USE OF TWO-PISTON SPLAT QUENCHING TO INVESTIGATE AND CHARACTERIZE THE IMPACT OF COMPOSITIONAL VARIATIONS ON RAPID SOLIDIFICATION MICROSTRUCTURES AND SUB-MICROSCALE FEATURES IN STAINLESS STEEL ALLOYS

by

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A DISSERTATION

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ABSTRACT

The objective of this dissertation was to use two-piston splat quenching (SQ) to investigate the impact of compositional modifications on the solidification and microstructure of rapidly solidified austenitic stainless steels (SS) and to demonstrate the ability of SQ to quickly and effectively simulate rapid solidification conditions similar to those found in powder bed fusion (PBF) additive techniques. PBF techniques like laser powder bed fusion (LPBF) are being implemented across a breadth of research and industrial applications to create parts with complex geometries and performance capabilities while pushing the current limits of processing conditions and understanding of material systems. In this work, SQ was used to experimentally produce rapid solidification in 20+ unique austenitic SS compositions with systematic variations of the chrome and nickel equivalency ratio (Cr/Ni_{eq}) through targeted compositional modifications. From the targeted change of Cr, Ni, and Mo concentrations in rapidly solidified SS alloys, the ferrite solidification mode was found to be the primary solidification mode at significantly lower Cr/Ni_{eq} than previously predicted for RS. Also, decreasing concentrations of Fe at a constant Cr/Ni_{eq} ratio (i.e., different Fe isopleths), or increased Mo concentrations at a constant Cr/Ni_{eq} ratio were found to suppress the ferrite to austenite massive transformation when compared to alloys with lower concentrations at the same Cr/Ni_{eq}. Using an established empirical relationship between cell size and cooling rate, the SQ technique was estimated to produce cooling rates between 10^6 and 10^8 K/s. Thermal gradients were extracted from 2-D heat transfer simulations of the SQ solidification event and used with these cooling rates to produce solidification rate estimates for SQ which were between 0.4-1.6m/s. The primary solidification
mode was observed to be the determining factor in which elements segregated to the cell
boundaries during RS, for which Cr and Mo were the main elements to segregate during primary
austenite solidification and Ni during primary ferrite solidification. Finally, the solidification
rates and conditions produced by SQ experiments resulted in similar microstructures, features,
and microsegregation to what was found in LPBF samples of the same feedstock.
DEDICATION

I dedicate this dissertation to my family, friends, and Man’s Best Friend. To my parents, Ron and Anne Hasenbusch, for being a limitless source of encouragement, motivation, and support throughout my entire academic career and life. To the rest of my family and friends, who have been there for me through every step of this journey. To my Irish Wolfhound, Theo, who put up with the late nights, long hours, and early mornings. Without all of you, none of this would have been possible.
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<thead>
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Material constant for empirical relationship</td>
</tr>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>AISI</td>
<td>American Iron Steel Institute</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminum</td>
</tr>
<tr>
<td>AM</td>
<td>Additive manufacturing</td>
</tr>
<tr>
<td>ANOVA</td>
<td>Analysis of variance</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>$\beta_0$</td>
<td>Interatomic distance length scale/diffusion coefficient</td>
</tr>
<tr>
<td>BCC</td>
<td>Body centered cubic</td>
</tr>
<tr>
<td>BCT</td>
<td>Body centered tetragonal</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscattered electron</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>$C_L$</td>
<td>Liquid composition</td>
</tr>
<tr>
<td>$C_L^*$</td>
<td>Liquid composition at interface</td>
</tr>
<tr>
<td>$C_0$</td>
<td>Initial composition</td>
</tr>
<tr>
<td>$C_S$</td>
<td>Solid composition</td>
</tr>
<tr>
<td>Cr</td>
<td>Chromium</td>
</tr>
<tr>
<td>$Cr_{eq}$</td>
<td>Chrome equivalence</td>
</tr>
<tr>
<td>$Cr/Ni_{eq}$</td>
<td>Chrome nickel equivalence ratio</td>
</tr>
<tr>
<td>d</td>
<td>Cell size</td>
</tr>
</tbody>
</table>
\(D_L\) Solute diffusion coefficient in the liquid
\(\delta\) Delta ferrite (BCC)
DED Directed-energy deposition
DTSA II Desktop Spectrum Analyzer II
EBM Electron beam melting
EBSD Electron backscatter diffraction
EDS/EDX Energy dispersive X-ray spectroscopy
EML Electromagnetic levitation
EMU Magnetic moment response
\(F_s\) Fraction solid
FBAM Fusion based additive manufacturing
FCC Face centered cubic
Fe Iron
FN Ferrite Number
G Temperature gradient
\(\gamma\) Austenite (FCC)
GTA Gas tungsten arc
HAADF High angle annular dark field
HED High energy density
HV High vacuum
ICP-OES Inductively coupled plasma optical emission spectrometry
IGA Inert gas atomization
IGF Inert gas fusion
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
</tr>
<tr>
<td>K</td>
<td>Partition coefficient</td>
</tr>
<tr>
<td>K&lt;sub&gt;eq&lt;/sub&gt;</td>
<td>Equilibrium partition coefficient</td>
</tr>
<tr>
<td>K&lt;sub&gt;v&lt;/sub&gt;</td>
<td>Velocity corrected partition coefficient</td>
</tr>
<tr>
<td>K*</td>
<td>Partition coefficient at the solid liquid interface</td>
</tr>
<tr>
<td>KCNSC</td>
<td>Kansas City National Security Campus</td>
</tr>
<tr>
<td>L</td>
<td>Liquid</td>
</tr>
<tr>
<td>LPBF</td>
<td>Laser powder bed fusion</td>
</tr>
<tr>
<td>M&lt;sub&gt;s&lt;/sub&gt;</td>
<td>Saturation magnetization based on composition (Gauss)</td>
</tr>
<tr>
<td>M&lt;sub&gt;L&lt;/sub&gt;</td>
<td>Equilibrium liquidus slope</td>
</tr>
<tr>
<td>m&lt;sub&gt;L&lt;/sub&gt;(V)</td>
<td>Non-equilibrium liquidus slope</td>
</tr>
<tr>
<td>Mn</td>
<td>Manganese</td>
</tr>
<tr>
<td>Mo</td>
<td>Molybdenum</td>
</tr>
<tr>
<td>M&lt;sub&gt;S&lt;/sub&gt;</td>
<td>Calculated</td>
</tr>
<tr>
<td>M&lt;sub&gt;Se&lt;/sub&gt;</td>
<td>Mean squared error</td>
</tr>
<tr>
<td>n&lt;sub&gt;x&lt;/sub&gt;</td>
<td>Sample size</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;eq&lt;/sub&gt;</td>
<td>Nickel equivalence</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute for Science and Technology</td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>n</td>
<td>Material constant</td>
</tr>
<tr>
<td>O</td>
<td>Oxygen</td>
</tr>
<tr>
<td>Oe</td>
<td>Magnetic field</td>
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<tr>
<td>Acronym</td>
<td>Definition</td>
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<td>---------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>PBF</td>
<td>Powder Bed Fusion</td>
</tr>
<tr>
<td>PDAS</td>
<td>Primary dendrite arm spacing</td>
</tr>
<tr>
<td>Pe</td>
<td>Peclet number</td>
</tr>
<tr>
<td>PS</td>
<td>Platen/splat</td>
</tr>
<tr>
<td>$Q_{\text{Tukey}}$</td>
<td>Calculated Q value</td>
</tr>
<tr>
<td>$Q_{\text{crit}}$</td>
<td>Q critical value</td>
</tr>
<tr>
<td>R</td>
<td>Solidification rate</td>
</tr>
<tr>
<td>ROI</td>
<td>Region of interest</td>
</tr>
<tr>
<td>RS</td>
<td>Rapid solidification</td>
</tr>
<tr>
<td>RSP</td>
<td>Rapid solidification processing</td>
</tr>
<tr>
<td>RVP</td>
<td>Rotary vain pump</td>
</tr>
<tr>
<td>SDAS</td>
<td>Secondary dendrite arm spacing</td>
</tr>
<tr>
<td>$\text{SE}_{\text{Anova}}$</td>
<td>Standard Error</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>$\sigma_U$</td>
<td>Measured saturation magnetization</td>
</tr>
<tr>
<td>$\sigma_F$</td>
<td>Saturation magnetization based on composition (emu/g)</td>
</tr>
<tr>
<td>S/L</td>
<td>Solid liquid</td>
</tr>
<tr>
<td>SLM</td>
<td>Selective laser melting</td>
</tr>
<tr>
<td>SQ</td>
<td>Two-piston splat quenching</td>
</tr>
<tr>
<td>SR</td>
<td>Segregation Ratio</td>
</tr>
<tr>
<td>SRM</td>
<td>Standard reference material</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>SS</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscope</td>
</tr>
<tr>
<td>( \dot{T} )</td>
<td>Cooling rate</td>
</tr>
<tr>
<td>( T^* )</td>
<td>Interface temperature</td>
</tr>
<tr>
<td>( T_f )</td>
<td>Pure metal melting point</td>
</tr>
<tr>
<td>( T_0 )</td>
<td>Temperature where FCC and BCC free energies are equal</td>
</tr>
<tr>
<td>TAC</td>
<td>Total alloy content</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>( U_x )</td>
<td>Mean</td>
</tr>
<tr>
<td>TKD</td>
<td>Transmission Kikuchi diffraction</td>
</tr>
<tr>
<td>UHP</td>
<td>Ultra-high purity</td>
</tr>
<tr>
<td>( V )</td>
<td>Solidification velocity</td>
</tr>
<tr>
<td>( V_0 )</td>
<td>Speed of sound</td>
</tr>
<tr>
<td>VSM</td>
<td>Vibratory sample magnetometry</td>
</tr>
<tr>
<td>( \bar{X} )</td>
<td>Absolute mean difference</td>
</tr>
<tr>
<td>YAG</td>
<td>Yttrium aluminum garnet</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>Length scale of the microstructure</td>
</tr>
<tr>
<td>WD</td>
<td>Working distance</td>
</tr>
</tbody>
</table>
ACKNOWLEDGMENTS

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CHAPTER 1: INTRODUCTION

1.1 Motivation

In the past two decades, the engineering and manufacturing world has experienced a metals additive manufacturing (AM) boom. Metal AM techniques are creating opportunities for both old and new alloy systems to be utilized in ways previously not feasible due to manufacturing limitations, material compatibility issues, or other restrictions. In particular, metallic fusion based additive manufacturing (FBAM) techniques such as laser powder bed fusion (LPBF), electron beam melting (EBM), and directed-energy deposition (DED) have been primary targets of a significant amount of this rapid growth by utilizing rapid solidification (RS) conditions during processing to create parts with complex geometries and unique microstructures and features. Austenitic stainless steels (SS) are a frequent candidate alloy series for FBAM processes partially due to the vast amount of previous research and knowledge about the alloy system, but also for the mixture of good strength, ductility, and corrosion resistance of the system. The potential applications of FBAM processes in industry are vast, ranging from decreasing the time and cost during rapid prototyping of a new part design to building one-off replacement parts or custom pieces to full-scale manufacturing of components for industries from aerospace to medical devices. The implementation of these techniques is occurring at increasing speeds across numerous facets of both industrial and research engineering fields in applications from prototyping to mass production and as the employment of these techniques becomes more widespread, the capabilities of the technologies will naturally be pushed to the limits. In order to successfully achieve the next step and drive beyond these limits in a manner
that is both fast and efficient, the ability to gain a deeper understanding of the effects that RS has on the material at the micro and nanoscale is essential.

FBAM processes of metallic materials relies on metallic powders and rapid solidification during the build process in order to produce finished parts with high densities, good material properties, and complex geometries. Some of the more recognizable FBAM processes are powder bed fusion (PBF), direct metal laser sintering (DMLS), and directed-energy deposition (DED) which use either a focused laser or electron beam to fuse thin layers of metal powder together to build 3-D parts. Over time, these applications have been shown to be successful in producing complex, three-dimensional parts using feedstock powder from a variety of alloys systems ranging from various SS to titanium and Inconel 625.

In particular, PBF process like selective laser melting (SLM), which is also referred to as laser powder bed fusion (LPBF), have been identified as flagship processes in the FBAM realm for producing high quality parts with near comparable mechanical properties compared to bulk materials using austenitic SS alloys. Austenitic SS alloys are of particular interest due to the combination of widespread use of these alloys across numerous industries and the significant amount of existing knowledge pertaining to manufacturing austenitic SS under non-equilibrium conditions, i.e., welding. The LPBF process is similar to other PBF processes in how it works, in which a high power laser will raster across a thin layer of metal powder guided by a control mirror. This results in a rapid melting then rapidly solidifying of the metal in the desired pattern for each layer, progressively building towards a solid final part. PBF regularly utilize raster speeds over 1m/s during part builds. [1-3] The process is performed by a computer program that controls multiple variables usually defined by inputs such as raster speed, powder layer thickness, laser power, etc. A schematic of a typical LPBF process is shown in Figure 1.1.1 from
the side. Not pictured, but important to mention is that during the build an inert shielding gas is usually applied to the surface (or an inert gas environment is used) to reduce oxygen uptake by the steel during melting and resolidification. Literature about LPBF produced austenitic SS parts generally report successful builds with a higher ductility, higher yield strength, improved hardness, and larger ultimate tensile strengths compared to traditional wrought or cast counterparts.\[^{[4-11]}\] These improvements in performance are largely attributed to the unique combination micro and nanostructural features formed as a result of the rapid solidification occurring during LPBF processes.\[^{[6, 9, 12-14]}\]

![Schematic of generic LPBF processing technique.][15]

Despite these promising advances in the performance of PBF processed SS, these processes need further refinement before true mainstream implementation can occur. PBF processes are ideal for producing complex geometry parts, but these can be susceptible to defects such as microcracking, balling, pores, and substandard surface quality.\[^{[11, 16-18]}\] As a result, parts are at higher risk of localized corrosion and experience reductions in plasticity and fatigue life.
Porosity also plays a large role in the mechanical properties where even a 1% porosity will noticeably impact the toughness and fatigue behavior of the part.\textsuperscript{[17]} While parts with complex geometries is useful, low quality surface finishes will increase the potential for corrosion to occur and can be difficult to improve post build.\textsuperscript{[19]} As these production techniques utilize faster solidification rates what worked previously at slower solidification rates may no longer apply. Many of these performance concerns can be related back to changes in the material properties and or microstructure caused by the large RS rates possible in PBF processes in the form of strengthening methods, grain structures, phase content, and composition gradients.

The RS inherent in PBF processes can significantly alter the microstructure morphologies and features compared to other solidification processes such as casting or welding. An example of possible differences in grain structure is shown in Figure 1.1.2A-C which compares the grain structures within the bulk of an as-cast sample and a LPBF sample of 316L. The as-cast material had large rectangular grains (Figure 1.1.2A) which were similar in size to the individual melt pools observed in the microstructure of the LPBF sample (Figure 1.1.2B) which had significantly smaller grains that were less rectangular than the as-cast grains. (Figure 1.1.2C) Figure 1.1.3A-B shows the grain structure of a different LPBF processed 316L sample from multiple angles. The grains in this LPBF sample show a directional growth preference parallel to the build direction (Figure 1.1.3B) as this was the primary direction of heat flow during solidification. As a result of PBF processes being multipass techniques that fuse many layers together to form a single, final piece, when looking at the cross section of the build direction the individual layer melt pools can observed and form an overlapping or cascading effect of the melt pool between layers. (Figure 1.1.2B) Cast and welded materials typically solidify with large equiaxed or dendritic solidification structures depending on the solidification rates, cooling rates, and temperature.
gradients involved in the specific production method used. Alternatively, PBF processes typically exhibit fine, cellular solidification structures that decrease in size as the solidification rate increases. \cite{20-24} The difference in solidification structures is shown visually in Figure 1.1.4A and C. RS rates resulting in a fine cellular solidification structure can also be achieved in some laser or electron beam welding processes like single-pass pulsed laser welding or surface-glazing. \cite{25-27} The effects of increased solidification rates and RS on the microstructure and material properties of SS alloys is discussed in greater detail in the literature review.

![Figure 1.1.2 Micrograph of as-cast (A) and LPBF (B) processed 316L SS showing the two different microstructures revealed using a 75% HNO₃ and 25% HCl etchant. Optical image showing grain structure in LPBF processed sample etched using picric acid and HCL. \cite{16}](image)

![Figure 1.1.3 EBSD grain structure maps of a 316L sample processed by LPBF looking at (A) the top of the build direction and (B) looking parallel to the build direction (vertical). \cite{17}](image)
Two-piston splat quenching (SQ) has the potential to be a cost-effective and efficient method to study new alloy compositions at similar RS rates and conditions to those found at the upper end of FBAM techniques. The metallic powders that many FBAM processes rely on require highly specialized equipment to produce, are costly to purchase in sufficient quantities for FBAM, can be difficult to source, commonly have long lead times, and require a specific size distribution to produce quality builds. In our experience, 30kg of custom alloyed \(<150\ \mu m\) powder cost near $1,000 per kg (total $30,000) to be purchased. The 30kg was necessary so that after separating out the 15-45\(\mu m\) powder, there was more than the minimum required 10kg of powder needed for LPBF experiments. This goes to show how researching new alloy systems directly with these techniques requires significant resources in terms of finances, time, and manpower. Unlike other alternative RS processes, SQ uses a very small sample size of ~0.1g, does not use metallic powders, and a single test can be completed in about an hour with replicate samples showing a reasonable degree of uniformity. Although SQ and other forms of splat cooling have been around since the mid-1900s, there is not a large amount of literature involving research where SQ was applied to SS alloys. As a result, a significant amount of the existing literature utilizes the non-equilibrium solidification conditions produced by traditional welding, laser or electron beam welding, or PBF techniques as a foundation for the SQ work. It is the goal
of this dissertation to demonstrate how two-piston splat quenching can be used as an effective tool to study the impacts of rapid solidification on microstructure formation, micro- and sub-macrostructure features, and cellular segregation behavior in 300 series type stainless steels across a wide range of Cr/Ni<sub>eq</sub> without requiring atomized powder or PBF systems.

1.2 Background and Literature Review

**Stainless steel metallurgy**

“Stainless steel” is a universally recognized term used as a catch-all for a multitude of ferrous alloy types that can be further broken down and divided into sub-classes based on the alloy composition and properties. In order for a metal to be considered stainless steel, there are two primary requirements; the primary element must be iron (Fe) and the alloy must contain at least 10.5 wt % chromium (Cr).<sup>[29]</sup> The Cr addition is critical to SS design as it is primarily responsible for the improved corrosion resistance compared to other ferrous alloys. The corrosion resistance comes from a passive chrome oxide layer that forms on the outer surface of the metal. Additionally, SS metals are typically alloyed with other elements as well, like Ni or Mn, to achieve specific material structure, properties, and performance. Under the SS heading, there exist multiple classes of SS ranging from austenitic and ferritic SS to duplex and precipitate strengthened SS, categorized by the American Society for Testing and Materials (ASTM) using a three-digit system. One of the most widely used classes of SS is the 300 series which are austenitic SS containing elevated concentrations of Ni compared to other series. 300 series SS provide enhanced corrosion resistance, improved high temperature performance, and have good weldability.<sup>[29]</sup> Some common examples are 304 and 310 SS which are used for applications from food processing to cryogenic vessels. Certain alloys within the 300 series, such as 316 and 317 SS, include the addition of molybdenum, between 2-3 and 3-4 wt% respectively, which
forms an additional passive surface oxide layer, further enhancing the pitting and corrosion resistance of the alloys. These alloys are employed in applications from surgical tools to nuclear reactors. The last modification of SS alloys is associated with the carbon content where regular alloys typically allow up to 0.08 wt% C there are low carbon steels that only allow 0.03 wt% C or less. The decrease in maximum carbon content reduces or eliminates sensitization effects by limiting the amount of C available to precipitate Cr carbides which are detrimental to material performance. Full compositional specification for multiple common 300 series SS alloys are listed in Table 1.2.1. The alloy design and modification process is complex and must be performed with careful consideration as it will impact material properties and performance from microstructure, phase, and corrosion resistance to weldability, yield strength, ductility, and hardness.

Table 1.2.1 ASTM A240-20a compositional specification for common 300 series SS alloys.

<table>
<thead>
<tr>
<th>Wt%</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>C</th>
<th>N</th>
<th>P</th>
<th>S</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>Balance</td>
<td>18.0-20.0</td>
<td>8.0-12.0</td>
<td>ND</td>
<td>&lt; 2.0</td>
<td>&lt; 0.75</td>
<td>&lt; 0.03</td>
<td>&lt; 0.10</td>
<td>&lt; 0.045</td>
<td>&lt; 0.03</td>
<td>ND</td>
</tr>
<tr>
<td>310S</td>
<td>Balance</td>
<td>24.0-26.0</td>
<td>19.0-22.0</td>
<td>ND</td>
<td>&lt; 2.0</td>
<td>&lt; 1.50</td>
<td>&lt; 0.08</td>
<td>ND</td>
<td>&lt; 0.045</td>
<td>&lt; 0.03</td>
<td>ND</td>
</tr>
<tr>
<td>316L</td>
<td>Balance</td>
<td>16.0-18.0</td>
<td>10.0-14.0</td>
<td>2.0-3.0</td>
<td>&lt; 2.0</td>
<td>&lt; 0.75</td>
<td>&lt; 0.03</td>
<td>&lt; 0.10</td>
<td>&lt; 0.045</td>
<td>&lt; 0.03</td>
<td>ND</td>
</tr>
<tr>
<td>317L</td>
<td>Balance</td>
<td>18.0-20.0</td>
<td>11.0-15.0</td>
<td>3.0-4.0</td>
<td>&lt; 2.0</td>
<td>&lt; 0.75</td>
<td>&lt; 0.03</td>
<td>&lt; 0.10</td>
<td>&lt; 0.045</td>
<td>&lt; 0.03</td>
<td>ND</td>
</tr>
<tr>
<td>321</td>
<td>Balance</td>
<td>17.0-19.0</td>
<td>9.0-12.0</td>
<td>ND</td>
<td>&lt; 2.0</td>
<td>&lt; 0.75</td>
<td>&lt; 0.08</td>
<td>&lt; 0.10</td>
<td>&lt; 0.045</td>
<td>&lt; 0.03</td>
<td>Ti=5*(C+N)</td>
</tr>
</tbody>
</table>

ND=Not defined

A variety of different methods have been developed over time to predict material properties like phase content and solidified composition. Binary and ternary phase diagrams are one commonly used tool to phase and composition of a solidified SS for slow, near-equilibrium processes. Austenitic SS is commonly based upon the Fe-Cr-Ni ternary phase diagram, which can be more difficult to visualize as a function of both composition and temperature. Another commonly used approach in stainless steel research is visualization of phase relationships using pseudo-binary phase diagrams or isopleths. Both phase diagrams and isopleths are
constructed from equilibrium thermodynamic calculations and principles, but isopleths can represent the phase relationships between more complex chemistries and temperatures. Isopleths predict the phase stability over a range of temperatures while the concentrations of two elements, a dependent and independent element, can be varied while the rest of the alloy’s composition remains constant. Similar to a phase diagram this is another tool to predict solidified compositions, predict solidified phase, or used to calculate equilibrium partition coefficients for more complex alloys. An example isopleth based on the ASTM A240 316L SS with 66% Fe was generated using ThermoCalc and can be found in Figure 1.2.1. It should be kept in mind that isopleths are still generated based on equilibrium thermodynamic calculations meaning the predictions will not necessarily be accurate for conditions that deviate heavily from equilibrium. However, these tools are still beneficial and can provide initial predictions of phase content and compositions for complex alloy systems.
Figure 1.2.1 Pseudo-binary isopleth for 66 wt% Fe 316L stainless steel generated using ThermoCalc.

One of the most closely connected aspects of alloy design lies in the relationships between the composition and crystal structure or phase. The two primary phases formed during solidification in SS are austenite and ferrite, which are face centered cubic (FCC) and body centered cubic (BCC) crystal structures respectively, and the two main alloying elements in 300 series SS, Ni and Cr, are austenite and ferrite promoting elements, respectively. The reason that 300 series SS have an increased Ni content is to enable greater concentrations of Cr to be added to an alloy while maintaining a primarily austenitic microstructure. In addition to Cr and Ni, other elements commonly found or added to 300 series alloys like Mn and Mo are also austenite or ferrite stabilizers, a full list is shown in Table 1.2.2. In some cases, an alloy is designed to
contain both phases for improved properties. For example, austenitic steels perform better in high temperature conditions and have better corrosion resistance compared to ferritic steels, but ferritic steels are less prone to solidification cracking due to irregular grain boundaries, making them easier to weld.\textsuperscript{[25]} Thus, understanding the composition-phase relationship during SS alloy design is necessary as the phase will impact the properties and performance of the final product.\textsuperscript{[31, 34]}

Table 1.2.2 Common alloying elements added to SS metals that are austenite (FCC) and ferrite (BCC) stabilizing, listed in no particular order.\textsuperscript{[31]}

<table>
<thead>
<tr>
<th>Austenite Stabilizing Elements</th>
<th>Ferrite Stabilizing Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni, Mn, C, N, Cu, Co</td>
<td>Cr, Mo, Nb, Ti, Si, Al, V, W</td>
</tr>
</tbody>
</table>

Phase formation and rapid solidification

In SS research equivalence equations are another common predictive tool that has been developed to estimate the phase formation in SS during solidification and are regularly used in welding research and application.\textsuperscript{[35]} These values are a numerical quantification of the tendency of the alloy to form specific phases based on certain elemental additions like those listed in Table 1.2.1. Multiple iterations of the equivalence equations that have been developed over time, refined with each new set of equations, dating back to Schaeffler in 1949.\textsuperscript{[35, 36]} The evolution of the equivalence equations and the significance of each element can be seen by looking at previously proposed equivalence equations, listed in Table 1.2.3. One of the more commonly used versions of these equations are the WRC-1992 equations developed based on earlier versions from DeLong and Schaeffler modified to more accurately capture the effects of Mn and Cu in phase stabilization and maintain accuracy across a wider range of austenitic SS compositions.\textsuperscript{[35]} The WRC-1992 equivalence equations account for the effects of austenite and ferrite stabilizing elements commonly used in the welding of SS alloys to calculate the Cr.
equivalence (Cr$_{eq}$) and Ni equivalence (Ni$_{eq}$) values. (Equations 1.2.1-2) A ratio of the Cr$_{eq}$ and Ni$_{eq}$ values can be taken to produce the Cr/Ni$_{eq}$ ratio and as a more general method of expressing the composition and a numerical value that can be used for phase estimates.

\[
\begin{align*}
\text{Cr}_	ext{eq} &= \text{Cr wt}\% + \text{Mo wt}\% + (0.7*\text{Nb wt}\%)
\end{align*}
\]

Equation 1.2.1

\[
\begin{align*}
\text{Ni}_	ext{eq} &= \text{Ni wt}\% + (35*\text{C wt}\%) + (20*\text{N wt}\%) + (0.25*\text{Cu wt}\%)
\end{align*}
\]

Equation 1.2.2

Table 1.2.3 Various Cr and Ni equivalence equations for SS alloys. $^{[35, 37-39]}$

<table>
<thead>
<tr>
<th></th>
<th>Cr Equivalence</th>
<th>Ni Equivalence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schaeffler 1949</td>
<td>Cr + Mo + 1.5<em>Si + 0.5</em>Nb</td>
<td>Ni + 30<em>C + 0.5</em>Mn</td>
</tr>
<tr>
<td>Delong 1974</td>
<td>Cr + Mo + 1.5<em>Si + 0.5</em>Nb</td>
<td>Ni + 30<em>C + 30</em>N + 0.5*Mn</td>
</tr>
<tr>
<td>Hammar 1979</td>
<td>Cr + 1.37<em>Mo + 1.5</em>Si + 2<em>Nb + 3</em>Ti</td>
<td>Ni + 0.31<em>Mn + 22</em>C + 14.2*N + Cu</td>
</tr>
<tr>
<td>WRC 1988</td>
<td>Cr + Mo + 0.7*Nb</td>
<td>Ni + 35<em>C + 20</em>N</td>
</tr>
<tr>
<td>WRC 1992</td>
<td>Cr + Mo + 0.7*Nb</td>
<td>Ni + 35<em>C + 20</em>N + 0.25*Cu</td>
</tr>
</tbody>
</table>

The WRC-1992 equations can be used with the WRC-1992 diagram to determine an estimated ferrite number (FN) of an alloy. (Figure 1.2.2) The FN is magnetically based unit used to determine ferrite content instead of percent ferrite that is measured using a standardized procedure set by the International Organization for Standardization (ISO) and can be considered approximately equal to the ferrite percent. $^{[36]}$ The benefits of using ferrite number are that it can be determined non-destructively and is measured using a calibration standard making comparison across samples possible. $^{[38]}$ Previous versions of the equivalence equations like the Schaeffler and Delong equations were found to incorrectly address the role of Mn and resulted in overpredictions of the FN in higher alloyed SS compositions. The WRC-1992 equivalence equations were proposed to provide improved predictions for the FN for dissimilar metal welds and cladding applications in particular. $^{[35]}$ It should be noted that the measured FN is affected by ferrite composition and, for alloys with ferrite percents above about 30%, the FN has been shown to need to be corrected or it can incorrectly predict ferrite percent. $^{[36, 40]}$
Using the WRC-1992 equations, equivalence values were calculated for various SS alloys found across some of the welding and RS literature and plotted in Figure 1.2.3. Additionally, the minimum and maximum \( \text{Cr}_{eq} \) and \( \text{Ni}_{eq} \) values for 316L SS were calculated with the WRC-1992 equations based on the range of possible compositions defined by the ASTM A240 specification.\(^{32}\) Using the WRC-1992 diagram, \( \text{Cr}_{eq} \) and \( \text{Ni}_{eq} \) corresponding to FNIs of 0, 24, and 100 have also been overlayed for reference. The refinement of the equivalence equations through multiple iterations leading up to the WRC-1992 equation set and broad adaptation of the equations across research and industry have provided a practical means for comparing SS alloys with different compositions.

Figure 1.2.2 WRC-1992 diagram with \( \text{Cr}_{eq} \) and \( \text{Ni}_{eq} \) equations and ferrite number predictions.\(^{35}\)
Solidification of SS under equilibrium conditions can undergo several different solidification paths based primarily on the alloy composition with respect to concentrations of stabilizing elements. There are five common solidification modes that typically occur in SS solidification during welding that are either fully austenite, fully ferrite, or a combination of the two. The five solidification modes are primary austenite (PA), austenite plus ferrite (AF), eutectic, ferrite plus austenitic (FA), and primary ferrite (PF) and are also detailed in Table 1.2.4 where $\delta$ is ferrite, $\alpha$ is austenite, and L is the liquid phase. The interdendritic phase formation in
the AF, eutectic, and FA solidification modes at slow cooling rates are caused by compositional changes during solidification that result in a shift of the stable solidifying phase. \cite{40, 48, 60} These three solidification modes can also experience sub-solidus transformations from ferrite to austenite. Estimations of what $\text{Cr}_\text{eq}$ and $\text{Ni}_\text{eq}$ values produce each solidification path are included on the WRC-1992-diagram in Figure 1.2.2. The ability to use isopleths and apply the equivalence equations to predict solidification path and microstructure across a wide range of SS alloy chemistries is incredibly useful, however, these methods can not be readily applied to rapid solidification conditions due to a number of reasons.

Table 1.2.4 Five equilibrium solidification paths for SS. $\delta$ is ferrite, $\alpha$ is austenite, and L is the liquid phase.

<table>
<thead>
<tr>
<th>Solidification Modes</th>
<th>Solidification Path</th>
<th>Solidification Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single phase ferritic (PF)</td>
<td>$L \rightarrow L + \delta \rightarrow \delta$</td>
<td>Ferrite is the primary and only phase to form during solidification.</td>
</tr>
<tr>
<td>Ferritic + Austenitic (FA)</td>
<td>$L \rightarrow L + \delta \rightarrow L + \delta + \alpha \rightarrow \delta + \alpha$</td>
<td>Ferrite is the primary phase to form during solidification but interdendritic/cellular austenite forms between dendrites/cells. Austenite provides sites for potential solid-state ferrite→austenite transformation.</td>
</tr>
<tr>
<td>Eutectic</td>
<td>$L \rightarrow L + \delta + \alpha \rightarrow \delta + \alpha$</td>
<td>Ferrite and austenite both solidify as primary phase from eutectic liquid. Ferrite prone to austenite solid-state transformation.</td>
</tr>
<tr>
<td>Austenitic + Ferritic (AF)</td>
<td>$L \rightarrow L + \alpha \rightarrow L + \delta + \alpha \rightarrow \delta + \alpha$</td>
<td>Austenite is the primary phase to form during solidification but interdendritic/cellular ferrite forms at dendrite/cell walls. Ferrite susceptible to solid state transformation to austenite.</td>
</tr>
<tr>
<td>Single phase austenitic (PA)</td>
<td>$L \rightarrow L + \alpha \rightarrow \alpha$</td>
<td>Austenite is the primary and only phase to form during solidification.</td>
</tr>
</tbody>
</table>

The solidification of austenitic stainless steel has been widely studied under solidification rates and cooling rates employed in casting and welding processes, nonetheless, rapid solidification in austenitic stainless steels is highly complex and still an active area of research with new contributions to the literature on a regular basis. \cite{59, 61-63} Estimated cooling rates for SS material for various solidification processes that span from $10^{-1}$ K/s to $10^6$ K/s are listed in Table 1.2.5. Initial works by J. C. Lippold and J. W. Elmer do well to highlight the impact that rapid solidification has on the solidification mode and microstructure formation in SS alloys with respect to Cr and Ni concentrations. Elmer et. al. mapped the Cr/Ni space between 1.15 and 2.15
using Fe-Cr-Ni ternary alloys while reporting on phase formation from melt spinning and electron beam surface melting of austenitic type stainless steel as it related to the E-B scan speed, Figure 1.2.4, including the five solidification paths that were observed. Note the X-axis is in Cr and Ni concentration no Cr/Ni\textsubscript{eq} for this plot. Work by J.C. Lippold and colleagues produced a similar map showing the same suppression of interdendritic phase formation at elevated laser scan speeds but replaced ternary alloys and Cr and Ni concentrations with various 300 series SS alloys and Cr/Ni\textsubscript{eq} values calculated with WRC-1992. (Figure 1.2.5)\textsuperscript{[44]} For RS conditions in the Lippold figure, the assumption is that the maximum growth rate to occur can not exceed the weld so the weld/beam speed can be treated equivalently to the max growth rate experienced in the sample.\textsuperscript{[44]} The data used to generate the “Lippold Map” was measured for solidification rates between 10 and 100 mm/s for various processing techniques like laser beam welding, EBW, and surface melting treatments while providing predictions for faster solidification rates.\textsuperscript{[44]} Other work in RS of SS supports the suppression of interdendritic phase, formation favoring single phase solidification, and the compression of the range of Cr/Ni\textsubscript{eq} values between fully austenitic and fully ferritic microstructures at elevated solidification rates.\textsuperscript{[25, 53, 64-67]} At higher solidification rates above 100mm/s, such as those expected in AM technologies like LPBF, the Elmer and Lippold maps are great tools for estimating solidification modes; but, they were made from a wide selection of 300 series alloys and the solidification modes at these rates are not as well studied, thus only predictions.

