Molten pool modeling, microstructure and grain refinement in Ti-alloys

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Molten pool modeling, microstructure and grain refinement in Ti-alloys

by

Michael Yesid Mendoza Londono

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

Major: Materials Science and Engineering

Program of Study Committee:
Peter Collins, Major Professor
Richard LeSar
Leonard Bond

Iowa State University
Ames, Iowa
2016

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DEDICATION

This research and thesis is dedicated to my family that with their unconditional love motivates me to set higher targets.
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<th>Description</th>
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<td>AM</td>
<td>Additive manufacturing</td>
</tr>
<tr>
<td>CAD</td>
<td>Computer aided design</td>
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<td>STL</td>
<td>stereolithography</td>
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ABSTRACT

It is known that titanium alloys are widely used in a variety of industries such as aerospace, automotive and biomedical. Good corrosion resistance and the high strength/weight ratio are among the properties that have made these alloys attractive for abovementioned industries. Although these alloys have been extensively investigated for the past decades, the growing demand, the high cost and the recent development of additive manufacturing techniques require better understanding of these alloys as well as the existing relationship between composition, processing and properties. The approach here is to model the molten pool dynamics, created during additive manufacturing processing of titanium alloys, via Comsol Multiphysics to assess key aspects such as grain growth direction and cooling rates. The Laser Engineered Net Shaping (LENS™), was used to produce a set of specimens to evaluate microstructure and grain refinement in the Ti-W system.

The computational results indicate the importance of are the fluid dynamics variables (e.g. Marangoni and buoyance effects) and the preferential grain growth in the $<001>_{\beta}$ direction. A compositionally graded titanium binary system (Ti-xW specimen ($0 \leq x \leq 30$ wt%)) was used to evaluate the influence of composition on grain refinement by applying the Easton & St. John model that shows how the grain refinement is mainly governed by the nucleant particles mechanism. In addition, a set of nine Ti-6wt%W specimens were deposited using LENS™ with different laser energy densities and the results shows how the energy density is proportional to the grain size due to two effects. The first effect is that as the energy density increases, the potential availability of nucleant particles can be reduced.
Second the energy density (represented by power in the model) is inversely proportional to the cooling rate which confirms the proportionality between grain size and energy density.
CHAPTER 1

INTRODUCTION

1.1 Thesis Organization

This thesis first describes the motivation to perform research related to titanium alloys. In the literature review a brief introduction to different additive manufacturing techniques is discussed. Numerical solutions of different physical phenomena are important to design, optimize and create devices or processes. The finite element method is a powerful tool to model several aspects in additive manufacturing techniques and has been widely used. COMSOL Multiphysics® is used as one of those tools with well acceptance in the industry. Also a review of microstructure and grain refinement in titanium alloys is described. Finally, a discussion and analysis of results from the Ti-W system and simulations are presented.

1.2 Motivation

The wide use of titanium alloys in aerospace, automotive and other industries demand the improvement of their properties and the simultaneous reduction in cost. In addition, the recent development of additive manufacturing techniques also requires a better understanding of their unique aspects to correlate composition, processing and properties.
CHAPTER 2

LITERATURE REVIEW

2.1 Additive Manufacturing

Additive manufacturing (AM) is defined as a general process to produce 3D objects. This technology is also called 3D printing. It incorporates a material feed stock and an energy source to create three-dimensional objects in layer by layer fashion. In the 1980’s, rapid prototyping was created as the first layer by layer method controlled by a computer aided design (CAD) file for prototype parts [1]. The CAD file contains the general geometry of the object and this geometry is sliced into a stereolithography (STL) file providing the necessary information to deposit each layer. Among the several advantages of AM process are rapid creation of models, less human interaction, complicated shape objects and time and cost reduction. However, due to rapid solidification and other unique aspects of the process, it is more difficult to understand the microstructure and the resultant properties.

2.2 Additive Manufacturing Techniques

AM processes can be classified by energy source (e.g. laser, electron beam) or by material feed stock (e.g. powder feed, wire feed) [2]. Table 1 shows general details of some additive manufacturing techniques. Despite the differences in some technical details the physics involved in each case are very similar.
Table 1. Some additive manufacturing techniques (AM)

<table>
<thead>
<tr>
<th>AM</th>
<th>Heat source</th>
<th>Feedstock source</th>
<th>Atmosphere</th>
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<td>LENS™</td>
<td>Laser</td>
<td>Metal Powder</td>
<td>Argon</td>
</tr>
<tr>
<td>EBAM™</td>
<td>Electron Beam</td>
<td>Wire</td>
<td>Vacuum</td>
</tr>
<tr>
<td>Direct Metal Laser Sintering (DMLS)</td>
<td>Laser</td>
<td>Metal powder</td>
<td>Nitrogen or Argon</td>
</tr>
<tr>
<td>Arc-based AM</td>
<td>Electric arc</td>
<td>Wire</td>
<td>Argon</td>
</tr>
<tr>
<td>Selective laser Sintering (SLS)</td>
<td>Laser</td>
<td>Metal powder (bed)</td>
<td>Nitrogen</td>
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</table>

This work is mainly focused on Laser Engineering Net-Shaping (LENS™) system and a small section on simulation of Electron Beam Additive manufacturing (EBAM™).

2.2.1 Electron beam additive manufacturing (EBAM™)

EBAM™ is an additive manufacturing technique that uses an electron beam as the heat source. A source wire is fed into the electron beam to create the molten pool in a vacuum chamber [3]. The vacuum provides a non-reactive environment, allowing the production of components of high purity materials. Fig. 1 shows a schematic view of the process [2].

The advantages of this process are high deposition rates and large build volumes [4]. However, the final component requires more machining than that deposits produced using powder based systems such as LENS™. An interesting aspect of this process is its future use in outer space, since it is conducted under vacuum [1].
2.2.2 Laser Engineering Net-Shaping (LENS™)

The LENS™ technology was developed by a cooperation between Sandia National Laboratories and Pratt & Whitney. In 1997, this technology was licensed by Optomec, Inc. Since 1997, LENS™ systems has been manufactured and distributed just by Optomec, Inc. [5] This additive manufacturing technique uses a laser beam as the heat source. A powder feed system supplies the metal powder required at the indicated level under the control of a regulated flow of mass. Instead of vacuum (i.e. that used for EBAM™), this process uses an argon atmosphere. This atmosphere keeps the moisture low and the levels of oxygen below 10ppm [6, 7]. Among the advantages of this process are that it can be used to repair as well as fabricate new parts, manipulation of more than one material (deposition of compositionally graded components) and the required machining for the final component is less. Fig. 2 shows a schematic view of the process [2].
2.3 Finite Element Analysis (FEA)

FEA is a numerical technique that captures complex conditions (e.g. boundary conditions) of a given problem, but with a solution that is the result of a numerical approximation [8]. This method was originally developed for structural analysis in mechanics. However, today it is used for the analysis of heat transfer, wave and ray optics, fluid flow and many others. Some of the popular packages are, ANSYS, ABAQUS, JMAG and COMSOL [8].

