

DISSERTATION

UNDERSTANDING AND UTILIZATION OF THERMAL GRADIENTS IN SPARK  
PLASMA SINTERING FOR GRADED MICROSTRUCTURE AND MECHANICAL  
PROPERTIES

Submitted by

Alexander David Preston

School of Advanced Materials Discovery

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Colorado State University

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Doctoral Committee:

Advisor: Kaka Ma

Chris Weinberger

Jamie Neilson

Paul Heyliger

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## ABSTRACT

### UNDERSTANDING AND UTILIZATION OF THERMAL GRADIENTS IN SPARK PLASMA SINTERING FOR GRADED MICROSTRUCTURE AND MECHANICAL PROPERTIES

Spark plasma sintering (SPS), also commonly known as electric field assisted sintering, utilizes high density electric currents and pressure to achieve rapid heating and significantly shorter sintering times for consolidating metal and ceramic powders, which could otherwise be difficult, time consuming, and energy intensive. SPS has attracted extensive research interests since the early 1990's, with the promise of efficient manufacturing of refractory materials, ultrahigh temperature ceramics, nanostructured materials, functionally graded materials, and non-equilibrium materials. Thermal gradients occur in SPS tooling and the samples during sintering, which can be a drawback if homogeneous properties are desirable, as the temperature inhomogeneity can lead to large gradients in microstructure such as porosity, grain size, and phase distribution. Many researchers have looked to mitigate or control these gradients by design and use of specialized tooling. However, the effect of the starting powder is relatively less investigated or overlooked. Feedstock powders can come in various shapes, particle size distributions, and surface chemistry. Effects of these powder characteristics on the SPS process and the consequent microstructure of the sintered parts remain as a gap in the fundamental knowledge of SPS. To fill in this gap, my research investigated the role of thermal gradients during SPS, and how the thermal gradients subsequently affect the location-specific pore distribution, and the consequent mechanical properties of the materials. From a practical point of

view, design and fabrication of a bulk sample with a fully dense surface and an engineered pore architecture in the sample interior via one-step SPS will enable mechanical properties unattainable via conventional processing of fully dense bulk materials, such as alike combination of lightweight, high surface hardness, and wear resistance, and high toughness.

Therefore, the overarching goal of my research was to provide fundamental insights into the material processing - microstructure - properties correlation so that the field assisted sintering technology can be advanced to control location-specific microstructure. To fulfill this goal, two metallic materials were selected in my study, austenitic stainless steel and commercially pure titanium, representing inherently heavy but widely used alloys, and a pure metal that is inherently lightweight, these materials were used to investigate the effects of powder morphology on the sintering behavior. The pure Ti was selected specifically to gain fundamental insight into the effect of powder shape on sintering, while mitigating the concern of alloying/precipitation events and integrating FEM with my experimental work.

This work identified a relationship between decreasing pore size and increasing yield strength in stainless steel, which was attributed to fine precipitate formation surrounding submicron pores inducing local stiffening. Whereas larger pores where precipitates were not found are concluded to not have the necessary driving force for the precipitation event to occur. Ball milled stainless steel powders with higher aspect ratios were also shown to have smaller porosity gradients in comparison to their spherical gas atomized counterparts. A thermal electric finite element model is also proposed which incorporates the master sintering curve to simulate densification as an alternative to the more computationally costly and difficult to parametrize fully coupled thermal-electric-mechanical finite element model. Results from the combined model indicate strong agreement with experimental results within 2% accuracy of measured

densification. Additionally, the model predicts higher porosity gradients for gas atomized powders in comparison to ball milled powders which is experimentally verified.

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Lastly, I would like to thank my wife, parents, family, and friends without their constant support, love, and generosity I would not be anywhere near where I am today.

## DEDICATION

To my wife and family, without their constant support and love I would not be half the person I am today.

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## CHAPTER 1 Literature Review and Goals of My Research

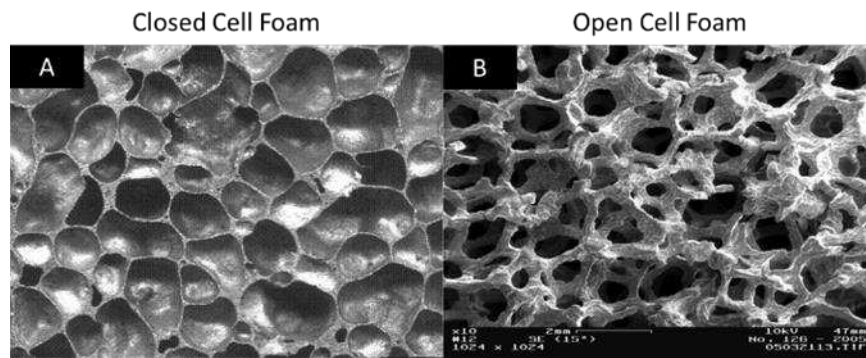
### 1.1 Introduction

Lightweight structural metals have become of increasing importance with each passing decade. With increasing need to further fuel efficiency in the automotive, aerospace, and defense industries to name a few. This has led to the rise in production of titanium, aluminum, magnesium, and their alloys in replacement of inherently heavier metals such as steel. However, the other option which has not been as extensively explored is the incorporation of porosity in the metallic structure, therefore lowering the metals overall density. This chapter supplies a literature review on the current production and research of porous metals, sintering mechanisms in powder metallurgy, spark plasma sintering, and the effects of powder characteristics. Based on this review, the overarching motivation and objectives of this research are outlined at the end of the chapter, with an overall goal of greater understanding of the impact that porosity has on mechanical behavior within metals, and how porosity can be further tailored to our benefit.

### 1.2 Porous Materials

Porous materials are important for applications in aerospace, energy, transportation, construction, electronics, biomedical and others, because of their advantages in weight savings, high permeability, high surface area, high impact energy absorption efficiency and so forth. Porous materials were first defined in two categories by Lorna J. Gibson and Micheal F. Ashby in 1987 as being either honeycombs or foams [1]. Foams can be further categorized into open cell foams and closed cell foams, as depicted in Figure 1:1. Open cell foams exhibit interconnected or continuous pores, whereas closed cell foams have pores entirely enclosed by the parent material. Because of these distinct differences in structure (i.e. open porosity vs closed porosity), there are also expected differences in both functional and mechanical behavior. Open

cell foams provide a high surface to volume ratio, superior permeability, and low sound conductivity, which make them excellent for catalysts, gas filters, and soundproofing materials. However, the mechanical properties of open cell foams are less desirable due to its interconnected porosity and potential for brittle fracture. In contrast, closed cell foams have a great potential in mechanical applications as the collapse of the enclosed and isolated pores upon compressive stresses provide improved plastic strain. This research is relevant to the closed pore structure.



**Figure 1.1:** Representative microstructure of (a) closed cell foams and (b) open cell foams [2]

Gibson and Ashby developed a series of mathematical models to predict the mechanical properties of foam materials, as shown in Table 1 [1], [3]. According to the Gibson-Ashby models, the Young's modulus and shear modulus of open cell foams are proportional to the relative density squared,  $\left(\frac{\rho^*}{\rho_s}\right)^2$ . In contrast, the modulus of closed cell foams depends on both the relative density and the volume fraction porosity, following a more complex polynomial relation. The yield strength of the open cell foams is proportional to the relative density to the two-thirds power, while the yield strength of closed cell foams is inversely proportional to the relative density. It is worth noting that neither the pore size nor the pore distribution is considered in the Gibson-Ashby models.

**Table 1. 1:** Elastic properties equations for both open and closed cell foams [1], [3]

| Open Cell Foams                                                                         | Closed Cell Foams                                                                                                                                                                             |
|-----------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\frac{E^*}{E_s} = C * \left(\frac{\rho^*}{\rho_s}\right)^2$                            | $\frac{E^*}{E_s} \approx C * \phi^2 * \left(\frac{\rho^*}{\rho_s}\right)^2 + (1 - \phi) * \left(\frac{\rho^*}{\rho_s}\right) + (\rho_s * \frac{1 - 2\nu}{E_s * (1 - \frac{\rho^*}{\rho_s})})$ |
| $\frac{G^*}{E_s} = C * \left(\frac{3}{8}\right) * \left(\frac{\rho^*}{\rho_s}\right)^2$ | $\frac{G^*}{E_s} \approx \left(\frac{3}{8}\right) * C \left[ \phi^2 * \left(\frac{\rho^*}{\rho_s}\right)^2 + (1 - \phi) * \left(\frac{\rho^*}{\rho_s}\right) \right]$                         |
| $\frac{\sigma_y^*}{\sigma_s} = C * \left(\frac{\rho^*}{\rho_s}\right)^{\frac{2}{3}}$    | $\frac{\sigma_y^*}{\sigma_s} = C * \left(\frac{\rho_s}{\rho^*}\right)$                                                                                                                        |

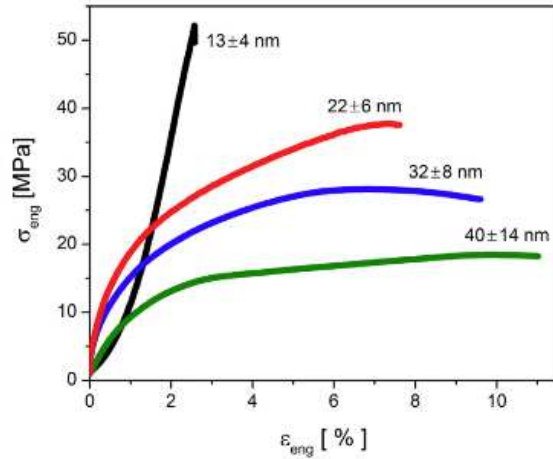
In Table 1,  $E^*$ ,  $G^*$ ,  $\nu$ ,  $\rho^*$ ,  $\sigma_y^*$ ,  $\sigma_s$ ,  $E_s$ ,  $\rho_s$ ,  $\phi$ , and  $C$  are the elastic modulus, the shear modulus, the Poisson's ratio, the density of porous material, the yield strength of the porous material, the plateau strength of the porous material, the Young's modulus of the parent material, the density of the parent material, the volume fraction porosity in the material, and a correction factor generally with a value of 1 or close to 1, respectively.

Previous experimental studies are in general agreement with the Gibson and Ashby equations for homogenous macro-porous metals, including aluminum [4], [5], titanium [6], [7], and stainless steels[8]–[10]. However, the Gibson-Ashby models still have several limitations. First, the distribution of pores is assumed to be uniform throughout the entire sample in the model, leading to overestimation of mechanical property values such as bulk modulus and hydrostatic yield strength [11]. To address this limit, additional models called “super cell models” were developed to better represent foams with heterogeneous microstructure. Interruption in the structural periodicity was incorporated in these super cell models [11]. Second, the Gibson-Ashby models are not readily adapted to the nanoscale. Due to the ultrahigh surface to volume ratio, the effect of free surfaces in nanoporous materials can no longer be ignored as they are at the macro and micro scales. As the ligament size decreases to the nanoscale, it is not feasible to

use bulk properties to characterize the ligament. The reduced coordination number of atoms on the ligament surface and redistribution of electrons effectively softened or stiffened the material [12]. Hodge *et al.* suggested that this change in ligament size also restricted the multiplication of dislocations severely, and subsequently changed the yield strength of the material. They found that Au foams with a relative density of 30% and ligament sizes ranging from 900 nm to 40 nm had yield strengths of ~10 MPa to ~100 MPa, respectively, whereas the Gibson-Ashby model would predict a yield strength of ~12 MPa for this material given its relative density, volume fraction porosity, and parent material properties [1], [13]. Hodge *et al.* then proposed a modified model that incorporates the effect of ligament size, known as the modified foam scaling equation [13]:

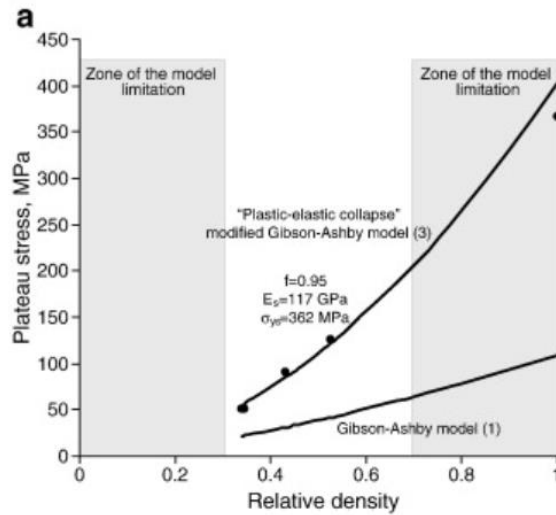
$$\text{EQ(1.1)} \quad \sigma^* = C_s \left[ \sigma_0 + k * L^{-\frac{1}{2}} \right] * \left( \frac{\rho^*}{\rho_s} \right)^{\frac{3}{2}}$$

Where  $\sigma^*$ ,  $\sigma_0$ ,  $C_s$ ,  $k$ , and  $L$  represent the foam's yield strength, the bulk material's yield strength, a fitting coefficient, a Hall-Petch type coefficient for theoretical yield strength of a material, and the ligament size, respectively. A few other studies showed that nanoporous open cell foams had larger yield strengths or elastic moduli than those of a fully dense bulk counterpart, and the experimental data agreed well with the modified foam scaling equation [14]–[16]. However, these nanoporous materials had very poor fracture performance, due to a ductile to brittle transition as ligament size was reduced. Luhrs *et al.* also found that the ductility of nanoporous Cu-Ni decreased as the average ligament size decreased from 40 nm to 13 nm; when the ligament size was 13 nm or below, the nanoporous Cu-Ni became brittle, as shown in Figure 1.2 [17]. The fracture mechanics of nanoporous materials still attract extensive researches [17]–[19].



**Figure 1.2:** Compression testing of nanoporous copper-nickel with varying ligament size [17]

Lastly, the Gibson-Ashby models are not intended for materials with relative densities outside the 30% to 70% range, as suggested in Figure 1.3 [3].



**Figure 1.3:** Gibson-Ashby equations predicted limitations [3]

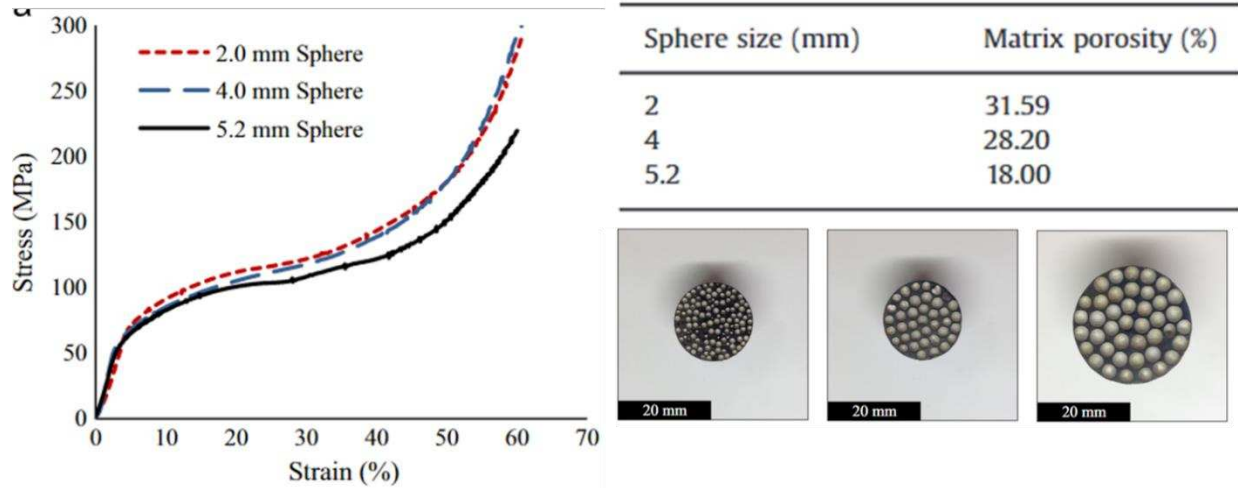
While foam materials with relative densities ranged from 30% to 70% have been extensively investigated, rarely are closed cell foams with densities between 70% and 90%. This is most likely because of the concern of crack nucleation at pores, with limited payoff in weight savings given the relative density is between 70%~ 90%. The fracture strength of a material decreases as its flaw size increases, according to Griffith's equation below [20].

$$\text{EQ(1.2)} \quad \sigma_f * \sqrt{a} = \sqrt{\frac{2E\gamma}{\pi}}$$

Where  $\sigma_f$ ,  $a$ ,  $E$ ,  $\gamma$  are the fracture stress, flaw size, Young's modulus, and surface energy, respectively. It should be noted that given a same overall relative density, the fracture strength can be increased when the flaw size is decreased. In addition, although pores are commonly regarded as preferential sites for crack nucleation, pores also have the potential to retard crack propagation by both blunting the crack tip as it propagates and deflecting the crack in a new direction if the pores have a fairly spherical shape [18]–[22]. The change in Cauchy stress due to crack blunting was first described in an equation derived by Irwin *et al.* in the 1950's:

$$\text{EQ(1.3)} \quad \sigma_{i,j} = \frac{K}{\sqrt{2\pi r}} * f_{i,j}$$

Where  $\sigma_{i,j}$ ,  $K$ ,  $r$ , and  $f_{i,j}$  are the Cauchy stress, stress intensity factor, distance from the crack tip, and a factor based on geometry, respectively. If a crack is infinitely sharp, at the tip of the crack, the Cauchy stress is close to infinity, i.e.,  $r \rightarrow 0$ ,  $\sigma_{i,j} \rightarrow \infty$ ; however, if the crack interacts with a secondary 3-D defect with a spherical shape, the curvature of the crack tip is increased. The increased crack tip curvature corresponds to a higher value of  $f_{i,j}$ , and consequently increases the critical stress required for crack propagation to continue [25]. Alvandi-Tabrizi *et al.* made macroporous stainless steel by sintering hollow stainless steel spheres with secondary powder as a matrix to bind the hollow spheres together [26]. They found that the size of the hollow sphere directly impacted the matrix porosity, as shown in Figure 1.4, even with each sample undergoing the same processing conditions. In addition, at quasi-static strain rates, the 2 mm spheres exhibited the highest yield stress. However, the overall volume fraction porosity for each sample or the effect of the spatial distribution of pores on the mechanical properties were not discussed in this study.