In the Lippold map, there was also a new solidification path titled “F/MA” which is similar to the FA solidification path but is where the material solidified as PF before undergoing a diffusionless, massive transformation while cooling from ferrite to austenite. At slower cooling rates this is a diffusion controlled transformation, but as cooling rates increase the at higher
cooling rates this becomes a diffusionless massive transformation. \cite{68-70} The phase transformation from ferrite to austenite can occur by either a peritectic transformation or a massive transformation at higher cooling rates. \cite{69, 71} \cite{68, 72} However, peritectic transformations require low temperature gradients and in FBAM processes the temperature gradients are very high. \cite{69} Temperature gradients in FBAM processes have been found to range anywhere from $10^3$-$10^8$ K/m during solidification. \cite{69} The F/MA transformation in rapidly solidified SS alloys has been concluded to be driven by the difference in free energies of the two phases caused by local undercoolings during RS. \cite{7, 53, 60, 69, 73} Therefore the aforementioned F/MA solidification path is formed by a solid state, diffusionless, massive transformation of ferrite to austenite.

Table 1.2.5 Cooling rate estimates for solidification occurring in various processing techniques. \cite{40, 74, 75}

<table>
<thead>
<tr>
<th>Process</th>
<th>Cooling Rate (K/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Directional Solidification</td>
<td>$10^{-1}$-$10^{1}$</td>
</tr>
<tr>
<td>Casting</td>
<td>$10^{0}$-$10^{2}$</td>
</tr>
<tr>
<td>Arc Welding</td>
<td>$10^{1}$-$10^{3}$</td>
</tr>
<tr>
<td>Atomization</td>
<td>$10^{0}$-$10^{5}$</td>
</tr>
<tr>
<td>Laser Beam Welding</td>
<td>$10^{2}$-$10^{6}$</td>
</tr>
<tr>
<td>Melt Spinning</td>
<td>$10^{4}$-$10^{6}$</td>
</tr>
<tr>
<td>Splat Quenching</td>
<td>$10^{5}$-$10^{8}$</td>
</tr>
<tr>
<td>Single Pulse Laser Melting</td>
<td>$10^{6}$-$10^{8}$</td>
</tr>
</tbody>
</table>
Figure 1.2.4 Principle solidification modes observed for increasing scan speeds in seven Fe-ternary alloys with varying Cr and Ni concentrations, modified from Elmer 1989. [26]
Solidification theory

This section will briefly review the key aspects of solidification theory with respect to solidification microstructures and rapid solidification. During many FBAM and welding processes, solidification initiates at a solid liquid (S/L) interface resulting in one of three morphologies: planar, columnar, or dendritic depending on factors such as solidification rate, thermal gradient, and composition distribution. Examples of each solidification morphology are shown in Figure 1.2.6. At large solidification rates the dendritic morphology no longer has time to form secondary dendrite arms and will form a cellular morphology, which resembles a smaller version of the columnar solidification shown in Figure 1.2.6B. The transition from slow planar to dendritic and cellular structures occurs due to local S/L interface instabilities that can be
influenced by temperature gradients, composition gradients, capillarity forces, dendrite tip radius, and large undercoolings. The transition from slow planar solidification to columnar morphology occurs once a critical velocity is reached and local perturbations form along the planar S/L interface. Constitutional supercooling states that the liquid phase is only thermodynamically stable if the temperature is above the liquidus temperature and below the liquidus temperature both solid and liquid phases should coexist. Thus, planar solidification fronts will break down into a cellular or dendritic form in order to have solid and liquid coexist, and that during solidification the region of solid and liquid will contain liquid below the liquidus temperature. The thickness of these regions can be impacted by local thermal and compositional gradients at the S/L interface and solidification velocity. The criteria for stable planar growth in the constitutional supercooling theory is listed in equation 1.2.3 where $G$ is temperature gradient, $R$ is growth rate, $\Delta T$ is the equilibrium freezing range, and $D_L$ is the diffusion coefficient of the solute in the liquid.

$$\frac{G}{R} \geq \frac{\Delta T}{D_L}$$  

Equation 1.2.3

As solidification rates increase the planar interface loses stability ($\Delta T/D_L$ is greater than $G/R$) and the solidification structure will transition away from planar solidification. Further increased levels of constitutional supercooling will cause the solidification morphology to transition from cellular to dendritic solidification. When solidification rates continue to increase, the dendrite size will decrease and the dendritic structure will eventually transition to a fine cellular solidification structure in which secondary dendrite arm formation is suppressed. Finally, when the cell spacing becomes critically small, the limit of stability for cellular growth is reached and planar solidification becomes the stable morphology again. This evolution of
solidification microstructures is well studied and covered in greater detail by Mullins, Tiller, Trivedi, Kurz, Giovanola, and Fisher to name a few. \[76, 78, 79, 81-83\]

Figure 1.2.6 Examples of (A) planar, (B) cellular, and (C) dendritic solidification morphologies observed in carbon tetrabromide using optical microscopy. \[84\]

RS begins when a critical velocity is reached, where the governing relationships previously used to describe solidification are no longer applicable. Solidification is generally considered rapid, for most metals at solidification rates above 10mm/s and faster or for cooling rates on the order of magnitude of 100K/s or greater. \[34, 82\] Solidification slower than this is stable solidification, following the relationship $\lambda^2 V = \text{constant}$ where $\lambda$ is the length scale of the microstructure and $V$ is the solidification velocity. Trivedi and Kurz define the transition to RS as an approximate critical velocity of the S/L interface, where the diffusion distance in the liquid at the S/L interface becomes smaller than the scale of solidification features. This can also be represented when the Peclet number ($Pe$) becomes larger than unity, where the Peclet number is a ratio of the solidification velocity ($V$) and length scale of the microstructure ($\lambda$) over 2 times the solute diffusion coefficient in the liquid ($D_L$) at the S/L interface, $Pe = \frac{V\lambda}{2D_L}$. \[82\] Another way to describe the Peclet number is as a ratio of the microstructural length scale and the diffusion length scale. Meaning during RS the range of solute diffusion in the liquid is smaller than the length scale of solidification morphology and solute redistribution becomes localized with
respect to the features.\textsuperscript{[82]} As the solidification rate increases and cell feature size continues to decrease, the transition from cellular back to planar solidification eventually occurs and is referred to as the absolute limit of stability for cellular solidification.\textsuperscript{[81]} However, these rates are above the normal range of expected solidification rates for most FBAM processes.\textsuperscript{[20-24]} The transition from and to planar solidification can be visualized in a plot of the Peclet number vs interface velocity, an example shown in Figure 1.2.7A for Ag-5Cu. In these plots $V_c$ is the velocity below which planar solidification is stable and $V_a$ the velocity above which planar solidification becomes stable again. The limit of stability (transition from or to planar solidification) is represented when the Peclet number rapidly decreases or increases respectively. Using the stability criteria for the S/L interface proposed by Mullins et. al., the absolute limit of stability was calculated by J.W. Elmer for RS in multiple EBM Fe-Cr-Ni metals.\textsuperscript{[40, 83]} The results were similar between different alloys and one set of results is shown in Figure 1.2.7B. Compared to Figure 1.2.7A, the upper absolute limit of stability is not predicted for this range of solidification rates up to 5-10m/s.
Figure 1.2.7 Calculated Peclet number vs solidification interface velocity showing stability of cellular solidification for (A) Ag-5Cu binary alloy \(^{[79]}\) and (B) Fe-28Cr-13Ni ternary alloy. \(^{[40]}\) In (A) \(V_C\) is the velocity below which planar solidification is stable and \(V_a\) the velocity above which planar solidification becomes stable again.

Variables like solidification rate and temperature gradient are critical when studying solidification in welding and other RS processes. The presence of compositional gradients in the liquid at the S/L interface is the basis for the previously mentioned compositional supercooling theory where the compositional gradients can be responsible for local S/L interface instabilities causing the planar to dendritic and cellular transition. Without detailing the entire theory, the
primary conclusion is that after the planar transition occurs, when both the solid and liquid phases are present there exist temperature and composition gradients between the liquid and solid during solidification and that the amount of constitutional supercooling will result in different solidification structures as the solidification velocity increases.\textsuperscript{[31, 76]} The solidification morphology is predicted by G/R where G is the temperature gradient, and R is the growth rate of the S/L interface.\textsuperscript{[31]} Additionally, by solving for G*R the cooling rates experienced can be calculated and used to represent the size of the solidification morphology, where larger values indicate smaller features. (Figure 1.2.8). Unfortunately, accurate in-situ or direct measurements of cooling rates, solidification rates, and temperature gradients are difficult to achieve in RSP, especially in production environments. However, these relationships can still be used for understanding the solidification event in RS by utilizing empirical relationships and simulations to provide estimates for values such as cooling rates or temperature gradients.

Figure 1.2.8 (A) Effect of increasing constitutional supercooling on solidification morphology and (B) solidification morphology predictions based on G/R. Figures are from Welding Metallurgy by S. Kou.\textsuperscript{[31]}
Empirical equations have been produced for a range of metallic systems based on the G*R relationship using experimentally measured thermal data and physical dendrite or cell measurements. These relationships have been measured for simple binary alloys like Al-4.5Cu to complex SS alloys like 201 SS, and 310 SS. One method for defining this relationship for a material involves measuring the cooling rate and cell size in slower solidification processes then extrapolating the results to higher solidification rates. The empirical relationship is generally reported as \( d = A(G*R)^{-n} \) where \( d \) is cell spacing, \( A \) and \( n \) are material constants, and \( G*R \) is the cooling rate. This is done because rapid cooling rates are difficult to measure during solidification. Previous work by Katayama & Matsunawa experimentally measured the cooling rate and cell size across a range of cooling rates in pulsed YAG laser welded and gas tungsten arc (GTA) welded 310 SS. They found good agreement between the empirical relationship generated from slower (\( 10^1-10^3 \) K/s) cooling rate measurements in GTA and faster cooling rates (\( 10^5-10^6 \) K/s) in the pulsed laser welds. Similar relationships have been proposed by other authors for similar SS materials using a combination of low and high cooling rate techniques and measured and predicted cooling rates. These empirical relationships from the literature are plotted in Figure 1.2.9. It should be noted that all except for one of the relationships are for the secondary dendrite arm spacing (SDAS), but during rapid solidification secondary dendrite arms do not have time to form, resulting in cellular solidification and the cell spacing ends up being used as the primary dendrite arm spacing (PDAS). When comparing the different relationships presented in Figure 1.2.9 it should be kept in mind that each was formed based on results from different solidification processing techniques and different SS alloy compositions. As a result, while the rate of change of the cooling rate with respect to cell size was relatively stable between different empirical relationships, differences in the unique
temperature gradients and solidification rates of each process resulted in variations of the specific cooling rates associated with each cell size.

There are a few concerns with using utilizing the cooling rate and cell size relationship at large cooling rates and using relationships extrapolated from slower cooling rate processes. For SS this relationship is verified by both experiment and theory for cooling rates up to $10^5$ K/s.\[77, 86, 89-92\] However, under RS conditions, the solidification morphology is heavily controlled by the solidification rate, not the temperature gradient.\[82\] This is shown in Peclet and dendrite tip radius calculations over a range of S/L interface velocities for various temperature gradients (Figure 1.2.7) where at high solidification velocities, before the absolute limit of stability was reached, the Peclet number and dendrite tip radius become insensitive to the temperature gradient.\[40, 78, 79, 82\] Although, Kurz and Fisher show results where larger temperature gradients produced smaller spacings than predicted for the same solidification rates.\[78\] This is why one must be careful when using extrapolated empirical relationships to get the cooling rate from cell size in high cooling rate processes. Additionally, while using G*R to express the cooling rate enables solidification rate calculations, if the temperature gradient of the technique used to develop the empirical relationship were not similar in magnitude to the process being measured, the resulting solidification rate calculation could be less accurate. The ability to estimate the cooling and solidification rates of solidification from the cell size is a powerful tool, but if used without careful consideration of the solidification event as a whole it can produce less accurate predictions.
Elemental segregation and diffusion

Many examples of solidification occur outside of the planar solidification regime (welding, PBF, etc.) and as a result experience elemental segregation on the macro or micro scale. Most solidification events can be described by one of three common solidification models and the associated composition profiles, shown in Figure 1.2.10 A-C. These models are A.) complete diffusion in the liquid phase and solid phase, B.) complete diffusion in the liquid phase with no solid diffusion (Scheil), and C.) partial diffusion in the liquid phase with no solid diffusion. The first model describes equilibrium solidification conditions. The second model is more complex and begins to capture some partitioning effects. However, both models predict the composition of the solid to either increase or decrease at increasingly faster rates over time, while the third model has an initial transient stage, steady state stage, and a final transient stage. During cellular and dendritic solidification these models can be applied to predict
microsegregation behavior between cells and dendrites. The application of the three solidification models to two microsegregation conditions, partition coefficient less than one and greater than one, are shown in Figure 1.2.10 D and E respectively. Composition profiles described by the limited liquid diffusion with no solid diffusion solidification model are typically what is observed in welded solidification structures.

Figure 1.2.10 Solute redistribution models for (A) solidification with complete liquid and solid diffusion, (B) complete liquid diffusion and no solid diffusion “Scheil”, and (C) limited liquid diffusion with no solid diffusion. Figures D and E show microsegregation composition profiles for each solute redistribution model with (D) partition coefficient less than 1.0 and (E) greater than 1.0 in cellular or dendritic structures. Figures are from *Welding Metallurgy* by S. Kou. [31]

Previous research of elemental segregation in SS alloys shows that of the major alloying elements, the primary elements expected to segregate during solidification (partition coefficients farthest from 1.0) are Cr (and Mo if present), or Ni and is controlled by the solidifying phase. This is caused by the rejection of solutes from the solid into the liquid during solidification and redistribution of solute in the liquid with respect to the dendrite or cell. Going back to the phase stabilizing elements listed in Table 1.2.2, Cr and Mo help stabilize ferrite solidification while Ni
helps stabilize austenite. Thus, during the solidification of one phase, elements that do not stabilize that phase are rejected during solidification in larger amounts. In welded 304L which has an austenitic microstructure, Cr and Ni segregation were observed, where Cr was found to be depleted at the subgrain (dendrite) core with increased concentrations at the subgrain (dendrite) boundary. The composition profile of Ni showed the opposite segregation response with increased levels of Ni present at the subgrain core and decreased levels at the subgrain boundary. In welded ferritic SS microstructures the opposite was reported, where Ni was found segregated to the dendrite wall and Cr to the dendrite center. In a similar study of GTA welded 300 series SS alloys, similar segregation of Cr and Ni was reported, and in Mo containing alloys, Mo showed similar segregation behavior to Cr in austenite. Due to the solute buildup at the S/L interface during solidification in SS the formation of interdendritic phases can occur. This happens at the boundaries between dendrites and cells as a result of a significant change in chemistry caused by solute redistribution during solidification.

In studies using rapid solidification processing (RSP) techniques like LPBF and HED, similar results are reported, where the segregation of Cr and Mo to the cell boundaries in austenite solidification is still observed. Unlike in GTA and other more slowly solidified microstructures, the initial transient region observed in RS structures is typically not observed. The formation in interdendritic phases has also been found to be suppressed at high solidification rates due to changes in the thermodynamic stabilities, and phase transformations that occur. Additionally, in some RS processes, solidified ferritic microstructures showed a lack of elemental segregation was reported at the cell boundaries. It has been reported that the Scheil-Gulliver model of solidification can provide reasonable first order estimates of segregation behavior in FBAM for rapidly solidified cellular segregation, equation
1.2.4. [22,97] In this equation $C_s$ is the composition of the solid, $k_{eq}$ is the partition coefficient, $C_0$ is the initial composition, and $f_S$ is the fraction of solid formed. However, the solution of the equation will change with how close to 1.0 the $f_S$ is solved for and the model does not factor in solid-state diffusion effects. As a result, the model can potentially result in inaccurate predictions of segregation but can be used as a first order estimate. [22]

$$C_s = k_{eq} \cdot C_0 \cdot (1-f_s)^{k_{eq}-1}$$  \hspace{1cm} \text{Equation 1.2.4}

Another value of interest when researching rapid solidification is the partition coefficient ($k$) and how it is affected by RS. The equilibrium partition coefficient ($k_{eq}$) can be calculated using binary phase diagrams as $C_s/C_L$ for a given composition, where $C_s$ is the composition of the solid and $C_L$ is the corresponding composition of the liquid. Under equilibrium conditions this can be re-written as $C_{Si}/C_{Sf}$, where $C_{Si}$ is the composition of the initial solid to form and $C_{Sf}$ is the composition of the final solid to form. $k$ values not equal to 1.00 indicate the element experienced some form of segregation during solidification. $k$ values less than 1.00 indicate the material initially solidified with less than equilibrium concentrations of that element and the excess was rejected from the solid into the liquid during solidification. As a result, higher concentrations were found in the last material to solidify. The alternate is true for $k$ values greater than 1.0. The $k_{eq}$ values for Cr, Ni, and Mo, three commonly added alloy elements in 300 series SS, during austenite and ferrite solidification are listed in Table 1.2.7. Unfortunately, these conditions are only applicable at equilibrium when there is complete diffusion in the solid and liquid.
Table 1.2.7 Equilibrium partition coefficients for Cr, Ni, and Mo in austenite and ferrite. \[40, 98, 99\]

<table>
<thead>
<tr>
<th></th>
<th>Austenite (FCC)</th>
<th>Ferrite (BCC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.80</td>
<td>1.05</td>
</tr>
<tr>
<td>Ni</td>
<td>1.05</td>
<td>0.82</td>
</tr>
<tr>
<td>Mo</td>
<td>0.65</td>
<td>~1.00</td>
</tr>
</tbody>
</table>

There is significant previous work that has been done to predict how increased solidification rates reduce the magnitude of segregation and shift $k$ values towards 1.0, or partitionless solidification. This is shown visually in Figure 1.2.11, where the relationship between $k_{eq}$ and $k_v$ approaches 1.0 as solidification rates increase and solidification morphology transitions from dendritic to cellular to planar. \[78\] When the equilibrium definition of $k=Cs/C_L$ for compositions on either side of the S/L interface is used under non-equilibrium conditions the result is the effective partition coefficient. \[60, 78\] Part of the Aziz Jackson Continuous Growth Model (CGM) uses equation 1.2.5 to calculate a velocity corrected partition coefficient using some material and process dependent constants that has a closed solution. \[100, 101\]

$$k_v = \frac{k_{eq} + \beta_0 * V}{1 + \beta_0 * V}$$

Equation 1.2.5

In this equation $k_{eq}$ is the equilibrium partition coefficient, $\beta_0$ is a ratio of the interatomic distance length scale to the liquid diffusion coefficient, and $V$ is the solidification velocity. For most metals, the interatomic distance length scale is between 0.5nm and 5nm. The liquidus slope ($m_L(V)$) and S/L interface temperature ($T^*$) of the material will also be effected by non-equilibrium solidification conditions and can be calculated using equations 1.2.6-7 respectively. \[34, 60\]

$$m_L(V) = \frac{m_L}{1 - k_{eq}} \left( 1 - k^* \left( 1 - \ln \left( \frac{k^*}{k_{eq}} \right) \right) \right)$$

Equation 1.2.6

$$T^* = T_f + m_L(V) * C_L^* + \frac{m_L^* V}{1 - k_{eq} * V_0}$$

Equation 1.2.7
V₀ is the speed of sound and Tₐ is the melting point. These two equations allow for better estimates for various properties such as freezing range and extended solubility limits due to rapid quenching. These equations were proposed for general use with binary alloy systems but could also be used with isopleths.

In addition to elemental segregation during solidification, one also must consider the possibility of post solidification, solid-state diffusion. Cr, Ni, and Mo were previously reported as segregating elements in austenite and ferrite solidification of 316L. Solid-state diffusion is a process that is controlled by the diffusion coefficient of each element, temperature, and time and unlike welding or casting processes where parts remain at high temperatures for significant amounts of time, PBF processes experience rapid cooling rates. As a result, there is a reduced duration where two of the necessary conditions are met for diffusion to occur, minimizing the distance over which diffusion could occur or eliminating the possibility. The solid state diffusion coefficients of Cr and Ni in austenite and ferrite differ significantly in which solute diffusion in austenite is lower for each element than in ferrite. This would indicate that if there was solid-state diffusion occurring in rapidly solidified microstructures it would likely happen in primary ferrite solidified microstructures compared to austenite microstructures. The diffusion coefficients and equations for diffusion coefficients at near liquidus temperatures for these elements are listed in Table 1.2.8. The largest diffusion coefficient value being for Ni
diffusion in ferrite. The larger diffusion coefficients of these elements in ferrite, in particular Ni, has been proposed as to why no cellular segregation has been previously reported for some rapidly solidified ferritic microstructures. [66, 70, 96]

Table 1.2.8 Average calculated diffusion coefficient at high temperatures for Cr in the austenite and ferrite phase of a duplex SS and Ni in the austenite and ferrite phase of Fe. [60, 96, 102-104]

<table>
<thead>
<tr>
<th>Diffusion Coefficient</th>
<th>Austenite (cm²/s) 1425 °C (a)</th>
<th>Ferrite (cm²/s) @ 1420 °C (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>$3 \times 10^{-9} : D=8 \times 10^{-2} * e^{(-58500/RT)}$</td>
<td>$1.7 \times 10^{-4} : D=0.06e^{(-50700/RT)}$</td>
</tr>
<tr>
<td>Ni</td>
<td>$2 \times 10^{-10} : D=9 \times 10^{-3} * e^{(-60000/RT)}$</td>
<td>$7.8 \times 10^{-5} : D=9.7e^{(-62700/RT)}$</td>
</tr>
</tbody>
</table>

LPBF features and other RSP techniques

LPBF was selected as the FBAM process of choice for this dissertation work due to its ability to generate high rates of solidification and frequent use in industry and existing literature on RS of austenitic SS alloys. As such, there are a few characteristic attributes that are commonly reported on for LPBF processed 316L SS that should be highlighted. LPBF processing can use laser travel speeds over 1m/s during the build process and can operate within solidification rates in the regime of 100-1,000 mm/s. [3, 7, 69, 105] At RS rates solidification morphology in LPBF material is typically entirely cellular and exhibits a preferential orientation towards the edge of the melt pool as this is the primary direction of heat flow during solidification. (Figure 1.2.12) [17, 69, 106] Dislocation pileup along the solidification cell boundaries is commonly reported in LPBF processed austenitic 316L microstructures. (Figure 1.2.13) [9, 12, 14, 17] Additionally, MnSi oxides that have been identified as the metastable phase, rhodonite, are also typically observed to decorate the cell boundaries in varying sizes for LPBF 316L depending on whether shielding gas was used or an inert chamber. (Figure 1.2.13 and 1.2.14) [12, 17, 107] Finally, elemental segregation in SLM processed 316L and other austenitic SS material is reported to be determined by the primary solidification phase. Austenitic 316L microstructures
are regularly reported to segregate primarily Cr and Mo to the cell boundaries with less significant amounts of Mn segregation also reported in some work. \[12, 13, 17, 108\] An example of this segregation behavior is shown in the EDS chemical maps in Figure 1.2.5.3 which also shows the presence of the MnSi oxides. Unlike elemental segregation in primary austenite, the cellular segregation behavior of primary ferrite solidified LPBF 316L material is not as widely investigated and when it is, Ni segregation to the cell boundaries was not always reported. \[8, 13, 17, 69, 109\] This has been suggested to be caused by already low amounts of Ni segregation produced during solidification and solid-state diffusion leading to a homogenization of the microstructure. \[53, 64\]

Figure 1.2.12 Two separate 316L samples produced via LPBF showing the etched solidification structure in (A) an optical micrograph \[20\] and (B) SEM image. \[3\]
Figure 1.2.13 TEM bright field (BF) images showing dislocation pileup and oxide particle formation at cell boundaries in an austenitic 316L microstructure produced via LPBF at (A) low and (B) high magnification. [17]

Figure 1.2.14 EDS chemical maps of cellular structure where Cr, Mo, and Mn were detected to segregate to cell boundaries in austenitic microstructure from LPBF 316L material. [17]

Currently, identifying the correct adjustments for key processing parameters in LPBF to control the final microstructure and performance of a build using any material is a difficult process. This optimization of processing parameters for new materials is typically accomplished
by implementing parametric studies where a few key parameters are systematically adjusted.\cite{2, 4, 14, 18} However, due to the high price tag of feedstock powders mentioned earlier and lengthy process required to clean and change powders in most LPBF machines these options are costly and time consuming regardless. Simulations can assist in this process guiding the parameter selection but are highly complex and, at least initially, need experimental data to be validated. This is where a greater understanding of the effects that rapid solidification has on the microstructure and material properties becomes so important.

Other RSP techniques that fall outside of the FBAM header and that are used when studying RS include metal powder atomization, melt spinning, splat and anvil experiments, Duwez gun experiments, and single pulse laser welding/surface melting. Laser/electron beam welding and single pass melts make use of the high-energy density of the sources to achieve cooling rates on the order of $10^5$-$10^6$ K/s for stainless steels.\cite{25, 40, 45} Melt spinning is a technique where a stream of molten metal is continuously deposited onto a chilled rotating drum. The drum material is typically Cu due to the good heat transfer properties and availability. The process requires kg of material to be melted and deposited but is capable of achieving cooling rates between $10^4$-$10^6$ C/sec.\cite{25, 110-112} Atomization produces metal powder that can undergo a range of cooling rates depending on the size of each particle but is a costly process that requires specialized equipment to make. General dendrite arm spacing to cooling rate relationships for some different metals are shown in Figure 1.2.15 along with the ranges of cooling rates over which different RSP techniques associated.\cite{74} There are a few different types of splat quenching experiments that can be used to produce RS such as the Duwez gun, chilled plate, hammer and anvil, and two-piston splat quench. Both the Duwez gun and Rotary Splat Quencher produce thin, discontinuous metal foils that are not suitable for measuring mechanical or solidification
properties, but they also achieve the highest cooling rates \(10^{10} \text{ K/s}\) of the four techniques mentioned.\(^{[113-117]}\) The piston and anvil and two-piston splat quench technique, however, produces more consistent, repeatable splat foils.\(^{[45, 73, 118]}\) Vitek, Ruhl, Inokuti, and Hayzelden provide estimates of the cooling rates for two-piston splat quenching to be on the order of \(10^5-10^8 \text{ K/s}\), theoretically reaching \(10^{10} \text{ K/s}\).\(^{[45, 73, 114, 117-121]}\)

![Diagram showing variation of dendrite arm spacing with cooling rate for different metals and the associated RSP techniques.]

**Figure 1.2.15** Variation of dendrite arm spacing with cooling rate for different metals and the associated RSP techniques.\(^{[74]}\)

Two-piston splat quenching

The focus of this dissertation work was on the utilization of two-piston splat quenching (SQ) to simulate rapid solidification in SS. Two-piston splat quenching also referred to as a magnetic-yoke piston apparatus will be referred to as SQ from here on, is an older method of simulating RS conditions where a sample is electromagnetically levitated, melted, dropped, and compressed or “splatted” between two Cu platens forming a rapidly cooled foil. Each platen is
mounted on the end of a steel rod which are simultaneously accelerated towards each other when triggered by the falling liquid droplet as it passes through the light relay. A schematic of the magnetic-yoke apparatus is shown in Figure 1.2.16. The SQ technique has several distinct attributes that separate it from other RS experimental techniques. By electromagnetically levitating and melting the sample, chances of heterogeneous nucleation occurring prior to the splat are minimal, there are fewer chances for melt contamination, there is a high degree of homogeneity in the melt, and homogenous nucleation can be controlled by the amount of supercooling or superheat applied to the droplet during levitation. Additionally, SQ is a relatively low cost experiment to run and can be completed in short amounts of time. Initial conditions for solidification in SQ are mostly fixed as prior to the splat event the sample is a known mass, volume, shape, and temperature. During the splat event, the liquid droplet is contacted by the platens and deformed, flowing rapidly outwards as it is solidifying, resulting in a complex solidification event. Splat quenching machines tend to be less complex than PBF machines which require galvo mirrors, lens cooling systems, powder spreaders, etc. and have fewer inputs that can be changed. The advantages of SQ make this technique ideal for assessing the RS response of alloys across a wide compositional space.
Figure 1.2.16 Magnetic-yoke piston apparatus similar to the one used in this dissertation.\cite{122}

Previous work has been done using SQ with various binary alloy systems to primarily study RS microstructures and bulk metallic glass formation. The previous work relating to Fe based binary systems include but are not limited to Fe-C, -Al, -Cu, -Ni, -Cr, -Mo, and -Mn.\cite{45, 114, 117, 119, 124, 125} Significant work by R. C. Ruhl et. al. investigating the key variables like splat thickness, heat transfer coefficients, and splat temperature that effect cooling rate in multiple splat cooling processes including SQ.\cite{114} This work also entailed modeling splat cooling under both ideal and Newtonian conditions.\cite{114} They reported cooling rates between $10^5$-$10^8$ K/s which showed good agreement between measured and calculated values.\cite{114, 117} A study by H. Jones later reported that for Fe on Cu splat quenching experiments cooling rates were between $10^4$ and $10^7$ K/s that are between near-ideal and non-Newtonian cooling conditions.\cite{45, 113} Work by Inokuti and Cantor used SQ to look at the effect of RS in Fe-Ni and Fe-Mn alloys and reported a suppression of the martensite transformation temperature and higher retention of
austenite in SQ material due to the large cooling rates.\cite{118, 126} In this study, as well as in piston and anvil quench experiments of Fe-25Ni performed by Kattamis et. al. and other SQ experiments, cooling rates are regularly reported between $10^5$ and $10^7$ K/s.\cite{45, 126, 127} The work by Kattamis et. al. also reported that elemental segregation between the cellular solidification structure was still observed at the high cooling rates in SQ samples.\cite{127} In other work on SQ of the Fe-Ni binary alloys, Hayzelden reported a small segregation free region at the onset of solidification that rapidly broke down into cellular solidification driven by the microsegregation of Ni.\cite{73}

One study by J. V. Wood et. al., used a modified Duwez gun with Fe-20Cr-25Ni ternary to detail the microstructure of hammer and anvil splat quenched samples.\cite{125} They chose this alloy to avoid the solid state ferrite to austenite transformation and ensure fully primary austenitic microstructure. In this work, as well as other SQ works the solidification microstructures were reported to be fine cellular that are more frequently reported as normal to the plane of the foil, i.e. in the direction of solidification.\cite{118, 125, 127} Another unique feature reported in samples produced by of two-piston splat quench experiments is the observation of two separate solidification fronts that meet in the middle of the sample as well.\cite{127, 128} This also appears in hammer and anvil samples, but can be biased to one side.\cite{45}

Very little work could be found on SQ of complex SS alloys, only one paper by J. M. Vitek et. al., that used a hammer and anvil splat quenching with three 300 series SS alloys (310, 308, and 312 SS).\cite{45} The Cr and Ni concentrations are as follows, 310SS-26.7Cr-21.5Ni, 308SS-20.5Cr-10.5Ni, and 312SS-30.2Cr-6.0Ni and equate to Cr/Ni$_{eq}$ values of 1.1, 1.6, and 3.1 respectively using Schaeffler 1949. Vitek et. al. reported that while 310SS was cooling rate insensitive and formed fully austenitic structures over the range of cooling rates 308 and 312SS
ranged from forming fully austenitic or fully ferritic microstructures at the highest cooling rates respectively to duplex structures at lower cooling rates. This is supported by the microstructure selection maps proposed by Lippold and Elmer in Figures 1.2.4 and 1.2.5. The higher cooling rate region was identified as regions near the splat surface or interface and the lower cooling rate region was at the splat quench interior. Other important observations were that laser welded 308SS had large 0.5µm diameter MnSi oxides that weren’t observed in the SQ 308 material and splat quenched 312SS formed Cr rich M_{23}C_{6} precipitates along the grain boundary.

1.3 Summary of Background and Literature Review

The impact of elevated solidification rates and cooling rates on microstructures in austenitic SS alloys is fairly well studied for the lower end of rapid solidification rates and are highly applicable to traditional welding or solidification processes. However, with the increased use of FBAM technologies across industry to create austenitic SS parts with complex geometries and the reliance of PBF processes on faster rapid solidification and cooling rates there is a critical need for further development of the understanding of the interplay between RS, composition, and microstructure sub-microscale features in SS alloys.

PBF processes are highly complex, techniques that use a laser focused to nm to µm in size to build parts on the order of cm to dm in size that have µm to mm level resolution with multiple variables which can be adjusted or controlled that will directly affect the build quality and microstructure of the finished part. Parametric studies to optimize build parameters for a new design or material in PBF are time consuming and costly to perform, requiring large amounts of feedstock material. SS alloy specifications for compositions have been purposefully designed for specific applications to achieve target microstructures and phase contents under equilibrium or near-equilibrium solidification conditions. However, even when limited to a single well studied,
material like 316L SS, current compositional specifications allow for a range of acceptable values that can potentially result in a 10% change of total alloying concentration for this material. While quantitative tools like the WRC-1992 equations can be used to represent an alloy chemistry and provide an estimate of the phase formation in the form of a FN, these methods are limited in compositions that they remain accurate over and do not accurately adjust for RS conditions. Additionally, microstructure prediction maps like those created by Lippold and Elmer show how RS will impact the solidification mode and final microstructure for a range of potential compositions up to between 10 mm/s and 100 mm/s. It must be remembered that these are still predictive tools and the effectiveness of these maps to predict the effects of RS are the most accurate for similar alloy compositions as the data used to generate them. Also, the solidification rates of interest for LPBF are in the 100-1,000 mm/s regime which are above the 10-100 mm/s beam travel speeds these plots are designed around. An alternative process for simulating RS rates in this 100-1,000 mm/s regime would provide a fast, cost effective alternative for investigating effects of RS on new alloy systems for use in LPBF and other FBAM processes.

SQ is potential alternative technique that is capable of producing RS conditions and high cooling rates in metals similar to those found in LPBF material. Thus, the possibility of using SQ to investigate RS in complex SS alloy systems for LPBF should be further investigated. SQ experiments can be performed quickly and at a fraction of the cost to trialing new alloy compositions in a LPBF system. Both techniques have estimated cooling rates between $10^5$ and $10^8$ K/s and are capable of achieving solidification rates in the 100-1,000 mm/s regime, approaching the absolute limit of stability for cellular growth. No expensive atomized powders are required for SQ experiments and custom alloy feedstock can be made or purchased for
experiments. SQ has also been previously shown to produce similar cellular solidification structures to those observed in LPBF melt pools. The SQ process is particularly relevant for this implementation as it occurs very quickly, capturing a single solidification event allowing for investigation of as close to the as solidified microstructure as possible. The lack of published literature involving SQ and complex SS alloys creates a unique opportunity to utilize SQ to study RS in austenitic SS alloys and apply the results to high solidification rate PBF processes. On the other hand, the wealth of literature that currently exists for PBF processing of 300 series austenitic SS like 304L and 316L will allow for detailed comparison of the RS microstructure produced by SQ to validate the use of SQ for this process. Additionally, the high degree of control and repeatability of the process allow for more direct comparison of any results with the modified variable. Using SQ to provide a faster method for investigating the composition-RS-microstructure relationship for individual alloy compositions will allow for more targeted modification of PBF operating parameters to achieve the targeted microstructure.

1.4 Research Objectives and Dissertation Structure

   Based on the challenges, literature, and opportunities previously described relating to rapid solidification of austenitic stainless steels as it pertains to fusion based additive manufacturing processes by laser powder bed fusion the technical objectives of the research discussed in this dissertation are defined as follows:

1.) Further explore and refine the current understanding of how compositional modifications of Cr and/or Ni impacts the solidification path and microstructure formation during rapid solidification for SS alloys with respect to the WRC-1992 Cr/Ni_{eq}.