When applying FEA for real engineering problems, there are some unknowns that we seek to solve. Those unknowns are useful to predict the behavior of the system. The
unknowns are also called field variables. Field variables include velocities in fluid mechanics, temperatures in heat transfer, and displacements in solid mechanics. The finite element method transforms the infinite number of field variables into a finite number via segmentation of the geometry into space elements. Each element has its field variables expressed by functions [8]. Those functions are in turn defined by specific nodal points that have one or more field variables depending on the physics associated with the problem. Finding and assembling the element properties to link to global properties and establishing the boundary conditions that results in a system of equations that may be solved to determine the unknowns [8].

An approximate solution of a simplified model is the foundation of the finite element analysis (FEA) [9]. The total number of nodal points times the dependent variables from the physics involves are known as the degrees of freedom. They are the finite number of parameters that characterize the approximated solution and this is called discretization. It is normally expected that when the finite number of elements are large or trend to infinite, the finite element solutions converge to a solution that is independent of the choice for the particular discretization [9].

2.4 COMSOL Multiphysics® Package

FEMLAB® was a software designed to solve engineering problems applying the finite element method until 2005 and now is known as Comsol Multiphysics® [10]. The basis of the software are laws of physics described in mathematical models that for space and time dependent situations are partial differential equations (PDEs)[11]. These laws include different conservations laws, laws of classical mechanics and laws of electromagnetism [11].
The mathematical models are discretized by the Finite Element Analysis (FEA), resulting in numerical models that are solved and then analyzed. The solution of partial differential equations (PDEs) is given by the function of field variables (unknowns), also called dependent variables. As mentioned before, they include velocities in fluid mechanics, temperatures in heat transfer or displacements in solid mechanics [8]. The independent variables $x, y, z$ and $t$ are the space and time description of the solution [11]. The solution to the PDEs is the description of a given system that provides the capability to predict the operation for a device or a process.

The physics involved in the system can have one or more PDEs and each equation can have several different solutions. Therefore, the initial and boundary conditions provide the system with a single solution to the PDEs. Boundary conditions are specific restrictions on the system such as surfaces, edges or points. The initial conditions define the state of the system at the beginning of a time-dependent process. The suitable assignation of those initial and boundary conditions to the system determine if the problem is well posed to result in a unique solution. All errors associated with the convergence in the finite element solution should be analyzed under the reasonableness of the physical configuration (initial and boundary conditions) and the discretization (meshing) [10].

Theoretically speaking, it is difficult to determine if a realistic model is well-posed or not to get convergence to a unique solution. For this reason, highly simplified models are implemented to do the analysis. The results from those simplified models are the “raw material” to understand and estimate the behavior of more realistic models. However, it is important to note that even very well-posed models may be significantly affected by small changes in the model data [11].
The focus of this work is on 2D simulations of molten pool for additive manufacturing techniques which implies the use of physics (modules in Comsol Multiphysics®) such as heat transfer and fluid dynamics. In fluid flow, the descriptions are based on the laws of conservation of momentum (Navier-Stokes equation) and mass (continuity equation). Heat transfer is based on the law of conservation of energy, where the three mechanisms of heat transfer are conduction, convection and radiation. A wider description of these physics (modules) is provided in the subsequent section.

2.4.1 Heat transfer module

The heat transfer module is based on the conservation of energy in a system. The three mechanisms of heat transfer such as conduction, convection (conduction and advection) and radiation as well as heat sources and heat sinks are the factors that contribute to the balance of energy formulation. Fig. 3 from the introduction manual to heat transfer module shows the three mechanisms involve in the physics [12].

![Fig 3: A solid surrounded by a fluid showing the three mechanisms of heat transfer [12]](image)

Conduction is a mechanism of heat transfer for objects that are in physical contact, it follows the Fourier’s law where the heat flux is proportional to the gradient of temperature.
The heat transfer by convection takes place when a fluid flow is literally transporting the heat. If such transportation of heat is caused by a spontaneous movement of the fluid due to differences in density for a gradient of temperature, it is called natural convection. On the other hand, when an external force is acting on the system creating the fluid flow, it is called forced convection. Radiation is the transfer of heat that does not require a physical contact to act. It is just a transmission of energy by electromagnetic radiation [12].

\[ \rho C_p \frac{\partial T}{\partial t} + \rho C_p u \cdot \nabla T + \nabla \cdot (-k \nabla T + q_r) = Q \]  

Eq. 1

The balance of energy is established with equation 1. The first term on the left side represents the change of temperature with time. For a steady state condition this term disappears. The second term is for the heat transfer by convection. The last term describes heat transfer by conduction and radiation. On the right side of equation 1 the \( Q \) represents the heat sources or sinks that could be present in the system [13].

The thermophysical properties are the coefficients of the terms in equation 1:
- \( \rho \) = fluid density (kg/m\(^3\))
- \( C_p \) = fluid heat capacity at constant pressure (J/(kg.K))
- \( K \) = fluid thermal conductivity (W/(m.K))
- \( u \) = fluid velocity field (m/s)
- \( Q \) = heat source (or sink) (W/m\(^3\))
- \( q_r \) = heat flux by radiation (W/m\(^2\))
2.4.2 Fluid Dynamics Module (single phase field)

Two conditions, namely laminar flow and compressible Newtonian fluid, are assumed for simplicity. The partial differential equations associated to the single phase fluid interfaces are equation 2 (conservation of momentum (Navier-Stokes equation)) and equation 3 (conservation of mass (Continuity equation)) [14]. The solution provides the fluid velocity and pressure of a given system.

\[
\rho \frac{\partial u}{\partial t} + \rho (u \cdot \nabla) u = \nabla \cdot \left[ p I + \mu (\nabla u + (\nabla u)^T) - \frac{2}{3} \mu (\nabla \cdot u) I \right] + F \\
\text{Eq. 2}
\]

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = 0 \\
\text{Eq. 3}
\]

\(T = \) absolute temperature

\(\rho = \) fluid density (kg/m\(^3\))

\(u = \) velocity vector (m/s)

\(p =\) pressure (Pa)

\(\mu = \) dynamic viscosity (Pa.s)

\(F = \) external forces applied to the fluid (buoyancy, Marangoni etc.)

\(I = \) identity matrix

both terms on the left side of Eq. 2 represent the inertial forces. On the right side, the first term represents the pressure forces, the second and third terms represent the viscous forces and the fourth term (F) represents the external forces applied to the system. For Eq. 3 the
first term on the left side that expresses the variation of density with time disappears when
the fluid is considered incompressible due to low variations in temperature [15].