**Figure 1.4:** Stress-strain curves for metallic foams with different pore sizes [26]

### 1.3 Sintering Mechanisms in Powder Metallurgy

This research utilizes powder metallurgy (PM) to synthesize the metallic closed cell foam.

Compared to bulk materials, powders are relatively unstable from a thermodynamic perspective.

A large driving force for diffusion is provided to the powders when energy is added during sintering. This allows the system to reach a state closer to or at equilibrium depending on the amount of energy given to the system and the total time the system is allowed to evolve towards equilibrium. The change in Gibbs free energy during sintering can be grouped into two different terms: the change in surface energy and the change in volumetric energy, shown in equation 4.

$$\text{EQ(1.4)} \quad \Delta G_{total} = G_V \Delta V + \gamma \Delta A$$

Where  $\Delta G_{total}$ ,  $G_V$ ,  $\gamma$ ,  $\Delta V$ , and  $\Delta A$  are the change in total Gibbs free energy, the volumetric free energy, the surface free energy, the change in volume, and the change in surface area. The equilibrium condition where the total change in Gibbs free energy is zero can therefore be written as:

$$\text{EQ(1.5)} \quad 0 = G_V dV + \gamma dA$$

Assuming the powder is spherical particle, the volumetric and surface area differentials can be written as:

$$\text{EQ(1.6)} \quad dV = 4\pi r^2 dr$$

$$\text{EQ(1.7)} \quad dA = 8\pi r dr$$

Where  $r$  is the radius of the particle. Combining equations 5-7, we find the following relationship:

$$\text{EQ(1.8)} \quad G_V = \gamma * \frac{8\pi r dr}{4\pi r^2 dr} = \gamma * \frac{2}{r}$$

This can further be rewritten as:

$$\text{EQ(1.9)} \quad G_v = \gamma * \left[ \left( \frac{1}{r_1} \right) + \left( \frac{1}{r_2} \right) \right]$$

Where  $1/r_1$  and  $1/r_2$  are the principal curvatures which can be used to describe a 3-D surface.

Therefore, the reduction in Gibbs free energy is driven by the change in curvature, leading to densification of the powder compact during the sintering process. The diffusion equation for sintering was derived via conservation of mass. The change in concentration with respect to time is equal to the total flux of the material in equation (10).

$$\text{EQ(1.10)} \quad \frac{\partial c}{\partial t} = \nabla \cdot J$$

Where  $c$ ,  $t$ , and  $J$  are defined as the concentration, time, and the mass flux. Fick's first law equates the mass flux based upon the concentration gradient, which is further scaled by a diffusion rate in equation (11).

$$\text{EQ(1.11)} \quad J = -D \nabla c$$

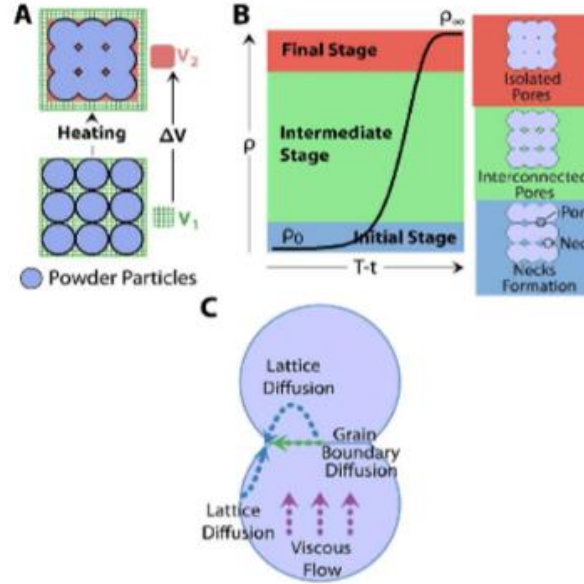
Where  $D$  is the diffusion rate of the material. The diffusion rate defined by the following Arrhenius equation:

$$\text{EQ(1.12)} \quad D = D_0 \exp \left( -\frac{Q}{RT} \right)$$

Where  $D_0$ ,  $Q$ ,  $R$ ,  $T$  are defined as a diffusion coefficient, activation energy, the gas constant, and temperature, respectively. The combination of equations 10-12 resulted in the general equation for downhill diffusion:

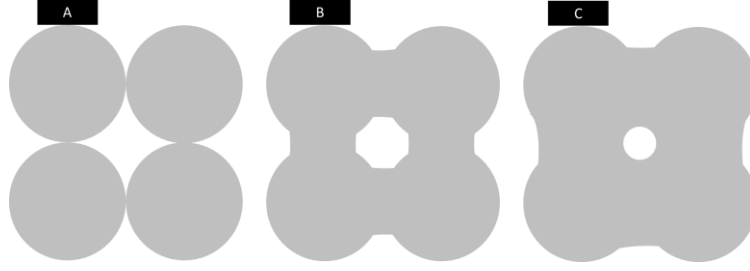
$$\text{EQ(1.13)} \quad \frac{\partial c}{\partial t} = \nabla \cdot [-D \nabla c]$$

Three distinct stages are observed during sintering, known as the initial stage, the intermediate stage, and the final stage, as illustrated in Figure 1.5.



**Figure 1.5:** Three densification stages during sintering and the associated diffusion mechanisms [27]

These three stages are defined by the relative density of the powder compact and the diffusion mechanism that dominates each stage. Surface diffusion dominates in the initial sintering stage, and necks form at the particle-particle contacts, as shown in Figure 1.6. Neck formation is driven by the reduction in the Gibbs free energy as necking lowers the curvature of the particles, according to equations (4-9).



**Figure 1.6:** Picture A shows initial particle packing, picture B shows neck formation and growth, and picture C shows a stable pore.

The amount of densification is minimal at the initial sintering stage where the pores remain interconnected. During the intermediate stage of sintering, volumetric diffusion dominates, as the increased temperature promotes vacancy formation and self-diffusion through the bulk of the particles. Consequently, the necking areas between powder particles grow, contributing to further densification. In addition, creep mechanism is activated by the increase in temperature at the intermediate sintering stage, which results in viscous flow of the powder particles and significant densification (relative density increased from ~ 55% to ~90%). At the intermediate stage of sintering, some pores maintain interconnectivity while others become isolated, depending on the relative curvature of the starting particles and the local relative density of the powder compact. In the final stage of sintering, the curvatures of the particle-particle contact areas become stable, which lowers the driving force for surface diffusion, and therefore, densification comes to a halt. Thermodynamically stable pores are sustained, the size and curvature of which depend on the total thermal energy within the powder compact, as well as the sintering time at a specified temperature. During this stage, grain boundary diffusion dominates, and grain growth occurs. The total grain boundary area is reduced at the final sintering stage, leading to the reduction of the total Gibbs' free energy of the system. The grain growth velocity at any spatial location on the grain boundary which is modeled based on its curvature:

$$\text{EQ(1.14)} \quad v = M\sigma\kappa$$

Where  $v$ ,  $M$ ,  $\sigma$ , and  $\kappa$  are the grain growth velocity, grain boundary mobility, the grain boundary energy and the sum of the principal curvatures. Assuming only normal grain growth occurs, the grain growth can be determined via the following equations:

$$\text{EQ(1.15)} \quad d^2 - d_0^2 = kt$$

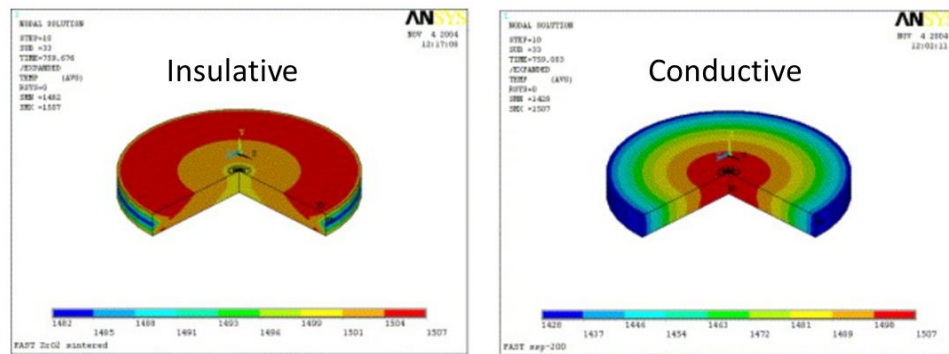
$$\text{EQ(1.16)} \quad k = k_0 \exp\left(-\frac{Q}{RT}\right)$$

Where  $d$ ,  $d_0$ ,  $k$ ,  $t$ ,  $k_0$ ,  $Q$ ,  $R$ ,  $T$  are final grain size, initial grain size, temperature dependent constant, time, experimentally fitted constant, grain boundary activation energy, gas constant, and temperature, respectively. Grain sizing classically is conducted via etching followed by a linear intercept method where a line of a given distance is drawn across a photo and then the divided by the number of intercepts yielding an average grain size.

#### 1.4 Spark Plasma Sintering

The sintering mechanisms discussed earlier apply to spark plasma sintering (SPS). SPS is a powder consolidation method used in this work that allows for high heating rates (<100<sup>0</sup>C/min) in comparison to conventional sintering techniques such as hot-pressing or free sintering. This is achieved via joule heating where direct current (DC) passes through tooling and the powder sample depending on the tooling and powder materials used. However, the role of DC that leads to thermal gradients in the SPS process has not been fully understood, leaving a fundamental gap in the field which restricts scalability and reproducibility when using the SPS for powder consolidation [28]. If the powder used is insulative, then we expect to see the highest temperature within the powder compact to occur at the edge of the sample, with the lowest temperature occurring at the center of the sample. This is due to the DC current passing through the graphite die which has a higher conductivity than the powder. But, if the powder is conductive and has a higher conductivity than the tooling, we would expect the current to move through the sample and would expect the highest temperature to be at the center of the sample

with the lowest temperature at its edge. Additionally, if the powder is conductive the fraction of electrical current flowing through the powder vs the die will substantially change during the sintering process. This is because as the metallic sample densifies it becomes more conductive from the elimination of porosity, meaning more current will flow through the sample and a larger electrical/thermal gradient occurs. Regardless of the powder being conductive or insulative, thermal gradients have been observed in both the powder and tooling, especially when scaled up leading to large gradients in microstructure [29], [30]. These thermal gradients for both a conductive and insulative material are illustrated in the figure below[30].



**Figure 1.7:** Thermal gradients present in both insulative and conductive samples

Futhermore, these trends in thermal gradients have been successfully identified via finite element method (FEM) and confirmed experimentally for SPS [31]–[36]. Most previous studies investigated why thermal gradients occur in the SPS including tooling geometries, heating rates, powder composition, initial density, and the electrical conductivity of the sample [37]–[39]. Axial thermal gradients are currently thought to be the result of tooling misalignment which causes the top and bottom surfaces of the sample to not experience the same temperature due to the sample not being centered in the Z-direction [40]. Radial thermal gradients are attributed to the current distribution and radiative heat loss from the surface of the die. Some groups such as Olevsky’s seek to eliminate thermal gradients within the sample in order to obtain a homogenous

microstructure as described in their study on constructing multiple complex parts from Ni powder in the SPS [41]. However, it is important to understand thermal gradients are not always undesirable. In fact, if controlled correctly they can lead to the synthesis of desirable heterogenous structures. In addition to high heating rates, the SPS process requires uniaxial pressure which ensures that a constant conductive pathway is maintained, and arcing does not occur during the run. The chamber is either under vacuum or filled with an inert gas during operation, which prevents any external reactions with either the tooling or the sample during the run.



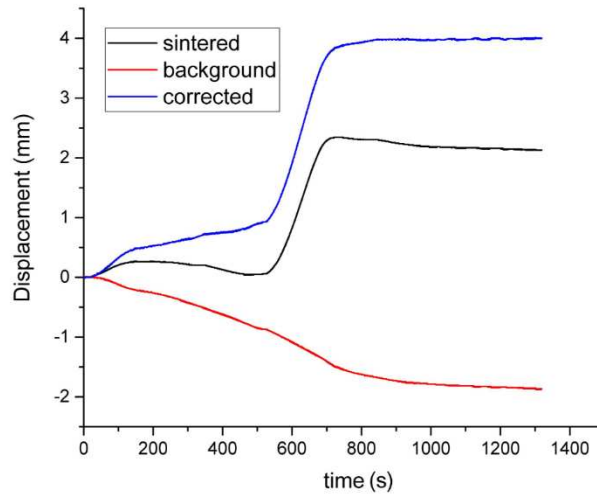
**Figure 1.8:** Spark Plasma Sintering machine located at the Factory

Pressure, heating rate, holding temperature, and holding time are essential variables for tunability and control of the densification process of the powder sample during SPS. During sintering, multiple parameters are recorded to allow for data analysis and further manipulation of the process. These include voltage, current, temperature, uniaxial force, displacement, displacement rate, and chamber pressure. Also knowing the consolidated final height of the

sample is essential to estimating the relative density of the sample during sintering via equation 17 below.

$$\text{EQ(1.17)} \quad \rho = \rho_f * \left[ \frac{h_f}{h_f + \text{disp}} \right]$$

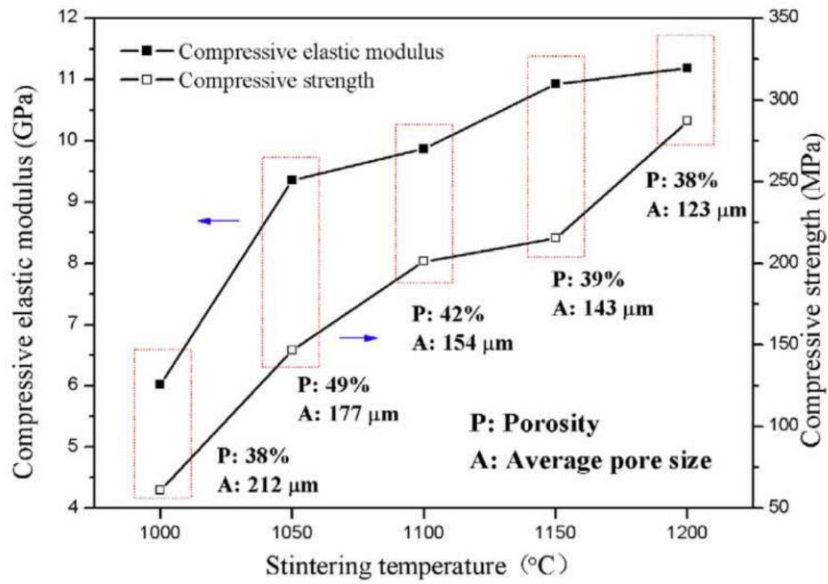
Where  $\rho$ ,  $\rho_f$ ,  $h_f$ , and  $\text{disp}$  are density, final density, final height, and displacement. Mapping the relative density vs temperature yields what is commonly known as a relative density curve. This allows the user to select a holding temperature to produce a sample with a desired density assuming all other variables mentioned prior other than temperature are held constant. An additional run is needed with only the tooling to extract thermal expansion information which can later be subtracted from a run with powder as illustrated in Figure 1.8.