2.) Examine the connections between the solidification path, solid state phase transformations, and microstructures of rapidly solidified SQ stainless steel samples.
3.) Establish cooling rate and solidification rate estimates for SQ samples using cell size measurements.
4.) Demonstrate the effectiveness of SQ at simulating RS conditions similar to PBF in austenitic SS alloys.
5.) Perform detailed analyses of the same 316L stainless steel material produced by both LPBF and SQ across multiple length scales to observe and quantify phase content, solidification path, cell size/spacing, and cellular microsegregation.
6.) Examine the potency of Mo at increasing concentrations as a ferrite promoter and with respect to the ferrite to austenite massive transformation at rapid solidification rates.

This dissertation is written using a journal-style format and is arranged accordingly. After the introduction, Chapter 2 is a general methods section providing greater detail about any analysis method or technique used in any of the articles that follow. Chapter 3 primarily addresses the influence of Cr and Ni on the phase and microstructure formation in objective one. This chapter also covers technical objective two and three, detailing the connection between the solidification path, and observed microstructure in rapidly solidified SS samples and providing solidification rate estimates. Chapter 4 works to address technical objectives four and five by presenting the numerous similarities between solidification structures, microstructures, and microsegregation in SQ and LPBF produced samples from the same feedstock. Chapter 5 reports on objective six and partially objective two covering the impact of various concentrations of Mo on the solidification path, microstructure, and cellular microsegregation at the same Cr/Ni<sub>eq</sub>. These chapters are then followed up with a conclusion chapter, Chapter 6, that summarizes the key findings from the entire body of research, provides suggestions for potential future studies to expand on current findings, and list final conclusions.
CHAPTER 2: METHODS

2.1 Alloy Design and Production

Alloy feedstocks were custom made for the work presented in this dissertation to achieve specific variations in alloy composition through controlled modification of alloying elements. Equivalency values were calculated using the WRC1992 set of equations. Our approach to investigating the effect of Cr and Ni was based in the use of isopleths. The Fe-Cr-Ni isopleth was readily simulated and provided a good initial prediction about the stable phases one would expect to form. Using these isopleths, the Cr and Ni can be varied systematically to track the predicted phase stability. This concept of how to vary the Cr and Ni was kept in mind when designing the alloy feedstock chemistries. Specific alloy compositions for the alloys used can be found in the individual chapters. A full list of the compositions for all alloys produced can be found in Appendix 7.1.1. Alloy compositions were designed based on the ASTM A240 specification for 316L SS with the intent of modifying only Fe, Cr, Ni, and Mo concentrations to achieve the targeted Cr//Ni_{eq} values.

Custom alloy feedstocks were made using high purity elements in the form of plates, powder, and pellets. (Table 2.1.1) Alloys were designed to target specific chemistries and produce 20g of feedstock that could be used for multiple splat quench experiments. Ni, Mo, Mn, Si, and C powder (when used) were weighed individually and mechanically mixed together prior to being pressed into a pellet. The powders were pressed into a pellet to reduce losses during arc melting. Fe and Cr were weighed out separately due to them not being in powder form. The use of C powder to alter the C content of the final alloy was attempted but was not successful.
Attempts were also made to use 1080 SS wire as a base metal replacing enough pure Fe to achieve the targeted C concentrations in the final alloy, however these were also unsuccessful.

Table 2.1.1 Pure elements used to make custom alloy feedstock for SQ with the purity, form, and supplier.

<table>
<thead>
<tr>
<th>Element</th>
<th>Purity (%)</th>
<th>Form</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>99.99</td>
<td>Pellet</td>
<td>Goodfellow and Kurt J. Lesker</td>
</tr>
<tr>
<td>Cr</td>
<td>99.98-99.99</td>
<td>Plate</td>
<td>Goodfellow and Kurt J. Lesker</td>
</tr>
<tr>
<td>Ni</td>
<td>99.99</td>
<td>Powder</td>
<td>Goodfellow</td>
</tr>
<tr>
<td>Mo</td>
<td>99.9</td>
<td>Powder</td>
<td>Goodfellow</td>
</tr>
<tr>
<td>Mn</td>
<td>99.5</td>
<td>Powder</td>
<td>Goodfellow</td>
</tr>
<tr>
<td>Si</td>
<td>99.99</td>
<td>Powder</td>
<td>Goodfellow</td>
</tr>
<tr>
<td>C - Powder</td>
<td>99.99</td>
<td>Powder</td>
<td>Goodfellow</td>
</tr>
<tr>
<td>C – 1080 SS</td>
<td>0.08</td>
<td>Wire</td>
<td>Goodfellow</td>
</tr>
</tbody>
</table>

An ABJ-900 GTA melter with water chilled Cu plate was used to melt and combine the mixed element pellet with the Cr and Fe and produce the feedstock. Powder pellet, Cr pieces, and Fe pieces were layered from bottom to top inside of a cleaned, circular reservoir on the Cu plate in the arc melter. The chamber was put under vacuum and backfilled with UHP Ar three times. During arc melting, a constant flow of Ar at 15L/min was used to maintain an inert environment. Prior to melting the charge, a piece of Ti was melted in the inert environment first to collect any remaining oxygen in the chamber. A 250A current supplied by a Miller XMT-450 power supply was used in the arc melting process. Once the charge had fully melted, heat was applied to the liquid pool for approximately 45 seconds while the electrode/arc was moved in a circular mixing motion to encourage homogenization in the sample. After the 45 seconds the arc was removed, and the sample allowed to solidify and cooled for one minute before it was flipped over and re-melted using the same applied heat technique described previously. This process was repeated a total of six times to encourage complete mixing of the elements and produce a homogeneous sample. The sample was allowed to fully cool, under vacuum for 20 minutes before being removed from the chamber. Arc melted samples (buttons) were cold rolled reducing
the buttons from ~25mm down to a plate, ~2.4mm thick. This thickness was required in order to make symmetric samples with the target mass for SQ experiments as sample symmetry improves levitation.

2.2 Feedstock Characterization

Feedstock material was characterized prior to splat quenching using a combination of inductively coupled plasma optical emission spectroscopy (ICP-OES) and IR spectroscopy via inert gas fusion (IGF) and combustion, as well as energy dispersive X-ray spectroscopy (EDS) in some cases. For ICP-OES and IGF analysis, pieces of feedstock material were sectioned from the rolled feedstock and sent to the team at Honeywell FM&T for chemical analysis. The bulk chemical analysis performed by Honeywell FM&T measured the concentrations of Fe, Cr, Ni, Mo, Mn, Si, P, Cu, V, B, Ti, Nb, and Al using primarily ICP-OES. IGF and combustion were used to measure C, N, S, O, and H concentrations which utilize IR spectroscopy.

The second method utilized qualitative EDS to look at the chemical homogeneity of the feedstock material. Unlike ICP-OES and IGF which were used for all feedstocks, this analysis method was only used on the first five produced. Sections of the arc melted feedstock were sectioned from the bulk feedstock prior to cold rolling. Samples were mounted in PolyFast, and standard grinding and polishing practices were used to prepare the surface for EDS investigation, finishing polishing with a 0.05um colloidal silica suspension. Data was collected using a JEOL 7000 SEM with an Oxford X-Max 80mm² EDS detector and analyzed using the AZTEC software. A combination of EDS maps and line scans were collected at various locations within the feedstock material.
2.3 Splat Quenching

For SQ experiments rolled feedstock was sectioned into cubes roughly 2.4mm x 2.4mm x 2.4mm in size, weighing approximately 105mg. Symmetric samples were found to produce the most stable levitation during electromagnetic levitation (EML) and melting. Prior to splat quenching samples were rinsed with acetone and dried using compressed air. An Edmund Buhler Ultra Rapid Quenching machine was used for all SQ. Once inside the chamber, the SQ machine was sealed and pumped down using a rotary vain pump (RVP) and backfilled with ultra-high purity (UHP) Ar three times. Following the roughing purges, the chamber was brought under a high vacuum (HV) of 5E-5 mPa for 45 minutes minimum, then backfilled with UHP Ar to and held at 600mPa. A foot pedal was used to activate on the electromagnetic field and begin levitation and melting of the sample. Upon reaching stable levitation the crucible was removed and the light trigger was activated. During this process a two-color pyrometer was used to measure the surface temperature of the droplet during levitation melting. The pyrometer utilized a 10ms sampling rate to ensure up to date temperature data was used during SQ experiment. A target superheat of 1600°C was used for all SQ experiments and was typically met within ±1%. When the target superheat was reached, the EML was stopped by releasing the foot pedal and the sample entered free fall. As it fell, the sample interrupted the light trigger, engaging the platens to create the splat event. A schematic of the splat quench machine is shown in Figure 2.3.1. The chamber was brought to atmosphere, and the splat quenched sample removed. The side of the SQ that was impacted by the left and right platen was marked and recorded. Some samples experienced movement during levitation, revolving around the interior of the coil during EML and as a result could fall off center. Both sides of a typical splat quench after removal from the machine are shown in (Fig. 2.3.2 A-B) A small disk was observed on the surface of splat
quenched samples and was used to indicate the region of interest (ROI). The disk was typically about 40% the total diameter of the SQ in size.

Figure 2.3.1 Schematic of two-piston splat quenching chamber setup.

Figure 2.3.2 Opposite sides of a single SQ. (A) is the side of the sample that was impacted by the left platen and (B) is the side of the sample that was impacted by the right platen. The right platen (B) impacted the liquid droplet before the left platen (A) causing the smaller disk that is observed in B and not A.
2.4 Splat Quench Sample Preparation

Splat quenched samples were cross sectioned through the middle of the disk and mounted with the cross section exposed. The XYZ coordinate system shown in Figure 2.3.2 remains accurate when looking at mounted splat quenches and has been updated to reflect the change in orientation in Figure 2.4.1. Samples were hot mounted in PolyFast using a Struers mounting press. PolyFast is an electrically conductive polymer used for ease of imaging in with electron microscopes that also has good edge retention during polishing. SQ cross sections were held up using spring clips and hot mounted at 25kN and 180°C for 6 minutes then cooled for 4 minutes. A visual of the mounted splat quench with axes defined is shown in Figure 2.4.1.

![Figure 2.4.1 Schematic of mounted SQ with ROI highlighted in red box.](image)

Hot mounted samples were ground and polished using a Pace Nano-1000 auto-polisher using the following grit progression: 320 grit, 600 grit, 1200 grit, 3µm colloidal silica, 1µm colloidal silica, and vibratory polished for 12 hours with a 0.02 µm colloidal silica suspension on a Pace 12” Giga-S Vibratory Polisher. SQ samples were hand ground to at least 1200 grit with the X-axis parallel to the tangent of grit paper rotation. If not done, the grinding pad would cause the SQ to be pulled over or smeared, artificially increasing the observed splat quench thickness. The smearing effect was less prominent when hand polishing, but not completely absent and slight smearing could occur if care was not taken.
2.5 Optical and Electron Microscopy

Optical images of the polished SQ cross section were taken using a Leica optical microscope. In samples that had been vibratory polished for a long period the ferrite and austenite phases were readily distinguishable. SQ samples were imaged across the entire diameter (X-axis) of the cross section as indicated in Figure 2.5.1. Optical phase quantification was performed using ImageJ to measure the area of the SQ and the area of the ferrite phase image across the entire SQ.

![Figure 2.5.1 Visual explanation of where optical images were taken for phase analysis.](image)

Qualitative EDS was again performed using a JEOL 7000 SEM with an Oxford X-Max 80mm² EDS detector and analyzed using the AZTEC software. Line scans were collected across the thickness of splat quenched samples, from the left platen splat (PS) interface to the right PS interface, inside the ROI using a step size of 0.5µm. Similarly, EDS chemical maps spanning from left to right PS interface were also collected from within the ROI of SQ samples.

Quantitative EDS with standards was used to investigate the chemical homogeneity between replicate splat quenches, between different microstructure regions within the same splat quench, and radially across the SQ. EDS spectra collected for quantitative EDS with standards were processed using the DTSA-II software developed by Dr. Nicholas Ritchie at NIST. Earlier work completed with Dr. Ritchie enabled the development of a set of operating conditions for use in this process to provide the most accurate results possible within the limitations of EDS. All data was collected at or near a probe current of 0.5nA (actual probe current was recorded and
used in calculations). Probe current was measured using a Faraday Cup with a 100µm aperture. NIST standard reference materials (SRM) were used for pure elemental references. All spectra were collected using the following: 0.5nA, 60 sec live time, 4 process time, 20keV beam energy, 40keV energy scale, 4096 channels, WD 9.5mm. Five, 60 second live time spectra were collected for each element (Fe, Cr, Ni, Mo, Mn, Si), as well as when collecting spectra from SQ samples. Carbon and nitrogen references were not used because of the poor energy resolution of EDS, particularly at low energies, and the difficulty quantifying light elements. Spectra from NIST SRM 316L material were also collected using the same processing conditions and used to aid in quantifying major element compositions within samples.

In DTSA II, material standards were created for the SRM pure elements and SRM 316L by combining the signal from the five separate spectra together. This was done to improve the count statistics and limit any potential of a contamination throwing off the spectra by sampling multiple areas. The most accurate quantification results were achieved using material standards from a combination of spectra collected from pure Mo, Mn, and Ni and Fe, Cr, and Si from the 316L SRM standard.

Backscatter electron (BSE) images were taken on a ThermoFisher Apreo SEM using an A+B detector. Electron Backscatter Diffraction (EBSD) scans were collected using a JEOL 7000 SEM, phosphor screen EBSD camera, and the Aztec software to process the collected Kikuchi patterns. Scans were taken at 70° pre tilt at 600X magnification using a probe current of 16 and step size 0.2um. In the phase maps, BCC ferrite is marked as red and FCC austenite is marked as blue. IPF-Y maps were used instead of IPF-X or IPF-Z because the Y-axis is the direction of solidification. KAM maps were set to a scale of 0° - 5° using 3X3 binning. The data was not cleaned or modified in post processing unless specifically stated.
It should be kept in mind that while EBSD provides valuable information, the technique is restricted in the total area it can scan by the time it takes to collect and process the data. EBSD scans and corresponding microstructure maps generated in this work represent a relatively small portion of the entire cross section of the sample. They are not indicative of the grain morphology or phase distribution throughout the entire sample. The EBSD scans for a splat quenched sample typically covered less than 1% of the entire cross section.

TEM foils were made from etched SQ samples using two methods. Method one was a FIB liftout using a TESCAN FIB or Quanta FIB. Foils were oriented perpendicular to the growth direction of the cellular structure producing a cross section of the cells when looked at in a TEM. A 15μm wide, 2 μm thick, platinum bar was deposited on top of the solidification cells at the location of interest, lifted out, attached to a Cu grid, and thinned to <150nm thick. The second method was using a Tenupol-5 Jet Polisher. This method used a 3mm disk punched out of the SQ foils. The solution was a 10% perchloric acid 90% acetic acid mixture at room temperature using 50V.

Bright field (BF) and scanning transmission electron microscopy high-angle annular dark-field (STEM-HAADF) images were collected using a TECNAI F-20 TEM operating at 200kV. BF images were taken both in focus and intentionally out of focus to highlight certain nanostructural features. STEM-HAADF images were collected using various short and long camera lengths between 50mm and 960mm. The longer camera length was used to better observe dislocations in STEM-HAADF imaging while the shorter camera length reduced our visibility of dislocations. STEM-EDX analysis was performed using an Optima T-60 Amtek detector and the TEAM analysis software. A combination of line scans and maps were collected to investigate the
different nano structural features of the samples. Specific details of how STEM-EDX data was processed are covered in each paper.

2.6 Etching and Cell Size Analysis

Electrolytic etching was used to reveal the cellular solidification structures in splat quenched material. The primary electrolyte used for etching was a 60/40 mix of 70% nitric acid and DI water. Samples were submerged in the solution and a DC power supply was used with a SS cathode and a sharpened tungsten electrode as the anode. The power supply was set to 1.25V using the voltage-controlled mode. Samples containing only primary austenite only needed to be etched for about 5 sec. Samples containing both primary austenite and F/MA required slightly more time typically around 10-20 seconds. Samples with all F/MA, mixed F/MA and ferrite, or all ferrite microstructures were etched at longer times until the cellular structure could be seen. In some ferrite samples, the microstructure had to be over etched to sufficiently reveal the cell structure.

A few other electrolytic etch solutions were explored. A 90/10 mixture of oxalic acid and DI water at 15V for approximately 50 seconds seemed to have an inverse etching behavior to the nitric acid etch. The oxalic acid did work to reveal the cell structure similar to nitric acid. However, using oxalic acid was found to produce results less consistency and did not define the cells as well as nitric acid. The other electrolyte explored was a mixture of 20g NaOH and DI water. This was specifically explored to try to reveal cell size in samples that were primary ferrite. We found some success with this electrolyte, however, again the results were less consistent and clear than when the nitric acid solution was used.

Etching of SQ samples was key to differentiating between primary austenite and F/MA microstructures. After EBSD had been performed, if the sample indexed as austenite, it was
etched using nitric acid and based on the response could be identified as either primary austenite or F/MA. We classified the two etching responses as type 1 cells and type 2 cells. Type 1 cells were cells that solidified as primary austenite and are identified by deep, clean outlines of the cells. The cells retain most of the columnar structure associated with cellular solidification. Type 2 cells were formed during primary ferrite solidification and were present in both F/MA microstructures and primary ferrite microstructures. These cells were identified by the coarser etch that does not penetrate as deeply into the cell boundaries and reveals a more needle like structure.

After cells were sufficiently etched, SEM images of the etched structures were collected. Macro images were collected at 1,000X at six different sites along the X-axis of the cross section identified in Figure 2.6.1 A. The regions associated with the six sites were chosen to span the length of the cross section with two sites in each of the areas of interest along the splat quench (center of ROI, edge of ROI, midway between ROI and outer edge). Each site was further divided evenly into 6 zones, 3 per solidification front. (Figure 2.6.1B) Zone 1 began at the left PS interface and zone 3 ended at the midline on the same solidification front. Zone 4 started on the other side of the midline and zone 6 ended at the right PS interface. Using ImageJ, individual cell size measurements were collected in each zone for each site.
A one-way analysis of variance (ANOVA) was used to analyze cell size measurements and assess whether the means of independent datasets were significantly different. A one-way ANOVA test was run for each site to compare the six individual zones using a 95% confidence index to generate the mean cell size and variances for each zone. If the P-value returned was less than 0.05 it could be concluded that at least one set of mean values were significantly different. To determine which zones had mean cell size values that were significantly different a Tukey-Kramer Post Hoc analysis was performed in which Zone 1 was tested against zone 2, zone 2 vs zone 3, zone 3 vs zone 4, etc. The absolute mean difference ($\bar{X}$) was calculated by taking the absolute value of the difference of the two means between the two zones. (Equation 2.6.1) The standard error ($SE_{ANOVA}$) was calculated using equations 2.6.2 using the mean squared error ($MS_{E}$) and sample size (n) for the two groups. The $Q_{Tukey}$ value was solved by dividing $\bar{X}$ by the $SE_{ANOVA}$ value. Lastly the $Q_{Crit}$ value was looked up on a standardized range $Q$ table using a 95%
confidence index for 6 groups and the specific degrees of freedom. $Q_{\text{Tukey}}$ could then be compared against $Q_{\text{crit}}$ and if $Q_{\text{Tukey}}$ was larger than $Q_{\text{Crit}}$ the mean of the two zones was determined to be significant.

\[
\bar{X} = |U_1 - U_2| \quad \text{Equation 2.6.1}
\]
\[
\text{SEANOVA} = \sqrt{\frac{M^2S_E}{2} \left( \frac{1}{n_1} + \frac{1}{n_2} \right)} \quad \text{Equation 2.6.2}
\]

### 2.7 Cooling Rate and Solidification Rate Estimations

Cell size measurements were used to estimate cooling rates using the empirical relationship described in equation 2.7.1 and material constants of $A=80$ and $n=0.38$ reported in work by Katayama and Matsunawa.\cite{25} In order to make solidification rate estimates from the cell size measurements, temperature gradients, $G$, that corresponded to the range of cooling rates estimated by the cell size were extracted from heat transfer simulations performed in ANSYS Fluent. These simulations were ran using a heat transfer coefficient of $h=10^7 \text{ W/(m}^2\text{*K)}$ determined from literatures.\cite{73, 114, 117, 121, 129} Heat transfer simulations using coefficients of $10^5$ and $10^6 \text{ (W/m}^2\text{*K)}$ were tested but produced cooling rates that were not high enough. To estimate the solidification rate equation 2.7.1 was modified into equation 2.7.2 by replacing cooling rate ($\dot{T}$) with $G \cdot R$ allowing for the solidification rate, $R$, to be solved for.

\[
d = A \cdot \dot{T}^{-n} \quad \text{Equation 2.7.1}
\]
\[
d = A \cdot (G \cdot R)^{-n} \quad \text{Equation 2.7.2}
\]

### 2.8 Vibratory Sample Magnetometry

Vibratory sample magnetometry (VSM) was used as a means to measure the primary ferrite content of individual splat quenches within the ROI. VSM works by applying a magnetic field (Oe) to the sample and measuring magnetic moment (emu) response of the sample. The literature shows good agreement for primary ferrite measurements in small samples using
VSM.[41, 130] This was performed using a Quantum Design Dynacool PPMS with non-magnetic, brass rods to hold the samples. The non-mounted half of the SQ was used for these measurements. Due to size limitations of the VSM chamber, a 3-5mm square was sectioned from the middle of the SQ and weighed. A visual representation of where this sample was taken from is represented by the black box in Figure 2.8.1. During VSM measurements the strength of the magnetic field was changed from 12,000 Oe to -12,000 Oe and back, recording the magnetic moment response. The step size used for varying the applied magnetic field was refined as it approached zero to improve measurement accuracy during increased change in the magnetic moment response. Step size was decreased from 100 Oe between ±5,000 and ±12,000 Oe, to 50 Oe between ±2,000 and ±5,000 Oe, and 25 Oe between ±2,000 and ±2,000 Oe The magnetic field range of 12,000 to -12,000 Oe was used to ensure the magnetic field fully saturated the sample, or came close to fully saturating the sample, i.e., where the magnetic moment response of the sample becomes linear. (Figure 2.8.2)

![Figure 2.8.1. Schematic of where VSM sample was taken from SQ.](image)
Figure 2.8.2. Example hysteresis loop from VSM measurement of a two-phase SS alloy.

To determine the primary ferrite content from the VSM measurement the saturation magnetization of a fully ferritic sample is needed. The saturation magnetization of ferrite can be estimated from the chemical composition of the material. There are a few different empirical relationships that can be used to calculate the saturation magnetization from the chemistry. We used the relationship developed by Merinov, et al. which accounts for Cr, Ni, Mo, Mn, and Si in the ferrite saturation magnetization calculation and is presented in Equation 2.8.1.  \[ \sigma_F = 21,600 - 275(\%Cr) - 330(\%Ni) - 280(\%Mn) - 610(\%Si) - 260(\%Mo) - 670(\%Ti) - 630(\%Al) \]  

In this equation \( \sigma_F \) is the saturation magnetization value for ferrite based on the chemistry. This equation outputs in units of Gauss and was converted to emu/g to match VSM data.

From the VSM data, the measured saturation magnetization of the sample was calculated and subtracted from the response leaving the maximum magnetic moment response. (Equation
2.8.2) This is divided by the mass of the sample measured earlier producing the sample’s saturation magnetization. By dividing the measured saturation magnetization by the calculated saturation magnetization of ferrite for that chemistry equals the wt % ferrite of the sample.

\[
\% \text{ Residual ferrite} = \frac{\sigma_u}{\sigma_F}
\]

Equation 2.8.2

Where \( \sigma_u \) is the measured saturation magnetization and \( \sigma_F \) is the calculated saturation magnetization for ferrite based on the chemistry.
CHAPTER 3: INVESTIGATION OF THE EFFECT OF CHROME AND NICKEL CONCENTRATIONS DURING TWO-PISTON SPLAT QUENCHING OF AUSTENITIC STAINLESS STEELS


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3.1 Abstract

For solidification rates at or near equilibrium solidification conditions the effects of chrome (Cr) and nickel (Ni) on stainless steel solidification modes and microstructures are well detailed, however, fusion-based additive manufacturing (FBAM) processes that rely on faster, more rapid solidification rates calls for a more in-depth understanding of the effects of rapid solidification on the solidification behavior and how these change with variations in alloy composition. Eleven custom stainless steel (SS) alloys with unique compositions based on 316L were made using targeted alloying element additions to generate feedstock with Cr/Ni_{eq} ratios ranging from 0.9-2.1. Two-piston splat quenching (SQ) was used to produce rapid solidification conditions similar to those achieved in powder bed fusion processes in a fraction of the time and cost of traditional methods. Employing heat transfer simulations, SEM, and STEM characterization techniques the SQ process was found to consistently produce solidification rates estimated to be between ~0.4-1.6m/s. Five unique solidification microstructures were identified within the rapidly solidified SQ samples. At rapid solidification rates, the primary ferrite solidification mode was found to occur at lower Cr/Ni_{eq} than previously predicted and the
primary ferrite phase was found in the microstructure of samples with lower Cr/Ni\textsubscript{eq} than previously predicted as well. SQ samples with compositions that were within the compositional specifications for 316L SS, an alloy which is commonly used in FBAM processes, demonstrated a wider range of potential solidification modes and microstructures that could form at rapid solidification rates than expected. By using SQ as a means to simulate rapid solidification conditions like those observed in FBAM processes, potential new alloy compositions can be screened faster and more cost effectively than purchasing and running test batches of the metallic powder.

3.2 Introduction

In order to better understand how rapid solidification conditions impact the microstructure of stainless steels (SS), there are a few key concepts that should be discussed ranging from solidification morphology and solidification mode to phase formation and alloy composition. Two of the most prevalent phases formed in low carbon SS are austenite and ferrite. The formation of these phases under equilibrium conditions is primarily decided by the concentrations of austenite and ferrite stabilizing elements used to alloy these steels with the two most prevalent being Cr and Ni. Ternary phase diagrams are useful for understanding and identifying the evolution of phase formation based on composition at a given temperature. Isopleths of the Fe-Cr-Ni system can be used to create pseudo-binary phase diagrams that can provide a two-dimensional visualization of the predicted phase and solidification path as a function of Cr and Ni concentrations and temperature given a single Fe concentration. \cite{7, 31, 40, 133}

However, pseudo-binary isopleths should be used with some caution as these are 2-D representations of a 3-D space which can potentially lead to the results being misinterpreted and should not be overly relied upon. \cite{66} Even so, constant pseudo-binary constant Fe isopleths have
been shown in multiple literatures sources to be significantly useful for producing equilibrium predictions and studying non-equilibrium solidification such as welding with Fe-Cr-Ni systems and SS alloys when this is kept in mind. [33, 42, 70, 96, 99, 134]

While isopleths provide a good estimation for simple alloys, for more complex steels, the use of Cr equivalence values (Cr_{eq}), Ni equivalence values (Ni_{eq}) values, and the Cr/Ni equivalence ratio (Cr/Ni_{eq}) are preferred. The Cr_{eq} and Ni_{eq} values account for the other stabilizing elements that are present in the alloy and the impact these elements have on solidification mode and phase formation during solidification of multicomponent stainless-steel alloys. The equivalence values consider other austenite stabilizers like C and N, and ferrite stabilizers like Mo and Nb. One of the more commonly accepted sets of equivalence equations for austenitic SS are the WRC 1992 equations, Eq 3.2.1 and 3.2.2. [35]

\[
\text{Cr}_{eq} = \text{Cr} + \text{Mo} + (0.7 \times \text{Nb}) \quad \text{Equation 3.2.1}
\]

\[
\text{Ni}_{eq} = \text{Ni} + (35 \times \text{C}) + (20 \times \text{N}) + (0.25 \times \text{Cu}) \quad \text{Equation 3.2.2}
\]

When studying solidification of stainless steel, particularly in welding, atomization, and fusion-based AM processes, these equations are used regularly to calculate the Cr/Ni_{eq}. [25, 44, 46, 50, 135]

Fusion-based additive manufacturing (FBAM) techniques for metallic materials, such as directed energy deposition (DED), electron beam melting (EBM), and laser powder bed fusion (LPBF) all can potentially experience very high cooling rates and solidification rates during processing. All of these RSP techniques form either dendritic or cellular solidification morphologies as a result of the high cooling and solidification rates. LPBF of stainless steel is capable of regularly producing cooling rates of \(10^5\) K/s and higher.[3, 5, 7, 10, 19, 44, 53, 88, 136] Other rapid solidification processing (RSP) techniques such as laser beam welding, melt spinning, pulsed laser welding, and surface glazing achieve similar cooling rates. [25, 27, 110, 133] Most FBAM
techniques require metal powder and implementing new powder chemistry is costly and time-consuming, taking weeks to months to make, and tens of thousands of dollars in material cost. Additionally, there is the time and cost associated with running trials of the new alloy to ensure it performs as expected and what additional processing may be required.

Two-piston splat quenching (SQ) is an older technique that utilizes electromagnetic levitation and metal platens to produce rapidly solidified thin foils. The cooling rates found in FBAM processes are similar to those produced by SQ. [45, 73, 113, 114, 121] The range of cooling rates that have been observed in SQ is typically from $10^5$-\(10^8\) K/s depending on experimental conditions. [115, 117, 120, 121, 137] SQ is a technique that electromagnetically levitates and melts a metallic sample to a desired superheat (or supercooling) condition before releasing the molten sphere and compressing the liquid it between two platens, typically copper. The process of testing a new material in a SQ apparatus is very fast and costs a fraction of what it would take to make and test atomized powder of a new chemistry. Also, through the modification of key experimental parameters of the SQ process such as sample material, platen material, platen surface finish, platen velocity (etc.) one could achieve cooling rates ranging anywhere from $10^4$ to $10^{10}$ K/s. [113-115, 117, 120]

Rapid solidification is defined by Kurz et. al. as a critical growth velocity of the S/L interface where diffusion becomes localized with respect to the microstructure. Another way of representing this is when the corresponding Peclet number ($P_E = \frac{V\lambda}{2D_L}$) becomes larger than unity. [82] This is represented by the ratio of velocity, $V$, and dendrite tip radius, $\lambda$, to two times the solute diffusion coefficient in the liquid. A general approximation for metals is a solidification rate around 10mm/s. Under equilibrium and near equilibrium conditions predictive tools for phase formation like isopleths and ternary phase diagrams can be readily applied in most
circumstances, however FBAM and other rapid solidification processes rely on solidification and cooling rates significantly above equilibrium conditions. Traditional solidification models used to predict microstructure or phase formation in near equilibrium condition processes, such as Scheil or WRC-1992, use assumptions that work well at slower solidification rates but are less accurate at rapid solidification rates. As solidification rates increase, local equilibrium at the S/L interface is lost and these traditional models do not account for the new phenomena such as solute trapping, micro-segregation, and the capillarity effect that occur at higher solidification rates. [82]

Previous work has been done to track the evolution of microstructures at increased solidification rates in austenitic SS alloys with various chemistries. It was found that as solidification rates increased, a single-phase solidification mode was favored over two-phase solidification in which secondary phases form. [26, 34, 44, 130] At rapid solidification rates SS alloys can potentially solidify with a primary austenite solidification mode or a primary ferrite solidification mode. These two solidification modes can potentially result in three different microstructures once solidified, primary austenite, primary ferrite, or austenite that solidified as ferrite and experienced a solid-state diffusionless massive transformation to austenite (F/MA) while cooling. Using a variety of alloy chemistries and RSP techniques microstructure prediction maps were generated covering the slower end of RS with predictions for how faster solidification rates will affect the microstructure. [40, 44] These plots use weld speed and solidification rate fairly interchangeably thanks to the key assumption that during welding, the tail of the melt pool is considered to be solidifying at the same rate as the weld. [26, 55] More recently, Bermejo et. al. studied a range of steels with Cr/Ni_{eq} values between 1.2 and 2.0 using single pass laser welding to produce various cooling rates and found good agreement with microstructure predictions
presented by Lippold, Elmer, Fukumoto, and Iamboliev. However, many of these previous studies focus primarily on cooling rates ranging between $10^3$-$10^5$ K/s and use either Fe-Cr-Ni ternary or SS with low amounts of alloying elements outside of Cr and Ni.

Measuring the cooling rates and solidification rates under rapid solidification conditions is an extremely difficult task and even more difficult to do so accurately. One way of estimating these rates is by extrapolating empirical relationships from slower cooling rates relating the dendrite arm spacing and cell spacing. A general form of this relationship can be seen in Equation 3.2.3 where $\dot{\gamma}$ is cooling rate, A and n are constants, and d is cell spacing.\[25]

$$d = A^*(\dot{\gamma})^{-n}$$
Equation 3.2.3

This has been shown to be robust and effective relationship for rapid cooling rates up until a critical cell size is reached where the solidification mode transitions from non-planar back to planar due to the solute length and capillarity length becoming comparable.\[78,79,82\] Work by Katayama et. al. found good agreement of measured cooling rate and cell spacing relationship to previous work and provided values for the A and n constants.\[25\] Furthermore, using a common relationship in welding, solidification rate can be estimated from this relationship by substituting the cooling rate with temperature gradient multiplied by solidification rate, $G*R$.\[31\] This relationship allows equation 3 to be manipulated to solve for R, solidification rate.

As the solidification rates achieved by many PBF techniques continues to increase, a solid understanding of how these rapid solidification rates effect the materials and microstructure of the solidified part is critical. In this paper, two-piston splat quenching was implemented to examine the rapid solidification process for austenitic SS at higher cooling rates than previously investigated. Differently from previous works, this work combines the two key influences on rapid solidification microstructures of SS spanning a range of rapid cooling rates and
compositional modifications to target specific Cr/Ni$_{eq}$ values. This approach allowed us to generate cooling rates at or above those observed in additive techniques such as EBM and LPBF for a many different alloy chemistries in a short amount of time. Detailed optical microscopy, electron microscopy, and magnetometry were employed to characterize the microstructures and measure changes in cell size and phase formation as a function of cooling rate and steel composition.

3.3 Methods

Feedstock generation

All splat quench experiments used custom made alloy feedstock designed with a focus on controlling the concentrations of the stabilizing elements considered in the WRC 1992 equations. These alloys were made using high purity metal powder and sheet (> 99.95%) from Goodfellows and Kurt J. Lesker. The powders were individually weighed out and mixed by hand before being pressed into a pellet. Arc melting was performed in an inert Ar environment with a constant flow of Ar, and prior to arc melting the material a piece of Ti was melted to collect any remaining oxygen in the chamber. After the initial melt the button was flipped over and re-melted multiple times to ensure the sample was completely mixed.

The arc melted material formed buttons that were cold rolled and part of each feedstock was removed and sent for a full bulk chemical analysis to be performed using a combination of inductively coupled plasma optical emission spectroscopy (ICP-OES), combustion analysis (CA), and inert gas fusion (IGF). IGF was used to measure N, O, and H while CA was used for C and S. The rest of the elements were measured via ICP-OES providing accurate compositional measurements of each element for every alloy.
Two-piston splat quenching

Cubes were sectioned from the rolled feedstock to make the samples used in splat quenching. An Edmund Buhler Ultra-Rapid Splat Quenching machine was used with ultra-high purity Ar as the inert gas and copper as the platen material. A two-color Fluke Endurance optical pyrometer was used to measure the temperature of the sample during levitation with a 10ms sampling frequency. Electromagnetic levitation was stopped and the sample allowed to fall when the target superheat of 1600°C was reached. As the sample fell it triggered a light barrier engaging the pistons to splat the molten droplet as it fell. The left and right sides were marked when the splatted sample was removed from the SQ machine. A schematic of the splat quench is shown in Figure 3.3.1A-B. Figure 3.3.1C is a splat quenched disk after being removed from the chamber.
Analysis and characterization

Splat quenched samples were prepared for microscopy using standard metallographic techniques. Splat quenched samples were cut in half longitudinally and hot mounted to expose the XY plane of the SQ. A schematic of the hot mounted sample is used in Figure 3.3.1D. Mounted samples were ground and polished with the SQ parallel to the tangent of the grinding and polishing pad to prevent smearing or bending of the sample. Samples were polished to a surface finish of 1µm by hand and vibratory polished using 0.02µm colloidal silica suspension for microscopy.
A combination of optical and electron microscopy was used to analyze the samples. Optical images were collected on a Leica optical microscope. Energy dispersive X-ray Spectroscopy (EDS) was performed on a JEOL 7000 SEM with an Oxford X-MAX 80mm² EDS detector. Electron Backscatter Diffraction (EBSD) scans were collected at a 70° tilt. EDS and EBSD data were processed using the Oxford AZTEC software. Backscatter electron images (BSE) images were collected using a Thermo-Fisher Apreo SEM. STEM-EDX line scans were collected using a TECNAI F-20 TEM operating at 200kV and an Optima T-60 Amtek detector.

