Development of Simultaneous Transformation Kinetics Microstructure Model with Application to Laser Metal Deposited Ti-6Al-4V and Alloy 718

THESIS

Presented in Partial Fulfillment of the Requirements for the Degree Master of Science in the Graduate School of The Ohio State University

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2013

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ABSTRACT

Laser based additive manufacturing has become an enabling joining process for making one-of-a-kind parts, as well as, repairing of aerospace components. Although, the process has been established for more than a decade, optimization of the process is still performed by trial and error experimentation. At the same time, deployment of integrated process-microstructure models has remained as a challenge due to some of the reasons listed below: (1) lack of good process models to consider the laser-material interactions; (2) inability to capture all the heat transfer boundary conditions; (3) thermo-physical-mechanical properties; and (4) robust material model. This work pertains to the development of robust material model for predicting microstructure evolution as a function of arbitrary thermal cycles (multiple heating and cooling cycles) that can be integrated into a process model.

This study focuses on the development of a material model for Ti-6Al-4V and Alloy 718. These two alloys are heavily used in turbine engines and undergo complex phase transformations, making them suited to developing a material model for laser metal deposition (LMD). The model uses simultaneous transformation kinetics (STK) theory to predict the transformation of one parent phase into several products. The model uses
calculated thermodynamic properties of the alloys for portions of the respective transformation characteristics. Being a phenomenological model there are several user defined calibration parameters to fit the predicted output to experimental data. These parameters modify the nucleation and growth kinetics of the individual transformations. Analyses of experimental LMD builds are used to calibrate the material model.

A Ti-6Al-4V build made on a room temperature substrate showed primarily colony alpha morphology in the bottom half of the build with a transition to basketweave alpha in the top half. An increase in hardness corresponding to the microstructural transition was observed. This sample had an average of 340 HV hardness. Analysis of the calculated thermal profiles at the location of the morphology transition showed a transition from cooling below the beta transus to cooling above the beta transus. The Ti-6Al-4V STK model was calibrated using the experimental data from this sample.

The substrate of a second build was heated above the Ti-6Al-4V beta transus. This build showed predominantly basketweave alpha without a microstructural transition. Large prior beta grains (>1mm) were observed growing epitaxially from the substrate. These large grains promoted the basketweave formation. Hardness testing showed an average of 344 HV. Samples built in this way were also fatigue tested in the as built condition. Results show that they match previous builds that had been stress relieved.

A third build was performed at room temperature on a substrate with large prior beta grains. This build showed basketweave morphology like the second build even though
the substrate was not thermally controlled. The hardness for this build averaged 396 HV which is ~50 HV higher than the previous two. This build shows that it may be possible to produce better mechanical properties by controlling the beta grain size rather than heating the substrate.

Eighteen Alloy 718 builds were made using proprietary processing conditions. All of these builds were analyzed for nano-scale γ’ and γ’’ precipitates. Two of the builds were similar but had different laser powers. The low laser power build did not show nano-scale precipitates. The higher power build did show small amounts (<3%) of nano-scale precipitates and a corresponding increase in hardness at their locations. The higher power build was used to develop the STK model for Alloy 718.

Sixteen of these builds were part of a design of experiments and are referred to as DOE samples. Eight of them have a single layer while the other eight have multiple layers. They were examined for nano-scale precipitates. The amounts of precipitates were correlated to hardness values and thermal profiles.
This document is dedicated to my family. Especially Dawn who pushed me to pursue a graduate degree.
ACKNOWLEDGMENTS

My sincere thanks go to Professor Suresh Babu for his mentoring. He believed in being able to train me in MSE from a ME background. He has taught me to be a proficient researcher by thinking for myself and applying my thoughts to see what happens. I am confident that the skills he has bestowed upon me will be of great use in my continuing career.

Thanks also to my committee member Professor Wolfgang Windl. Thank you especially for your help during my term as a MSE 205 TA.

Thank you to all of my fellow graduate students for insight and companionship. Special thanks to Jeff Rodelas and Tapasvi Lolla for their help with electron microscopy and general phase transformation knowledge. Also thanks to Avinash Prabu for his work on the beta grain growth model and ongoing LMD experiments.

I would like to thank Anil Chaudhary and Applied Optimization for support of the CIMJSEA at OSU, which sponsored this work. Thanks also to Matt Keller at AO for his work with the thermal modeling.
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CHAPTER 1: INTRODUCTION

Laser metal deposition (LMD) is an enabling process in the repair of high value aerospace parts. There is a high material and machining cost for these complex components [1]. As a result, cost savings can be realized by reusing these parts after service by localized repair techniques [2]. Due to the complex geometry of these parts (such as blisks) and tight geometric tolerance (distortion must be minimized), normal welding methods (gas tungsten arc welding) are not viable. LMD presents a potential solution to this problem through the following advantages: (a) low heat input (< 500 Watts); (b) ability to vary the composition in small scales (< 2 mm); and (c) reduced distortion [2]. LMD works by spraying powdered metal into a small molten weld pool created by laser, followed by rapid solidification (>2000K/s initial cooling rate) [3]. The deposition apparatus consists of a fiber laser and powder delivery system. This beam is rastered around, in a layer-by-layer fashion, to build up a 3D part. Each layer may contain many linear and/or curvilinear weld beads. The path sequences for these beads and layers are often designed based on part geometry and geometrical precision and seldom based on microstructural homogeneity. It is well known that repeated heating and cooling cycles results in complex microstructural evolutions and resulting mechanical heterogeneity [4]. Mechanical heterogeneity must be avoided to make successful repairs.
Microstructure modeling that uses the thermal transients as input present a viable solution to controlling the microstructural evolution. By simulating the thermal history of a LMD build and predicting the resultant microstructure adjustments can be made to the build parameters before a physical build is ever made. To develop a phenomenological microstructure model builds must be made to provide calibration data. Microstructural analysis of these builds allows for the output of the model to be fitted to the experimental data.

Ti-6Al-4V and Alloy 718 are two alloys that are heavily used in aerospace applications. Titanium alloys account for around 33% of the weight in aerospace engines. Ti-6Al-4V is used in components up to 315°C, such as blisks and blades [5, 6]. Alloy 718 is widely used in turbine applications up to 650°C [7, 8]. This alloy represented over 50% by weight of the rotating part forgings used by GE aviation [7]. With these large amounts of these alloys used in turbine engines it is desirable to have repair processes that minimize downtime while maintaining structural integrity. Currently, repairs are done by replacing entire components with new ones. Repair processes using LMD have potential to reduce cost by only replacing the damaged or worn out portion of a part [1]. This minimizes downtime while preserving the structural integrity of the component outside of the repair area. As mentioned above the microstructural evolutions during the repeated thermal cycles of LMD must be better understood before this process can become commonplace. Therefore, the focus of the current research is to enhance this understanding using computer modeling of the thermal and microstructural evolutions.
The layout of this thesis will be as follows. The second chapter will be a background literature review. This will cover the state of the art in additive manufacturing, microstructure modeling and background information about Ti-6Al-4V and Alloy 718. The third chapter will present the research objectives. The fourth chapter will overview the experimental procedures and equipment that was utilized. The fifth chapter will describe the development of the STK microstructure model and its limitations. The results and discussions will be presented in chapters six and seven covering Ti-6Al-4V and Alloy 718, respectively. These chapters will cover the simulated thermal profiles from the LMD builds, the hardness measurements, microstructural observations, and calibration and results of the STK model. Conclusions and future work will follow the results chapters. The source code for the STK model will be presented in Appendix A for Ti-6Al-4V and Appendix B for Alloy 718.
CHAPTER 2: BACKGROUND

2.1 Modeling

2.1.1 Overall Transformation Kinetics

Overall transformation kinetics are used for modeling the change from one phase to another or the precipitation of a product phase from a parent. The theory accounts for the changing nucleation and growth rates as the transformation proceeds. The classical Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation is used for finding the extent of transformation.

Most of the phenomenological materials models have been based on the classical general theory of nucleation [4, 9, 10]. This theory provides a simple and elegant method for tracking an isothermal transformation as a function of time while allowing nucleation events to happen randomly throughout the volume. This is illustrated schematically in Figure 2.1 for a hypothetical volume transforming from beta to alpha phase. The left image is at the initial time, $t_0$ with the parent phase, $\beta$ and three small units of $\alpha$ phase (blue regions) that have nucleated and are in the process of growing. During a short time, $\Delta t$, some more $\alpha$ (orange color) has been allowed to nucleate and grow without accounting for neighboring particles. The total of these new particles is known as the extended volume. Since the nucleation events are random through the volume a potential
situation of hard-impingement exists between new nuclei and already pre-existing $\alpha$ regions. This is obviously not possible. Therefore, real volume fraction of a phase must be calculated from this extended volume. The methodologies for this correction are discussed below which is based on classical JMAK formulations.

![Figure 2.1. Schematic illustration of nucleation and growth of product ($\alpha$) phase into parent ($\beta$) phase with hard impingement](image)

The overall transformation for one phase can be calculated using the JMAK equation (equation 1)[11, 12]. Here $dV_\alpha$ is the actual change in volume of the $\alpha$ phase, $dV^e_\alpha$ is the extended volume or the total volume that could transform for the time step, and $V$ is the total volume of the sample. Therefore, $\left(\frac{V_\alpha}{V}\right)$ is the volume fraction of $\alpha$. By subtracting the volume fraction of $\alpha$ from 1, we have the probability of finding untransformed $\beta$ phase.

$$dV_\alpha = \left(1 - \frac{V_\alpha}{V}\right) dV^e_\alpha$$  \hspace{1cm} (1)
The change in extended volume $dV^e_\alpha$ is calculated by equation 2. Here the first part of the equation calculates the volume of a spherical particle. The growth rate and nucleation rate per unit volume are given by $G$ and $I$, respectively. The nuclei incubation time is given by $\tau$.

$$dV^e_\alpha = \left( \left( \frac{4\pi}{3} \right) G^3 (t - \tau)^3 \right) IV d\tau$$  \hspace{1cm} (2)

By integrating equation 2 the total extended volume of alpha can be calculated as seen in equation 3.

$$V^e_\alpha = \left( \frac{4\pi V}{3} \right) \int_{\tau=0}^{t} G^3 I (t - \tau)^3 \, d\tau$$  \hspace{1cm} (3)

By integrating equation 1, the real volume fraction can be calculated as a function of the extended volume fraction as seen in equation 4 [11, 13]. This allows for the calculation of the extent of transformation from $\beta$ to $\alpha$ as a function of the nucleation rate, growth rate and time. At every time step, the extended volume is allowed to grow without consideration of impingement and is then corrected.

$$\frac{V_\alpha}{V} = 1 - \exp \left\{ - \frac{V^e_\alpha}{V} \right\}$$  \hspace{1cm} (4)

2.1.2 Simultaneous Transformation Kinetics

In the current work, the simultaneous transformation kinetic (STK) framework is based on a paper by Jones and Bhadeshia published in 1997 [11]. Jones and Bhadeshia
developed these equations for steel to describe the decomposition of austenite into several ferrite morphologies. The STK model is based around an adaptation of the JMAK equations. This adaptation allows for modeling of the transformation of one parent phase into several product phases at the same time. The standard JMAK theory only allows for the transformation of one parent into one product. In the STK model each product phase has its own nucleation and growth parameters and at each time step is allowed to simultaneously grow unimpeded. The actual volume transformed is then calculated in the same way as described above for the JMAK theory.

Equation 1 can be modified to allow for the simultaneous transformation as seen in equation 5 [11, 13]. This example shows equations for only two transformations occurring but they can be expanded to allow for more. The change in the extended volumes would be calculated by equation 2.

\[
dV_\alpha = \left(1 - \frac{V_{a}+V_{\beta}}{V}\right) dV_{a}^{\alpha}
\]

\[
dV_\beta = \left(1 - \frac{V_{a}+V_{\beta}}{V}\right) dV_{\beta}^{\alpha}
\]

Two product phases growing from one parent phase is illustrated in Figure 2.2. The blue circles represent \(\alpha_1\) that has nucleated at \(t_0\). After an increase in time \(\alpha_1\) has grown and the \(\alpha_2\) (orange circles) has begun nucleating. Now there are two different morphologies forming at the same time. STK accounts for this by solving simultaneous equations for each of the product-phase morphologies being evaluated.
Equation 5 can be represented by equation 6 to provide a way to deal with any number of simultaneous transformations. These equations are useful for computer implementation [11]. In this equation, $\Delta V_j$ is the change in real volume for the $j^{th}$ phase-morphology at time $t$ while $V_i$ is the real volume of the $i^{th}$ phase-morphology at time $t$ and the total original volume of the parent phase is represented by $V$. The total volume of each transformed phase-morphology is given by $V_{j,t+\Delta t}$. The number of product phase morphologies being evaluated is represented by $n$. This means that each product-morphology would be given a number and this equation would be solved simultaneously for each one. Implementation of equation 6 was done within a software framework, which allows microstructure predictions for a given thermal cycle. This will be discussed in Chapter 4.
The overall transformation equations and therefore the STK equations are based on isothermal transformations. Therefore, the Laser Metal Deposition (LMD) thermal profiles must be broken into smaller time intervals for every temperature, thus creating small isothermal steps. The principle of additivity is applied to allow for the isothermal transformation kinetics to be applied to a continuous cooling situation [4, 12]. This principle allows for the extent of transformation to be calculated for each small isothermal step. Equation 7 shows how the isothermal steps are added together. In this equation \( t_i(T) \) is the amount of isothermal time it takes to reach an extent of transformation \( \zeta_i \). The time for the non-isothermal transformation is given by \( t \). Here \( t \) would be defined as the real time and \( t_i(T) \) would be the equivalent time. The concept of equivalent time will be discussed next.

\[
\int_0^t \frac{dt}{t_i(T)} = 1
\]

Figure 2.3 illustrates how a thermal profile can be broken into smaller time \((dt)\) and temperature \((dT)\) steps. Finer time-steps will lead to predictions with lower error. In contrast, large time steps will produce “saw-tooth” results with large error. At every time step, equation 6 is evaluated to calculate the extent of transformation simultaneously for all of the desired product morphologies.
As the transformation proceeds in real time from one isothermal step \((n)\) to the next \((n+1)\) an equivalent time must be calculated for the \(n+1\) step. A schematic showing the first few transformation steps from beta to alpha during cooling is seen in Figure 2.4. Three isothermal transformation temperatures are shown, \(T_1\), \(T_2\), and \(T_3\). As the temperature decreases the transformation follows different paths because the kinetics are different at different temperatures. The transformation starts at point \(O\) and proceeds along the curve for \(T_1\) until it reaches point \(A\). At this point the temperature decreases to \(T_2\) and the extent of transformation remains the same. However, it takes less time to reach the same extent on the \(T_2\) curve. Therefore, the equivalent time from \(O\) to \(B\) must be
calculated so the transformation can continue from \( B \) to \( C \). At point \( C \) the same process occurs as the temperature decreases to \( T_3 \). The extent of the transformation as a function of the actual time can be seen in the right plot. It can be seen how the slope of the curve changes as the temperature decreases (time increasing).

![Diagram](image)

Figure 2.4. Schematic diagram illustrating the use of equivalent time and the additive nature of a transformation during cooling. Adapted from [4].

The model developed by Jones and Bhadeshia takes the shape of the precipitates into account when calculating the nucleation and growth rate. For example, the allotriomorphic ferrite is modeled as discs that grow on both sides of the parent austenite boundary. Further, the growth rate of the faces parallel to the grain boundary plane is
three times higher than the face normal to the plane. This means the allotriomorphic ferrite will spread along the austenite grain boundaries much faster than it will grow normal to them. The STK model developed in this work does not take the shape of the precipitates into account. In this model they are simply presented as spheres. This is because obtaining an accurate result is dependent on diffusion calculations. However, running a diffusion modeling software such as DICTRA® was found to be too time consuming. The current STK code contains a function to approximate the diffusion data through an iterative process. However, this process does not converge much of the time and causes the program to crash. Therefore, the growth rate calculation in the current code uses Zener’s approximation to define the paraequilibrium at the beta/alpha interface.

2.1.3 Thermal Modeling

The thermal model used in this work was developed by Applied Optimization and is titled Simulation of Additive Manufacturing Processes (SAMP). In this work SAMP is used to calculate the thermal history within the build and substrate during LMD. SAMP models the laser-material interaction at every time step using finite element modeling. The simulation is set up by defining parameters to control the deposit path; number of layers; laser power, speed, and spot size; temperature dependent material properties; and powder volume rate and velocity. The additive process is simulated by adding elements along the path defined by the user. After setting up the simulation the software allows for monitoring of the simulation progress and the ability to stop and restart the simulation at any time [3, 14].
Data can be extracted from the simulation by query of nodes within the mesh. This data is extracted in a tabular format. For this work only temperature vs. time was extracted. The locations of the nodes for extraction were selected as close as possible to the physical location defined by the microstructural analysis to be described later. This methodology allows for the direct correlation of microstructural distributions to the associated thermal profile at these locations.

2.2 Additive Manufacturing
Additive manufacturing (AM) is a relatively new process. It first became available in the late 1980s [15]. Unlike traditional manufacturing methods, which are subtractive, AM adds material in a layer-by-layer fashion. Typically some machining operation is needed to produce the final shape, thus parts produced with AM are referred to as “near net shape” [4, 16].

Additive manufacturing processes were originally envisioned as a method of rapid prototyping. The parts were built without mechanical properties in mind. They were simply a way for designers and engineers to hold and see a part before devoting significant resources to mass production tooling. The fit and function of assembled parts could be checked. Soon, potential markets were seen where AM could be used to produce new parts or perform repairs on existing parts. With AM limited production runs or even one-off parts are no longer more costly than producing millions. Further, repair could be done to costly parts and eventually repair done locally without having to wait for parts to be shipped around the world [17, 18].

13
Multiple processes exist that fall into the AM category. The standardized terminology can be found in ASTM F2792 – 12a [19]. This work focuses on processes for creating metallic parts. Below laser sintering, laser melting, laser metal deposition, electron beam freeform fabrication, and shaped metal deposition will be defined and compared.

2.2.1 Laser Sintering
Laser sintering is a powder bed process. A schematic of this machine can be seen in Figure 2.5. The bed of metallic powder can be seen on the left platen. This platen moves downward as the part is built to keep the distance between the part and the laser the same. The laser rasters in the desired path to fuse the powder together. After a layer is complete the deposition mechanism pushes powder from the right platen to the left one to add a new layer of powder. This process is repeated until the part is complete.

Figure 2.5. Schematic for laser sintering and laser melting [20].
Laser Sintering is known commercially under two trade names [15]. Selective laser sintering was developed by researchers at the University of Texas at Austin [21]. Direct metal laser sintering is marketed by EOS as the EOSINT M 250 system with a CO$_2$ laser [22].

The Laser Sintering process entails only partial melting of the powder [15]. To obtain the best consolidation of pre-alloyed powder the operator must adjust the parameters to operate in the mushy zone. Even when processed in this way problems such as porosity and heterogeneous mechanical properties are common. A post-processing treatment is usually performed to obtain desired properties [15].

2.2.2 Laser Melting

Laser Melting is the same as laser sintering in machinery and procedure but it completely melts the powder [15]. Complete melting allows for fully dense parts without post-processing [23]. A higher energy density than that in Laser Sintering is needed to provide complete melting of the powder.

There are three commercial trade names for Laser Melting. The first is Direct Metal Laser Sintering by EOS. This uses the same name as the Laser Sintering system by EOS but uses different processing and a fiber laser [15]. The product is the EOSINT M 280. The second is Selective Laser Melting which is primarily used in Europe [24]. The third is LaserCusing by Sauer Product GmbH [25].
2.2.3 Laser Metal Deposition

Laser metal deposition (LMD) differs from Laser Sintering and Laser Melting because it is a powder spray system instead of a powder bed system [15]. In this system a laser is focused on a substrate to create a melt pool. Powder is then fed, coaxially, into the path of the laser and the melt pool. The substrate moves in the x and y directions to create a build in a layer by layer fashion. The powder is fed with a shielding gas (usually Ar). Shielding gas is also fed through the laser column to keep powder particles away from the optics.

The powder spray process allows for different powders to be incorporated into the same build. By having multiple powder feed systems the powder flow rates can be adjusted to adjust the composition. Parts manufactured in this manner are called functionally graded materials (FGMs) [15, 26]. FGMs can have their composition spatially tailored to have their properties match what is needed for the local stress level within the part.
LMD is a versatile process that can be used to produce new parts as well as repair existing parts [15, 18, 27]. Its ability to be used as a repair technology makes it the technology utilized for the present work. In the aerospace industry, LMD allows for expensive parts to be repaired rather than replaced, presenting a significant cost savings to the operator.

LMD is mainly known by two trade names [15]. Direct Metal Deposition (DMD) developed by Mazumder’s research group at the University of Michigan [28]. The DMD system includes a closed loop feedback control [27, 29, 30]. The next trade name is Laser Engineered Net Shaping (LENS®). This system was developed by Sandia National Laboratory and Optomec Inc. [18, 31].

2.2.4 Electron Beam Freeform Fabrication
This process is similar to LMD except it uses an electron beam as a heat source and metallic wire instead of powder (Figure 2.7). The builds are carried out under a vacuum so there is no interference with the electron beam. Electron Beam Freeform Fabrication was developed by the NASA Langley Research Center [32, 33].
2.2.5 Shaped Metal Deposition (SMD)
Shaped Metal Deposition uses either a Metal Inert Gas (MIG) or Tungsten Inert Gas (TIG) welding system with a wire feeder [9, 34]. Since this process uses traditional welding technology the heat input is much higher than a laser system. However, the MIG and TIG systems are considerably less expensive than a laser system. This system is most similar to multipass welding. RAPOLAC is a European consortium that is performing research into SMD for aerospace applications [35].

2.2.6 Hot Isostatic Pressing (HIP)
The HIP process is often used with additive manufacturing processes in order to improve the mechanical properties. It is necessary for fully dense parts from Laser Sintering [15]. Hot Isostatic Pressing works by subjecting the part to heat and pressure simultaneously. The pressure is uniform around the entire part. Pressures range from 15,000 to 45,000 psi
and temperatures can be up to 2500 °C [36]. These temperatures and pressures allow voids and cracks to be healed within the material thereby improving the mechanical properties.

2.3 Ti-6Al-4V

2.3.1 Alloy Information

The current research pertains to Ti-6Al-4V alloy containing around 10% β phase (BCC) and 90% α phase (HCP) at room temperature [4]. This alloy transforms to 100% β phase at around 1273K (referred to as the β-transus) [4, 37]. On cooling below this temperature, the β phase begins decomposing into α phase (Figure 2.8). The alpha phase can form in several morphologies [allotriomorphic grain boundary alpha (α_{GB}), Widmanstätten alpha: basketweave (α_{BW}) & colony-α, massive (α_{m}) and martensitic (α’)] depending on the prior-beta grain size and the cooling rate from the β-transus (Figure 2.9). The effect of cooling rate on the alpha morphology can be seen schematically in Figure 2.10. Line AB shows heating from the α+β region to the β region. Line CD shows that the fastest cooling will result in martensite. Intermediate cooling (line CE) will result in massive alpha. Slow cooling (line CF) will result in primary alpha (colony and basketweave). The typical cooling rates required to produce the different morphologies were referenced by Kelly [4]. For the allotriomorphic and Widmanstätten variants, a cooling rate of <20K/s is necessary. Massive takes place when the cooling rate is between 20 and 410K/s. The martensitic transformation occurs when the cooling rate is higher than 410K/s.
Figure 2.8. Schematic diagram showing the transformations from beta to alpha during continuous cooling. (a) Single beta grain. (b) As the temperature falls below the beta transus grain boundary alpha begins forming at the prior-beta GB. (c) Further cooling leads to GB alpha fully decorating the grain. (d) Alpha begins to consume the beta grain interior as colony alpha. (e) Further undercooling will lead to basketweave alpha formation [4].
Figure 2.9. Optical micrographs showing the variety of alpha morphologies that can form on cooling.

Figure 2.10. Schematic showing the transformations that occur in Ti-6-4 during different heating and different cooling rates [4].
As seen in Figure 2.8b the first alpha to nucleate is the allotriomorphic grain boundary alpha. This morphology forms continuous films along the prior-beta grains. The GB alpha shares orientation with the prior-beta grain boundary. The alpha has a burgers orientation relationship of \( \{110\}_\beta//\{0001\}_\alpha \) and \( <11\overline{2}0>\_\alpha//<111>_\beta \) with the beta. Since there are six different \( \{011\} \) planes in beta and two alignments of \( <11\overline{2}0>\_\alpha//<111>_\beta \) for each beta plane, there are 12 possible crystallographic variants [4, 38].

After all of the grain boundaries have been covered, alpha sideplates begin forming epitaxially (Figure 2.8d) from the grain boundary alpha. These sideplates are known as colony alpha because their parallel laths share crystallographic orientation with each other. This orientation is dependent on the crystallographic orientation that the GB alpha has taken with respect to the beta.

The shift from colony to basketweave is dependent on the beta grain size and cooling rate [4]. The basketweave laths appear to have random orientations (Figure 2.8e). This is due to more of the 12 crystallographic variants being visible a given micrograph. With small beta grains and slow cooling rates colony is likely to consume all of the beta before the undercooling is high enough for basketweave to form. The combination of larger beta grains and higher cooling rates will lead to primarily basketweave formation.

If the cooling rate is high enough (>20K/s [4]) a diffusionless massive or martensitic reaction can take place. If the temperature falls below the martensite start temperature of 848K before all of the beta has been consumed then the remaining beta will transform to
martensite. The effect of cooling rate on the diffusional alpha transformation can be seen in Figure 2.11. Deviation from equilibrium is only slight for 0.1 and 1K/s cooling rates. The 10 and 20K/s cooling rates have large deviations but the large amount of undercooling increases the driving force for the transformation and allows the fraction of alpha to nearly reach equilibrium values before the martensite start temperature ($M_s = 848K$). Here it can be seen that above 50K/s there is just over 30% of the volume has transformed to alpha leaving a large amount of beta that can undergo martensitic transformation. A cooling rate $\geq 400$K/s fully suppresses the diffusional transformation.

![Diagram illustrating the transformation from beta to alpha under equilibrium conditions and several cooling rates](image)

Figure 2.11. Diagram illustrating the transformation from beta to alpha under equilibrium conditions and several cooling rates [4].
2.3.2 LMD

During continuous cooling from a single thermal cycle one alpha morphology will dominate depending on the conditions. However, during LMD, the repeated heating and cooling cycles result in dissolution and growth of the different alpha morphologies. Past work with this alloy has shown visible macroscopic banding across the width of the build (Figure 2.12) [4, 9, 39-41]. Kobryn et. al interpreted these bands as colonies of secondary alpha with varying grain size and correlated to specific thermal cycles [39]. Baufeld reported that these bands form from excursions in temperature below and above the beta-transus [41].

Kelly also found “characteristic layers” throughout the build [4]. He defined this characteristic layer as a region of nominal material and a layer band that is repeated throughout the structure. Between each layer band there is basketweave alpha while the layer band contains colony alpha. Since the characteristic layer was not found in the last three layers he identified theses layers as a transient region. He further concluded that the characteristic layer does not fully develop until three subsequent layers are deposited. Therefore, a layer $n$ does not form the characteristic microstructural features until $n+3$ is deposited on top of it.
Due to the repeated heating and cooling cycles, spatial variations of microstructure and mechanical properties have been reported. Brandl et al. reported a 1-4 kN lower failure force in the as-built condition than plate material during a punch test [40]. Alcisto et al observed a 7-14% reduction in strength and 53% reduction in elongation, in the as-built condition, compared to that of wrought material [42]. Kobryn and Semiatin demonstrated that even after stress relieving, LMD parts do not match the properties of cast part [43].

Kobryn and Semiatin studied the difference in mechanical properties for different loading directions for LMD builds that had been stress relieved and Hot Isostatic Pressed. Their work (Figure 2.13) shows that the fatigue strength varies depending on the loading direction even after stress relieving. The S-N curve was generated using cylindrical
dogbone tension samples. The total length measured 76mm, the gage length was 13.5mm, and the gage diameter was 5mm. The fatigue life for the z-direction (empty triangles) survives lower stress and nearly an order of magnitude fewer cycles compared to the x and y-directions (empty boxes and diamonds). At best the stress relieved parts match the fatigue properties of cast parts. In order to improve the LMD fatigue properties a HIP’ing process had to be performed. This process allows the properties in all directions to be shifted into the “cast plus HIP” and “wrought anneal” regimes (filled shapes).

Figure 2.13. Fatigue data showing disparity between directional fatigue life for stress relieved LMD Ti-6-4 parts. It can also be seen that the properties can be improved by HIP’ing process [6, 43].

2.3.3 Microstructural Characterization
In order to develop and calibrate the STK model microstructure of the samples must be characterized. The method of characterization must also be quantifiable. This gives
experimental volume fractions that the model can be calibrated to. Given the complex multi-scale microstructure features in Ti-6-4 multiple characterization methods were used. The measurement of the μm to mm scale beta grain size was suited to the methods described in ASTM E112 [44]. The method used counted the intercepts of concentric circles with the grain boundaries.

The smaller μm scale alpha constituent needed each morphology volume fraction spatially tracked through the deposit. Since no commercially available software is capable of this analysis, manual point counting was used as described in ASTM E562 [45]. This method involved overlaying a 10x10 grid on optical micrographs. This grid gave 100 intersection points where the underlying microstructure would be recorded. By knowing where the micrograph came from within the build, a map could be generated to visualize the changing microstructure.
Ongoing research in the field of automated microstructure characterization is being performed Dr. Hamish Fraser’s group at OSU. Tiley and Searles have published work on procedures for characterizing titanium microstructures [46, 47]. This work employs serial sectioning techniques using the focused ion beam SEM. This allows the 3D structure of the grains to be analyzed. Their work involves methods for measuring the alpha lath size, the volume fraction of Widmanstätten alpha, the volume fraction of GB alpha, and prior β grain size. Recently, Sosa et. al have worked on developing 3D microstructural characterization techniques [48]. This technique uses two-point correlation to help determine the orientation of alpha lathes in optical micrographs.
2.3.4 Modeling
A number of papers have been written on different thermal and microstructure modeling approaches including traditional Johnson-Mehl-Avrami-Kolmogorov (JMAK) overall transformation kinetic theories, which considers the nucleation, growth, and dissolution of alpha phase within beta phase.

The current work is largely based on this work from Kelly’s PhD thesis published in 2004. Kelly developed a thermal model able to calculate the thermal transients within a 3D model of an 18-layer build. Kelly’s microstructure model utilizes JMAK theory (in a sequential fashion, without allowing for overlap of phase transformations) to provide estimations of the alpha fractions throughout the build [4].

In 2008 Charles developed a finite element model capable of predicting Ti-6Al-4V microstructure evolution during TIG metal deposition for an 11 layer build [9]. The thermal model used provides information for a 2D section through the center of the build. The model utilizes a modified JMA equation to provide predictions for the diffusional alpha transformations. In her work, kinetic constants were adopted from Kelly’s 2002 work.

Teixeira et al. have developed a microstructure model based on JMAK theory that is applicable to continuous cooling after forging for near-beta alloys [49]. This model takes beginning beta grain size into account for the kinetics of $\alpha_{GB}$. This model also considers the interactions between grain boundary alpha and intragranular alpha using a simultaneous transformation kinetic framework.
Crespo et al. have developed a model based on JMAK theory that was extended to predict mechanical properties based on microstructure [50]. Their model considers the transformation from beta to primary alpha for cooling rates less than 410K/s. For cooling rates higher than 410K/s their model considers a combination of primary alpha and martensite. This model predicts the microstructure as a fraction of $\alpha$ and $\alpha'$ and calculates the yield stress, Young’s modulus and hardness. The yield stress is calculated based on the contributions by alpha and beta which are combined as weighted stresses in the microstructure. The Young’s modulus and hardness were found by looking up the value based on the fraction of beta present before quenching.