2.5 Modeling of Molten Pool Dynamics

Different models by finite element analysis have been developed to understand the
physics and predict the behavior of liquid metal depositions in several additive
manufacturing techniques under certain parameters. A pioneer 2D numerical model for
convection diffusion of matter in steels described how the particles are melted as soon as
they reached the molten pool [16]. Picasso and Hoadley [17] are possibly the first authors
taking into account the fluid motion and the liquid-gas interface changes. Toyserkani et al.
proposed a 3D transient model to understand the correlation between deposition geometry
and laser changes with time [18]. Pinkerton and Li presented a model that is able to track a
multiple-layer deposition. However, it assumes the thermophysical properties are
independent of temperature [19]. A 3D model using ABAQUS 6.7 was proposed to
understand the temperature distribution and melt pool dimensions. It uses cell activation to
represent the material addition and all properties are temperature-dependent, but it neglects
the fluid flow [20]. Morville et al. [21] developed a model that includes all fluid motion
aspects such as buoyancy and Marangoni. The mass addition is also considered and the
molten pool shape is described by a moving mesh Arbitrary Lagranian Eulerian (ALE)
method in a multilayer deposition. The thermophysical properties are temperature-dependent
and melting and solidification phase changes are also included. However, this model uses the
Boussinesq approximation instead of the full compressible formulation of the Navier-Stokes
equation for the buoyance term and the computational cost is very high.
In the present work, two simplified models apply the equations of conservation of energy, momentum and mass. It includes the buoyancy effect, but instead of using the Boussinesq approximation, it uses the full compressible formulation of the Navier-Stokes equation. The Benard-Marangoni effect is also included, but the molten pool shape and size evolution is not tracked to avoid the complexity and computational cost of using the deformed geometry or moving mesh. In contrast it uses a predefined geometry based on literature and experimental observations. The final aspect is that the computational cost is very low, allowing a calculation to be concluded in about 40 minutes. The objective of the EBAM™ model is to see the thermal distribution in the molten pool. However, the LENS™ model is intended to calculate cooling rates.

2.6 Microstructure and Grain Refinement in Titanium Alloys

Titanium has two allotropic forms, below 882 °C it is hexagonal close-packed and above 882 °C it is body-centered cubic structure [22]. In the aerospace and offshore oil and gas industries titanium and its alloys are widely used due to their good corrosion resistance and the high strength/weight ratio. Among titanium alloys, Ti-6Al-4V is the most widely used alloy, employed even in biomedical applications due to the good bulk mechanical properties [23]. Titanium alloys can be classified into three main groups [24]. The classification for titanium alloys is based on the resultant phases at room temperature as a result of compositional variations, and they are α and near α alloys, α + β alloys and β alloys.

The alloys Ti−3Al−2.5V, Ti-5Al-2.5Sn, Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo are considered into the group of α and near α alloys. The α alloys are commercially pure
titanium (CP) that has a variation of grades based on iron and oxygen content. These alloys contain elements that promote the stabilization of the $\alpha$ phase (e.g. Al, O, N, C, Sn) as well as small addition of elements that promote the $\beta$ phase (e.g. Mo, W, Nb, V) [24].

The $\alpha + \beta$ alloys are those with both phases stable at room temperature. The fraction of $\beta$ is more considerable compared to the first group due to greater additions of $\beta$ stabilizer alloy elements. Ti-6Al-4V is the most common alloy in this category. The microstructure of laser-deposited Ti-6Al-4V consists columnar prior $\beta$ grains with Widmanstätten $\alpha$ laths outlined in retained $\beta$ [25].

The $\beta$ alloys comprises those alloys whose metastable $\beta$ phase is stable at room temperature by quenching and without martensite formation. The solute concentration of $\beta$ stabilizers is greater than that of other two group. The alloys Ti-10V-2Fe-3Al and Timetal 21S (Ti-15Mo-2.7Nb-3Al-0.2Si) are good examples of this category. Alloys in this group offer reasonable cold rolling capabilities [24].

2.6.1 Grain refinement in titanium alloys

The grain refinement via addition of alloying elements in conventionally produced titanium alloys has been studied by several researchers due to the associated improvements of mechanical properties including strength and ductility. The grain refinement of cast alloys is typically due to the presence of inoculants, other compositional effects, and cooling rate. However, more recently considerations related to composition as the effects of thermodynamic parameters such as the growth restriction factor $Q$ and the undercooling factor $P$, defined in equations 4 and 5 as:

$$Q = m_i C_0(k - 1)$$ 

Eq. 4
where $k$ is the partition coefficient and $m_1$ is the slope of the liquidus curve [1, 26]. Some of the previous studies have focused on the contribution of a given solute species as a promoter of constitutional undercooling through the growth restriction factor $Q$. For instance, Tamirisakandala et al. [27] reported the effect of boron on the grain refinement of as-cast Ti-6Al-4V and Ti-6242 and Bermingham et al. [28] studied the same effect for as-cast commercially pure titanium. In these studies, an interpretation of the factor $Q$ is that the boron solute is rejected in front of the solid-liquid interface, forming a boron rich undercooled region that restricts the growth of pre-existent nuclei and necessarily increases the probability to activate new nuclei.

Applying a similar analysis, Easton and St. John [29, 30] developed a model for Al and Mg alloys to evaluate the grain refinement through a semi-empirical relationship that involves the contribution from the solute and the nuclei effects on grain size. The simplified equation is expressed in Eq. 6,

$$d = a + \frac{b}{Q}$$

where $d$ is the diameter of the grain, $a$ is the y-intercept, defined by Eq. 7,

$$a = \frac{1}{(\rho. f)^{1/3}}$$

In equation 7 $\rho$ is the density of nucleant particles and $f$ is the activated fraction of particles, thus the $a$ term is inversely proportional to the maximum number of activated nuclei. The term $b$ is defined as $b_1\Delta T_n$ where $b_1$ is a constant and $\Delta T_n$ is the undercooling necessary to
activate nucleation. Higher values of $b$ (the slope) represent lower potency of nuclei as they require a high undercooling ($\Delta T_n$) to be activated [29].

In experimental results of Easton and St. John for aluminum alloys [30] and magnesium alloys [31] the model was found to be in good agreement with the data. Additionally in more recent research work conducted by Bermingham et al. [28], the same model was applied to Ti refined by additions of silicon. The results were also in agreement with the Easton and St. John model, suggesting that it is also applicable to Ti alloys.

