire or powder-cored wire system might be necessary. Thermodynamic calculations will also be required to verify that no brittle phases are formed at intermediate compositions.

A final area for investigation is process economics. The EBSFF process will never be more than a laboratory curiosity unless it results in a cost reduction for a given level of performance. It is likely that manufacturing costs will be higher for EBSFF than conventional processing, at least for long production runs; however, the present work has shown that the microstructural benefits of EBSFF may provide performance gains that would allow them to be sold at a premium price. Furthermore, there is also the possibility that inspection and product liability costs may be reduced if EBSFF-based approaches for removing non-metallic inclusions are successful.
## APPENDIX A: CHEMICAL ANALYSES

<table>
<thead>
<tr>
<th>Element</th>
<th>VAR</th>
<th>Wire</th>
<th>EBSFF</th>
<th>Plate</th>
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<tr>
<td>Carbon</td>
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<td>0.040 wt%</td>
<td>0.037 wt%</td>
<td>0.047 wt%</td>
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<tr>
<td>Oxygen</td>
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<td>56</td>
<td>22</td>
<td>8</td>
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APPENDIX B: ACRONYMS

EBSFF: Electron Beam Solid Freeform Fabrication
VIM: Vacuum Induction Melting
VAR: Vacuum Arc Remelting
ESR: Electro-Slag Remelting
HIP: Hot Isostatic Press
EBCHR: Electron Beam Cold-Hearth Remelting
3DP: Three-dimensional Printing
SLS: Selective Laser Sintering
NDT: Non-destructive Testing
LCF: Low Cycle Fatigue
DTA: Differential Thermal Analysis
SEM: Scanning Electron Microscope
EDS: Energy Dispersive (X-ray) Spectroscopy
STEM: Scanning Transmission Electron Microscope
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BIOGRAPHICAL NOTE

The author was born on July 22, 1968 in Pittsburgh, Pennsylvania. His parents are Emily and Edward Matz. He has one sister and one brother, five and ten years younger, respectively. He attended North Allegheny High School and graduated in 1986. He received the Eagle Award from the Boy Scouts of America in 1986. He received his Bachelor's degree in Metallurgical Engineering and Materials Science from Carnegie-Mellon University in December, 1990. While a student there, he was employed for four terms as a Co-op Metallurgist with the Allegheny Ludlum Steel Corporation, now a part of Allegheny-Teledyne International. He received the Master's Degree in Materials Science and Engineering from the Massachusetts Institute of Technology in August, 1993. He is a member in good standing of the following technical societies: the American Society for Metals (1988), The Materials Society of the American Institute of Mining, Metallurgical and Petroleum Engineers (1988), the Society of Automotive Engineering (1988), and Sigma Xi (1994).