### 2.4 Inconel 718

#### 2.4.1 Alloy Information

Alloy 718 is a precipitation strengthened Nickel-based superalloy. The gamma matrix has a FCC crystal structure with a lattice parameter of $a=0.356\text{nm}$. Gamma double prime ($\gamma''$; Ni$_3$Nb) is the primary strengthening precipitate. Metastable $\gamma''$ has a DO$_{22}$ crystal structure with lattice parameters $a=0.365\text{nm}$ and $c=0.746$. Gamma prime ($\gamma'$; Ni$_3$(Al,Ti)) also contributes to strengthening but forms to a lesser extent due to the low amounts of Al and Ti. $\gamma'$ has a L1$_2$ crystal structure and a lattice parameter of $a=0.356\text{nm}$. Since the lattice parameters of $\gamma''$ and $\gamma'$ are so close to that of $\gamma$ they are coherent with the matrix.

Several other precipitates can form including MX carbides (usually NbC), laves (Ni$_2$Nb), and delta (also Ni$_3$Nb but incoherent with DOa crystal structure). NbC has a FCC structure with a lattice parameter of $a=0.443\text{nm}$. Laves has a hexagonal structure with lattice parameters of $a=0.467\text{nm}$ and $c=0.771\text{nm}$. The above lattice parameters were
found by Knorovsky et al.[51]. The lattice mismatch between these particles and the matrix makes them incoherent. The formation of these other precipitates can be detrimental because they consume Nb that could otherwise be used for γ” formation.

Above 650ºC the γ” precipitates will begin being replaced by delta. Alloy 718 is widely used for parts where welding is necessary because the sluggish γ” precipitation prevents strain age cracking [7, 8, 52]. Precipitation in Alloy 718 during short aging times has been investigated by Alam et al. and this work will be used for comparison with the current LDM builds [53].

Alloy 718 typically undergoes solutionizing to dissolve the laves phase and reduce segregation. This is followed by an aging heat treatment to precipitate γ” and γ’. A typical heat treatment schedule consists of: solution annealing at 1000ºC for 1 hour followed by a water quench; aging at 717ºC for 8 hours; furnace cooling to 620ºC and aging at 620ºC for 10 hours followed by air cooling [54]. The material in this study is in the as deposited condition. Therefore a heterogeneous microstructure is expected along with detrimental phases present. The thermal profiles for the samples presented here will be compared to an aging temperature range of 620-720ºC (893-993K) [54-56]. Since most of the literature data involves either unaged or fully aged material the thermal data for this comparison will be presented as a histogram so the amount of time spent in the aging temperature range can be evaluated. This will allow for justification for the state of the microstructure and amount of γ”/ γ’. A TTT diagram for Alloy 718 can be seen in
Figure 2.15. This shows that γ’’ has a wide range of temperatures that it can form at. It also shows that γ’’ begins forming almost immediately in the aging process.

Figure 2.15. TTT diagram for Alloy 718 [8].

Knorovsky et al. investigated the solidification sequence for Alloy 718 [51]. They found that the following reactions occur as the material cools from liquid: first proeutectic γ forms; followed by a γ/NbC eutectic at ~1250ºC; the next step is continued γ solidification; finally, there is a γ/laves eutectic at ~1200ºC. This work also consisted of elemental analysis to determine how the elements segregate during solidification. The main alloying element of interest is Nb because it is needed form γ’’. They found Nb to have a partition coefficient of 0.5, this means that it segregates strongly to the liquid. So the first liquid to solidify (dendrite core) will be depleted in Nb while the last liquid to
solidify (dendrite boundaries) will be enriched. They found the dendrite cores to contain ~2.6wt.% Nb and the maximum solubility of Nb in γ to be ~9.3wt.%. The laves precipitate at the dendrite boundaries contains around 22.4wt% Nb. Similar results for the Nb segregation were found by Patel and Antonsson [57, 58].

Knorovsky et al. created the solidification diagram seen in Figure 2.16. This diagram does not consider the small amount of NbC they found in their study. The numbered points indicate measurements that were performed using differential thermal analysis and chemical analysis. Point 3 is the average core composition of 2.6wt.%, point 4 is the average eutectic composition of 19.1wt.%, point 5 is the maximum solubility of Nb in γ (9.3wt.%), and point 6 is the maximum solubility of Nb in Laves (22.4wt.%). This diagram helps schematically show how the first liquid to solidify is depleted of Nb and the last to solidify is enriched. If a part that has solidified in this way is aged the strengthening precipitates will only form along the dendrite boundaries because that is where the necessary alloying elements have segregated to. This would lead to heterogeneous mechanical properties throughout the material. This is the reason solutionizing treatments are usually performed before aging.
2.4.2 LMD

Inconel 718 produced with LMD has been the subject of a relatively few studies. Mechanical properties have been tested in the aged and unaged condition by Tabernero et. al [59]. They produced samples using different cladding strategies (different deposition paths) and then performed tensile tests. They found that the path of the laser has a significant effect on the strength and found that the best strength is achieved by aligning the laser path with the main stress direction. They also found that a homogenization and aging treatment improved the tensile strength and ductility by as much as 100%. Even after aging, the mechanical properties of the LMD parts were at best 75% those of wrought material.

Amsterdam produced LENS® builds with 718 and performed tensile and fatigue tests [60]. Their samples were solutionized and aged. They found their yield strength and ultimate tensile strength to be in agreement with literature values for wrought aged
material. The fatigue samples also matched literature values. However, they found macro defects in the builds that are detrimental to the fatigue life.

Balazic et. al have produced prototype blisk (bladed disk) blades as well as experimental repairs to blades using 718 [61]. Unfortunately their report did not include mechanical testing data.

Kong et. al made 718 builds with varying parameters and then classified the build quality [62]. To assess the build quality they used parameters such as crack length, lack of fusion, porosity, and penetration. By using a design of experiments software package they were able to find a combination of parameters that gave the lowest heat input while maintaining high deposition rate and build quality. This is important for repairs in order to keep build time short (cost down) and distortion to a minimum.

Baufeld et. al performed experiments using shaped metal deposition (SMD) with 718 [63]. Entire flat dogbone tensile specimens were machined out of the SMD build. The samples had dimensions of 25 x 8 x 3mm. They varied the strain rate to see if it had an effect on the strength and found no correlation. They compared the SMD yield strength and UTS to published data for other processes (LMD, electron beam deposition, and casting). They found the SMD yield strength to be the lowest while their UTS was only above casting. However, SMD had the best ductility.

Zhao et. al studied LMD 718 and the effect of different powders on the mechanical properties [64]. They compared gas atomized (GA) and plasma rotation electrode
preparation (PREP) powders. Their samples underwent a standard aging heat treatment. They found more porosity and lower stress rupture life using the GA powder. They found the tensile test results for both powders in the aged condition to match those of wrought 718.

Blackwell produced LMD builds which were tensile tested after various heat treatments [55]. The effect of Hot Isostatic Pressing (HIP’ing) was also analyzed. The tensile tests were performed on samples with the build direction parallel to the loading direction as well as with the build direction perpendicular. The parallel samples placed the interface between the build and substrate at the middle of the sample in order to investigate any weakness at the interface. They found the as-deposited samples to have low yield strength in both directions. The UTS for the perpendicular sample was 350 MPa higher than the parallel one. The rest of the samples showed strengths on par with wrought material. However, the ductility of the LMD parts was lower than the wrought value though. It was found that the parallel samples failed in the deposit material and not at the interface. After HIP’ing the samples showed slightly lower strengths but much improved ductility.

2.4.3 Microstructure Characterization
Obtaining an overall view of the microstructure in an as-built 718 LMD build is difficult because of the spatial heterogeneity combined with multiple length scales. It will be shown that the 718 samples have significant elemental segregation which leads to areas with a high concentration of precipitates and areas of low concentration. Depending on the thermal gradient and growth rate different solidification structures will form during
cooling. It will be seen that some of the samples analyzed here have varying solidification structures in the bottom and top of the build. This is shown schematically by Kou in Figure 2.17 [65]. This shows how the solidification structure changes from planar to equiaxed as a function of the temperature gradient and growth rate. The solidification structure is important to being able to characterize the strengthening precipitates in this material.

![Figure 2.17. Schematic of different solidification morphologies as a function of temperature gradient (G) and growth rate (R) [65].](image)

2.4.4 Modeling

No literature was found regarding a precipitation model for 718. The commercial software JMatPro does have the ability to predict the phase fraction of precipitates. The capabilities of the software include thermodynamic properties over a range of
temperatures, solidification diagrams, evolution of $\gamma'$ & $\gamma''$ during isothermal aging at 720ºC, and the calculation of CCT and TTT diagrams [66].

The software TC-PRISMA is able to provide information about precipitation using thermodynamic and kinetic databases. The software calculates the nucleation, growth, dissolution, and coarsening of particles in a matrix. Currently applicable to isothermal conditions but application to cooling conditions will be implemented in the future. As of the writing of this document this software was not available at OSU for evaluation.
CHAPTER 3: OBJECTIVES

The main objective for this research is to develop a material model for Ti-6Al-4V and Alloy 718. To develop a phenomenological model samples that were built with different proprietary parameters were analyzed. Additional objectives include:

1. Examining the relationship between hardness and microstructure in LMD builds.
2. For Ti-6Al-4V examine the effect of controlling the thermal environment during the LMD build. Specifically, the effect on fatigue life was investigated.
3. Develop methodologies for characterizing the spatial microstructure variation in LMD builds.
CHAPTER 4: EXPERIMENTAL PROCEDURE

4.1 Polishing Procedure

Ti-6Al-4V samples were polished using the following procedure. After sectioning, the samples were ground using a belt grinder to remove any large scratches. If large defects were still apparent hand grinding was done using 320 or 400 grit paper. From here the samples were ground using 600 grit followed by 800 grit paper. The final step was 8+ hours on a vibratory polisher using 0.2 µm colloidal silica. Following the vibratory polish the samples were thoroughly cleaned with water and several minutes in an ultrasonic bath using ethyl alcohol. The samples were then ready to be used in the SEM or etched for optical microscopy.

Inconel 718 samples were polished the same as the Ti-6Al-4V samples up to the 800 grit step. Following this they were prepared using diamond polishing compound (in a sequence of 6µm → 3µm → 1µm) followed by around 4 hours on a vibratory polisher with colloidal silica. The samples were then cleaned in the same way at the titanium samples. These samples were then etched to remove either the matrix or γ’/γ’’. To remove the matrix an electrolytic etch of 15g CrO₃ 150mL H₃PO₄ 20mL H₂SO₄ at 6v for ~30s was used. To remove the γ’/γ’’, the samples were swabbed with 61.0% Lactic acid, 85%; 46.6% Nitric acid, 69%; 2.4% Hydrofluoric acid, 49% for ~45s.
4.2 Optical Microscopy
Optical microscopy was performed using an Olympus GX-51 metallograph. This microscope allows for up to 100x magnification. This microscope is interfaced with a PC to take digital micrographs and make measurements of features. This microscope was used to measure hardness indents made manually.

4.3 Hardness
Micro-hardness measurements were made using manual and automated techniques. The manual indents were made using a Leco M-400-H1 manual micro-indenter. This machine allows for individual indents or a short line of indents to be made. It is also very useful for tracing the interface between a LMD build and substrate. Indents made with this machine are measured with the optical microscope using the procedure found in ASTM E385-10E2. [67]

Automatic micro hardness measurements were made with a Leco LM-100AT machine. This machine allows for grids of thousands of indents to be made and measured. This allows for spatial variation of hardness to be measured as a contour map. Frequency distributions can also be generated from the data.

The spatial maps were generated by a program implemented in Igor Pro™. The spatial maps are presented as contour plots where each indent is given a color depending on its hardness value. The program also uses a smoothing algorithm to fill in data between points.
4.4 Overview of SEM Imaging Techniques

There are several different SEM imaging techniques that were utilized to provide the desired information. Each of these provides key data and on combining the same, a comprehensive understanding of microstructure evolution can be described. This equipment was utilized in the OSU Campus Electron Optics Facility (CEOF).

4.4.1 Backscatter Electron Detection (BSE)

BSE is useful because it provides contrast between different compositions. In Ti-6-4 this allows retained beta to be detected in the final microstructure. The beta appears brighter than alpha in these images because it contains high vanadium concentrations. It is well known that during $\beta \rightarrow \alpha$ transformations, vanadium partitions to beta while aluminum partitions to alpha. Since V has a higher atomic number (23) than Al (13), it backscatters electrons more strongly and leads to the brighter appearance of $\beta$ phase in the BSE imaging mode. Backscattering occurs when electrons from the electron beam penetrate the surface of the specimen and through elastic scattering events have come back out of the specimen.[68] Elements with high atomic number backscatter electrons more effectively due to their larger electron cloud.

4.4.2 Energy-Dispersive X-ray Spectroscopy (EDS)

EDS allows for the chemical composition of a sample to be analyzed. This is done by detecting the unique x-rays that are given off by different elements when they are impinged by high-energy electrons. An X-ray is emitted from an atom when an electron beam ejects an electron from the inner shell of the atom. This puts the atom in an
energetic state, which is remedied by an electron from the next higher energy band filling the spot of the ejected electron. This process leaves the atom still at a higher energy than its ground state. The difference is made up by emitting an x-ray at a characteristic energy. [68] Since each element releases x-rays of different characteristic energies, this technique can be used to differentiate between the different elements in a specimen. This is done by comparing the spectrum of the detected x-ray energies (Figure 4.1) to reference values for the elements. Information can be gathered in a single point fashion or by a scan along a defined line. The line scan, combined with a SEM image provides a visual way of seeing how a sample’s composition changes with position.

Figure 4.1: Example of the x-ray spectrum for a Ti-6Al-4V sample collected by EDS
4.4.3 Electron Backscatter Diffraction (EBSD)

EBSD provides crystallographic information by directing the electron beam to the surface of a tilted sample. The electron beam moves in a raster pattern around the desired scan area while the computer records the diffraction patterns created by the interaction of the beam with the sample. The diffraction patterns are created from electrons that are backscattered in two cones. These cones create patterns when they intersect a phosphor screen inside the SEM chamber. The patterns consist of parallel lines (Kikuchi lines) that intersect at various points [see Figure 7]. The Kikuchi lines represent the crystallographic planes and the points where they intersect are the zone axes of the crystal. By comparing, or indexing, the recorded patterns to reference patterns the software can determine the crystallographic orientation of the phase.

Figure 4.2: Example of a diffraction pattern formed by EBSD
The recorded data can be presented in several different ways. First is the image quality map. This quantifies how well the collected patterns were indexed using the sum of the Hough transform peaks. The Hough transform peaks are used to digitally analyze the diffraction pattern and allow the software to index the pattern. This means that if the collected pattern could not be confidently matched to a reference one, that point will result in lower image quality. A map of the image quality of all the points gives information on how accurate the data is. Next is the Inverse Pole Figure map, which illustrates the orientation of the grains using different colors. This is useful for seeing which grains share the same orientation. Lastly, a phase map can be produced to spatially illustrate where different phases are in a sample. In the case of Titanium, alpha has HCP crystal structure and beta has BCC crystal structure. Therefore, EBSD can be used to differentiate between these phases.

4.4.4 Through Lens Detector (TLD)

The TLD is found on the Sirion SEM. This detector is a very efficient secondary electron collector. This allows for extremely high resolution imaging [19]. This detector was utilized to see the nano-scale $\gamma'$/$\gamma''$ precipitates in IN718.
CHAPTER 5: MODEL DEVELOPMENT

General aspects of the model development that pertain to both Ti-6Al-4V and Alloy 718 will be presented here. The calibration procedure, governing equations, and limitations will be discussed.

5.1 Calibration Procedure
The model contains a number of calibration parameters. The titanium model contains 10 parameters while the 718 model contains 16. The parameters will be described in section 6.2 and 7.2 for Ti-6Al-4V and 718, respectively. These parameters are used for fitting the predictions to the experimental data. They modify the nucleation and growth characteristics of the transformations. In this way one species can be promoted over another.

An iterative procedure was used to calibrate each model. After analyzing the experimental microstructure a single thermal cycle was inputted into the model. The calibration parameters were adjusted until the output matched the experimental data for that node. Thermal profiles from other nodes were then inputted into the model to check their output using the same calibration parameters. If the output did not match the experimental data then the parameters were adjusted to obtain reasonable results for all of the nodes.
5.2 Governing Equations

The following equations have been implemented into the STK model. The source code can be seen in the appendices with comments referring to the equations in this section. In this way the equations can be presented using conventional nomenclature and not model specific variables. Within the model these equations are evaluated at every time step and the results are either stored or used in another equation.

5.2.1 Extent of Transformation

The extent of transformation reports how much of the parent phase has transformed into a given product. It is given as a fraction from 0 to 1. The extended volume is found by equation 8.

\[ V = I_0 \cdot \frac{8\pi}{15} \cdot (\alpha_3^*)^3 \cdot t^\frac{5}{2} \]  

(8)

Here the nucleation rate is given by \( I_0 \) is the nucleation rate, \( \alpha_3^* \) is the growth rate, and \( t \) is the time during that isothermal step.

Nucleation Rate

The nucleation rate and growth rate are calculated at this point to feed into the actual volume equation. Equation 9 calculates the nucleation rate.

\[ I_0 = n_0 \cdot e^{-\frac{q}{kT}} \]  

(9)
Where $n_0$ is the number of nucleation sites per unit volume. This is a user inputted value for calibrating the model. $Q$ is the activation energy for the transformation, $k$ is the Boltzmann constant and $T$ is the temperature in Kelvin. The activation energy is calculated by equation 10 \[ Q = \frac{16\pi \gamma^3}{3\Delta G^2} \] Here $\gamma$ & $\Delta G$ are the surface energy and free energy change, respectively. The surface energy is a user inputted value for calibration. The change in free energy is obtained from equilibrium curves that are a function of temperature.

**Growth Rate**

The growth rate ($\alpha^*_3$) is found by equation 11 \[ \alpha^*_3 = \frac{(X_0 - X_e)}{2(X_\beta - X_e)} \cdot \sqrt{\frac{D}{t}} \] Here $X_0$ is the bulk parent concentration, $X_e$ is the parent interface concentration, and $X_\beta$ is the product interface concentration. All concentrations are in moles. $D$ is the diffusivity of the rate limiting element and $t$ is the time.

**5.2.2 Equivalent Time Calculation**

Since the thermal profiles are being evaluated as small isothermal steps that are being added together equivalent times must be calculated. As described in the background chapter (Figure 2.4) the equivalent time gives the amount of time the current extent of
transformation would take at the new temperature. First the volume of product at the
previous step is calculated using equation 12.

\[ V_{old} = -\alpha_{eq} \ln(1 - \zeta_{old}) \]  

(12)

Here \( V_{old} \) is the old volume of the product, \( \alpha_{eq} \) is the equilibrium alpha fraction, and \( \zeta_{old} \)
is the old extent of transformation. Now the equivalent time can be calculated by solving
for \( t \) in equation 9. This is shown in equation 13.

\[ t_{equiv} = \left( \frac{V_{old}}{l_{0}^{\alpha_{eq}^{\frac{1}{3}}} \zeta_{old}^{\frac{2}{3}}} \right)^{\frac{2}{5}} \]  

(13)

Here the old volume that was calculated in equation 12 is divided by the nucleation
rate and growth rate for the current temperature.

### 5.2.3 Simultaneous Transformations

After the extended volumes of the phases have been calculated the change in real
volume can be evaluated using equation 6. These equations were explained in the
background and are reprinted here.

\[ \Delta V_j = \left( 1 - \frac{\sum_{i=1}^{n} V_i}{V} \right) \Delta V_j^e \]  

(6)

\[ V_{j,t+\Delta t} = V_{j,t} + \Delta V_j \text{ for } j = 1 \ldots n \]

In this equation, \( \Delta V_j \) is the change in real volume for the \( j^{th} \) phase-morphology at time \( t \)
while \( V_i \) is the real volume of the \( i^{th} \) phase-morphology at time \( t \) and the total original
volume of the parent phase is represented by $V$. The total volume of each transformed phase-morphology is given by $V_{j,t+\Delta t}$. The number of product phase morphologies being evaluated is represented by $n$.

5.3 Model Limitations

5.3.1 Equilibrium Data

Equilibrium data was used to calculate the free energy of transformation, the solute concentration in each phase, and the phase fraction. This was done as a simplification to develop the prototype STK model. Further research into the non-equilibrium conditions of the LMD process is necessary to develop an understanding of build sensitivity to these conditions.

One of the major deficiencies of using equilibrium data is that the model does not account for solute segregation during transformation. Therefore the model does not account for Al segregating to alpha and V segregating to beta in Ti-6Al-4V. Likewise, it does not account for Nb segregating to the interdendritic regions of Alloy 718. This is important because in the case of 718 the enrichment leads to higher precipitation kinetics. This affects the number and size of the strengthening precipitates in the LMD build. One way this could be accounted for is by utilizing DICTRA® to model the solute diffusion during multiple heating and cooling cycles.

5.3.2 Cannot Spatially Predict Grain Boundary Locations

In the case of Ti-6Al-4V epitaxial growth of the beta grains leads to columnar grains that coarsen with the height of the build. While modeling of the beta grain size is the subject
of current research it does not tell where in the build one could locate the beta grain boundaries. This is important for knowing where colony is likely to form versus basketweave.
CHAPTER 6: TI-6AL-4V

This chapter will contain information about the Ti-6Al-4V STK model and three LMD builds. The builds are identified as Ti-1, Ti-2, and Ti-3. The first two builds (Ti-1 and Ti-2) were made by a third party and build parameters have not been shared with OSU for intellectual property reasons. The third build (Ti-3) was built at OSU and full build parameters are known.

6.1 Ti-6Al-4V Thermodynamic Data
The following thermodynamic data was found using Thermo-Calc® version R with the SSOL4 database [69]. The data was calculated by Thermo-Calc® by stepping through a range of temperatures. The composition used was Ti-6.0Al-4.0V wt%. This alloy specific data was incorporated into the STK model using curves fitted to the Thermocalc® data.

6.1.1 Driving Force
The free energy as a function of temperature was found for the $\beta \rightarrow \alpha$ transformation. Figure 6.1 shows that as the temperature decreases below the beta transus the driving force increases. The output from Thermocalc® is in the format DGM/RT. In the STK code this data is multiplied by -1 and then multiplied by R (8.3144725) and the current temperature. This gives the driving force in J/mole.
6.1.2 Equilibrium Phase Fraction

The equilibrium phase fraction for alpha and beta was found. The data is shown in Figure 6.2 between room temperature and the beta transus. Above the beta transus the fraction of beta is 1.0. At temperatures below the beta transus the beta begins decomposing into alpha. The transformation is complete around 800K with the volume containing ~0.9 alpha and ~0.1 beta [4].
Figure 6.2. Equilibrium phase fraction for Ti-6Al-4V. Alpha is the red trace and beta is the dashed blue trace.

The equilibrium phase fraction is utilized by the code to determine if the alpha precipitates are to grow or dissolve. If the current amount of alpha is lower than the equilibrium value then growth can occur. If the current amount is higher than the equilibrium value then dissolution must occur. The kinetics of dissolution during heating are different than the precipitation. Kelly studied this for multiple thermal cycles using time resolved X-ray diffraction [37]. Using a heating and cooling rate of 20K/s he found that alpha does exist above the beta transus. For true application to this work in-situ observation of the transformation must be done at higher heating and cooling rates. In this model when dissolution occurs the amount of alpha is simply reset to the equilibrium value. This is a simplification and further research is a recommendation for future work.
6.1.3 Equilibrium Phase Composition

For Ti-6Al-4V the equilibrium phase concentration of vanadium in alpha and beta was found. Vanadium is the rate limiting element in the diffusion based transformation [4, 70]. Figure 6.3 is a plot of the vanadium concentration as a function of temperature for alpha and beta in equilibrium.

![Figure 6.3. Equilibrium vanadium concentration for alpha and beta as a function of temperature.](image)

The data in the STK model was converted from weight percent to mole fraction using equation 14. Here $X$ is the mole fraction, $w\% (i)$ is the weight percent of the element in
question, \( M_i \) is the molecular mass of the element (50.942 g/mol for V), and \( M_{\text{total}} \) is the total molecular mass of the system (45.86 g/mol for Ti-6Al-4V)

\[
X = w\%_0(i) \frac{M_{\text{total}}}{M_i}
\]  

(14)

### 6.2 Model Calibration Parameters

The model calibration is performed by varying the model’s parameters to fit the experimental microstructure data. The Ti-6-4 model contains 10 parameters. A list of the parameters with a short description and the variable name in the model (in italics) followed by the units is listed below:

- **Variables controlling model predictions**
  - Number of grain boundary nucleation sites
    - Modifies how easily GB alpha forms. Effectively controls beta grain size
    - \( N_{\text{zero}} \) [\#*m\(^{-3}\)*s\(^{-1}\)]
  - Number of nucleation sites for basketweave and colony
    - Allows for modification of how likely it is for these morphologies to start growing
    - \( N_{\text{zeroWid}}, N_{\text{zeroCol}} \) [\#*m\(^{3}\)*s\(^{-1}\)]
  - Acceleration factors for basketweave and colony
    - Accelerates the growth rate of these morphologies in order to fit to the experimental data
    - \( \text{AccFactor}, \text{AccFactorCol} \) [unitless]
  - Surface energy
    - Determines the magnitude of the activation energy
    - \( \text{SurfEnerImp} \) [J/m\(^2\)]
  - Strain energies
    - Determines how much undercooling is required to form
    - \( \text{StrainEnergy}, \text{StrainEnergyCol} \) [J/mole]
  - Ratio of massive to martensite
    - Determines the ratio of massive alpha to martensite
    - \( \text{RatioOfMassMart} \) [unitless]
Factor to control martensite formation
  - *MartBPara*

6.3 Ti-1 Sample Information

6.3.1 As Received Build
The build was made on the edge of a plate with dimensions of 152x200x3.2mm. The plate had a semicircular area machined out of it and the LMD process was used to fill the area in. The build can be seen in Figure 6.4a. The build was sectioned down the center of the build with the cutting direction parallel to the build direction (Figure 6.4b). The microstructural features of this section will be discussed later in this chapter. The section view represented as a meshed 3D model can be seen in Figure 6.4c. This model represents the output of SAMP. Figure 6.4c contains a coordinate system to orient the reader. The build direction (vertical direction) is the z-direction. The length of the build (out of page) is the x-direction. The depth of the build (across the page) is the y-direction. Discrepancies can be seen between the shape of the 3D model and the actual build. In the actual build the width of the build is wider than the substrate and the top has rounded corners. This occurs because the material flows during the build. SAMP uses a finite element model and does not account for fluid flow.
6.3.2 Region Definition

In order to quantify the spatial microstructural distributions, the sample was divided into regions starting near the substrate and moving up toward the top of the sample (see Figure 6.5). These regions are 1mm high by 2mm wide. The regions were outlined on the sample by making indents on the surface. Dividing the sample into regions provided a convenient method for keeping track of where micrographs came from in order to perform point counting.

The point counting micrographs were taken in such a way to fill in each of the rectangular regions. In this way a continuous view of the microstructure could be formed from the bottom to top of the build.

Throughout this chapter these regions will be referred to when addressing the spatial variation in hardness and microstructure in the build.
6.4 Ti-1 Results and Discussion

6.4.1 Thermal Profiles
Thermal profiles were extracted from the SAMP simulation for this build. The SAMP simulation was performed by Applied Optimization and only the extracted thermal data was provided to OSU. The nodes for data extraction were selected as close to the physical coordinates of the point counting micrographs as possible.

The thermal data presented in this section will all refer to temperatures extracted from the middle of the build. Figure 6.6 plots the percent difference in temperature between a node in the middle of the build and a node at the outside edge for region 1 and 7. It can be seen that the temperature only varies significantly between the middle of the build and the
outside edge during the beginning of the build. After the initial difference the variation decreases to below 20% for any point in time.

Figure 6.6. Percent difference in temperature between a node in the middle of the build and outside of build for region 1 (a) and region 7 (b).

The simulated thermal data for several regions can be seen in Figure 6.7. It can be seen how the temperature of already deposited regions increases each time a new layer is deposited. However, the effect from subsequent layers is diminished as the build progresses and a larger “buffer” is created. The number of layers can be inferred by the number of large fluctuations in the bottom region. For this build it appears there are 19 layers. Focusing on region 1, it can be seen that each layer reheats this region above the beta transus for a period of time until region 7. Region 1 does have very quick excursions
above the beta transus even after region 7 is deposited but it is unlikely they have any effect on the microstructure because they are so short. It can also be seen that region 7 and 10 spend most of their time above the beta transus. Ultimately, at the end of the build, region 1 cools from below the beta transus while the other two regions cool from above the beta transus. None of the regions cool below the Ms temperature until the very end of the build.

![Simulated thermal T-t data illustrating the thermal evolution during the LMD build. Horizontal lines show the liquidus, beta transus, and martensite start temperature.](image)

**Figure 6.7.** Simulated thermal T-t data illustrating the thermal evolution during the LMD build. Horizontal lines show the liquidus, beta transus, and martensite start temperature.

The cooling rates at the end of the build vary spatially as well. They are compared in Table 6.1. The cooling rate in region 1 is lower (15K/s) than it is in region 10 (25K/s). By comparing these cooling rates to the plot in Figure 2.11 the likelihood of the diffusional
transformation completing can be evaluated. All of the regions below region 5 will cool below 20K/s and so it is possible that the diffusional transformation will fully complete. This means martensite is unlikely to form because all of the available beta has transformed. Region 5 and above cool fast enough that the diffusional transformation does not complete. Therefore it is possible that some martensite will be present. However, the volume fraction of martensite would be low because the diffusional transformation would have nearly completed.

Table 6.1. Final cooling rates for thermal profiles in Figure 6.7.

<table>
<thead>
<tr>
<th>Location</th>
<th>Cooling Rate (K/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region 1</td>
<td>15</td>
</tr>
<tr>
<td>Region 5</td>
<td>20</td>
</tr>
<tr>
<td>Region 7</td>
<td>23</td>
</tr>
<tr>
<td>Region 10</td>
<td>25</td>
</tr>
</tbody>
</table>

By focusing on the thermal cycles at the end of the build the region where the build transitions from cooling below the beta transus to above can be determined. Figure 6.8 details these thermal cycles. It can be seen that the transition occurs in region 5. Region 4 begins cooling from around 1220K. The beginning of region 5 cools from just below the
beta transus (~1268K) while the end of region 5 cools from above the beta transus (~1320K). All of the subsequent regions will cool from above the beta transus.

![Graph showing thermal profiles in different regions at end of Ti-1 build. Transition in cooling from below or above the beta transus can be seen in region 5.]

**Figure 6.8.** Thermal profiles in different regions at end of Ti-1 build. Transition in cooling from below or above the beta transus can be seen in region 5.

### 6.4.2 Microhardness

A microhardness map of the substrate and build was created using a Leco LM-100AT machine. Figure 6.9 illustrates the data in an image format with the colors representing different Vickers hardness numbers. The indents were made with a spacing of 150μm and a force of 100g. The map indicates a significant softening of the substrate in the HAZ. The other observation to be made is the increase in hardness above the dashed line. This represents a change in the physical properties of the build. These hardness variations are in agreement with data from Kelly based on microstructures achieved with different cooling rates [4]. For colony microstructure, as seen near the substrate of the current
build, Kelly reported 305 ±14 HV after a primary heat treatment and 328 ±53 HV after a secondary heat treatment. This corresponds to the lower regions with a range of ~300-350 HV. For basketweave microstructure, as seen in the upper regions of the current build, he reported 314 ±23 HV for a primary heat treatment and 332±18 HV after a secondary heat treatment. This corresponds to a range of ~350-380 HV in the upper regions of the experimental build.

Figure 6.9: Microhardness map of Ti-1 build. Black dashed line shows transition from soft to harder region. Red dashed line indicates interface of build and substrate.
The shape of the build-substrate interface is not flat due to melt-back. The original height of the substrate is actually at the top of the red dashed line. Heat buildup causes the interface to become curved.