To select an alloying element as a grain refiner for Ti-based alloys some aspects should be considered. For example, B and Si both have the ability to reduce the grain size [27, 32]. Certainly it has to be effective in small additions to avoid deleterious results in the microstructure evolution [33] or the mechanical properties [34] beyond a certain composition limit $c_0$. When considering grain size by itself, it is clear that the growth restriction factor $Q$ should be high to promote fine grain sizes. Several solute elements in small amounts with a high growth restriction factor $Q$ have been evaluated in the past such as beryllium with the $Q$ factor of $72C_0$ [35], Boron with the $Q$ factor of $66C_0$ [28], and silicon with the $Q$ factor of $21.7C_0$ [33]. Tungsten is among the elements with a high $Q$ factor of about $22.65C_0$, which has been largely neglected in the literature. These elements, as well as other potential binary systems [35] are given in Table 2. Generally, the Ti-W system is ignored due to the high melting point of W (3540 K) and the high density of 19.25 g/cm$^3$ [36]. The unmelted W particles in the build are classified as high-density inclusions, for which advanced titanium melt practices have been designed to eliminate. In conventional melting processes, W shows a strong solute partitioning in Ti and leads to compositionally inhomogeneous structures, reducing the technical advantages for aerospace applications. However, as noted above, it
does have the potential to reduce the grain size due to its high growth restriction factor, which may be of benefit in certain applications.

Table 2. Calculated values for several elements in titanium

<table>
<thead>
<tr>
<th>Element</th>
<th>m₀</th>
<th>k</th>
<th>Q = m₀(k-1)C₀</th>
<th>P = m₀(k-1)C₀/k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>-2.1</td>
<td>→1</td>
<td>→0C₀</td>
<td>→0C₀</td>
</tr>
<tr>
<td>B</td>
<td>-66</td>
<td>→0</td>
<td>66C₀</td>
<td>660C₀</td>
</tr>
<tr>
<td>Be</td>
<td>-92</td>
<td>0.21</td>
<td>72C₀</td>
<td>343C₀</td>
</tr>
<tr>
<td>C</td>
<td>70</td>
<td>6.4</td>
<td>378C₀</td>
<td>59C₀</td>
</tr>
<tr>
<td>Cr</td>
<td>-8.1</td>
<td>0.81</td>
<td>1.54</td>
<td>1.85C₀</td>
</tr>
<tr>
<td>Cu</td>
<td>-10.6</td>
<td>0.39</td>
<td>6.5C₀</td>
<td>16.6C₀</td>
</tr>
<tr>
<td>Fe</td>
<td>-18</td>
<td>0.79</td>
<td>3.8C₀</td>
<td>4.8C₀</td>
</tr>
<tr>
<td>Mo</td>
<td>8.9</td>
<td>1.5</td>
<td>4.5C₀</td>
<td>2.96C₀</td>
</tr>
<tr>
<td>Nb</td>
<td>10</td>
<td>1.25</td>
<td>2.5C₀</td>
<td>2C₀</td>
</tr>
<tr>
<td>Si</td>
<td>-32.5</td>
<td>0.35</td>
<td>21.7C₀</td>
<td>62C₀</td>
</tr>
<tr>
<td>V</td>
<td>-4.7</td>
<td>→1</td>
<td>→0C₀</td>
<td>→0C₀</td>
</tr>
<tr>
<td>W</td>
<td>15.1</td>
<td>2.5</td>
<td>22.65C₀</td>
<td>9.06C₀</td>
</tr>
</tbody>
</table>

Additionally, W is an isomorphous β-stabilizer and does not form intermetallic compounds, in contrast with B, Be, and Si (see Fig. 4(a-d)). It is also important to mention that during additive manufacturing; strong solute partitioning will not operate at the same level as in conventional melt/ingot processes. In this study, the operating mechanism with regards to the grain refinement effect of W has been explored as a model alloying element to Ti, across a wide composition range, via a compositionally graded Ti-xW specimen (0 ≤ x ≤ 30 wt%) which was produced using Laser Engineered Net Shaping (LENS™) technology.

1 The m, k, Q, and P are all ‘average’ values from phase diagrams, or as reported in the literature.
Fig 4: Phase diagrams of (a) Ti-B (b) Ti-Be (c) Ti-Si (d) Ti-W.
CHAPTER 3

PROCEDURE

3.1 EBAM™ and LENS™ Models

The proposed 2D finite element models emulating the parameters of EBAM™ and LENS™ systems implement the conservation of energy, momentum and mass equations. The thermophysical properties\(^2\) (temperature dependent) [21, 37] and parameters used in both models for the calculations are summarized in Table 3 (for EBAM™ system) and Table 4 (LENS™ system). The liquid phase region (assumed laminar flow and compressible Newtonian fluid) includes the buoyancy and Marangoni effects. The set of equations are coupled and solved using the commercial package COMSOL Multiphysics®.

3.2 Compositional Gradient Ti-xW (0 ≤ x ≤ 30 wt%) and 9 Depositions of Ti-6W (wt%)

A compositionally graded Ti-xW (0 ≤ x ≤ 30 wt%) specimen was produced using an Optomec LENS™ 750 at the University of North Texas from high purity elemental metal powders of Ti (99.9% pure, −150 mesh from Alfa Aesar) and W (99.8% pure, plasma spray grade from Micron Metals). In this first AM system, the laser is a fixed optic Nd:YAG laser with a wavelength of 1064nm provided by US Laser Corp. The laser was operated between 350-500W power, and the argon atmosphere was kept below 20ppm oxygen. In addition, a series of Ti-6wt%W alloys were deposited using an Optomec LENS™ system at Ames.

\(^2\) Ti-6Al-4V thermophysical properties (temperature dependent) are used due to the wide availability of information about this Ti-Alloy.
Laboratory. In this second AM system, the laser is a fiber optic Nd:YAG laser with a wavelength of 1064nm provided by IPG. The IPG laser was operated between 183-367W power, and the argon atmosphere was kept below 5ppm oxygen.

Table 3. Parameters used for the EBAM™ system model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small square</td>
<td>0.007</td>
<td>( w_0 (m) )</td>
</tr>
<tr>
<td>Big square</td>
<td>0.01</td>
<td>( h_0 (m) )</td>
</tr>
<tr>
<td>Emissivity</td>
<td>0.4</td>
<td>( \varepsilon )</td>
</tr>
<tr>
<td>Dynamic viscosity</td>
<td>( 4 \times 10^{-3} )</td>
<td>( \mu_0 (Pa.s) )</td>
</tr>
<tr>
<td>Electron beam exposure length</td>
<td>0.0035</td>
<td>( r_0 (m) )</td>
</tr>
<tr>
<td>Electron Beam power</td>
<td>( 1 \times 10^7 )</td>
<td>( P (W/m^2) )</td>
</tr>
<tr>
<td>Thermocapillary coefficient</td>
<td>( -2.7 \times 10^{-4} )</td>
<td>( \gamma (N/m.K) )</td>
</tr>
<tr>
<td>Liquidus temperature</td>
<td>1923</td>
<td>( T_L (K) )</td>
</tr>
<tr>
<td>Density (Liquid phase)</td>
<td>( 5227.6-0.688*T(K) )</td>
<td>( \rho_l (Kg/m^3) )</td>
</tr>
<tr>
<td>Density (solid phase)</td>
<td>( 4462.6-0.1425*T(K) )</td>
<td>( \rho_s (Kg/m^3) )</td>
</tr>
<tr>
<td>Thermal conductivity (Liquid phase)</td>
<td>( -12.752+0.024*T(K) )</td>
<td>( \lambda_l (W/(m.K)) )</td>
</tr>
<tr>
<td>Thermal conductivity (Solid phase)</td>
<td>( 3.5127+0.0127*T(K) )</td>
<td>( \lambda_s (W/(m.K)) )</td>
</tr>
<tr>
<td>Specific heat capacity (Liquid phase)</td>
<td>831</td>
<td>( c_p (J/(Kg.K)) )</td>
</tr>
<tr>
<td>Specific heat capacity (Solid phase)</td>
<td>( 412.7+0.1801*T(K) )</td>
<td>( c_p (J/(Kg.K)) )</td>
</tr>
</tbody>
</table>