**Figure 1.9:** Displacement curves from an SPS experiment [42]

These relative density curves allow for the study of porous materials using the SPS process. While most studies using spark plasma sintering have focused on minimizing grain growth and fully dense materials, some SPS studies have been centered around investigating foam structures. Groups have studied how changes in SPS parameters can change the final structure of open cell foams, but most of these studies do not attempt any mechanical testing [43]–[46]. Other studies such as that done by Dudina *et al*, did limited mechanical behavior testing via compression

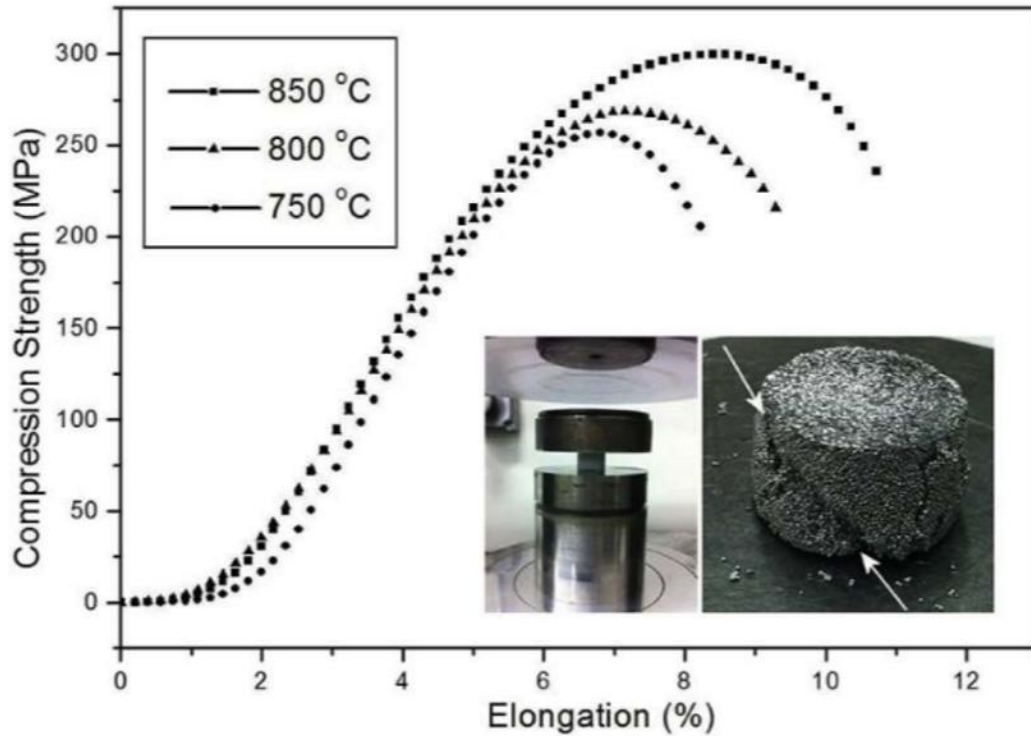
testing, but do not consider pore distribution or average pore size [44]. Zhang *et al.* studied open cell Ti foams with porosity volume fractions between 38% and 58% with large pores  $50\mu\text{m}$  to  $500\mu\text{m}$  in size, the foam was synthesized via SPS and also incorporated the use of a secondary phase that is vaporized during sintering leaving pores in its place [47]. This study found that both decreasing pore size and decreasing volume fraction porosity lead to higher compressive elastic modulus and higher compressive strength in Figure 1.9 below.



**Figure 1.10:** Compressive strength and elastic modulus of open foam titanium samples with varying volume fraction porosity and average pore size.

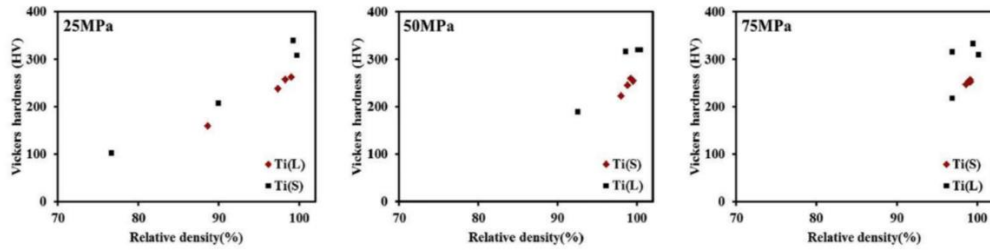
Comparing the sample sintered at  $1000^{\circ}\text{C}$  and the sample sintered at  $1200^{\circ}\text{C}$ , we observe the same volume fraction porosity, but with a change in average pore size. This decrease in pore size comes with increases in both the compressive strength and compressive elastic modulus. This study also did not discuss any porosity gradient within the sample. Yamenoglu *et al.* conducted a study on a  $\text{Ti5Al2.5Fe}$  alloy which used different holding temperatures of  $750^{\circ}\text{C}$ ,  $800^{\circ}\text{C}$ , and  $850^{\circ}\text{C}$  to synthesize samples with isolated porosity varying between 29.1% to 28.4% volume

fraction porosity [48]. Their results indicated increasing yield strength and compressive strength with decreasing volume fraction porosity which can be seen in Figure 1.10.



**Figure 1.11:** Compressive strength of Ti5Al2.5Fe with varying volume fraction porosities.

This study focused on volume fraction of pores without investigating either pore distribution or average pore size. Motsi *et al.* also conducted experiments on pure titanium but looked at materials with higher relative density ranging from  $\approx 76\%$  to 100%, only one sample was below 90% relative density [49]. The method they used to control the relative density was by changing the average particle size and pressure, while keeping holding temperatures constant. They conducted microhardness testing and found an increase in hardness with a decrease in relative density regardless of the pressure or initial particle size used as depicted in Figure 1.11.



**Figure 1.12:** Hardness vs relative density sintered at multiple pressures

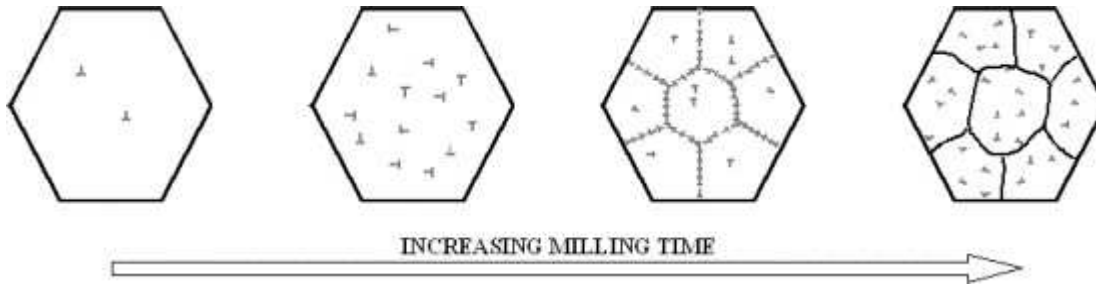
Motsi *et al.* did not discuss the average pore size or porosity distribution throughout the samples. To my knowledge, there has only been one paper to actively investigate the radial porosity created by the SPS due to thermal gradients [50]. They concluded the shape of the radial porosity distribution and radial temperature distribution were similar. However, they did not consider pore size and the relative density was calculated via axial displacement. This leaves some large fundamental gaps in research using SPS as the process for powder consolidation, including the influence of thermal gradients on different porosity characteristics, the effect of pore size on mechanical properties within the 70%-90% relative density regime, and the effect of pore distribution on mechanical properties.

### 1.5 Effect of Powder Characteristics

The characteristics of the powder play a key role in the sintering behavior and the microstructure of the final solid material. The three predominant characters of the starting powder are: chemical composition, microstructure, and morphology. The chemical composition controls a large portion of how sintering occurs in the system as these local chemical gradients change the local chemical potentials that drive diffusion. Equations (4-16) include intrinsic properties such as activation energy, surface energy, and volumetric energy, all of which are connected to local chemical composition and work towards lowering the Gibbs free energy via sintering. However, these properties are all dependent upon the microstructure which is inclusive of the homogeneity of the sample at both the macro and micro scale. These inhomogeneities can

give rise to gradients and abnormalities across a sample. The powder morphology refers to the shape and size of the particle. Gas atomized (GA) particles generally start off with a powder size range on the order of a 100  $\mu\text{m}$  and are round. GA powders are formed by melting the parent material and then forcing a fine distribution of droplets within a cooling inert gas which rapidly cools the droplets. This rapid cooling of the liquid droplets forms spherical powders which are commonly used as a feedstock material for powder metallurgy. Both the size and shape of these feedstock powders can be varied via powder processing. Powder processes used in this work include sieving, planetary ball milling, and cryomilling. Sieving is used to get specific powder size ranges. Sieving must be done multiple times with the individual sieve plus powder weights recorded to assure powder flow between sieves has stopped and the captured distribution is accurate. Therefore, this method can be used as a tool to analyze a size distribution of a starting powder or to only use a specific size distribution for experiments.

Planetary ball milling is a method of changing a feedstock's size, morphology and microstructure. Powder is loaded into a milling jar with balls which act as the grinding media in the system and these jars are then subsequently loaded into the ball mill. The jars are then rotated at a high RPM around the center of the mill; however, the jars are also able to rotate around their own center during milling. This high energy milling causes a large amount of plastic deformation to the powder as it is compressed against jar walls and between balls. The plastic deformation is caused by two forms of stress: compressive and shear [51]. This plastic deformation leads to a high dislocation density in the powder during milling which evolves into the reduction of grain size via dislocation pile up and annihilation cycles as shown in Figure 1.12.



**Figure 1.13:** Grain refinement during milling. [52]

Reduction in grain size leads to an increase in hardness and yield strength which can be described by the Hall-Petch equations:

$$\text{EQ(1.18)} \quad \sigma_y = \sigma_0 + \frac{k}{\sqrt{d}}$$

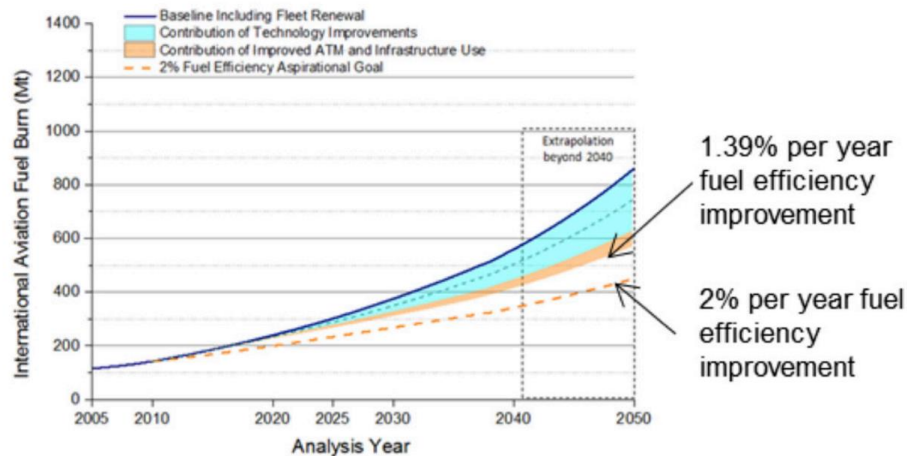
$$\text{EQ(1.19)} \quad H = H_0 + \frac{k}{\sqrt{d}}$$

Where  $\sigma_y$ ,  $\sigma_0$ ,  $H$ ,  $H_0$ ,  $k$ , and  $d$  are yield strength, material constant strength, hardness, material constant hardness, fitting coefficient, and grain size. Planetary ball milling can also reduce particle size via fracture and will change the morphology of the particle depending on ball size, process control agent (PCA) used, as well as the amount of time milling occurred.

Cryomilling is another mechanical milling technique that can change the particle size, morphology, and microstructure of metallic powders. Liquid nitrogen is used to keep the milling temperature around -185°C. The liquid nitrogen directly contacts the powder during milling, which may change the composition of the powder via nitriding. After the mill has been cooled, feedstock powder is also loaded into the container. Similar to planetary ball milling, plastic deformation occurs due to high resolved stresses from both compression and shear [51]. This leads to dislocation pile up, but without enough thermal energy for the dislocations to annihilate, the dislocation density grows extraordinarily quickly. This causes reduction in grain size to occur at a much faster rate than standard milling, allowing grain sizes starting in the micron range to be reduced to the nanometric range in a matter of hours instead of days [52].

## 1.6 Motivation

From the practical point of view, the primary motivation of my work is to create light-weight structures with improved or equivalent mechanical properties compared to fully dense counterparts. Lightweight materials and structures are important for our society for many reasons, including but not limited to: increasing fuel efficiency, reducing environmental damage by lowering CO<sub>2</sub> during processing, and increasing a materials specific strength. The need for increased fuel efficiency is and will continue to be a very pressing subject for many forms of transportation such as the automobile, aerospace, defense, and space industries. Figure 1.13 below, shows the gap between expected fuel burned by international flights (orange solid fill) with 1.39% annual improvement in efficiency each year. The figure also shows the limit on fuel burn for airplane travel to be carbon neutral assuming other carbon offsets (orange dashed line) which calls for an annual efficiency improvement of 2% per year according to the ICCT (International council of clean transportation) [53].



**Figure 1.14:** Projected international aviation fuel burn assuming 1.39% annual fuel efficiency improvement in orange, and the necessary 2.0% annual fuel efficiency in black for a carbon neutral form of transportation according to the ICCT

The value of lowering the weight and therefore increasing fuel efficiency are large in some areas such as the aerospace industry and astronomical in others such as the space industry. In

order to do this, there are two paths forward: use lower density materials such titanium, aluminum, magnesium, etc., or create structures with lower density by incorporating porosity. As previously discussed, open cell foams have been and continue to be extensively researched, but they still have their own set of problems and limitations. Some of these include a lengthy non-environmentally friendly processing route, brittle to ductile fracture transitions with nanometric foams, limited material options when using dealloying which requires an immiscible system and leaves only a monolithic system post leeching, and scalability. However, limited research has been done with closed cell foams specifically within the 70%-90% relative density range. This range allows for a reduction in weight of 10%-30%, while also allowing for many more processing techniques such as metallic foaming, metal sphere sintering, and powder metallurgy. While crack propagation is of concern for materials within this regime, we believe the risks can be mitigated with careful control of flaw size, shape, and distribution. Lastly, results shown by Alvandi-Tabrizi, *et al.* from North Carolina State University indicate there may be a scaling law between pore size and mechanical behavior which has not been explored for closed cell foams [26]. As discussed above, researchers have focused on either fully dense structural materials, namely 95-99% dense, or highly porous materials such as metal foams (volume percent porosity higher than 30%). Introducing pores effectively reduces the weight of the components, potentially leading to increased specific strength and impact toughness. For a given overall porosity, reducing the pore size to the submicron and nanoscale regime can improve strength and deformability. Therefore, control of pore distributions will enable further tunability of mechanical properties and enable lightweight structures, as well as advance our fundamental understanding of porous materials. Specifically, design and fabrication of a bulk sample with a fully dense surface, which still provides high hardness, wear resistance and corrosion resistance,

and an engineered pore architecture in the sample interior (e.g., with submicron pores and radially descending local volume fraction from internal center to surface) in one-step SPS will advance the material's mechanical properties (specific strength, impact energy absorption efficiency, damping capability) to levels unattainable via conventional processing of fully dense bulk structural materials.

## 1.7 Research Goal

Based on the literature review above, effects of starting powder characteristics on the SPS process and the consequent microstructure of the sintered parts remain as a fundamental knowledge gap, thus limiting the advance of SPS technique for more precise control of material microstructural evolution. To fill in this knowledge gap, the overarching goal of my research was to provide fundamental insights into the material processing - microstructure - properties correlation so that the field assisted sintering technology can be advanced to control location-specific microstructure, particularly how to control pore distributions. The hypothesis was that the starting powder characteristics would induce different extents of thermal gradients in SPS, which subsequently affect the diffusion kinetics and creep behavior behind the densification, leading to location-specific pore characteristics, e.g., size and volume fraction. More specifically, this project aims to answer the following questions: (1) What is the predominant factor that controls the local distribution of pores, temperature or temperature gradient? (2) How can the FEM of temperature distributions in the sample during SPS be integrated into the experimental study of microstructure to predict location-specific pore distribution? (3) What material-dependent factor(s) need to be identified for the prediction of location-specific pore distributions? By answering these questions, we are able to predict porosity gradients that occur during the SPS process, which further guide the selection of processing parameters.