The frequency distribution for Ti-1 is in Figure 6.10. The figure does not include data for the substrate. The hardness is concentrated between 300 and 380 HV with an average of 340 HV.

![Hardness Frequency Distribution](image.png)

Figure 6.10. Hardness frequency distribution for the Ti-1 build. Does not include substrate data.

### 6.4.3 Optical Microscopy

Optical micrographs will be presented in this section of the Ti-1 sample. These micrographs will provide higher magnification views of regions 2, 5, 6, and 8 and the top of the build (Figure 6.5).
Figure 6.11 shows the microstructure in the bottom of the build (region 2). The edge of the build is shown in Figure 6.11a and the middle is shown in Figure 6.11b. Both areas feature primarily colony alpha with some grain boundary alpha along the prior beta grain boundaries. The main difference between the edge and the middle is the size of the prior beta grains. The edge has larger prior beta grains. This is likely due to path that the laser took.

Figure 6.11. Micrographs from region 2. The edge of the build (a) and middle of build (b) are seen. GB alpha is seen on prior beta grain boundaries with colony alpha filling the grain interiors.

The microstructure of region 5 is seen in Figure 6.12. The edge of the build is seen in Figure 6.12a while the middle is seen in Figure 6.12b. This region represents the beginning of the transition from primarily colony to primarily basketweave alpha. This region has much larger prior beta grains than region 2 and therefore has less grain boundary alpha. This reduction in grain boundary alpha reduces the epitaxial nucleation
sites for colony alpha. The microstructure here is still mostly colony alpha though. However, many more orientations are seen in comparison to region 2. This indicates that intragranular nucleation was taking place but the undercooling was not high enough for only basketweave alpha to form. This allows for alpha sideplates to form alongside these intragranular laths.

In Figure 6.12a the microstructure could nearly be classified as basketweave alpha however most of the laths are found in groups, making them colonies. Many overlapping and intersecting colonies can be seen due to the minimal grain boundary area. A large colony alpha formation can be seen in Figure 6.12b along the grain boundary. However, as the distance from the grain boundary increases basketweave alpha can also be seen.

Figure 6.12. Micrographs from region 5. The edge of the build (a) and middle of build (b) are seen. GB alpha with colonies are apparent with some basketweave.
The microstructure of region 6 is seen in Figure 6.13. The edge of the build is in Figure 6.13a and the middle is in Figure 6.13b. This region represents the final stages of the transition to primarily basketweave alpha. No prior beta grain boundaries can be seen in either micrograph. This allows for easier basketweave alpha formation because there is essentially no grain boundary alpha for colony nucleation. There are still some packets of colony that have formed in this region.

![Micrographs from region 6. The edge of the build (a) and middle of build (b) are seen. Both areas show primarily basketweave](image)

The microstructure in region 8 consists of primarily basketweave alpha (Figure 6.14). The edge is seen in Figure 6.14a and the middle is seen in Figure 6.14b. The beta grain size here has reached its maximum for this sample. The formation of basketweave alpha is the preferred morphology for the beta grains size and thermal conditions.
An interesting microstructure feature is seen in Figure 6.14b. It appears that basketweave is seen on the left side of the prior beta grain boundary and martensite is seen on the right. Since the thermal conditions in this area have to be essentially the same it is not possible that the cooling rate variation between these two grains was enough to have martensite formation in one and not the other. This region did not cool below the Ms temperature until the very end of the build. The cooling rate (>20K/s) supports that some martensite could be present. A similar phenomenon was observed by Baufeld et al. and their optical micrographs have the same appearance [41]. They concluded that even though the alpha morphology has a martensitic grid-like appearance it is not martensite. This is because they found retained beta surrounding the alpha laths which would not be present if the transformation was diffusionless. In addition they found the laths to have the same chemical composition. In order to verify the same morphology is present on both sides of this grain boundary SEM imaging techniques were used.
The top of the build can be seen in Figure 6.15. The beta grain size is so large at this point that only four grains can be seen across the build. The seemingly different morphologies can be seen in the different prior beta grains. It can also be seen that the microstructure seen in region 8 is continuous all the way to the top. The reasoning for this is that all of the regions above region 5 cooled from above the beta transus. Therefore the microstructure can be consistent through all of these regions. Further insight into the resultant microstructure will be discussed with the analysis of the thermal profiles.

Figure 6.15. Top of Ti-1 build (Regions 8-10). Large prior beta grain size and basketweave alpha are observed.

### 6.4.4 SEM Characterization of Region 2

Figure 6.16 contains BSE micrographs that illustrate the microstructure contained in region 2 [see Figure 6.5 for the location of these regions] from the bottom of the build. Parallel colony alpha laths can be seen as well as retained beta, represented by the lighter...
color surrounding the alpha laths. This retained beta was previously undetected in optical microscopy, because the size of these ribs is around 0.3μm. Grain boundary alpha can be seen decorating the prior-beta grain boundaries.

![BSE micrographs from region 2. (a) Low magnification of region, prior-beta grains can be seen as well as colony alpha microstructure. (b-c) Consists higher magnification on the grain boundaries. (d) Is an even higher magnification of picture (c) where the outline of beta around the alpha laths is clear.](image)

To verify that the light regions are beta and EDS line scan was performed. The scan was set up to traverse a prior-beta grain boundary and several of the alpha laths in the region. Figure 6.17 shows the area scanned on top, with the white line being the scan line, and the results below. The graph shows that when the scan line crosses the light regions of the
image, there is a corresponding increase in V and decrease in Al. Therefore it can be concluded that the light regions are in fact retained beta.

Figure 6.17. EDS line scan data. On top is an BSE image of the scan region with the white line representing the scan line. On the bottom is the data from the scan with the peaks in V representing beta.

Figure 6.18 contains EBSD data for region 2. The qualitative view of the quality of the scan data is shown in Figure 6.18a. It represents how closely the scanned pattern matches the reference pattern, how easily the pattern could be indexed. This image has good overall image quality, meaning the patterns could be indexed as either alpha or beta. Figure 6.18b is the Inverse Pole Figure (IPF) map, which shows the crystallographic data.
It can be seen that the laths in the colonies of alpha share the same orientation in space (same color in crystallographic triangle). The IPF map also illustrates how the laths grow from the prior-beta boundaries toward the interior of the prior-beta grain. Further work is required to evaluate the same with respect to relative misorientation of beta grains that form in every layer.

Figure 6.18. (a) IQ map illustrating the parallel colony alpha laths growing from prior-beta boundaries. IPF map illustrating how the colonies share crystal orientations. (c) Phase map showing where beta was detected in the scan.

Lastly, Figure 6.18c is a phase map that illustrates alpha with red and beta with green color. Here the beta is seen in a discontinuous fashion due to a limitation with the step.
size between points with the SEM. Since size of retained beta within the ribs (around 0.3μm wide) are the same size as that of the scanning step (0.3μm), the beta appears discontinuous. This is because on one row the beam could land on the beta rib and index as beta while on the next row the beam could land on alpha and index as such. Also, EBSD software cannot index effectively close to the prior-beta grain boundary areas, because the diffraction pattern contains information form alpha grain (HCP) and the adjacent beta (BCC) rib. Nevertheless, when viewed in conjunction with image quality map, it can be seen that the beta (~4.3% of the scanned area) always outlines the alpha laths. It is possible that this percentage would increase if the step size is reduced and the beta is indexed in an efficient fashion. From the work with the SEM, the presence of retained beta in this region has been confirmed as well as the shared crystallographic orientation of the alpha colonies with the grain boundary alpha.

6.4.5 SEM Characterization of Region 8
As mentioned earlier, the Region 8 was selected for further characterization with the SEM, because optical microscopy (see Figure 6.14b) suggested martensite in one beta grain and basketweave in the adjacent grain. The SEM analyses may be able to validate the above suggestion. The α’ martensite has a HCP crystal structure and forms due to a displacive (aka diffusionless) transformation at higher undercooling. Therefore, it is often found at samples cooled with high rates from the beta transus temperature. The displacive transformation leads to retained strain within the matrix and a composition that is same as that of parent beta phase. Another type of martensite that can form is α’’ with an
orthorhombic structure. The $\alpha''$ martensite is expected in alloys with high amounts of beta stabilizers. In our analyses, there is no evidence for $\alpha''$ martensite due to lack of diffraction patterns that are consistent with orthorhombic structure [38]. The BSE image of the selected area is shown in Figure 6.19a. From this image, it can be seen that there is a contrast difference between each side of the grain boundary but the morphology of the alpha laths appears to be the same. In comparison with region 2, the alpha here has basketweave morphology. This is qualified by the entangled, random structure of the laths. The laths in this region also have a much higher aspect ratio (ratio of length to width) than in the bottom region.

![Figure 6.19](image)

Figure 6.19. (a) Low mag BSE image of region 8 prior beta grain boundary showing basketweave morphology. (b) High mag BSE image of region 8 showing presence of secondary alpha.

The other feature apparent from the BSE image is the presence of very fine secondary alpha as seen in Figure 6.19b. The relative size difference between secondary and
primary alpha is apparent (marked by arrows). The secondary alpha was not quantified in this work and only its presence is being stated here as an observation. Secondary alpha was also reported by Baufeld et al. [41]. These secondary alpha laths can be important to strengthening the alloy and therefore their presence should be a subject of further investigation.

The chemical composition of the left matrix, right matrix and grain boundary was examined using EDS point scans. This uses the same technology as the line scan but the electron beam is focused on one point while the composition is quantified. The data from this study is presented in Figure 12 with a set of bars for Al, V and Fe. The blue bars represent left of the grain boundary, red, on the boundary, and green, right of the boundary. It can be seen that there is not a significant difference between the left and right matrices for any of the elements. At the grain boundary there is an increase in V and decrease in Al, which could indicate the presence of retained beta along the boundary. The lack of difference between the matrices is significant to the detection of martensite because martensite is formed by a diffusionless process. Therefore, if martensite were present, the composition would be the same as that of beta and have a higher V content.
Finally, an EBSD scan was performed in this same area and the data is presented in Figure 6.21. The image quality map (Figure 6.21a) illustrates there is no relative difference in image quality between the left and right matrices. This is important for the detection of martensite because martensite will produce a lower image quality relative to that of an area that is not martensite. This is due to the heavily dislocated nature of martensite since it is a shear, diffusionless transformation [4]. Many factors can affect the image quality, which means this method cannot be used to absolutely determine if an area is martensite. However, by scanning both sides of the grain boundary in one scan, the IQ of each side can be compared relative to the other for a valid test of martensite.
Figure 6.21: (a) IQ map illustrating little relative difference across beta grain boundary. IPF map illustrating the crystal orientations across beta grain boundary. (c) Phase map showing where beta was detected in the scan

Figure 6.21b is the IPF map for this scan. Here the colors illustrate a difference in orientation from the left to right of the boundary. The left qualitatively contains more laths oriented with [0001] and [10\bar{1}0] while the right contains laths oriented with [2\bar{1}10] and a mixture of the other directions. The orientation differences indicate that the prior-beta grains had different orientations, during their growth in the [100] direction as seen in Figure 6.22, thereby affecting the orientation of the transformed alpha. This is because alpha can form on six different \{011\} beta planes with 2 possible alignments, leading to 12 possible variants (Burger’s orientation relationship: \{110\}_\beta/\{0001\}_\alpha and <111>\_\beta
//<11\bar{2}0> a). Therefore, the orientation relationship between alpha and beta leads to the overall difference in orientation for the alpha on either side of this grain boundary. While the orientations are different, the morphology is consistent on both sides with high aspect ratio, randomly* oriented laths.

![Diagram](image.png)

**Figure 6.22**: Representation of \(\beta\) grain orientation variations during growth

Figure 6.21c is the phase map for the scan with red representing alpha and green representing beta. The beta is randomly distributed around the matrix and only accounts for 1.4% of the area. This is consistent with the high magnification BSE image in Figure 9b where no significantly brighter spots are seen. It can be concluded that the upper regions do not contain martensite and are nearly 100% basketweave. There is a very small amount of retained beta present.

* In crystallographic criteria, they are not random. They appear random due to the formation of many variants of \(\alpha\)-laths within the \(\beta\)-grain
6.4.6 Prior-Beta Grain Size

The prior-beta grains in this build are observed as small near the substrate and increasing in size in the vertical direction in a columnar fashion (see Figure 6.24). The beta grains coarsen during the deposit because of preferential epitaxial growth [12, 71]. This is explained with a schematic diagram in Figure 6.23).

![Diagram showing the effects of cooling rates on beta grain size](https://example.com/diagram)

Figure 6.23: Representation of beta dendrites and grains forming after cooling from the liquidus

At the beginning of the LMD process, when the first layer is started, there are two ways that the beta grains can begin growing. By epitaxial or nonepitaxial growth. If the grains below the melt pool are heated above the beta transus then epitaxial growth will occur because the BCC crystal structure can continue. This would lead to faster coarsening of the beta grains because there would be fewer orientations competing.
However, if the area below the melt pool does not exceed the beta transus then those grains will remain alpha and nonepitaxial growth will occur. This means the beta coming out of the liquid will require nucleation and growth because of the HCP crystal structure in the substrate. There are numerous equiaxed grains in the substrate and so nucleation occurs easily with numerous orientations as the first layer \((n-1)\) cools through the liquidus \([71]\). As these \(\beta\)-dendrites grow in the \(<100>\) direction some of these dendrites will be shut out due to hard impingement with other grains with higher velocity. This is because the \(<100>\) dendrites that are aligned with the direction of maximum temperature gradient will be the ones with the highest growth rate or velocity. When layer \(n\) is deposited there are numerous grains for epitaxial beta growth because \(n-1\) is still above the beta transus. The epitaxial growth will occur easiest on the grains in the previous layer that have their \(<100>\) direction most aligned with the direction of the highest temperature gradient. When the \(n+1\) layer is deposited, there are once again numerous epitaxial sites, however, smaller in number than layer \(n\). This leads to a situation in which every layer will have diminishing number of epitaxial sites that are preferable for continued growth as the next layer is added. This occurs until only a few grains have the best orientation and those grains continue up through the rest of the build.

This can be seen schematically in Figure 6.24. The overlaid lines start off small and equiaxed. In the first few layers they are still equiaxed but have increased in size. Subsequently they start elongating. Competitive growth occurs and eventually a few grains win out and grow up through the remainder of the build.
Figure 6.24. Macroscopic image with schematic overlay illustrating the elongation and increase in prior-beta grain size.

In addition, the coarsening of the beta grains also occurs based on the cooling rate during solidification. In a layer close to the substrate, the initial solidification experiences a cooling rate of around 2333K/s this leads to fine dendrite arm spacing. As the build progresses, the cooling rate from the liquidus becomes lower (around 461K/s in the middle and 405K/s at the top) which leads to coarser dendrite arm spacing (see Figure
6.23) [71]. Due to time spent above the beta transus, the dendrites coalesce with each
other to form one large grain therefore the dendrite arm spacing cannot be measured.

Figure 6.25 contains data for the variation in beta grain size. The data was collected using
a method in ASTM E112-10 using a grid of horizontal lines [44]. Horizontal lines were
overlaid at different heights in the build. The intersection points with the grain boundaries
were counted and the number of intersections per unit length was converted into average
grain diameter. As can be seen in the figure, the beta grains increase in size by more than
an order of magnitude from the bottom regions to the top. The reason that the grain size
decreases in region 8 is because there is a new grain that comes into view (top of Figure
6.24). This has the effect of decreasing the size of the existing grains. This extreme
spatial variation must be accounted for in the material model.

![Graph showing beta grain size variation](image)

Figure 6.25. Beta grain sizes measured in different regions for Ti-1.
A prototype beta grain growth model has been developed by a fellow researcher at OSU. This model begins with an initial grain size that is inputted by the user. The thermal profiles from SAMP are used as input. As the temperature varies through the duration of the build, the model allows the beta grain size to grow incrementally according to equation 15. Here $D_{i+1}$ is the grain diameter for the current layer while $D_i$ is the diameter for the previous layer. $Q$ is the activation energy, $M$ is mobility, and $\Delta t$ is the change in time. For subsequent layers, the model looks at the grain size in the previous layer to simulate epitaxial growth.

$$D_{i+1} = D_i + M \cdot \exp \left( -\frac{Q}{RT} \right) \cdot \left( \frac{1}{D_i} \right)^{n-1} \cdot \Delta t$$  \hspace{1cm} (15)

The output of the beta grain growth model compared with the experimental data can be seen in Figure 6.26. The model has good correlation with the measured data until region 7. At this region, a new grain is visible in the micrograph. The model does not successfully predict this that thus there is a deviation. Further work on the calibration of this model is necessary and will be continued at OSU.
6.4.7 Microstructure Characterization Results
Through point counting and SEM characterization, spatial maps of the morphologies were created as seen in Figure 6.27. These maps illustrate the percentage of alpha morphology as a color with red representing the highest percentage and blue, the lowest. Maps were created for the colony alpha, basketweave alpha and grain boundary alpha. Through the SEM work it was determined that martensite is not present in this sample. The percentage of grain boundary Widmanstätten was very small (<1%) per region in the bottom half of the build and therefore not reported. Lastly, the massive morphology is very difficult to distinguish and therefore not included in the map [4].
The maps show that in regions 1-4 there is nearly 100% colony alpha which transitions into a mixture of colony and basketweave in region 5. This mixture of basketweave and colony ends at region 6 and primarily basketweave continues to the top at region 9. Some areas have been identified with pockets of colony toward the center of the sample in these upper regions. The concentration of colony in the lower regions with smaller beta grains is because the colony laths grow out of the grain boundary alpha. The grain boundary alpha nucleates first because of high diffusivity along the beta grain boundaries. Given additional undercooling parallel laths form perpendicular to the grain boundary alpha. Even as the beta grain size increases the alpha retains colony morphology because of temperature fluctuations below the beta transus and low undercooling. In the upper regions, the combination of high undercooling and large beta grain size provides enough
driving force for intragranular nucleation. Since the beta grains are large in this area, the colony growth along the grain boundaries is not fast enough to fill the entire beta grain. Therefore, intragranular nucleation begins as the temperature drops, resulting in the observed basketweave structure. As mentioned earlier, the transition from colony to basketweave corresponds (see Figure 6.28b) to a change in cooling from below the beta transus to above.

The grain boundary alpha map shows there is a very small (<10%) amount of it concentrated in the bottom, center of the build. The amount of grain boundary alpha is inversely proportionate to the prior-beta grain size because as the grains become larger their boundary area becomes smaller.
Through the microstructural analysis, it was found that there is a morphological change in region 5 from primarily colony alpha to basketweave alpha. The analysis of the thermal cycles (Figure 6.28b) in this area revealed that at the bottom of region 5 the final cooling step occurs from below the beta transus while at the top of the region the cooling occurs from above the beta transus. This transition in alpha morphology occurs after the beta grain size has increased. This indicates a complex interaction in this region between the beta grain size and final cooling step.

In the lower regions the alpha morphology is sensitive to the number of cycles around the beta transus. This serves to provide more and more alpha to “pin” the beta grains, effectively raising the local beta transus temperature [4]. On repeated heating and cooling not all the alpha is dissolved, which makes continued alpha growth easier [37]. This is possible because during cooling the nucleation step can be skipped if there is preexisting alpha and epitaxial growth can occur. This serves to stabilize the colonies of alpha in the bottom layers. This means that as the final cooling step is approached there is more colony alpha in these regions even though the temperature is very close to the beta transus.

The microstructure of region 5 indicates a metastable condition occurring between colony and basketweave, resulting in the transition seen in the microstructural analysis. This represents the area of the build where the regions below are in “steady state” and not thermally affected enough by subsequent layers to produce dissolution of the alpha that has formed. This “steady state” region area would increase or decrease depending on the
number of vertical layers produced. From this work it cannot be theorized how this region would be affected by additional horizontal layers.

In the regions above region 5, the number of cycles around the beta transus is fewer and the final cooling occurs from a peak temperature above the beta transus. This indicates that until the final cooling step the microstructure is primarily beta. On cooling rapidly from this temperature, the driving force is high enough for intragranular nucleation of basketweave α-phase morphology. This finding is important because it can be used to provide guidance about how to control the microstructure more effectively. If a build can be made in which the entire build stays above the beta transus until the end of processing, a fully basketweave microstructure can be obtained in the build (this will be shown for sample Ti-2). Likewise, if each layer were allowed stay below the beta-transus temperature before the final cooling, predominantly colony alpha microstructure can be attained.

6.4.8 Calibration based on Microstructure Close to the Substrate

The first set of calibrations was performed to match the morphology in the bottom of the build changing parameters mentioned above. The experimental data is compared to the predictions in Figure 6.29. Although it was known that the results would not match for the entire build, these calibrations provide a baseline for understanding the fidelity of the model. The initial calibration was using one node close to the substrate. The parameters were adjusted until the prediction matched the experimental microstructure for this node.
These parameters were then applied to the rest of the nodes in the overall build. Resulting values of the parameters are presented (see Table 6.2).

![Figure 6.29: Colony microstructure maps comparing experimental (a) to predicted (b) for first run.](image)

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<th>Value</th>
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Table 6.2. List of modeling parameters for 1st run for Ti-1. Same parameters are used for all regions.
The map on the left side (Figure 6.29a) is for the experimental data, while the right (Figure 6.29b) is for the model predictions. The different colors on the map represent the different percentages of colony alpha present. From comparison of the two it can be seen that the overall trend from bottom to top agrees, however, the magnitude of the predicted data is not correct. Both maps show a trend from high concentration at the bottom to low at the top. The scale for the experimental data ranges from 0-100% while the predicted scale ranges from 65-80%. This means that for the top of the build where both maps have purple, the experimental contains 0% colony while the predicted contains 65%.

6.4.9 Position Dependent Calibration and Results
Analysis of experimental microstructure (see section 5.4.7), it is obvious that there is an abrupt transition in morphology mid-way in the build. Above region 5, predominantly basketweave morphology was observed. In contrast, below the region 5, majority of colony alpha is observed. In order to represent this transition with the model, two sets of calibration parameters were utilized (i.e., one set for regions 1-5 and another set for regions 6-10). The results of this calibration exercise are shown in Figure 6.30a. Here it is apparent that the predictions match the experimental values much better.
Table 6.3. List of modeling parameters for 2\textsuperscript{nd} run for Ti-1. Different parameters are listed for regions 1-5 and regions 6-10.

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The calibration parameters are listed in Table 6.3. The parameters for regions 1-5 remain the same as the first calibration run. In order to promote basketweave in regions 6-10, the following parameters were adjusted: The Nzero term was decreased from 8x10\(^{19}\) to
$1 \times 10^{17} \text{ m}^{-3} \text{s}^{-1}$ to reflect the reduction in grain boundary nucleation sites due to the larger beta grain size. NzeroWid was increased from $5 \times 10^{18}$ to $1 \times 10^{23} \text{ m}^{-3} \text{s}^{-1}$ to provide more sites for basketweave nucleation. NzeroCol was decreased from $1 \times 10^{24}$ to $8 \times 10^{15} \text{ m}^{-3} \text{s}^{-1}$. SurfEnerImp was decreased from 0.08 to 0.001 J/m$^2$. This lowered the surface energy for all morphologies. The StrainEnergy was increased from 600 to 1000 J/mole to lower the starting temperature for the basketweave transformation. StrainEnergyCol was increased from 100 to 600 J/mole to lower the starting temperature for colony. The AccFactor was increased from 5 to 6 and the AccFactorCol was reduced from 20 to 5 to push the growth rate of basketweave in front of colony. The MartBPara and RatioofMassMart were kept the same.

The data in Figure 6.30 may suggest a gradual transition region in the microstructure in the middle of the build. However, this is an artifact of the smoothing algorithm with the mapping function of the plotting package. The actual transition from colony to basketweave is very sharp, going from ~73% colony (at the end of region 5) to ~90% basketweave (at the start of region 6). This transition region is difficult to model exactly in the current prototype version, since mixture of basketweave and colony dispersed was observed throughout the transition region.

**6.5 Ti-2 Sample Information**

Ti-2 was built with the use of a heater to maintain the substrate and build above the beta transus. Applied Optimization performed a number of simulations with SAMP to optimize the temperature of the substrate. Using this data a heater system was
implemented into the build chamber. The purpose of this build was to investigate how the microstructure could be controlled using thermal management and the effect of the resultant microstructure on fatigue properties.

6.5.1 Ti-2 As Received Build
The Ti-2 build was deposited on top of a cylindrical substrate. The cylinder is 22.2mm in diameter. The build is a square that is slightly offset from the middle of the cylinder as seen in Figure 6.31a. Ridges are also visible going across the build. These features could be from the high temperature during the build. The build was then sectioned by first cutting normal to the axis of the cylinder and then cutting across the ridges seen along the top of the build. The two sections before mounting and polishing can be seen in Figure 6.31b.

![Figure 6.31. Ti-2 build in the as received condition (a) and after sectioning (b).](image)
6.6 Ti-2 Results and Discussion

6.6.1 Thermal Profiles
Simulated thermal profiles for this build are in Figure 6.32. The temperatures for all the layers in the build stay above the beta transus until the end of the build. All layers cool together at around 15K/s. This lets all the layers transform from beta to alpha at the same time. The microstructure of this build will be shown to be predominantly basketweave morphology.

![Simulated thermal profiles for Ti-2](Figure 6.32)

Figure 6.32. Thermal profiles for sample Ti-2. Temperatures stay above the beta transus until the end of the build.

6.6.2 Microhardness
A microhardness map for Ti-2 was created with 150μm spacing between indents and a 100g force. The map can be seen in Figure 6.33. It can be seen that there is some
variation throughout the build. However, when compared to the map for Ti-1 (Figure 6.9) there is not a transition from soft to hard in the z-direction. This is because the microstructure in this build is predominantly basketweave through the entire build.

The substrate interface is shown by the dashed red line. There is not a transition in hardness at the interface as in Ti-1. This is because the epitaxial large beta grain growth started in the substrate and continued up through the build.

The frequency distribution of hardness for the build can be seen in Figure 6.34. The average hardness is 344 HV. The hardness ranges from ~280 to ~440 HV. The hardness distribution is concentrated between 320 and 360 HV.

![Figure 6.33. Hardness map for Ti-2. The substrate interface is denoted by the red dashed line.](image)
6.6.3 Optical Microscopy

For this sample, only optical microscopy was utilized because it was determined by the study of Ti-1 that the necessary information could be obtained without using the SEM. A macro view of Ti-2 can be seen in Figure 6.35. There is not a clear interface between the substrate and the deposit. Since the substrate was heated above the beta transus during the build the beta grains are large and the epitaxial growth in the deposit takes away the interface definition. The columnar prior beta grains in this build begin from the height of the substrate and continue up to the top of the build. These large prior beta grains and keeping the deposit above the beta transus leads to a primarily basketweave microstructure.
Figure 6.35. Macro view of sample Ti-2. The dashed red line indicates the height of the substrate.

It is also clear from Figure 6.35 that this sample does not exhibit horizontal layer bands. This is similar to what was seen in Ti-1. It is in contrast to many samples seen in literature. Kelly, Kobryn, and others observed repeated banding across their LMD samples [41, 72, 73].

The micrographs in Figure 6.36 show the middle of the build from the bottom to the top. This figure illustrates that the microstructure in the build is relatively consistent. The microstructure in the bottom of the build is represented by Figure 6.36a. Some equiaxed prior beta grains can be seen in the bottom of the micrograph. The start of the epitaxial columnar beta grains can be seen in the middle of the micrograph. These prior beta grains are outlined by a thin layer of allotriomorphic alpha. This grain boundary alpha provides nucleation sites for a small amount of colony alpha around the perimeter of the grains.
The interior of the grains contains basketweave alpha. Figure 6.36b represents the middle of the build. There are no equiaxed prior beta grains seen in this region. A columnar prior beta grain can be seen becoming wider as it moves up the build. As the grain become larger the amount of colony alpha along the edge reduces and the amount of basketweave increases. Figure 6.36c-d is representative of the microstructure near the top of the build. Here the prior beta grains size is larger and so there is very little grain boundary and colony alpha. The microstructure is predominantly basketweave.

Figure 6.36. Optical micrographs from the middle of the build starting at the substrate (a) through the top (b-d). Basketweave alpha is the primary morphology. Small amounts of colony can be seen coming from GB alpha.
The bottom of the build contains more colony alpha (Figure 6.36a-b) than the middle or top (Figure 6.36c-d). However, this amount of colony is less than that seen in the bottom of Ti-1. In the current sample the beta grains are larger and so the colony alpha begins to form along the grain boundaries but cannot completely fill the grain interior before basketweave does.

6.6.4 Prior-Beta Grain Size

The prior-beta grain size in this sample was measured in the same way as Ti-1. The measurements were done in 1mm increments from the substrate. The grains start at over 1mm and there is an upward trend. There is less of a change in grain size in this build compared to Ti-1. The thermal management used in this build allowed the grains to start at a large size. This allowed the formation of primarily basketweave alpha through the build.

Figure 6.37. Variation in prior beta grain size in Ti-2.
6.6.5 Ti-2 Model Results
The model was run for one thermal profile from the build. Since the temperature of all
the layers remains above the beta transus until the end of the deposition one profile is
valid for all the layers. The model used the calibration parameters for regions 6-10 of Ti-
1 (Table 6.3). The final results of the model can be seen in Table 6.4. As expected,
basketweave is the predominant morphology. There is a small amount (6.31%) of colony
present. This is acceptable since there are pockets of colony alpha throughout the build.
The amount of grain boundary alpha being less than 5% is also acceptable.
Allotriomorphic alpha is seen along the prior beta grains and this small amount is
reasonable without quantification. The model predicts no martensite or massive products.
This means all of the beta that is available for transformation has transformed by the Ms
temperature.

<table>
<thead>
<tr>
<th>Grain Boundary (%)</th>
<th>Colony (%)</th>
<th>Basketweave (%)</th>
<th>Martensite (%)</th>
<th>Massive (%)</th>
<th>Beta (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.27</td>
<td>6.31</td>
<td>87.09</td>
<td>0.00</td>
<td>0.00</td>
<td>3.33</td>
</tr>
</tbody>
</table>

6.6.6 Impact of Processing Above Beta Transus
Additional samples were made with the same processing conditions as Ti-2. These
samples were created in order to investigate the impact on fatigue properties. It was
hypothesized that the absence of layer bands and the absence of a transition would lead to improved fatigue properties.

Fatigue testing in the z-direction was performed on four samples that were processed above the beta transus. The testing was done in the as processed condition, no additional heat treatment was performed. The results of this testing can be seen in Figure 6.38. The data from the current testing has been overlaid on the chart from Kobryn presented in Figure 2.13 [43]. The current samples are outlined by the red dashed line. It can be seen that three of the samples are in the cast part regime. There is one outlier that failed prematurely (sample 4). The red arrow is indicating how the as-built parts that have been beta-processed surpass the fatigue properties of the stress-relieved z-direction parts. The current parts match the stress-relieved x & y parts from the literature. While still not matching the parts that have been Hot Isostatically Pressed, with further research it may be possible to push as built parts closer to the wrought annealed regime (upper right) of this chart.
Figure 6.38. Chart comparing fatigue data of beta-processed samples (red dots) to literature values. Adapted from [43]

6.7 Ti-3 Sample Information
Ti-3 was built using the Laser Engineered Net Shaping (LENS®) system at OSU. This build was performed to see the effect of large prior-beta grains in the substrate on the final microstructure in the build. It was hypothesized that the large prior-beta grains would allow epitaxial growth from the substrate and produce primarily basketweave morphology in the build.

The substrate used was a section from a casting riser with prior-beta grains between 0.5 and 2mm. The substrate had a diameter of 47.6mm and a thickness of 14.3mm. The build was performed on an Optomec 750 LENS® machine with a fiber laser at OSU. A CAD model of the build was built with Solidworks and sliced by the LENS® machine. The
slices were set so the hatch patterns would be 180° from each other (Figure 6.39). The machine parameters for this build are in Table 6.5.