In both of these LENS™ systems, a computer-aided design (e.g. CAD) file is used, from which a tool path is extracted for the subsequent laser deposition of a three dimensional specimen. The CAD file is converted and sliced into layers with a nominal thickness of
0.25 mm. Each layer consists of multiple parallel lines with a nominal hatch width of ~0.38 mm. The tool path that is generated based upon these variables is used to control the motorized stages for in-plane motion (x-y directions) and a deposition head consist of focusing lens and powder nozzles mounted on the motorized stage that provides motion in z direction. The 2D (x,y) in-plane motion of the stage accompanied by -z vertical motion of the deposition head produce near-net-shape metallic pieces.

Table 4. Parameters used for the LENS™ system model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate width</td>
<td>0.003</td>
<td>w₀(m)</td>
</tr>
<tr>
<td>Substrate height</td>
<td>0.003</td>
<td>h₀(m)</td>
</tr>
<tr>
<td>Emissivity</td>
<td>0.4</td>
<td>ε</td>
</tr>
<tr>
<td>Dynamic viscosity</td>
<td>4 x 10⁻³</td>
<td>μ₀(Pa.s)</td>
</tr>
<tr>
<td>Laser beam radius</td>
<td>5 x 10⁻⁴</td>
<td>r₀(m)</td>
</tr>
<tr>
<td>Laser power</td>
<td>183-259-367</td>
<td>P(watts)</td>
</tr>
<tr>
<td>Thermocapillary coefficient</td>
<td>-2.7 x 10⁻⁴</td>
<td>γ (N/m.K)</td>
</tr>
<tr>
<td>Absorption*</td>
<td>15%</td>
<td>----</td>
</tr>
<tr>
<td>Liquidus temperature</td>
<td>1923</td>
<td>T_L(K)</td>
</tr>
<tr>
<td>Density (Liquid phase)</td>
<td>5227.6-0.688*T(K)</td>
<td>ρ_l(Kg/m³)</td>
</tr>
<tr>
<td>Density (solid phase)</td>
<td>4462.6-0.1425*T(K)</td>
<td>ρ_s(Kg/m³)</td>
</tr>
<tr>
<td>Thermal conductivity (Liquid phase)</td>
<td>-12.752+0.024*T(K)</td>
<td>λ(W/(m.K))</td>
</tr>
<tr>
<td>Thermal conductivity (Solid phase)</td>
<td>3.5127+0.0127*T(K)</td>
<td>λ(W/(m.K))</td>
</tr>
<tr>
<td>Specific heat capacity (Liquid phase)</td>
<td>831</td>
<td>c_p (J/(Kg.K))</td>
</tr>
<tr>
<td>Specific heat capacity (Solid phase)</td>
<td>412.7+0.1801*T(K)</td>
<td>c_p (J/(Kg.K))</td>
</tr>
</tbody>
</table>

* Laser absorption based on experimental results from other authors [38].
Two separate aspects of this research were conducted. The first research activity used the fixed-optic laser equipped with two powder feeders to assess the influence of W on the microstructure, in particular on the grain size. To conduct this first research activity, the LENS™ is equipped with two independently controlled powder feeders which were loaded with pure Ti powder in powder feeder #1 and with a Ti–30 wt% W mechanically mixed elemental powder blend in powder feeder #2. An inert gas (here Ar) carries the powders from powder feeders into a controlled atmosphere box. The fluidized powders are injected (via four convergent Cu nozzles) into a localized melt pool created by a focused high energy Nd:YAG laser. A 6 mm thick Ti-6Al-4V substrate was used as the base for laser deposition of the powder blend and in-situ alloying. The dimensions of the graded specimen deposit were 38 mm × 25 mm × 12 mm in form of a rectilinear solid. The independently computer controlled powder feeders allow for pre-programmed incremental changes in the relative mass flow rate from powder feeders and consequently variation in the local composition along the length of the sample.

For the second research activity the LENS™ system with fiber-optic laser was used to assess the influence of processing parameters on the microstructure. Specifically, in this second study the travel speed was changed between ~8.5mm/sec and ~12.5mm/sec to vary the energy density between ~149 kJ/cm³ and ~448 kJ/cm³ [39]. A total of nine depositions were made with a range of energy densities. The geometry of these deposits are cylinders with a diameter of 7.62mm and a height of 12.7mm.

Following depositions, the deposits were sectioned from the substrate. These were then prepared for materials characterization using conventional metallographic techniques. The sections were ground using 240-800 grit wet/dry SiC abrasive papers followed by
polishing using a 0.04 μm colloidal silica suspension. Following preparation, the specimens were then cleaned using a different solutions including acetone, water-surfactant mixture, water, and methanol. Imaging of the microstructure was carried out using a FEI™ Quanta 250 FE-SEM equipped with field emission gun (FEG) source and backscatter detector. The local compositions along the graded specimen were determined by standardless energy dispersive spectroscopy (EDS) and reported to the nearest whole wt.%. Average grain size measurements following the Planimetric procedure [40] were conducted for further analysis and interpretation.
4.1 EBAM™ Model

Comsol Multiphysics® can help understand the temperature distribution into the molten pool. This understanding could help to indicate the preferential direction of the solidification front that is parallel to the greatest gradient of temperature in the molten pool. This approach has an exposure time of 0.5s to the heat source from a total modeling time of 1s as shown in Fig. 5. This exposure time is an estimation from the scanning velocity of the electron beam and the size of the molten pool.

Fig. 5: Exposure time to the heat source of 0.5s.
The geometry of the model, initial temperatures and the used material are schematized in Fig. 6.

Fig. 6: Geometry of the model.