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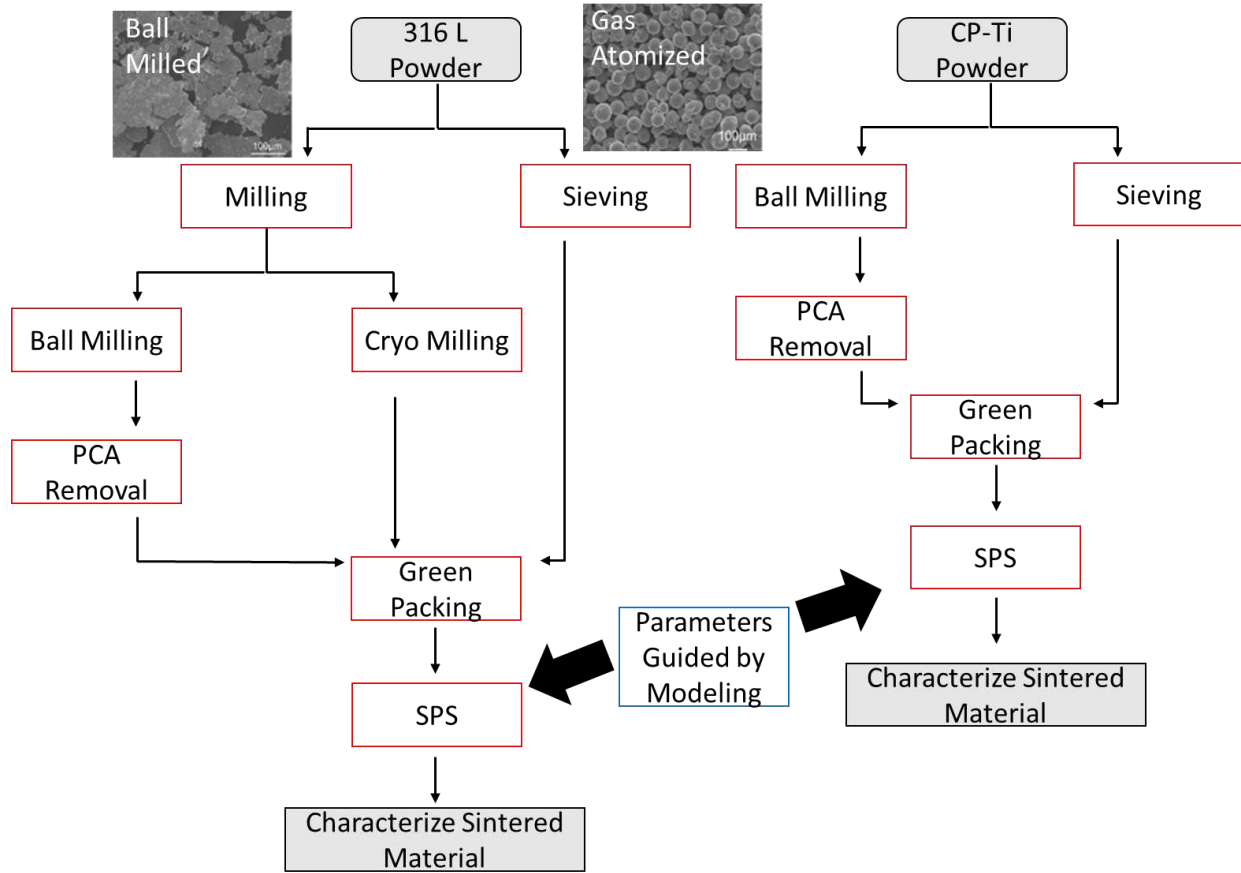
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## CHAPTER 2 General Approach

This chapter will describe the general approach in my study, including experimental strategy, modeling basis, and characterization methods. More explicit procedures and details are provided in individual chapters.

### 2.1 Experimental Strategy

In this study two different powdered materials were utilized, austenitic stainless steel 316 L (SS 316L) and commercially pure titanium (CP-Ti). Stainless steel was chosen as a representative of an inherently heavy alloy which could greatly benefit from lower density; while commercially pure titanium was chosen as an already lightweight unalloyed metal which is a popular choice among industries where specific strength is of utmost concern. These powders were sometimes sieved to collect a specific size distribution or ball milled to change their overall morphology. Milling and sieving allowed me to identify the impact of powder characteristics on the sintering process and porosity characteristics. During ball milling a process control agent (PCA), steric acid, was implemented for some studies to reduce cold welding of the powder, this was removed after milling by rinsing the powders multiple times in 200 proof ethanol, the powders were then subsequently heated to 100°C to remove residual moisture. After which, powders were green packed at 40 MPa within a graphite die and loaded into the spark plasma sintering system, where the system was heated at rates between 50°C/min to 150°C per minute with pressure ranging from 10 to 40 MPa. The system was then allowed to cool, and the sample was removed from the SPS when temperatures were below 100°C at the die surface. Samples were then removed from the die, followed by grinding and polishing for characterization. This general procedure is illustrated in the figure below.

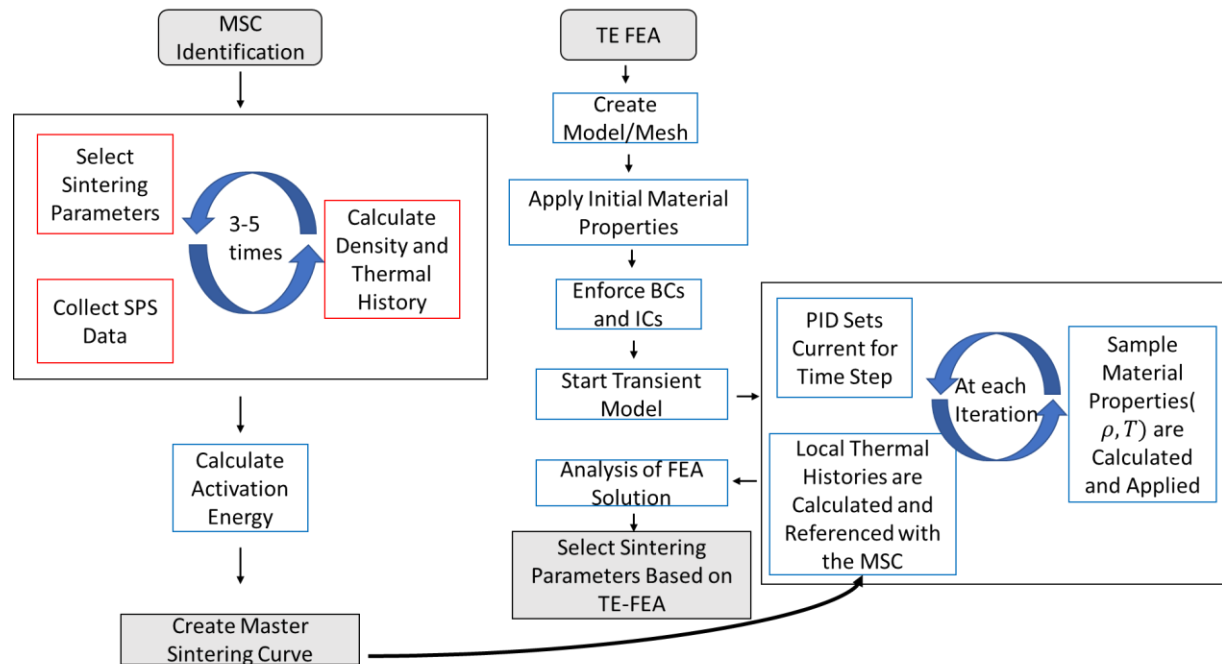


**Figure 2.1:** General experimental approach flowchart, where blue boxes represent computational steps and red boxes represent experimental steps

## 2.2 Modeling Basis

The modeling used in this study is confined to two parts, the master sintering curve (MSC) and thermal-electric finite element analysis (TE FEA) model. The MSC is a process that allows a researcher to accurately predict density based on thermal history of a material, while the TE FEA model is the simulation which is implemented to predict the location specific thermal history of a material based upon sintering parameters. In this study, the master sintering curve is first created with small scale 20 mm diameter samples which are sintered at multiple heating rates where the displacement, time, and temperature are all recorded during the sintering run. The activation energy is then determined by minimizing the mean residual square between the

experimental densification curves with respect to the experimental thermal history. Matlab scripts (Appendix D1-D4) are then used for identification of the activation energy for the powder. The TE FEA model is then implemented to simulate the thermal and electrical conditions of the SPS during a sintering run for a larger 66 to 70 mm diameter sample. For the simulation to work current needs to be an input at the start of each time interval during the simulation, this is done by simulating a proportional-integral-derivative controller within a subroutine (Appendix E1) which is called by the FEA software ABAQUS. The PID controller increases or decreases the current based upon the temperature of a simulated thermal couple to approximate a sintering run with prescribed conditions. Another subroutine (Appendix E1) is then used to predict the density at each simulated node within the FEA model based on the experimentally verified MSC. Finally, a larger 66 to 70 mm diameter sample is created to verify the simulated results.



**Figure 2. 2:** General modeling approach flowchart, where blue boxes represent computational steps and red boxes represent experimental steps.

### 2.3 Characterization Methods

This study characterized both the materials microstructure and mechanical properties in order to get a holistic understanding of the impact of powder characteristics and sintering environment on the final sintered sample. A key to the success of this study was to fully understand all aspects of porosity. To first determine the entire volume fraction of porosity within a sample, both geometric density and Archimedes density were taken which allows for the calculation of relative density and helps us to understand the densification of the sample during the SPS process. However, this doesn't tell us how the pores are distributed which can be related to thermal gradients and impact mechanical/functional properties, in order to determine this aspect both SEM and Micro-CT were used. SEM allows us to determine the distribution at a single site regardless of the pore size, where as Micro-CT can give us more statistically significant data by measuring larger areas, but is unable to detect pores which are smaller than 10 microns. To characterize the pore shape and size, SEM was once again implemented with multiple images taken at a specific location and then analyzed using image J software.

In addition to pores the composition and general microstructure were important to determine within this study. X-ray diffraction characterized any change of phase/ grain refinement occurred during the ball milling process, both of which have great impact on the mechanical properties of the material. While, energy dispersive X-ray spectroscopy was implemented to look for local changes of composition, specifically at pore and particle interfaces. To determine local grain size two methods were used, the first was a classic etching followed by SEM imaging process; the second, was electron back-scatter diffraction (EBSD), both were instrumental in relating the local mechanical properties to local grain structure.

The mechanical testing within this study was performed at multiple length scales, testing performed at the micro level allowed for fine evaluation at specific locations such as interfaces.

These tests provided information about the materials hardness and wear resistance using nanoindentation and nano scratch testing. While testing at the macroscopic level allowed us to understand how the material would behave as a whole, inclusive of porosity and other defects. The tests performed at this level included compression testing and microhardness testing which gave vital information on the materials overall yield strength, ductility, toughness, and hardness. More details about the characterization methods are described within each chapter.

## CHAPTER 3 Effect of powder particle size on pore size and distribution and the resultant mechanical properties of austenite stainless steels

My research started with studying the effects of powder particle size on the pore formation in an austenite stainless steel during sintering, and how the pore size and distribution affected the mechanical properties at different length scales. Austenitic stainless steel 316 L powder was selected as a representative of inherently heavy alloys, which would greatly benefit from design of pore architecture to achieve high strength to weight ratios. To investigate the effect of powder particle sizes, starting powders were sieved to get different particle size ranges, with different morphologies, and then loaded to the die in a layered pattern to make bulk samples via spark plasma sintering. This chapter presented a thorough characterization of pore features, including total volume percent, size, shape, spacing, and surface area, in contrast to many other studies that only investigated the overall pore volume fraction. Additionally, the mechanical properties of those samples were investigated at multiple length scales to investigate the effect of pore characteristics, including macroscale compression testing, Vickers micro-indentation, nanoindentation and nanoscratch. Results suggested incorporating submicron pores improved both the yield strength and strength to weight ratio.

### 3.1 Introduction

Lightweight structural materials are essential for aerospace and transportation industries in order to bolster fuel efficiency. While some metals are inherently lightweight because of their low densities, such as Mg ( $1.74 \text{ g/cm}^3$ ) and Al ( $2.70 \text{ g/cm}^3$ ) [1], other metals or alloys, like stainless steel and Ni alloys, are intrinsically heavy due to their high atomic mass, yet possess superior corrosion resistance, and high temperature strength that are not available in Mg or Al alloys. Incorporating pores is an alternative approach to enable lightweight structural materials.

The development of metal foams is a typical example [2–5]. The challenge is how to sustain the mechanical properties of the porous materials in comparison to its fully dense counterparts. In general, current understanding of the mechanical behavior of porous materials is based on the Gibson-Ashby models, which suggest that the elastic modulus and yield strength of a porous material are proportional to its relative density, given below [6]:

$$\text{EQ (3.1)} \quad \frac{E^*}{E_s} \approx C_E \phi^{n_e}$$

$$\text{EQ (3.2)} \quad \frac{\sigma^*}{\sigma_{ys}} \approx C_\sigma \phi^{n_e}$$

In these equations,  $E^*$ ,  $E_s$ ,  $\sigma^*$ ,  $\sigma_{ys}$ , and  $\phi$  represent the modulus of the porous material, the modulus of the fully dense material, the yield strength of the porous material, the yield strength of the fully dense material, and the relative density of the porous material, respectively.  $C_E$ ,  $C_\sigma$  and  $n_e$  are constants depending on the material, loading conditions and whether the porous material is open-cell or closed-cell.

The Gibson-Ashby models show good agreement with experimental results for macroporous metallic foams in which pores are homogeneously distributed, including Al [7, 8], Ti [9, 10] and stainless steels [11–13]. However, the Gibson-Ashby models have several limitations. First, the distribution of pores are assumed to be uniform throughout the entire sample in the model, which may lead to over- or underestimation of mechanical properties [14]. Second, the Gibson-Ashby models were not intended for materials with relative densities outside of the 30% to 70% range, as originally suggested by Ashby [15]. In addition, these models solely considered the overall relative density of the material, thereby overlooking the effects of pore shape, size, and local distribution. Previous studies revealed that yield strength and elastic modulus of open-cell foams increased with decreasing ligament size [16–21]. Some studies reported that local work-hardening occurred in these open cell foams due to higher local strains

present at the nanometric ligaments, leading to local slip band formation and increased yield strength [22, 23]. Nevertheless, the correlation between pore characteristics (i.e. shape, size, and distribution) and mechanical properties in closed-cell porous metals is relatively unknown. To provide insight into the correlation between pore characteristics and mechanical properties, austenitic stainless steel 316L (SS 316L) was chosen as a representative of inherently heavy metals in this study. Stainless steels are the most common materials used in construction, transportation, medical, food, and energy industries, primarily due to their low costs (e.g., SS 316L is around \$4.36/kg) and remarkable corrosion resistance [24]. However, stainless steels have a low specific yield strength due to their high densities, 7.6 to 8.0 g/cm<sup>3</sup> [25]. For example, the specific yield strength of a AISI type SS 316L annealed sheet is 36.2 MPa·cm<sup>3</sup>/g, in contrast to an annealed Al7075 alloy (51.6 MPa·g/cm<sup>3</sup>) and annealed Ti6Al4V (187.4 MPa·g/cm<sup>3</sup>) [1]. Therefore, it is imperative to investigate the effectiveness of incorporating pores to reduce the weight of stainless steels for a given volume, without sacrificing the mechanical properties. Spark plasma sintering (SPS) was utilized to fabricate SS316L samples with a variety of pore characteristics in this study, because of its rapid sintering rates and capability to control porosity [26]. SPS utilizes a combination of pulsed DC current and mechanical pressure to densify a powder compact encapsulated by a set of highly conductive die and punches, typically graphite. The presence of high-amperage pulsed DC current in SPS enables high heating rates, >100°C/min, short sintering time length (several minutes), and thus, minimal grain growth [27]. Therefore, SPS is predominantly used for developing ultrafine grained or nanostructured materials [28, 29]. Recently, several studies applied SPS to develop metal foams. Yang *et al.* investigated the compressive mechanical behavior of an alumina/aluminum titanate composite foam fabricated by SPS and reported that the foam with an average pore diameter of 15 μm

achieved a flexural strength of 154.2 MPa [30]. Yamenoglu *et al.* reported that the yield strength and compressive strength of closed-cell titanium alloy foams, also fabricated by SPS, increased as the volume percentage of pores decreased, which could be predicted by the Gibson-Ashby models [31]. Work by Zhang *et al.* on open cell Ti foams with porosity ranged from 38% to 58% and large pore sizes (50 $\mu$ m to 500 $\mu$ m in diameter) revealed that decreasing pore diameter and reducing porosity lead to higher elastic modulus and higher compressive strength [32]. The pore sizes in these studies were all above micron scale.