![Diagram of Even Layers and Odd Layers](image)

**Figure 6.39.** Top down schematic view of hatches for Ti-3 showing how they are offset 180°.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Power</td>
<td>350W</td>
</tr>
<tr>
<td>Travel Speed</td>
<td>635mm/min</td>
</tr>
<tr>
<td>Feed Rate (Hopper motor speed)</td>
<td>3 RPM</td>
</tr>
</tbody>
</table>

**Table 6.5.** Parameters for Ti-3 build.

### 6.8 Ti-3 Results and Discussion

#### 6.8.1 Microhardness

A microhardness map for Ti-3 was created with 150μm spacing between indents and a 200g force (Figure 6.40). The hardness in this build is higher than that seen in Ti-1 and
Ti-2. The color scale for in this figure is consistent with those for Ti-1 and Ti-2 even though the hardness goes higher than 400 HV. Any area that is above 400HV in Figure 6.40 appears red. This allows for easy comparison of this build to the previous ones. While Ti-1 and Ti-2 have small regions of red values nearly half the area for Ti-3 is red. This high hardness is likely due to the 100% basketweave microstructure that is observed.

![Figure 6.40. Hardness map for sample Ti-3. The substrate interface is denoted by the black dashed line.](image)

The frequency distribution for the Ti-3 build is seen in Figure 6.41. The distribution is centered between 375 and 425 HV. The Ti-3 build has an average hardness of 396 HV with a minimum of 352 HV and a maximum of 568 HV. The average hardness in Ti-3 is around 50 HV higher than the average hardness for Ti-1 (340 HV) and Ti-2 (344 HV).
6.8.2 Optical and SEM Characterization

Optical and SEM imaging was used to observe the microstructure of Ti-3. Figure 6.42 is an optical macrograph showing the regions where further examination with the SEM is desired. Columnar prior beta grains can be seen extending from the substrate to the top of the build. The grains do not expand in width very much compared with Ti-1. Large equiaxed prior beta grains filled with colony alpha can be seen in the substrate.
SEM characterization was performed to examine the details in the microstructure that were not clear with the optical microscope. The optical microscopy suggested that the sample could contain entirely basketweave microstructure but the features were too small to be distinguished optically. The images in Figure 6.43 show completely basketweave structure throughout the build. Prior beta grain boundaries can be seen in R2 and R4. Continuous grain boundary alpha is not seen on these grain boundaries though. No equiaxed prior beta grains can be seen, similar to Ti-2.
Figure 6.43. SEM micrographs of Ti-3. From R1 (a), R2 (b) and R4 (c) as denoted in Figure 6.42.

6.8.3 Prior-Beta Grain Size

The prior-beta grain size in this build was measured the same way as Ti-1. The build starts out with columnar prior-beta grains directly from the substrate. This is due to the large prior-beta grains in the substrate. Even though the grains in the substrate are large (~500-2000µm) the columnar grains in the build do not match their full size. The grain size starts at around twice as large as that in Ti-1 and increases with the height of the build. The increase is around 500µm. The grain size in Ti-3 never reaches the minimum size of Ti-2 (>1000µm). This is because the build did not stay at high temperature throughout the deposit to allow for the beta grains to grow. Even with the beta grains
being smaller than those in Ti-2 basketweave alpha and a higher hardness is seen throughout Ti-3. This is likely because Ti-3 cooled faster than Ti-2 because there was not an external heat source keeping the build hot.

![Figure 6.44. Prior-beta grain size variation in Ti-3.](image)

**6.9 Ti-3 Conclusions**

Ti-3 is significant because it illustrates that it is possible to obtain a fully basketweave microstructure without maintaining the temperature above the beta transus. By using a substrate with large prior-beta grains (>1mm) it is possible to suppress the grain boundary and colony alpha morphologies. The hardness map for Ti-3 shows regions that are significantly harder (>50HV higher) than Ti-1 or Ti-2. It may be possible to use this method to bring the properties closer to those of wrought material without Hot Isostatic Pressing or stress relieving. Mechanical testing must be done to see if the higher hardness correlates to improved mechanical properties.
CHAPTER 7: ALLOY 718

This chapter will contain information about the Alloy 718 STK model and the associated LMD builds. These builds were made by a third party and build parameters have not been shared with OSU. The builds are identified as Ni-1 and Ni-2. Sixteen additional builds have been analyzed as part of a design of experiments (DOE#1 - #16). These samples were built with different proprietary processing parameters. All of the samples were investigated for nano-scale precipitates. The amount of precipitates is correlated to the spatial hardness. Calibration of a STK model to predict the fraction of precipitates was performed by inputting thermal profiles from the samples.

In this chapter the Ni-1 and Ni-2 results will be directly compared. The results for the DOE samples will be presented after the Ni-1 and Ni-2 sections. The DOE results will be compared separately from Ni-1 and Ni-2.

7.1 Alloy 718 Thermodynamic Data
The following thermodynamic data was found using Thermo-Calc® version R with the TTNI7 database [69]. The data was calculated by Thermo-Calc® by stepping through a range of temperatures. The composition used in Thermo-Calc® was Ni-18.2Cr-19Fe-5.08Nb-3.13Mo-0.97Ti-0.51Al-0.12Si-0.02C-0.003B. This alloy specific data was incorporated into the STK model using curves fitted to the Thermo-Calc® data.
7.1.1 Driving Force

The free energy as a function of temperature was found for the $\gamma \rightarrow \text{Laves}$, $\gamma \rightarrow \text{NbC}$, $\gamma \rightarrow \gamma'$, and $\gamma \rightarrow \gamma''$ transformations. Figure 7.1 shows that as the temperature decreases the driving force for all precipitates increases. The driving force for NbC has the largest value by far. However, the amount of carbon in the system is so low that only small amounts of NbC form. The other driving forces are tightly grouped until around 775K. Here the driving force for laves increases at a faster rate than $\gamma'$ or $\gamma''$. Here the driving force for $\gamma''$ also increases above that for $\gamma'$. This means that if the composition is favorable more of the phase with the highest driving force will form.

Figure 7.1. Chart of driving forces as a function of temperature for Alloy 718.
The output from Thermo-Calc® is in the format DGM/RT. In the STK code this data is multiplied by -1 and then multiplied by R (8.3144725) and the current temperature. This gives the driving force in J/mole.

7.1.2 Equilibrium Phase Fraction

The equilibrium phase fraction for each precipitate as a function of temperature was found. Delta was not considered in this calculation because it will prevent the formation of metastable γ’’ under equilibrium conditions. The data is shown in Figure 7.2. At high temperature the system is completely gamma. NbC is the first precipitate to begin forming. Thermo-Calc® is reporting the solvus of NbC at ~1700K. However, Knorovsky reported a γ/NbC eutectic at ~1525K. Since there is very little carbon in the system the amount of NbC stays low, reaching a maximum of ~0.002. The next precipitate to form is γ’’ at ~1215K. The fraction of γ’’ increases to ~0.1 at room temperature. At ~1175K γ’ begins forming. It reaches a maximum of ~0.13 at room temperature. Finally, laves begins forming at ~588K. This solvus is also abnormally low compared to Knorovsky’s work. He reported a γ/laves eutectic temperature of ~1417K. The amount of laves at room temperature is ~0.12. The solvus temperatures for the NbC and Laves eutectics are different than those in physical experiments because the equilibrium calculations are not accounting for segregation of elements. The calculated temperatures indicate the solvus if the composition remains at the nominal values throughout solidification.
Figure 7.2. Chart of phase fractions as a function of temperature.

This phase fraction data is used by the model to determine if the precipitates are able to grow or if dissolution must take place. If the amount of a phase at the current time step is less than the equilibrium amount then further growth is allowed. If the amount is more than the equilibrium amount then dissolution takes place. As in the Ti-6Al-4V model the dissolution is simplified by resetting the current phase fraction to the equilibrium value. Future work in modeling the dissolution is recommended.

7.1.3 Equilibrium Phase Composition

Since real time diffusion calculations are not possible the equilibrium phase compositions were found. This data will represent the concentration of elements at the interface
between γ and the precipitate. The concentration of the slowest diffusing element in each phase is considered. For γ′′ and laves the formation is dependent on Nb diffusion. The formation of γ′ is dependent on Al diffusion. Delta is not reported here because the calculation failed to run in Thermo-Calc®. Delta is also not seen in the samples discussed here.

The concentration of Nb as a function of temperature for γ′′ and γ in equilibrium can be seen in Figure 7.3. Figure 7.4 shows the concentration of Al for γ′ and γ in equilibrium. Figure 7.5 shows the concentration of Nb for NbC and γ in equilibrium.

![Figure 7.3. Concentration of Nb between γ′′ and γ in equilibrium over a range of temperatures](image-url)
Figure 7.4. Concentration of Al between $\gamma'$ and $\gamma$ in equilibrium over a range of temperatures

Figure 7.5. Concentration of Nb between NbC and $\gamma$ in equilibrium over a range of temperatures
For the STK model the concentration data was converted from weight percent to mole fraction. This was done using equation 16. Where \( X \) is the mole fraction, \( w\%(i) \) is the weight percent of the element in question, \( M_i \) is the molecular mass of the element (92.906g/mol for Nb and 26.982g/mol for Al), and \( M_{total} \) is the total molecular mass of the system (57.96g/mol for 718)

\[
X = w\%(i) \frac{M_{total}}{M_i}
\]  

(16)

### 7.2 Model Calibration Parameters

The STK model for 718 is calibrated by adjusting the parameters listed below to fit the experimental data. The 718 model contains 16 parameters. A short description of the physical meaning of the parameter is given and then the actual parameter name from the Igor code is listed.

- **Variables controlling model predictions**
  - Number of nucleation sites for \( \gamma' \), \( \gamma'' \), NbC, Laves, and Delta
    - Allows for modification of how likely it is for these morphologies to start growing
    - \( N\text{zeroGP}, N\text{zeroGDP}, N\text{zeroNbC}, N\text{zeroLaves}, N\text{zeroDelta} \) [#m^-3s^-1]
  - Acceleration factors for \( \gamma' \), \( \gamma'' \), NbC, Laves, and Delta
    - Accelerates the formation of these morphologies in order to fit to the experimental data
    - \( Acc\text{FactorGP}, Acc\text{FactorGDP}, Acc\text{FactorNbC}, Acc\text{FactorLaves}, Acc\text{FactorDelta} \) [unitless]
  - Surface energy
    - Determines the magnitude of the activation energy
    - \( Surf\text{EnerImp} \) [J/m^2]
  - Strain energies for \( \gamma' \), \( \gamma'' \), NbC, Laves, and Delta


- Determines how much undercooling is required to form

### 7.3 Quantifying Nano-scale Particles

Since \(\gamma^\prime\) and \(\gamma\) are nano-scale particles it is difficult to characterize their spatial variation within a large-scale LMD build. However, the micron-scale solidification structure gives hints to the nano-scale precipitate concentration because the areas where the precipitates are concentrated appear brighter. This provides a method of getting an average precipitate concentration that is in line with the length scale of the data being inputted to the model. It will be shown that the amount of \(\gamma^\prime\) and \(\gamma\) varies in both the height and the width of the build. A traverse of the width reveals that the \(\gamma^\prime/\gamma\) concentration increases at the dendrite boundaries and reduces to virtually zero at the dendrite cores. Since the extracted thermal profile covers many microns in area a technique had to be devised to generate an average amount of \(\gamma^\prime/\gamma\) for the large area.

In order to find this average low magnification (~750x) micrographs (Figure 7.6a) were taken corresponding to the extracted thermal cycles and then high magnification (50,000x) micrographs (Figure 7.6c) where taken from various locations within the low-mag micrograph. These high-mag images were analyzed for \(\gamma^\prime\) and \(\gamma\) (Figure 7.6d) while the low-mag images were analyzed for area that could support \(\gamma^\prime/\gamma\) precipitation (Figure 7.6b). The images were analyzed following a method of automated particle analysis described by Payton [74]. The technique will be covered in detail in Chapter 6.
Figure 7.6. Schematic illustrating process of quantifying $\gamma'/\gamma''$ in the Low-mag overview (a). The low-mag image after threshold operation (b). High-mag image of dendrite boundary (c). High-mag image after threshold operation (d).

7.4 Ni-1 Sample Information
Ni-1 is a multi-layer build that was deposited on the edge of a thin substrate. A SAMP thermal simulation was performed by Applied Optimization using the proprietary build parameters. It was found that this build had a lower overall temperature than Ni-2. As a result, less time was spent in the aging temperature range. This led to minimal $\gamma'/\gamma''$ formation. It will be seen that there are particles that could be the beginning of $\gamma'/\gamma''$ formation but they are not well defined.
7.4.1 As Received Build

The deposit was received by OSU as a section of a larger build. The original build dimensions are unknown. The as received sample can be seen in Figure 7.7a. This build section has dimensions of 11.5mm x 4.0mm. The build was also sectioned along a plane denoted by the red dashed line to have two samples from this build. A schematic of where the build was sectioned can be seen in Figure 7.7b. The plane at 6.4mm from the left edge is denoted by the red dashed lines. This plane corresponds to the section cut made by the dashed line in Figure 7.7a. This schematic also shows the coordinates of temperature extraction points. These points were chosen on the two sectioned planes at the bottom (interface of substrate), middle, and top of the build. A point was taken from the center and outside at each of these locations to give a total of 12 thermal profiles.

Figure 7.7. Photograph (a) of as received Ni-1 sample. Schematic (b) showing where sectioned faces are as well as points where thermal data was extracted.
7.5 Ni-1 Results and Discussion

In this section data will be presented from the thermal simulation, optical microscopy, hardness mapping, and SEM. The thermal data will be analyzed to show how much time was spent in the isothermal aging temperature range for this alloy. Data from optical micrographs can be used to analyze the solidification structures. SEM will be used for the majority of the characterization since the strengthening precipitates (γ' / γ'') are so small.

7.5.1 Thermal Data

The thermal data simulated by SAMP for the Ni-1 build is seen below in Figure 7.8. It can be seen that this build took around 1200s to complete. The number of layers in the build can be inferred by the number of major thermal undulations. Here this build would have 10 layers. This chart shows the thermal history for a location (point 2) at the interface between the build and substrate in red, in the middle of the build (point 4) in orange, and the 9th layer in blue (point 6). The nominal aging temperature range (893-993K) for A718 is shown by the dashed horizontal lines. It can be seen that the bottom layer would experience much more time at elevated temperature than a top layer. It stands to reason that enough time spent in the aging temperature range would allow γ'/ γ'' to form. It also appears that an external thermal management system may have been used. This is because after the deposit starts the temperature never drops below a value of around 600K. This allows the bottom layers to stay above a preset temperature and for all
of the layers to cool together at the end of the build. Indeed, this is the case at the end of this build.

![Figure 7.8. Simulated thermal history (a) for bottom (point 2), middle (point 4), and top (point 6) of Ni-1 build.](image)

A frequency distribution for the temperatures in the bottom and top of Ni-1 can be seen in Figure 7.9. In this chart, the higher the frequency of a temperature, the longer the time spent at that temperature. Here it can be seen that neither location spends much time in the aging range. Most of the time is spent in the 600-850K temperature range for both locations. It will be shown that there is almost no $\gamma'/\gamma''$ precipitation in this sample. This can be compared to the Ni-2 sample in the next section.
Figure 7.9. Chart showing distribution of temperatures in the bottom (point 2) and top (point 6) of the Ni-1 build.

7.5.2 Microhardness Data
The microhardness map seen in Figure 7.10 for sample Ni-1. The dashed line represents the boundary between the substrate and build. It can be seen that the build is harder than the substrate, indicating that some strengthening has occurred. However, it will be seen that strengthening precipitates are not seen in this build. Therefore the hardening in the build could be from clustering of precipitate forming elements before the precipitates form.
A frequency distribution of the hardness values in the build can be seen in Figure 7.11. This data represents the deposit only, the substrate data has been removed. The build varies in hardness from 255HV to 369HV with an average hardness of 322HV. The frequency distribution shows that the highest frequency is between 310HV and 330HV.
7.5.3 Optical Microscopy

A macrograph of the Ni-1 build can be seen in Figure 7.12. This image shows that the interface with the substrate is not flat. This is due to meltback when the laser is depositing on the edges. Lighter colored bands can be seen crossing the width of the build. These are likely small heat affected zones that are formed when previous layers are reheated. Since these bands do not show up in the hardness map (Figure 7.10) it is assumed that they do not affect the mechanical properties. Black diamonds have been overlaid on the macrograph to show spatially where thermal profiles were extracted from the SAMP model.
Figure 7.12. Macrograph of Ni-1 build. Diamonds indicate areas where thermal profiles were extracted.

7.5.4 SEM Characterization

SEM characterization was carried out with the Sirion SEM using the through lens detector (TLD). This detector allows for very high magnification so the nano-scale precipitates in this alloy can be imaged. The sample was prepared by dissolving the matrix with an electrolytic etch consisting of 15g CrO$_3$ 150mL H$_3$PO$_4$ 20mL H$_2$SO$_4$ at 6v for ~30s.

Figure 7.13a illustrates the microstructure at the bottom of the Ni-1 build. This relatively low-magnification image shows a somewhat columnar dendritic structure. The large precipitates (laves and carbides) can be seen along the interdendritic boundaries. In order to investigate the presence of $\gamma'$/$\gamma''$ high-mag images were taken in the interdendritic
regions (Figure 7.13b). A large precipitate can be seen in the bottom of the image. In the matrix surrounding this precipitate nano-scale particles can be seen. However, they are not well defined. They could be the start of $\gamma'/\gamma''$. Well defined $\gamma'/\gamma''$ particles will be seen in the Ni-2 sample.

Figure 7.13: Low-mag micrograph (a) from bottom of Ni-1 build. Columnar dendritic structure can be seen. High-mag micrograph (b) from bottom of Ni-1 build. No defined $\gamma'/\gamma''$ precipitates are seen.
Moving to the top of the build, Figure 7.14a shows that the large precipitates now appear to form in an equiaxed fashion. This change from dendritic to equiaxed is most likely due to a different thermal gradient seen in the bottom and top of the build. The structure seen here is similar to a “rafted structure” seen by Clark et al. [16]. They observed columnar dendrites in the X-Z plane and a “rafted structure” when they viewed a transverse section (X-Y plane). Since this rafted structure is seen in Ni-1 in the Y-Z plane, it is possible that the dendrites are now growing in the X-Y plane. This could be caused by a change in the path of the laser during the deposition. Figure 7.14b is a high-mag micrograph from the top of the build near one of the large precipitates. Here, as in the bottom, there is a lack of $\gamma'/\gamma''$. 
Figure 7.14: Low-mag micrograph (a) from top of Ni-1 build. Equiaxed structure is seen. High-mag micrograph (b) from top of Ni-1 build. Lack of nano-scale precipitates.

The lack of nano-scale precipitation in this build can be rationalized by looking at the thermal profiles. Figure 7.8 and Figure 7.9 show that neither the bottom or top of this build spend a significant amount of time in the aging temperature range. Therefore it would not be expected to see $\gamma'$/$\gamma''$ precipitates.
7.6 Ni-2 Sample Information
Ni-2 is a multi-layer build that was deposited on the edge of a thin substrate. A SAMP thermal simulation was performed by Applied Optimization using the proprietary build parameters. This build had a higher overall temperature than Ni-1 and spent more time in the aging temperature range. Therefore γ'/γ'' did form in this build. However, the particles are spatially heterogeneous due to elemental segregation during solidification.

7.6.1 As Received Build
The deposit was received by OSU as a section of a larger build. The original build dimensions are unknown. The as received section can be seen in Figure 7.15a. The rounded corner is likely due to heat buildup and high temperature at the edge of the build. The received build section has dimensions of 12.6mm x 5.6mm. This sample was sectioned again along the dashed red line. Figure 7.15b schematically shows the location of the section planes with reference to the left edge of the build. This schematic also shows the locations where thermal data was extracted from the SAMP simulation.
Figure 7.15. Photograph (a) of as received Ni-2 sample. Schematic (b) showing where sectioned faces are as well as points where thermal data was extracted.

7.7 Ni-2 Results and Discussion

7.7.1 Thermal Data
The thermal history for the bottom (point 2), middle (point 4), and top (point 6) can be seen in Figure 7.16. This build appears to have 10 layers, the same as Ni-1. It can be seen that this build takes around 1200s to complete. This build was made with a higher laser power than Ni-1 and so the overall temperature is higher. Thermal management was implemented in this build as well. The temperature in this build does not go below ~700K after the initial transient period. This management system keeps all of the layers around the same temperature as they cool. This can be seen during the build as well as at the end. In the microstructure analysis it will be seen that the $\gamma'$ / $\gamma''$ precipitation in the bottom regions is supported by the amount of time the bottom layer spends in the nominal aging
range. Similarly, for the top layers, the shorter time spent in the aging temperature range leads to the smaller precipitation field as seen as will be seen later.

Figure 7.16. Simulated thermal history (a) for bottom (point 2), middle (point 4), and top (point 6) of Ni-2 build.

Figure 7.17 schematically shows the total amount of time spent in the aging temperature range for the bottom and top of the build. It can be seen that while the aging temperature range does not have the highest frequency, it is significantly higher than that seen in the Ni-1 build. It will be shown that this leads to an increase in the nano-scale precipitation in Ni-2 compared to Ni-1.
7.7.2 Microhardness Data

The hardness map for the Ni-2 sample is presented in Figure 7.18. The interface of the build and substrate is denoted by the dashed line. It can be seen that the substrate and bottom of the build are harder than the top of the build. This is because these regions were held in the aging temperature range for more time than the top. The SEM characterization of this sample will show that these harder regions correlate to increased $\gamma'/\gamma''$ precipitation.
Figure 7.18. Microhardness map for Ni-2 build. Dashed red line indicates interface with substrate.

Figure 7.19 shows the frequency distribution for Ni-2 deposit. The hardness data for the substrate has been taken out of this distribution. The build varies in hardness from 250HV to 374HV with an average hardness of 301HV. Even though this sample has $\gamma'$/$\gamma''$ precipitates where Ni-1 did not, it has a lower average hardness than Ni-1. This could be because the precipitates are segregated in certain regions. This leads to a larger variation in the hardness.
7.7.3 Optical Microscopy

An optical macrograph for Ni-2 can be seen in Figure 7.20. Similarly to Ni-1, the interface with the substrate is not flat. Meltback can be seen more prominent on the right side than the left. This is likely due to the path of the laser. This build does not exhibit the lighter bands seen in Ni-1 (Figure 7.12). This could be because Ni-2 was kept at a higher temperature than Ni-1. Thereby keeping the previous layers above the temperature where these bands form. The black diamonds on the image have been overlaid to show where thermal profiles have been extracted from the SAMP model.
7.7.4 SEM Characterization

This sample was prepared and characterized the same way as the Ni-1 sample. The bottom of the Ni-2 build features large precipitates in a columnar dendritic arrangement (Figure 7.21a). These precipitates have formed along the interdendritic regions. A lighter colored field can be seen surrounding the large particles. This field denotes where there concentration of $\gamma'/\gamma''$ particles. The red box on Figure 7.21a shows the region for Figure 7.21b while the green box is the region for Figure 7.21c. The dendrite core is
shown at high-mag in Figure 7.21b. It can be seen that there is no γ'/γ''. This is in contrast to the interdendritic region (Figure 7.21c) where strong precipitation can be seen.

![Figure 7.21](image)

Figure 7.21. Low-mag micrograph (a) from bottom of Ni-2 build. Columnar dendritic microstructure is seen. High-mag micrographs showing lack of precipitation in dendrite core (b) and strong precipitation in interdendritic region (c).

The top of the build can be seen in Figure 7.22a. Here the large precipitates appear equiaxed instead of columnar dendritic. The particles could appear this way because they have changed orientation as described for Ni-1. If the top of the sample were viewed in
the x-y plane it is possible there would be columnar dendrites. Also of note is the absence of the lighter colored fields around the precipitates. This indicates that the $\gamma'/\gamma''$ precipitation will not be as strong in the top regions. A high-mag micrograph near one of the large precipitates reveals that this is true. Figure 7.22b shows that the $\gamma'/\gamma''$ precipitation in this region is not as strong as the bottom.

![Low-Mag](image1)
![High-Mag](image2)

Figure 7.22. Low-mag micrograph (a) from top of Ni-2 build. Equiaxed microstructure can be seen. High-mag (b) near one of the large precipitates shows irregular shaped $\gamma'/\gamma''$. 

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The reason that the brighter fields are not seen in the top region is because of two factors. The first being lack of time at high temperature for the Nb rich laves and NbC to partially dissolve and enrich the surrounding area with Nb. The second being lack of time spent in the aging temperature range for the $\gamma'/\gamma''$ precipitates to form. The combination of these factors led to the lack of nano-scale precipitates in the top regions.

7.7.5 $\gamma'/\gamma''$ Quantification in Ni-2
The Ni-2 sample has been used for quantification of the amount of $\gamma'/\gamma''$ because it has the strongest precipitation of the samples analyzed thus far. This makes it good for testing the quantification methods and calibrating the STK model. To quantify the $\gamma'/\gamma''$ a different etchant was used to dissolve the precipitates while leaving the matrix intact. The etchant was 61.0% Lactic acid, 85% 46.6% Nitric acid, 69%; 2.4% Hydrofluoric acid, 49% for ~45s. Using this etchant provides better contrast between the precipitates and the matrix, allowing for easier computerized image processing. The Sirion SEM with the TLD was still used for this work.

To provide an average $\gamma'/\gamma''$ concentration over a large length scale micrographs were taken at low and high magnification. The low magnification micrograph would have several areas selected to have high magnification micrographs taken. In this way the high magnification micrographs could be analyzed to find the concentration of $\gamma'/\gamma''$ while the low magnification micrographs could be analyzed to find the areas that contained $\gamma'/\gamma''$.
\(\gamma''\) precipitates. These numbers can then be combined to find an average of the nano-scale particles over a micron length scale.

For the bottom of the build a low-mag overview image can be seen in Figure 7.23a. The interdendritic regions can be seen as the brighter areas. These brighter areas are where \(\gamma'/\gamma''\) precipitates can form. The dendrites appear as columns mostly aligned with the z-axis of the build. Larger laves and carbide precipitates can be seen in this micrograph as well.

An example of one of the high-mag images from within Figure 7.23a can be seen in Figure 7.23b. Here the \(\gamma'/\gamma''\) precipitates are seen as black spots on a grey background (matrix). This in contrast to the \(\gamma'/\gamma''\) seen in Figure 7.13c with the chromic etch. Here the precipitates appear brighter than the background.

Figure 7.23. Low magnification overview (a) for bottom region of Ni-2. Example of high magnification (b) micrograph in interdendritic region.
The overview micrograph for the middle of Ni-2 can be seen in Figure 7.24a. The brighter fields in the interdendritic regions are less prominent than those in the bottom of the build. An example of the high-mag images from this area can be seen in Figure 7.24b. Qualitatively the precipitation in this micrograph appears to be about the same as that seen in bottom region (Figure 7.23b).

![Figure 7.24. Low magnification overview (a) for middle region of Ni-2. Example of high magnification (b) micrograph in interdendritic region.](image)

Figure 7.25a shows the overview micrograph for the top of the build. The laves and carbide particles are present but they are not surrounded by the brighter fields. This suggests that there will not be $\gamma'/\gamma''$ in this region. Indeed, when the high-mag micrograph (Figure 7.25b) is analyzed, there are no $\gamma'/\gamma''$ precipitates. There are bright particles seen across the matrix. These are likely particles of colloidal silica that did not come off after polishing. They are present in the bottom and middle micrograph also but are not as noticeable because of the numerous precipitates.
From the low-mag overview images, the area where it is possible to form $\gamma'/\gamma''$ can be quantified. The data from these analyzed images can be seen in Table 7.1. The bottom of the build has more potential for forming nano-scale precipitates. The middle is around 10% less while the top shows 0% area to form $\gamma'/\gamma''$. This contradicts the findings with the electrolytic etch where it was reported that the top regions did show some precipitation. With this etch there was almost no $\gamma'/\gamma''$ precipitation in these regions.

Table 7.1. Percentage of area where it is possible to form $\gamma'/\gamma''$.

<table>
<thead>
<tr>
<th>Region</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom</td>
<td>33%</td>
</tr>
<tr>
<td>Middle</td>
<td>23%</td>
</tr>
<tr>
<td>Top</td>
<td>0%</td>
</tr>
</tbody>
</table>
The data from each of the high-mag micrographs is presented in Table 7.2. There is a large variation in the particle count and area percentage depending on where the image was taken from. If the image was taken near one of the laves or carbide particles, the concentration of $\gamma'/\gamma''$ is higher. If the image came from closer to the dendrite core, the $\gamma'/\gamma''$ concentration will be lower. The average column in Table 2 represents all of the area percentages for each region averaged together. This gives an average for the amount of $\gamma'/\gamma''$ in the dendrite boundaries.

<table>
<thead>
<tr>
<th>Image</th>
<th>Particle Count</th>
<th>Area Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom 03</td>
<td>4531</td>
<td>11.18</td>
</tr>
<tr>
<td>Bottom 05</td>
<td>3948</td>
<td>7.49</td>
</tr>
<tr>
<td>Bottom 06</td>
<td>1664</td>
<td>2.95</td>
</tr>
<tr>
<td>Bottom 08</td>
<td>3514</td>
<td>7.14</td>
</tr>
<tr>
<td>Bottom 09</td>
<td>2900</td>
<td>5.58</td>
</tr>
<tr>
<td><strong>Bottom Average</strong></td>
<td></td>
<td><strong>6.87</strong></td>
</tr>
<tr>
<td>Middle 02</td>
<td>3006</td>
<td>6.77</td>
</tr>
<tr>
<td>Middle 03</td>
<td>3233</td>
<td>9.06</td>
</tr>
<tr>
<td>Middle 04</td>
<td>1288</td>
<td>2.77</td>
</tr>
<tr>
<td><strong>Middle Average</strong></td>
<td></td>
<td><strong>6.20</strong></td>
</tr>
</tbody>
</table>

*Note: Top region not included because no $\gamma'/\gamma''$ was observed
Table 7.3 combines the data in Table 7.1 and Table 7.2 to give an overall average for the amount of $\gamma'/\gamma''$ in each low-mag micrograph. This illustrates how small the $\gamma'/\gamma''$ is in this sample. Devaux found the amount of $\gamma$ to be 4% and the amount of $\gamma''$ to be 15% during isothermal aging [52].

Table 7.3. Results showing the overall average of $\gamma'/\gamma''$ for each region

<table>
<thead>
<tr>
<th>Region</th>
<th>Area where PPTs Possible</th>
<th>Avg. Area of PPTs</th>
<th>Overall Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom (pt. 2)</td>
<td>33%</td>
<td>6.87%</td>
<td>2.29%</td>
</tr>
<tr>
<td>Middle (pt. 4)</td>
<td>23%</td>
<td>6.20%</td>
<td>1.42%</td>
</tr>
<tr>
<td>Top (pt. 6)</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
</tbody>
</table>

7.7.6 Calibration values for STK model

The values in Table 7.4 were used for the initial results that follow. Currently the predictions of $\gamma'$ and $\gamma''$ are the only ones that are active. The code is in place in the framework for the other precipitates but since they have not been quantified they are not currently being predicted. The surface energy value has been found in literature for $\gamma''$ but not for the other precipitates. This value is currently being used for the nucleation rate
calculation for all of the precipitates. This will need to be updated to reflect the fact that the different particles have different surface energies.