To predict the temperature distribution in the molten pool, two different conditions were evaluated. In the first condition (see Fig. 7(a)) the model applied just the Heat Transfer module (ht) which involves the three mechanisms of heat transfer. On the other hand, in addition to the three mechanisms of heat transfer previously considered, the second condition included the buoyance and Marangoni effects through the Fluid Dynamics module (see Fig 7(b)). Finally, a comparative analysis to understand the differences between the two conditions, followed by an identification of the preferential direction of the greatest thermal gradient was performed.
Three specific times 0.2s-0.6s-0.8s from the time-dependent solution are presented to evaluate the thermal gradients along several directions under both aforementioned conditions. The times 0.2s and 0.6s are selected because they represent the maximum power at the beginning and at the end of heat source exposure. The time 0.8s is selected because it represents the solidification stage when the heat source is removed. Fig. 7 shows the resultant isotherms at 0.2s. The left molten pool is under the first condition and the right molten pool under the second condition. At first glance the isotherms on left side are more uniform, showing little perturbation on their shape. In contrast, the right side shows more deformed isotherms due to the Marangoni and buoyance effects. It is clear that those effects are important and should be considered to evaluate the thermal distribution in a molten pool. In order to identify the preferential direction of the greatest thermal gradient, several straight lines (blue, green, red and light blue) are imposed in Fig. 7 and plot in Fig. 8 to evaluate the temperature along their respective distance (towards the molten pool).

Fig. 7: Molten pool isotherms at 0.2s (a) No fluid dynamic effects (b) with fluid dynamic effects.
Fig. 8: Temperature vs distance curves for imposed lines (color lines) of molten pool at 0.2s (a) No fluid dynamic effects (b) with fluid dynamic effects.
The thermal gradients (slope) for each selected direction are presented in Fig. 8. The color of each curve matches with the color of the imposed lines in Fig. 7 (e.g. the horizontal line is blue on both figures). As a first observation all directions in the first condition (see Fig. 8(a)) have a very similar thermal gradient. On the second condition (see Fig. 8(b)) the thermal gradients for the horizontal and inclined (16.7°) directions (blue, red and light blue) are greater than for the vertical direction (green line). Comparing the two conditions is also qualitative observable that the thermal gradients for condition 2 are greater than condition 1. Therefore, from time 0.2s can be extracted that the preferential direction for the greatest thermal gradient is the horizontal direction and it is more realistically represented by the model at condition 2 which includes those fluid flow effects. Under this premise the subsequent analysis is more focused on the second condition.

Another result from this analysis is the apparent expansion of the molten pool on its width and shrinking on its depth as reported in other studies [41]. The black vertical line (see Fig 7(a)(b)) that stands for the surface reference point at the solid/liquid interface indicates a small displacement to the left of the interface located at 0.01m according to the geometry of the model (see Fig. 6). However, the model assumes a predefined geometry to avoid the complexity of the deformed mesh. Therefore, the displacement of the solid/liquid interface guided by the isotherms is just an approximation that shows a simple trend and not an accurate position of the mentioned interface. The analysis for the thermal gradient along the set of directions inward the molten pool is then performed using the predefined position of the solid/liquid interface.
Fig. 9: Molten pool isotherms at 0.6s (a) No fluid dynamic effects (b) with fluid dynamic effects.

At the time of 0.6s, the isotherms at condition 1 (see Fig. 9(a)) shows again a more uniform shape compared with the more perturbed shape under condition 2 (see Fig. 9(b)). Due to the apparent more disrupted distribution of the isotherms, two more inclined lines are imposed at different angles with respect to the vertical direction (21.8° and 81.5°) to observe the thermal gradient. In Fig. 10(b), the gradient of temperature (second condition) for the horizontal and all inclined lines (blue, red and purple) is lesser than the vertical line (green line). This result indicates that at 0.6s the preferential direction for the greatest thermal gradient is the vertical direction.
Fig. 10: Temperature vs distance curves for imposed lines (color lines) of molten pool at 0.6s (a) No fluid dynamic effects (b) with fluid dynamic effects.
Fig. 11: Molten pool isotherms at 0.8s (a) No fluid dynamic effects (b) with fluid dynamic effects.

At 0.8s the thermal gradients (see Fig. 12(b)) for the horizontal and inclined lines (blue, light blue and red) are lesser than for the vertical line (green line). Consequently, as similarly reported at the previous time of 0.6s, this results at 0.8s indicate that the preferential direction for the greatest thermal gradient is the vertical direction (z direction). As a first conclusion, it is clear that the physical phenomenon is better represented or at least more realistic by the second condition where the fluid flow effects are under consideration. Also even when at the beginning of the time dependent simulation (0.2s) the preferential direction was the horizontal, this trend changed to be more favorable to the vertical direction at 0.6s and 0.8s times. Those times represent the moment where the exposure to the heat source is being removed (solidification stage). Therefore, the results indicate that the grain growth is more favorable towards the <001> direction in additive manufacturing techniques, that despite the technical differences, the physics involved is the same. As a complementary result Fig. 13 show the fluid flow at several times.
Fig. 12: Temperature vs distance curves for imposed lines (color lines) of molten pool at 0.8s (a) No fluid dynamic effects (b) with fluid dynamic effects.
4.2 LENS™ Model

A 2-Dimensional thermal model was also developed to determine the maximum temperature and the cooling rate [42] in a molten pool created during LENS™ process. This approach has an exposure time of 0.07s from a total modeling time of 0.1s as shown in Fig. 14. Similarly, as for the EBAM™ model the exposure time is estimated based on the laser scanning velocity and molten pool size. Also the geometry of the model, initial temperatures and the used material are schematized in Fig. 15.
Fig. 14: Exposure time to the heat source of 0.07s.

Fig. 15: Geometry of the model.

The calculations were carried out at three different powers 183W, 259W and 367W for the same conditions parameters. The last times where the heat source exposure is removed were
selected to evaluate the maximum temperature and then calculate the cooling rates for each case. Fig. 16 shows one of the temperature profile for the condition of 183W and a time of 0.09s. The resultant cooling rates are 6530 K/s for 183W, 5980 K/s for 259W and 5560 K/s for 367W. These calculated cooling rates are in well agreement with the specific range of $10^3$ and $10^4$ K/s for rapid solidification in LENS™ process reported by Zheng et al. from experimental [43] and computational results [2, 44]. The maximum temperatures in the molten pool calculated by the Comsol Multiphysics® model are 2652 K, 2876 K and 3209 K for the heat source powers of 183W, 259W and 367W respectively. The average thermal gradient for the power of 367W is 5050 K/cm. An experimental 3D spatial reconstruction of thermal characteristics in LENS™ process reported by Kriczky et al. [45] shows maximum temperatures of 2818 K and average thermal gradient of 7871 K/cm for a measured power of 350W. The 3D thermal reconstruction was acquired by a sequence of coaxial images of individual layers with a Stratonics, Inc. optical sensor, and the deposited material was Ti-6Al-4V. Comparing our computational results with the experimental results from literature, it is observable that the calculated maximum temperatures and thermal gradients are in close agreement. In addition, other computational results of maximum temperature reported by Thijs et al. [46] are in the order of 3000 K for a single layer. The cooling rate results from the Comsol model indicate that inasmuch the power is increased the cooling rate decreases. It is also important to note that the cooling rate is inversely proportional to the grain size [47, 48]. Therefore, the grain size increases as the power (energy density)$^3$ increases.