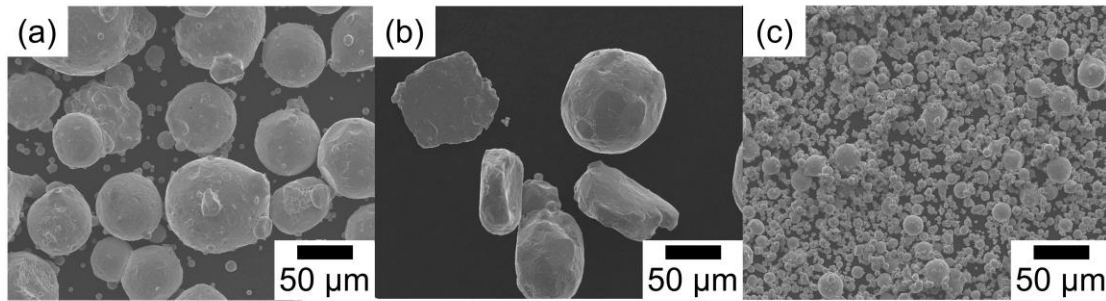
Given that pore characteristics are influential in the mechanical properties, it is also important to investigate how the pore characteristics can be controlled during processing. Therefore, the present work has two-fold objectives: (1) to investigate if and how the feedstock powder characteristics (particle size and morphology) affect the pores formed in the sintered bulk samples, which will enable future control of pore characteristics; (2) to elucidate the effect of pore characteristics on mechanical properties. To achieve these two goals, austenitic stainless steel 316L samples with intentional pores of varying diameters and distributions were fabricated by spark plasma sintering using starting powders with different morphologies. Characterization of pore features was addressed on the pore size, shape, interpore spacing, and pore surface area, in addition to the total volume percentage. The mechanical properties of those samples were investigated at multiple length scales, including macroscale quasi-static compression testing, microhardness testing, nanoindentation and nanoscratch.

## 3.2 Materials and Methods

### 3.2.1 Powder processing and selection

To investigate the effect of powder morphology on the densification behavior and the consequent pore formation, three types of SS316L powders with different shapes and particle sizes were

selected. The first was commercial gas atomized powder (Carpenter Powder Products) with a spherical shape and a particle size range of 38  $\mu\text{m}$  to 158  $\mu\text{m}$ , as shown in Fig. 3.1a. This first type of powder is referred to as GA1 thereafter. The GA1 powder was sieved to get three different particle size ranges: 38  $\mu\text{m}$  to 75  $\mu\text{m}$ , 75  $\mu\text{m}$  to 106  $\mu\text{m}$ , and 106 to 150  $\mu\text{m}$ . The second powder was a cryomilled powder with plate-like shape, as shown in Fig. 3.1b. The cryomilled powder was obtained by ball milling the GA1 powder for 8 hours in liquid nitrogen using an attrition mill. The cryomilled powder exhibited the same particle size range (38  $\mu\text{m}$  to 158  $\mu\text{m}$ ) as the GA1 powder, but different morphology and reduced grain size [33]. The third type of powder was another commercial gas atomized powder (Carpenter Powder Products) with a narrow particle size distribution range and fine particle sizes (average diameter  $\sim 5 \mu\text{m}$ ), as shown Fig. 3.1c. This finer gas atomized powder is referred to as GA2 hereafter.

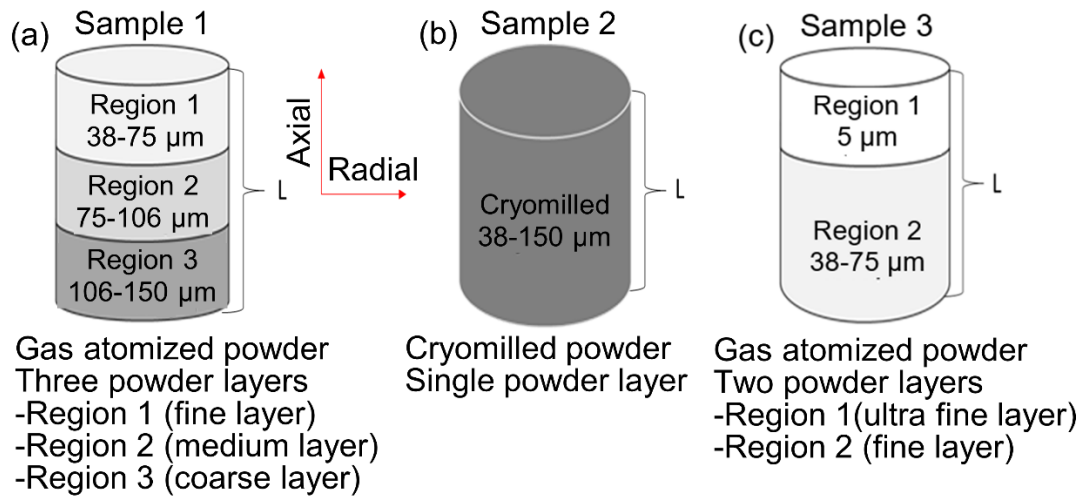


**Figure 3.3:** SEM images of (a) GA1 powder, (b) cryomilled powder, and (c) GA2 powder.

### 3.2.2 Sintering

Three different samples were made via SPS (Fuji Dr.Sinter 3.20 MKIV) with different feedstock powder packing patterns as shown in Fig. 3.2. The first sample (S1) was made from the sieved GA1 powder, consisting of three layers with the powder particle size increasing from top to bottom (Fig. 3.2a). The three layers in S1 are noted as Region 1 (R1), Region 2 (R2) and Region 3 (R3). The second sample (S2) was made from the cryomilled powder with a particle size range

of 38-150  $\mu\text{m}$  (Fig. 3.2b). The third sample (S3) was composed of a layer of GA2 powder and a layer of 38  $\mu\text{m}$  to 75  $\mu\text{m}$  GA1 powder (Fig. 3.2c). The latter was used as a substrate to keep a consistent sample height,  $L$ , with the other two samples. S1 and S2 were sintered under the same conditions in order to investigate how change in powder morphology affects pore characteristics in the sintered bulk samples. The heating rate during sintering was 100°C/min, with a 1-minute hold at 100°C to burn off any moisture within the powder and a 6-minute hold at 1100°C for densification. During sintering, the samples were subjected to a constant pressure of 20 MPa. S3 had the same sintering schedule except a lower pressure, 15 MPa, which was chosen to avoid total pore closure given the smaller starting particle size.



**Figure 3.4:** Strategic packing of feedstock powders. Samples 1 and 3 used a layered structure with different powder particle sizes in each layer, while sample 2 used one wide range of particle size.

### 3.2.3 Specimen preparation

The cross-sections of the different samples or regions described in section 3.2 were prepared for metallography and hardness testing (nanoindentation and microhardness). Cross sections were ground using SiC papers with grits of 180, 600, 800, and 1200, followed by polishing using high

viscosity diamond suspension of sizes 3 $\mu\text{m}$ , 1 $\mu\text{m}$ , 0.25 $\mu\text{m}$ , and 0.05 $\mu\text{m}$ . After polishing, a small piece was cut from each sample/region and etched by electrochemical polishing using 10wt% oxalic acid for 30-second intervals to reveal grain boundaries. The un-etched cross sections were used for nanoindentation. Compression testing specimens were machined from each bulk sample using electronic discharge machining (EDM). Three 4mm x 4mm x L sections parallel to the axial direction were machined from the center of each bulk sample, where L is the total length of the bulk sample as depicted in Fig. 3.2. The rectangular faces parallel to the axial direction were then ground using SiC papers with 600, 800, and 1200 grits followed by polishing with high viscosity diamond suspension of sizes 3 $\mu\text{m}$  and 1 $\mu\text{m}$  to achieve mirror-like surface finishing prior to compression testing. Three subsized specimens were then cut from each section to a final dimension of approximately 4mm x 4mm x 6 mm (ASTM E9-09) for compression testing at room temperature [34].

### 3.2.4 Microstructure characterization

X-ray diffraction (XRD) was implemented to determine which phases were present in each bulk sample, using a scanning  $2\theta$  range of 15°-120° with a step size of 0.02° and a scan rate of 1 step/s. The grain size, pore distribution, and chemical composition in the samples were characterized via scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). Nine images were analyzed per region to determine the grain size using the average grain intercept method. SEM images were obtained using a JEOL JSM-6500F field emission scanning electron microscope to characterize the pore characteristics. ImageJ software was implemented to perform the imaging analysis. The relative density, or the volume percentage of pores, of different samples/regions were estimated by both Archimedes and geometric methods using a Radwag XA 110/2x scale.

### 3.2.5 Mechanical Testing

The mechanical properties of the samples were tested at multiple scales, including nanoindentation testing, nanoscratch testing, microhardness testing, and macroscopic compression testing. It is worth noting that the loading modes experienced by the materials under indentation is not simply compression. While the material underneath the indenter probe is subjected to compressive stresses, the deformation of the indented area causes tensile and shear stresses on the material in the subsurface and the area surrounding the indents as the probe penetration depth increases. Nanoindentation was conducted using a Hysitron Ti Premier equipped with a Berkovich probe. Eleven 3x3 arrays of nanoindents were performed for each region, giving a total of 99 indents per region to ensure repeatability. The nanoindentation parameters are: a loading rate of 533  $\mu\text{N/s}$  with a maximum force of 8000  $\mu\text{N}$  held for 10 seconds, followed by an unloading rate of 533  $\mu\text{N/s}$ . Nanoscratch testing was conducted using the Hysitron Ti Premier equipped with a conical probe of tip radius  $\sim 1.15 \mu\text{m}$ , to achieve a consistent interaction volume regardless of the tip orientation. Microhardness testing was conducted using a Pace HV-1000Z microhardness tester equipped with a Vickers indenter. At least 20 indents were performed in each region with the indents spaced 10x the diameter of indent away from each other. Three scratches were performed per region spaced at least 10x scratch widths apart to investigate the wear resistance. The normalized lateral force was calculated with the following equation [35]:

$$\text{EQ (3.3)} \quad \frac{F_L}{F_N} = \beta \sqrt{\frac{F_N}{R^2 H}}$$

in which  $F_L$ ,  $F_N$ ,  $\beta$ ,  $R$ , and  $H$  represent the normalized lateral force, normal applied force, force constant, tip radius, and the depth of the scratch, respectively.

Quasi-static compression tests were carried out using an MTS Landmark system at a strain rate of  $10^{-3}$ /s. A preload of 0.05 kN was used for each sample to ensure contact prior to testing. The force (F) and crosshead displacement ( $\Delta L$ ) were recorded during testing and then converted to engineering stress ( $\sigma_E = \frac{F}{A}$ ) and engineering strain ( $\epsilon_E = \frac{\Delta L}{L_0}$ ) using the measured cross-sectional area A and initial length  $L_0$ . True stress - true strain curves were not used in this study because the sample volume is not conserved in porous materials that are subjected to compressive load, as the pores collapse during compression. Therefore, the scope of this work focused on the yield strength and specific yield strength rather than the plastic strain. Two sub-sized compression testing specimens from each region were tested. The compression tests were manually stopped at engineering strain of 0.3. All samples sustained integrity at this strain without fracture.

### 3.3. Results

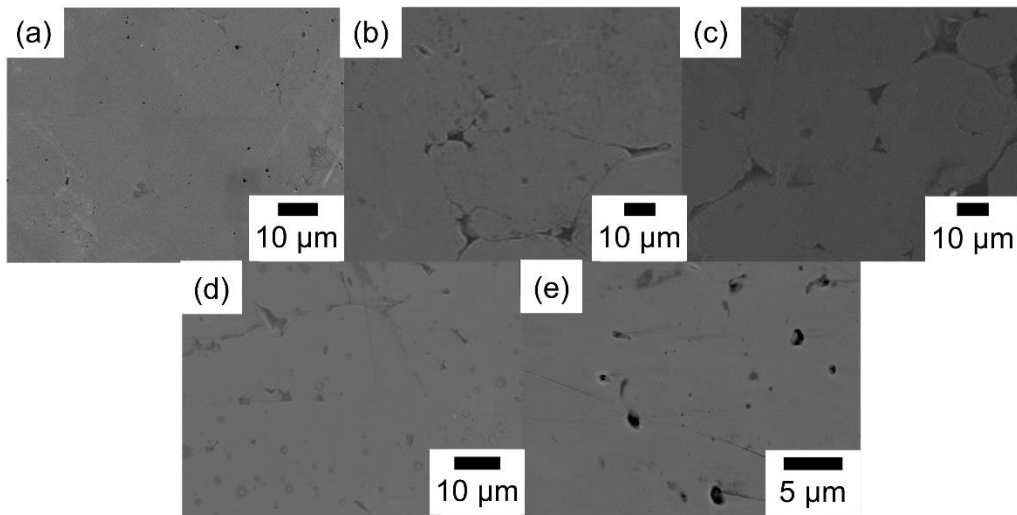
#### 3.3.1 Microstructure

The pore characteristics in different regions of Sample 1 were demonstrated in Fig. 3.3 a-c. Sample one region one (S1R1) showed a relatively high density with the presence of submicron pores (Fig. 3.3a). The pore diameter ranged from 147 nm to 980 nm with an average value of 247 nm. Sample one region two (S1R2) exhibited pores ranging from 1.6  $\mu\text{m}$  to 23  $\mu\text{m}$  in diameter with an average of 4.9  $\mu\text{m}$  (Fig. 3.3b). In contrast, region 3 of sample 1 (S1R3) showed a significantly higher volume percentage of pores with a larger size (a range of 5.6  $\mu\text{m}$  - 52  $\mu\text{m}$  with an average value of 12.6  $\mu\text{m}$ ) than S1R1 and S1R2, as displayed in Fig. 3.3c. The changes in pore characteristics in different regions of S1 suggest that coarse starting powder resulted in a higher volume percentage of pores and a larger pore size (S1R3) than those regions sintered from fine starting powder (S1R1 and S1R2). Sample 2 (S2) exhibited a relatively homogeneous microstructure throughout the entire sample compared to S1, as the feedstock powder was not

separated into distinct regions in S2. The pore size in S2 ranged from 926 nm to 10.6  $\mu\text{m}$  with an average of 5.8  $\mu\text{m}$  (Fig. 3.3d). Sample 3 region 1 (S3R1) shows submicron pores like S1R1, with an average pore size of 472 nm, as shown in Fig. 3.3e. The average pore spacing were estimated based on Eq (4) below, assuming equal spacing between pores.

$$\text{EQ (3.4)} \quad S = \left( \frac{\pi r^2}{\phi} \right)^{\frac{1}{2}},$$

where  $S$  is the spacing between pores,  $\phi$  is the relative density, and  $r$  is the average pore radius in that region. According to this estimation, the average pore spacings in S1R1 and S3R1, 1.3  $\mu\text{m}$  and 2.8  $\mu\text{m}$ , respectively, are significantly smaller than those in the other regions, which are  $\sim 19$   $\mu\text{m}$  or greater. The quantitative pore characteristics in various samples are provided in Table 1. It is noted that uncertainty exists in porosity measurements. This work combined Archimedes' method and geometric density measurements, as well as analysis of SEM images, to estimate the porosity and pore sizes. Rather than a single average value, standard deviations in volume percentages of pores and the range of the pore size observed in SEM were provided in Table 1.

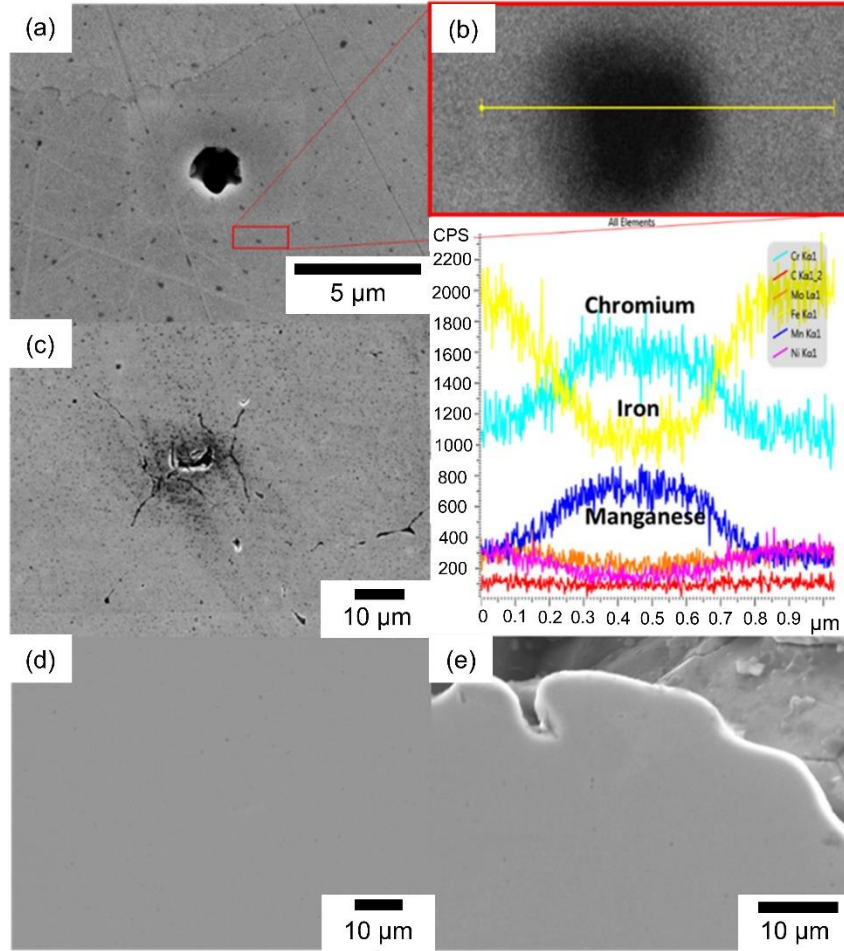


**Figure 3.5:** Representative microstructures (SEM images) showing pore size and shape in (a) S1R1, (b) S1R2, (c) S1R3, (d) S2, and (e) S3R1.