Quantitative SEM-EDS using standards and DTSA-II was utilized to perform highly accurate compositional measurements between individual splat quenches and between phases. A NIST SRM multi-element metals block was used for pure elements and NIST SRM 1155 for nominal 316L. Spectra were collected at five different locations for 60 seconds at a 9.5mm working distance for each sample using point scans. In DTSA II, standard references were created for Fe, Cr, Ni, Mo, Mn, and Si using pure elements and 316L SRM material.

Vibratory sample magnetometry (VSM) was performed using a Quantum Design Dynacool PPMS. A magnetic field was applied with one full cycle from 12,000 Oe to -12,000 Oe and back with the magnetic moment response of the sample recorded. Samples used for VSM were approximately 3-5mm squares sectioned from the radial center of the other half of the splat quenched disk. Using the equation presented in work by Merinov (Equation 3.3.1) the saturation magnetization of each sample was calculated as if it were fully ferrite.\textsuperscript{[41, 130-132]}

$$\sigma_F = 21,600 - 275(\%Cr) - 330(\%Ni) - 280(\%Mn) - 610(\%Si) - 260(\%Mo) - 670(\%Ti) - 630(\%Al)$$  \hspace{1cm} \text{Equation 3.3.1}

In this equation $\sigma_F$ is the theoretical saturation magnetization value for a fully magnetic sample based on the chemistry. This equation outputs in units of Gauss and was converted to emu/g.
Using equation 3.3.2 and dividing the measured saturation magnetization $\sigma_U$ by the calculated saturation magnetization $\sigma_F$ for that composition, the wt % ferrite was calculated.

$$\% \text{ Residual ferrite} = \frac{\sigma_U}{\sigma_F}$$  \hspace{1cm} \text{Equation 3.3.2}

Samples were electrolytically etched in a 60/40 solution of 70% nitric acid and DI water using a 1.25V potential applied to the polished surface of the sample. Etching times ranged from 5-20 seconds depending on the microstructure response. Once etched, samples were imaged using a Thermo-Fisher Apreo SEM at six different regions across the cross section. The images were imported into the software ImageJ. Each of the six sites was separated into six zones, three per solidification front, to track the evolution of cell diameter throughout solidification. Cell size measurements were checked for statistical relevance using a one-way ANOVA test as described in Chapter 2.6.

Simulation

2-D heat transfer simulations were completed in ANSYS Fluent to simulate solidification in the SQ process. A 35µm wide by 110µm long rectangle was used to represent a section of a single solidification front in the final shape of the splat quenched sample. Simulations were performed using heat transfer coefficients of $10^5$, $10^6$, and $10^7$ W/m$^2$K as these values have each been suggested in previous literature as estimates for the SQ process.\textsuperscript{[73, 114, 117, 121, 129]} The heat transfer simulations using coefficients of $10^5$ and $10^6$ W/m$^2$K were found to produce cooling rates that were not high enough when compared to the cooling rate estimates from the cell size measurements, so these simulation results were not included. The temperature gradients for each cooling rate of interest were extracted from the simulation that used the $10^7$ W/m$^2$K heat transfer coefficient.
3.4 Results

Microscale and sub-microscale chemical analysis

The bulk chemistry of near half of the alloys was within the ASTM A240 compositional specification for 316L material. Bulk chemical analysis of the custom feedstocks provided a full compositional analysis of each splat quench sample. The compositional results for each feedstock are reported in Table 3.4.1 along with the calculated WRC-1992 Cr\textsubscript{eq}, Ni\textsubscript{eq}, and Cr/Ni\textsubscript{eq} values are included as well. Alloys 3-7 met the ASTM A240 composition specification for 316L stainless steel.\cite{32} Alloys 8 and 9 were very close to meeting the specification with only 0.2 and 0.1 wt% over the maximum allowed Cr concentration respectively. Alloy 10 almost met the specification; however, the Ni concentration was 0.8 wt% low. Feedstocks that fit within the A240 specification for 316L are marked in Table 3.4.1 with an asterisk next to the alloy number.

Table 3.4.1 Bulk chemical analysis of custom alloy feedstock compositions used for SQ experiments.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>N</th>
<th>C</th>
<th>Nb</th>
<th>Cu</th>
<th>Ti</th>
<th>Cr\textsubscript{eq}</th>
<th>Ni\textsubscript{eq}</th>
<th>Cr/Ni\textsubscript{eq}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>58.6</td>
<td>17.30</td>
<td>19.90</td>
<td>2.24</td>
<td>1.43</td>
<td>0.48</td>
<td>0.002</td>
<td>0.008</td>
<td>0.000</td>
<td>0.009</td>
<td>0.003</td>
<td>19.54</td>
<td>20.22</td>
<td>0.97</td>
</tr>
<tr>
<td>2</td>
<td>70.9</td>
<td>12.60</td>
<td>12.40</td>
<td>2.08</td>
<td>1.31</td>
<td>0.36</td>
<td>0.033</td>
<td>0.009</td>
<td>0.007</td>
<td>0.316</td>
<td>0.003</td>
<td>14.68</td>
<td>13.45</td>
<td>1.09</td>
</tr>
<tr>
<td>3*</td>
<td>65.7</td>
<td>17.20</td>
<td>13.00</td>
<td>2.34</td>
<td>1.52</td>
<td>0.20</td>
<td>0.002</td>
<td>0.018</td>
<td>0.000</td>
<td>0.007</td>
<td>0.002</td>
<td>19.54</td>
<td>13.67</td>
<td>1.43</td>
</tr>
<tr>
<td>4*</td>
<td>65.0</td>
<td>17.80</td>
<td>12.90</td>
<td>2.77</td>
<td>1.10</td>
<td>0.44</td>
<td>0.020</td>
<td>0.003</td>
<td>0.000</td>
<td>0.000</td>
<td>0.010</td>
<td>20.57</td>
<td>13.41</td>
<td>1.53</td>
</tr>
<tr>
<td>5*</td>
<td>68.0</td>
<td>17.20</td>
<td>11.10</td>
<td>2.22</td>
<td>1.10</td>
<td>0.38</td>
<td>0.010</td>
<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>19.42</td>
<td>11.34</td>
<td>1.71</td>
</tr>
<tr>
<td>6*</td>
<td>68.3</td>
<td>17.20</td>
<td>10.60</td>
<td>2.26</td>
<td>1.10</td>
<td>0.46</td>
<td>0.020</td>
<td>0.003</td>
<td>0.000</td>
<td>0.000</td>
<td>0.010</td>
<td>19.46</td>
<td>11.11</td>
<td>1.75</td>
</tr>
<tr>
<td>7*</td>
<td>67.9</td>
<td>18.00</td>
<td>10.30</td>
<td>2.31</td>
<td>1.10</td>
<td>0.40</td>
<td>0.030</td>
<td>0.002</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>20.31</td>
<td>10.97</td>
<td>1.85</td>
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<tr>
<td>8</td>
<td>67.7</td>
<td>18.20</td>
<td>10.30</td>
<td>2.27</td>
<td>1.10</td>
<td>0.40</td>
<td>0.010</td>
<td>0.002</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>20.47</td>
<td>10.57</td>
<td>1.94</td>
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<tr>
<td>9</td>
<td>66.9</td>
<td>18.10</td>
<td>10.50</td>
<td>2.92</td>
<td>1.10</td>
<td>0.42</td>
<td>0.010</td>
<td>0.002</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>21.02</td>
<td>10.77</td>
<td>1.95</td>
</tr>
<tr>
<td>10</td>
<td>69.8</td>
<td>16.80</td>
<td>9.20</td>
<td>2.20</td>
<td>1.51</td>
<td>0.52</td>
<td>0.002</td>
<td>0.007</td>
<td>0.000</td>
<td>0.007</td>
<td>0.003</td>
<td>19.00</td>
<td>9.49</td>
<td>2.00</td>
</tr>
<tr>
<td>11</td>
<td>61.0</td>
<td>23.00</td>
<td>11.80</td>
<td>2.31</td>
<td>1.40</td>
<td>0.49</td>
<td>0.002</td>
<td>0.008</td>
<td>0.000</td>
<td>0.008</td>
<td>0.005</td>
<td>25.31</td>
<td>12.12</td>
<td>2.09</td>
</tr>
</tbody>
</table>

* Composition is within ASTM A240 specification for 316L stainless steel

Quantitative EDS using NIST standards and multi-physics-based simulations found no measurable differences in the composition of major alloying elements between feedstock and splat quenched samples. Due to the mass of splat quenched samples being below the minimum requirements for the bulk chemical analysis techniques, quantitative EDS was used to investigate the post splat composition of major alloying elements (Fe, Cr, Ni, Mo, Mn, Si). Good agreement
was found between the pre-splat feedstock composition (Table 3.4.1) and post-splat sample composition (Table 3.4.2) for the major alloying elements. Due to the limited resolution of EDS the concentration of minor/trace elements could not be assessed. The compositions calculated using quantitative EDS in Table 3.4.2 are averages of the quantification of multiple spectra from the same sample with the one standard deviation reported. The slight differences in elemental concentrations between replicate splat quenches of the same feedstock are indistinguishable from variation between quantifications results. Thus, individual splat quenched samples from the same feedstock should be considered to have the same chemical composition as the feedstock for the primary alloying elements.

Table 3.4.2 Compositions calculated using quantitative EDS technique and standard deviation reported between replicates of alloys 4, 8, and 9 in wt%.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-2</td>
<td>64.3 ± 0.13</td>
<td>18.0 ± 0.04</td>
<td>13.6 ± 0.13</td>
<td>2.9 ± 0.04</td>
<td>1.1 ± 0.04</td>
<td>0.4 ± 0.00</td>
</tr>
<tr>
<td>4-3</td>
<td>64.4 ± 0.19</td>
<td>18.0 ± 0.05</td>
<td>13.5 ± 0.11</td>
<td>2.8 ± 0.07</td>
<td>1.0 ± 0.04</td>
<td>0.4 ± 0.02</td>
</tr>
<tr>
<td>8-1</td>
<td>67.4 ± 0.50</td>
<td>17.9 ± 0.21</td>
<td>10.5 ± 0.18</td>
<td>2.2 ± 0.07</td>
<td>1.1 ± 0.06</td>
<td>0.4 ± 0.03</td>
</tr>
<tr>
<td>8-3</td>
<td>67.2 ± 0.29</td>
<td>17.8 ± 0.20</td>
<td>10.6 ± 0.17</td>
<td>2.3 ± 0.06</td>
<td>1.1 ± 0.07</td>
<td>0.4 ± 0.01</td>
</tr>
<tr>
<td>9-1</td>
<td>67.4 ± 0.25</td>
<td>18.1 ± 0.11</td>
<td>10.6 ± 0.15</td>
<td>2.8 ± 0.06</td>
<td>1.1 ± 0.07</td>
<td>0.4 ± 0.01</td>
</tr>
<tr>
<td>9-2</td>
<td>67.5 ± 0.28</td>
<td>18.1 ± 0.16</td>
<td>10.6 ± 0.16</td>
<td>2.9 ± 0.07</td>
<td>1.1 ± 0.07</td>
<td>0.4 ± 0.02</td>
</tr>
<tr>
<td>9-3</td>
<td>67.1 ± 0.21</td>
<td>18.0 ± 0.11</td>
<td>10.6 ± 0.07</td>
<td>2.9 ± 0.07</td>
<td>1.1 ± 0.07</td>
<td>0.4 ± 0.01</td>
</tr>
</tbody>
</table>

SEM-EDX line scans performed across the thickness of the SQ sample showed no observable chemical gradients. The line scans spanned the Y-axis of the mounted samples from PS interface to PS interface and crossed the sample midline. The raw signal intensity data was used to generate ratios of signal intensities for Cr/Fe and Ni/Fe signals. The plotted signal ratios for Cr/Fe and Ni/Fe are shown in Figures 3.4.2A and 3.4.2B respectively. The samples were found to be chemically homogenous as the line scan data showed no observable segregation or compositional gradients across the thickness of SQ samples.
Sub-microscale investigation of splat quenched samples revealed two different types of elemental segregation at the cell boundaries. While segregation wasn’t observed at the microscale in the SEM, sub-microscale analysis via STEM-EDX line scans revealed elemental segregation to the cell boundaries. Two different elemental segregation responses were observed in SQ samples. Primary austenite solidification resulted in the segregation of mainly Cr and Mo to the cell boundaries, with a subsequent decrease in the signal intensity of Fe at the cell boundary as well. The concentration of Ni was observed to remain stable across the primary austenite solidified cell boundaries. In primary ferrite solidification, the only element detected to segregate to the cell boundary was Ni. The signal intensities of Cr and Mo were observed to remain mostly stable across the cell boundaries. There was a similar decrease in the Fe signal at the primary ferrite solidified cell boundaries as to what was observed in the type 1 cell segregation, but less intense. The two different segregation responses can be observed in STEM-EDX line scans in Figure 3.4.3A and B. Figure 3.4.3A is from primary austenite solidified material while Figure 3.4.3B is from primary ferrite solidified material. The segregating elements in each of the segregation responses measured align with what has been reported.

Figure 3.4.2. Ratio of signal intensities of (A) Cr to Fe and (B) Ni to Fe for alloys 1-3, 10, and 11 across the thickness of splat quenched sample.
previously in the literature for elemental segregation to cell boundaries in rapidly solidified 300 series SS. [7, 13, 65, 66, 95, 130]

![Fe-16.9Cr-11.7Ni Cr/Ni\textsubscript{eq} 1.53 Solidification Mode – Primary Austenite Microstructure - Austenite](A) ![Fe-18.1Cr-10.5Ni Cr/Ni\textsubscript{eq} 1.95 Solidification Mode – Primary Ferrite Microstructure - Ferrite](B)

Figure 3.4.3 Fe, Cr, Ni, and Mo X-ray signal intensities collected from STEM-EDX line scans in the TEM showing sub-microscale segregation in (A) primary austenite solidified (type 1) cells and (B) primary ferrite solidified (type 2) cells.

**Phase content**

VSM measurements of the central region of splat quenched samples were used to measure the bulk wt% ferrite and showed increased ferrite content with increasing Cr/Ni\textsubscript{eq} values. Ferrite was first detected with VSM in SQ samples with a Cr/Ni\textsubscript{eq} of 1.71 and increased in concentration in samples with higher Cr/Ni\textsubscript{eq}. The wt% ferrite calculated for the samples can be found in Table 3.4.3. Asterisk have been placed next to SQ samples that are within the A240 specification for 316L SS. The bulk ferrite content between replicate splat quenches from the same feedstock was found to vary, in some cases significantly up to 50 wt%. It should be noted that the calculated wt% ferrite is for only the inner region of SQ samples, not the entire sample. Also, part of the wt% ferrite calculation involves using an empirical relationship (Equation 3.3.1)
that was designed to work for a range of compositions, to estimate the saturation magnetization based on composition.

Table 3.4.3. Range of ferrite contents and average ferrite contents calculated by VSM and optical image analysis from multiple SQ replicates of each composition.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr/Ni_{eq}</th>
<th>WRC-1992 FN</th>
<th>VSM (Wt% Ferrite)</th>
<th>Optical (Area % Ferrite)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Min-Max</td>
<td>Average</td>
</tr>
<tr>
<td>1</td>
<td>0.97</td>
<td>0</td>
<td>0.0-0.0*</td>
<td>0.0*</td>
</tr>
<tr>
<td>2</td>
<td>1.09</td>
<td>0</td>
<td>0.0-0.0*</td>
<td>0.0*</td>
</tr>
<tr>
<td>3</td>
<td>1.43</td>
<td>2</td>
<td>0.0-0.0*</td>
<td>0.0*</td>
</tr>
<tr>
<td>4</td>
<td>1.53</td>
<td>6</td>
<td>0.0-0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>1.71</td>
<td>9</td>
<td>0.3-0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>6</td>
<td>1.75</td>
<td>10</td>
<td>0.6-0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>7</td>
<td>1.85</td>
<td>15</td>
<td>3.4-22.0</td>
<td>9.9</td>
</tr>
<tr>
<td>8</td>
<td>1.94</td>
<td>18</td>
<td>2.5-13.2</td>
<td>7.9</td>
</tr>
<tr>
<td>9</td>
<td>1.95</td>
<td>20</td>
<td>39.9-91.4</td>
<td>62.8</td>
</tr>
<tr>
<td>10</td>
<td>2.00</td>
<td>16</td>
<td>55.9-57.3*</td>
<td>56.6*</td>
</tr>
<tr>
<td>11</td>
<td>2.09</td>
<td>45</td>
<td>100-100*</td>
<td>100*</td>
</tr>
</tbody>
</table>

*Data from a single replicate SQ sample.

Optical images of highly polished splat quenched samples were used to obtain an understanding of the spatial distribution of the austenite and ferrite phases within the material. The range of ferrite area percentages measured for different splat quenched samples using optical microscopy are shown in Table 3.4.3. The EBSD phase maps were used to identify austenite and ferrite regions in the optical microscope images. Ferrite was identified as the darker regions and austenite was the lighter regions observed. (Figure 3.4.4) The amount of austenite and ferrite varied between splat quenched samples and individual solidification fronts. The two optical images in Figure 3.4.4 are from the same splat quench sample and show examples of the phase contrast seen between austenite and ferrite at the radial center (A) vs. the outer edge (B). The ferrite content was found to be highest near the radial edges of splat quench samples where more
austenite formed near the radial center and conversely austenite was found in higher
concentrations near the radial center of the splat quenches. No ferrite was observed in the optical
analysis of alloys 1-4. Ferrite microstructures were first observed in small amounts in alloys 5
and 6, along the PS interface near the outer edges of the SQ. As the Cr/Ni_{eq} of the alloys
increased more ferrite was found closer to the radial center of the SQ. Alloys 7 and 8 formed
higher concentrations of ferrite than 5 and 6, spanning anywhere from ~3-22\%. The spatial
evolution of austenite content with respect to radial position is shown in the two plots in Figure
3.4.5 for SQ sample 9-1 and the corresponding optical images of 9-1 in Figure 3.4.4A and B.

Figure 3.4.4 Optical images from SQ 9-1 (A) near the radial center and (B) near the outer edge.
The lighter regions are austenite, and the darker regions are ferrite.
EBSD scans of splat quenched samples were used to determine the phases present in solidified samples. As a reminder, the EBSD scans covered less than 1% of the cross section and were taken near the radial center of the SQ so it should be kept in mind that the phase maps captured are only representative of a small area of the sample. Representative phase maps generated from the EBSD data are shown in Figure 3.4.6 where 3.4.6A through 3.6.6F are SQ samples with increasing Cr/Ni\textsubscript{eq} values. The fully austenitic microstructures that were observed in the optical images of alloys 1-4 were also observed in EBSD scans for those alloys. (Figure 3.4.6A) Alloys 5 and 6 were found to be dual phase as in the optical images, forming ferrite towards the outer radius of the SQ samples along the PS interface. As a result of the EBSD scans being performed near the radial center of the splat quenches, most of the regions scanned were fully austenitic for alloys 5 and 6. Mixed austenite and ferrite microstructures were found in EBSD scans of SQ alloys 7-10. (Figure 3.4.6B-E) Finally, fully ferritic microstructure was observed in SQ alloy 11. (Figure 3.4.6F) In dual-phase samples that formed predominantly austenite microstructures, ferrite preferentially formed at the PS interface before the middle of the SQ.
Figure 3.4.6. EBSD Phase map of SQ samples with increasing Cr/Ni$_{\text{eq}}$ values from (A) 1.53 to (F) 2.09. Austenite is represented by blue, and ferrite is represented as red. White dotted lines indicate midline location.

BSE images and inverse pole figures (IPF) generated from the EBSD scans show the grain structure and morphology in splat quenched samples. The splat quench event creates two independent solidification fronts that meet, usually, in the middle of the splat quench forming a midline throughout the sample. These solidification fronts form independently of each other and produce independent grain structures. The smallest grains generally formed along the PS interface, where solidification initiated, and grew in size moving towards the midline. This region was only a few micrometers deep before the grain size began to increase and evolve into; progressively larger equiaxed grains, transitioned into long columnar grains, or formed massive grains. Examples of the different grain morphologies can be seen in the IPF-Y maps in Figure
3.4.7 and BSE images in Figure 3.4.8. Twin grain boundaries were observed in fully austenitic samples and the austenitic regions of dual phase splat quenches (Figures 3.4.7A-D). Fully ferritic and ferritic regions of dual phase samples showed no observable twinning. (Figure 3.4.7E-F) Additionally, the BSE images in Figure 3.4.8 show two examples of how, depending on the position along the X-axis within the SQ sample, different grain morphologies could be found. This was observed for both fully austenitic material, Figure 3.4.8A-B, and in fully ferritic material, Figure 3.4.8C-D. There was no relationship observed between radial position and grain morphology in SQ samples.

Figure 3.4.7. IPF-Y map of different possible grain structures observed in SQ samples. The most prominent microstructure is listed with the alloy chemistry for each map as follows: (A) Alloy 2 – primary austenite, (B) alloy 4 – primary austenite and F/MA, (C) alloy 7 – F/MA and primary ferrite, (D) alloy 9 – F/MA and primary ferrite, (E) alloy 10 – primary ferrite and F/MA, and (F) alloy 11 – primary ferrite.
Figure 3.4.8. BSE images of different grain morphologies observed at different locations along the X-axis within the same SQ from (A-B) alloy 2 and (C-D) alloy 11.

**Etching**

Electrolytic etching revealed primary austenite cellular solidification and primary ferrite cellular solidification structures in splat quenched samples. While primary ferrite microstructures could be differentiated from austenite using either optical microscopy or EBSD, these techniques are unable to differentiate between primary austenite and F/MA microstructures. However, the two microstructures can be identified via the etching response of the sample from the type of cell structure observed. The two cell structures will be referred to as type 1 cells and type 2 cells.
Type 1 cells are cells that solidified as primary austenite and are characterized by a deep etch at the cell boundary that produces a clean outline of the cells. (Figure 3.4.9A) These cells retain the columnar structure associated with cellular solidification. Type 2 cells solidify as primary ferrite and were found in both F/MA and primary ferrite microstructures. These cells are identified by a rougher etch that does not penetrate the cell boundary as deeply. (Figure 3.4.9B) The two cell types were also confirmed by the different microscale segregation behaviors discussed earlier, where type 1 segregates primarily Cr with some Ni and Mo while type 2 segregates only Ni. Alloys 1 and 2 were fully type 1 cells and alloys 5-11 were entirely type 2 cells. Only splat quenches from alloys 3 and 4 exhibited both type 1 and type 2 cells. In Figure 3.4.9C both types of cells are shown in the same sample, the sample is over etched to clearly reveal both types.

Cells formed in the general direction of heat flow from midline to PS interface, but never formed perpendicular to the direction of heat flow (radial center to edge). Solidification cells were found to be independent of grain orientation which can be seen when looking closely at Figure 3.4.9B, where some of the grain boundaries can be observed cutting through the solidification cells. This was confirmed by IPF maps of lightly etched samples.

Figure 3.4.9. (A) Alloy 1 - Type 1 cells, (B) alloy 9 - type 2 cells, (C) alloy 3 - type 1 and 2 cells.
Cell size measurements

The mean diameter of solidification cells formed during splat quenching were found to range between 0.12µm and 0.44µm, depending on the location along the Y-axis, within the splat quenched sample. The range of minimum and maximum mean cell sizes for each SQ sample are listed in Table 3.4.4. The largest cells were found at the radial center of the splat quench, closest to the midline, Y=0. The smallest cells were typically located away from the radial center, along the PS interface. Mean cell size increased going from PS interface towards the midline. This increase is visible in Figure 3.4.10 which shows the histogram of alloy 4 cell measurements where the mean cell size increases as it progresses towards the midline. In this plot, the mean cell sizes and variances of each zone were averaged together for sites 1-6 to create an average mean cell size and variance for each zone and plotted for three replicate SQ of the same alloy composition. The error bar values are two times the average variance of each zone. While the plot shows how the range of mean cell sizes of individual SQ samples from the same alloy feedstock could vary, the range of mean cell sizes for SQ samples overall was very consistent. The one-way ANOVA test compared six zones per test (site) and resulted in P-values consistently well below 0.05. The Tukey-Kramer post-hoc analysis was performed on a subset of the 11 alloy compositions for alloys 4-9 to determine which of the mean cell sizes were significantly different between zones 1-2, 2-3, 4-5, and 5-6 at each site. In Table 3.4.5 the percentage of mean cell sizes that were significantly different between zones is shown. The mean cell size between zones was significantly different 82% of the time for the four zone comparisons previously mentioned. As zones 3-4 are part of two separate solidification fronts, the average percentage of significantly different means was calculated with and without comparing zones 3-4. The mean cell size could increase on average between 0.08 µm to 0.19µm.
from the PS interface to the midline, and could range between 0.15µm-0.29µm within a single SQ. The average minimum mean cell size was 0.16µm and could fluctuate ±0.04µm while the average maximum mean cell size was 0.38µm ±0.06µm. No relationship was observed between the feedstock chemistry and the range of cell sizes measured for major alloying elements.

Table 3.4.4. Range of measured cell size in SQ samples and associated estimated ranges for cooling rates and solidification rates.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr/Ni&lt;sub&gt;eq&lt;/sub&gt;</th>
<th>Cell Size (µm)</th>
<th>Cooling Rate (K/s)</th>
<th>Temperature Gradient (K/µm)</th>
<th>Solidification Rate (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.97</td>
<td>0.15 - 0.37</td>
<td>1.1E+07 - 1.5E+08</td>
<td>29-152</td>
<td>390 - 1210</td>
</tr>
<tr>
<td>2</td>
<td>1.09</td>
<td>0.13 - 0.38</td>
<td>1.0E+07 - 2.4E+08</td>
<td>28-202</td>
<td>390 - 1210</td>
</tr>
<tr>
<td>3</td>
<td>1.43</td>
<td>0.14 - 0.36</td>
<td>1.2E+07 - 1.9E+08</td>
<td>29-172</td>
<td>410 - 1130</td>
</tr>
<tr>
<td>4</td>
<td>1.53</td>
<td>0.12 - 0.42</td>
<td>7.6E+06 - 3.6E+08</td>
<td>20-229</td>
<td>390 - 1570</td>
</tr>
<tr>
<td>5</td>
<td>1.71</td>
<td>0.16 - 0.41</td>
<td>8.1E+06 - 1.3E+08</td>
<td>21-137</td>
<td>390 - 1010</td>
</tr>
<tr>
<td>6</td>
<td>1.75</td>
<td>0.15 - 0.39</td>
<td>9.7E+06 - 1.6E+08</td>
<td>25-152</td>
<td>390 - 1110</td>
</tr>
<tr>
<td>7</td>
<td>1.85</td>
<td>0.14 - 0.38</td>
<td>1.0E+07 - 2.0E+08</td>
<td>26-172</td>
<td>390 - 1200</td>
</tr>
<tr>
<td>8</td>
<td>1.94</td>
<td>0.15 - 0.43</td>
<td>7.1E+06 - 1.7E+08</td>
<td>18-152</td>
<td>390 - 1130</td>
</tr>
<tr>
<td>9</td>
<td>1.95</td>
<td>0.12 - 0.44</td>
<td>7.0E+06 - 3.6E+08</td>
<td>18-229</td>
<td>390 - 1570</td>
</tr>
<tr>
<td>10</td>
<td>2.00</td>
<td>0.17 - 0.32</td>
<td>1.7E+07 - 1.2E+08</td>
<td>38-125</td>
<td>470 - 1000</td>
</tr>
<tr>
<td>11</td>
<td>2.09</td>
<td>0.16 - 0.29</td>
<td>2.3E+07 - 1.3E+08</td>
<td>44-125</td>
<td>540 - 1050</td>
</tr>
</tbody>
</table>
Figure 3.4.10. Averaged mean cell size from multiple sites for each zone across thickness of SQ sample for three replicates of alloy 4.

Table 3.4.5 Percentage of cell size means that were determined to be significantly different from post-hoc analysis between neighboring zones for alloys 4-9.

<table>
<thead>
<tr>
<th>Zones Compared</th>
<th>Alloy 4</th>
<th>Alloy 5</th>
<th>Alloy 6</th>
<th>Alloy 7</th>
<th>Alloy 8</th>
<th>Alloy 9</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 1-2</td>
<td>90.9</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>81.3</td>
<td>94.1</td>
<td>94.4</td>
</tr>
<tr>
<td>Zone 2-3</td>
<td>73.3</td>
<td>56.3</td>
<td>64.3</td>
<td>71.4</td>
<td>88.9</td>
<td>75.0</td>
<td>71.5</td>
</tr>
<tr>
<td>Zone 3-4</td>
<td>61.5</td>
<td>42.9</td>
<td>16.7</td>
<td>35.7</td>
<td>46.7</td>
<td>50.0</td>
<td>42.2</td>
</tr>
<tr>
<td>Zone 4-5</td>
<td>90.0</td>
<td>57.1</td>
<td>61.5</td>
<td>85.7</td>
<td>83.3</td>
<td>84.6</td>
<td>77.1</td>
</tr>
<tr>
<td>Zone 5-6</td>
<td>66.7</td>
<td>80.0</td>
<td>100.0</td>
<td>86.7</td>
<td>88.9</td>
<td>90.9</td>
<td>85.5</td>
</tr>
<tr>
<td>Average</td>
<td>75.9</td>
<td>66.2</td>
<td>67.7</td>
<td>76.1</td>
<td>77.1</td>
<td>78.9</td>
<td>73.6</td>
</tr>
<tr>
<td>Average without 3-4</td>
<td>80.2</td>
<td>73.3</td>
<td>81.5</td>
<td>86.0</td>
<td>85.6</td>
<td>86.2</td>
<td>82.1</td>
</tr>
</tbody>
</table>

The mean cell sizes were used to calculate estimates for cooling rates and solidification rates using the empirical relationship provided by Katayama et. al. discussed previously.\cite{25}
cooling rates estimated from the range of mean cell sizes were between $7.0 \times 10^6$ and $3.6 \times 10^8$ K/s. (Table 3.4.4) An estimate of the corresponding solidification rates was made using a combination of the measured cell sizes, literature data on SS, and simulation of heat transfer during the splat quench event. Temperature gradients corresponding to the estimated cooling rates were extracted from the heat transfer simulation and ranged between 18 and 229K/µm. (Table 3.4.4). A full table of the temperature gradients and cooling rates from the simulation is listed in Appendix 7.1.2. The solidification rate estimates were primarily between 390-1,200 mm/s, with two reaching up to 1,570mm/s.

3.5 Discussion

The phase content and solidification mode of splat quenched stainless steel is significantly impacted by the alloy composition, even within the allowable ASTM A240 specification. At all solidification rates the concentration of alloying elements has a significant effect on the phases formed. Higher solidification rates tend to favor single phase solidification modes and the transition region separating fully austenitic and fully ferritic solidification shrinks. [34, 82] This is shown in works by Lippold and Elmer and based on the ASTM A240 ranges for 316L compositions, many of the Cr/Ni$_{eq}$ values are near or within the transition region between the two microstructures at rapid solidification rates. [40, 44] As a result of a smaller transition region, small changes to alloy chemistry like those given for 316L can lead to significant changes in the microstructure formation.

Five basic microstructures, based upon phase content, could be found in SQ samples: all primary austenite, all primary ferrite, all transformed austenite (F/MA), primary austenite and F/MA, and primary ferrite and F/MA. At very low Cr/Ni$_{eq}$ ($X < 1.1$) alloys 1 and 2 formed all primary austenite microstructures confirmed by EBSD and the type 1 cells observed after
etching. Between alloys 2 and 3 there occurs a transition from a completely primary austenite microstructure to a mixed primary austenite and F/MA microstructure. The presence of both type 1 and 2 cells observed in alloy 3 indicated a mixed microstructure even though it indexed as completely FCC. (Figure 3.4.6C) Alloy 4 (1.53 Cr/Ni_{eq}) was almost entirely F/MA with a small number of local regions of primary austenite near the PS interface. None of the custom alloy SQ samples formed an entirely F/MA microstructure due to the large range of solidification rates experienced during SQ. Alloy 5 and alloy 6 with Cr/Ni_{eq} of 1.71 and 1.75 were almost entirely F/MA, but small amounts of primary ferrite were present at along the PS interface near the radial edge of where cell sizes were the smallest and solidification rates were the fastest. Alloys 5 and 6 are within the ASTM A240 specification for 316L SS and have nearly identical chemistries with the only major difference being ~0.5 wt% more Ni in alloy 6 vs. alloy 5. For alloys 7 and 8, even though the Cr/Ni_{eq} varied by almost 0.1, the average phase contents were similar. Both formed microstructures around 10-15% ferrite, but alloy 8 had 0.2 wt% more Cr and 0.02 wt% less N. Alloys 8 and 9 showed a major difference in phase content with alloy 9 forming between 40-90% ferrite compared to alloy 8 forming 6-18% ferrite. Alloy 9 has 0.1 wt% less Cr, 0.2 wt% more Ni, and 0.6 wt% more Mo, but the Cr/Ni_{eq} are 1.94 and 1.95. Alloys 9 and 10 formed similar microstructures and phase contents, but alloy 10 had lower concentrations of Cr, Ni, Mo, and N.

At very high Cr/Ni_{eq} (X > 2.0) alloy 11 formed all primary ferrite.

The phase content was found to vary, significantly for some alloys, based upon the location in the SQ sample. Varying phase content in splat quenched samples is seen in Figure 3.4.5 which showed the spatial distribution of austenite within a SQ sample. Distributions similar to this were observed in all samples where both austenite and ferrite were present. The difference of phase content based on location is most likely caused by differences in the solidification rate.
within the splat quench sample. In the optical phase quantification, for dual-phase splat quenches, it was consistently observed that the ferrite concentration increased away from the radial center of the splat quench. (Figure 3.4.5) It was also observed that primary ferrite typically formed along the PS interface initially and expanded away from the interface as ferrite content increased. This behavior is best illustrated by the EBSD phase maps in Figure 3.4.6B and C. In the cell size measurements, the mean cell size at the PS interface were measurably smaller than the cells along the midline. (Figure 3.4.10). As previously mentioned, larger cell sizes mean lower cooling rates and solidification rates. Based on the cell size distribution indicating that largest cooling rates were at the PS interface and the observed preferential formation of ferrite microstructure along the PS interface it is concluded that the higher cooling rates near the PS interface suppressed the ferrite to austenite massive transformation.