---

$^3$ Energy density is defined as: $\rho_{\text{energy}} = \frac{P}{v \cdot \text{layer spacing} \cdot \text{hatch width}}$ where $P$ is the laser power, $v$ is the velocity of the laser, $\text{layer spacing}$ is the layer spacing, and $\text{hatch width}$ is the distance between passes.
4.3 Grain Refinement in a Compositional Gradient Ti-xW (0 ≤ x ≤ 30 wt%)  

The reduction of grain size has shown to optimize the strength or corrosion fatigue resistance for some Ti-alloys [26]. Texture is another problem that can be reduced by promoting nucleation of new equiaxed grains due to the contribution of the constitutional undercooling. Backscattered electron micrographs taken along the graded specimen from the regions with the local average compositions of 5%W, 13%W and 25%W are shown in figure 17. In the three micrographs the features are α laths within prior β grains, regardless of the variation in size and the phase fraction. At first glance, it is evident that inasmuch the tungsten content increases, the grain size is getting reduced and the shape is more equiaxed. However, a brief discussion about
previous studies related to grain refinement in titanium alloys will be useful to understand the approach and the applicability of the Easton & St. John model on the Ti-xW analysis.

Fig. 17: Backscatter SEM micrographs corresponding to the local average compositions of (a) Ti-5W, (b) Ti-13W, (c) Ti-25W.

In a study performed by Bermingham et al., a significant grain refinement on Ti-Si alloy (from 600 to 200 µm) was observed with small addition of Si (i.e. 0.05-0.9 wt%) [33]. On their analysis, they compared the grain refinement results with another study performed on the same Ti-Si system by Zhu et al. [32]. Additions of silicon up to 2.75 wt% caused an even greater grain refinement (up to 92%) in the system. The Easton and St. John equation (grain size vs the inverse of $Q$) for both studies is schematically shown in Fig. 18 for comparison. As observed in figure 18, the slope ($b$ term in the model) of the plot by Bermingham et al. is much lower than that of Zhu et al. which means that the potency of nuclei (inversely proportional to the necessary undercooling to activate nucleation $b = b_1 \Delta T_n$) is greater in their work. The projected y-intercept $a$ is lower for the Zhu et al. curve, indicating that the number of activated nucleant particles is higher.
The Bermingham conclusion for such comparison is that the refinement for Zhu et al. according to the curve comes from a high population of low potency nuclei and the refinement from his study comes from a low population of high potency nuclei [33]. However, Bermingham et al. did not provide the explanation for the slope discrepancy on the curves for the same Ti-Si system. A possible reason could be the proportionality between the undercooling factor expressed as $P = 62C_0$ (Ti-Si system) and the $b$ term of the Easton and St. John equation. The range of composition for the Zhu’s work (up to 2.75 wt%) was greater than for the Bermingham’s work.

![Graph showing the Easton & St. John model for two different Ti-Si studies.](image)
The understanding of the Easton & St. John model [29, 30] is important because it allows (via the \(b\) term) a preliminary prediction of the potency of nuclei for the given system. Also the term \(a\) provides information related to the role of the nucleant particles. In this specific cases for Ti-Si system the curves are straight lines which means that the population of nucleant particles is constant. Nevertheless, the origin of those nucleant particles was unclear. Bermingham et al. did not observe any silicide compounds in the microstructure and the Ti-Si phase diagram does not show any intermetallic to be present in the liquid before the primary solidification [33]. On the other hand, Zhu et al. reported titanium silicide (Ti\(_5\)Si\(_3\)) just after a composition of 1.33wt\% and it occurs after the primary solidification which means that they cannot act as nucleant particles. Therefore, the possible origin of those nucleant particles should be from impurities in the base material or the silicon additions [33].

The different results for the same system shows that more studies related to grain refinement via solute additions are required [33]. A study performed previously by Tamirisakandala et al [27] on the Ti-B system, showed how the solute mechanism through the growth restriction factor is driving the grain refinement. However, this study omitted the nucleant particles population mechanism. Regarding the fact that the nucleant-mechanism should be always considered, Bermingham et al. [28], performed another study on the same Ti-B system to take into a count the nucleant mechanism. They found that the predominant mechanism is the solute addition, validating the initial assumptions made by Tamirisakandala for this specific case.

Bermingham et al. posed a more general approach to evaluate the mechanisms involve in the grain refinement in titanium alloys [26]. The approach presents two scenarios. The first scenario is a solute-based mechanism where the grain refinement is increasing with solute content until reaching a saturation point that depends of a pre-established nucleant particles
population available (see Fig. 19(a)). On the other hand, the second scenario is a nuclei-based mechanism where the solute addition is increasing the nucleant particles population which in turn increases the grain density (grain refinement) without the previous saturation point (see Fig. 19(b)). The two possible scenarios in Fig. 19 are implemented in this research work to assess the grain refinement in the Ti-W system.

![Fig. 19: Schematic representation of a) Solute-based mechanism and b) nuclei-based mechanism](image)

To implement the discussed concepts about the two different possible scenarios that potentially reveal the governing grain refinement mechanism in Ti-W system, the $Q$ factor should be calculated and the corresponding Easton and St. John curve should be plotted. The expected Easton and St. John curve for Ti-W system with an undercooling factor expressed as $P = 11.2C_0$ and tungsten additions that increase the nuclei population (unmelted particles), is a curve with a high slope and a continuous decay in the projected y-intercept. Fig. 20(a) shows the grains size vs the solute addition of tungsten.
Fig. 20: Plots of a) grain size as a function of W concentration. (b) Easton and St. John model

It can be seen that the most probable grain refinement scenario for Ti-W system is the second scenario, i.e. nuclei-based mechanism (see Fig. 20(a) and 19(b)). Despite the high growth restriction factor of $Q = 22.65$, the second scenario (b) has the best agreement for Ti-W system. The $m$ parameter is higher at very low concentrations of tungsten. However, the Easton & St. John model has the assumption that the parameters $m$ and $k$ are independent of the solute concentration [49]. Therefore, the growth restriction factor is proportional to the solute content.
and the general value of 22.65 is a reasonable value. Fig. 20(b) shows the implementation of the model on the Ti-W data. The slopes of tangential lines on the curve are as high as expected from the high growth restriction factor. However, the continuous decay in the projected y-intercept \(a\) inasmuch the solute content increases (lower \(1/Q\)) indicates that the nucleant particles population in increasing proportionally with that solute addition. The constant presence of unmelted particles in additive manufactured Ti-W alloys is an indicative of the origin of those new nucleant particles (see Fig. 22).