Table 7.4. Table showing calibration parameters based on Ni-2 quantification

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$\gamma''$</th>
<th>$\gamma'$</th>
<th>NbC</th>
<th>Laves</th>
<th>Delta</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleation Sites</td>
<td>2.5E18</td>
<td>8E18</td>
<td>1E18</td>
<td>1E5</td>
<td>1E10</td>
<td>#*m^{-3}*s^{-1}</td>
</tr>
<tr>
<td>Surface Energy</td>
<td>0.095</td>
<td>0.095</td>
<td>0.095</td>
<td>0.095</td>
<td>0.095</td>
<td>J/m²</td>
</tr>
<tr>
<td>Strain Energy</td>
<td>300</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>J/mole</td>
</tr>
<tr>
<td>Acceleration Factor</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

7.7.7 Results from STK Model for Ni-2

The thermal profiles for the bottom, middle, and top of the Ni-2 sample have been processed by the prototype 718 STK framework. The framework was developed and the initial calibration performed based on the data for the bottom of the build. Figure 7.26 illustrates the output from the model for the bottom (point #2 in Figure 7.15b). Here the thermal history can be seen in the bottom of the chart and the fraction of $\gamma'$ and $\gamma''$ can be seen in the upper plot. This shows that the model is accounting for the precipitates growing incrementally. Once enough time has been spent in the aging temperature range, the precipitates will begin nucleating and growing. However since the temperature is not fixed, the fraction does not increase linearly. Before 600s the temperature gets high.
enough that the precipitates dissolve. After 600s the bottom has cooled enough that the precipitates that nucleate are stable and are not all dissolved in the high temperature excursions. As time progresses, the precipitates will continue to nucleate and grow when the thermal conditions are favorable. This leads to the step pattern of the plot. This schematically shows the mechanism that would be expected during the LMD process.

![Chart of Temperature vs. time and fraction of $\gamma'(GP)$ and $\gamma''(GDP)$ vs time.](image)

Figure 7.26. Chart of Temperature vs. time and fraction of $\gamma'(GP)$ and $\gamma''(GDP)$ vs time.

The results from the STK model from three locations can be seen in Table 7.5. The values of the $\gamma' + \gamma''$ can be compared experimental data in Table 7.3. The prediction for the bottom point is slightly over (0.19% more) the experimental data. The prediction for
the middle point has a large deviation. The experimental amount is 1.42% while the prediction is 0.016%. The top point has good agreement also. No \( \gamma' \) or \( \gamma'' \) was found experimentally and the model is predicting 0.001%.

Table 7.5. Predicted values of \( \gamma'(GP) \) and \( \gamma''(GDP) \) for different locations.

<table>
<thead>
<tr>
<th>Location</th>
<th>Gamma (%)</th>
<th>GP (%)</th>
<th>GDP (%)</th>
<th>GP+GDP (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point 2 (Bottom)</td>
<td>97.503</td>
<td>0.544</td>
<td>1.938</td>
<td>2.482</td>
</tr>
<tr>
<td>Point 4 (Middle)</td>
<td>99.794</td>
<td>0.009</td>
<td>0.007</td>
<td>0.016</td>
</tr>
<tr>
<td>Point 6 (Top)</td>
<td>99.803</td>
<td>0.001</td>
<td>0.000</td>
<td>0.001</td>
</tr>
</tbody>
</table>

For the middle of the build the relation between the precipitate fraction and temperature can be seen in Figure 7.27. At the beginning of the traces the precipitates have a maximum value of \(~0.0004\). At 1160s the temperature increases above 1200K and the precipitate fraction immediately drops to zero. This means that the temperature has increased to a point where the equilibrium precipitate fraction is zero. Since the dissolution in the model is simulated by resetting the precipitate fraction to the equilibrium value, the precipitate fractions become zero. As the build cools the precipitate fraction increases to its final value of 0.00016. This is a deficiency in the model because it is not likely that the precipitates dissolve instantaneously. Since the temperature excursion is so short it is likely that the precipitates would not dissolve very much. This is a result of using equilibrium data for governing the model predictions.
However, this equilibrium data must be used until further research is done into the in-situ transformations during LMD. In the meantime EDS can be performed to find the solute enriched composition at the dendrite boundaries. This new composition can then be put in Thermo-Calc® and the thermodynamic data can be calculated. The A718 model can be modified with this data to simulate the precipitation conditions at the dendrite boundaries. It is possible that this would provide better correlation to the experimental data before performing in-situ research.

Figure 7.27. Detail of end of build for point 4. T-t data shown on bottom and fraction of γ’ and γ’ shown on top.

7.8 Analysis of 16 Design of Experiments Samples
OSU received 16 design of experiments (DOE) samples from AO. 8 of the samples are single layer and 8 are multi-layer. The sample numbers can be seen in Table 7.6. Each
build was done on the edge of a coupon that measured 50x50x2.2mm. The path geometry is not known but it can be inferred that there are multiple paths in each layer because of multiple peaks seen in the thermal profiles. One thermal profile from each sample has been extracted from the SAMP simulation of the build and provided to OSU. This profile was extracted from the center of the build at the interface of the deposit and substrate. The micrographs are from approximately the same location as the extracted thermal profile.

Table 7.6. Sample numbers corresponding to single layer or multi-layer DOE builds.

<table>
<thead>
<tr>
<th>Single Layer</th>
<th>DOE # 1, 3, 5, 7, 10, 12, 14, 16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multi-Layer</td>
<td>DOE # 2, 4, 6, 8, 9, 11, 13, 15</td>
</tr>
</tbody>
</table>

7.8.1 DOE Thermal and Microstructure Results

DOE #1

DOE #1 is a single layer build. The thermal profile can be seen in Figure 7.28a. This build was completed relatively quickly with little time spent in the nominal aging temperature range. This build would be expected to show very little precipitation. Indeed, as can be seen in Figure 7.28b, there are only a few carbide/laves precipitates seen. The gamma grain structure can be seen here with the grains less than 50μm in size. Smaller
scale $\gamma'/\gamma''$ precipitates were not observed in this sample, therefore there are not any higher magnification micrographs.

![Figure 7.28. Thermal profile for DOE #1 (a). Low magnification micrograph (b) showing lack of precipitates.](image)

**DOE #2**

DOE #2 is a multilayer build whose thermal profile can be seen in Figure 7.29a. This build takes around 500s. After a short “ramp-up” period in the beginning the temperature does not fall below 993K. This temperature corresponds with the upper limit of the isothermal aging temperature range. Since very little time is spent in the aging range it is expected that there would be very little precipitation. Figure 7.29b is a low magnification image showing laves and carbide precipitates. These are discontinuous and there are small precipitate fields surrounding some of these precipitates. Looking closer at the eutectic products and the precipitate fields (Figure 7.29c & d) it can be seen that there is a low concentration of $\gamma'/\gamma''$ precipitates. They are clustered close to the eutectic products.
A gamma grain can be seen in Figure 7.29c and it can be seen that the eutectic products have formed at the grain boundaries.

Figure 7.29. Thermal profile for DOE #2 (a). Microstructure overview (b). Detail view of blue box (c). Detail view of red box (d) showing \( \gamma' / \gamma'' \) particles near eutectic particles.

**DOE #3**

DOE #3 is a single layer build. The build’s thermal profile can be seen in Figure 7.30a. It appears that this build had four paths evidenced by the four peaks in the thermal profile. This build is not expected to have appreciable \( \gamma' / \gamma'' \) precipitation since very little time
was spent in the aging temperature range. Figure 7.30b shows a number of eutectic particles. Some of these have grown together to form continuous chains. Brighter precipitate fields are not seen between the particles though. Figure 7.30c & d are high magnification images near the eutectic particles. They show that there is no $\gamma'/\gamma''$ precipitation in this build. The black areas in Figure 7.30c are contamination on the surface of the sample. This contamination is likely due to oils picked up during preparation.

Figure 7.30. Thermal profile for DOE #3 (a). Microstructure overview (b). Detail view near eutectic product (c). Detail view of red box (d).
DOE #4

DOE #4 is a multi-layer build. Figure 7.31a shows the thermal profile for this build. It can be seen that after 200 seconds the temperature is controlled and does not drop below 750K until the end of the build. This sample spends the entirety of the deposit time cycling in and out of the aging range. In the beginning this will allow precipitates to form on cooling but they are likely to be dissolved on the subsequent heating cycle. As the build progresses the maximum temperature decreases and the precipitates become more stable. The resultant microstructure is seen in Figure 7.31b-d. The overall structure is seen in Figure 7.31b with large carbide/laves precipitates, primarily along the dendrite boundaries. Fields of lighter contrast can be seen surrounding these precipitates and it will be seen that these fields contain γ'/γ'' precipitates. Figure 7.31c is a higher magnification micrograph from the area selected in the blue box of the previous image. Here γ'/γ'' precipitates can be seen with their concentration decreasing as the distance away from the large precipitates increases. The γ'/γ'' precipitation field extends at most 2μm away from the large precipitates. Figure 7.31d is a higher magnification image from the area selected by the red box in the previous image. The various morphologies of the γ'/γ'' can be seen, with some being spherical and some being disc shaped. Qualitatively, the precipitate concentration here appears to be less than in the Ni-2 sample previously analyzed.
DOE #5

DOE #5 is a single layer build. From analysis of the thermal profile (Figure 7.32a) it appears that there are 4 paths in the layer. It can be seen that there is very little time spent in the aging temperature range. The low magnification image in Figure 7.32b shows a number of eutectic particles. Some of the particles have grown together to form chains. Precipitate fields are not seen. The high magnification image (Figure 7.32c) confirms that there are no γ'/γ'' particles. The black spots on the surface are contamination, likely due to oils picked up during preparation of the sample.
DOE #6

DOE #6 is a multi-layer build. The thermal profile is seen in Figure 7.33a. It is not possible to determine how many layers or the number of paths per layer. This build was given no time to cool off between layers. After the initial transient portion where the build is heating up the temperature does not drop below ~950K. This provides the maximum amount in time in the aging temperature range for this build. The low-mag image (Figure 7.33b) illustrates the morphology of the eutectic products. The eutectic
particles in this build appears to be aligned in columnar dendritic shapes. These dendrites are likely aligned parallel to the direction of maximum temperature gradient. Figure 7.33c shows that γ'/γ'' particles are found near the eutectic products. The field of particles extends less than 1μm away from the eutectic particle. Figure 7.33d is a detail view of the area denoted by the red box in Figure 7.33b. This shows an area that is not near eutectic particles that contains γ'/γ'' particles.

Figure 7.33. Thermal profile for DOE #6 (a). Microstructure overview (b) showing eutectic particles. Detail view near eutectic particle (c) showing γ'/γ'' precipitates. Detail view of red box (d) showing γ'/γ'' precipitates away from eutectic particles.
DOE #7

DOE #7 is a single layer build. Once this build was started the temperature (Figure 7.34a) was kept above the lower limit for the aging temperature range (893K). This processing would give the possibility of having precipitates form. However, the high temperature excursions and short build time prevent precipitates from forming. Figure 7.34b shows that there are very few precipitates present in this sample. The fields indicating $\gamma'/\gamma''$ precipitation surrounding the large precipitates are not observed here. Figure 7.34c is a higher magnification micrograph confirming the lack of $\gamma'/\gamma''$ precipitation.

Figure 7.34. Thermal profile for DOE #7 (a). Low and high magnification micrographs (b & c) showing eutectic particles and lack of $\gamma'/\gamma''$. 
DOE #8

DOE #8 is a multi-layer build. The thermal profile is seen in Figure 7.35a. The number of layers and number of paths per layer cannot be determined by this plot. After the initial transient the temperature of the build does not drop below 893K. This gives the maximum amount of time in the aging temperature range. Figure 7.35b shows the morphology of the eutectic particles in this build. Most of the particles are singular but some have grown together to form continuous chains. There is not a clear dendritic structure seen. The blue box is shown in detail in Figure 7.35c. Here γ'/γ'' particles can be seen surrounding the eutectic products. These particles extend around 1μm into the surrounding matrix. Figure 7.35d shows evidence of γ'/γ'' particles that are away from the eutectic products. They appear to have formed along a γ grain boundary.
Figure 7.35. Thermal profile for DOE #8 (a). Microstructure overview (b) showing eutectic particles. Detail view of blue box (c) showing γ'/γ'' precipitates. Detail view along grain boundary (d) showing γ'/γ'' precipitates away from eutectic particles.

**DOE #9**

DOE #9 is a multi-layer build. The thermal profile is seen in Figure 7.36a. The minimum temperature in this sample stabilizes around 893K after a short transient period at the beginning of the build. It is not possible to determine how many layers or paths per layer this build has. A low magnification is seen in Figure 7.36b. This image shows the distribution of the eutectic particles. As in the other builds there are some areas where these precipitates have grown into continuous chains. The areas seen in Figure 7.36c & d
are denoted by the blue and red boxes. Figure 7.36c is a high-magnification image showing the distribution of $\gamma'/\gamma''$ particles around the larger eutectic particles. The $\gamma'/\gamma''$ extend around 1µm into the matrix. Figure 7.36d shows a cluster of eutectic particles with $\gamma'/\gamma''$ in the space between.

Figure 7.36. Thermal profile for DOE #9 (a). Microstructure overview (b) showing eutectic particles. Detail view of blue box (c) showing $\gamma'/\gamma''$ precipitates near eutectic a particle. Detail view of red box (d) showing $\gamma'/\gamma''$ precipitates field around eutectic particles.
DOE #10

DOE #10 is a single layer build. The thermal profile is seen in Figure 7.37a. It appears that this build has 6 paths within the layer. After the first 2 cycles the minimum temperature stabilizes around 850K. Figure 7.37b illustrates the distribution of the eutectic products at low-magnification. Figure 7.37c is a high-magnification image near a group of the eutectic particles. No $\gamma'/\gamma''$ precipitates are seen.

Figure 7.37. Thermal profile for DOE #10 (a). Microstructure overview (b) showing eutectic particles. Detail view near eutectic particles (c) showing lack of $\gamma'/\gamma''$ precipitates.
DOE #11

DOE #11 is a multi-layer build. The temperature in this build (Figure 7.38a) was maintained above the upper limit of the aging temperature range. This means that precipitation can occur but it will not be very strong. The upper limit does not indicate the solvus temperature for γ'/γ'''. The overview micrograph in Figure 7.38b shows that the large precipitates (carbides & laves) are equiaxed and appear to be mostly along the gamma grain boundaries. Lighter contrast precipitation fields are not seen in these micrograph. Figure 7.38c is a higher magnification micrograph near some of the large precipitates. Here γ'/γ''' can be seen in a very low concentration. These particles appear to be aligned with the gamma grain boundaries. This indicates that this sample was in the very early stages of precipitation as it will happen along the grain boundaries before occurring intragranularly.
Figure 7.38. Thermal profile for DOE #11 (a). Low magnification overview (b) showing few eutectic particles. Detail view near eutectic particles (c) showing beginning of $\gamma'/\gamma''$ precipitation along grain boundaries.

**DOE #12**

DOE #12 is a single layer build. From the thermal profile (Figure 7.39a) it appears to have 4 paths in this layer. The build time is the shortest in this set of samples. This explains the small amount of eutectic product seen in Figure 7.39b. This sample is void of any $\gamma'/\gamma''$ as seen in Figure 7.39c.
Figure 7.39. Thermal profile for DOE #12 (a). Low magnification overview (b) showing few eutectic particles. Detail view near eutectic particles (c) showing lack of γ’/γ’’ precipitation.

**DOE #13**

DOE #13 is a multi-layer build. The minimum temperature in this build stabilizes around 893K (Figure 7.40a) after a transient period that is longer than that seen in other samples. This transient period may affect the formation of γ’/γ’’ because it spends less time in the aging temperature range. Eutectic particles can be seen in the low-magnification image (Figure 7.40b). There are no brighter precipitate fields are seen in this image. Figure 7.40c & d show more detail closer to the eutectic particles. It can be seen that the γ’/γ’’ extends around 0.5 μm into the matrix surrounding the eutectic particles. The γ’/γ’’
particles in this sample appear less defined than in other samples. This could be because of the longer transient period.

Figure 7.40. Thermal profile for DOE #13 (a). Low magnification overview (b) showing eutectic particles. Detail view near eutectic particle (c) showing γ'/γ'' precipitation. Higher magnification (d) near eutectic particle showing γ'/γ'' particles.

**DOE #14**

DOE #14 is a single layer build that appears to have 4 paths (Figure 7.41a). The minimum temperature in this build never reaches the nominal aging temperature range.
Figure 7.41b is a low-magnification image showing the eutectic particles in the build. These particles are primarily equiaxed. The high-magnification image (Figure 7.41c) confirms that $\gamma'/\gamma''$ particles are not present.

Figure 7.41. Thermal profile for DOE #14 (a). Low magnification overview (b) showing few eutectic particles. Detail view near eutectic particles (c) showing lack of $\gamma'/\gamma''$ precipitation.

**DOE #15**

DOE #15 is a multi-layer build. The number of layers cannot be determined through the thermal profile (Figure 7.42a). The temperature in the bottom layer stabilizes around
893K after a relatively long transient period. Figure 7.42b is a low-magnification image where the distribution of eutectic particles can be seen. These particles have a mixture of equiaxed and elongated morphologies. Figure 7.42c is a high-magnification image near one of the eutectic particles. Very small $\gamma'/\gamma''$ might be present. They are not as numerous or large as those seen in other builds.

Figure 7.42. Thermal profile for DOE #15 (a). Low magnification overview (b) showing eutectic particles. Detail view near eutectic particles (c) showing lack of $\gamma'/\gamma''$ precipitation.
DOE #16

DOE #16 is a single layer build that appears to have 6 paths within that layer (Figure 7.43a). The minimum temperatures in this build do not make it into the aging temperature range. The distribution of eutectic particles can be seen in the low-magnification image (Figure 7.43b). These particles have equiaxed and elongated morphologies. The high-magnification image in Figure 7.43c shows a lack of $\gamma'/\gamma''$ particles.

Figure 7.43. Thermal profile for DOE #16 (a). Low magnification overview (b) showing eutectic particles. Detail view near eutectic particles (c) showing lack of $\gamma'/\gamma''$ precipitation.
7.8.2 Hardness Measurements

Hardness traverses were performed along the vertical height of the samples. A spacing of 150μm between indents was used. The indents were made using a Leco M-400-H1 manual micro-indenter. The indents were measured using an Olympus GX-51 metallograph. The diagonals of the indent were measured and the hardness values were calculated using ASTM E385-10E2 [67]. Since only the bottom thermal profiles are available to OSU only hardness values at that location are reported here to find correlation with the thermal profiles (Figure 7.44). It can be seen that there is an 80 HVN difference between the lowest and highest hardness.

![Bottom Layer Hardness](image)

Figure 7.44. Chart of hardness in bottom layer of samples.
7.8.3 $\gamma'/\gamma''$ Quantification in DOE Samples

The multi-layer DOE samples had their $\gamma'/\gamma''$ quantified using the same method as Ni-2. The results for the average $\gamma'/\gamma''$ in a low magnification micrograph are seen in Figure 7.45. The single-layer builds are not included here because $\gamma'/\gamma''$ was not observed in them. The amounts measured are all less than 1.0%. The amounts in DOE #11, 13, and 15 are not confirmed. There are some precipitates observed in the samples but they could not be quantified. Therefore they have been set equal to the amount found in DOE #2 which had the lowest quantifiable amount.

![Quantification Results for DOE Samples](image)

Figure 7.45. Chart showing measured amounts of $\gamma'$ (GP) + $\gamma''$ (GDP).
7.8.4 STK Model Results

Below are the results from the STK model for each of the DOE thermal profiles seen above. These results (Figure 7.46) show the final percentage of $\gamma' + \gamma''$ at the end of the build compared to the experimental data. The $\gamma''$ and $\gamma'$ fractions were added together since they have not been differentiated experimentally. The model was run with the parameters seen in Table 7.7. The parameters are the same as those used for Ni-2 except the number of nucleation sites was reduced. This was done because the when the parameters for Ni-2 were used the model was predicting much higher amounts of $\gamma''/\gamma'$ than were seen experimentally.

Figure 7.46. Results from STK model for DOE sample thermal profiles.
Table 7.7. Table showing calibration parameters based on DOE sample quantification

<table>
<thead>
<tr>
<th>Parameter</th>
<th>γ’’</th>
<th>γ’</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleation Sites</td>
<td>13E16</td>
<td>18E16</td>
<td>#<em>m⁻³</em>s⁻¹</td>
</tr>
<tr>
<td>Surface Energy</td>
<td>0.095</td>
<td>0.095</td>
<td>J/m²</td>
</tr>
<tr>
<td>Strain Energy</td>
<td>300</td>
<td>600</td>
<td>J/mole</td>
</tr>
<tr>
<td>Acceleration Factor</td>
<td>3</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Appropriately, the model predicts no precipitation in the single layer builds. The model predicts that precipitation will occur in all of the multi-layer builds except for #2 and #11. The temperature in these samples remained above the nominal aging temperature range through most of the build and therefore the model does not predict precipitates. Experimentally, very small amounts of precipitates are seen in #2 and #11.

7.9 DOE Sample Discussion

7.9.1 Build Duration Effect on Precipitation

It can be seen that none of the single layer builds contain any γ’/γ’’. With the longest build taking around 100 seconds (DOE #7); there simply isn’t enough time at high temperature for precipitation to occur. The early stages of precipitation in Alloy 718 were investigated by Alam et al. [53]. They found that clusters of atoms that form γ’ and γ’’ begin forming as soon as 120 seconds of aging. These clusters are the precursors to the
\(\gamma'/\gamma''\) precipitates. After 120s the majority of these clusters only contain 5-8 atoms.

Aging for 120s produced minimal hardening over the quenched samples with a value around 215 HVN. Further aging of 500s shows \(\gamma'/\gamma''\) beginning to co-precipitate. This stage also showed an increase in hardness to around 240 HVN.

In the DOE samples it is seen that the number of layers (build time) affects the precipitation and therefore the hardness. Results with the same trend seen by Alam et al. were observed. The average hardness for the single layer builds is 246 HVN while the average for the multi-layer builds increased to 265 HVN.

It is unclear why the single layer builds are harder than ones aged for 120s by Alam. One hypothesis is that elemental segregation during solidification is allowing more/larger clusters of solute atoms to form. These clusters are precursors to \(\gamma'\) and \(\gamma''\). Alam hypothesizes that these clusters provide some hardening before precipitation occurs.

Since these solute atoms have a higher concentration in the interdendritic regions there is likely to be an increase in the number and size of the clusters and a corresponding increase in hardness.

The average hardness of the multi-layer builds also shows an increase over the value reported by Alam. This could be because of the segregation effect discussed for the single layer builds allowing for precipitates to form more easily. For a 500s aging they found \(\gamma'\) to be 2-3 nm in size and the \(\gamma''\) to be 2-5 nm. However, the precipitates seen in the DOE samples are 6-16 nm in size. Particles of this size were not seen by Alam et al. until they
aged a sample for 5000s. This treatment gave an increase in volume fraction of $\gamma'/\gamma''$ as well as an increase in size to 5-15 nm for $\gamma'$ and 10-15 nm for $\gamma''$. They reported a hardness of $\sim$380 HVN for 5000s aging time. While the multi-layer builds ranged between 400s and 1000s of build time, they spent significantly less time in the aging temperature range. However, we see particles that are on par in size with those seen after 5000s of isothermal aging on a solutionized sample. This suggests that the segregation of the precipitate forming elements enhances the precipitation kinetics. Since the particles are not homogenously distributed the full hardening effect is not realized.

7.9.2 Thermal Effect on Precipitation

In all of the multi-layer builds it can be seen that after a transient period at the beginning of the build the temperature stabilizes and does not fall below a set minimum value until the end of the build. This is done as an attempt to control/promote the precipitate formation.

The first group that will be discussed are samples where the minimum temperature is above 1000K. DOE #2 and #11 are in this category. Both samples have small, non-continuous eutectic particles. DOE #2 has small precipitate fields around some of the eutectic particles while they are not present in #11. There are some $\gamma'/\gamma''$ particles in DOE #11 but only along what appear to be the $\gamma$ grain boundaries. DOE #2 contains more $\gamma'/\gamma''$ particles as they extend in small fields around the eutectic particles. The hardness for DOE #2 and #11 are the lowest of the multi-layer builds with values of 228 HVN and
230HVN, respectively. The temperature in these builds is simply too high to allow for strong $\gamma'/\gamma''$ precipitation.

The next group of samples are ones where the minimum temperature is between 893-993K and the build time is less than 500s. DOE #6, #8, and #15 are in this category. The eutectic precipitates in these samples can be seen aligned along the dendrite boundaries. The values for the hardness of DOE #6, #8, and #15 are 251, 260, and 290 HVN, respectively.

DOE #6 and #8 show $\gamma'/\gamma''$ precipitates surrounding the eutectic products. $\gamma'/\gamma''$ particles are also seen not close to the eutectic particles. These two samples are the only ones with precipitation occurring away from the eutectic particles. This suggests that the thermal conditions in these samples were favorable to precipitation in less enriched areas. $\gamma'/\gamma''$ particles are seen in DOE #15 but they are not clearly defined. It is possible that these particles are in the early stages of forming. This is likely because it has a short build time but the transient period is extended compared to the other samples.

The last group of samples consists of ones that have a build time longer than 500s and minimum temperature less than 893K. DOE #4, #9, and #13 are in this category with hardness values of 263, 293, and 308 HVN, respectively. The eutectic particles in these samples are seen lined up along the dendrite boundaries. Precipitate fields are seen around some of the eutectic particles in all three of these samples. All of these samples exhibit $\gamma'/\gamma''$ particles around the eutectic particles.
The hardness of DOE #9 and #13 are the highest out of the group. Quantitatively, #9 contains more $\gamma'/\gamma''$ than #13.

In general it was observed that when more time was spent between 893K and 993K more $\gamma'/\gamma''$ precipitation occurred, resulting in higher hardness. This holds true for most of the samples but there are some anomalous results. These include DOE #4, #6, #8, #9, #13, and #15. Samples 4, 6, and 8 are not as hard as would be expected. These samples quantitatively have more precipitates than some of the harder samples. DOE #9, #13, and #15 are anomalous because they are harder than expected. They all contain fewer precipitates than #6 but have higher hardness. #9, #13, and #15 have 42HVN, 57HVN, and 39HVN higher hardness than #6, respectively.

**7.9.3 Model Predictions Correlate to Hardness**

The STK model was run for the DOE sample thermal profiles. The output compared to the experimental data is visible in Figure 7.46. The model results can be used to predict when precipitation will occur seeing as no $\gamma'/\gamma''$ precipitates were seen in the single layer builds and appropriately the model predicts no $\gamma'/\gamma''$ precipitates. It can also be seen by comparing Figure 7.44 and Figure 7.46 that the model output correlates with the measured hardness reasonably.

The softest samples are the single layer builds. This is because of a lack of $\gamma'/\gamma''$. Correspondingly, the model predicts no precipitation in these samples. One anomaly to this trend is DOE #3 because even though no $\gamma'/\gamma''$ was observed and none is predicted
by the model yet the hardness is higher than the rest of the single layer builds. It is possible that the hardness could be higher due to solute clustering as a precursor to precipitation.

The model also successfully predicts that there would be very low precipitation in DOE #2 and #11. These samples have a correspondingly low hardness.

The model predicts different levels of $\gamma' / \gamma''$ precipitation for the rest of the samples (#4, #6, #8, #9, #13, and #15). However, the amount of precipitates does not necessarily correlate to if one sample will be harder or softer than another. For example DOE #9 has the highest precipitate fraction but it doesn’t have the highest hardness. DOE #13 has the highest hardness but lower precipitate fraction than #9.
CHAPTER 8: CONCLUSIONS AND FUTURE WORK

The primary objective of this research was to develop a microstructure model for Ti-6Al-4V and Alloy 718. Toward that end a prototype model has been developed for each alloy system. The conclusions formed from the results are presented below. Following the conclusions recommendations for future work are presented.

8.1 Conclusions

8.1.1 Ti-6Al-4V

1. Ti-1 exhibited a spatial variation in microstructure and hardness. The sample was predominantly colony alpha with some grain boundary alpha in the bottom half. This transitioned to predominantly basketweave alpha in the top half. The change in microstructure led to an increase in hardness in the top half.

2. The transition in microstructure and hardness was found to be a result of an increase in prior beta grain size in combination with the last thermal cycle cooling from above the beta transus. The regions that were basketweave remained beta until the end of the build and upon cooling transformed to basketweave because of the small amount of grain boundary area.

3. The microstructure data from Ti-1 was used to calibrate the STK model for Ti-6Al-4V. The microstructure transition could not be accurately modeled with one
set of calibration parameters. This is because the model does not have logic included to predict the beta grain size and the resultant change in transformation kinetics. Therefore two sets of calibration parameters were developed, one for the bottom half of the build and one for the top half.

4. Ti-2 was built while keeping the substrate above the beta transus. This resulted in a microstructure that is predominantly basketweave alpha. Very little grain boundary and colony alpha were observed because of the large beta grains that started epitaxially from the substrate. This sample did not exhibit the transition in hardness that was seen in Ti-1.

5. Fatigue testing on builds similar to Ti-2 showed an increase in fatigue life over testing in literature. The Ti-2 group of samples in the z-direction had life in the as built condition comparable to stress-relieved parts from literature. This exemplifies how process modeling can be used to improve properties and potentially eliminate a post-build heat treatment.

6. Ti-3 was built to investigate the effect of having large prior beta grains in the substrate at room temperature. Epitaxial growth was observed in this sample but the beta grain size was not as large as those in Ti-2. This sample showed basketweave microstructure throughout the sample. Grain boundary and colony alpha were not detected. Hardness in this sample averaged ~50 HV higher than Ti-1 or Ti-2. This could be because of finer alpha laths due to higher cooling rate as a result of a thicker substrate.
8.1.2 Alloy 718

Samples Ni-1 and Ni-2

1. $\gamma'/\gamma''$ precipitates were found in Ni-2 but not Ni-1. This is due to the longer time spent in the aging temperature range (893-993K) by Ni-2. The precipitates were found in the bottom and middle but not top of Ni-2. Precipitates were found along the dendrite boundaries because of Nb segregation to liquid during solidification.

2. An increase hardness corresponding to the $\gamma'/\gamma''$ fraction was found in the bottom of Ni-2. The hardness of Ni-1 showed an increase around the middle of the build. This could be due to solute clustering before precipitation occurs.

3. The $\gamma'/\gamma''$ precipitates were quantified in Ni-2 using a selective etch and computer image analysis. These techniques were used to give an average of the nano-scale precipitates over a larger length scale.

4. A prototype STK model for Alloy 718 was developed. The model was calibrated to the Ni-2 sample to predict $\gamma'/\gamma''$. The remaining phases possible in 718 were disabled for this run due to lack of quantification and parameters. The model correctly predicts 0% $\gamma'/\gamma''$ when using thermal profiles from Ni-1.

DOE Samples

1. No $\gamma'/\gamma''$ precipitates were found in the single layer builds. This is an effect of the short build times for these builds.

2. Time spent in the aging temperature range has an effect on the formation of precipitates. If the build stays too hot $\gamma'/\gamma''$ will not form even if the build takes
longer than 500s. It was also observed that the best precipitation occurred when
the minimum sustained temperature was within the aging temperature range and
the build time was 500s or longer.

3. Even in the multi-layer builds the volume fraction of $\gamma' / \gamma''$ is much less than
0.01. This is likely because of the shorter build times when compared with Ni-2.

4. The STK model that was developed provides a quantitative indication of if $\gamma' / \gamma''$
will form. The model successfully predicts that precipitation will occur for the
multi-layer builds and not the single-layer builds. The amounts of precipitates
predicted in the multi-layer builds correlated well with the experimental values
after changing the number of available nucleation sites in the model.

8.2 Future Work

1. Develop a beta grain growth model for Ti-6Al-4V. This model can be coupled
with the STK model to allow for the automatic transition of the from colony to
basketweave in builds similar to Ti-1.

2. For the general STK model an automatic calibration iteration routine should be
implemented. This would allow the researcher to input the experimental
microstructure data into the model and the model would automatically run
iterations of different parameters to converge on a solution. The current method of
performing the iteration manually was able to find parameters that gave
reasonable correlations but it is possible that other solutions exist.
3. Research into dissolution modeling. Since particle dissolution is currently handled by resetting the volume fraction to the equilibrium value complete dissolution of a phase can happen instantaneously when the temperature rises above the dissolution temperature. In reality this does not happen because it takes time for the particles to dissolve back into the matrix. This also means that when the temperature comes back down there are more nucleation sites which enhance the precipitation kinetics. Modeling of the solute concentration profiles across the particle/matrix interface during heating must be done. It is possible that DICTRA® could be used for this task.