The range of cell sizes measured in splat quenched samples are of a similar magnitude with cell sizes for rapid solidification and for previously reported for LPBF of SS. As previously mentioned, cell sizes reported for LPBF of stainless steel are typically between 0.3µm and 1.3µm and can be extended lower depending on processing parameters. [1, 3, 95, 108, 139, 140] The range of cell sizes observed in SQ overlaps with the lower end of that range. Using the cell size to cooling rate relationship discussed previously, cooling rate estimates for two-piston splat quenching were between 7.0*10^6 K/s and 3.6*10^8 K/s. The fastest cooling rates were regularly located at the PS interface while the slowest were near the midline. Again, these cooling rates partially overlap with the higher end of those commonly reported in LPBF of steel which is estimated to be between 10^5 and 10^8 K/s. [1, 7, 88] Lastly, from the mean cell size measurements, the solidification rate estimates for SQ were between ~0.4 and 1.6m/s, which are similar in magnitude to what can be produced at the upper end of LPBF. [5, 20, 95]
These results have shown that the primary ferrite microstructure and F/MA microstructures occurred in alloys with a wider range of Cr/Ni$_{eq}$ than previously predicted at these rapid solidification rates and that increased rapid solidification rates reduced the range of Cr/Ni$_{eq}$ in which the F/MA microstructure was observed. The increase in compositional range for the F/MA microstructure is visualized in Figure 3.5.1 by using a modified version of J.C. Lippold’s microstructure selection map for 300-series stainless steel. The data used to generate this plot is consolidated in Table 3.5.1. In previous studies, theoretical and experimental work has been done detailing why single-phase solidification is favored at rapid solidification rates primarily due to effect on solute redistribution behavior and local undercoolings at the solid liquid interface/dendrite tip. As a result of these different phenomena affecting the solidification process, at rapid solidification rates, fully ferritic solidification microstructures formed at lower Cr/Ni$_{eq}$ values when compared to slower solidification rates. Also, fully austenitic microstructures were found in material with Cr/Ni$_{eq}$ values above what is predicted for slower solidification rates. The microstructures observed in the splat quenched samples were formed at solidification rates between 390 and 1,600mm/s, a range of solidification rates that are well into the FBAM rapid solidification regime of interest (10mm/s and above). As a result, the microstructures observed were expected to differ from slower solidification rate predictions in a similar manner to what has been reported previously. In this modified microstructure selection map, the X- and Y-axis have been extended to include Cr/Ni$_{eq}$ values down to 0.9 and solidification rates up to 10,000mm/s respectively. Using the culmination of results shown in Table 3.5.1 each sample has been added to the modified Figure 3.5.1 at the respective Cr/Ni$_{eq}$ value with the corresponding observed microstructures and range of solidification rates. We found that during rapid solidification, partial F/MA microstructures
formed in SQ samples with a large range of Cr/Ni\textsubscript{eq} values, between 1.43 and 2.00. The transition to a complete primary austenite solidification mode would be expected to occur in alloys with Cr/Ni\textsubscript{eq} values between of 1.43 and 1.09, but partial primary austenite was observed in samples with Cr/Ni\textsubscript{eq} values up to 1.54. Finally, in areas where the smallest cells were observed, small amounts of primary ferrite began forming in samples with Cr/Ni\textsubscript{eq} values as low as 1.71. It should be noted that the Fe content of each alloy was tracked, however there was no observable effect on mean cell size or microstructure for the alloys studied.
Figure 3.5.1 Modified microstructure prediction map based on work by Lippold et. al. [44] The microstructures that were observed in SQ samples for each alloy feedstock are plotted at the corresponding Cr/Ni$_{eq}$ and estimated range of solidification rates based on cell size measurements. Alloy composition is identified by the number above each set of data points.

Table 3.5.1 Summary table of data used to generate Figure 3.5.1.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr/Ni$_{eq}$</th>
<th>Solidification Rate (mm/s)</th>
<th>Solidification Mode</th>
<th>Microstructures</th>
<th>Ferrite Content (Area %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.97</td>
<td>390 - 1210</td>
<td>Primary Austenite</td>
<td>Austenite</td>
<td>0.0-0.0</td>
</tr>
<tr>
<td>2</td>
<td>1.09</td>
<td>390 - 1210</td>
<td>Primary Austenite</td>
<td>Austenite</td>
<td>0.0-0.0</td>
</tr>
<tr>
<td>3</td>
<td>1.43</td>
<td>410 - 1130</td>
<td>Primary Austenite + Primary Ferrite</td>
<td>Austenite + F/MA</td>
<td>0.0-0.0</td>
</tr>
<tr>
<td>4</td>
<td>1.53</td>
<td>390 - 1570</td>
<td>Primary Austenite + Primary Ferrite</td>
<td>Austenite + F/MA</td>
<td>0.0-0.0</td>
</tr>
<tr>
<td>5</td>
<td>1.71</td>
<td>390 - 1010</td>
<td>Primary Ferrite</td>
<td>F/MA + Ferrite</td>
<td>0.2-0.7</td>
</tr>
<tr>
<td>6</td>
<td>1.75</td>
<td>390 - 1110</td>
<td>Primary Ferrite</td>
<td>F/MA + Ferrite</td>
<td>0.6-1.5</td>
</tr>
<tr>
<td>7</td>
<td>1.85</td>
<td>390 - 1200</td>
<td>Primary Ferrite</td>
<td>F/MA + Ferrite</td>
<td>6.7-18.1</td>
</tr>
<tr>
<td>8</td>
<td>1.94</td>
<td>390 - 1130</td>
<td>Primary Ferrite</td>
<td>F/MA + Ferrite</td>
<td>6.3-16.2</td>
</tr>
<tr>
<td>9</td>
<td>1.95</td>
<td>390 - 1570</td>
<td>Primary Ferrite</td>
<td>F/MA + Ferrite</td>
<td>57.0-84.8</td>
</tr>
<tr>
<td>10</td>
<td>2.00</td>
<td>470 - 1000</td>
<td>Primary Ferrite</td>
<td>F/MA + Ferrite</td>
<td>62.8-97.3</td>
</tr>
<tr>
<td>11</td>
<td>2.09</td>
<td>540 - 1050</td>
<td>Primary Ferrite</td>
<td>Ferrite</td>
<td>100-100</td>
</tr>
</tbody>
</table>
Splat quenching did not produce observable chemical gradients in bulk SQ samples but did result in microscale segregation to cell boundaries. SQ samples were homogenous when analyzed longitudinally and through the middle of the SQ. Elemental segregation was not observed during SEM-EDX between solidification cells most likely due to the small cell sizes in splat quenched samples and even smaller cell boundary thickness. Generally, the interaction volume of EDX in an SEM is around 1µm while the typical cell size was around 200-400nm.\textsuperscript{141} When these length scales are compared to the interaction volume is much larger than the cell features. However, STEM-EDX line scans showed the segregation of primarily Cr and Mo to cell boundaries during primary austenite solidification. In primary ferrite solidification, Ni was the primary element to segregate to the cell boundary. The elemental segregation responses due to the two different solidification modes are previously reported in rapid solidification and FBAM literature.\textsuperscript{7, 9, 13, 24, 65, 66} Although primary ferrite and F/MA are not the same phase, the F/MA microstructure originally solidified as ferrite prior to transforming to austenite. This shared solidification mode was observed in the etching response of the splat quenched samples where type 2 cells formed in both primary ferrite and F/MA microstructures but type 1 cells were only observed in primary austenite.

The observed ranges of Cr/Ni\textsubscript{eq} with which the different solidification modes and microstructures were observed for the SS alloys investigated in this study, strongly suggests that compositional specifications for metal powders to be used in PBF should be amended to avoid the formation of unintended phases and/or microstructures in the final product. 316L is specifically formulated to form primarily austenite with small amounts of ferrite to reduce the potential of solidification cracking. Too much ferrite and the mechanical properties and corrosion resistance will suffer. Form a fully austenitic microstructure and there is greater
potential for cracking to occur. Of the samples that were within the A240 specification for 316L, combinations of primary austenite and F/MA microstructures and combinations of F/MA and primary ferrite were observed with up to 20% primary ferrite measured in higher Cr/Ni$_{eq}$ SQ samples. At the elevated solidification rates studied, most of the 316L specification actually solidified as ferrite and transformed into austenite with only alloys 3 and 4 containing any primary austenite. Also, the three alloys that were slightly outside of the specification with high Cr/Ni$_{eq}$ (alloys 8-10) formed anywhere from 20 to >90% ferritic microstructures. See Appendix 7.1.3 for complete list of Cr/Ni$_{eq}$, microstructures, and solidification phases for each SQ. The various possible microstructures that can form during rapid solidification within the specification highlights the need for more refined compositional tolerances in order to ensure the formation of the intended microstructure and phase of the final part.

One possible explanation for why the F/MA microstructure was observed in SQ alloys with a wider range of Cr/Ni$_{eq}$ than previously predicted is due to the higher cooling rates of SQ ($10^6$-$10^8$K/s) compared to the data used to generate the Lippold plot (around $10^3$-$10^5$K/s).\textsuperscript{[44]} The ferrite to austenite massive transformation that makes the F/MA microstructure occurs when a temperature is reached in the two phase regime in which the free energies between the two phases are equal.\textsuperscript{[70, 99]} Higher cooling rates means the transformation temperature of ferrite to austenite will be reached faster than at lower cooling rates. Since the temperature gradient and cooling rates are also related to cooling rate, differences in these values between the SQ process and methods used to generate the Lippold plot could also attribute to differences in the range of Cr/Ni$_{eq}$ where the F/MA microstructure formed. Additionally, further cooling below the transformation temperature in SS has been shown to significantly increase the driving force for the transformation to occur.\textsuperscript{[70]} Thus, the larger cooling rates produced in SQ resulted in the
formation of F/MA microstructures over a wider range of Cr/Ni\textsubscript{eq} than previously predicted by generating a larger driving force for transformation.

The results discussed in this study show the potential of splat quenching to be used as an alloy screening tool for FBAM techniques, particularly LPBF. The solidification cell morphology of a SQ sample is similar to those observed in LPBF processes. The range of cell size measured in SQ samples is fairly consistent and, in targeted areas of the sample, resulted in cells similar in size to those observed in LPBF.\textsuperscript{[1, 7, 88]} The combination of F/MA and primary austenite microstructures have previously been reported in LPBF material of 316L.\textsuperscript{[7]} Thus, it can be concluded that SQ produces cooling and solidification rates along similar magnitudes as LPBF techniques around $10^6$ – $10^8$ K/s and 390-1,600mm/s. While a direct comparison of the two techniques would provide a definitive answer, based on these results and the literature referenced, two-piston splat quenching is a potentially viable tool to simulate RS for PBF processes.

3.6 Conclusion

This study details the use of two-piston splat quenching to investigate microstructure formation at rapid solidification for SS. A variety of SS with Cr/Ni\textsubscript{eq} spanning 0.9 to 2.1 were produced and researched for this study. Detailed microscopy and characterization were used to connect changes in phase content, cell size, and segregation to alloy composition. In this research, we have noted the following:

1. Under rapid solidification conditions, multiphase microstructures (e.g., primary austenite-F/MA and F/MA-primary ferrite) are observed over a much wider compositional range than previously predicted. The original Lippold diagram provided predictions for expected solidification microstructures based on solidification rate data covering up to
10-100mm/s. Our results spanned the 390-1,200 mm/s solidification rate regime and found F/MA microstructures formed over a significantly wider range of Cr/Ni$_{eq}$, 1.43 and 2.0. Fully primary austenitic microstructures are concluded to begin forming between 1.43 and 1.09 Cr/Ni$_{eq}$, with partial primary austenite forming in samples with Cr/Ni$_{eq}$ as high as 1.54. Primary ferrite began to form in small quantities at very high solidification rates in samples with a Cr/Ni$_{eq}$ as low as 1.71. The microstructure/solidification mode deviations from previously predicted Cr/Ni$_{eq}$ ranges are theorized to be caused by the differences in cooling rate and solidification conditions of SQ with the methods used to produce the data used in the Lippold plot.

2. Splat quenched samples were shown to be chemically homogeneous, within detectable limits for primary alloying elements, across a given splat quenched sample on the microscale, but sub-microscale elemental segregation was found at cell boundaries. For primary austenite solidification (type 1 cells), Cr segregation was most notable with some Ni and Mo segregation to cell boundaries. For primary ferrite solidification (type 2 cells), Ni was the only detected segregating element. This segregation behavior was observed in both primary ferrite and transformed austenite (F/MA) microstructures.

3. The range of measured cell sizes in splat quenched samples spanned from 0.12 and 0.44µm and was unaffected by changes in alloy composition. The range of cell sizes in SQ samples was shown to be similar to the smaller range of commonly reported cell sizes in LPBF literature. The corresponding cooling rates estimated from this range of cell sizes were between $7.0 \times 10^6$ to $3.6 \times 10^8$ K/s. While more difficult to quantify, the estimated solidification rates were between 390-1,200 mm/s. These cell sizes, cooling rates, and solidification rates for splat quenched stainless steel are comparable to the
upper end of solidification rates and cooling rates commonly reported LPBF processed SS.

4. Splat quenching produces similar microstructures and cellular segregation to other SS produced by rapidly solidified fusion based additive manufacturing techniques and could, therefore, provide an effective tool for screening alloys of interest for fusion based additive manufacturing techniques. The elemental segregation to cell boundaries observed in type 1 and type 2 cells produced by splat quenching was very similar to reported cellular segregation observed in LPBF and other rapid solidification techniques from the literature.

5. Material specifications for austenitic stainless steel, like ASTM A240 for 316L, may need to be further refined when processing steels within the upper end of solidification rates experienced in fusion based additive manufacturing in order to achieve the intended microstructure. For more traditional manufacturing methods, the range of compositions allowed by the ASTM A240 specification for 316L steel would result in nearly complete austenite formation. During rapid solidification, higher Cr//Ni_{eq} values possible within the specification can promote microstructures in excess of 50% primary ferrite. Alternatively, lower Cr//Ni_{eq} can produce either primary austenite or a mixture of primary austenite and massively transformed austenite (F/MA) as solidification rates decrease.

3.7 Acknowledgement

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CHAPTER 4: A COMPARISON OF SUB-MICROSCALE CELLULAR SEGREGATION IN RAPIDLY SOLIDIFIED STAINLESS STEEL VIA TWO-PISTON SPLAT QUENCHING AND LASER POWDER BED FUSION


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4.1 Abstract

Fusion based additive manufacturing (FBAM) techniques leverage rapid solidification (RS) conditions to create parts with complex geometries, unique micro and nanoscale morphological features, and cellular elemental segregation. Three custom alloy compositions with Cr/Ni\textsubscript{eq} values ranging from 1.53 to 1.95 were produced via arc melting and processed using laser powder bed fusion (LPBF) and two-piston splat quenching (SQ) to achieve RS rates estimated between 0.4 m/s and 0.8 m/s. Using both SEM and TEM, micro and nanoscale imaging and analysis techniques were utilized to achieve high resolution images, perform phase identification, and measure elemental segregation across solidification cell boundaries in the various microstructures formed during RS. Similar microstructure features were observed in rapidly solidified stainless steels produced by both LPBF and SQ processing including phase and microstructure identification, oxide particles, cell size, and segregation behavior. Larger oxide particles were found in the LPBF samples than the SQ samples. Also, primary austenite solidification cells from the LPBF sample exhibited dislocation pileup along the cell boundaries that was not found in any of the other microstructures or SQ samples. The targeted adjustment of
Cr and Ni concentrations to control the Cr/Ni$_{eq}$ values were similar to the allowable ranges of the ASTM A240 specification and resulted in no observable impact to the cell size, oxide particle size, or magnitude of segregation. The average segregation ratio values showed that the amount of Ni segregation in the primary ferrite solidified microstructures did not significantly differ between the three custom alloys, regardless of Cr/Ni$_{eq}$ or RS processing technique. SQ is demonstrated as an alternative processing technique that can be used as a screening tool for new alloy compositions which is capable of simulating RS rates, microstructures, and conditions similar to LPBF.

4.2 Introduction

Powder bed fusion (PBF) processing techniques rely heavily on rapid solidification (RS) to create parts with complex geometries that would not be feasible through traditional production processes. Austenitic stainless steels are commonly used in PBF processing with great success to create high strength parts with good corrosion resistance and thermo-mechanical properties. These properties are achieved partially as a result of the unique micro and sub-microstructures formed by rapid solidification (RS). Cooling rates and solidification rates experienced during PBF processing can vary extensively based on the material and build parameters, for example, stainless steels processed via laser powder bed fusion (LPBF) typically achieve cooling rates between $10^3$ and $10^7$ K/s. However, the relationship between composition, microstructure, and rapid solidification is not fully understood, so before new alloys can be used, they must be investigated to ensure the desired properties will be achieved after RS. The metallic powder used in PBF processes requires specialized equipment to make, can cost thousands of dollars to purchase in sufficient quantities for PBF, and generate waste from required size distributions that are necessary for consistent and quality results. Also, the PBF
equipment must be emptied and cleaned when changing alloy compositions. These factors make testing new alloy compositions a costly and time-consuming processes.

RS that occurs during fusion-based additive manufacturing (FBAM) processes such as PBF, enables the formation of unique micro and sub-microscale structure and features in stainless steels. Most FBAM stainless steels are characterized by the cellular solidification structures that can form as a result of RS. The solidification structure can be observed by etching a polished cross section, or by using TEM bright field (BF) imaging. In BF images of 316L, the solidification structure is outlined by networks of dislocations along the cell boundaries.[14] The dislocation networks result in a sub-structure within the microstructure. [7, 9, 12-14, 24, 108, 144] Along with the dislocation pileup, nanoscale oxide particles have also been found along the cell boundaries.[7, 9, 12, 14, 24, 145] These oxide particles were identified as Mn enriched Si oxides, or Rhodonite (MnSiO₃) and have been found to range in size between 10 and 300nm. [8, 9, 14, 17, 107] In some studies, other Cr-rich oxides have also been reported, but these were not found as frequently. [8, 95] The MnSi oxides are reported to act as Zener pinning sites at the cell boundaries for the dislocation pile up and are partially responsible for the improved material properties. [95, 107] In rapidly solidified austenitic stainless steels the segregation of Cr, and if present, Mo to the cell boundaries has been repeatedly reported. [7, 9, 13, 95] The segregation of these heavy elements to cell boundaries has also been suggested to contribute to improved material properties. [9, 12, 95] The ability of RS processing to produce microstructures and features that are distinctly different from what occurs at slower solidification rates creates an opportunity for current metallic systems to be implemented in new ways.

Rapid solidification is known to affect the resultant phase/microstructure formed at certain compositions in austenitic stainless steels and, in some cases, this deviation from the
equilibrium predicted microstructure can significantly impact the properties of the final product. Stainless steel and RS literature use equivalence equations, such as WRC-1992, to quantitatively represent a materials tendency to form either austenite or ferrite microstructures based on the chemical composition. Higher solidification rates were found to increase the range of equivalence values where austenite and ferrite solidification was stable, reducing the predicted two-phase region. Rapid solidification rates tend to produce single phase solidification of austenite or ferrite, typically resulting in three possible microstructures; primary austenite (PA) from austenite solidification, primary ferrite (PF) from ferrite solidification, and austenite formed from a massive transformation of ferrite (F/MA). The effect of RS on the ranges of equivalence values where these microstructures form is critical to understand when performing FBAM processes in order to ensure the desired material properties in the finished part.

Microscale cellular segregation that occurs during RS in welding and FBAM processes changes when rapid solidification rates are reached. In slower solidification rate processes of austenitic stainless steel, such as arc welding, Cr and Ni exhibit an inverse segregation behavior where Cr becomes enriched at cell boundaries and depleted at the cell center, and Ni enriched at the cell center and depleted along the cell boundaries. The opposite segregation response was observed in ferritic microstructures where there was Ni enrichment at boundaries and Cr at cell centers. This difference in elemental segregation in which Cr is rejected during austenite solidification and Ni is rejected during ferrite solidification is explained by Cr being a ferrite stabilizer and Ni being an austenite stabilizer. This type of segregation is under the assumption of the limited diffusion in the liquid with no solid diffusion model. The segregation at the cell center is referred to as an initial transient region and the segregation at the cell
boundary is the final transient region. When electron beam welding (EBW) was used, which has a much higher solidification rate, the initial transient region was no longer observed but the final transient region remained.[53, 65, 66] In a different study of austenitic 316L, produced by SLM where the solidification rates are higher than conventional arc welding, the enrichment of Cr, Ni, Mo, and Mn was reported at the cell boundaries with no observable change in composition within the cell body.[17] Similarly, in LPBF processed austenitic 316L material, Voisin et. al. reported both Cr and Mo segregation to the cell boundaries.[12] This study did not mention the Ni or Mn response at the cell boundaries. The variation in reported segregation profiles found in rapidly solidified stainless steels further highlights the need for a better understanding of how RS changes solidification microstructures in various processing methods.

Along with micro-segregation, the possibility of solid-state diffusion after solidification has been previously proposed. During separate studies by Brooks and Iamboliev, they reported rapidly solidified ferritic structures where cell boundaries were homogenous after solidification and solid-state diffusion was used to explain the resulting lack of observed segregation at the RS cell boundaries.[53, 65, 66] There are multiple factors that can impact whether solid-state diffusion will occur, such as crystal structure, element, distance, and temperature. The amount of solid-state diffusion that can occur in a solidified material will change based on the phase, as the diffusion properties of elements is different in austenite vs ferrite.[7, 53, 65] Also, whether solid-state diffusion will occur or to what degree is dependent on the processing technique and conditions, as sufficient time and temperature are required. Although, micro-segregation in rapidly solidified stainless steel has been reported in the solidified microstructures, the possibility that the observed segregation has been modified by solid-state diffusion must also be considered.
Several solidification models have been developed and or modified to simulate rapid solidification conditions more accurately using correction factors or by incorporating phenomena such as solid-liquid boundary diffusion and solute trapping. At equilibrium solidification rates, tools such as phase diagrams and the lever rule generally predict solidification segregation well. More complex, non-equilibrium solidification models, such as Scheil, are useful for simulations at intermediate solidification velocities and can produce first order estimates for the low end of rapid solidification. As solidification rates increase, prior assumptions about diffusion and interface kinetics are no longer accurate requiring velocity corrected models such as the continuous growth model presented by Aziz. These typically combine models addressing effects such as undercooling, dendrite tip radius, and the absolute limit of stability with larger models to improve results. Additionally, to validate these models, a more comprehensive understanding of rapid solidification for stainless steels may well require the study of many, different alloy compositions which span the microstructure space from PA – F/MA – PF. To do so, will require an efficient means of producing a variety of stainless steels, performing rapid solidification experiments, and characterizing the result RS microstructure.

Two-piston splat quenching (SQ) is a useful tool for generating samples with RS rates similar to PBF processes. The technique requires very little feedstock (<1 gram) to perform experiments, feedstock does not need to be in powder form, and experiments can be completed from start to finish in a matter of a couple hours. By comparison, a standard LPBF build process requires several kilograms of powder to be produced by a series of atomization experiments and subsequent powder sizing and characterization, costing significantly more time and capital. The SQ process utilizes rapid solidification to create thin foils with high cooling rates and cellular solidification structures. SQ is capable of achieving cooling rates beginning around $10^4$ K/s.
and increasing up to $10^8$ K/s or higher under the right circumstances. Such a wide range in cooling rates is achievable through targeted modification of key experimental parameters such as sample size, surface roughness, and platen material.

This paper compares the RS microstructures produced by LPBF and SQ experiments using a variety of stainless steel alloys which span the microstructure space between primary austenite (PA), F/MA, and primary ferrite (PF). The solidified materials were examined using a combination of micro and nanoscale analysis techniques to assess microstructure, solidified phase, elemental segregation, and micro/nanostructural features. Unlike in previous works, this paper discusses the similarities and differences between microstructures for a single alloy chemistry produced with two unique rapid solidification processes and investigates the potential relationship between the Cr/Ni$_{eq}$ and elemental segregation in multiple alloys and microstructures produced by SQ. In addition, the segregation ratios estimated from experimental results will be compared to both simulated. Detailed imaging using scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission electron microscopy high-angle annular dark-field (STEM-HAADF) was performed, and analysis using electron backscatter diffraction (EBSD) and STEM energy dispersive X-ray spectroscopy (EDX) measurement techniques were implemented to examine the samples at the micro and nanoscales. Finally, this paper demonstrates that the SQ technique can be used as an effective means to efficiently explore the RS microstructure space similar to LPBF for stainless steels.

4.3 Methods

Alloy production and rapid solidification processing

A total of three different alloy compositions were produced in this investigation that had increasing Cr/Ni$_{eq}$ ratios of 1.53, 1.71, and 1.95 using the WRC 1992 equivalence equations.
Alloy 1 was a 316L type stainless steel that was within the ASTM-A240 composition specification had been processed via LPBF. Alloys 2 and 3 were produced using high purity raw material that was arc melted together to achieve homogenous feedstock with the targeted chemistries. All raw material purities were 3N or higher. Iron was in the form of 1/8” pellets and Cr sputtering targets were used for alloying while the rest of the material was in powder form and pressed into a pellet. Alloy compositions were measured after arc melting and rolling using the following bulk chemical analysis techniques: inductively coupled plasma optical emission spectroscopy (ICP-OES), combustion analysis (CA), and inert gas fusion (IGF). A portion of the LPBF material was sectioned and used for SQ experiments of that alloy composition. Three replicate samples were made from each alloy composition using SQ. SQ was performed in an UHP Ar environment. For the SQ experiments, the samples were electromagnetically levitated, melted, and brought to a target temperature of 1600°C before being released and splatted between two Cu platens to create the thin foils.

Sample preparation

To prepare samples for TEM and STEM analysis both SQ and LPBF samples were cross sectioned and mounted in the electorally conductive hot mount material PolyFast. The LPBF sample was cut through the middle to expose melt pool cross sections. SQ produced thin foil disk samples that were sectioned longitudinally through the middle, as if cutting a coin in half, and mounted with the cross section exposed. (Figure 2.4.1) All mounted samples were ground and polished to a 1µm finish then either electrolytically etched in a 60/40 solution of 70% nitric acid and DI water using a DC power supply at 1.25V to reveal solidification microstructure, or vibratory polished to a 0.02µm finish for EBSD.
TEM foils were made via focused ion beam (FIB) lift outs from etched samples. FIB lift outs were performed using either a TESCAN LYRA FIB-FESEM or FEI Quanta 3D Dual Beam, both of which use a gallium ion source. First a region of interest was identified, where a group of cells were aligned and in-plane. In splat quenched samples this was within the radial center of the splat quench. For LPBF material the region of interest was within the interior of the build away from any edges. A focused ion beam was used to deposit a bar of platinum perpendicular to the orientation of the solidification cells to produce a cross section of the cells when viewed in the TEM. The TEM foil was then cut and lifted out from the sample and attached to a Cu grid. The foil was thinned until the thickness was 150nm or less was achieved.

SEM imaging and analysis

An SEM was employed for high resolution imaging of the etched cell structure and to perform EBSD analysis of polished samples. Images were collected on a Thermo-Fisher Apreo SEM while EBSD was completed using a JEOL 7000 SEM and the software Aztec produced by Oxford. In splat quenched samples images and EBSD scans were collected from the radial center of the splat quench. Images and EBSD scans of LPBF material were from the interior of the sample build. The cell size was measured for the LPBF and SQ samples and solidification rates were estimated to be between 0.4 and 0.8m/s. This was achieved using the empirical relationship between cell size and cooling rate from work by Katayama et. al. and heat transfer simulations to convert the cell size to cooling rate to solidification rate.\textsuperscript{[25, 27]} (Chapter 3)

TEM and STEM-HAADF imaging and STEM-EDX

All TEM and STEM work was performed on an FEI TECNAI F-20 microscope at 200kV. Bright field and STEM-HAADF images were collected using the GMS III software. Camera lengths used for STEM-HAADF imaging were 50mm and 100mm.
STEM-EDX line scans were collected from each sample using a single tilt low background beryllium sample holder. STEM-EDX was performed using an EDAX Optima-T-60 windowless detector and analyzed using the EDAX-TEAM software. Analysis performed used integrated counts under peak for each element and were automatically background subtracted, but peak deconvolution was not performed. To reduce artifacts in the signal intensity line profiles a ratio of signals was taken for each element vs the Fe signal. This reduced any change in signal intensity due to changes in foil thickness.

ThermoCalc simulations

The thermodynamic modeling software Thermo-Calc 2022a was used to run multiple solidification models for each alloy feedstock being studied. Simulations were performed using the classic Scheil solidification module (Equation 4.3.1) where \(C_s\) is the composition of the solid, \(k_{eq}\) is the equilibrium partition coefficient, \(C_0\) is the initial composition, and \(f_s\) is the fraction solid. \(^{[31]}\)

\[
C_s = k_{eq} * C_0 * (1 - f_s)^{k_{eq}-1}
\]

Equation 4.3.1

The velocity modified Scheil with solute trapping module was also used to perform solute trapping simulations at three different rapid solidification rates 0.1m/s, 1.0m/s, and 5.0m/s. All simulations were completed using the TCFE8 Steels/Fe-alloys database. The allowed phases in each simulation were restricted to only the liquid phase and the observed primary solidification phase of that alloy. This was done to account for the change in primary solidification phase caused by rapid solidification and to reflect what was observed in the experimental results. The classic Scheil and Scheil with solute trapping model were ran to 95% completion. The Scheil with solute trapping module utilizes a modified version of previous work
by Aziz and Jackson that presented an equation for a velocity corrected partition coefficient shown in Equation 4.3.2. [100, 101, 146]

\[ k_V = \frac{k_0 + \beta_0 V}{1 + \beta_0 V} \]  

Equation 4.3.2

In this equation, \( k_V \) is the velocity corrected partition coefficient, \( k_\text{eq} \) is the equilibrium partition coefficient, \( V \) is the solidification front velocity, and \( \beta_0 \) is a ratio between the interatomic distance length scale and diffusion coefficient. A modified version is used in the ThermoCalc model to solve for the partitioning coefficient at increased solidification rates.

Segregation ratio calculation

The partition coefficient, \( k_\text{eq} \), is commonly presented as shown in Equation 4.3.3, where \( C_S \) is the concentration of an element present in the solid, and \( C_L \) is the concentration of the same element in the liquid.

\[ k_\text{eq} = \frac{C_S}{C_L} \]  

Equation 4.3.3

For equilibrium and near equilibrium solidification conditions, \( C_L \) can be replaced with the concentration of the respective element in the final solid to solidify. However, under rapid solidification conditions when solving for the partition coefficient, \( C_L \) can not be replaced with the concentration in the final solid due to phenomena like undercooling, cell tip radius, and diffusion in the liquid and solid to name a few. Instead, the ratio of initial vs final concentration, which was once partition coefficient, now is the segregation ratio.

In order to quantify the amount of segregation, segregation ratios were measured using experimental data from multiple cells in each microstructure and compared with thermodynamic simulations. When calculating the segregation ratio from solidification simulations \( C_S \) was the initial composition and \( C_L \) was the final composition of the solidified phase. For the experimental data, integrated and background subtracted X-ray signal intensities from individual
line scans were used in place of composition. This was done because of difficulties associated with precisely and accurately converting STEM-EDX data into elemental compositions for complex alloys. The average signal intensity from the cell center was used as $C_S$ and the signal intensity at the cell boundary was $C_L$. The segregation ratio was not calculated using the ratio of signal vs Fe signal data in order to provide a more accurate representation of the individual segregation of each element. In cases where the signal intensities were skewed by TEM foil thickness, the signal intensity at the base of the peak (identified using the ratio of signal vs Fe data) was used instead of the cell center to reduce thickness effects.

4.4 Results

Microstructures and cellular morphology

The three stainless steel alloys used in this study had similar compositions that spanned a range of Cr/Ni$_{eq}$ values from 1.53 to 1.95 through varied Cr, Ni, and Mo concentrations. The measured individual alloy compositions are listed in Table 4.4.1 along with the WRC-1992 equivalence values and Cr/Ni$_{eq}$ ratios for each alloy. Alloys 1 and 2 were within the ASTM A240 compositional specification for 316L SS which defines a range of allowable concentrations for Cr, Ni, and Mo. Alloy 3 almost met the specification, but contained 0.1 wt% Cr more than allowed for 316L SS. The only other major compositional difference between the alloys was that the concentration of C in alloy 1 was an order of magnitude greater than in alloys 2 and 3, but still below the 0.03 wt% upper limit for low carbon SS.
Table 4.4.1 Measured bulk chemistry analysis results for feedstock alloys 1-3 with equivalence values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>N</th>
<th>C</th>
<th>Cruisine</th>
<th>Ni eq</th>
<th>Cr/Ni eq</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - LPBF</td>
<td>67.1</td>
<td>16.90</td>
<td>11.70</td>
<td>2.55</td>
<td>1.20</td>
<td>0.53</td>
<td>0.020</td>
<td>0.018</td>
<td>0.000</td>
<td>0.040</td>
<td>0.000</td>
</tr>
<tr>
<td>1 - SQ</td>
<td>67.1</td>
<td>16.90</td>
<td>11.70</td>
<td>2.55</td>
<td>1.20</td>
<td>0.53</td>
<td>0.020</td>
<td>0.018</td>
<td>0.000</td>
<td>0.040</td>
<td>0.000</td>
</tr>
<tr>
<td>2 - SQ</td>
<td>68.0</td>
<td>17.20</td>
<td>11.10</td>
<td>2.22</td>
<td>1.10</td>
<td>0.38</td>
<td>0.010</td>
<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>3 - SQ</td>
<td>66.9</td>
<td>18.10</td>
<td>10.50</td>
<td>2.92</td>
<td>1.10</td>
<td>0.42</td>
<td>0.010</td>
<td>0.002</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

EBSD phase mapping was used to identify austenite and ferrite phases in the rapidly solidified samples produced by LPBF and SQ processing. Alloy 1 samples that were processed using LPBF and SQ both produced fully austenitic microstructures. A fully austenitic microstructure was observed in the SQ alloy 2 samples at the center, and small amounts of ferrite were found at the radial edges of the sample. It should be noted that the PA and F/MA microstructures are both crystallographically austenite and can not be distinguished when using EBSD. In the EBSD phase analysis alloy 3, both austenite and ferrite were found in significant amounts seen in Figure 4.4.1D. Ferrite concentrations in these samples varied with respect to radial position in the SQ with more ferrite being observed away from the radial center. This is covered in greater detail in previous work on SQ stainless steel microstructures. (Chapter 3) Figure 4.4.1A-D contains phase maps for each of the four samples where blue is austenite and red is ferrite. In the phase map shown in Figure 4.4.1A, patterns that could not be matched are shown as white instead of black dots, as in Figures 4.4.1 B-D, because the first phase map was exported using a different software than the rest. In Figures 4.4.1A-C, small amounts of ferrite are indicated at the grain boundaries of the austenitic material. This was due to low quality Kikuchi patterns generated at the grain boundaries that were mis-indexed by the software and can be ignored.
Electrolytic etching exposed the cellular solidification structure of each sample and also used to differentiate the PA microstructure from F/MA microstructure. Two distinctly different cell types were observed. Type 1 cells were identified by a strong etching response at the cell boundary while the body of the cell remained mostly unaffected. Type 2 cells were characterized
by a less defined etching response, with cell boundaries being weakly etched and more of the cell body being affected. PA was identified by type 1 cells while both PF and F/MA microstructures formed type 2 cells. Examples of the two cell types can be found in Figure 4.4.2 A-H. While it was observed in EBSD phase maps that LPBF and SQ alloy 1 were fully austenitic, both type 1 and 2 cells were observable in the samples after etching. (Figure 4.4.2A-D) In LPBF alloy 1, type 1 cells consistently formed along the bottom edge of the weld pool and type 2 cells formed closer to the interior/top of the weld pool. In the corresponding SQ sample from alloy 1, type 1 cells were observed along the PS interface while type 2 cells formed along the interior (middle) of the sample. In both processing techniques the type 1 cells formed where cooling rates and solidification rates were predicted to be the largest and type 2 cells in the areas where lower cooling rates were expected. Alloys 2 and 3 formed only type 2 cells, regardless of if the sample indexed as austenite or ferrite in EBSD. The cellular structures for these two samples are shown in Figure 4.4.2E-H. In previous work, in-depth cell size analysis for the LPBF and SQ processed alloy 1 and SQ alloys 2 and 3 was performed and found a conservative overlap in cell sizes observed between approximately 0.20-0.40µm in diameter. (Chapter 3) These translate to cooling rate estimates between 9.3*10^6 – 7.7*10^7 K/s and solidification rate estimates between ~390mm/s and 830mm/s. In order to achieve a more detailed comparison of the nanostructural features between samples, TEM and STEM analysis of type 1 and type 2 cells in LPBF and SQ alloy 1, and type 2 cells from FMA in alloy 2 and PF in alloy 3 were performed.
Figure 4.4.2 Type 1 and Type 2 cells observed in: (A, B) LPBF alloy 1, (C, D) SQ alloy 1, (E, F) SQ alloy 2, (G, H) SQ alloy 3.
TEM and STEM-HAADF images

BF and STEM-HAADF imaging of PA in LPBF and SQ samples revealed mostly similar micro and sub-microscale structures and features between the two processing methods. The cellular solidification structures were easily observable in BF and STEM-HAADF images of the PA microstructure (type 1 cells) from LPBF produced alloy 1. The cell boundaries were identified in BF by the dislocation pileup at the cell boundaries, which could also be seen in the STEM-HAADF images, Figure 4.4.3 A-D. This type of dislocation buildup along the cell boundaries is characteristic of LPBF and other PBF processed austenitic stainless steels. In addition to the dislocation pileup, a network of oxide particles could also be observed that formed along the cell boundaries. The oxide network was most easily observed in the STEM-HAADF images but could be observed in BF images by over or under focusing the image. In Figure 4.4.3B, the image was intentionally under-focused to make the oxides more visible through the dislocation pileup. Cell boundaries were not always constrained by grain boundaries and were found across and along grain boundaries. The size of the oxides formed in this material ranged from ~5nm in diameter at the smallest to ~100nm in diameter for the larger oxides. Oxide particles were found primarily along the cell boundaries and sometimes at grain boundaries but not all of the time.