4.4 The Ti-6W Alloy – Effect of Energy Density in LENS™ Processing

4.4.1 Unmelted particles

A theoretical calculation performed with the heat capacity equation for Ti-6Al-4V (temperature dependent) and including its latent heat of fusion to estimate the energy density required to melt and heating up to 3209 K for a Ti-alloy (Ti-6Al-4V), gives a result of 10.8 kJ/cm\(^3\). This value of energy density represents an absorption of \(\sim 8\%\) from an applied energy density of 149kJ/cm\(^3\) (lowest energy density used in the Ti-6W system). This result shows a reasonable agreement with the experimental absorption lower than 15% reported by Peyre et al. [38]. The relationship between unmelted particles and energy density is shown in Fig. 21 and 22. The trend is evident, inasmuch the energy density increases the fraction of unmelted particles decreases. If the unmelted particles decrease, the population of nucleant particles theoretically speaking should also decreases. Thus from this perspective the grain size should increases proportionally to the energy density. As expected the as-deposited microstructure corresponding to the lowest energy density level 2.4MJ/in\(^3\) (\(\sim 149 \text{ kJ/cm}^3\)) contains multiple lack of fusion regions of different sizes (see Fig. 22(a)).
Fig. 21: Fraction of unmelted particles as a function of energy density.

Fig. 22: Backscatter electron micrographs for two deposited specimens (a) 2.4MJ/in³ (~149 kJ/cm³) and (b) 7.4MJ/in³ (~448 kJ/cm³).
The compositional variation along the specimens can be tracked through the contrast in the backscatter electron micrographs. The contrast is governed by the atomic mass of the present elements. For this reason, the brighter regions correspond to regions that are more tungsten rich, while the darker gray regions correspond to regions that are tungsten lean. This tendency is clear in Fig. 22(a), as well as Fig. 23, which was acquired from a specimen deposited at 5.4 MJ/in³ (~328 kJ/cm³). The darker (Ti-rich) regions (see Figs. 22(a) and 23(a)) tend to be near the bottom of the molten pools and near W particle clusters, which may be due to the combination of lower superheats and local heat extraction of the W particles, which require additional energy to reach their melting points and then melt. Fig. 23(b) shows how the variations in composition have a direct effect on phase transformations. The brighter regions (W rich regions) has a less fraction of $\alpha$ laths compared with darker regions (Ti rich region). This effect is explained by the $\beta$ stabilizer effect of tungsten.

Fig. 23: Backscatter electron micrographs for a specimen deposited at 5.4 MJ/in³ (~328 kJ/cm³).
4.4.2 Tungsten effect on local chemistry

Fig. 23 has a series of insets identify as a-1, a-2, and a-3. Those insets show a cellular or dendritic structure with a length scale of ~10µm. It is expected that the growing direction of those dendrites is along the direction that has the greatest thermal gradient as a morphological instability. As indicated in the initial simulation with COMSOL Multiphysics®, the direction of greatest thermal gradient corresponds to the <001>β direction. However, the inset (a-2) shows a slightly inclination in the preferential direction of growing. A possible reason for this deviation could be a complex interaction between adjacent molten pools during the remelting process or an unpredictable effect from the fluid dynamics.

Fig. 24: Backscatter electron micrographs with the compositional variations (at energy density of 7.4MJ/in³) (~448 kJ/cm³).
Fig. 24 shows a series of micrographs taken at increasing magnifications, and culminating in Fig. 24(d). In figures 24(c-e) the compositional variation across the columnar grain is evident and is analyzed using standardless EDS for the line shown in Fig. 24(d). The periodic structure (~7 µm) (see Fig 24(e)) from the standardless energy dispersive spectroscopy shows a variation ranged from ~5.5 to 6.5 wt%W. These results correspond with the classical definition of a morphological instability and confirm the preferential grain growth direction parallel to the greatest thermal gradient. In addition, the dendrite arm spacing extracted from the periodic structure (~ 7 µm) is in good agreement with the predicted range of 5-14 µm from a microscale Lattice Boltzmann-Cellular Automata (LB-CA) model that proceeds with the combined fluid flow, solute transport, and solidification for a binary Ti-6 wt%W alloy melt. (M. Rolchigo, private communication, September 9, 2016).

**4.4.3 Effect of power on grain size**

To evaluate the effect of power on the average *minimum* grain size, Fig. 25(a) shows grain size vs energy density. It is clear that as the energy density increases the grain size also increases. Fig. 25(b) shows the measured grain size with the corresponding cooling rate calculated previously by the COMSOL Multiphysics® model. Both results converge to the proportionality between grain size and energy density (inversely proportional to cooling rate). This proportionality between the average minimum grain size and the energy density (represented by the power) may be affected by two main factors. As the energy density increases the population of unmelted particles is less, which suggest a less availability of nucleant particles to increase the grain density (reducing the grain size). The second factor is related to the molten pool size. As the energy density increases the molten pool size also increases. Therefore, the
cooling rates should decrease with the molten pool size, as is effectively observed in the
calculation performed with the computational model.

Fig. 25: Grain size as a function of (a) energy density) and (b) cooling rate.
CHAPTER 5

CONCLUSIONS

This work was based on several critical aspects related to additive manufacturing processing from two different approaches. The first approach was via simulation where the analysis of temperature distribution and the cooling rates in the molten pool were evaluated. The second approach was the deposition of several Ti-W specimens to observe the energy density and compositional effects on the microstructure.

The temperature profile of molten pool, modeled using COMSOL Multiphysics®, shows how important are the fluid dynamics effects (buoyance and Marangoni) on the resultant isotherms. It was shown that the preferential grain growth direction at $<001>_{\beta}$ is promoted by the fluid dynamic effects and the same phenomenon was observed in the Ti-6W specimens. A compositionally graded Ti-xW specimen ($0 \leq x \leq 30$ wt%) was produced using LENS™ to study the grain refinement effect of tungsten and the associated mechanisms in Ti-based alloys. A significant reduction in the grain size was observed from $> 170 \mu m$ to $\sim 30 \mu m$ with addition of up to 23 wt% W. To understand the operating mechanisms of grain refinement, the Easton and St. John model was applied which fitted well for Ti-W system. A comparison of previous results from other researchers provided the understanding to predict the tendency of the curve and then separate the concepts of the solute-based mechanism and the nuclei-based mechanism to reduce the grain size. The Ti-W system did not show any indication of grain refinement saturation point in the studied composition range. The nuclei population is increasing with the solute addition and the significant $Q$ factor of 22.65$C_0$ is consistent with the second scenario, but with a considerable
additional solute effect. Therefore, the Easton and St. John model is a good method to analyze and interpret the grain size refinement in additively manufactured Ti-based alloys.

The relationship between energy density and grain size from the nine specimens revealed the tendency to increase the prior beta grain size inasmuch energy density is augmented. The more absorbed energy the greater is the size of the molten pool which in turn implicates lower cooling rates. The decreasing cooling rates calculated using the COMSOL Multiphysics® simulation are concordant with the increasing prior beta grain size across the studied energy density range.
REFERENCES