4. Develop integration with diffusion model to account for element segregation during transformations. In the case of Alloy 718 this is important for knowing when supersaturation makes precipitation easier.

5. Investigate surface energies for laves, delta, and NbC for the Alloy 718 STK code.

6. Use TEM to differentiate between the γ’ and γ’’. This would allow for a ratio between the two to be established for Alloy 718 LMD builds.

7. Development of automated microstructure characterization techniques for Ti-6Al-4V will increase the accuracy of the experimental data. Manual point counting carries inherent error because it only looks at a portion of the total microstructure. The error can be decreased by increasing the number of points on each
micrograph. However, this increases the fatigue rate (and subsequently the error rate) of the researcher.

8. The development of automated characterization would make serial sectioning viable. The current work only focused on one cross section per sample which only gives a 2D view of the microstructure. Serial sectioning would allow for a 3D view to be built up. In the case of Ti-6Al-4V this would allow the changes in the beta grains to be tracked through a volume. For Alloy 718 the evolution of the dendrites could be observed through the volume.

9. For 718 investigate the heat treatment response for various initial number and spacing of \( \gamma' \) and \( \gamma'' \). Since different build parameters produce different precipitate quantities investigating how they respond to different direct aging times and temperatures would be useful.

10. Develop tests using the Gleeble that simulate the LMD thermal cycling. These tests would allow for comparison to the actual build microstructure. They would also allow for samples that are spatially homogeneous over a larger area than seen in the LMD samples.
REFERENCES


60. Amsterdam, E., Evaluation of the microstructure and mechanical properties of laser additive manufactured gas turbine alloys Ti-6Al-4V and Inconel 718, 2010, National Aerospace Laboratory NLR.

Innovative design for sustainability in manufacturing and management, 2010: p. 574-582.


#pragma rtGlobals=1  // Use modern global access method.

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// Current Version: 15

// For Center for Integrative Materials Joining for Energy Applications
// The Ohio State University, Columbus, Ohio 43221

----------------------------
Function DeploySTKThermalCycle(TempW, TImeW)
Wave/D TempW, TImeW
// This contatins the array of the the temperature and time from SAMP
// This may be very bumpy and also may contain lot of noise, so we have to smooth it out

// Here copies of the temperature wave are made to store all the fraction data from calculations
Duplicate/o TempW FractionBeta      // Tracks the fraction of beta Phase
Duplicate/o TempW FractionGB       // Tracks the fraction of Grain Boundary
Duplicate/o TempW FractionWid      // Tracks the fraction of Basketweave
Duplicate/o TempW FractionCol      // Tracks the fraction of Colony
Duplicate/o TempW FractionMart     // Tracks the fraction of Martensite
Duplicate/o TempW FractionMass     // Tracks the fraction of Massive
Duplicate/o TempW OverallFraction  // Tracks the fraction of Total Alpha
Duplicate/o TempW Dummy

// Initializing the arrays and getting rid of the temperature information in the duplicated wave
FractionBeta = 0
FractionGB = 0
FractionWid = 0
FractionCol = 0
FractionMart = 0

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FractionMass = 0
OverallFraction = 0
Dummy = 0

// Setting up some dummy variables to track things
// These get modified in each and every time step

Variable BetaFraction = 0
Variable GBFraction = 0
Variable WidFraction = 0
Variable ColFraction = 0
Variable MartFraction = 0
Variable MassiveFraction = 0
Variable TotalFraction = 0 // All alpha
Variable TotalAlphaBefore = 0
Variable TotalAlphaNow = 0

// Now Set the Initial Microstructure assuming we have room temperature microstructure
// It should reset as soon as the temperature goes to melting point
// First data point is room temperature microstructure
// This is necessary if you are tracking changes just due to heat treatment
// for example in substrate where you did not melt
FractionBeta[0] = 0.1
FractionGB[0] = 0.4
FractionWid[0] = 0.5
FractionCol[0] = 0
FractionMart[0] = 0
FractionMass[0] = 0
OverallFraction[0] = 0.9
Dummy[0] = 0.9
Variable PrevTime = 0
Variable TempK = 0

// Parameters for the materials models
// There are 10 calibration parameters
// we need to change to correlate to the experimental data

// Grain Boundary nucleation sites
Variable NZero = 1e17 // this is related to beta grain size, increase it if you have small beta grain size
// Basketweave nucleation sites
Variable NZeroWid = 1e20 // increase for more basketweave nucleation sites
// Colony nucleation sites
Variable NZeroCol = 1e16 // increase for more colony nucleation sites
// Surface energy for beta to alpha transformation
Variable SurfEnerImp = 0.01
// Strain energy for grain boundary alpha
Variable StrainEnergy = 800 // J/mole
// Strain energy for colony and basketweave alpha
Variable StrainEnergyCol = 300 // J/mole
// Acceleration factor for basketweave growth rate
Variable AccFactor = 20 // Increase to accelerate basketweave growth
// Acceleration factor for colony growth rate
Variable AccFactorCol = 5       // Increase to accelerate colony growth
// Ratio of massive to martensite
Variable RatioOfMassMart = 0.05
// Martensite
Variable MartBPara = 1.1e-2   // Increase this to increase martensite formation rate

// Parameters for the materials models
// are evaluated by calculating the TTT diagram

Wave tttgb
duplicate/o tttgb ttwid
Duplicate/o tttgb tttcol
    ttwid = CalculateExtentAlphaWid(y, NZeroWid, SurfEnerImp, StrainEnergy, AccFactor, 10^x)
    tttgb = CalculateExtentAlpha(y, NZero, SurfEnerImp, 10^x)
    tttcol = CalculateExtentAlphaCol(y, NZeroCol, SurfEnerImp, StrainEnergyCol, AccFactorCol, 10^x)
// they should be visable in the graph to see the relative positons

Variable LastExtent  = 0
Variable PreviousExtent  = 0
Variable PreviousAlphaFraction  = 0
Variable TimeVal= 0
Variable TimeINcre = 0
Variable GrowthMode = 1   // 1 means grow // -1 means dissolve
Variable start = 1
Variable final = numpnts(TempW)-1
Variable EquilFraction = 0
print start, final
Variable NewDummy
Variable MsTemp = 848   // in K from Kelly Thesis

Do

// -----------------------------Let us get the initial or previous microstructure

    BetaFraction = FractionBeta[start-1]
    GBFraction = FractionGB[start-1]
    WidFraction = FractionWid[start-1]
    ColFraction = FractionCol[start-1]
    Mart Fraction = FractionMart[start-1]
    MassiveFraction = FractionMass[start-1]
    TotalFraction = OverallFraction[start-1]

    TempK = TempW[start]
    EquilFraction = Equilibri um(TempK, 2)

    if (EquilFraction >= TotalFraction) // yes you can form alpha
        GrowthMode = 1
    else
        GrowthMode = -1
    endif
Dummy = EquilFraction

// Now consider the growth mode
if (GrowthMode == 1) 
  // Calculate increment to GB Alpha
  PreviousExtent = GBFraction/EquilFraction
  PrevTime = 0
  if ((PreviousExtent >= 0) && (PreviousExtent <= 1))
    PrevTime = FindEquivalentTimeAlpha(TempK, NZero, SurfEnerImp, GBFraction)
    if (Prevtime >= 0)
      TimeIncr = (TimeW[0] - TimeW[1])
      TimeVal = PrevTime + TimeIncr
      FractionGB = EquilFraction*
    endif
  endif

  // Calculate increment to Basketweave Alpha
  PreviousExtent = WidFraction/EquilFraction
  if ((PreviousExtent >= 0) && (PreviousExtent <= 1))
    PrevTime = FindEquivalentTimeWid(TempK, NZeroWid, SurfEnerImp, StrainEnergy, AccFactor, WidFraction)
    if (Prevtime >= 0)
      TimeIncr = (TimeW[0] - TimeW[1])
      TimeVal = PrevTime + TimeIncr
      FractionWid = EquilFraction*
    endif
  endif

  // Calculate increment to Colony Alpha
  PreviousExtent = ColFraction/EquilFraction
  if ((PreviousExtent >= 0) && (PreviousExtent <= 1))
    PrevTime = FindEquivalentTimeCol(TempK, NZeroCol, SurfEnerImp, StrainEnergy, AccFactorCol, ColFraction)
    if (Prevtime >= 0)
      TimeIncr = (TimeW[0] - TimeW[1])
      TimeVal = PrevTime + TimeIncr
      FractionCol = EquilFraction*
    endif
  endif

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endif
endif

 MartFraction = MartensiteFraction(MsTemp, TempK, BetaFraction, MartBPara)
 FractionMart[start] = MartFraction

 MassiveFraction = RatioOfMassMart*MartensiteFraction(MsTemp, TempK, BetaFraction, MartBPara)
 FractionMass[start] = MassiveFraction

 //--------------------------------------------------------
 // Growth Calculation is over
 //--------------------------------------------------------
 // Above we assume each morphology is growing on its own
 // We have taken care of the overall transformation kinetics for each morphology
 // But when each morphology competes, the fraction has to be corrected
 // We need to invoke the equation 12 is Jones and Bhadeshia paper
 // we have 5 morphologies
 // GB, Basketweave, Col, Mart and Massive
 //--------------------------------------------------------

 Make/o/N= 5 ChangeinExtended, ChangeinReal, RealVolumeOld
 Variable DummyVariable
 ChangeinReal = 0
 ChangeinExtended = 0
 RealVolumeOld = 0
 ChangeinExtended[0] = FractionGB[start] - FractionGB[start-1]
 RealVolumeOld[0] = FractionGB[start-1]
 RealVolumeOld[1] = FractionWid[start-1]
 RealVolumeOld[2] = FractionCol[start-1]

NewDummy = CalculateRealVolume(BetaFraction, ChangeinExtended, ChangeinReal, RealVolumeOld) // ChangeinReal is calculated

// Reset occurs now
FractionGB[start] = ChangeinReal[0] + FractionGB[start-1]

BetaFraction = 1 - FractionWid[start] - FractionGB[start] - FractionMart[start] - FractionCol[start] // What was the last beta fraction

OverallFraction[start] = 1 - FractionBeta[start]

endif

//*************************
// ------------------------------------------
// Now let us consider the dissolition mode // needs more work here
// Right now we are reseting to the equilfraction; but this may be artificial
// 'This needs little more thought and discussion based on
// IN-situ characterization
// 'This is not correct and great fudge!
// Must fix in the second version
//------------------------------------------

Variable RatioGB = FractionGB[start-1]/TotalFraction
Variable RatioWid = FractionWid[start-1]/TotalFraction
Variable RatioMart = FractionMart[start-1]/TotalFraction
Variable RatioCol = FractionCol[start-1]/TotalFraction
Variable RatioMass = FractionMass[start-1]/TotalFraction

if (RatioGB <0)
    RatioGB = 0
endif
if (RatioWid <0)
    RatioWid = 0
endif
if (RatioMart <0)
    RatioMart = 0
endif
if (RatioCol <0)
    RatioCol = 0
endif
if (RatioMass <0)
    RatioMass = 0
endif

Make/0/n=4 RatiosNow
RatiosNow[0] = RatioGB
RatiosNow[1] = RatioWid
RatiosNow[2] = RatioCol
RatiosNow[3] = RatioMart

// Dissolution is taken care
if (GrowthMode == -1)
    FractionGB[start] = RatioGB * EquilFraction
    FractionWid[start] = RatioWid * EquilFraction
    FractionCol[start] = RatioCol * EquilFraction
    FractionMart[start] = RatioMart * EquilFraction
    FractionMaSS[start] = RatioMass * EquilFraction
endif

//------------------------------------------
start += 1
While (start <= final)
    Duplicate/o Dummy EquilFractionWave
End

//-----------------------------------------------------
// This is based on Magee theory
//-----------------------------------------------------
Function MartensiteFraction(Ms, Temperature, BetaFraction, MartBPara)
    Variable Ms, Temperature, BetaFraction, MartBPara
    Variable Fraction = 0
    Variable b = MartBPara // 1.1e-2 // For steels it is 1.1e-2
    Fraction = 1 - exp(-b*(Ms - Temperature))
    if (Fraction < 0)
        Fraction = 0
    endif
    return Fraction
End

//-----------------------------------------------------
// Here you can slow down the martensite fraction based on remaining beta
// This will work as long as the change in extended volume are small
// if it is not, we will see large jumps (saw tooth type increases)
// This will introduce errors
// So to make sure you have not significant error accumulation
// make sure that your temperature intervals are not too large
// that means in steep temperature gradients the time interval has to be small
// Equation 12 of Jones and Bhadeshia paper
// Implementation of equation 6 in chapter 4
//-----------------------------------------------------

Function CalculateRealVolume(BetaFraction, ChangeinExtended, ChangeinReal, RealVolumeOld)
    Variable BetaFraction; Wave ChangeinExtended, ChangeinReal, RealVolumeOld
    Variable Start = 0
    Variable final = numpnts(ChangeinExtended)-1
    Variable totalfraction = 0

// Function used in growth mode only, change in extended cannot be negative

Do
    if (ChangeinExtended[start] < 0)
        ChangeinExtended[start] = 0
    endif
    totalfraction += RealVolumeOld[start]
    start +=1
While (start <= final)

Variable BracketTerm = totalfraction/1 // Dividing by 1 because it is assumed that the total volume is 1
if (BracketTerm >= 1)
    BracketTerm = 0.99999999
endif

start = 0
Do
    ChangeinReal[start] = (1-(BracketTerm))*ChangeinExtended[start]
    start +=1
While (start <= final)
return 0
End

//--------Overall Transformation Kinetics----------
// Assuming it as sphere
// Based on Babu Paper from MST 1995
// Geometry has to be changed later
//--------Overall Transformation Kinetics----------

///----Grain Boundary Alpha-------------------------
// This is implementation of Equation 8 in Chapter 4
Function CalculateExtentAlpha(TempK, NZero, SurfEnerImp, timeval)
Variable TempK, NZero, SurfEnerImp, timeval
Variable Izero = CalcNuclRate(TempK, NZero, SurfEnerImp)
Variable Rate = CalcGrowthRate(TempK, 0)
Variable EqAlpha = Equilibrium(TempK, 2)
Variable Extent = 0
Variable ActualVolume = Izero*(8*Pi/15)*(Rate^3)*(timeval^(5/2))
extent = 1 - exp(-ActualVolume/EqAlpha) // we need to consider the site saturation above 0.5 there will be no nuclei!
if (extent >=1 )
    extent = 1
endif
Return Extent
    // Return Extent*EqAlpha (real alpha)
End

//Implementation of equation 12 and 13 in chapter 4
Function FindEquivalentTimeAlpha(TempK, NZero, SurfEnerImp, PreviousFraction)

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Variable TempK, NZero, SurfEnerImp, PreviousFraction
Variable Izero = CalcNuclRate(TempK, NZero, SurfEnerImp)
Variable Rate = CalcGrowthRate(TempK, 0)
Variable EqAlpha = Equilibrium(TempK, 2)
Variable OldExtent = PreviousFraction/EqAlpha
if (oldExtent >=1)
    OldExtent = 0.9999
endif
Variable OldVolume = -1*EqAlpha*ln((1-OldExtent))
//derived from this expression extent = 1 - exp(-ActualVolume/EqAlpha)
Variable NewTime = (OldVolume/(Izero*(8*Pi/15)*(Rate^3))*(timeval^(5/2))) // derived from this
ActualVolume = Izero*(8*Pi/15)*(Rate^3)*(timeval^(5/2))
    if (numtype(NewTime) !=0)
        NewTime = -1
    endif
Return NewTime
// Return Extent*EqAlpha (real alpha)
End

//===Basketweave Alpha-----------------------------
// This is implementation of Equation 8 in Chapter 4
Function CalculateExtentAlphaWid(TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, timeval)
Variable TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, timeval
Variable Izero = CalcNuclRateWid(TempK, Nzero, SurfEnerImp, StrainEnergy)
Variable Rate = CalcGrowthRateWid(TempK, 0, AccFactor)
Variable EqAlpha = Equilibrium(TempK, 2)
Variable Extent = 0
Variable ActualVolume = Izero*(8*Pi/15)*(Rate^3)*(timeval^(5/2))
//print Izero, Rate, timeval
extent = 1 - exp(-ActualVolume/EqAlpha)
// we need to consider the site saturation above 0.5 there will be no nuclei!
Return Extent
// Return Extent*EqAlpha (real alpha)
End

//Implementation of equation 12 and 13 in chapter 4
Function FindEquivalentTimeWid(TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, PreviousFraction)
Variable TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, PreviousFraction
Variable Izero = CalcNuclRateWid(TempK, Nzero, SurfEnerImp, StrainEnergy)
Variable Rate = CalcGrowthRateWid(TempK, 0, AccFactor)
Variable EqAlpha = Equilibrium(TempK, 2)
Variable OldExtent = PreviousFraction/EqAlpha
if (oldExtent >=1)
    OldExtent = 0.9999
endif
Variable OldVolume = -1*EqAlpha*ln((1-OldExtent))
//derived from this expression extent = 1 - exp(-ActualVolume/EqAlpha)
Variable NewTime = (OldVolume/(Izero*(8*Pi/15)*(Rate^3)))*(timeval^(5/2)) // derived from this
ActualVolume = Izero*(8*Pi/15)*(Rate^3)*(timeval^(5/2))
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if (numtype(NewTime) !=0)
    NewTime = -1
endif
Return NewTime
End

// Implementation of equation 8 in chapter 4
Function CalculateExtentAlphaCol(TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, timeval)
    Variable TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, timeval
    Variable Izero = CalcNuclRateWid(TempK, Nzero, SurfEnerImp, StrainEnergy)
    Variable Rate = CalcGrowthRateWid(TempK, 0, AccFactor)
    Variable EqAlpha = Equilibrium(TempK, 2)
    Variable Extent = 0
    Variable ActualVolume = Izero*(8*Pi/15)*(Rate^3)*(timeval^(5/2))
    //print Izero, Rate, timeval
    extent = 1 - exp(-ActualVolume/EqAlpha)
    // we need to consider the site saturation above 0.5 there will be no nuclei!
    Return Extent
End

//Implementation of equation 12 and 13 in chapter 4
Function FindEquivalentTimeCol(TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, PreviousFraction)
    Variable TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, PreviousFraction
    Variable Izero = CalcNuclRateWid(TempK, Nzero, SurfEnerImp, StrainEnergy)
    Variable Rate = CalcGrowthRateWid(TempK, 0, AccFactor)
    Variable EqAlpha = Equilibrium(TempK, 2)
    Variable OldExtent = PreviousFraction/EqAlpha
    if (oldExtent >=1)
        OldExtent = 0.9999
    endif
    Variable OldVolume = -1*EqAlpha*ln((1-OldExtent))
    //derived from this expression extent = 1 - exp(-ActualVolume/EqAlpha)
    Variable NewTime = (OldVolume/(Izero*(8*Pi/15)*(Rate^3))^2/5) // derived from this ActualVolume = Izero*(8*Pi/15)*(Rate^3)*(timeval^(5/2))
    if (numtype(NewTime) !=0)
        NewTime = -1
    endif
    Return NewTime
End

// Classical Nucleation Theory-----------------------
// Molar volume = 10.64e-6 m^3/mole of titanium
// For Ti6Al4V
// This is implementation of equation 9 in Chapter 4
Function CalcNuclRateWid(TempK, Nzero, SurfEnerImp, strainenergy)
    Variable TempK, Nzero, SurfEnerImp, strainenergy

// Kelvin, Cal/mole, Const, m^3/mole, J/m^2 = per m^3
Variable D ActivEnergy, RateNucleation, R, CriticalRadius
// Molar volume for HCP Titanium
Variable MolarVolume = 10.64e-6
Variable FreePerMoleNorm = -1*CalculateDGM(TempK) // Normalized and multiply by -1 for
// sign convention
Variable RValue = 0.3144725 // J/K/Mole
Variable FreePerMole = FreePerMoleNorm*Rvalue*TempK // Now this is in J/Mole
Variable D k = 1.3806E-23 // J/kelvin
if(FreePerMole <= -1*strainenergy)
  //This is implementation of equation 10 in chapter 4
  ActivEnergy = 16*(22/7)*(SurfEnerImp^3) / (3*(FreePerMole*(8.314/1.98)/MolarVolume)^2)
  RateNucleation = Nzero * exp(- ActivEnergy/ (k*(TempK)) )
  CriticalRadius = -2*SurfEnerImp/(FreePerMole*(8.3142/1.98)/MolarVolume)
  If (RateNucleation >= INF)
    RateNucleation = NaN
  Endif
else
  RateNucleation = NaN
  CriticalRadius = NaN
endif
// Has to modify for the mobility variation with temperature
Variable TMelt = 1972.28 // From ThermoCalc
RateNucleation *= exp(-142.188*Tmelt/6.023e23)
return(RateNucleation)
End

//------------------------------
// This is OK for allotriomprhic ferrite
// Bulk Parent Concentration: O_Bar
// Partent Interface Concentration: O_MetInc
// Product Interface Concentration: O_IncMet
// Product Concentration is same as Interface concentration
//-----------------------------
// This is an approximation, since we cannot couple with ThermoCalc and DicTra yet
// Ideally the fluxes should be balanced.
// We need to get TQinterface
//-----------------------------
// Diff is going to be in the units of m2/s
// It should be the slowest diffuser in the allow
//------------------------------
Function CalcGrowthRateWid(TempK, Mode, AccFactor)
  Variable TempK, Mode, AccFactor
  Variable Diff = CalculateDiffRateBeta(TempK)
  Variable Al_Bar_Mole = 1.0198e-1 // From ThermoCalc calculations wt to mole fraction
  Variable V_Bar_Mole = 3.6010e-2 // From ThermoCalc calculations wt to mole fraction
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Variable Ti Bar Model = 8.6201e-1  // From ThermoCalc calculations wt to mole fraction
Variable O IncMet = VanadiumEqConc(tempk, 1)
Variable O bar = V Bar_Mole
Variable O MetInc = VanadiumEqConc(tempk, 0)
Variable Alpha = 0
Variable supersaturation = (O IncMet - O bar)/(O IncMet - O MetInc)
if (mode ==0)
    //This is implementation of equation 11 in chapter 4
    Alpha = sqrt(2)*(( supersaturation )) * sqrt(diff) // this is different from the dilute condition
    if (Alpha < 0)
        Alpha = 0.0
    endif
endif
if (mode ==1)
    Alpha = CalculateParabolic(O IncMet,O bar,O MetInc,DIFF)
endif
return(Alpha*AccFactor)
End

//-------------------Classical Nucleation Theory------------------/
// Molar volume = 10.64e-6 m^3/mole of titanium
// For Ti6Al4V
//Implementation of equation 9 in chapter 4
//-------------------Nucleation Rate for Grain Boundary Alpha-------------------
Function CalcNuclRate(TempK, Nzero,SurfEnerImp)
// Here FreePerMole is for beta to alpha transformation
Variable/D TempK, Nzero, SurfEnerImp
    // Kelvin, Cal/mole, Const, m^3/mole, J/m^2 = per m^3
Variable/D ActivEnergy, RateNucleation, R, CriticalRadius
    // Molar volume for HCP Titanium
Variable MolarVolume = 10.64e-6
Variable FreePerMoleNorm = -1*CalculateDGM(TempK)  // Normalized and multiply by -1 for sign convention
Variable RValue = 08.3144725 // J/K/Mole
Variable FreePerMole = FreePerMoleNorm*Rvalue*TempK  // Now this is in J/mole
Variable/D k = 1.3806E-23  // J/kelvin
if(FreePerMole <= 0.000)
    // This is implementation of equation 10 in chapter 4
    ActivEnergy = 16*(22/7)*(SurfEnerImp^3) / ( 3*(FreePerMole*(8.314/1.98/MolarVolume)^2)
    RateNucleation = Nzero * exp(- ActivEnergy/ (k*(TempK)) )
    CriticalRadius = - 2*SurfEnerImp/(FreePerMole*(8.3142/1.98)/MolarVolume)
    If (RateNucleation >= INF)
        RateNucleation = NaN
    Endif
else
    RateNucleation = NaN
    CriticalRadius = NaN
endif
// Has to modify for the mobility variation with temperature
Variable TMelt = 1972.28 // From ThermoCalc
RateNucleation *= exp(-142.188*TMelt/6.023e23)

return(RateNucleation)

End

//-----------------------------------------------
//----------------
// 0: Simple Aron's growth Law---------
//-----------------
// This is OK for allotriomprhic ferrite
// Bulk Parent Concentration: O_Bar
// Partent Interface Concentration: O_MetInc
// Product Inteface Concentration: O_IncMet
// Product Concentration is same as Interface concentration
//--------
// This is an approximation, since we cannot couple with ThermoCalc and DicTra yet
// Ideally the fluxes should be balanced.
//--------------------
// Diff is going to be in the units of m2/s
// It should be the slowest diffuser in the alloy
//-----------------------------------------------

Function CalcGrowthRate(TempK, Mode)
Variable TempK, Mode
Variable Diff = CalculateDiffRateBeta(TempK)
Variable Al_Bar_Mole = 1.0198e-1 // From ThermoCalc calculations wt to mole fraction
Variable V_Bar_Mole = 3.6010e-2 // From ThermoCalc calculations wt to mole fraction
Variable Ti_Bar_Model = 8.6201e-1 // From ThermoCalc calculations wt to mole fraction
Variable O_IncMet = VanadiumEqConc(tempk, 1)
Variable O_bar = V_Bar_Mole
Variable O_MetInc = VanadiumEqConc(tempk, 0)
Variable Alpha = 0
Variable supersaturation = (O_IncMet - O_bar)/(O_IncMet - O_MetInc)
if (mode ==0)
    //Implementation of equation 11 in chapter 4
    Alpha = sqrt(2)*(( supersaturation )) * sqrt(diff) // this is different from the dilute condition
endif
if (mode ==1)
    Alpha = CalculateParabolic(O_IncMet,O_bar,O_MetInc,DIFF)
endif
return(Alpha)
End

//-----------------------------------------------
// This is based on Mucig46 and based on the Kinsman
// Parabolic growth rate calculation
// Not currently used because it does not converge on a solution
//-----------------------------------------------

Function CalculateParabolic(XGAG,XBAR,XAGA,DIFF)
Variable/D XGAG, XBAR, XAGA, DIFF

Variable/D Ges, PrevGes, Omega, Dum1, Der, sqrp, Error, Alpha

\[
\text{sqrp} = \text{sqrt}(\pi)
\]
\[
\text{Ges} = 0.51466 \\
\text{Ges IS A GUESS}
\]

\[
\text{Omega} = \frac{\text{XAGA}-\text{XBAR}}{\text{XGAG}-\text{XAGA}}
\]

Variable condition = 0
Variable condition1 = 0
Variable condition2 = 0
Variable FirstLoop = 0

Make/O/N=400 dummyPara; Setscale x -1, 1, dummyPara
dummyPara = \left(10^x\right) \left(\exp\left(\left(10^x\right)^2\right)\right) \left(1-\text{erf}\left(10^x\right)\right) - \frac{\text{Omega}}{\text{sqrp}}
if (Diff < 0)
    \text{return} (\text{NaN})
endif
do
do
\text{Dum1} = \text{Ges} \left(\exp(\text{Ges} \times \text{Ges})\right) \left(1-\text{erf}(\text{Ges})\right) - \frac{\text{Omega}}{\text{sqrp}}
\text{Der} = \left(\exp(\text{Ges} \times \text{Ges})\right) \left(1 + 2 \times \text{Ges} \times \text{Ges}\right) \left(1-\text{erf}(\text{Ges})\right) - \frac{\text{Ges} \times 2}{\text{sqrp}}
\text{prevGes} = \text{Ges}
\text{Ges} -= \left(\text{Dum1} / \text{Der}\right)
\text{Error} = \text{abs}(\text{Ges} - \text{PrevGes})
if (\text{Error} < 1E-11)
    \text{Alpha} = \text{Ges} \times 2 \times \text{sqrt}(\text{Diff})
    \text{condition} = 1
    \text{condition1} = 1
endif
if (\text{firstloop} > 20)
    // Print "Using Approximation"
    \text{Ges} = \text{CalBisectionAlpha}(\text{Omega}, \text{sqrp})
    // Print "Ges obtained by that method", ges
    if (\text{Ges} > 0)
        \text{alpha} = \text{Ges} \times 2 \times \text{sqrt}(\text{Diff}) // \text{NaN it is a fudge}
    else
        \text{alpha} = \text{NaN}
    endif
    \text{condition1} = 1
    \text{condition} = 1
endif
\text{FirstLoop} += 1
while(\text{condition1} == 0)
    while(\text{condition} == 0)
        \text{return}(\text{Alpha})
End

//---------------------------------------------------------------
\text{Function CalBisectionAlpha}(\text{Omega}, \text{sqrp})
\text{Variable Omega, sqrp}
\text{Variable FirstLogGes, SecondLogGes, logGesIncre}
Variable FirstGes, SecondGes
Variable FirstValue, SecondValue
Variable condition = 0, condition1 = 0, iteration = 0
Variable maxLogGes = 0.74, MinlogGes = -3
logGesIncre = abs(MinlogGes - maxLogGes)/50
FirstLogGes = -3
SecondLogGes = FirstLogGes + logGesIncre
Do
FirstGes = 10^FirstLogGes; SecondGes = 10^SecondLogGes
FirstValue = FirstGes * (exp(FirstGes * FirstGes)) * (1 - erf(FirstGes)) - (Omega/sqrp)
SecondValue = SecondGes * (exp(SecondGes * SecondGes)) * (1 - erf(SecondGes)) - (Omega/sqrp)
if (FirstLogGes >= maxLogGes) // no solution
    return(10^maxLogGes)
    condition = 1
endif
if (abs(FirstValue) < 1e-9) //
    return(FirstGes)
    condition = 1
endif
if (iteration > 50) //
    return(FirstGes)
    condition = 1
endif
condition1 = 0
do
if ((FirstValue <= 0) & (SecondValue <= 0)) // both values are below zero
    if ((0 - SecondValue) < (0 - FirstValue)) // second value is closer to zero
        FirstLogGes = SecondLogGes
        SecondLogGes = FirstLogGes + logGesIncre
    else
        // first value is close to zero
        FirstLogGes += logGesIncre
        SecondLogGes = FirstLogGes + logGesIncre
    endif
// print "both are below zero the next", FirstLogGes, SecondLogGes
condition1 = 1
iteration += 1
endif
if ((FirstValue > 0) & (SecondValue > 0)) // both values are above zero
    if ((0 - SecondValue) > (0 - FirstValue)) // second value is closer to zero
        FirstLogGes = SecondLogGes
        SecondLogGes = FirstLogGes - logGesIncre
    else
        // first value is close to zero
        FirstLogGes -= logGesIncre
        SecondLogGes = FirstLogGes + logGesIncre
    endif
// print "both are above zero the next ges", FirstLogGes, SecondLogGes
condition1 = 1
iteration += 1