The primary austenite microstructure (type 1 cells) produced by SQ in alloy 1 were similar to the PA from the LPBF material but exhibited smaller oxide particles and lacked the dislocation pileup observed in LPBF. The SQ PA sample formed a similar oxide network along the cell boundaries, like in the LPBF material, that was visible in both BF and STEM-HAADF images. (Figure 4.4.4) Unlike the LPBF sample, no dislocation pileup at the cell boundaries was observed in SQ PA material. Although, under-focusing the BF image was still required to
observe the oxides. The oxide particles that formed in the PA SQ material did not form as large as in the LPBF PA, only ranging from ~5nm to ~30nm in diameter. The oxides in SQ PA were found along cell boundaries and at grain boundaries when they were the same. While SQ PA exhibited cellular solidification and a network of oxides along the cell boundaries similar to LPBF, the oxide particles formed were not as large, and no observable dislocation pileup along the cell boundaries are what features differed between the PA microstructures formed by LPBF and SQ.
Figure 4.4.3 Primary austenite microstructure (type 1 cells) in alloy 1 produced by LPBF. (A-B) TEM-BF images and (C-D) STEM-HAADF images. Image B and D are higher magnification to show detail that is difficult to resolve at lower magnification. Image B was intentionally under-focused to make oxides more visible through dislocation pile-up.
Figure 4.4.4 Primary austenite microstructure (type 1 cells) in alloy 1 produced by SQ. (A-B) TEM-BF images and (C-D) STEM-HAADF images. Image B and D are higher magnification to show detail that is difficult to resolve at lower magnification. Images A and B were intentionally under-focused to make oxides more visible.

BF and STEM-HAADF images of the F/MA microstructures (type 2 cells) from LPBF and SQ alloy 1 were more similar than the PA microstructures, where the only difference was how large of oxide particles formed in the LPBF vs SQ material. The network of oxides was observable in the F/MA samples from both LPBF and SQ material. As described earlier, the oxide network that outlined the cell boundaries was observed in STEM-HAADF images.
normally and BF images more easily by under-focusing the image. (Figure 4.4.5 A-D) Unlike in the LPBF produced PA, dislocation pileup at the cell boundaries was not observed in LPBF produced F/MA samples. The oxides that formed in the LPBF F/MA material were similar in size to what was observed in PA, ~5 to ~100nm in diameter. The same was true for SQ FMA where the oxides ranged from ~5 to ~30nm. The F/MA microstructures in LPBF and SQ processed alloy 1 were more similar than the PA microstructures since no dislocation pileup was observed in either sample, however, the size range of oxides in the LPBF material was still larger than in the SQ material.
TEM foils of F/MA and PF microstructures (both type 2 cell) from SQ samples of alloys 1-3 showed no observable change in the sub-microscale structure and features with respect to change in composition or phase (F/MA or PF). In the BF and STEM-HAADF images of alloy 2 (Figure 4.4.6 A-B) and alloy 3 (Figure 4.4.6 C-D) no dislocation pileup was observed along the cell boundaries similar to in alloy 1. The oxide network that formed along the cell boundaries was the primary method of identifying the cellular structure. Still, the BF images needed to be under-focused to make the oxide network readily visible. The size range of oxides observed in
alloys 2 and 3, like in alloy 1, ranged from ~5 to ~30nm in diameter. No significant change was observed in the sub-microscale structure and features between the F/MA alloy 2 material and PF alloy 2 material.

Figure 4.4.6. Under-focused BF-TEM and STEM-HAADF images of type 2 cells from (A-B) the F/MA microstructure in SQ alloy 2 material and (C-D) the primary ferrite microstructure in SQ alloy 3 material.

**STEM-EDX: LPBF and SQ alloy 1**

STEM-EDX line scans of the PA microstructures produced by SQ and LPBF in alloy 1 revealed that Cr and Mo were the two primary elements that segregated to the cell boundaries.
during primary austenite solidification. (Figure 4.4.7) Line profiles of the integrated and background subtracted signal intensities across solidification cells showed increased signal intensities for primarily Cr and Mo of the major alloying elements, and a decrease in Fe signal at the cell boundaries. This was observed in the STEM-EDX line profiles plotted in Figure 4.4.7 of PA cells from LPBF material (4.4.7A-C) and SQ material (4.4.7D-F). The red lines in Figures 4.4.7A and D represent the area where the line scans were collected. Figures 4.4.7B and E are the integrated and background subtracted signal intensities of Fe, Cr, Ni, Mo, Mn, Si, and O from the line scan across the solidification cell marked in Figures 4.4.7A and D. Here the increase in Cr and Mo signal, as well as the decrease in Fe signal are visible, while the Ni signal shows no significant change in intensity at the cell boundaries. In Figure 4.4.7C and F, the ratio of signal intensities for Cr/Fe, Ni/Fe, and Mo/Fe are plotted for the same line. As mentioned in the methods section, a ratio of signal intensity vs Fe signal intensity was plotted to account for the changes in intensity resulting from changes in foil thickness. In Figures 4.4.7C and F, it is more easily observed that the intensity of Cr, Ni, and Mo remain stable throughout the body of the solidification cell. There was no observable change in signal intensity until the cell boundary was approached where segregation is seen. The segregation of Cr and Mo in PA from both LPBF and SQ samples typically occurred within ~30nm on either side of the boundary. In the ratio of signal plot, the Cr/Fe, Ni/Fe, and Mo/Fe ratios were found to increase across the cell boundaries. This result differed from what was observed in the individual element signal intensities where only Cr and Mo signal increased at the cell boundaries. The increase in Ni/Fe ratio was attributed to the decrease in Fe signal, not an increase in Ni. It was also observed that, in addition to increased Cr and Mo signal intensity at the cell boundaries, in some line scans, the intensity of the Mn and Si signals also increased. However, the increase in Mn and Si was not consistently observed and
was not present in all line scans. There are a few potential explanations for this that are covered in the discussion section.

Figure 4.4.7. STEM-EDX line scans across type 1 solidification cell boundaries in alloy 1 produced by (A-C) LPBF and (D-F) SQ.

The F/MA microstructures produced by LPBF and SQ in alloy 1 were also very similar in segregation behavior where Ni was the only observable element to segregate to the cell
boundaries. Ni was the only element that experienced an increase in signal intensity across cell boundaries in the F/MA microstructures of LPBF and SQ samples. STEM-HAADF images with line scan locations indicated, signal intensity plots, and the ratio of signal intensity vs Fe plots from both line scans are shown in Figure 4.4.8 A-F for the F/MA microstructures. Similar to the PA microstructures, the signal intensity remained stable throughout the cell body and only began to change when the cell boundary was approached. Unlike the PA segregation, the decrease in Fe signal was not as intense, so there was no observed increase in Cr/Fe and Mo/Fe signals when the ratio of signal intensities was plotted. The large variation in X-ray counts seen in Figure 4.4.8E were caused by variations in the sample thickness that occurred during FIB thinning, also known as curtaining. The curtaining is visible in the STEM-HAADF image in Figure 4.4.8 D. The effects of curtaining are eliminated when the signal intensity of each element was plotted in a ratio against the Fe signal intensity, Figure 4.4.8F. Ni segregation in F/MA occurred over a greater distance from the boundary in LPBF than SQ, typically 150-200nm on either side of the cell boundary in LPBF and between 50-100nm in SQ samples. Both of these distances are larger than what was observed for Cr and Mo in PA microstructures.
Figure 4.4.8. STEM-HAADF images and STEM-EDX line profiles from cell boundaries in the F/MA microstructure formed by the primary ferrite solidification mode for (A-C) LPBF alloy 1 material and (D-F) SQ alloy 1 material.

Using results from multiple STEM-EDX line scans, average segregation ratios were calculated to quantify the intensity of Cr, Ni, and Mo segregation in the PA and F/MA microstructures in LPBF and SQ processed alloy 1 samples. The average values and one
standard deviation are listed in Table 4.4.2. In PA produced by LPBF and SQ, the segregation ratio for Cr and Mo were almost the same. The average value for Cr in LPBF was 0.94 ±0.01 and in SQ was 0.92 ±0.02. The segregation ratios for Mo in PA from LPBF and SQ were also close, at 0.84 ±0.01 and 0.82 ±0.03 respectively. The average segregation ratios and standard deviations for each element in PA for alloy 1 produced by LPBF and SQ are listed in Table 4.4.2A. The difference in the estimated average segregation ratios of Cr and Mo between LPBF and SQ were not large enough to be significantly different. The average segregation ratio of Ni in the PA microstructures from LPBF and SQ alloy 1 was 0.97 ±0.02 for both samples. While it is possible that a small amount of Ni segregation could be occurring, more extensive STEM-EDX analysis is required to confirm.

In LPBF and SQ produced F/MA microstructures from alloy 1, Ni was the only observed element to segregate to the cell boundaries. The average segregation ratios of Cr in the F/MA microstructures were near or equal to 1.00, indicating no meaningful segregation of Cr occurred. The segregation ratio of Mo in F/MA was slightly lower than 1.00 at 0.97 ±0.02. Similar to Ni in PA, whether a small amount of Mo segregation occurred or not can not be determined from the current data. Table 4.4.2B lists the average segregation ratios calculated for each element in the F/MA microstructures. Unlike in PA, the average segregation ratios of Mn and Si in F/MA were much closer to 1.00 for both LPBF and SQ sample. Possible causes for the difference of Mn and Si segregation ratios between PA and F/MA microstructures will be addressed in the discussion section.
Table 4.4.2 Average segregation ratio estimates and standard deviations in (A) PA and (B) F/MA microstructures from LPBF and SQ alloy 1. Green bar represents primary segregating element in the respective microstructure.

<table>
<thead>
<tr>
<th>A</th>
<th>Alloy 1 PA Microstructure</th>
<th>Solidification Mode - Primary Austenite</th>
<th>LPBF</th>
<th>Segregation Ratio</th>
<th>SQ</th>
<th>Segregation Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.94 ± Stdev 0.01</td>
<td>0.92 ± Stdev 0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.98 ± Stdev 0.02</td>
<td>0.97 ± Stdev 0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.84 ± Stdev 0.01</td>
<td>0.82 ± Stdev 0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.90 ± Stdev 0.02</td>
<td>0.90 ± Stdev 0.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.92 ± Stdev 0.03</td>
<td>0.91 ± Stdev 0.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>B</th>
<th>Alloy 1 F/MA Microstructure</th>
<th>Solidification Mode - Primary Ferrite</th>
<th>LPBF</th>
<th>Segregation Ratio</th>
<th>SQ</th>
<th>Segregation Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>1.01 ± Stdev 0.02</td>
<td>1.00 ± Stdev 0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.91 ± Stdev 0.03</td>
<td>0.92 ± Stdev 0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.97 ± Stdev 0.01</td>
<td>0.97 ± Stdev 0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.99 ± Stdev 0.01</td>
<td>0.98 ± Stdev 0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.96 ± Stdev 0.02</td>
<td>0.97 ± Stdev 0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

STEM-EDX: SQ alloy 1-3

STEM-EDX data from the F/MA microstructure of SQ alloy 2 and PF microstructure of alloy 3 produced very similar segregation profiles as in F/MA from LPBF and SQ alloy 1. Again, Ni was the only element observed to segregate to the cell boundaries during solidification in the F/MA and PF microstructures. The signal intensity remained stable throughout the body of the cell until approaching the cell boundary. The distance from the cell boundary that Ni segregation occurred was similar to what was observed in SQ alloy 1, between 50-100nm typically. Figure 4.4.9 presents line profiles from two different line scans of the PF microstructure from alloy 3. Figure 4.4.9A-C spans a complete solidification cell while Figure 4.4.9D-F shows a line scan across the cell boundary with significantly higher counts. In both of these line profiles the increase in Ni signal and decrease in Fe signal are visible across the cell boundaries. Line profiles of the ratio of signal intensity vs Fe in Figure 4.4.9C and F and show slight increases to the ratio of Cr/Fe and Mo/Fe as a result of the decrease in Fe, but significant increases in individual Cr or Mo signals were not seen. Figure 4.4.10A-D show representative line profiles using the ratio of signal intensity vs Fe for Cr, Ni and Mo in the F/MA and PF microstructures for each alloy.
Figure 4.4.9. Line scan across two primary ferrite solidified, ferrite cell boundaries in SQ alloy 3. (A, D) STEM-HAADF images of where the line scans were collected from, (B, E) integrated and background subtracted signal intensity line profile, and (C, F) ratio of signal intensity vs Fe line profile.
Figure 4.4.10. Line scan profiles using a ratio of signal intensities vs Fe signal intensity across cell boundaries in: (A) LPBF F/MA alloy 1, (B) SQ F/MA alloy 1, (C) SQ F/MA alloy 2, and (D) SQ PF alloy 3.

The average segregation ratios were calculated for the F/MA and PF microstructures in alloys 1-3 respectively, and when compared were found to be measurably indifferent regardless
of microstructure, composition, or processing technique. The average segregation ratio of Cr was consistently at or near 1.00, while Mo, Mn, and Si ranged from 0.96-0.99 and although the average segregation ratio for these elements across microstructures/techniques were not identical, the differences between them were not significant. The only element with a segregation ratio significantly different from 1.00 in the FMA and PF microstructures was Ni. The average segregation ratio ranged from 0.89-0.92. A direct comparison of the average segregation ratios for each microstructure condition can be found in Table 4.4.3. The segregation ratio of Ni in F/MA from LPBF was not measurably different from the values for Ni in the various SQ samples. Additionally, the average values of segregation ratios were not measurably different between the F/MA and PF microstructures or different alloy compositions.

Table 4.4.3. Average segregation ratio and standard deviation for elements in F/MA microstructures in alloys 1 and 2, and primary ferrite in alloy 3. Green bar highlights primary segregating element in the respective microstructure.

<table>
<thead>
<tr>
<th>Element</th>
<th>Alloy 1 F/MA Microstructure</th>
<th>Alloy 2 F/MA Microstructure</th>
<th>Alloy 3 PF Microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solidification Mode - Primary Ferrite</td>
<td>Solidification Mode - Primary Ferrite</td>
<td>Solidification Mode - Primary Ferrite</td>
</tr>
<tr>
<td></td>
<td>LPBF</td>
<td>SQ</td>
<td>SQ</td>
</tr>
<tr>
<td>Cr</td>
<td>1.01 ± Stdev 0.02</td>
<td>1.00 ± Stdev 0.02</td>
<td>0.99 ± Stdev 0.03</td>
</tr>
<tr>
<td>Ni</td>
<td>0.91 ± Stdev 0.03</td>
<td>0.92 ± Stdev 0.02</td>
<td>0.90 ± Stdev 0.04</td>
</tr>
<tr>
<td>Mo</td>
<td>0.97 ± Stdev 0.01</td>
<td>0.97 ± Stdev 0.02</td>
<td>0.97 ± Stdev 0.02</td>
</tr>
<tr>
<td>Mn</td>
<td>0.99 ± Stdev 0.01</td>
<td>0.98 ± Stdev 0.02</td>
<td>0.97 ± Stdev 0.04</td>
</tr>
<tr>
<td>Si</td>
<td>0.96 ± Stdev 0.02</td>
<td>0.97 ± Stdev 0.02</td>
<td>0.98 ± Stdev 0.03</td>
</tr>
</tbody>
</table>

STEM-EDX: Oxide particles

STEM-EDX line scans across the oxide particles identified the oxides as MnSi oxides in both the LPBF and SQ material. Figure 4.4.11A-B present the composition line profiles from a line scan spanning a single oxide particle in the PA microstructure from LPBF alloy 1 and Figure 4.4.11 C-D for PA from SQ alloy 1. In both cases, the signal intensity decreased for Fe, Cr, Ni,
and Mo while passing over the oxide and the Mn, Si, and O signals increased. In Figure 4.4.12, a higher magnification line scan of one of the larger oxide particles observed in LPBF material showed a similar increase in the Mn, Si, and O signals. Similar signal intensity responses were observed in both large and small oxide particles in each sample.

![Figure 4.4.11 STEM-HAADF images and background subtracted, (AB) integrated signal intensity line profiles from a small oxide particle in LPBF alloy 1 material and (CD) in SQ alloy 1 material.](image-url)
Thermodynamic simulations

Thermodynamic simulation results were used to estimate the segregation ratio for individual elements in the primary solidification phases experienced in each alloy under multiple different solidification conditions. When using Scheil, as the system approaches complete solidification the final compositions become a function of how close to complete solidification the model is ran, meaning the solution can potentially greatly over or underpredict segregation. The simulations used in this work were stopped at 95% complete. The segregation ratios from classic Scheil solidification were the farthest from 1.0 of all simulations, predicting the most segregation for each element. The results from the Scheil with solute trapping module that were
ran at 0.1 m/s were the same as from the classic Scheil simulation results. This is due to the solidification rate not being fast enough to invoke solute trapping. When a 1 m/s solidification rate was used, the model predicted less segregation shown by segregation ratio values closer to 1.0 for all elements. Lastly, at 5 m/s, even less segregation was predicted than in the 1 m/s simulation with stabilizing elements (Cr and Mo in primary austenite solidification and Ni in primary ferrite solidification) approaching segregation ratios of 1.00. However, the segregation ratios predicted for the other elements were still farther from 1.00 than what was observed experimentally. (Table 4.4.4). The segregation ratios from simulations and experimental data for both primary solidification modes observed in alloys 1-3 are presented in Table 4.4.4A-D. In the PF solidification simulations, Table 4.4.4B-D, the segregation ratio values for Cr and Mo were found to be closer to what was observed experimentally than the values for Cr and Mo were in PA simulations. In general, the segregation ratios from simulations more closely matched the experimental estimates for elements that stabilized the primary solidification phase being simulated. (I.e., Ni in PA and Cr and Mo in PF) Additionally, although the values for Mn and Si showed greater deviation from the experimental values, this trend was still observed as the segregation ratio of Mn in PA simulations was closer to 1.00 than Si, and vice versa during PF simulations. The larger overall disagreement in Mn and Si was likely caused by the restriction of allowed phases to only liquid and the primary phase.
Table 4.4.4 Individual element segregation ratios calculated from Thermo-Calc solidification simulations using the Scheil module and Scheil with solute trapping module at 1m/s and 5m/s solidification rates compared with experimentally measured segregation ratios for the (A) PA solidification mode and (B-D) PF solidification mode for each alloy composition, alloy 1-3 respectively. Simulations were ran to 95% solidified.

<table>
<thead>
<tr>
<th>A</th>
<th>Alloy 1 - PA Microstructure</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Solidification Mode - Primary Austenite</td>
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<tr>
<td></td>
<td>Thermo-Calc Simulation</td>
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<tr>
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<td>PA</td>
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<tr>
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<td>Scheil</td>
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<tr>
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<tr>
<td>Ni</td>
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<td>Mo</td>
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<tr>
<td>Mn</td>
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<td>Si</td>
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<table>
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<tr>
<td></td>
<td>Solidification Mode - Primary Ferrite</td>
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<tr>
<td></td>
<td>Thermo-Calc Simulation</td>
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<tr>
<td></td>
<td>PF</td>
</tr>
<tr>
<td></td>
<td>Scheil</td>
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<tr>
<td>Mn</td>
<td>0.42</td>
</tr>
<tr>
<td>Si</td>
<td>0.57</td>
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4.5 Discussion

Comparison of LPBF and SQ samples
Splat quenching process produced samples with very similar RS microstructures and sub-microscale features to LPBF processed samples of the same composition despite having different thermal histories during processing. It should be noted that the LPBF and SQ comparison presented here was for only a single composition (alloy 1). Although the processing techniques varied, the two samples produced microstructures that indexed as fully austenitic during EBSD analysis that were actually mixed microstructures consisting of both primary austenite and massively transformed austenite (F/MA). This was confirmed by the etched response, solidification structures, and elemental segregation observed in each. (Figures 4.4.1 and 2) The LPBF and SQ samples were morphologically different when observed after etching due to the different processing conditions. In LPBF, a laser is rastered across a thin layers of metal powder causing the loose powder to melt and resolidify as one piece. An overlapping raster pattern is typically used to melt and resolidify more loose powder with a portion of the previous melt pool. This results in at least part of the previously melted and solidified material to undergo the melt and solidification process multiple times. Additionally, while there are parts of the original melt pool that may only solidify once, there is a large amount of energy and heat being introduced to the solidified material from adjacent melt pools, and future layers. Thus, the bulk of the material will experience multiple heating and cooling cycles before cooling to room temperature once the build is complete. \[^{10, 17}\] Alternatively, in SQ samples are melted and solidified only once and only experience a single heating and cooling cycle before cooling to room temperature rapidly after solidification. \[^{73, 118}\] The two techniques also differ with respect to geometric constraints. In LPBF, heat is extracted primarily through contact with the previous melt pool/layer where as in SQ, the liquid is in forced contact against the surface of the Cu platens during the splat event. Regardless of the differences in morphological appearances, earlier work demonstrated that the
two techniques produced solidification cells over a range of sizes that primarily overlapped between 0.20 and 0.40µm in diameter with similar solidification rate estimates between 0.4 and 0.8m/s.

The sub-microscale structures and features of the PA and FMA microstructures in both LPBF and SQ differed only slightly. During TEM analysis of the LPBF and SQ alloy 1 samples, regardless of whether the TEM foil contained the PA or F/MA microstructures, MnSi oxides of various sizes always formed along the cell boundaries. (Figures 4.4.3-5) The MnSi oxides ranged in size from 5-30nm in both the PA and F/MA microstructures for SQ material. However, in the LPBF material, the oxides formed over a larger size range from ~5 to ~100nm in diameter. (Figures 4.4.11-12) This size range is similar to the size ranges that have been previously reported for MnSi oxides in LPBF processed 316L. \[9, 12, 14, 19, 95\] These oxides have been previously identified as MnSiO\(_3\), Rhodonite.\[9, 12-14, 107\] One possible explanation for the formation of larger oxide particles in the LPBF material compared to the SQ material has to do with the differences in thermal histories associated with each process. The material in LPBF undergoes multiple heating and cooling cycles before the finished part is complete while SQ is a single rapid solidification and cooling event.\[5\] The longer period exposed to elevated temperatures would result in a higher mobility and promote a coarsening of the oxide particles. Work by F. Yan et. al. showed that when LPBF processed 316L was heat treated at 1200°C for 30 minutes the rhodonite particles increased in size.\[107\] The other difference was related to dislocation pile-up along cell boundaries in the PA microstructure. This feature has been reported previously in rapidly solidified austenitic 316L material processed via LPBF as a distinctive microstructure feature and would not necessarily be expected in the SQ material.\[3, 7, 9, 13, 95\] Dislocation pileup at the cell boundaries in LPBF is thought to be caused by either oxide
particles acting as Zener pinning sites for dislocations or segregation of heavy elements (Ex. Cr and Mo) to cell boundaries having a pinning effect on dislocations. [9, 95, 107, 150] During an LPBF build the material experiences repeated heating and cooling, and melting and resolidifying of the part causing non-uniform thermal expansion and contraction which would lead to lattice strain. [5, 19] Dislocations would be formed by the material in an attempt to accommodate and relax the lattice strain that built up during processing. Since SQ is a single thermal cycle technique there is less driving force for dislocations to be generated and could explain why dislocation pileup at the cell boundaries was not observed in the SQ material. [9, 10, 12, 108, 151] However, this does not explain the lack of dislocation network in the F/MA microstructures from LPBF material. The lack of dislocations in the LPBF F/MA microstructure could be a result of ferrite crystal structure being able to accommodate fewer dislocations compared to the austenite structure, or that the dislocations are destroyed/relaxed during the solid-state transformation from ferrite to austenite due to the increase in lattice volume that occurs.

The elemental segregation observed in the PA microstructures showed Cr and Mo as the primary elements that segregated to the cell boundaries. (Figure 4.4.7) The segregation ratios that were calculated from this data represent the magnitude of segregation in Cr and Mo across cell boundaries and were not measurably different between LPBF and SQ samples. (Table 4.4.2) Similarly, in the F/MA microstructure, Ni was the only observed segregating element and the segregation ratios of Ni were not measurably different for the LPBF sample vs the SQ sample. (Figure 4.4.8, Table 4.4.2) In PA, the segregation ratio of Ni was estimated to be 0.97 ±0.02, not 1.00 even though Ni is an austenite stabilizer. In welding literature about segregation in austenitic 316L SS, Ni is regularly reported to segregate away from the dendrite/cell boundaries and be enriched at the dendrite/cell centers (K>1.0). [31, 65] Based on the standard deviation and
error from EDX collection a deviation of this size is not significantly large enough to be differentiated as significant segregation and while minor Ni segregation in rapidly solidified PA has been reported in previous studies of RS of 316L SS, it generally is not mentioned.\cite{7, 13, 17}

Similarly, while segregation ratios of Mo in the F/MA and PF microstructures were 0.97 ±0.02 on average, Mo is a ferrite stabilizer and this small difference from 1.0 is not enough to be considered significant Mo segregation.

The segregation distance of Ni from the cell boundaries in F/MA microstructures of LPBF and F/MA and PF microstructures in SQ material were observably larger than the distance over which Cr and Mo segregated in PA microstructures. Also, the distance over which Ni segregated from the cell boundary in the LPBF material was larger than in the SQ material. It has been previously suggested that in ferrite solidified RS microstructures Ni can experience solid-state diffusion, reducing the amount of segregation at the cell boundaries.\cite{7, 53, 65} Solid-state diffusion would not be expected in a PA solidified microstructure because the diffusivity of elements in austenite is significantly smaller than in ferrite.\cite{65, 130, 152, 153} If the time where the conditions for solid-state diffusion in a SQ sample were smaller than in LPBF sample this could explain why the Ni segregation distance found in LPBF material was larger than in SQ material. However, it would not explain why a difference in magnitude of segregation ratios was not observed. In a direct comparison of the micro and sub-microscale structures and features same alloy processed using LPBF and SQ, the samples were similar with the three main differences being that: oxide particles in SQ microstructures did not form as large as in LPBF, dislocation pileup along the cell boundaries was observed in only the LPBF PA microstructure, and Ni segregation in the LPBF F/MA microstructure occurred over a greater distance from the cell boundaries than in SQ F/MA microstructures.
Comparison of SQ primary ferrite solidified microstructures with different Cr/Ni$_{eq}$

The sub-microscale structures and features, and segregation in the two primary ferrite solidified microstructures (F/MA and PF) from SQ alloys 1, 2, and 3 were unaffected by changes in the Cr/Ni$_{eq}$ values. The three alloy compositions had Cr/Ni$_{eq}$ value of 1.53, 1.71, and 1.95 and all experienced some amount of primary ferrite solidification that resulted in either F/MA or PF as the final phase. (Figures 4.4.1 and 2) MnSi oxide particles formed a network that outlined the cellular solidification structures were observed in all both the F/MA and PF microstructures. The size of oxides that formed in each SQ sample was consistently between 5 and 30nm in diameter. (Figures 4.4.4-6, 11, and 12). Additionally, although the three alloys had different concentrations of Ni, the magnitude of Ni segregation from primary ferrite solidification represented by the segregation ratio was found to not significantly differ. (Figure 4.4.9 and 10) From these results, it can be concluded that the amount of Ni segregation was not significantly affected by the targeted variations in Cr/Ni$_{eq}$ between the three different alloys, or the two microstructures formed by primary ferrite solidification.

The increases in the Mn and Si X-ray signals at cell boundaries in some line scans of PA from LPBF and SQ are likely not elemental segregation for a number of reasons. To begin with, the increase in Mn and Si signal at the cell boundaries was not present at all of the cell boundaries. Additionally, the increase in Mn signal could be caused by the increase in Cr signal at the cell boundary due to the overlap of the Cr kα and Mn kβ energy lines. This is supported by the lack of Mn and Si signal increase at the cell boundaries and segregation ratios in F/MA and PF microstructures. Another possible cause for the increase in Mn and Si signal is the presence of the MnSi oxides found along the cell boundaries and differentiating a signal increase from this vs segregation is difficult. Finally, it should be kept in mind that Mn is an austenite promoter and
Si is a ferrite promoter, so the segregation of both elements in single phase would not be likely. It is for these reasons that the increases in Mn and Si signals observed across some cell boundaries in PA microstructures should not be considered to be from cellular segregation without further investigation.

Thermo-Calc solidification simulations

Some potential causes for the differences between segregation ratio estimates from rapid solidification simulations and experimental results are due to the fraction solid value used in Scheil simulations or possible homogenization from solid-state diffusion. The amount of segregation predicted by both classic and solute trapping Scheil solidification simulations was overestimated for most elements when compared to the experimental results. It is possible that for rapid solidification in LPBF and SQ, Scheil solidification will more accurately simulate the processes when solved to a lower amount of solidification rather than 95%. Also, these simulations were ran with only the liquid and primary solidification mode (austenite or ferrite) being allowed to form in order to simulate single phase solidification. So, if what would normally be eutectic or peritectic conditions are being reached, the accuracy of the model could be affected. Although the solidification rate estimates used for LPBF and SQ are below where complete solute trapping is expected the observed increasing of segregation ratio values towards 1.00 for Ni in PA and Cr and Mo in PF are promising. Previous work in FBAM and laser welding discusses the possibility of cellular Ni segregation to be fully homogenized in PF as Ni does have a higher diffusion coefficient in ferrite compared to austenite. Similarly, the diffusion coefficients of Cr and Mo are also larger in ferrite vs austenite. Given the larger diffusion coefficients in ferrite, it could be suggested that after solidification there was sufficient solid-state diffusion to homogenize Cr and Mo across the cell boundaries, but the greater amount
of Ni segregation could not be completely homogenized, and the amount observed experimentally is what remained. However, further investigation and modeling of potential solid-state diffusion in the primary solidification phases in order to verify if this is the case.

4.6 Conclusions

In conclusion, this paper presents a detailed comparison between two rapid solidification (RS) processing techniques for austenitic stainless steel, two-piston splat quenching (SQ) and laser powder bed fusion (LPBF), to characterize and discuss the similarities and differences of various micro and sub-microscale features. Three alloys were used that had Cr/Ni$_{eq}$ ratios between 1.53 and 1.95 and spanned most of the composition space of the AISI A240 spec for 316L stainless steel. The results found that LPBF and SQ processing techniques produced very similar material in terms of elemental segregation, solidification morphology, oxide particles, microstructure, and sub-microscale structures and features. Extensive electron microscopy and EDX analysis, as well as computational thermodynamic modeling were used to estimate individual element segregation ratios in primary austenite and primary ferrite solidification. In this research we have noted the following:

1. Splat quench (SQ) processing of stainless steel material produced similar microscale and sub-microscale rapidly solidified features as those observed in the same material processed using laser powder bed fusion (LPBF). The size range of solidification cells that formed in both materials overlapped between 0.20 and 0.40µm in diameter suggesting solidification rates between 0.4 and 0.8m/s. Elemental segregation to the cell boundaries of Cr and Mo in PA and Ni in F/MA microstructures were mostly consistent between LPBF and SQ. Segregation ratio estimates from the segregation of Cr and Mo in PA were not measurably different between LPBF and SQ material, and the same was
found for Ni in the FMA microstructures. However, the distance that Ni segregated from the cell boundaries was observably larger in LPBF than in SQ, possibly due to differences in thermal history allowing for greater solid-state diffusion in the LPBF sample. MnSi oxides formed along the cell boundaries in both microstructures ranging from 5-30 nm in SQ material and 5-100nm in LPBF material. Also, dislocation pile-up along the cell boundaries was observed only in the LPBF PA microstructure.

2. Increasing the Cr/Ni$_{eq}$ ratio over a range of 1.53 and 1.95 in SQ processed stainless steels did not notably change the sub-microscale features observed in the RS nanostructure. There was no significant change in the range of cell sizes in SQ microstructure of alloys with increased Cr/Ni$_{eq}$ values. The size range of MnSi-rich oxides that formed in the SQ samples were not affected by the changes in Cr/Ni$_{eq}$ or microstructure. The segregation of Cr and Mo, or Ni that occurred in each sample was controlled by the primary solidification phase (primary austenite or primary ferrite). The average segregation ratio of Ni in primary ferrite solidified SQ microstructures was found to not be measurably impacted by changes in the alloys Cr/Ni$_{eq}$ ratio over a range of 1.53 to 1.95. Also, Ni segregation in F/MA microstructures was not measurably different from Ni segregation in PF microstructures.

3. Similar to as observed in the experimental results, segregation ratio estimates from rapid solidification simulations were not significantly impacted by changes in the alloys composition or Cr/Ni$_{eq}$ ratio over a range of 1.53 to 1.95. Classic Scheil solidification predictions overestimated the amount of segregation that was observed in LPBF and SQ samples. The modified Scheil with solute trapping module produced segregation ratio values closer to experimental estimates, but even at higher solidification rates, were still
farther from 1.00 than measured experimentally. This difference could be explained by solid-state diffusion reducing the amount of segregation at the cell boundaries, but further investigation should be performed to confirm.