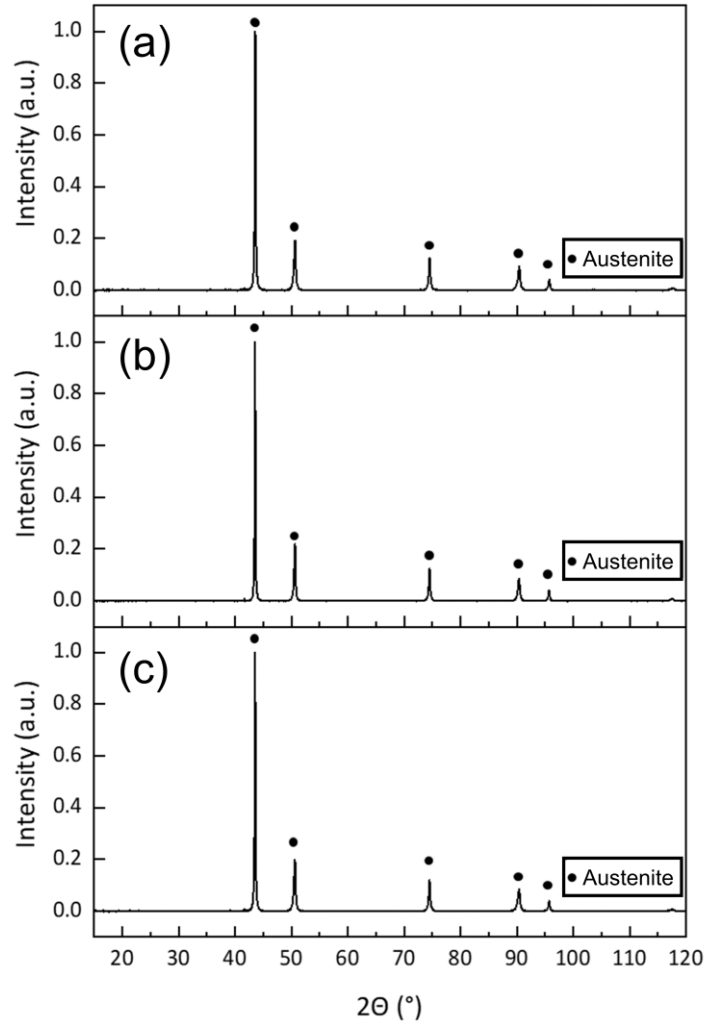
**Table 3.1:** Summary of the microstructural characteristics in different samples/regions.

| Sample ID | Volume percentage of pores (%) (Archimedes) | Volume percentage of pores (%) (Geometric) | Average pore size and size range ( $\mu\text{m}$ ) | Average interpore spacing ( $\mu\text{m}$ ) | Total Pore surface area ( $\text{cm}^2$ ) | Average grain diameter ( $\mu\text{m}$ ) |
|-----------|---------------------------------------------|--------------------------------------------|----------------------------------------------------|---------------------------------------------|-------------------------------------------|------------------------------------------|
| S1R1      | $10.9 \pm 0.6$                              | $9.8 \pm 1.2$                              | 0.25<br>(0.15 - 0.98)                              | 1.3                                         | 2.5                                       | $4.2 \pm 1.1$                            |
| S1R2      | $21.3 \pm 0.7$                              | $18.8 \pm 0.9$                             | 4.9<br>(1.6 - 23)                                  | 19                                          | 0.25                                      | $3.6 \pm 0.93$                           |
| S1R3      | $23.2 \pm 1.2$                              | $21.1 \pm 0.8$                             | 13<br>(5.6 - 52)                                   | 48                                          | 0.11                                      | $4.5 \pm 1.2$                            |
| S2        | $11.9 \pm 0.9$                              | $9.5 \pm 1.1$                              | 5.8<br>(0.93 - 11)                                 | 30                                          | 0.12                                      | $1.4 \pm 0.85$                           |
| S3R1      | $8.9 \pm 1.0$                               | $7.6 \pm 1.0$                              | 0.47<br>(0.27 - 1.4)                               | 2.8                                         | 1.1                                       | $1.1 \pm 0.62$                           |

(Cr, Mn)-rich precipitates with diameters that ranged from 100 nm to 400 nm were present in the regions surrounding the submicron pores in S1R1, as shown in Fig. 3.4a. The EDS line scans (Fig. 3.4b) showed an evident drop in Fe accompanied with the increase in Cr and Mn contents across the precipitates. These nanoscale precipitates were also observed in the areas surrounding small pores in S1R2 (Fig. 3.4c). However, the (Cr, Mn)-rich precipitation or segregation was not observed in the pore-free regions or in the regions adjacent to large pores, as shown in Fig. 3.4d and 4e. The precipitation phenomenon surrounding pores were also observed in previous studies on iron based systems with high contents of chromium, in which the pore size was  $\sim 10\mu\text{m}$ - $20\mu\text{m}$  [36, 37]. The XRD patterns (Fig. 3.5) show that all three samples are primarily austenitic, without detectable peaks of martensite or any other secondary phases. This is consistent with the SEM observation, which affirms that the precipitates were not widely spread through the samples.

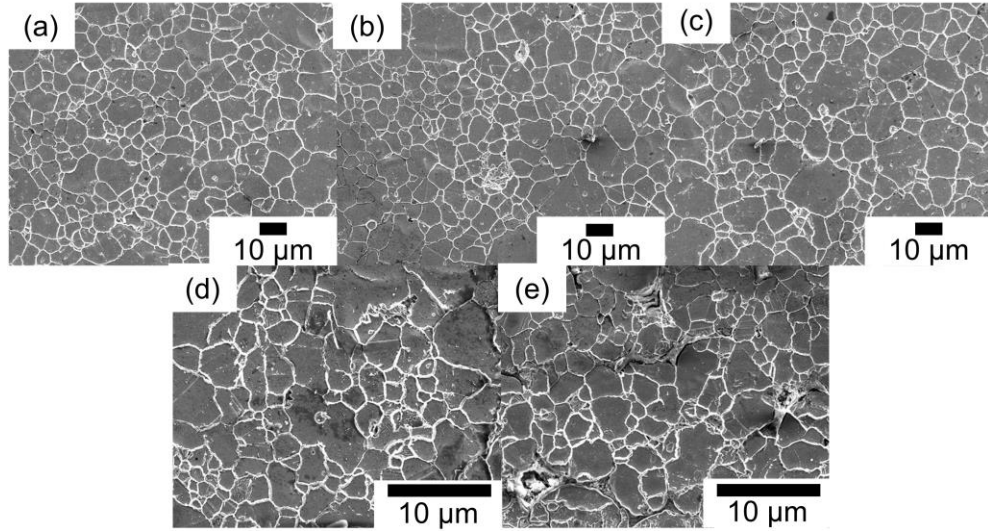


**Figure 3.6:** (a) SEM of an area surrounding submicron pores in S1R1, (b) EDS line scan of a precipitate in S1R1, (c) area containing fine pores in S1R2, (d) area containing no pores in S1R2, and (e) area adjacent to large pores in S1R2.



**Figure 3.7:** XRD patterns indicating present phases. (a) S1, (b) S2, (c) S3

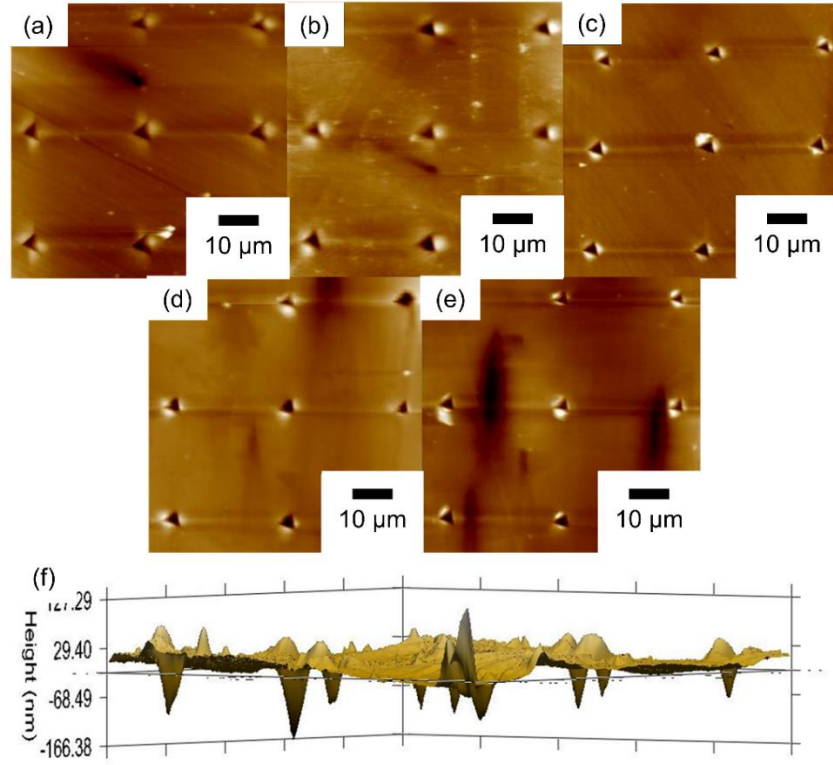
Fig. 3.6 shows representative grain structures of the various samples or regions. The average grain diameter of S1R1, S1R2 and S1R3 was  $4.2\ \mu\text{m}$ ,  $3.6\ \mu\text{m}$ , and  $4.5\ \mu\text{m}$ , respectively. S2 exhibited a finer grain structure (average grain diameter  $\sim 1.4\ \mu\text{m}$ ) as the feedstock powder (cryomilled powder) had a finer grain size than gas atomized powder [33, 38, 39]. S3R1 also exhibited a fine grain structure, with an average grain size of  $1.1\ \mu\text{m}$ .



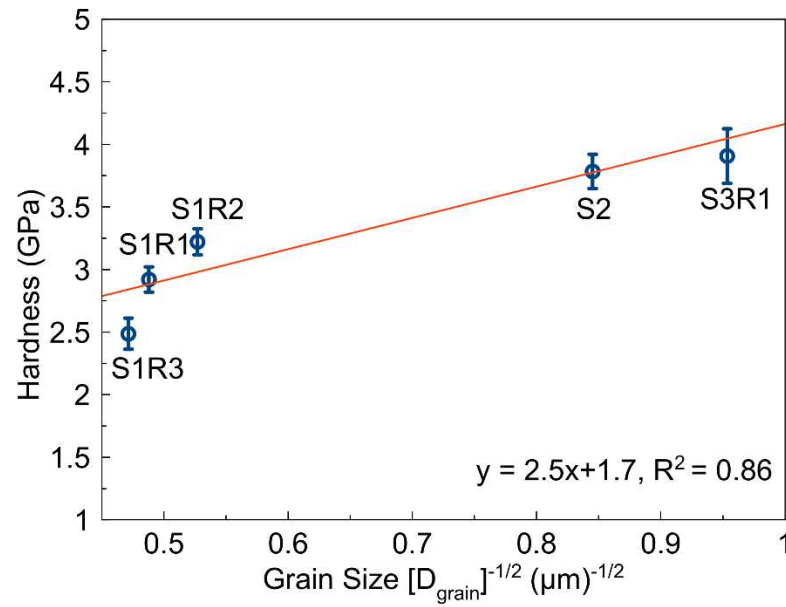
**Figure 3.8:** Scanning electron microscopy images of the etched samples showing the grain boundaries. (a) S1R1, (b) S1R2, (c) S1R3, (d) S2, and (e) S3R1.

### 3.3.2 Hardness

The hardness of the samples was measured by both nanoindentation and micro-Vickers testing. Representative scanning probe microscopy (SPM) images of the post-nanoindentation samples are shown in Fig. 3.7. The nanoindentation hardness results are provided in Fig. 3.8. Within sample 1, region 2 showed the highest hardness compared to S1R1 and S1R3, because of the smallest grain size in S1R2. S2 and S3R1 showed higher hardness values than all three regions in S1. These observations were expected according to grain boundary strengthening mechanism, i.e., the Hall-Petch relation. Initial analysis of the data did not provide a clear correlation between the pore size and the nanoindentation hardness, as the length scale of those nano-indents is too small to include pores.

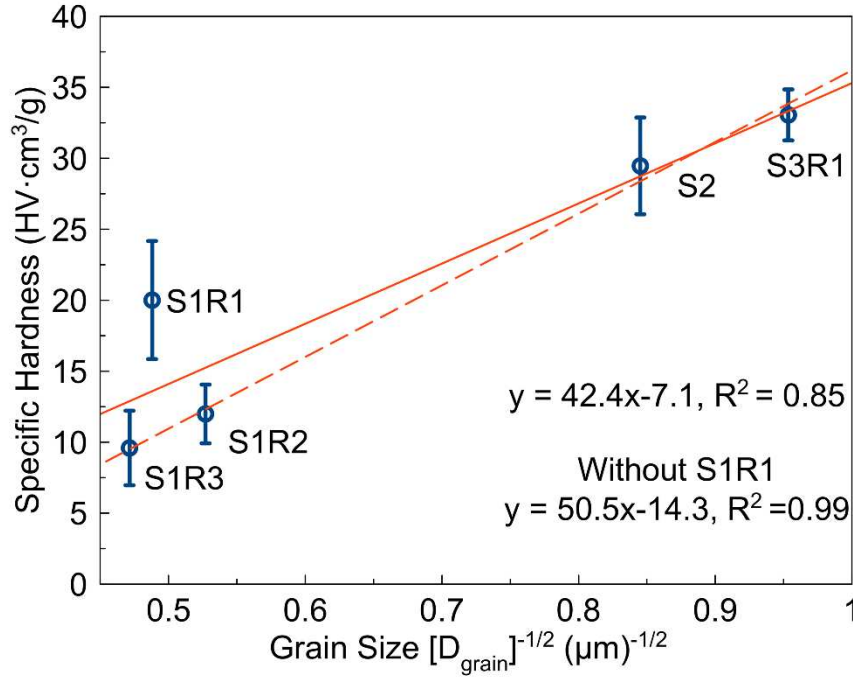


**Figure 3.9:** SPM imaging of nanoindentation sets on sample surface, (a) S1R1, (b) S1R2, (c) S1R3, (d) S2, (e) S3R1, and (f) a 3-D rendering of a nanoindentation set from SPM imaging.



**Figure 3.10:** Hardness measured by nanoindentation vs. the average grain size $^{-1/2}$ .

Vickers microhardness tests were performed to make indents with a length scale of about a hundred microns. Given the large interaction volume in microhardness testing compared to the nanoindentation, the volume percentage of pores became an important factor, as the total surface area being impacted by the probe directly depends on the force required to plastically deform the surface of the material. The force required to achieve a same displacement as that for a fully dense counterpart decreased with increasing volume percentage of pores underneath the sample surface, leading to a lower microhardness. Taking the volume percentage of pores into account, the specific microhardness, i.e., the microhardness divided by the density, were plotted against the grain size, as shown in Fig. 3.9. To examine the Hall-Petch relation for those SS316L materials with a relative density ranged from 80% to 90%, lower than what is commonly defined as fully dense materials (>95%), linear fitting was performed to the data of specific microhardness vs. (average grain size)<sup>-1/2</sup> in Fig. 3.9. When all five data points were included for the fitting, the data point for S1R1 showed the largest residual from the best fitted trend line, making it appear to be an outlier. Therefore, an additional linear fitting trend line was provided in the plot, excluding the data point for S1R1. The solid trend line included the data of S1R1 while the dashed trend line did not include S1R1. Based on S1R1 having the largest residual from the original all-data-included fitting line (solid line in Fig. 3.9) and that the dashed trend line has a higher value of the R<sup>2</sup> than the solid trend line, it suggested that S1R1 was an outlier that exhibited a specific hardness higher than what was predicted from Hall-Petch relation. This is attributed to the nano- or submicron pores present in S1R1, which is further discussed in section 3.3.1. Note that the same analysis was done for microhardness, which also showed that S1R1 was an outlier.