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```c
endif
if ((FirstValue > 0) && (SecondValue <= 0))  // First value above zero
    logGesIncre *= 0.4
    FirstLogGes = logGesIncre
    SecondLogGes += logGesIncre
    // Printf "near the solution F %G->%G\r",FirstValue, SecondValue
    // Printf "Iterating between %G and %G \r", FirstLogGes, SecondLogGes
    condition1 = 1
    iteration +=1
    if(abs(FirstLogGes - SecondLogGes) < 1e-5)
        return(FirstGes)
    endif
endif
if ((FirstValue <= 0) && (SecondValue > 0))   // Second value above zero
    logGesIncre *= 0.4
    FirstLogGes += logGesIncre
    SecondLogGes -= logGesIncre
    // Printf "near the solution F %G->%G\r",FirstValue, SecondValue
    // Printf "Iterating between %G and %G \r", FirstLogGes, SecondLogGes
    condition1 = 1
    iteration +=1
    if(abs(FirstLogGes - SecondLogGes) < 1e-8)
        return(FirstGes)
    endif
endif
while (condition1 == 0)
    while(condition == 0)  // condition not met
        end
    //-----------------------------------------------
    Function CalculateParabolicMod(XGAG,XBAR,XAGA,DIFF)
    Variable/D XGAG,XBAR,XAGA,DIFF
    Var variable/D Ges,PrevGes, Omega, Dum1, Der, sqrp, Error, Alpha, Point
    sqrp = sqrt(Pi)
    Ges = 0.51466  // GES IS A GUESS
    VALUE OF ALPHA1/(2*SQRT(D))
    Omega = (XGAG-XBAR)/(XGAG-XAGA)
    Variable condition = 0
    Variable condition1 = 0
    Variable condition2 = 0
    Variable FirstLoop = 0
    Variable condition3 = 0
    Make/O/N=20 ErrorW GesValue;  GesValue = NaN; ErrorW= NaN
    if (Diff <0)
        return(NaN)
    endif
do
do
    Dum1=Ges*(exp(Ges*Ges))*(1-erf(Ges))-(Omega/sqrp)
    Der =exp(Ges*Ges)*(1 + 2*Ges*Ges)*(1-erf(Ges))-(Ges*2/sqrp)
```

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prevGes = Ges
Ges = (Dum1/Der)
Error = abs(Ges - PrevGes)
ErrorW[firstloop] = Error; GesValue[firstloop]=Ges
If (Firstloop >= 2)
    If ((ErrorW[firstloop] > ErrorW[firstloop-1]) && (condition3 == 0) )
        Point = firstloop - 1
    condition3 = 1
    // print "the points is", Point
endif
endif
if (Error < 1E-11)
    Alpha = Ges*2*sqrt(Diff)
endif
if (firstloop > 20)
    if (Ges > 0)
        alpha = Ges*2*sqrt(Diff) // NaN it is a fudge
    else
        alpha = NaN
    endif
    condition1 = 1
    condition = 1
endif
FirstLoop += 1
while(condition1 ==0)
    while(condition == 0)
        return(Alpha)
    End
End
Function ApproxGesCalculation(ErrorWave,GesWave, Point)
Wave ErrorWave,GesWave; Variable Point
Wave w_coef
Wavestats/Q ErrorWave; Point = V_minloc
CurveFit/Q line ErrorWave(Point-2,Point) /X=GesWave
return(-w_coef[0]/w_coef[1])
End
End
//---------------------------Simple Arrhenius Law------------------------
// Based on Semiatin 2004 Met Trans A paper
// Thermodynamic factors are ignored here
// Diffusion of Vanadium in Beta Phases
// As per Dictra the diffusivity in beta phase is fast
// Here we can assume that the back diffusion in alpha is less
// So the growth rate will be controlled by diffusion in beta
Among the vanadium and aluminum
Diffusivity of vanadium is slow
so let us use this value
Returns in m²/s

Function CalculateDiffRateBeta(TempK)
Variable/D TempK
Variable D_Zero=1e5
Variable QW = 17460
Variable Rval = 1
Variable Result = D_Zero*exp(-QW/TempK)
// this is in (micron)^2 so multiply by 1e-12
Variable Diff = Result*1e-12
Return Diff
End

Curves representing equilibrium phase fractions

Curve fitted to thermodynamic calculations
In principle we need to couple with TC calculations
This is based on SSOL4 Database
PhaseFraction[0] is liquid
PhaseFraction[1] is beta
PhaseFraction[2] is alpha
Function Equilibrium(TempK, Mode)
Variable TempK, Mode
Variable LiquidFraction = 0
Variable BetaFraction = 0
Variable AlphaFraction = 0
Make/o/N=3 PhaseFra
if (tempk >= 1972.3)
  LiquidFraction = 1
  BetaFraction = 0
  AlphaFraction = 0
  PhaseFra[0] = LiquidFraction
  PhaseFra[1] = BetaFraction
  PhaseFra[2] = AlphaFraction
endif
if ((TempK >= 1967.6) & (tempk <=1972.3)) // Above the solidus
  LiquidFraction = -422.58 + 0.21476*TempK
  BetaFraction = 1 - LiquidFraction
  AlphaFraction = 0
  PhaseFra[0] = LiquidFraction
  PhaseFra[1] = BetaFraction
  PhaseFra[2] = AlphaFraction
endif
if ((TempK >= 1201) && (tempk < 1967.6))
    LiquidFraction = 0
    BetaFraction = 1
    AlphaFraction = 0
    PhaseFra[0] = LiquidFraction
    PhaseFra[1] = BetaFraction
    PhaseFra[2] = AlphaFraction
endif

if (TempK < 1201) // below the solidus
    LiquidFraction = 0
    AlphaFraction = 0.96737 + 3.8801/(1+exp(-(TempK-1281.2)/69.56))
    BetaFraction = 1 - AlphaFraction
    PhaseFra[0] = LiquidFraction
    PhaseFra[1] = BetaFraction
    PhaseFra[2] = AlphaFraction
endif

Variable Value = 0
if (mode == 0)
    Value = LiquidFraction
endif
if (mode == 1)
    Value = BetaFraction
endif
if (mode == 2)
    Value = AlphaFraction
endif
return value
End

// -------------------------------
// Vanadium Concentration in moleFraction
// Returns in Kelvin
Function CalculateTzero(Vanadium)
Variable Vanadium
// Return 1119.35
Variable Result = NaN
if (Vanadium <= 0.28601)
    Make/o/N=4 PolyWave
    PolyWave={1274.7,-4548.4,8174,-11316}
    Result = poly(PolyWave,Vanadium)
endif
Return Result
End
// -------------------------------
// Now we need to calculate the tie line
// Here we assume the tie line will always go through the bulk composition
// Ideally you need to calculate this with mass balance and allowing for
// Tie line shift
// These concentrations obtained using equilibrium calculations
// If it is mode == 0; get the vanadium concentration in alpha
// if it is mode == 1; get the vanadium concentration in beta
// Ideally this needs to be coupled with ThermoCAlc
// Now it is polynomial fit similar to Vitek Approach

Function VanadiumEqConc(tempK, Mode)
Variable/D tempK, Mode
Make/o/N=6 polyWave
Variable Result = 0
If (mode==0)  // Vanadium in Alpha
    polyWave={-0.012898,0.00020772,-1.094e-06,2.4103e-09,-2.1429e-12,6.5354e-16}
    Result = poly(polyWave,TempK)
endif
If (mode==1)  // Vanadium in Beta
    If (tempK > 1201.22)
        result = NaN
    endif
    if ( ((tempK>= 787) && (tempK <= 1201.22))
        Make/o/N=3 NewPolyWave
        NewPolyWave={-0.072745,9.2602,0.0037045}
        Result= NewPolyWave[0]+NewPolyWave[1]*exp(-NewPolyWave[2]*tempK)
    endif
    if (tempK < 787)
        Make/o/N=4 NewPolyWave
        NewPolyWave={1.0043,-0.83224,713.95,89.789}
    endif
    if (Result <= 0)
        Result = 0
    endif
Return Result
End

// Calculate the driving force for Ti6Al4V
// Here again only applicable for Ti6Al4V
// Ideally you need to couple with ThermoCalc to get as a function of composition
// Returns DGM/RT

Function CalculateDGM(TempK)
Variable TempK
Make/o/N=5 FitWave
FitWave = {-0.11473,3.7738,0.0028975,10.284,0.010664}
Variable Result = 0
if (TempK <= 1200.85)
    Result = FitWave[0]+FitWave[1]*exp(-FitWave[2]*TempK)+FitWave[3]*exp(-FitWave[4]*TempK)
else
    Result = 0
endif
Return Result
End

// -------------------------Graphing operations below this point---------------------------------------
Window Graph3() : Graph
    PauseUpdate; Silent 1 // building window...
    Display /W=(445,340,1075,835) DissolutionRate,Growth_GB_Alpha
    ModifyGraph log(left)=1
EndMacro

Window Data_Anil() : Table
    PauseUpdate; Silent 1 // building window...
    Edit/W=(5,44,510,251) timeW,temperature
    ModifyTable format(Point)=1
EndMacro

Window Graph1() : Graph
    PauseUpdate; Silent 1 // building window...
    Display /W=(177,55,1080,504) temperature vs timeW
    ModifyGraph mode=3
    SetAxis bottom 70.9610631578947,330.284094736842
EndMacro

Window Graph0() : Graph
    PauseUpdate; Silent 1 // building window...
    Display /W=(862,260,1409,645) Nucl
    AppendToGraph/R Growth_GB_Alpha
    ModifyGraph lSize(Growth_GB_Alpha)=2
    ModifyGraph log(left)=1,log(right)=1
    Label left "Nucleation Rate"
    Label bottom "Temperature (K)"
    Label right "Growth Rate"
EndMacro

Function ExtentToVolumeFraction(extent, tempk)
    Variable extent, tempk
    Variable EqAlpha = Equilibrium(TempK, 2) // From Phase Diagram
    Return (EqAlpha*extent)
End

Window Graph1new() : Graph
    PauseUpdate; Silent 1 // building window...
    Display /W=(450,268,1351,603) temperature vs timeW
    AppendToGraph temperature_SS

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AppendToGraph/R FractionGB vs timeW
ModifyGraph mode(temperature)=3,mode(temperature_SS)=4
ModifyGraph marker(temperature)=8
ModifyGraph rgb(temperature_SS)=(0,0,0)
EndMacro

Window Graph4() : Graph
PauseUpdate; Silent 1  // building window...
Display /W=(260,133,1143,560) temperature_SS vs temperature_ss_time
AppendToGraph/R FractionGB vs temperature_ss_time
AppendToGraph/R FractionWid vs temperature_ss_time
AppendToGraph/R FractionMart vs temperature_ss_time
AppendToGraph/R Dummy vs temperature_ss_time
ModifyGraph lSize(FractionGB)=2,lSize(FractionWid)=2,lSize(FractionMart)=2
ModifyGraph rgb(FractionGB)=(1,16019,65535),rgb(FractionWid)=(0,0,0)
Cursor/P A FractionMart 2600
ShowInfo
EndMacro

Window Graph2() : Graph
PauseUpdate; Silent 1  // building window...
Display /W=(669,295,1082,680)
AppendMatrixContour TTTGB
ModifyContour TTTGB autoLevels={0,1,11}, moreLevels={0.01}, rgbLines=(65535,0,0)
AppendMatrixContour TTTWid
ModifyContour TTTWid autoLevels={0,*,.11}, moreLevels={0.01}, rgbLines=(0,0,0)
ModifyGraph lStyle('TTTWid=0.9')=3
ModifyGraph mirror=2
Label left "Temperature (K)"
Label bottom "Log(Time, s)"
SetAxis left 500,1200
SetAxis bottom -1.4
Legend/CN=text0/J/F=0/A=MC/X=-28.48/Y=-37.15 ";(TTTGB=0.1)"
"TTTGB=0.1\r\n(TTTGB=0.9) "TTTGB=0.9\r\n(TTTWid=0.1) "TTTWid=0.1"
"TTTWid=0.9) "TTTWid=0.9"
EndMacro

Window Table1() : Table
PauseUpdate; Silent 1  // building window...
Edit/W=(5,44,604,431) Te10,Ti10,alphafraction
ModifyTable format(Point)=1
EndMacro
APPENDIX B: ALLOY 718 STK IGOR PRO SOURCE CODE

#pragma rtGlobals=1 // Use modern global access method.

//-------------------------------
//Contacts:
//   Dr. Suresh Babu: babu.13@osu.edu
//   Kurt Makiewicz: Makiewicz.2@osu.edu

// For Center for Integrative Materials Joining for Energy Applications
// The Ohio State University, Columbus, Ohio 43221
//-------------------------------
// Current Version: 5
//-------------------------------
// Material Model Function
// This module will take the following input
// Alloy: A718
// Input Variables
//-------------------------------

Function DeploySTKThermalCycle(TempW, TImeW)
Wave/D TempW, TImeW
// This contains the array of the temperature and time from AO
// This may be very bumpy and also may contain lot of noise, so we have to smooth it out

//-------------------------------
// Copies of the temperature wave are made to store all the fraction data from calculations
//-------------------------------
Duplicate/o TempW FractionGamma       // Tracks the fraction of Gamma Phase
Duplicate/o TempW FractionGP          // Tracks the fraction of Gamma Prime
Duplicate/o TempW FractionGDP         // Tracks the fraction of Gamma Double Prime
Duplicate/o TempW FractionNbC         // Tracks the fraction of NbC
Duplicate/o TempW FractionLaves       // Tracks the fraction of Laves
Duplicate/o TempW FractionDelta       // Tracks the fraction of Delta
Duplicate/o TempW OverallFraction     // Tracks the fraction of that has transformed
Duplicate/o TempW Dummy
Duplicate/o TempW GrowthMode1

Make/N=1/D/o Node_Name
Make/N=1/D/o GDP_out
Make/N=1/D/o GP_out
Make/N=1/D/o NbC_out
Make/N=1/D/o Laves_out
Make/N=1/D/o Delta_out
Make/N=1/D/o Gamma_out
Make/N=1/D/o Temp_out
Make/N=1/D/o Time_out

// Initializing the arrays and getting rid of the temperature information in the duplicated wave
FractionGamma = 0
FractionGP = 0
FractionGDP = 0
FractionNbC = 0
FractionLaves = 0
FractionDelta = 0
OverallFraction = 0
Dummy = 0

// Setting up some dummy variables to track things
// This gets modified in each and every time step
Variable GammaFraction = 0
Variable GPFraction = 0
Variable GDPFraction = 0
Variable NbCFraction = 0
Variable LavesFraction = 0
Variable DeltaFraction = 0
Variable TotalFraction = 0  // All precipitates
Variable TotalPPTBefore = 0
Variable TotalPPTNow = 0

// Now Set the Initial Microstructure assuming we have room temperature microstructure
// It should reset as soon as the temperature goes to melting point
// first data point is room temperature microstructure
// This is necessary if you are tracking changes just due to heat treatment
// for example in substrate where you did not melt
FractionGamma[0] = 1.0
FractionGP[0] = 0.00
FractionGDP[0] = 0.0
FractionNbC[0] = 0.0
FractionLaves[0] = 0.0
FractionDelta[0] = 0
OverallFraction[0] = 0.0
Dummy[0] = 0.0
Variable PrevTime = 0
Variable TempK = 0

// Parameters for the materials models; there are 16 Calibration parameters

// Nucleation Site Terms
Variable NZeroGP = 8e18 // Changes GP Nucleation Sites
Variable NZeroGDP = 2.5e18 // Changes GDP Nucleation Sites
Variable NZeroNbC = 1e18 // Changes NbC Nucleation Sites
Variable NZeroLaves = 1e5 // Changes Laves Nucleation Sites
Variable \( N_{\text{ZeroDelta}} = 1 \times 10^10 \) // Changes Delta Nucleation Sites

Variable \( \text{SurfEnerImp} = 0.095 \) // Changes surface energy. Currently uses value for GDP

// Strain Energy Terms
Variable \( \text{StrainEnergyGP} = 600 \) // J/mole for GP
Variable \( \text{StrainEnergyGDP} = 300 \) // J/mole for GDP
Variable \( \text{StrainEnergyNbC} = 600 \) // J/mole for NbC
Variable \( \text{StrainEnergyLaves} = 600 \) // J/mole for Laves
Variable \( \text{StrainEnergyDelta} = 600 \) // J/mole for Delta

// Growth Rate Acceleration Factors
Variable \( \text{AccFactorGP} = 1 \) // Acceleration factor for GP.
Variable \( \text{AccFactorGDP} = 3 \) // Acceleration factor for GDP.
Variable \( \text{AccFactorNbC} = 1 \) // Acceleration factor for NbC
Variable \( \text{AccFactorLaves} = 1 \) // Acceleration factor for Laves.
Variable \( \text{AccFactorDelta} = 1 \) // Acceleration factor for Delta.

Variable \( \text{LastExtent} = 0 \)
Variable \( \text{PreviousExtent} = 0 \)
Variable \( \text{PreviousPPTFraction} = 0 \)
Variable \( \text{TimeVal} = 0 \)
Variable \( \text{TimeINcre} = 0 \)
Make/N=7/D/o GrowthMode // Provides storage for the growth mode for each PPT
GrowthMode = 1 // 1 means grow // -1 means dissolve
Variable \( \text{start} = 1 \)
Variable \( \text{final} = \text{numpnts}(\text{TempW}) - 1 \)
Make/N=7/D/o EquilFraction
EquilFraction = 0
print start, final
Variable \( \text{NewDummy} \)

Do

// Let us get the initial or previous microstructure

\[
\begin{align*}
\text{GammaFraction} & = \text{FractionGamma[start-1]} \\
\text{GPFraction} & = \text{FractionGP[start-1]} \\
\text{GDPFraction} & = \text{FractionGDP[start-1]} \\
\text{NbCFraction} & = \text{FractionNbC[start-1]} \\
\text{LavesFraction} & = \text{FractionLaves[start-1]} \\
\text{DeltaFraction} & = \text{FractionDelta[start-1]} \\
\text{TotalFraction} & = \text{GPFraction} + \text{GDPFraction} + \text{NbCFraction} + \text{LavesFraction} + \\
\end{align*}
\]

\[
\text{TempK} = \text{TempW[start]} \\
\text{EquilFraction}[0] = \text{Equilibrium}(\text{TempK}, 0) // Equilibrium total PPT fraction \\
\text{EquilFraction}[1] = \text{Equilibrium}(\text{TempK}, 1) // Equilibrium Gamma fraction \\
\text{EquilFraction}[2] = \text{Equilibrium}(\text{TempK}, 2) // Equilibrium GP fraction \\
\text{EquilFraction}[3] = \text{Equilibrium}(\text{TempK}, 3) // Equilibrium GDP fraction \\
\text{EquilFraction}[4] = \text{Equilibrium}(\text{TempK}, 4) // Equilibrium NbC fraction
\]

if (EquilFraction[0] >= TotalFraction) // yes you can form PPTs
    GrowthMode[0] = 1
else
    GrowthMode[0] = -1
endif

if (EquilFraction[2] >= GPFraction) // yes you can form GP PPTs
    GrowthMode[2] = 1
else
    GrowthMode[2] = -1
endif

if (EquilFraction[3] >= GDPFraction) // yes you can form GDP PPTs
    GrowthMode[3] = 1
else
    GrowthMode[3] = -1
endif

if (EquilFraction[4] >= NbCFraction) // yes you can form NbC PPTs
    GrowthMode[4] = 1
else
    GrowthMode[4] = -1
endif

if (EquilFraction[5] >= LavesFraction) // yes you can form Laves PPTs
    GrowthMode[5] = 1
else
    GrowthMode[5] = -1
endif

if (EquilFraction[6] >= DeltaFraction) // yes you can form Delta PPTs
    GrowthMode[6] = 1
else
    GrowthMode[6] = -1
endif

Dummy[start] = EquilFraction[0]

//-------------------------------
// Now let us consider the growth mode
//-------------------------------

//-------------------------------
// Calculate increment to GP
//-------------------------------

if (GrowthMode[2] == 1) //*************************
    PreviousExtent = GPFraction/EquilFraction[2]
    PrevTime = 0
    if ((PreviousExtent>=0) && (PreviousExtent <=1))

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PrevTime = FindEquivalentTimeGP(TempK, NZeroGP, SurfEnerImp, StrainEnergyGP, AccFactorGP, GPFraction)
if (Prevtime >= 0)
    TimeINcre = (TImeW[start] - TImeW[start-1])
    TimeVal = PrevTime + TimeINcre
    FractionGP[start] = EquilFraction[2]*
CalculateExtentGP(TempK, NZeroGP, SurfEnerImp, StrainEnergyGP, AccFactorGP, timeval)
endif
endif

//---------------------------------------------------------------
// Calculate increment to GDP
//---------------------------------------------------------------
if (GrowthMode[3] == 1) //*************************
    PrevTime = 0
    TimeINcre = 0
    PreviousExtent = GDPFraction/EquilFraction[3]
    if ((PreviousExtent>=0) && (PreviousExtent <=1))
        PrevTime = FindEquivalentTimeGDP(TempK, NZeroGDP, SurfEnerImp, StrainEnergyGDP, AccFactorGDP, GDPFraction)
    endif
endif

//---------------------------------------------------------------
// Calculate increment to NbC
//---------------------------------------------------------------
if (GrowthMode[4] == 1) //*************************
    PrevTime = 0
    TimeINcre = 0
    PreviousExtent = NbCFraction/EquilFraction[4]
    if ((PreviousExtent>=0) && (PreviousExtent <=1))
        PrevTime = FindEquivalentTimeNbC(TempK, NZeroNbC, SurfEnerImp, StrainEnergyNbC, AccFactorNbC, NbCFraction)
    endif
endif

//---------------------------------------------------------------
// Calculate increment to Laves
if (GrowthMode[5] == 1)

    PrevTime = 0
    TimeINcre = 0
    PreviousExtent = LavesFraction / EquilFraction[5]

    if ((PreviousExtent >= 0) && (PreviousExtent <= 1))
        PrevTime = FindEquivalentTimeLaves(TempK, NZeroLaves, SurfEnerImp, StrainEnergyLaves, AccFactorLaves, LavesFraction)
        if (Prevtime >= 0)
            TimeINcre = (TimeW[start] - TimeW[start-1])
            TimeVal = PrevTime + TimeINcre
        endif
    endif

endif

Calculate Increment to Delta

if (GrowthMode[6] == 1)

    PrevTime = 0
    TimeINcre = 0
    PreviousExtent = DeltaFraction / EquilFraction[6]

    if ((PreviousExtent >= 0) && (PreviousExtent <= 1))
        PrevTime = FindEquivalentTimeDelta(TempK, NZeroDelta, SurfEnerImp, StrainEnergyDelta, AccFactorDelta, DeltaFraction)
        if (Prevtime >= 0)
            TimeINcre = (TimeW[start] - TimeW[start-1])
            TimeVal = PrevTime + TimeINcre
        endif
    endif

endif
Make/o/N= 5

Variable Dummy

Gamma = 1 - FractionGP[start-1] - FractionGP[start-1] - FractionLaves[start-1] - FractionDelta[start-1] - FractionNbC[start-1] // What was the last Gamma fraction

ChangeinReal = 0
ChangeinExtended = 0
RealVolumeOld = 0

ChangeinExtended[0] = FractionGP[start] - FractionGP[start-1]

RealVolumeOld[0] = FractionGP[start-1]
RealVolumeOld[1] = FractionGDP[start-1]
RealVolumeOld[2] = FractionNbC[start-1]
RealVolumeOld[4] = FractionDelta[start-1]

NewDummy = CalculateRealVolume(Gamma = FractionGP[start-1], ChangeinExtended, ChangeinReal, RealVolumeOld) // ChangeinReal is calculated

// print GammaFraction, "now"
// Reset occurs now

FractionGP[start] = ChangeinReal[0] + FractionGP[start-1]
FractionGDP[start] = ChangeinReal[1] + FractionGDP[start-1]

-----------------------
// Now let us consider the dissolution mode // needs more work here
// Right now we are reseting to the equilfraction; but this may be artificial
// Must fix in the second version
-----------------------

Variable RatioGP = FractionGP[start-1]/TotalFraction
Variable RatioGDP = FractionGDP[start-1]/TotalFraction
Variable RatioLaves = FractionLaves[start-1]/TotalFraction
Variable RatioNbC = FractionNbC[start-1]/TotalFraction
Variable RatioDelta = FractionDelta[start-1]/TotalFraction

if (RatioGP < 0)
    RatioGP = 0
endif
if (RatioGDP < 0)
    RatioGDP = 0
endif
if (RatioLaves < 0)
    RatioLaves = 0
endif
if (RatioNbC < 0)
    RatioNbC = 0
endif
if (RatioDelta < 0)
RatioDelta = 0
endif
Make/o/n=5 RatiosNow
RatiosNow[0] = RatioGP
RatiosNow[1] = RatioGDP
RatiosNow[2] = RatioNbC
RatiosNow[4] = RatioDelta
// Dissolution is taken care
if (GrowthMode[2] == -1)
endif
if (GrowthMode[3] == -1)
    FractionGDP[start] = RatioGDP*EquilFraction[3]
endif
if (GrowthMode[4] == -1)
    FractionNbC[start] = RatioNbC*EquilFraction[4]
endif
if (GrowthMode[5] == -1)
endif
if (GrowthMode[6] == -1)
endif
OverallFraction[start] = 1 - FractionGamma[start]

//------------------------------------------
Growthmode1[start] = GrowthMode
//-----------------------------------------
// start +=1
dif
While (start <= final)
Duplicate/o Dummy EquilFractionWave
End

//------------------------------------------
// This will work as long as the change in extended volume are small
// if it is not, we will see large jumps (saw tooth type increases)
This will introduce errors
So to make sure you have not significant error accumulation
make sure that your temperature intervals are not too large
that means in steep temperature gradients
the time interval has to be small
Equation 12 of Jones and Bhadeshia paper
Implementation of equation 6 in chapter 4

Function CalculateRealVolume(GammaFraction, ChangeinExtended, ChangeinReal, RealVolumeOld) // ChangeinReal is calculated
Variable GammaFraction; Wave ChangeinExtended, ChangeinReal, RealVolumeOld
Variable Start = 0
Variable final = numpnts(ChangeinExtended) - 1
Variable totalfraction = 0

// In growth mode only,
// Change in extended cannot be negative

Do
    if (ChangeinExtended[start] < 0)
        ChangeinExtended[start] = 0
    endif
    totalfraction += RealVolumeOld[start]
//print totalfraction, GammaFraction, realvolumeold[start], start, "now2"
    start += 1
While (start <= final)

Variable BracketTerm = totalfraction / 1
if (BracketTerm >= 1)
    BracketTerm = 0.99999999
endif
//print BracketTerm
start = 0
Do
    ChangeinReal[start] = (1 - (BracketTerm)) * ChangeinExtended[start]
//print changeinreal[start], "Change in Real at", start
    start += 1
While (start <= final)
return 0
End

------------Overall Transformation Kinetics--------------
// Assuming it as sphere
// Based on Babu Paper from MST 1995
// Geometry has to be changed later
------------Overall Transformation Kinetics--------------
// Extent Transformed for GP

// Implementation of equation 8 in chapter 4
Function CalculateExtentGP(TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, timeval)
  Variable TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, timeval
  Variable Izero = CalcNuclRate(TempK, NZero, SurfEnerImp, StrainEnergy, 1)
  Variable Rate = CalcGrowthRateGP(TempK, 0, AccFactor)
  Variable EqGP = Equilibrium(TempK, 2)
  Variable Extent = 0
  Variable ActualVolume = Izero*(8*Pi/15)*(Rate^3)*(timeval^(5/2))
  extent = 1 - exp(-ActualVolume/EqGP) // we need to consider the site saturation above 0.5 there will be no nuclei!
  if (extent >=1)
    extent = 1
  endif
  Return Extent
End

// Equivalent Time for GP

// Implementation of equation 12 and 13 in chapter 4
Function FindEquivalentTimeGP(TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, PreviousFraction)
  Variable TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, PreviousFraction
  Variable Izero = CalcNuclRate(TempK, NZero, SurfEnerImp, StrainEnergy, 1)
  Variable Rate = CalcGrowthRateGP(TempK, 0, AccFactor)
  Variable EqGP = Equilibrium(TempK, 2)
  Variable OldExtent = PreviousFraction/EqGP
  if (oldExtent >=1)
    OldExtent = 0.9999
  endif
  Variable OldVolume = -1*EqGP*ln((1-OldExtent)) // derived from this expression extent = 1 - exp(-ActualVolume/EqAlpha)
  Variable NewTime = (OldVolume/(Izero*(8*Pi/15)*(Rate^3))^2/5) // derived from this ActualVolume = Izero*(8*Pi/15)*(Rate^3)*(timeval^(5/2))
  if (numtype(NewTime) !=0)
    // print TempK, NZeroGP, SurfEnerImp, PreviousFraction, OldExtent
    NewTime = -1
  endif
  Return NewTime
End

// Extent Transformed for GDP

// Implementation of equation 8 in chapter 4
Function CalculateExtentGDP(TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, timeval)
Variable TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, timeval
Variable Izero = CalcNuclRate(TempK, Nzero, SurfEnerImp, StrainEnergy, 2)
Variable Rate = CalcGrowthRateGDP(TempK, 0, AccFactor)
Variable EqGDP = Equilibrium(TempK, 3)
Variable Extent = 0
Variable ActualVolume = Izero*(8*Pi/15)*(Rate^3)*(timeval^(5/2))
//print Izero, Rate, timeval
extent = 1 - exp(-ActualVolume/EqGDP)
// we need to consider the site saturation above 0.5 there will be no nuclei!
Return Extent
// Return Extent*EqGDP (real alpha)
End
//-----------------------------------------------
// Equivalent Time for GDP
//-----------------------------------------------
// Implementation of equation 12 and 13 in chapter 4
Function FindEquivalentTimeGDP(TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, PreviousFraction)
Variable TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, PreviousFraction
Variable Izero = CalcNuclRate(TempK, Nzero, SurfEnerImp, StrainEnergy, 2)
Variable Rate = CalcGrowthRateGDP(TempK, 0, AccFactor)
Variable EqGDP = Equilibrium(TempK, 3)
Variable OldExtent = PreviousFraction/EqGDP
if (oldExtent >=1)
    OldExtent = 0.9999
endif
Variable OldVolume = -1*EqGDP*ln((1-OldExtent))
// derived from this expression extent = 1 - exp(-ActualVolume/EqAlpha)
Variable NewTime = (OldVolume/(Izero*(8*Pi/15)*(Rate^3))*(timeval^(5/2)))^(2/5) // derived from this ActualVolume = Izero*(8*Pi/15)*(Rate^3)*(timeval^(5/2))
if (numtype(NewTime) !=0)
    NewTime = -1
endif
Return NewTime
End
//-----------------------------------------------
// Extent Transformed for NbC
//-----------------------------------------------
// Implementation of equation 8 in chapter 4
Function CalculateExtentNbC(TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, timeval)
Variable TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, timeval
Variable Izero = CalcNuclRate(TempK, Nzero, SurfEnerImp, StrainEnergy, 3)
Variable Rate = CalcGrowthRateNbC(TempK, 0, AccFactor)
Variable EqNbC = Equilibrium(TempK, 4)
Variable Extent = 0
Variable ActualVolume = Izero*(8*Pi/15)*(Rate^3)*(timeval^(5/2))
//print Izero, Rate, timeval
extent = 1 - exp(-ActualVolume/EqNbC)
// we need to consider the site saturation above 0.5 there will be no nuclei!

Return Extent