4.7 Acknowledgement

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CHAPTER 5: INFLUENCE OF MOLYBDENUM ON RAPID SOLIDIFICATION

MICROSTRUCTURE AND MICROSEGREGATION IN PRIMARY FERRITE SOLIDIFIED STAINLESS STEEL

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5.1 Abstract

The development of austenitic stainless steels using targeted alloy additions for a variety of applications has made them common place across a wide range of industries and as a result of these alloys being so familiar, they are often the first materials used when adapting new processing techniques. For applications in which a high degree of corrosion resistance is required austenitic stainless steels with varying levels of molybdenum will be utilized. The rapid cooling and solidification rates that occur during fusion based additive manufacturing processes like powder bed fusion cause a fundamental shift in the solidification behavior of the material typically resulting in single phase solidification. While the effect that the two most common stainless steel alloying elements, Cr and Ni, have on the microstructure has been fairly well documented across a range of solidification conditions, the impact of alloying elements like molybdenum are not as well understood at rapid solidification rates. For this study, four custom stainless steel alloy feedstocks were designed and made with targeted modification of the Cr and Mo concentrations to maintain a constant Cr/Ni_{eq} ratio of ~1.7. Two-piston splat quenching was used to produce rapidly solidified material from each feedstock where the solidification mode,
phase, and cell size where investigated. Solidification rates were estimated to be between 0.4 and 1.5 m/s. A comparison of the microsegregation and partitioning behavior of Cr, Ni and Mo in ferrite solidified material was also performed for the different alloy compositions. Variations of the Mo concentration between feedstocks showed no measurable influence on the solidification/cooling rates, solidification morphology, or the partitioning of Mo in rapidly solidified material. However, higher concentrations of Mo were found to significantly increase the amount of ferrite phase in the microstructure by suppressing the ferrite to austenite massive transformation.

5.2 Introduction

Austenitic stainless steels (SS) are widely implemented across many industries for applications where welding is used to join parts due to the alloys ease of weldability, high strength, thermal properties, and good corrosion resistance compared to low alloy and ferritic steels. In situations where even greater corrosion resistance is required, the addition of molybdenum to the alloy in the solid solution can be made to improve pitting resistance and enlarge the passive region of the alloy.\cite{29,32} It has also been reported that the added Mo forms a Mo-rich oxide stable film which also acts to improve corrosion resistance.\cite{30} Austenitic SS and super austenitic SS are commonly used to create parts that will require welding to produce parts that are strong with excellent corrosion resistance. However, due to the melting and solidification that occurs as part of the fusion process, the material is prone to microsegregation during resolidification which can dramatically impact the material performance, decreasing both strength and corrosion resistance.\cite{99} In austenitic SS alloys, Cr and Mo are the primary major alloying additions which are prone to microsegregation, forming zones that are either rich or
depleted of Cr and/or Mo within the resolidified area. [19, 99] These depleted zones are at a higher risk of localized corrosion due to lower amounts of Cr and Mo.

When processes like laser powder bed fusion (LPBF) and directed energy deposition (DED) were introduced for metal fusion based additive manufacturing, the material properties of austenitic SS made them a prime candidate. Similar to welding, processes like LPBF and DED are fusion based but rely on significantly higher cooling and solidification rates compared to what is typically found in traditional welding processes. [6, 7, 20-22, 99, 150, 154] Cooling rates for PBF processes are estimated to reach between $10^6$ and $10^7$ K/s. [69] These rapid solidification (RS) conditions can result in the formation of different microstructures, features, and segregation behavior depending on the composition of the alloy. The relationship between solidification rate and microsegregation dictates that as the solidification rate increases the amount of segregation that will occur decreases, and at high enough solidification rates (estimated around 10m/s) solute trapping can occur in which there is no segregation. [82] However, PBF processes are generally found to have solidification rates between 0.01-1m/s, not reaching the solute trapping solidification rates and are susceptible to less but still some degree of microsegregation. [13, 69, 95, 108, 140]

Elemental partition coefficient can be used to identify which elements are expected to segregate during solidification and how intense the segregation will be. Common alloying elements used in SS such as Cr, Ni, and Mo have been found to have different partition coefficients depending on the solidification phase. Based on the equilibrium partition coefficients shown in Table 5.2.1, in austenite, Cr and Mo segregate into the liquid while in ferrite Ni segregates into the liquid. However, for RS conditions the equilibrium partition coefficients do not remain an accurate method for predicting the amount of segregation that will occur.
RS has also been shown to impact the solidification phase stability and microstructure differently compared to slower solidification rates. For austenitic SS, as the solidification rates increase and RS conditions are reached, single phase solidification becomes the stable form of solidification. \cite{34,41,44} At RS rates SS material will solidify and form either primary austenite, primary ferrite, or ferrite that massively transforms to austenite (F/MA) during cooling. While a large amount of work has previously been done to study the change in solidification microstructure with respect to Cr and Ni at various concentrations and RS rates, limited work has been done relating to how different Mo concentrations impact solidification behavior at RS rates. Previous research by T. D. Anderson et. al. looked at the effect of Mo concentrations between 0 and 10 wt% for Fe-Cr-Ni-Mo filler metals at cooling rates around 30K/s using gas tungsten arc welding (GTAW) on phase formation and elemental segregation. \cite{99} They reported that at these cooling rates, Mo showed an equivalent ferrite stabilizing strength as Cr for 0-10 wt% Mo and identified a shift in solidification mode from ferrite with dendritic austenite to fully ferritic at \(\text{Cr}_{\text{eq}}/\text{Ni} \) around 1.7. An additional part of this study used high energy density (HED) laser welds on a smaller subset of samples to investigate the effect of elevated cooling rates, reaching estimated rates up to \(10^5\) K/s. For this part of the study, it was concluded that alloys near the eutectic were prone to forming F/MA microstructures with no observable Mo segregation. However, the impact of increased Mo concentrations on the final microstructure at these higher cooling rates was not concluded.
Table 5.2.1 Equilibrium partition coefficients for Cr, Ni, and Mo in austenite and ferrite. Cr and Ni partition coefficients in austenite and ferrite are from equilibrium phase diagrams for Fe-Cr-Ni ternary alloys \cite{40}. The Mo value for austenite is from an Fe-Ni-Mo ternary and the ferrite value is from ThermoCalc. \cite{98, 99}

<table>
<thead>
<tr>
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<th>Austenite (FCC)</th>
<th>Ferrite (BCC)</th>
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<tbody>
<tr>
<td>Cr  \cite{40}</td>
<td>0.80</td>
<td>1.10</td>
</tr>
<tr>
<td>Ni  \cite{5, 40}</td>
<td>1.05</td>
<td>0.74</td>
</tr>
<tr>
<td>Mo  \cite{98, 99}</td>
<td>0.65</td>
<td>~1.00</td>
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The combination of the ability of PBF processes to achieve very high cooling and RS rates, the different solidification paths and microstructures formed at RS rates compared to slower solidification, and the difference of Cr, Ni, and Mo segregation behaviors in austenite vs ferrite leads to the following questions. In rapidly solidified austenitic SS alloys: does the potency of Mo as a ferrite stabilizer remain equal to Cr at elevated solidification rates, does variation in the Mo concentration impact the microstructure or the F/MA to ferrite boundary, and will the segregation behavior of Mo during ferrite solidification be impacted by increased concentrations of Mo in the alloy composition? In this paper these questions were investigated using two-piston splat quenching (SQ) to create rapidly solidified samples of four custom alloy feedstocks with Cr/Ni\textsubscript{eq} of \~1.7 and Mo concentrations between 2 and 8 wt\%. This analysis is unlike in previous work because of the utilization of SQ to generate large RS rates similar to those observed at the upper end of PBF techniques to investigate the impact of different Mo concentrations on the boundary between FMA and ferrite at these rates. Analysis was performed using optical microscopy and various electron microscopy techniques in both the SEM and TEM to observe and measure the microstructure and phase content, estimate cooling rates and solidification rates, and investigate the cellular microsegregation of each alloy.
5.3 Methods

Alloy production, splat quenching, and sample preparation

The four SS alloys used in this study were designed to target a Cr/Ni\textsubscript{eq} ratio of 1.7 by varying Cr and Mo content while maintaining similar Fe and Ni concentrations between individual alloy feedstocks. High purity elements of 99.9\% or greater were used when making the feedstock. Ni, Mo, Mn, and Si powders were individually measured and mechanically mixed together before being pressed into a pellet. Fe and Cr, in the form of pellets and plate respectively, were used for the remainder of the alloy chemistry. All of the ingredients were arc melted under a constant flow of ultra-high purity (UHP) Ar to form the alloy feedstock. Cuboidal shaped samples were sectioned from the alloy feedstock for SQ experiments. Additional material was removed and used for ICP-OES, IGF, and combustion chemical analysis techniques to be performed. Cr\textsubscript{eq}, Ni\textsubscript{eq}, and Cr/Ni\textsubscript{eq} values were all calculated based on the WRC-1992 equations. Full detail of the alloy development and arc melting process are described in Section 2.1 of this dissertation as well as, Section 3.3. and 4.3.

Alloy feedstock was sectioned into cuboidal samples for SQ experiments where three replicate samples were performed for each alloy composition. Each SQ sample was approximately 2.3mm x 2.3mm x 2.3mm in size and targeted a mass of 105mg. Samples were levitated, melted, and heated to a target superheat temperature of 1600 °C in an inert UHP Ar environment at 600mPa. After SQ event the thin foil samples were removed from the apparatus and cross sectioned. More information about the SQ experiments can be found in Section 2.3 as well as a schematic of SQ apparatus.

Multiple preparation methods were used for sample analysis. Most SQ samples were prepared for characterization by cross sectioning the thin foil, mounting it in a semi-conductive
polymer, and mechanically grinding and polishing the surface. Samples were polished down to a 0.02µm finish using a vibratory polisher with a colloidal silica solution for the final step. The highly polished samples were used for optical, SEM-EDS, and SEM-EBSD analysis. Electrolytic etching was performed to reveal the solidification structure using a 60-40 nitric acid to DI water solution and a DC power supply at 1.3V with a tungsten electrode for 5-20 seconds. TEM samples were made using two different techniques. The first method was a FIB-lift out across a region of solidification cells that were oriented in the direction of solidification. The foil was attached to a Cu grid and thinned using a gallium source to <150nm thick. Alloy D1 was the only sample prepared using this technique. Alternatively, the remaining samples were prepared for TEM analysis using the Tenupol-5 twin jet electropolish. For this process, 3mm disks were punched out of the center of unmounted SQ foils. The samples were thinned using a solution a 10% perchloric acid and 90% acetic acid mixture using 50V at room temperature. This was the primary method of sample preparation for TEM in this study.

Electron microscopy and characterization

A combination of optical microscopy and SEM were used to analyze the SQ samples. Images were collected with the optical microscope of mounted, vibratory polished samples where the brightness and contrast were adjusted to allow for distinction between the solidified ferrite and austenite phases. Images were taken using a Leica optical microscope at high magnification spanning the cross section for each SQ replicate and using ImageJ were processed to measure the area % ferrite with respect to position.

EDX and EBSD were performed on a JEOL 7000 SEM, using an Oxford X-Max 80mm² detector and EBSD detector respectively. SEM imaging was performed on a Thermo-Fisher Apreo SEM. To measure the solidification cell size, sets of SEM images of etched
microstructures were collected from multiple sites that spanned the entire thickness of the SQ samples (from one PS interface through the other). Each site was divided into 6 sections and individual solidification cell diameters were measured in each section. An average of 50 measurements were collected from each zone and used to calculate a mean cell size for that zone. This method was similar to the process used to measure cell size described in Chapter 2.6 but utilizes two sites, one at the radial center and one towards the outer radius, instead of six sites.

Quantitative SEM-EDX was performed using NIST standards and the software DTSA-II to determine the concentration of major alloying elements in alloy D3. Elements included in the quantification were Fe, Cr, Ni, Mo, Mn, and Si. NIST pure element standards and NIST 316L standard reference material were used for as spectra references in the DTSA-II quantification. The quantification results from 10 different spectra were averaged for each element. Complete details of how the spectra were collected and processed for quantitative EDS are described in Section 2.5.

As mentioned earlier a combination of FIB-lifouts and jet polished samples were used in the TEM analysis of these material. A TECNAI F-20 200kV TEM was used for imaging and STEM-EDX. BF images were collected intentionally under-focused to highlight nano-oxides. STEM-HAADF images were taken at 100mm camera length. STEM-EDX line scans were collected on an Optima T-60 Amtek detector and the TEAM software.

Simulation and segregation ratio calculations

Isopleths were generated using CALPHAD ThermoCalc software with the TCFE8 Steels/Fe-alloys database. Isopleths were generated at 2, 4, and 8 wt% Mo, where the stable composition was 66Fe-1.1Mn-0.4Si and Cr and subsequently Ni were varied. An isopleth was also generated for alloy feedstock D4 using the same method but used 60% Fe instead of 66%.
The calculations were performed with the possible phases restricted to liquid, austenite, and ferrite. The minor alloying elements like C and N were not included in the calculations due to the very low concentrations.

The relationship between cooling rate and cell spacing has been well defined in the previous sections and in previous literature so it will only be covered briefly in this section. For this work, the cell size vs cooling rate relationship proposed by Katayama and Matsunawa was used in which the material constants were A=80 and n=0.38. The 2-D heat transfer simulations performed in ANSYS Fluent described in Chapter 3.3 were used to estimate the temperature gradient associated with predicted cooling rates. Combining the cell size and cooling rate relationship with the heat transfer simulations estimates for the solidification rate were produced.

Segregation ratios (SR) for Cr, Ni, and Mo were calculated using the STEM-EDX line scan data to assess microsegregation between solidification cells. The SR was measured from line scan data by taking a ratio of the integrated X-ray signal intensity for each element at the center of the solidification cell and the integrated X-ray signal intensity for that element at the boundary of the cell. Each line scan was plotted using a ratio of the integrated X-ray signal intensity for the individual element vs the integrated X-ray signal intensity for Fe to reduce any artifacts from channeling or sample thickness. Careful attention was used when processing line scans that had channeling or thickness artifacts. For these data sets, the element vs Fe signal plots were used to identify where segregation began and the position was noted. The average signal intensity for each element was calculated using this position to represent the signal intensity from the cell center. This could be done because like in Chapter 4 the ratio of element signal intensity vs Fe across the cell body remained stable up to the point where segregation began so the signal intensity just prior to that point should be the same as at the center. While typically the ratio of
signal intensity vs Fe is used for these calculations, decreases in the intensity of the Fe signal at the cell boundary could artificially increase the magnitude of segregation or lead to false segregation, so the elemental signal intensity was used.

5.4 Results

Composition and microstructure phase analysis

The composition of the four custom alloy feedstocks produced for this study were all near the target compositions and equivalence values. The WRC-1992 Cr/Ni_eq values of all four feedstocks were 1.72±0.02. Full chemistries and equivalence values are shown in Table 5.4.1. From D1 to D2, Cr is substituted nearly 1:1 for Mo while Fe and Ni concentrations remain similar between alloys. Some variation can be observed between the Mn and Si values; however, these are not factors in the WRC-1992 equations. The difference in C concentrations between the two alloys is minimal as well, but the difference in N is not as small. This resulted in a larger Ni_eq for D1 than D2. D3 had twice the Mo content as D2 and four times that of D1 while maintaining Fe and Ni values similar to D1 and D2. Again, there were slight difference in Mn and Si concentrations compared to D1 and D2, but they did not impact the equivalence values. Unlike D1-D3, alloy D4 was similar to D2 in Mo content and had a Cr/Ni_eq of 1.72 but had significantly more Cr and Ni at the expense of Fe compared to the other alloys. As a result, D4 had a Cr_eq of 23.4 and Ni_eq of 13.6 compared to the 19.3-20.8 Cr_eq and 11.0-12.3 Ni_eq in alloys D1-D3. Also, although the composition of D3 was measured using quantitative EDS with standards, which has been previously shown to be able to achieve accurate compositions for heavier elements, N and C concentrations still could not be accurately determined due to resolution limits of the EDS technique. An average value for N and C were taken from the three
other alloys and used in equivalence calculations for D3. As a result, the \( Cr_{eq} \), \( Ni_{eq} \), and \( Cr/Ni_{eq} \) values for D3 are approximations.

Table 5.4.1 Alloy compositions measured using ICP-OES, IGF, combustion, and quantitative SEM-EDS with Standards and DTSA-II.

<table>
<thead>
<tr>
<th>Alloy name</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>N</th>
<th>C</th>
<th>( Cr_{eq} )</th>
<th>( Ni_{eq} )</th>
<th>( Cr/Ni_{eq} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>68.0</td>
<td>17.20</td>
<td>11.10</td>
<td>2.22</td>
<td>1.10</td>
<td>0.38</td>
<td>0.010</td>
<td>0.001</td>
<td>19.42</td>
<td>11.34</td>
<td>1.71</td>
</tr>
<tr>
<td>D2</td>
<td>68.0</td>
<td>15.10</td>
<td>10.80</td>
<td>4.22</td>
<td>1.61</td>
<td>0.28</td>
<td>0.002</td>
<td>0.004</td>
<td>19.32</td>
<td>10.98</td>
<td>1.76</td>
</tr>
<tr>
<td>D3*</td>
<td>64.9</td>
<td>13.0</td>
<td>12.0</td>
<td>7.9</td>
<td>1.5</td>
<td>0.4</td>
<td>0.004**</td>
<td>0.005**</td>
<td>20.82</td>
<td>12.24</td>
<td>1.70</td>
</tr>
<tr>
<td>D4</td>
<td>61.4</td>
<td>19.50</td>
<td>13.20</td>
<td>3.87</td>
<td>1.70</td>
<td>0.29</td>
<td>0.003</td>
<td>0.010</td>
<td>23.37</td>
<td>13.61</td>
<td>1.72</td>
</tr>
</tbody>
</table>

* Alloy composition measured via quantitative EDS with standards, not IGF, ICP, and combustion.

** N and C concentrations were not measured but were assigned an average value based on other custom alloy feedstocks generated.

Four isopleths generated based on the target compositions show the effect of increasing Mo concentrations on equilibrium predicted phase stability during solidification. The 2 and 4 wt% Mo isopleths were fairly similar, the primary differences were: the phase boundaries shifted ~2wt% towards lower Cr values, the freezing zone for FCC got larger, and the liquidus temperature of the austenite phase decreased slightly. (Figure 5.4.1A-B) A larger difference was observed between the isopleths for 4 and 8 wt% Mo. In Figure 5.4.1B-C, a translation of the stable phase boundaries towards lower Cr concentrations was again observed. However, near the melting temperature the magnitude of translation was larger than just the 4% increase in Mo. The liquidus temperature for the austenite phase decreased and the freezing zone of the liquid + FCC region increased in size, similar to going from 2 to 4 wt%. Additionally, in the 8 wt% Mo isopleth, the slope of the liquidus for the FCC phase is positive, up to the liquid + two phase region, where previously it was primarily negative after the liquid + two phase region. The isopleth based on feedstock D4 was calculated as well and showed that when the Fe content was lowered and Cr and Ni concentrations increased, the two phase region increased in size and the
liquidus temperature decreased. For these alloy compositions, the isopleths predict D1 and D2 will form a mixture of FCC and BCC down to 1300 °C below which they form only austenite. The equilibrium isopleth predictions for alloy D3 and D4 where slightly different from D1 and D2, predicting higher initial solidus temperatures where the BCC + liquid region was stable before the liquid + FCC + BCC. Also, the FCC + BCC region was stable down to approximately 1150 °C before only FCC became the stable phase. It should be remembered that equilibrium isopleths should be treated as approximations when discussing solidification paths and reality will further deviate for non-equilibrium RS conditions. However, these isopleths can still provide the user with an first order understanding for how the changes in alloy composition impact the phase stability of each alloy. The isopleths could be modified to better account for the RS conditions using equations like equation 1.2.6 and 1.2.7 which could result in more accurate predictions.
Using a combination of EBSD and optical microscopy analysis the SQ microstructures revealed a significant difference between the phase content and ferrite concentrations of each alloy. In the EBSD phase maps shown in Figure 5.4.2A-D where austenite is blue and ferrite is
shown as red, the phases present in alloys D1-D4 respectively were identified. The phase maps shown are representations of the observed microstructure and were used to identify the phase(s) present for ferrite area % analysis completed using the optical images. Characteristic optical micrographs from SQ samples of D1-D4 are shown in Figure 5.4.3 A-D. The two phase nature of the samples can be most easily observed in Figure 5.4.2B where ferrite is forming along the PS interface while the middle is F/MA, and in Figure 5.4.3 B where the darker regions are ferrite and the lighter regions are austenite.

Figure 5.4.2 EBSD phase maps from alloys D1-D4. Blue represents austenite and red represents ferrite.
The ferrite content of SQ samples increased when Mo content was increased from 2 to 4 to 8 wt% while a similar Fe isopleth and Cr/Ni_{eq} values were maintained. The 2 wt% Mo alloy D1 contained < 1.0 area % ferrite indicating the microstructure was entirely F/MA. The 4 wt% Mo alloy D2 exhibited more ferrite, between 6.4 and 8.5 area%. Differently than D1 and D2, the 8 wt% Mo alloy, D3, formed an almost entirely ferritic microstructure (99.5+ area % ferrite). Lastly, the ferrite content of alloy D4, which was similar to D2 but had more Cr and Ni and less Fe, was found to be effectively 100%. Area percent ferrite averages were calculated from full
cross section optical images for all three replicates of each alloy feedstock and can be found in Table 5.4.2. The ferrite content with respect to radial position for the D2 SQ replicates was plotted in Figure 5.4.4 where the radial positions for the three replicate samples have all been normalized with respect to SQ diameter. From this plot it was observed that near the radial center of all three replicate SQ’s for D2 the ferrite content was the lowest and in general, as the outer radius of the SQ was approached, more ferrite was formed. Similarly, in SQ D1 samples, the small amount of ferrite observed occurred at the platen splat (PS) interface near the outer radius of the sample.

![Figure 5.4.4](image.png)

Figure 5.4.4 Measured area ferrite phase percent measured from optical images relative to radial position spanning the full cross section for the three replicate SQ D2 samples.
Table 5.4.2 Average area percent ferrite values for all replicate SQ samples.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>D1</th>
<th>D2</th>
<th>D3</th>
<th>D4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Mo</td>
<td>68Fe-2Mo</td>
<td>68Fe-4Mo</td>
<td>65Fe-8Mo</td>
<td>61Fe-4Mo</td>
</tr>
<tr>
<td>SQ 1</td>
<td>0.2</td>
<td>8.5</td>
<td>99.8</td>
<td>100.0</td>
</tr>
<tr>
<td>SQ 2</td>
<td>0.7</td>
<td>8.0</td>
<td>99.5</td>
<td>99.8</td>
</tr>
<tr>
<td>SQ 3</td>
<td>0.4</td>
<td>6.4</td>
<td>99.8</td>
<td>100.0</td>
</tr>
<tr>
<td>Area % Ferrite</td>
<td>0.2-0.7</td>
<td>6.4-8.5</td>
<td>99.5-99.8</td>
<td>99.8-100</td>
</tr>
<tr>
<td>WRC-1992 FN prediction</td>
<td>10</td>
<td>10</td>
<td>11</td>
<td>18</td>
</tr>
</tbody>
</table>

Cell size measurements, cooling rate estimates, and solidification rate estimates

Each of the four alloys used for SQ experiments showed evidence of primary ferrite solidification and resulted in either primary ferrite or massively transformed austenite that transformed from ferrite as it cooled, or a mixture of both. The massive austenite transformation or F/MA microstructure has been previously identified and is well reported in RS literature. The FMA austenite microstructure was differentiated from primary austenite solidified material using the solidification cells revealed by electrolytic etching. Examples of the etched cellular structures for each alloy are shown in Figure 5.4.5 A-D. A couple of things to note, the area of SQ D3 in Figure 5.4.5 C was slightly over etched compared to D1 and D2, and the D4 etch was harder to reveal due to the higher alloying content. Both images were still usable for measuring solidification cell diameters. Also, in the images a visible difference in the cell size at the PS interface vs the midline of the SQ sample can be observed. This increase in cell size moving towards the midline was also observed in the SQ samples and is also discussed in Chapter 3. The range of mean cell sizes measured were between 0.12µm and 0.36µm. While there were slight differences in the minimum and maximum mean cell sizes between compositions these were not significant and the range of cell sizes were similar to what was found previously in Chapter 3. Table 5.4.3 lists the maximum and minimum mean cell sizes that were recorded for each alloy composition. From the earlier discussed cell size to cooling rate relationship the range of cell
sizes produce cooling rates estimated between $1.3\times10^7$ and $3.4\times10^8$ K/s with solidification rates estimated between 410-1,490 mm/s. It should be noted that because of the log-log nature of the relationship and the very small cell sizes being used, slight changes in the cell diameter resulted in significant increases in the cooling rate and solidification rate estimates.
Figure 5.4.5 Etched solidification microstructure from SQ alloys D1-D4. (A-D respectively)
Sub-microscale features and cellular segregation

The BF and STEM-HAADF images collected in the TEM of samples from the four alloys revealed similar sub-microscale structures and features such as oxide particles and cellular microsegregation. To remind the reader, TEM samples for alloys D2-D4 were made using jet polishing while the TEM foil for alloy D1 was a FIB-liftout. The cellular solidification structures were readily visible in the TEM in both BF and STEM-HAADF images due to the outline of MnSi oxide particles that populated the cell boundaries. BF images were intentionally under-focused to make the oxide particles more visible. STEM-HAADF imaging showed the oxide particles along the cell boundaries as has been previously observed in rapidly solidified SS. BF images from D1-D4 are shown in Figure 5.4.6A-D and STEM-HAADF in Figure 5.4.7A-D. As with previously examined SQ SS alloys, the oxide particles were limited in size, peaking at around 30nm in diameter at most. Also, it was qualitatively observed that, in alloy D3, there was a fewer number of MnSi oxides along the cell boundaries D1 and D2 and D4.

Table 5.4.3 Table of range of mean cell diameters, estimated cooling rates, and estimated solidification rates.

<table>
<thead>
<tr>
<th>Alloy Name</th>
<th>Alloy Content</th>
<th>Cell Size (µm)</th>
<th>Cooling Rate (K/s)</th>
<th>Solidification Rates (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>Fe-17.2Cr-11.1Ni-2.2Mo</td>
<td>0.16-0.36</td>
<td>1.3E+07 - 1.4E+08</td>
<td>410-1000</td>
</tr>
<tr>
<td>D2</td>
<td>Fe-15.1Cr-10.8Ni-4.2Mo</td>
<td>0.15-0.33</td>
<td>1.6E+07 - 1.7E+08</td>
<td>460-1120</td>
</tr>
<tr>
<td>D3</td>
<td>Fe-13.0Cr-11.6Ni-8.0Mo</td>
<td>0.14-0.33</td>
<td>1.6E+07 - 2.3E+08</td>
<td>460-1180</td>
</tr>
<tr>
<td>D4</td>
<td>Fe-19.5Cr-13.2Ni-3.9Mo</td>
<td>0.12-0.32</td>
<td>1.8E+07 - 3.4E+08</td>
<td>470-1490</td>
</tr>
</tbody>
</table>
Figure 5.4.6 Intentionally under focused BF images of solidification cells in SQ alloys D1-D4. (A-D respectively)
Figure 5.4.7 STEM-HAADF cross section images of cellular solidification structure in SQ alloys D1-D4. (A-D respectively) Coral-like artifacts visible in D are a result of pitting of the sample from the jet polish.

Analysis of the STEM-EDX line scans indicate that during primary ferrite RS the amount of Mo segregation that occurred was invariant to Mo content (between 2-8%) or Fe isopleth, but there was a possible change in the behavior of Ni segregation. (Table 5.4.4) The SR of Cr in all
four alloys was consistently 1.00 as no segregation was observed. A similar trend was observed with Mo, which had a SR of 0.98 in the 2, 4, and 8 wt% Mo alloys. (Table 5.4.4) In most but not all of the line scans, a small increase in the X-ray signal intensity from Mo at cell boundaries, as well as in the Mo/Fe signal intensities, could be identified but given the standard deviations for the SR values between 0.1 and 0.2, the 0.98 SR of Mo can not easily be differentiated from 1.00. However, more importantly, the SR for Mo was highly consistent between each alloy and Mo composition and showed no observable change in segregation behavior as a result. (Figure 5.4.8B) On the other hand, the amount of Ni measured to segregate did show some variation. The three SRs and the standard deviations calculated for each alloy and the equilibrium partition coefficients are listed in Table 5.4.4. The average Ni SR increased from 0.92 in alloy D1 to 0.94 in D2 and to 0.96 in alloy D3 and D4 as seen in the box and whisker plot in Figure 5.4.8A.
Table 5.4.4 Table of measured segregation ratios X-ray signal intensity collected by EDX line scans for Cr, Ni, and Mo in each alloy, as well as the equilibrium partition coefficient for reference.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>Mean Segregation Ratio</td>
<td>1.00 ± 0.01</td>
<td>Mean Segregation Ratio</td>
<td>1.00 ± 0.01</td>
<td>Mean Segregation Ratio</td>
</tr>
<tr>
<td></td>
<td>Standard Deviation (σ)</td>
<td>0.01</td>
<td>Standard Deviation (σ)</td>
<td>0.01</td>
<td>Standard Deviation (σ)</td>
</tr>
<tr>
<td>Ni</td>
<td>Mean Segregation Ratio</td>
<td>0.92 ± 0.02</td>
<td>Mean Segregation Ratio</td>
<td>0.94 ± 0.01</td>
<td>Mean Segregation Ratio</td>
</tr>
<tr>
<td></td>
<td>Standard Deviation (σ)</td>
<td>0.02</td>
<td>Standard Deviation (σ)</td>
<td>0.01</td>
<td>Standard Deviation (σ)</td>
</tr>
<tr>
<td>Mo</td>
<td>Mean Segregation Ratio</td>
<td>0.98 ± 0.02</td>
<td>Mean Segregation Ratio</td>
<td>0.98 ± 0.01</td>
<td>Mean Segregation Ratio</td>
</tr>
<tr>
<td></td>
<td>Standard Deviation (σ)</td>
<td>0.02</td>
<td>Standard Deviation (σ)</td>
<td>0.01</td>
<td>Standard Deviation (σ)</td>
</tr>
</tbody>
</table>

Figure 5.4.8 Box and whisker plot showing the spread of segregation ratios from line scan data of Ni (A) and Mo (B) for each alloy composition.

5.5 Discussion

The targeted modification of alloy composition where Mo was substituted 1:1 for Cr, as weighted in the WRC-1992 equivalence equations, in a constant a Cr/Ni_eq of ~1.7, revealed a significant shift in the microstructure at RS rates. The ferrite content between replicates for each alloy was fairly consistent. Going from 2.2 to 4.2 wt% Mo between alloys D1 and D2 resulted in an increase from <1% primary ferrite to between 6-8% primary ferrite on average across the cross section of the SQ samples. In D2, areas away from the center radius of the samples reached between 20-30 area % ferrite. (Figure 5.4.4) In work by Vitek et. al., which used the slower solidification rate hammer and anvil splat quenching technique, they also reported variation in phase content with respect to radial position of the SQ. [45] Similar results were found in SQ.
samples of alloys 7-9 in Chapter 3 in which the center of the splats were found to have more austenite (F/MA) while the outer radius had more ferrite. Plots showing the distribution of the austenite content across the cross section are in Appendix 7.2.1. One possible explanation for why this occurs is based on previous findings that increased solidification rates could suppress the ferrite to austenite massive transformation at the PS interface, similarly this could also be due to increased solidification rates away from the radial center. It could be possible that during the complex chaotic event as the liquid droplet spreads out across the platen the solidification conditions change and as the material gets farther away from the initial impact site (radial center) along the platen surface, faster solidification rates can be achieved. In photos extracted from high speed footage of the splat event in Appendix 7.3.1A, a potential shift possibly similar to this can be observed as the sample is compressed by the platens. Further analysis of the cell size data with respect to phase content and radial position would be necessary to confirm whether there was a statistically significant difference in the cell size (and solidification rate) as a function of radial position. Additionally, the ferrite was observed to form preferentially along the interface regions of the SQ samples where the cell size was the smallest (Figure 5.4.5) and cooling rates and solidification rates were estimated to be the highest (Table 5.4.3). These results are consistent with what has been previously observed in SQ samples, discussed fully in Chapter 3. Ferrite formation along the PS interface can be observed most clearly in alloy D2 in Figures 5.4.2 and 3. Furthermore, at 8 wt% Mo the microstructure was 99.5+% ferrite. When more Cr and Ni were added in place of Fe, the more highly alloyed 4 wt% Mo D4 alloy showed similar results to D3 at a lower Mo content, producing similar, fully ferritic microstructures.

Our results suggest that under RS conditions the ferrite stabilizing effect of Cr and Mo are not 1:1 for Mo contents between 2-8 wt%. WRC-1992 predictions for D1-D3 predict the
alloys all to have FNs between 10-11 and D4 to have a FN of 18, as seen in Table 5.4.2. However, this is an overprediction for D1, and significant underpredictions for D3 and D4, only being close for D2 samples. The alloys are within the applicable Cr\textsubscript{eq} and Ni\textsubscript{eq} value ranges for the WRC-1992 diagram it can be noted that the predicted FNs are low enough that they can be considered approximately equal to % ferrite. One possible reason the FN predictions for these alloys were not accurate is that the cooling rate/solidification rates in SQ are much higher than solidification rates that occur in traditional welding processes which the WRC-1992 diagram was designed around.

The change in Cr and Mo composition can not be completely credited with driving the differences in the phase content that were measured due to the variation in the amount of C and N between the alloy feedstocks as C and N are both potent austenite stabilizers. These variations work out to relatively small changes in the Ni\textsubscript{eq} of between 0.1 to 0.3, or about a 3% change at most. Additionally the amount of Mn was also not the exact same between feedstocks, and although Mn is not included in the WRC-1992 equations it is also an austenite promoter.\textsuperscript{[31]} However, when the change in C, N, and Mn concentrations is compared to the measured ferrite content, the C and Mn levels were higher in the alloys that had more ferrite. While N levels decreased between D1 and D2 there was no significant difference between N levels in D2 and D4. Alternatively, when the ferrite content increased from D1 to D2 to D4, there was a decrease in Si levels even though Si is a ferrite stabilizer. D3 concentrations were not included in the comparison since the values for C and N were averaged from D1, D2, and D4 and the Mn and Si concentrations were only measured using quantitative EDS with standards. Based on these variations it is unlikely the difference in C, N, Mn, and Si significantly contributed to the difference in phase content between alloys.
Previous work by T. D. Anderson et. al. showed that in HED weld microstructures of SS with Mo contents between 0 and 10 isopleths were a reasonably good predictive tool for the microstructure.\textsuperscript{[99]} It was observed experimentally that at RS conditions the Mo content in an alloy did impact the final microstructure by increasing the amount undercooling required for the massive ferrite to austenite transformation to occur. In work by Perricone et. al. on laser welded Mo-bearing steels discusses that the isopleth can be modified to include new boundary roughly in the middle of the FCC+BCC stable region that represents the point where the two phases have equal free energies at a given temperature.\textsuperscript{[70]} The temperature at which the nominal composition crosses this line is defined as $T_0$. It is stated that the optimum conditions for the massive transformation to occur at low undercoolings in the stable two phase region, a high $T_0$ value and a high melting temperature. If the isopleths for D1-D4 were modified similar to this in which a new midline was generated down the center of the FCC+BCC region, the $T_0$ temperature would decrease as Mo concentration increased similar to how the temperature decreased where the nominal composition reached the stable FCC phase described earlier.