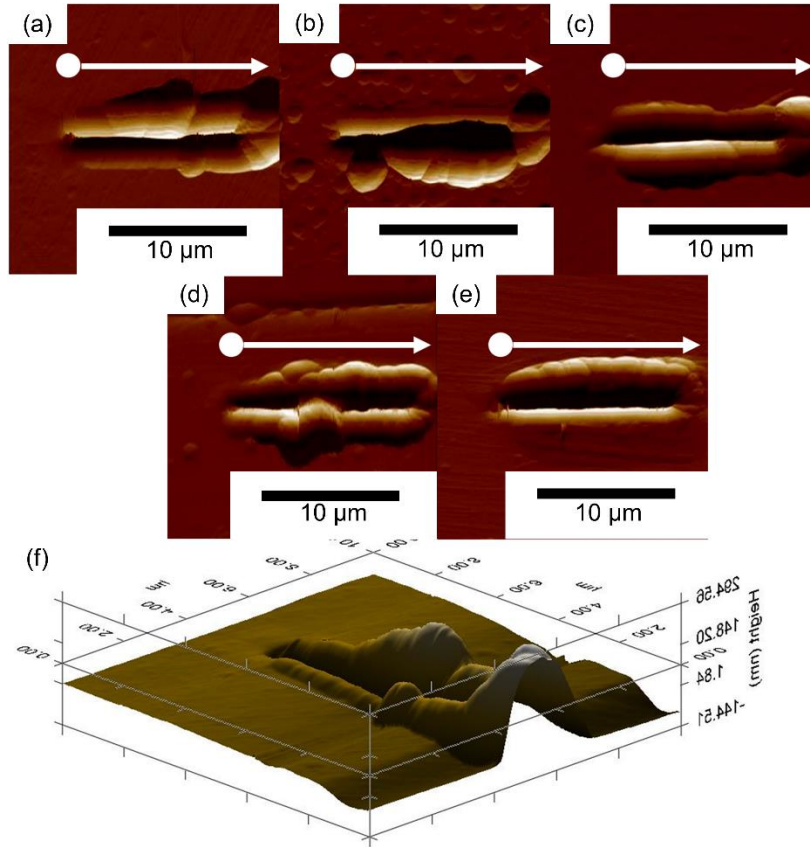


**Figure 3.11:** Specific hardness values acquired via microhardness testing vs the average grain size<sup>1/2</sup>.

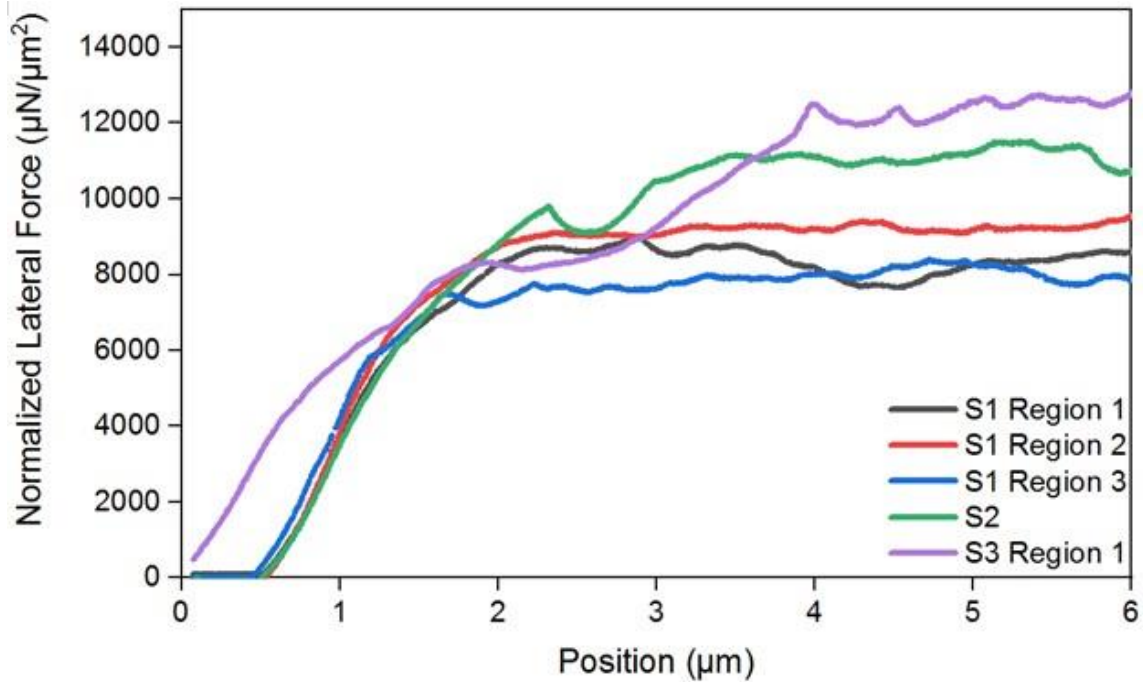
### 3.3.3 Nanowear behavior

Fig. 3.10 displays representative SPM images of the nanoscratches on each sample and the pile-up of materials on the sample surface. The normalized lateral forces as a function of the probe position during the nanoscratch testing are shown in Fig. 3.11. It is important to note that the material removed from the sample surface piled up on the probe tip before the scratch length reached  $\sim 3 \mu\text{m}$ , leading to increasing normalized lateral force (Fig. 3.11). When no more net material was added to the pileup, the normalized lateral force reached a steady state. Only the steady-state lateral forces were used to compare the wear resistance. A higher normalized lateral force means higher wear resistance, as it takes more force to move the conical probe across the sample surface. During scratch testing, both plastic deformation depth and elastic deformation depth were recorded. The plastic deformation depth ranged from 100 nm to 159 nm and the elastic deformation depth ranged 182 nm to 205 nm. The height of material pileup was in the

range of 103 nm to 272 nm. First, to investigate the effect of grain size, S1R1, S2, and S3R1 were compared to each other as they had a same level of porosity (volume percentage approximately ~ 10%, Table 1). S3R1 had the highest normalized lateral force after the 1  $\mu\text{m}$  position during the scratch testing because of smallest grain size. In contrast, S1R1 exhibited the lowest normalized lateral force, which corresponded to its largest grain size. Therefore, the wear resistance of the samples at nanoscale is inversely proportional to the grain size when the total porosity is at the same level. To investigate the role of pores in the nanowear behavior, the three regions in S1 were compared to each other. S1R2 had a higher porosity with a larger pore size than S1R1; yet it experienced the highest normalized lateral force among the three regions as it had the smallest grain size. S1R1 and S1R3 had a similar grain size range considering the standard deviation while S1R1 had a lower porosity with much smaller pore sizes. S1R1 showed a higher lateral force than S1R3 for most of the scratch length. Therefore, it is reasonable to suggest that the wear resistance at nanoscale increases with decreasing pore size and porosity. However, grain diameter is the dominant factor that determines the nanowear behavior.



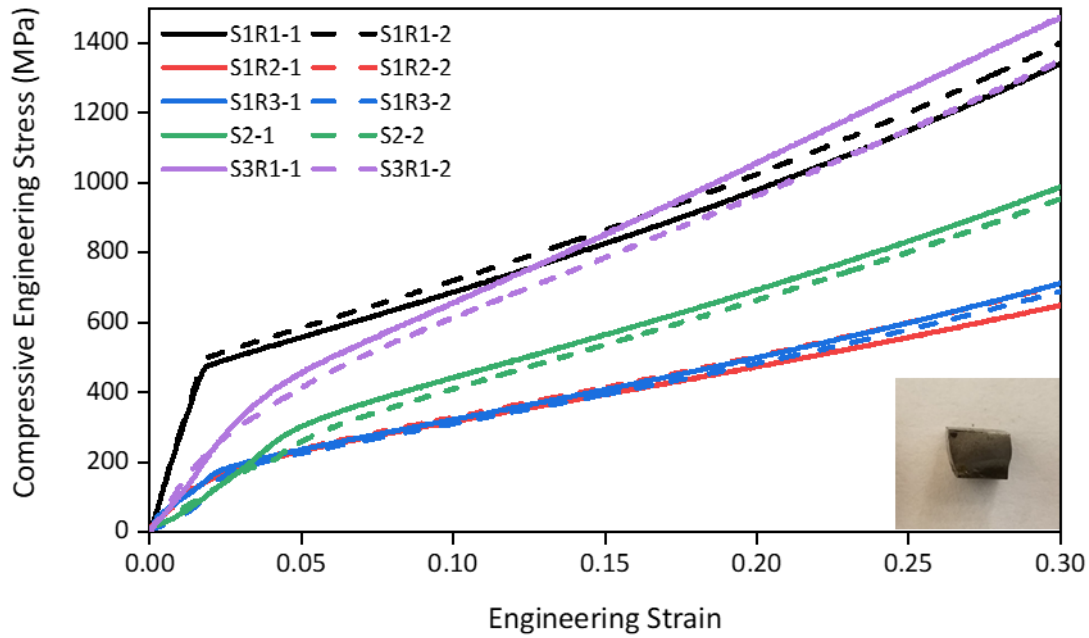
**Figure 3.12:** Representative SPM images of scratches from each region (a) S1R1, (b) S1R2, (c) S1R3, (d) S2, (e) S3R1, and (f) a 3-D rendering of a nanoscratch from SPM imaging. The arrows show the scratch directions.



**Figure 3.13:** The normalized lateral force as a function of the scratch length.

### 3.3.4 Quasi-static compression behavior

The compressive stress–strain curves are shown in Fig. 3.12. All samples responded to compression testing with significant plasticity. The testing was manually stopped after a strain of 0.3 due to sample barreling as depicted in Fig. 3.12. The corresponding mechanical properties, including 0.2% offset yield strength, specific yield strength, and compressive strength at strain of 0.3, are provided in Table 2. S1R1 exhibited the highest yield strength despite that it did not have the smallest grain size nor the highest relative density. Specifically, S2R1 has a much smaller grain size (1.4 μm) than S1R1 (4.2 μm) and a similar volume percentage of pores. However, S2 only exhibited a yield strength of 273 MPa while S1R1 had a yield strength of 482 MPa. S3R1 exhibited both a smaller grain size and a lower volume percentage of pores than S1R1, yet a slightly lower yield strength (402 MPa).



**Figure 3.14:** Compressive engineering stress – engineering strain curves of the samples.

**Table 3.2:** Average mechanical properties obtained from quasi-static compression tests.

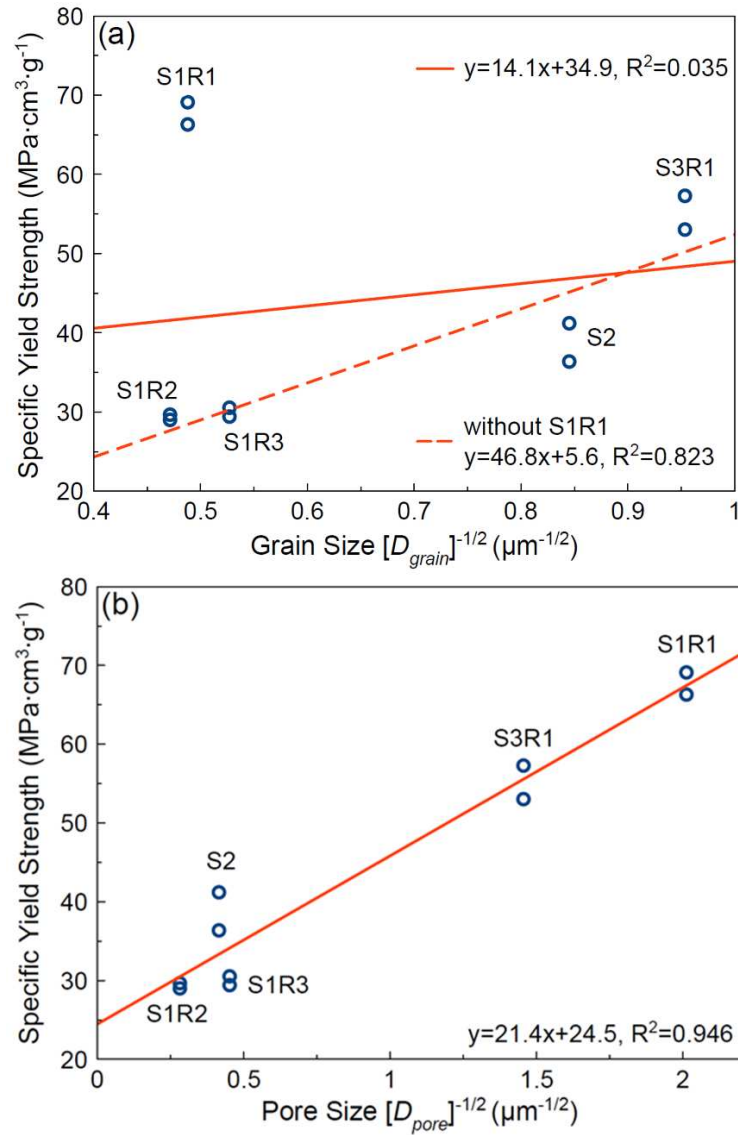
| Specimen    | Yield strength<br>(MPa) | Specific yield<br>strength<br>(MPa·cm <sup>3</sup> /g) | Compression<br>strength at 0.3<br>strain (MPa) |
|-------------|-------------------------|--------------------------------------------------------|------------------------------------------------|
| S1 Region 1 | 482                     | 67.7                                                   | 1370                                           |
| S1 Region 2 | 189                     | 29.9                                                   | 674                                            |
| S1 Region 3 | 180                     | 29.3                                                   | 700                                            |
| S2 Region 1 | 273                     | 38.8                                                   | 970                                            |
| S3 Region 1 | 402                     | 55.2                                                   | 1412                                           |

These results indicated that, in addition to grain size and relative density, the pore size played a significant role in the yield strength, which has not been well studied in the existing literature.

One goal of our present work was to fill in this gap. It was observed that initially S3R1 (grain diameter 1.1  $\mu\text{m}$ , pore diameter  $\sim 472$  nm) showed a lower strength than S1R1 (grain diameter 4.2  $\mu\text{m}$ , pore diameter  $\sim 247$  nm). When the compressive strain reached  $\sim 0.18$ , the strength of S3R1-1 started to outperform S1R1-1. Consequently, S3R1-1 had the largest compression strength at a true strain of 0.3. After the yield point, plastic deformation occurred and initiated pore collapse, i.e., the volume percentage of pores decreased as plastic deformation continued in compression tests. Therefore, a critical strain point was present at which grain boundary strengthening became dominant mechanism so that S3R1-1 became stronger than S1R1-1. S2, the sample made from cryomilled powder, exhibited an intermediate yield strength and compressive strength (at true strain = 0.3), lower than S1R1 and S3R1 but higher than S1R2 and S1R3, which also corresponded to its intermediate pore size (diameter  $\sim 5.4$   $\mu\text{m}$ ) and volume percentage of pores (11.9%) despite its fine grain size (diameter  $\sim 1.4$   $\mu\text{m}$ ). To exclude the effect of pore volume on the yield strength so that the influence of grain size and pore size can be assessed separately, specific yield strength was plotted against grain size (Fig. 3.13a) and pore size (Fig. 3.13b). Like what was observed in microhardness (Fig. 3.9), S1R1 appears to be an outlier compared to the rest of the data set of specific strength in Fig. 3.13a. S1R1 exhibited a higher specific yield strength than that was predicted from Hall-Petch. Therefore, the grain size effect in strengthening cannot be simply assessed by Hall-Petch relation in materials containing significant pores. Interestingly, the specific yield strength ( $\frac{\sigma_y}{\rho}$ ) and the pore diameter ( $D_{pore}$ ), as shown in Fig. 3.13b, showed a strong Hall-Petch type correlation,  $\frac{\sigma_y}{\rho} = 24.5 + \frac{21.4}{\sqrt{D_{pore}}}$ , with the linear fitting  $R^2$  value of approximately 0.95. It was discovered, for the first time, that the specific yield strength and the pore diameter exhibited such a quantitative correlation. It is worth noting that the number of data is yet limited to completely verify this correlation, and an

appropriate pore size range needs to be identified to apply this Hall-Petch type correlation.

Therefore, this new finding will intrigue additional research in this field.



**Figure 3.15:** Specific yield strength as a function of (a) grain diameter-1/2 and (b) pore diameter<sup>1/2</sup>.

It is also noted that the Young's modulus also varied among the different samples or regions, which was initially attributed to the different relative densities according to the Gibson-Ashby model (Eq1). However, S1R1 and S3R1 showed different Young's modulus although the two

regions had similar relative densities. The average pore diameter of S1R1 (~247 nm) is about half that of S3R1 (~472 nm). Therefore, for the same overall relative density, the elastic modulus of the material can be improved by reducing pore size. This is attributed to both localized precipitation around the pores and potentially stiffening of the pore surface.