// Return Extent*EqNbC (real alpha)

End

//-------------------------------
// Equivalent Time for NbC
//-------------------------------

//Implementation of equation 12 and 13 in chapter 4
Function FindEquivalentTimeNbC(TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, PreviousFraction)
    Variable TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, PreviousFraction
    Variable Izero = CalcNuclRate(TempK, Nzero, SurfEnerImp, StrainEnergy, 3)
    Variable Rate = CalcGrowthRateNbC(TempK, 0, AccFactor)
    Variable EqNbC = Equilibrium(TempK, 4)
    Variable OldExtent = PreviousFraction/EqNbC
    if (oldExtent >= 1)
        OldExtent = 0.9999
    endif
    Variable OldVolume = -1*EqNbC*ln((1-OldExtent))
    //derived from this expression extent = 1 - exp(-ActualVolume/EqAlpha)
    Variable NewTime = (OldVolume/(Izero*(8*Pi/15)*(Rate^3)))^(2/5) // derived from this ActualVolume = Izero*(8*Pi/15)*(Rate^3)*(timeval^(5/2))
    if (numtype(NewTime) != 0)
        NewTime = -1
    endif
    Return NewTime
End

//-------------------------------
// Equivalent Time for Laves
//-------------------------------

//Implementation of equation 12 and 13 in chapter 4
Function FindEquivalentTimeLaves(TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, timeval)
    Variable TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, timeval
    Variable Izero = CalcNuclRate(TempK, Nzero, SurfEnerImp, StrainEnergy, 4)
    Variable Rate = CalcGrowthRateLaves(TempK, 0, AccFactor)
    Variable EqLaves = Equilibrium(TempK, 5)
    Variable Extent = 0
    Variable ActualVolume = Izero*(8*Pi/15)*(Rate^3)*(timeval^(5/2))
    //print Izero, Rate, timeval
    extent = 1 - exp(-ActualVolume/EqLaves)
    // we need to consider the site saturation above 0.5 there will be no nuclei!
    Return Extent
End

//-------------------------------
// Equivalent Time for Laves
//-------------------------------

//Implementation of equation 12 and 13 in chapter 4
Function FindEquivalentTimeLaves(TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, PreviousFraction)
Variable TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, PreviousFraction
Variable Izero = CalcNuclRate(TempK, NZero, SurfEnerImp, StrainEnergy, 4)
Variable Rate = CalcGrowthRateLaves(TempK, 0, AccFactor)
Variable EqLaves = Equilibrium(TempK, 5)
Variable OldExtent = PreviousFraction/EqLaves
if (oldExtent >=1)
    OldExtent = 0.9999
endif
Variable OldVolume = -1*EqLaves*ln((1-OldExtent))
//derived from this expression extent = 1 - exp(-ActualVolume/EqAlpha)
Variable NewTime = (OldVolume/((Izero*(8*Pi/15)*(Rate^3)^((2/5)))*(timeval^((5/2)))))
// derived from this ActualVolume = Izero*(8*Pi/15)*(Rate^3)*(timeval^((5/2)))
if (numtype(NewTime) !=0)
    NewTime = -1
endif
Return NewTime
End

// Extent Transformed for Delta
// Implementation of equation 8 in chapter 4
Function CalculateExtentDelta(TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, timeval)
Variable TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, timeval
Variable Izero = CalcNuclRate(TempK, NZero, SurfEnerImp, StrainEnergy, 5)
Variable Rate = CalcGrowthRateDelta(TempK, 0, AccFactor)
Variable EqDelta = Equilibrium(TempK, 6)
Variable Extent = 0
Variable ActualVolume = Izero*(8*Pi/15)*(Rate^3)*(timeval^((5/2)))
//print Izero, Rate, timeval
//extent = 1 - exp(-ActualVolume/EqDelta)
// we need to consider the site saturation above 0.5 there will be no nuclei!
//Return Extent
// Return Extent*EqDelta (real alpha)
End

// Equivalent Time for Delta
// Implementation of equation 12 and 13 in chapter 4
Function FindEquivalentTimeDelta(TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, PreviousFraction)
Variable TempK, NZero, SurfEnerImp, StrainEnergy, AccFactor, PreviousFraction
Variable Izero = CalcNuclRate(TempK, NZero, SurfEnerImp, StrainEnergy, 5)
Variable Rate = CalcGrowthRateDelta(TempK, 0, AccFactor)
Variable EqDelta = Equilibrium(TempK, 6)
Variable OldExtent = PreviousFraction/EqDelta
if (oldExtent >=1)
    OldExtent = 0.9999
endif
Return NewTime
End
//endif
//Variable OldVolume = -1*EqDelta*ln((1-OldExtent))
//derived from this expression extent = 1 - exp(-ActualVolume/EqAlpha)
//Variable NewTime = (OldVolume/(Izero*(8*Pi/15)*(Rate^3)))^(2/5) // derived from this ActualVolume
= Izero*(8*Pi/15)*(Rate^3)*(timeval^(5/2))
//if (numtype(NewTime) !=0)
//    NewTime = -1
//endif
//Return NewTime
End

////////-Classical Nucleation Theory--------------
// Molar volume = 6.717e-6 m^3/mole
// For A718

//Implementation of equation 9 in chapter 4
Function CalcNuclRate(TempK, NZero,SurfEnerImp, StrainEnergy, Mode)
// Here FreePerMole is for gamma to PPT transformation
// Molar volume for A718
Variable/D TempK, NZero, SurfEnerImp, StrainEnergy, Mode
// Kelvin, Cal/mole, Const, m^3/mole, J/m^2 = per m^3
Variable/D ActivEnergy, RateNucleation, R, CriticalRadius
Variable MolarVolume = 6.717e-6
Variable FreePerMoleNorm = -1*CalculateDGM(TempK, Mode)  // Normalized and multiply by -1 for sign convention
Variable RValue = 08.3144725 // J/K/Mole
Variable FreePerMole = FreePerMoleNorm*Rvalue*TempK  // Now this is is in J/Mole
Variable/D k = 1.3806E-23 // J/kelvin
if(FreePerMole <= -1*StrainEnergy)
//Implementation of equation 10 in chapter 4
ActivEnergy = 16*(PI)*(SurfEnerImp^3) / (3*(FreePerMole*(RValue/1.98)/MolarVolume)^2)
RateNucleation = NZero * exp(- ActivEnergy/ (k*(TempK)) )
CriticalRadius = - 2*SurfEnerImp/(FreePerMole*(RValue/1.98)/MolarVolume)
If (RateNucleation >= INF)  
        RateNucleation = NaN
Endif
else
RateNucleation = NaN
CriticalRadius = NaN
endif
// Has to modify for the mobility variation with temperature
Variable TMelt = 1972.28 // From ThermoCalc
RateNucleation *= exp(-142.188*TMelt/6.023e23)
return(RateNucleation)
End

//-------------------Modes:
//-------------------0: Simple AAaron's growth Law--------
// ------------------1: based on Kinsman and Aaronson--------
// This is OK for allotriomprhic ferrite
// Bulk Parent Concentration: O_Bar
// Parent Interface Concentration: O_MetInc
// Product Interface Concentration: O_IncMet
// Product Concentration is same as Interface concentration
//--------
// This is an approximation, since we cannot couple with ThermoCalc and DicTra yet
// Ideally the fluxes should be balanced.
// Tried to run Dictra in the back, found too much time consuming
// Need work Later on
// Errors may be little; however for academic publishing need further work
// We need to get TQinterface
//-------------------
// Diff is going to be in the units of m2/s
// It should be the slowest diffuser in the allow
//-----------------------------------------------

// Growth Rate for GP
function CalcGrowthRateGP(TempK, Mode, AccFactor)
    variable TempK, Mode, AccFactor
    variable Diff = CalculateDiffRate(TempK, 1)
    variable Al_Bar_Mole = 1.0955e-2 // From ThermoCalc calculations wt to mole fraction
    variable O_IncMet = AluminumEqGP(tempk, 1)
    variable O_bar = Al_Bar_Mole
    variable O_MetInc = AluminumEqGP(tempk, 0)
    variable Alpha = 0
    //Implementation of equation 11 in chapter 4
    variable supersaturation = (O_IncMet - O_bar)/(O_IncMet - O_MetInc)
    if (mode == 0)
        Alpha = sqrt(2)*(supersaturation) * sqrt(diff) // this is different from the dilute condition
        if (Alpha < 0)
            Alpha = 0.0
        endif
    endif
    if (mode == 1)
        Alpha = CalculateParabolic(O_IncMet, O_bar, O_MetInc, DIFF)
    endif
    return(Alpha*AccFactor)
End

// Growth Rate for GDP
function CalcGrowthRateGDP(TempK, Mode, AccFactor)
    variable TempK, Mode, AccFactor
    variable Diff = CalculateDiffRate(TempK, 2)
    variable Nb_Bar_Mole = 3.169e-2 // From ThermoCalc calculations wt to mole fraction
    variable Nb_IncMet = AluminumEqGP(tempk, 1)
    variable Nb_bar = Nb_Bar_Mole
    variable Nb_MetInc = AluminumEqGP(tempk, 0)
    variable Nb_Alpha = 0
    //Implementation of equation 11 in chapter 4
    variable supersaturation = (Nb_IncMet - Nb_bar)/(Nb_IncMet - Nb_MetInc)
    if (mode == 0)
        Nb_Alpha = sqrt(2)*(supersaturation) * sqrt(diff) // this is different from the dilute condition
        if (Nb_Alpha < 0)
            Nb_Alpha = 0.0
        endif
    endif
    if (mode == 1)
        Nb_Alpha = CalculateParabolic(Nb_IncMet, Nb_bar, Nb_MetInc, DIFF)
    endif
    return(Nb_Alpha*AccFactor)
End
Variable O_IncMet = NiobiumEqGDP(tempk, 1)
Variable O_bar = Nb_Bar_Mole
Variable O_MetInc = NiobiumEqGDP(tempk, 0)
Variable Alpha = 0

//Implementation of equation 10 in chapter 4
Variable supersaturation = (O_IncMet - O_bar)/(O_IncMet - O_MetInc)
if (mode ==0)
    Alpha = sqrt(2)*((supersaturation)) * sqrt(diff) // this is different from the dilute condition
else
    Alpha = 0.0
endif
if (mode ==1)
    Alpha = CalculateParabolic(O_IncMet,O_bar,O_MetInc,DIFF)
endif
return(Alpha*AccFactor)

//-----------------------------------------------
// Growth Rate for NbC
//-----------------------------------------------
Function CalcGrowthRateNbC(TempK, Mode, AccFactor)
    Variable TempK, Mode, AccFactor
    Variable Diff = CalculateDiffRate(TempK, 2)
    Variable Nb_Bar_Mole = 3.169e-2 // From ThermoCalc calculations wt to mole fraction
    Variable O_IncMet = NiobiumEqNbC(tempk, 1)
    Variable O_bar = Nb_Bar_Mole
    Variable O_MetInc = NiobiumEqNbC(tempk, 0)
    Variable Alpha = 0

    //Implementation of equation 10 in chapter 4
    Variable supersaturation = (O_IncMet - O_bar)/(O_IncMet - O_MetInc)
    if (mode ==0)
        Alpha = sqrt(2)*((supersaturation)) * sqrt(diff) // this is different from the dilute condition
    else
        Alpha = 0.0
    endif
    if (mode ==1)
        Alpha = CalculateParabolic(O_IncMet,O_bar,O_MetInc,DIFF)
    endif
    return(Alpha*AccFactor)
End

//-----------------------------------------------
// Growth Rate for Laves
//-----------------------------------------------
Function CalcGrowthRateLaves(TempK, Mode, AccFactor)
    Variable TempK, Mode, AccFactor
    Variable Diff = CalculateDiffRate(TempK, 2)
Variable Nb_Bar_Mole = 3.169e-2  // From ThermoCalc calculations wt to mole fraction
Variable O_IncMet = NiobiumEqLaves(tempk, 1)
Variable O_bar = Nb_Bar_Mole
Variable O_MetInc = NiobiumEqLaves(tempk, 0)
Variable Alpha = 0
// Implementation of equation 10 in chapter 4
Variable supersaturation = (O_IncMet - O_bar)/(O_IncMet - O_MetInc)
if (mode ==0)
    Alpha = sqrt(2)*(( supersaturation )) * sqrt(diff)  // this is different from the dilute condition
    if (Alpha < 0)
        Alpha = 0.0
    endif
endif
if (mode ==1)
    Alpha = CalculateParabolic(O_IncMet,O_bar,O_MetInc,DIFF)
endif
return(Alpha*AccFactor)
End

//---------------------------------------------------------------
// This is based on Mucg46 and based on the Kinsman
//---------------------------------------------------------------
Function CalculateParabolic(XGAG,XBAR,XAGA,DIFF)
    Variable/D XGAG,XBAR,XAGA,DIFF
    Variable/D Ges,PrevGes, Omega, Dum1, Der, sqrp, Error, Alpha
    sqrp = sqrt(Pi)
    Ges = 0.51466  // GES IS A GUESS VALUE OF ALPHA1/(2*SQRT(D))
    Omega = (XGAG-XBAR)/(XGAG-XAGA)
    Variable condition = 0
    Variable condition1 = 0
    Variable condition2 = 0
    Variable FirstLoop = 0
    Make/O/N=400 dummyPara; Setscale x -1, 1, dummyPara
    dummyPara = (10^x)*(exp((10^x)*(10^x)))*(1-erf((10^x)))-(Omega/sqrp)
    if (Diff <0)
        return(NaN)
    endif
    do
do
    Dum1=Ges*(exp(Ges*Ges))*(1-erf(Ges))-(Omega/sqrp)
    Der =exp(Ges*Ges)*(1 + 2*Ges*Ges)*(1-erf(Ges))-(Ges*2/sqrp)
    prevGes = Ges
    Ges -= (Dum1/Der)
    Error = abs(Ges - PrevGes)
    if (Error < 1E-11)
Alpha = Ges*2*sqrt(Diff)
condition =1
condition1 = 1
endif
if (firstloop > 20)
// Print "Using Approximation"
Ges = CalBisectionAlpha(Omega,sqrp)
// Print "Ges obtained by that method", ges
if (Ges > 0)
alpha=   Ges*2*sqrt(Diff) // NaN it is a fudge
else
alpha = NaN
endif
condition1 = 1
condition = 1
endif
FirstLoop += 1
while(condition1 ==0)
while(condition == 0)
return(Alpha)
End
//-------------------------------------
Function CalBisectionAlpha(Omega,sqrp)
Variable Omega,sqrp
Variable FirstLogGes, SecondLogGes, logGesIncre
Variable FirstGes , SecondGes
Variable FirstValue, SecondValue
Variable condition =0, condition1 = 0, iteration = 0
Variable maxLogGes = 0.74, MinlogGes = -3
logGesIncre = abs(MinlogGes - maxLogGes)/50
FirstLogGes = -3
SecondLogGes = FirstLogGes + logGesIncre
Do
FirstGes = 10^FirstLogGes; SecondGes=10^SecondLogGes
FirstValue = FirstGes*(exp(FirstGes*FirstGes)) *(1-erf(FirstGes))-(Omega/sqrp)
SecondValue = SecondGes*(exp(SecondGes*SecondGes)) *(1-erf(SecondGes))-(Omega/sqrp)
if (FirstLogGes >= maxLogGes) // no solution
return(10^maxLogGes)
condition = 1
endif
if (abs(FirstValue) < 1e-9) //
return(FirstGes)
condition = 1
endif
if (iteration > 50) //
return(FirstGes)
condition = 1
endif
condition1 = 0
do
if ((FirstValue <= 0) %& (SecondValue <= 0)) // both values are below zero

If \((0 - \text{SecondValue}) < (0 - \text{FirstValue})\) \quad // \text{second value is closer to zero}

\[
\text{FirstLogGes} = \text{SecondLogGes} \\
\text{SecondLogGes} = \text{FirstLogGes} + \log\text{GesIncr}
\]

else
\quad // \text{first value is close to zero}

\[
\text{FirstLogGes} += \log\text{GesIncr} \\
\text{SecondLogGes} = \text{FirstLogGes} + \log\text{GesIncr}
\]

endif

// print "both are below zero the next", FirstLogGes, SecondLogGes
condition1 = 1
iteration +=1
endif

if ((\text{FirstValue} > 0) \&\& (\text{SecondValue} > 0)) \quad // both values are above zero

If \((0 - \text{SecondValue}) > (0 - \text{FirstValue})\) \quad // second value is closer to zero

\[
\text{FirstLogGes} = \text{SecondLogGes} \\
\text{SecondLogGes} = \text{FirstLogGes} - \log\text{GesIncr}
\]

else
\quad // first value is close to zero

\[
\text{FirstLogGes} -= \log\text{GesIncr} \\
\text{SecondLogGes} = \text{FirstLogGes} + \log\text{GesIncr}
\]

endif

// print "both are above zero the next ges", FirstLogGes, SecondLogGes
condition1 = 1
iteration +=1
endif

if ((\text{FirstValue} > 0) \&\& (\text{SecondValue} <= 0))  \quad // First value above zero

\[
\text{logGesIncr} *= 0.4 \\
\text{FirstLogGes} -= \log\text{GesIncr} \\
\text{SecondLogGes} += \log\text{GesIncr}
\]

// Printf "near the solution F %G<->%G",Firstvalue, Secondvalue
// Printf "Iterating between %G and %G \r", FirstLogGes, SecondLogGes
condition1 = 1
iteration +=1
if(abs(FirstLogGes - SecondLogGes) < 1e-5)
   return(FirstGes)
endif
endif

if ((\text{FirstValue} <= 0) \&\& (\text{SecondValue} > 0))   \quad // Second value above zero

\[
\text{logGesIncr} *= 0.4 \\
\text{FirstLogGes} += \log\text{GesIncr} \\
\text{SecondLogGes} -= \log\text{GesIncr}
\]

// Printf "near the solution F %G<->%G",Firstvalue, Secondvalue
// Printf "Iterating between %G and %G \r", FirstLogGes, SecondLogGes
condition1 = 1
iteration +=1
if(abs(FirstLogGes - SecondLogGes) < 1e-8)
   return(FirstGes)
endif
endif

while (condition1 == 0)
while(condition == 0) // condition not met
end
//-----------------------------------------------

Function CalculateParabolicMod(XGAG,XBAR,XAGA,DIFF)
Variable/D XGAG,XBAR,XAGA,DIFF

Variable/D Ges,PrevGes, Omega, Dum1, Der, sqrp, Error, Alpha, Point

sqrp = sqrt(Pi)
Ges = 0.51466 // GES IS A GUESS VALUE OF ALPHA1/(2*SQRT(D))

Omega = (XGAG-XBAR)/(XGAG-XAGA)
Variable condition = 0
Variable condition1 = 0
Variable condition2 = 0
Variable FirstLoop = 0
Variable condition3 = 0

Make/O/N=20 ErrorW GesValue; GesValue = NaN; ErrorW= NaN
if (Diff <0)
    return(NaN)
endif

do
    do
        Dum1=Ges*(exp(Ges*Ges))*(1-erf(Ges))
        Der =(exp(Ges*Ges)*(1 + 2*Ges*Ges))*(1-erf(Ges))
        prevGes = Ges
        Ges = (Dum1/Der)
        Error = abs(Ges - PrevGes)
        ErrorW[firstloop] = Error; GesValue[firstloop]=Ges
        If (Firstloop >= 2)
            If ((ErrorW[firstloop] > ErrorW[firstloop-1]) %& (condition3 == 0) )
                Point = firstloop - 1
                condition3 = 1
                // print "the points is", Point
            endif
        endif
        if (Error < 1E-11)
            Alpha = Ges*2*sqrt(Diff)
            condition1 =1
            condition1 = 1
        endif
        if (firstloop > 20)
            Ges = ApproxGesCalculation(ErrorW,GesValue, Point)
            if (Ges > 0)
                alpha= Ges*2*sqrt(Diff) // NaN it is a fudge
            else
                alpha = NaN
            endif
            condition1 = 1
            condition = 1
        endif

        229
FirstLoop += 1
while(condition1 == 0)
while(condition == 0)
return(Alpha)
End
//---------------------------------------------------------------
Function ApproxGesCalculation(ErrorWave, GesWave, Point)
Wave ErrorWave, GesWave; Variable Point
Wave w_coef
Wavestats/Q ErrorWave; Point = V_minloc
CurveFit/Q line ErrorWave(Point-2, Point) /X=GesWave
return(-w_coef[0]/w_coef[1])
End
//---------------------------------------------------------------

//---------------Simple Arrhenius Law-----------------
// Based on Semiatin 2004 Met Trans A paper
// Thermodynamic factors are ignored here
// Returns in m^2/s
//---------------------------------------------------------------
Function CalculateDiffRate(TempK, Mode)
Variable/D TempK, Mode
Variable D_Zero, QW, Rval, Result, Diff
if (mode == 1) //Diffusion of Al in Gamma
    D_Zero=1e7
    QW = 30000
    Rval = 8.314
    Result = D_Zero*exp(-QW/Tempk)
    // this is in (micron)^2 so multiply by 1e-12
    Diff = Result*1e-12
    Return Diff
endif
if (mode == 2) //Diffusion of Nb in Gamma
    D_Zero=8.8e-5
    QW = 272e3
    Rval = 8.314
    Result = D_Zero*exp(-QW/(Rval*Tempk))
    Diff = Result
    Return Diff
endif
//if (mode == 3) //Diff for NbC
//   D_Zero=8.8e-5
//   QW = 272e3
//   Rval = 8.314
//   Result = D_Zero*exp(-QW/(Rval*Tempk))
//   Diff = Result
//   Return Diff
//endif
230
//
//if (mode == 4) //Diff for Laves
//    D_Zero = 8.8e-5
//    QW = 272e3
//    Rval = 8.314
//    Result = D_Zero*exp(-QW/(Rval*Tempk))
//endif

End

// Equilibrium phase fractions with all phases active
// Curve fitted to thermodynamic calculations
// In principle we need to couple with TC calculations
// This is based on TTNi7 Database
// PhaseFraction[0] is Gamma
// PhaseFraction[1] is GDP
// PhaseFraction[2] is GP
// PhaseFraction[3] is Laves
// PhaseFraction[4] is NbC
// PhaseFraction[5] is Delta

// Delta is not currently considered

Function Equilibrium(TempK, Mode)
    Variable TempK, Mode
    Variable eq_Gamma_Fraction = 0
    Variable eq_GDP_Fraction = 0
    Variable eq_GP_Fraction = 0
    Variable eq_Laves_Fraction = 0
    Variable eq_NbC_Fraction = 0
    Variable eq_Delta_Fraction = 0
    Make/o/N=6 PhaseFra

    // Fitted Curves
    // For NbC
    Make/o/N=7 W_coef
    W_coef={0.0024757,-4.1008e-006,1.2999e-008,-1.8998e-011,1.3345e-014,-3.7009e-018,5.743e-023}

    // For GDP
    Make/o/N=9 W_coef1
    W_coef1={-1.3227,0.020173,-0.00011989,3.922e-007,-7.7575e-010,9.5236e-013,-7.0997e-016,2.9443e-019,-5.2129e-023}

    // For GP
    Make/o/N=7 W_coef2
    W_coef2={-0.26555,0.0038787,-1.5533e-005,3.2658e-008,-3.7869e-011,2.2855e-014,-5.6339e-018}
//For Laves
Make/o/N=5 W_coef3
W_coef3={-1.2709,0.011335,-3.331e-005,4.2596e-008,-2.1223e-011}

//Does not consider liquid formation. Even if above melting temperature, only gamma is present
if (tempk >= 1702.11)
    eq_Gamma_Fraction = 1
    PhaseFra[0] = eq_Gamma_Fraction
    PhaseFra[1] = eq_GDP_Fraction
    PhaseFra[2] = eq_GP_Fraction
    PhaseFra[3] = eq_Laves_Fraction
    PhaseFra[4] = eq_NbC_Fraction
    PhaseFra[5] = eq_Delta_Fraction
endif

//Start of NbC Formation
if ((TempK >= 1214.86) && (tempk <= 1702.11))
    eq_NbC_Fraction = poly(W_coef,TempK)
    eq_Gamma_Fraction = 1 - eq_NbC_Fraction
    PhaseFra[0] = eq_Gamma_Fraction
    PhaseFra[1] = eq_GDP_Fraction
    PhaseFra[2] = eq_GP_Fraction
    PhaseFra[3] = eq_Laves_Fraction
    PhaseFra[4] = eq_NbC_Fraction
    PhaseFra[5] = eq_Delta_Fraction
endif

//Start of GDP Formation
if ((TempK >= 1178.63) && (tempk <= 1214.86))
    eq_NbC_Fraction = poly(W_coef,TempK)
    eq_GDP_Fraction = poly(W_coef1,TempK)
    eq_Gamma_Fraction = 1 - eq_GDP_Fraction - eq_NbC_Fraction
    PhaseFra[0] = eq_Gamma_Fraction
    PhaseFra[1] = eq_GDP_Fraction
    PhaseFra[2] = eq_GP_Fraction
    PhaseFra[3] = eq_Laves_Fraction
    PhaseFra[4] = eq_NbC_Fraction
    PhaseFra[5] = eq_Delta_Fraction
endif

//Start of GP formation
if ((TempK >= 588.5) && (tempk < 1178.63))
    eq_NbC_Fraction = poly(W_coef,TempK)
    eq_GDP_Fraction = poly(W_coef1,TempK)
    eq_GP_Fraction = poly(W_coef2,TempK)
    eq_Gamma_Fraction = 1 - eq_GDP_Fraction - eq_NbC_Fraction - eq_GP_Fraction
    PhaseFra[0] = eq_Gamma_Fraction
    PhaseFra[1] = eq_GDP_Fraction
    PhaseFra[2] = eq_GP_Fraction
    PhaseFra[3] = eq_Laves_Fraction
    PhaseFra[4] = eq_NbC_Fraction
    PhaseFra[5] = eq_Delta_Fraction
endif
PhaseFra[2] = eq_GP_Fraction
PhaseFra[3] = eq_Laves_Fraction
PhaseFra[4] = eq_NbC_Fraction
PhaseFra[5] = eq_Delta_Fraction
endif

//Start of Laves formation
if (TempK < 588.5)
    eq_NbC_Fraction = poly(W_coef,TempK)
    eq_GDP_Fraction = poly(W_coef1,TempK)
    eq_GP_Fraction = poly(W_coef2,TempK)
    eq_Laves_Fraction = poly(W_coef3,TempK)
    eq_Gamma_Fraction = 1 - eq_GDP_Fraction - eq_NbC_Fraction - eq_GP_Fraction - eq_Laves_Fraction
endif

PhaseFra[0] = eq_Gamma_Fraction
PhaseFra[1] = eq_GDP_Fraction
PhaseFra[2] = eq_GP_Fraction
PhaseFra[3] = eq_Laves_Fraction
PhaseFra[4] = eq_NbC_Fraction
PhaseFra[5] = eq_Delta_Fraction
endif

Variable PPTFraction = eq_GDP_Fraction + eq_GP_Fraction + eq_Laves_Fraction + eq_NbC_Fraction + eq_Delta_Fraction
Variable Value = 0
if (mode ==0)
    Value = PPTFraction
endif
if (mode ==1)
    Value = eq_Gamma_Fraction
endif
if (mode ==2)
    Value = eq_GP_Fraction
endif
if (mode ==3)
    Value = eq_GDP_Fraction
endif
if (mode ==4)
    Value = eq_NbC_Fraction
endif
if (mode ==5)
    Value = eq_Laves_Fraction
endif
if (mode ==6)
    Value = eq_Delta_Fraction
endif
return value
End
// Now we need to calculate the tie line
// Here we assume the tie line will always go through the bulk composition
// Ideally you need to calculate this with mass balance and allowing for
// Tie line shift
// We obtained these concentrations using equilibrium calculations considering only gamma and the phase
// of interest to be active. This is not necessarily correct
// several precipitates rely on Nb and their respective solvus temperatures will affect the Nb content
// available for PPT formation.

//***Update 7/9/2012 Revised curve fits because mole fractions were off by a factor of 100

// If it is mode == 0; get the Aluminum concentration in Gamma
// if it is mode == 1; get the Aluminum concentration in GP
// Ideally this needs to be coupled with ThermoCalc
// Now it is polynomial fit similar to Vitek Approach

Function AluminumEqGP(tempk, Mode)
Variable/D tempk, Mode
Make/o/N=5 polyWave
Variable Result = 0
If (mode==0) // Al in Gamma
    If (tempK >= 1178.63)
        result = 0.010955658
    endif
    If (tempK < 1178.63)
        polyWave = [0.0059142, -4.4851e-005, 1.2275e-007, -1.46e-010, 6.5217e-014]
        Result = poly(polyWave,TempK)
    endif
endif

If (mode==1) // Al in GP
    If (tempK >= 1178.63) // Above GP Solvus
        result = NaN
    endif
    if (tempK < 1178.63) // Below GP Solvus
        Make/o/N=5 NewPolyWave
        NewPolyWave = [0.039105, 4.0597e-005, -8.7233e-008, 6.7219e-011, -1.2128e-014]
        Result = poly(NewPolyWave,TempK)
    endif
endif

if (Result <= 0)
    Result = 0
endif

Return Result
End
Function NiobiumEqGDP(tempK, Mode)
Variable/D tempK, Mode
Make/o/N=5 polyWave
Variable Result = 0
If (mode==0) //Nb in Gamma
    If (tempK >= 1218.3)
        Result = 0.0316906
    endif
    If (tempK < 1218.3)
        polyWave = {0.028592,-0.00021075,5.5462e-007,-6.2358e-010,2.5583e-013}
        Result = poly(polyWave,TempK)
    endif
endif
If (mode==1) //Nb in GDP
    If (tempK >= 1218.3) //Above GDP Solvus
        Result = NaN
    endif
    if (tempK < 1218.3) //Below GDP Solvus
        Make/o/N=5 NewPolyWave
        NewPolyWave = {0.11966,0.00016672,-2.5225e-007,1.3241e-010,7.3736e-016}
        Result = poly(NewPolyWave,TempK)
    endif
endif
if (Result <= 0)
    Result = 0
endif
Return Result
End

Function NiobiumEqNbC(tempK, Mode)
Variable/D tempK, Mode
Make/o/N=3 polyWave
Variable Result = 0
If (mode==0) //Nb in Gamma
    If (tempK >= 1702.11)
        Result = 0.0316906
    endif
    If (tempK < 1702.11)
polyWave= \{0.030708,-4.8995e-007,4.094e-010\}
Result = poly(polyWave,TempK)
endif

If (mode==1) // Nb in NbC
  If (tempK >= 1702.11) // Above NbC Solvus
    result = NaN
  endif
  if (tempK <= 1702.11) // Below NbC Solvus
    Make/o/N=3 NewPolyWave
    NewPolyWave= \{0.55759,3.2576e-005,-3.7014e-010\}
    Result = poly(NewPolyWave,TempK)
  endif
endif

if (Result <= 0)
  Result = 0
endif
Return Result
End

// *****************************************************************************
//**********For now this is copied from NbC because Laves data did not calculate correctly
// If it is mode == 0; get the Niobium concentration in Gamma
// if it is mode == 1; get the Niobium concentration in Laves
// *****************************************************************************
Function NiobiumEqLaves(tempk, Mode)
Variable/D tempk, Mode
Make/o/N=3 polyWave
Variable Result = 0
If (mode==0) // Nb in Gamma
  If (tempK >= 1702.11)
    result = 0.0316906
  endif
  If (tempK < 1702.11)
    polyWave= \{0.00030708,-4.8994e-009,4.0939e-012\}
    Result = poly(polyWave,TempK)
  endif
endif

If (mode==1) // Nb in Laves
  If (tempK >= 1702.11) // Above NbC Solvus
    result = NaN
  endif
  if (tempK <= 1702.11) // Below NbC Solvus
    Make/o/N=3 NewPolyWave
    NewPolyWave= \{0.0055759,3.2576e-007,-3.7014e-010\}
  endif
endif
Result = poly(NewPolyWave,TempK)
endif
endif

if (Result <= 0)
    Result = 0
endif

Return Result
End

// Calculate the driving force for A718
// Here again only applicable for A718
// Returns DGM/RT
// Function CalculateDGM(TempK, Mode)
Variable TempK, Mode
Variable Result = 0

//DGM for GP
If(Mode==1)
    Make/o/N=3 FitWave
    FitWave = {-0.42137,6.5861,0.002309}
    Result = FitWave[0]+FitWave[1]*exp(FitWave[2]*TempK)
Endif

//DGM for GDP
If(Mode==2)
    Make/o/N=5 FitWave
    FitWave = {-0.49166,5.9739,0.0020558,16.342,0.0080744}
    Result = FitWave[0]+FitWave[1]*exp(-FitWave[2]*TempK)+FitWave[3]*exp(-FitWave[4]*TempK)
Endif

//DGM for NbC
If(Mode==3)
    Make/o/N=7 FitWave
    FitWave = {78.267,-0.48605,0.0013001,-1.7641e-006,1.2754e-009,-4.6965e-013,6.9301e-017}
    Result = poly(FitWave,TempK)
Endif

//DGM for Laves
If(Mode==4)
    Make/o/N=9 FitWave
    FitWave = {362.87,-3.3087,0.013076,-2.891e-005,3.8997e-008,-3.2872e-011,1.6932e-014,-4.8808e-018,6.0378e-022}
    Result = poly(FitWave,TempK)
Endif

//DGM for Delta

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If(Mode==5)
Endif

if(Result <= 0)
    Result = 0
endif

Return Result
End