While the concentration of Mo was observed to influence the microstructure phase content, no significant effect on the cell size or microstructure feature size was found. The range of mean cell sizes measured from splat quenched samples of different feedstock compositions were not significantly different. This means that the addition of increased levels of Mo had no significant, detectable effect on the range of solidification cell sizes produced by SQ. In Chapter 3, similar results were found for a wide range of SS alloy chemistries with $\text{Cr}/\text{Ni}_{\text{eq}}$ ranging from 0.97-2.09. By combining the microstructure phase contents with the range of cell sizes measured, the observed microstructures were plotted at the estimated solidification rate ranges for each alloy based on Mo content in Figure 5.5.1. The solid lines between the FA, Ferrite +
Widmanstatten Austenite, and F/MA phases are based on the boundaries/predictions on the “Lippold” diagram for Cr/Ni_{eq} of 1.73. Dashed lines were used for Mo content above 4% because the materials considered when building the diagram contained very few Mo-bearing alloys and typical 300 series SS do not exceed 4% Mo. D4 was marked with triangles instead of circles because the composition is at a significantly different Fe isopleth (higher amounts of Cr and Ni) than the other three alloys, which even though it only had 4 wt% Mo like D2, it formed fully ferritic microstructures like D3. As previously discussed, the solidification cell size was measurably smaller at the platen splat (PS) interface compared to the middle of the SQ and a smaller cell size translates to larger solidification rates. In this work, as well as in Chapter 3, ferrite microstructures were observed to form near the PS interface before the middle of the SQ. Thus, based on the location of the ferrite formation, ferrite solidified at higher solidification rates. A summary of the solidification rate estimates, microstructures, solidification modes, and phase contents can be found in Appendix 7.1.4.
The increased concentrations of Mo were also found to have no observable effect on the solidification microstructure when observed in the TEM and STEM. All four alloys were found to display a similar network of MnSi oxides along cell boundaries. These oxide networks were visible in both BF and STEM-HAADF images of Figures 5.4.6 and 7 and in previous work on SQ SS alloys in Chapter 4. The size of the oxides was again consistent between alloys showing no observable variation. It was noticed that in alloy D3, there appeared to be qualitatively fewer oxide particles along the cell boundaries compared to D1, D2, and D4. This could potentially be
linked to the increased concentration of Mo in alloy D3 reducing the mobility of Mn and Si due
to the low diffusivity of Mo making it more difficult for the MnSi oxides to form. However, no
clear cause for this reduction in frequency of MnSi oxides was immediately identified and more
samples would need to be analyzed to confirm the observation.

The last area of interest for this study was whether the change in Mo content of the alloys
would impact the segregation behavior of primary ferrite. The equilibrium partition coefficients
for Cr, Ni, and Mo predict that during primary ferrite solidification Ni, which has an equilibrium
partition coefficient of 0.82, would be the only major element to segregate as the equilibrium
partition coefficient values of Cr and Mo were both near 1.0 as they are both ferrite stabilizing
elements. In all four alloys, regardless of Mo content, the average segregation ratios for Mo were
nearly identical at 0.98. While the SR of Mo was consistently below 1.00 for each alloy, there is
uncertainty whether the segregation is valid or significant based on the standard deviations of the
average values. From this it can be concluded that no measurable change in the amount of Mo
that segregated with respect to the Mo concentration of the alloy. There may have been
difference observed in the segregation behavior of Ni between the alloys. The most Ni
segregation occurred in the 2% Mo alloy D1 producing an average SR of 0.92. The least
segregation of Ni was found in alloys D3 and D4 with SR of 0.96 for both. D2 had an average
SR of 0.94 between the three alloys. It should be noted that the sample used in TEM analysis of
D1 was a FIB liftout while D2-D4 were jet polished samples. As a result, it is possible that in the
thinned area of the jet polished samples the cells were not oriented as precisely out of plan or
perpendicular to the thinned area compared to what was produced by FIB-liftout. One of the only
similar studies found that contained analysis of microsegregation in SQ ferrous material was
work by Kattamis et. al., which used a levitation splat quenching apparatus. They reported a SR
of Ni in Fe-25Ni samples of 0.97 which was much closer to a partitionless coefficient of 1.00 than their stated equilibrium partition ratio for Ni of 0.74. [127] Unlike for the Mo segregation, Ni was found to segregate to the cell boundaries in all four alloy compositions, but given the close proximity of the SR ratios, difference in sample preparation, and deviations associated with each average segregation ratio, further investigation would be required to determine if the differences in SR of Ni with increasing Mo contents was valid. One possible explanation for this decrease in Ni segregation could be related to the amount of time where solid state diffusion can occur. Based on what was observed in the isopleths, the transformation temperature from ferrite to austenite decreased by about 50°C from D1 to D2 and by over 100°C from D2 to D3 and 4. Given that the diffusion coefficient of Ni is higher in ferrite than austenite, Table 1.2.4.2, the lower transformation temperatures would allow more time for Ni to diffuse and would present as less segregation.

5.6 Conclusions

In conclusion, this paper investigates the effect of varied Mo content between 2-8 wt% in splat quenched rapidly solidified SS alloys with Cr/Ni_{eq} of approximately 1.7 with respect to the solidification phase, microstructure, sub-microscale features, and cellular microsegregation. Four, custom Mo bearing SS alloy feedstock compositions were made for SQ experiments containing either 2, 4, or 8 wt% Mo. The results showed that for RS SS at a Cr/Ni_{eq} of 1.7, the microstructure formed is likely influenced by both the Mo concentration, as well as total Cr and Ni content of the alloy. Extensive optical microscopy, electron microscopy, and STEM-EDX analysis were used to estimate individual element segregation ratios in rapid primary ferrite solidified microstructures. From this investigation we have concluded the following:
1.) In SQ samples from all four alloys compositions, only primary ferrite solidification was observed to occur, however, the amount of ferrite in each sample was impacted by the Mo concentration. It was also observed that at lower Fe isopleths (i.e., increased concentrations of Cr and Ni while maintaining the same Cr/Ni<sub>eq</sub>), also resulted in higher levels of ferrite in the final microstructure.

2.) Variation in the alloy Mo concentrations between 2 and 8 wt% did not cause a significant change in the range of mean solidification cell sizes formed by splat quenching which spanned from 0.12µm – 0.36µm in diameter. Thus, changes in the Mo concentration of the feedstock did not significantly impact the solidification rates estimated for SQ which ranged between 410-1490mm/s.

3.) At the sub-micron scale, almost no differences could be discerned in the microstructures between alloys of various Mo concentrations. The one exception was that fewer oxides were observed in the 8 wt% Mo material compared to the others possibly due to the slow diffusivity of Mo and there being higher concentrations of it.

4.) STEM-EDX measurements of rapidly solidified splat quench samples produced a consistent average segregation ratio of 0.98 for Mo that was independent of Mo content. However, the amount of Mo segregation was very minor if present, and almost not measurably different from 1.0. The average segregation ratio for Ni in each alloy was significantly different from 1.00 but less consistent between alloys and ranged from 0.92-0.96.

5.7 Acknowledgement

I would like to acknowledge Katherine Ziska for her assistance collecting and analyzing optical micrographs for phase analysis. This work was funded by Honeywell Federal Manufacturing & Technologies under Contract No. DE-NA0002839 with the U.S. Department of
Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a nonexclusive, paid up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for the United States Government purposes.
CHAPTER 6: SUMMARY, FUTURE WORK, AND CONCLUSIONS

6.1 Summary

Two-piston splat quenching (SQ) has been presented as a fast and effective means to study the effects of rapid cooling and solidification conditions in new alloy compositions that does not require complex processing methods or atomized metal powder. This technique was implemented to study RS in 20+ unique SS alloy compositions, for which various aspects of the solidification microstructures were analyzed over a series of studies including a comparison of the RS results from SQ samples with LPBF processed material of the same feedstock. The SQ technique was capable of producing multiple samples in a short period of time with replicates showing a high degree of repeatability between samples. The primary takeaways that were found relating to SQ processed material were: 1) SQ produced RS and cooling rates similar in magnitude to those measured in LPBF processed SS samples of the same feedstock. 2) Solidification rate estimates for the SQ technique were typically between 0.4-1.6m/s based on cell size measurements and heat transfer simulations. 3) Primary ferrite solidification and the F/MA and ferrite microstructures formed at much lower Cr/Ni\text{eq} than previously predicted at these solidification rates. 4) The primary segregating elements observed in the cellular microsegregation were determined by the solidification mode.

SQ experiments utilized electromagnetic levitation melting with a water cooled Cu coil in an inert Ar environment to melt SS samples of custom alloy compositions and to produce rapidly solidified samples. An Edmund Buhler Ultra-Rapid Quencher with a two color optical pyrometer was used to measure sample temperatures prior to the splat event for all SQ experiments. Splat
conditions including superheat temperature, initial sample mass, coil design, and drop distance were kept constant for all experiments to ensure consistency between samples. The custom feedstock alloys were designed as Mo bearing austenitic SS targeting specific Cr/Ni\textsubscript{eq} ratios through modification of Fe, Cr, Ni, and Mo additions. Samples were analyzed with respect to solidification path, microstructure, and microsegregation using optical and multiple electron microscopy techniques.

The first study was focused on using SQ to investigate how modifications of Cr and Ni concentrations effected the rapidly solidified microstructures (Chapter 3: Investigation of the Effect of Chrome and Nickel Concentrations During Two-Piston Splat Quenching of Austenitic Stainless Steels). This study involved producing custom alloy feedstocks based on the ASTM A240 compositional specification for 316L SS, that encompassed the range of Cr/Ni\textsubscript{eq} ratios for which the predicted microstructures went from fully austenitic to fully ferritic, represented by Cr/Ni\textsubscript{eq} values between 0.97-2.09. (Table 3.4.1) This study also included observations and trends found in SQ produced samples in general. SQ samples were found to be chemically indistinguishable from the parent feedstock as well as between replicate samples for major alloying elements. (Table 3.4.2) Additionally, the SQ samples were found to be chemically homogenous throughout the thickness of the SQ. (Figure 3.4.2) However, there was measurable segregation between the solidification cells of Cr and Mo for primary austenite solidified material and Ni in primary ferrite solidified material at the sub-micron scale. (Figure 3.4.3) A variety of grain structures were also observed within the SQ microstructures including columnar, equiaxed, and large grains. (Figure 3.4.7 and 3.4.8) Rapidly solidified SQ samples experienced fully cellular solidification and repeatably produced mean cell ranging between 0.11 \( \mu \text{m} \) and 0.44\( \mu \text{m} \). (Table 3.4.4) This range of cell sizes translated to solidification rates on the order of
magnitude of 0.4-1.6m/s. Cell size, and thus cooling rate and solidification rate were found to be independent of the Cr/Ni_{eq} in SQ samples. It was also observed that smaller cells formed along the platen splat (PS) interface and larger cells at the center of the SQ samples indicating a decreasing gradient in solidification rate as the samples solidified. (Figure 3.4.10) Ferrite formed preferentially along the PS interface where larger solidification rates were found. (Figure 3.4.6) The phase content of ferrite and F/MA (austenite) was also shown to vary with radial position in SQ samples in which the ferrite content increased towards the outer radius of SQ. (Figure 3.4.4 and 5) Overall, it was observed that primary ferrite was found in solidified SQ samples with Cr/Ni_{eq} down to 1.71 and F/MA microstructures were observed in samples with Cr/Ni_{eq} between 1.43 and 2.00. (Figure 3.5.1) For alloys within the compositional specification for 316L at the upper end of the Cr/Ni_{eq} values, significantly greater amounts of ferrite were found in the microstructure than predicted by WRC-1992 diagram.

In the second study, a comparison of the microstructure, sub-microscale features, and microsegregation between SQ and LPBF produced material of the same composition was performed while also looking at the change in microsegregation with respect to Cr/Ni_{eq} (Chapter 4: A Comparison of Sub-Microscale Cellular Segregation in Rapidly Solidified Stainless Steel Via Two-Piston Splat Quenching and Laser Powder Bed Fusion). In the first part of this study, LPBF processed SS with a Cr/Ni_{eq} of 1.53 was used as feedstock for SQ experiments and the SQ samples were compared to the LPBF samples. The SQ samples possessed a smaller mean cell size than the LPBF material, however the two techniques produced overlapping cell sizes between approximately 0.2 and 0.4μm indicating similar solidification rates were experienced by both materials. Both techniques produced similar microstructures that were crystallographically fully austenite but were actually a mixture of F/MA and primary austenite microstructures.
The two microstructures were identified by differences in how the two regions responded to electrolytic etching and the differences in segregating elements measured in STEM-EDX. The segregation of Cr and Mo in the primary austenite solidified material was not measurably different between the LPBF and SQ material, with average segregation ratios of 0.93 for Cr and 0.83 for Mo. The primary difference between the primary austenite microstructures of samples produced by the two techniques were that the LPBF samples had a network of dislocation pileup along the cell boundaries that was not present in the SQ austenite. In contrast, no dislocation pileup was observed at the cell boundaries in the LPBF or SQ F/MA regions of the microstructure. The segregation ratios of Ni in the two samples were not measurably different, both around 0.91. It should be noted that the distance over which Ni segregation occurred in the LPBF material was larger than in the SQ F/MA material, both of which were larger than the segregation distance of Cr and Mo in austenite. The wider range of segregation in the F/MA microstructures was attributed to the increased solid state diffusion coefficients of Cr, Ni, and Mo in ferrite compared to austenite. The larger segregation distance of Ni in the LPBF vs the SQ material was attributed to different thermal profiles affecting the solid-state diffusion of Ni after solidification for LPBF processing compared to the single heat and cool cycle of SQ. A consistent difference between the LPBF and SQ samples were that the MnSi oxides formed in the LPBF material could reach significantly larger sizes, around 100nm, where as in the SQ microstructures the largest observed was about 30nm. A potential explanation for the different oxide particle sizes was due to the different thermal histories with LPBF remaining at elevated temperatures longer than SQ samples. Two other custom feedstock compositions that had Cr/Ni$_{eq}$ of 1.71 and 1.95 were splat
quenched and the segregation response in the F/MA and PF microstructures were compared to what was observed in the LPBF and SQ F/MA microstructures. Consistent with the SQ 1.53 Cr/Ni\textsubscript{eq} sample, the MnSi oxide size did not exceed 30nm in either of these new compositions and Ni was the primary element to segregate to the cell boundary. The amount of Ni segregation in primary ferrite solidified F/MA and ferrite microstructures was not measurably influenced by the change in Cr/Ni\textsubscript{eq} of the alloy. Overall, the amount of segregation of Cr and Mo, and Ni in the respective phases of rapidly solidified SQ and LPBF material were much less than predicted for equilibrium conditions, meaning that the solidification rates are approaching partitionless solidification, but have not reached it. (Table 4.4.4) High solidification rates can enable the use of SS alloys with higher Cr/Ni\textsubscript{eq} values while still producing fully austenitic material and eliminating the harmful microsegregation of the protective elements, Cr and Mo.

The third study focused particularly on the modification of Mo content while maintaining the same Cr/Ni\textsubscript{eq} and Fe concentration to assess the effect of Mo concentrations on solidification during RS conditions (Chapter 5: Influence of Molybdenum on Rapid Solidification Microstructures and Microsegregation in Primary Ferrite Solidified Stainless Steel). This was achieved by performing SQ experiments on custom alloys with Mo concentrations of 2, 4, and 8 wt\% where Cr was used as the balance element. Additional comparison was made between the 4 wt\% Mo alloy and a separate 4 wt\% Mo alloy that had increased amounts of Cr and Ni. The results showed that the solidification rates produced during SQ experiments were unaffected by changes in Mo concentrations, similar to what was found in Chapter 3 with Cr and Ni. (Table 5.4.3) At the Cr/Ni\textsubscript{eq} 1.7 the primary solidification phase was not altered by the compositional changes between the alloys, all of which solidified as primary ferrite. Alternatively, at this Cr/Ni\textsubscript{eq} the microstructure phase content was significantly impacted by increased concentrations
of Mo. (Figure 5.5.1) For the three alloys near the same 66 wt% Fe isopleth, a small increase in the amount of ferrite occurred from <1% to near 7% going from alloy D1 to D2. However, the 8 wt% Mo alloy, D3, was found to contain a fully ferritic microstructure. In a separate comparison of the phase content of the two 4 wt% Mo alloys, D2 and D4, D4 which was along the 60 wt% Fe isopleth (higher levels of Cr and Ni) also produced fully ferritic microstructures. (Figure 5.4.1-3) While the primary solidification phase was unchanged between alloys, increased amounts of Mo and higher levels of Cr and Ni at the same Mo content (lower Fe isopleth) were found to stabilize ferrite formation and prevent the ferrite to austenite massive transformation. (Figure 5.4.1-4 and Table 5.4.2) When observed in BF and STEM-HAADF images the microstructures of the different alloys were very similar with the only notable difference being qualitatively there were less oxide particles along the cell boundaries in the 8 wt% Mo alloy compared to the others. (Figures 5.4.6 and 7) The microsegregation of Mo in primary ferrite solidified material showed no observable consequence from increased concentrations of Mo, or Cr and Ni concentrations, consistently averaging a segregation ratio of just under 1.0 at 0.98. (Table 5.4.4) Alternatively, there may have been an effect on the segregation behavior of Ni as a result of increased Mo concentrations, as the average SR of Ni was closer to 1.0 for the 8 %Mo and higher alloyed 4 %Mo samples than in the regular 4 %Mo and 2 %Mo alloys. (Figure 5.4.8) While the significance of the difference in Ni segregation ratios was not assessed, there was a noticeable trend in the results that warrants further investigation. (Figure 5.4.8) One possible explanation if this difference is real could be that due to lack of the F/MA transformation in the fully ferritic samples there was more time for solid-state diffusion of Ni compared to in the F/MA material. However, if this were true then a similar trend should have been observed between then F/MA and ferrite samples studied in Chapter 4.
This dissertation has expanded and improved the current scientific understanding of the relationship between rapid solidification, microstructure and solidification phase, and alloy composition for Mo bearing austenitic stainless steels and demonstrated that two-piston splat quenching can be used as an effective means of simulating rapid solidification rates similar to those found at the upper end of PBF processes. While previous investigations using two-piston splat quenching or similar splat processes have been performed on Fe-X binary systems or Fe-Cr-Ni ternary alloy systems, the work in this dissertation is the first to investigate the effects of RS with respect to targeted compositional variations in complex SS alloys across a wide range of the Cr/Ni\(_{eq}\) space and compare the results to a PBF process. The work in this dissertation presents several impactful takeaways as a result of utilizing this unique technique: primary ferrite solidification occurred in SQ processed alloys with Cr/Ni\(_{eq}\) as low as 1.43, the F/MA transformation was more prevalent than previously estimated at rapid solidification rates between 0.4 and 1.6 m/s, and similar microstructures and microsegregation behavior was observed in the austenite and F/MA microstructures of LPBF and SQ samples with only a few minor differences. The work in Chapter 4 comparing the rapid solidification microstructures and microsegregation response of SQ processed SS to the same material processed using LPBF is the first of its kind in the literature. From this work, a better understanding of the conditions in which SQ can be used to investigate the effects on solidification and microstructure for new alloy compositions at rapid solidification rates have been identified. The successful implementation of the SQ process to simulate rapid solidification rates across multiple SS alloys provides a path forward for future research of rapid solidification in a breadth of different alloy systems.
6.2 Recommendations for Future Work

While a significant number of unique alloy compositions were involved in the research included in this dissertation, there were multiple compositions that could be made to further fill out the Cr/\textit{Ni}_{eq} space and/or explore alternate Fe isopleths that would make for ideal samples to study in a continuation of this work. The two areas in particular would be around Cr/\textit{Ni}_{eq} between 1.1 and 1.5 which were underexplored in the dissertation work but contained the boundary/transition from ferrite solidification to austenite solidification at these RS conditions. This space is of key importance because of the microsegregation of Cr and Mo that occurs in primary austenite solidification but does not occur in primary ferrite solidification and can lead to local sensitivity to corrosion in rapidly solidified parts.\textsuperscript{155} This investigation would aim to better identify the range of Cr/\textit{Ni}_{eq} values where the primary solidification phase transitions from austenite to ferrite as well as possibly evaluate the solidification rate sensitivity of the transition.

In a similar vein, alloys with the same Cr/\textit{Ni}_{eq} as those studied between 1.53 and 2.00 could be made with increased or decreased amounts of Cr and Ni and or Mo compared to the existing samples. The majority of the research presented in this dissertation was along a single isopleth (Fe alloy content). Some of the data in Chapter 5 suggests that the phase stability may be significantly altered by total alloy content (TAC) on a different isopleth. The WRC-1992 diagram would also support the idea that the TAC/isopleth matters as the predicted FNs do not maintain the same Cr/\textit{Ni}_{eq} as Cr_{eq} and Ni_{eq} increase. The very informative work of Lippold combined data from multiple different isopleths (Fe content levels) and alloying elements, so there is some uncertainty of the effects of Cr/\textit{Ni}_{eq} vs TAC on solidification phase stability at rapid solidification. These alternate isopleth alloys would provide a comparison of the phase content of the microstructures at low and high Cr and Ni contents or different Mo contents and
would help to further the understanding of the ferrite to austenite transformation. To achieve this, more quantitative analysis would need to be performed in order to better elucidate the fundamental relationships between RS processing and the observed microstructure/phase. Assuming multiple transitions from F/MA to ferrite microstructures are captured by this work, the amount of undercooling required for the massive transformation to occur for each chemistry could be predicted by equilibrium isopleths generated with ThermoCalc and could be utilized to provide a better experimental estimate for undercooling and temperature gradients produced during splat quenching. These results could then be compared to existing undercooling estimates for SQ and RS processes to allow for more accurate microstructure predictions and be used in the development of a RS nucleation and growth kinetics model for stainless steels.

Another potential area for future work involves comparing microsegregation and microstructure phase content to more LPBF variants of SQ processed alloy compositions. In the work performed for this dissertation only one alloy composition was compared between SQ and LPBF and while the results were reasonably similar, a comparison of LPBF material at a few different Cr/Ni$_{eq}$ such as 1.71 and 1.95 would be beneficial in confirming the findings from the 1.53 Cr/Ni$_{eq}$ alloy. This study would involve measuring the microstructure phase content of the LPBF samples using optical microscopy and EBSD and performing STEM-EDX to measure the segregation behavior of the two new LPBF samples. By further investigating the similarities and differences between rapidly solidified material from SQ and LPBF of the same feedstock chemistry the effectiveness and validity of SQ to simulate RS for new alloy compositions in LPBF or other PBF processes can be highlighted.

As fusion based additive manufacturing methods become more prevalent in a variety of industrial applications so will the need to screen new alloy compositions to understand the
effects of RS on the alloy and this provides significant future research potential. In particular, SQ could be used to study some of the more unique alloy systems such as titanium alloys, Inconel alloys, or high entropy alloys which are very costly to purchase or produce as atomized powder. Preliminary investigations into prominent relative alloy binary or ternaries would be used to identify compositions and phases of interest and the susceptibility of those phases to the effects of RS. Another aspect of this potential work involves accounting for differences in thermal properties between austenitic SS and new alloy systems, meaning the results from SQ would need to be compared against PBF processed versions of the same material to ensure the rates and findings were consistent between the two.

Direct modification of the Cu platens used in SQ experiments to alter the solidification conditions or gain a greater understanding of the solidification event during the “splat” is another area of potential future work. Two different modifications would be proposed for this work. The first modification would be the removal of this layer of material from one platen equal to 50µm deep and approximately 2.5cm in diameter. This would modify the splat event by creating a predefined space that contained the splat event, also reducing or eliminating the jetting of excess material and ideally would produce splat samples with identical thicknesses. This would be a potentially useful modification because if the thickness of the SQ could be controlled than the user has subsequent control over the cooling rate and solidification rate. The second modification would involve placing a network of temperature probes just under the platen surface to capture the spatial heat transfer from the liquid droplet through the platen. This would be achieved by making a 3x3 grid layout of small holes drilled into the back of the platen, stopping just before the surface. High refresh rate thermocouples would be imbedded at the bottom of the holes on the back of the platen surface. To minimize interferences from installing
the thermocouples Cu rods will be used to backfill the holes and ensure optimum contact between the thermocouple and the back of the platen surface. This information could be used to improve heat transfer simulations and as an alternate means of estimating the cooling rates experienced during SQ.

One last proposal for possible future work would be the incorporation of the atomized 316L type powder used for LPBF experiments into the research. In instances where the powder is available or will be required for PBF builds the powder can be used to investigate the microstructure and phase information for a single composition across a significantly wider range of cooling rates and solidification rates than SQ or LPBF, all be it lower. Heat transfer and solidification of an atomized metal particle are well reported on for stainless steel alloys.\textsuperscript{[56, 82, 156, 157]} The atomization of metal powder produces particles anywhere from 1 to 2\(\mu\)m to 100s \(\mu\)m in diameter which each experience a different cooling rate that can be calculated using equations presented in the literature.\textsuperscript{[74]} In the proposed work, the powder would be sieved and sorted into various size groups established based on the difference in predicted cooling rates. The powder would be prepared for metallographic analysis and etched to reveal the solidification structure and allow for measurement of the solidification cells. Solidification cells would be measured with respect to the diameter of the parent particle and cooling rate estimates would be made using the empirical relationship and compared to the calculated values. Additionally, the temperature gradients would be calculated for the atomized powders and used to estimate the solidification rate which, if it were large enough, could potentially allow for a comparison between similar solidification rates in SQ and powder material.
6.3 Conclusions

In conclusion, the primary objective of this research was analysis and characterization of the microstructure/sub-microscale structure, phase content, solidification path, and microsegregation behavior of rapidly solidified, splat quenched austenitic stainless steels with respect to targeted compositional variations. The purpose of this investigation was to demonstrate the feasibility of two-piston splat quenching as a means to simulate rapid solidification conditions similar to PBF processes for screening new alloy compositions faster and cheaper, without requiring atomized powder. A range of custom feedstock compositions were designed to have Cr/Ni\text{eq} that span from fully austenitic to fully ferritic microstructure, based upon predictions at rapid solidification rates. The effects of variations in major alloying element compositions at rapid solidification rates were analyzed with respect to solidification rate, microstructure, solidification phase, and microsegregation. Key results of using SQ to simulate rapid solidification in Mo bearing austenitic stainless steels are summarized by the following points:

1. Under RS conditions, multiphase microstructures (e.g., primary austenite-F/MA and F/MA-primary ferrite) were observed over a much wider compositional range than previously predicted. Our results focused on the solidification rate regime above 0.1 m/s and found the F/MA microstructure, which has a primary ferrite solidification mode, formed over a significantly wider range of Cr/Ni\text{eq} ratios, i.e., 1.43 to 2.00 than previously predicted. Also, primary ferrite microstructures were initially observed forming in small quantities at very high solidification rates in samples with a Cr/Ni\text{eq} as low as 1.71.
2. The range of mean cell sizes (spanning 0.11 to 0.44µm) in splat quenched samples was not significantly different between SQ samples, regardless of the alloy composition or Cr/Nieq. The cooling rates were estimated to be in the range of $7.0 \times 10^6$ to $3.6 \times 10^8$ K/s and the corresponding solidification rate estimates were between 390-1,610 mm/s.

3. Comparison between LPBF and SQ processed samples of the same composition showed the samples were mostly similar with respect to solidification phases, microstructure, and microsegregation. The cell sizes, cooling rates, and solidification rates for SQ SS were also similar in magnitude to measured and literature values for LPBF processed SS. The only differences were observed in the geometry of the solidification structure due to differences in thermal history and processing method, the presence of dislocations pileup along the cell boundaries in LPBF primary austenite, and the observation of larger oxide particles in both primary austenite and F/MA microstructures of LPBF samples compared to SQ samples.

4. Compositional specifications for austenitic stainless steels, like ASTM A240 for 316L, may need to be further refined when processing steels within the upper end of solidification rates experienced in powder bed fusion techniques in order to achieve the intended microstructure. For more traditional manufacturing methods, the range of compositions allowed by the ASTM A240 specification for 316L steel would result in between 0 and 25% ferrite formation. During rapid solidification, higher Cr/Nieq values that are possible within the specification resulted in complete ferrite solidification with microstructures in excess of 50% primary ferrite.

5. Elemental segregation to the cell boundaries of either Cr and Mo or Ni were observed depending on solidification mode. Segregation of primarily Cr and Mo to the cell
boundaries was found in primary austenite solidified microstructures and the segregation of primarily Ni was found in primary ferrite solidified materials. The relative segregation ratio of each element was independent of the Cr/Ni_{eq} of the alloy and of the concentration of Cr, Ni, or Mo.

6. In SS alloys near the eutectic composition, at the same Cr/Ni_{eq}, increasing concentrations of Mo suppressed the ferrite to austenite massive transformation temperature low enough that the transformation did not occur, allowing fully ferritic microstructures to form. Similarly, the same Mo concentration with a lower Fe isopleth (increased Cr and Ni at the same Cr/Ni_{eq},) had similar results stabilizing the ferrite in SQ samples.
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### APPENDIX

#### 7.1 - Tables

Table 7.1.1 compositional analysis results for all custom feedstock alloys produced.* composition measured using quantitative EDS.

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*Composition measured using quantitative EDS.
Table 7.1.2 Cooling rates and temperature gradients extracted from 2D heat transfer simulations.

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<td>64.4</td>
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</table>

* Value extrapolated based on simulation data
### Table 7.1.3 Equivalence, phase, microstructure table for Chapter 3 alloys.

| Fe     | Cr     | Ni  | Mo  | Cr2N | N2 | SX Sample | Predicted Phase at 900°C | Observed Subsolidification Microstructure | Primary Solidification Mode | Primary Austenite | Primary Ferrite | Primary Bainite | Primary Nitride | F1A | F2A | F3A | F4A | Phase observed in EBSP | Wt. % Ferrite Content (Optical) | Wt. % Ferrite Content (EDS) |
|--------|--------|-----|-----|------|-----|-----------|---------------------------|------------------------------------------|------------------------------------------|---------------------|----------------|---------------|---------------|---------------|-----|-----|-----|-----|--------------------------|---------------------------|-----------------------------|
| 0.45   | 0.45   | 0.45| 0.45| 0.45 | 0.45| A1.1      | Balanced Austenite        | Balanced Austenite                       | Balanced Austenite                       | Balanced Austenite | Balanced Austenite | Balanced Austenite | Balanced Austenite | 0.0 | 0.0 | 0.0 | 0.0 | Balanced Austenite       | 0.00                       | 0.00                        |
| 0.45   | 0.45   | 0.45| 0.45| 0.45 | 0.45| A1.2      | Balanced Austenite        | Balanced Austenite                       | Balanced Austenite                       | Balanced Austenite | Balanced Austenite | Balanced Austenite | Balanced Austenite | 0.0 | 0.0 | 0.0 | 0.0 | Balanced Austenite       | 0.00                       | 0.00                        |
| 0.45   | 0.45   | 0.45| 0.45| 0.45 | 0.45| A1.3      | Balanced Austenite        | Balanced Austenite                       | Balanced Austenite                       | Balanced Austenite | Balanced Austenite | Balanced Austenite | Balanced Austenite | 0.0 | 0.0 | 0.0 | 0.0 | Balanced Austenite       | 0.00                       | 0.00                        |
| 0.45   | 0.45   | 0.45| 0.45| 0.45 | 0.45| A1.4      | Balanced Austenite        | Balanced Austenite                       | Balanced Austenite                       | Balanced Austenite | Balanced Austenite | Balanced Austenite | Balanced Austenite | 0.0 | 0.0 | 0.0 | 0.0 | Balanced Austenite       | 0.00                       | 0.00                        |
| 0.45   | 0.45   | 0.45| 0.45| 0.45 | 0.45| A1.5      | Balanced Austenite        | Balanced Austenite                       | Balanced Austenite                       | Balanced Austenite | Balanced Austenite | Balanced Austenite | Balanced Austenite | 0.0 | 0.0 | 0.0 | 0.0 | Balanced Austenite       | 0.00                       | 0.00                        |
| 0.45   | 0.45   | 0.45| 0.45| 0.45 | 0.45| A1.6      | Balanced Austenite        | Balanced Austenite                       | Balanced Austenite                       | Balanced Austenite | Balanced Austenite | Balanced Austenite | Balanced Austenite | 0.0 | 0.0 | 0.0 | 0.0 | Balanced Austenite       | 0.00                       | 0.00                        |
| 0.45   | 0.45   | 0.45| 0.45| 0.45 | 0.45| A1.7      | Balanced Austenite        | Balanced Austenite                       | Balanced Austenite                       | Balanced Austenite | Balanced Austenite | Balanced Austenite | Balanced Austenite | 0.0 | 0.0 | 0.0 | 0.0 | Balanced Austenite       | 0.00                       | 0.00                        |
| 0.45   | 0.45   | 0.45| 0.45| 0.45 | 0.45| A1.8      | Balanced Austenite        | Balanced Austenite                       | Balanced Austenite                       | Balanced Austenite | Balanced Austenite | Balanced Austenite | Balanced Austenite | 0.0 | 0.0 | 0.0 | 0.0 | Balanced Austenite       | 0.00                       | 0.00                        |
| 0.45   | 0.45   | 0.45| 0.45| 0.45 | 0.45| A1.9      | Balanced Austenite        | Balanced Austenite                       | Balanced Austenite                       | Balanced Austenite | Balanced Austenite | Balanced Austenite | Balanced Austenite | 0.0 | 0.0 | 0.0 | 0.0 | Balanced Austenite       | 0.00                       | 0.00                        |
| 0.45   | 0.45   | 0.45| 0.45| 0.45 | 0.45| A1.10     | Balanced Austenite        | Balanced Austenite                       | Balanced Austenite                       | Balanced Austenite | Balanced Austenite | Balanced Austenite | Balanced Austenite | 0.0 | 0.0 | 0.0 | 0.0 | Balanced Austenite       | 0.00                       | 0.00                        |
| 0.45   | 0.45   | 0.45| 0.45| 0.45 | 0.45| A1.11     | Balanced Austenite        | Balanced Austenite                       | Balanced Austenite                       | Balanced Austenite | Balanced Austenite | Balanced Austenite | Balanced Austenite | 0.0 | 0.0 | 0.0 | 0.0 | Balanced Austenite       | 0.00                       | 0.00                        |
| 0.45   | 0.45   | 0.45| 0.45| 0.45 | 0.45| A1.12     | Balanced Austenite        | Balanced Austenite                       | Balanced Austenite                       | Balanced Austenite | Balanced Austenite | Balanced Austenite | Balanced Austenite | 0.0 | 0.0 | 0.0 | 0.0 | Balanced Austenite       | 0.00                       | 0.00                        |
| 0.45   | 0.45   | 0.45| 0.45| 0.45 | 0.45| A1.13     | Balanced Austenite        | Balanced Austenite                       | Balanced Austenite                       | Balanced Austenite | Balanced Austenite | Balanced Austenite | Balanced Austenite | 0.0 | 0.0 | 0.0 | 0.0 | Balanced Austenite       | 0.00                       | 0.00                        |
| 0.45   | 0.45   | 0.45| 0.45| 0.45 | 0.45| A1.14     | Balanced Austenite        | Balanced Austenite                       | Balanced Austenite                       | Balanced Austenite | Balanced Austenite | Balanced Austenite | Balanced Austenite | 0.0 | 0.0 | 0.0 | 0.0 | Balanced Austenite       | 0.00                       | 0.00                        |

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Table 7.1.4 Equivalence, phase, and microstructure table for Chapter 5 alloys.

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<th>Ni</th>
<th>Mo</th>
<th>Cr$_{eq}$</th>
<th>Ni$_{eq}$</th>
<th>Cr/Ni$_{eq}$</th>
<th>Predicted Phase at 500mm/s</th>
<th>Phase observed in EBSD</th>
<th>Observed Solidification Microstructure</th>
<th>Primary Solidification Mode</th>
<th>Area % Ferrite Content (Optical)</th>
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</thead>
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<td>2.22</td>
<td>19.42</td>
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<td>F/MA</td>
<td>Ferrite</td>
<td>Primary Ferrite</td>
<td>Primary Ferrite</td>
<td>100.0</td>
</tr>
</tbody>
</table>
Figure 7.2.1 Spatial distribution of austenite (F/MA) content for alloys A7-9 Chapter 3. (A-C)
Figure 7.2.2 Cell size means for Chapter 3 alloys 4-9 with 95% CI using individual standard deviations. (A-F)
7.3 - Images

Figure 7.3.1 High speed frame captures of two different SQ events. Symmetric platen impact is shown in (A), and staggered impact is shown in (B).