### 3.4. Discussion

#### 3.4.1 Effect of feedstock powder morphology on pore formation

The microstructure of different regions in S1 reveals that the pore size and the volume percentage of pores increases with increasing feedstock powder particle size. The densification rate increases as the starting powder particle size decreases because of the higher surface energy to volume energy ratio and thus, a larger thermodynamic driving force compared to that of coarser feedstock powder. This phenomena was also reported on Ti alloys and Mg[40–42]. The shape of the starting powder also affects the formation of pores during SPS. The cryomilled powder had less dense packing in the initial powder compact due to its plate-like shape, compared to the spherical GA1 powder. As a result, the pores in S2 exhibited an irregular shape (Fig. 3.3d) in contrast to the near-round pores in S1R1 (Fig. 3.3a), although S1R1 and S2 were sintered to the same stage indicated by their similar level of porosity (Table 1). In addition, the pore size in S1R1 is significantly smaller than that in S2. On the other hand, S2 has a higher overall relative density than the entire S1 sample, attributed to the accelerated sintering caused by the larger surface area to volume ratio, and thus, higher surface energy of the cryomilled powder than the spherical GA1 powder. This agrees with Guan *et al.* who depicted higher relative densities with samples sintered using cryomilled Mg powder in comparison to gas atomized Mg powder, when identical SPS parameters were used [43]. Our findings suggest that strategic selection and packing of the starting powder is an alternative effective approach to

control the pore characteristics in the bulk materials made by SPS, in addition to tuning the SPS processing parameters. This is particularly important for design of graded pore distribution for functionally graded materials in one-step processing.

### 3.4.2 Effect of pore characteristics on mechanical properties

When the classical Hall-Petch relation, EQ(5) below, was applied to assess the specific microhardness against the average grain size to the negative one-half power,  $(\frac{1}{\sqrt{d}})$ , the linear fitting gave a coefficient of determination  $R^2$  of 0.85 (Fig. 3.9).

$$\text{EQ(2.5)} \quad H = H_0 + \frac{K_H}{\sqrt{d}},$$

where  $H, H_0, K_H, d$  are specific hardness, specific hardness resulted from lattice friction, Hall-Petch coefficient, and grain diameter, respectively. When the data of S1R1 was excluded as an outlier, the Hall-Petch relation fitting gave a significantly higher coefficient of determination  $R^2$  of 0.99 and  $K_H = 50.5 \text{ HV} \cdot \mu\text{m}^{1/2} \cdot \text{cm}^3/\text{g}$  for specific hardness. Then using the grain diameter of S1R1 and EQ(5), it was expected that S1R1 would have a specific hardness of  $\sim 10.1 \text{ HV} \cdot \text{cm}^3/\text{g}$ . However, the experimentally measured hardness of S1R1 is almost twice of the value predicted by Hall-Petch type model. We also evaluated the microhardness data as a function of  $(\frac{1}{\sqrt{d}})$ , which showed a greater deviation from the Hall-Petch relation ( $R^2 < 0.5$ ). The deviation from the Hall-Petch relation was attributed to the non-negligible porosity (10% or higher) in the samples, which was intentionally made in the current study to investigate pore effect.

In addition to grain boundaries, it is well known that multiple other factors contribute to strengthening in metals, such as dislocations, second-phase particles, precipitates, and twinning. S1R1 was made from gas atomized powders and the SPS process did not involve severe plastic deformation. Thus, dislocation strengthening is negligible. XRD and SEM results suggested that

no martensite or deformation twinning was present in S1. However, (Cr, Mn)-rich precipitates were present adjacent to small pores. Hence, the submicron pores in S1R1 play an influential role in strengthening the material by stiffening the local structure surrounding the pores and facilitating the formation of precipitates. For a given volume of pores, smaller pores lead to larger surface area to volume ratios. Using the volume percentage of pores and average pore size provided in Section 3.3.1, with the assumption of a spherical pore shape, the internal pore surface area was estimated via:

$$\text{EQ(3.6)} \quad V_{(1-\phi)} = V_T(1 - \phi)$$

$$\text{EQ(3.7)} \quad I_A = \frac{V_{(1-\phi)}}{3} r$$

Where  $V_{(1-\phi)}$ ,  $V_T$ ,  $\phi$ ,  $r$ , and  $I_A$  are total volume of pores, total volume of a sample, the relative density, radius of a pore, and total pore surface area, respectively. The results are provided in Table 1. Although S3 has a similar level of pore volume percentage and a finer grain size than S1R1, the local stiffening effect is more significant in S1R1 as the total internal pore surface area in S1R1 is approximately twice that of S3R1. Consequently, S1R1 exhibited a higher yield strength that did not follow the Hall-Petch relation. In addition, previous modeling work showed that nanometric voids contributed to strengthening by interactions with dislocations [44–46]. Dou *et al.* modeled the interaction of edge dislocations with nanometric voids in a Fe-Ni-Cr system, and they found that dislocations were pinned at the nanopore surface, and thus, a higher local stress was required for depinning the dislocations to continue the motion, leading to local strengthening [47]. Furthermore, (Cr, Mn)-rich precipitates were observed in the regions surrounding the small pores. It has been well established that (Cr, Mn)-rich precipitates strengthen stainless steels [48–51]. It is reasonable to correlate the amount of the precipitates to the total pore surface area. As S1R1 exhibited dominantly submicron pores and the highest pore

surface area to volume ratio and S3R1 showed the second highest value, it is anticipated that these two types of samples contain a relatively high concentration of (Cr, Mn)-rich precipitates, which further explains higher yield strength observed in S1R1 and S3R1 compared to the other samples. The concentration of precipitates around pores can be explained by increased flux of vacancies from the pore during sintering [52, 53]. This causes a driving force for mass diffusion towards the pores as described by Boiko et al:

$$\text{EQ(3.8)} \quad F = \frac{kT\nabla C_v}{C_0},$$

where  $F, k, T, \nabla C_v, C_0$  are the driving force, Boltzmann's constant, temperature, local vacancies concentration, and equilibrium vacancy concentration, respectively. As the mobilities of different elements are not the same in stainless steel, segregation of Cr and/or Mn occurs as the pore is filled by bulk diffusion and surface diffusion. Additionally, the concentration of local vacancies is inversely proportional to the radius of the pore [52, 53]:

$$\text{EQ(3.9)} \quad \nabla C_v = \frac{C_0 \omega \gamma}{kTr^2},$$

where  $\omega, \gamma, r$  are atomic volume, specific surface energy, and pore radius, respectively.

According to Eq (8) and (9), smaller pores, i.e. lower values of  $r$ , have a higher concentration of local vacancies, leading to a higher driving force for mass transport and eventually, segregation of certain elements near the pore surface. In contrast, large pores (high values of  $r$ ) inherently have a lower driving force for mass flow, which explains why little (Cr, Mn)-rich precipitation were observed in the area adjacent to larger pores. Some studies in the field of open-cell porous metals showed that the pore spacing directly correlated to the thickness of the ligament between nodes, and the local work hardening rate was increased due to formation of shear bands within the nanoscale ligaments [16–21]. It is generally known that pores lead to increased local work

hardening rates and a decrease in plasticity. Under the compressive load in the current study, all samples exhibited significant plasticity (plastic strain > 0.3) without fracture.

The results provided in Section 3.3.2 suggested that the effect of pore characteristics on the mechanical properties varied with the length scale at which the mechanical testing was performed. At a submicron length scale, the hardness determined from nanoindentation predominantly relies on the grain size and follows the Hall-Petch relationship, with a  $R^2$  of 0.86 (Fig. 3.8), whereas the volume percentage of pores and the pore size did not exhibit a clear influence. The nanoindents have a length of 1~2  $\mu\text{m}$  and a penetration depth ranging from 147 nm to 223 nm. The interaction volume between the probe and the material surface is limited so that the volume percentage of the pores have a negligible effect on the hardness unless a pore is coincidentally located right underneath the indent location. When the pore size is larger than the indent size (S1R2, S1R3 and S2), the pore size did not affect the nanoindentation hardness as the locations of indents were selected to avoid the pores to meet the requirement of flat surface for nanoindentation. In the case where the pore diameter was at a submicron scale (S1R1 and S3R1), it was possible that the indentation was carried out on a location where nanopores and/or precipitates were present. Then the plastic deformation in this occasion may require a higher force due to the stiffened atomic structure surrounding the pore, or interaction with the precipitate. At the micro-scale, the Vickers hardness exhibited dependence on both grain size and volume percentage of pores due to the larger interaction volume in microhardness tests than that for the nanoindentation. Therefore, specific hardness was assessed instead of hardness to exclude the effect from pore volume fraction, as discussed in Section 3.2.1.

At the macro-scale, the specific yield strength determined from the quasi-static compression testing did not increase linearly with decreasing  $(\frac{1}{\sqrt{d}})$ , as the Hall-Petch linear fitting gave a  $R^2$

of only 0.042 (Fig. 3.13a). However, when S1R1 was excluded as an outlier, a much stronger coefficient of determination of 0.89 was obtained (Fig. 3.13a). Despite its larger grain diameter (4.2  $\mu\text{m}$ ) than both S2 and S3R1 (1.4  $\mu\text{m}$  and 1.1  $\mu\text{m}$ , respectively), S1R1 outperformed the other samples in terms of specific strength though they had a similar volume percentage of pores. In addition, the dependence of the specific yield strength on the pore diameter (Fig. 3.13b) clearly followed a Hall-Petch type correlation with a  $R^2$  of 0.95. In other words, the yield strength linearly increased as a function of the pore diameter to the negative one-half power. This was the first time that a quantitative correlation between pore diameter and yield strength was established in austenitic stainless steel. If Hall-Petch relation was used to predict the specific strength of S1R1 assuming the pore size did not influence the strength:

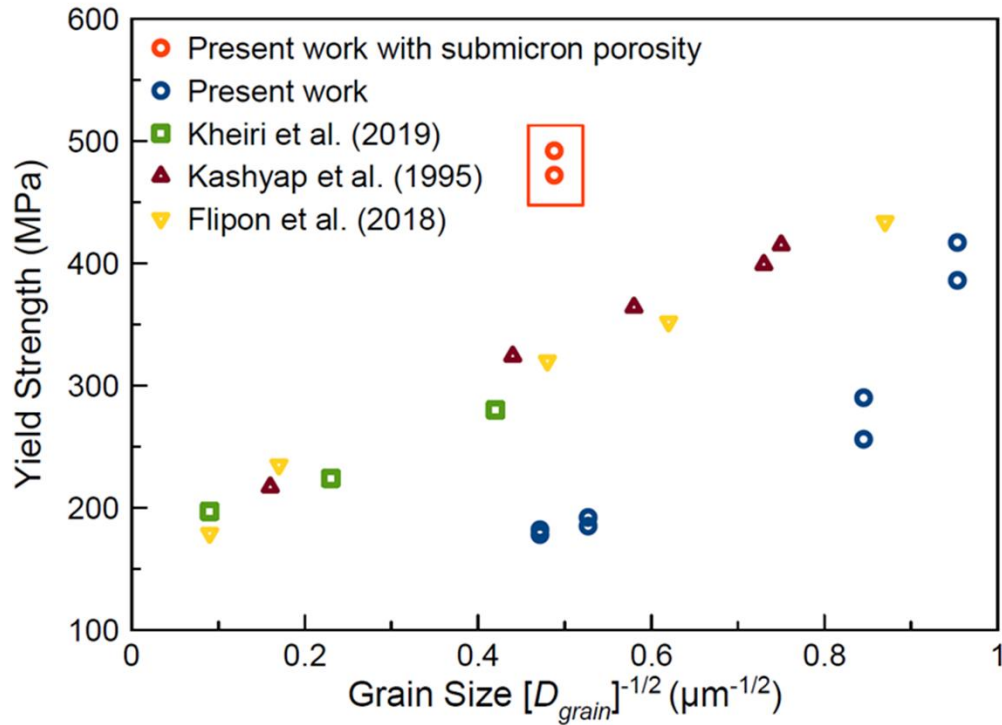
$$\text{EQ(3.10)} \quad \sigma_y = \sigma_0 + \frac{K_y}{\sqrt{d}},$$

where  $\sigma_y, \sigma_0, K_y, d$  are specific yield strength, specific friction stress, Hall-Petch coefficient, and grain diameter, respectively, then the predicted specific strength of S1R1 would be approximately 30  $\text{MPa}\cdot\text{cm}^3/\text{g}$ , much lower than the experimental result ( $\sim 68 \text{ MPa}\cdot\text{cm}^3/\text{g}$ ). Therefore, the Hall-Petch relation was not suitable for samples containing a significant amount of submicron pores. These findings suggest that submicron pores can make stainless steels stronger and meanwhile lighter for a given volume.

### 3.4.3 Comparison to other studies

The stainless-steel materials that contained submicron pores (S1R1) in the present work outperform fully dense stainless steels in other studies in yield strength, including those having finer grain sizes than S1R1, as shown in Fig. 3.14 [54–56]. The stainless steels samples in the present work, except S1R1, showed a similar Hall-Petch coefficient (slope of the linear fitting curve) to the literature data. The yield strength values of S1R2, S1R3, and S2 are lower than

those of the 316 stainless steels with a similar grain size reported in [54–56] , which is due to the porosity according to Gibson-Ashby model. However, S1R1 exhibited almost twice yield strength compared to those reported in the literature, which have the same grain size and are fully dense (relative density > 95%).



**Figure 3.16:** Comparison of yield strength - grain size correlation between select literature data and the results from present study.

Taking the porosity into account, S1R1 exhibited a specific yield strength ( $67.7 \text{ MPa}\cdot\text{cm}^3/\text{g}$ ), higher than two times the traditional fully dense SS316 counterparts ( $25.6 \text{ MPa}\cdot\text{cm}^3/\text{g}$ ). This was expected, attributed to the finer grain structure achieved by SPS. In addition, the specific yield strength achieved in the present work is superior compared to other studies where the SS 316L material was also fabricated by SPS. For example, Flipon *et al.* studied the impact of grain size on the yield strength of SS316L materials with relative densities of >95% and found that grain boundary strengthening occurred to different extents as the grain size decreased [56]. They

divided the grain diameter to three different regimes with different Hall-Petch coefficients. Using the Hall-Petch coefficients found in Flippen *et al.*'s work, the predicted yield strength for a sample containing an average grain diameter of 4.2  $\mu\text{m}$  is  $\sim 300\text{MPa}$ . Using the relative density found in S1R1 (89.1%), this is equivalent to a specific yield strength of  $\sim 42\text{ MPa}\cdot\text{cm}^3/\text{g}$ ; however, S1R1 in our study had a specific yield strength of  $\sim 68\text{ MPa}\cdot\text{cm}^3/\text{g}$ . We attribute the difference in these values,  $\sim 26\text{ MPa}\cdot\text{cm}^3/\text{g}$ , to the strengthening effects from a stiffened atomic structure surrounding the submicron pores and the precipitates that form around the pores. The specific strength achieved in the stainless steels containing submicron pores also outperformed the annealed 7075 aluminum, an alloy which is ubiquitous with the aerospace industry for its specific strength with a raw material unit price higher than SS 316L, as shown in Table 3. Furthermore, the SS316 samples containing submicron pores in the present work had a higher compressive strength (S1R1  $\sim 1370\text{ MPa}$  and S3R1  $\sim 1412\text{ MPa}$ ) than the Ti-6Al-4V alloy, at less than a quarter of the material cost. Hence, the incorporation of submicron pores is a feasible approach to develop cost-effective lightweight structural materials.

**Table 3.3:** Comparison of material cost and mechanical properties

| Material             | Cost            | Specific Yield Strength<br>[1]             | Compression Strength<br>[1] |
|----------------------|-----------------|--------------------------------------------|-----------------------------|
| SS 316 L (annealed)  | \$4.36/kg [24]  | $25.6\text{ MPa}\cdot\text{cm}^3/\text{g}$ | 515 MPa                     |
| Ti-6Al-4V (annealed) | \$21.20/kg [57] | $175\text{ MPa}\cdot\text{cm}^3/\text{g}$  | 860 MPa                     |
| 7075 Al (annealed)   | \$5.51/kg [58]  | $51.6\text{ MPa}\cdot\text{cm}^3/\text{g}$ | 276 MPa                     |

### 3.5. Summary

The current work provided insight into the effect of pore characteristics on the mechanical properties of austenitic stainless steels. SPS was utilized to achieve different pore characteristics and grain sizes in the stainless steels. Varying the particle size and the shape of the starting

powder can be utilized to control the formation of pores with diverse characteristics (volume percentage, size, and shape) in the sintered samples. The effect of pores on the mechanical properties depends on the length scale of mechanical testing. Several concluding remarks are provided below.

- At nanometric length scales, both hardness and wear resistance are predominantly controlled by grain size as predicted from the Hall-Petch relation, while the effect from the pores is not straightforward due to the limited interaction volume in the materials.
- At meso- and macro- scales, the Hall-Petch relation no longer predicts the strength accurately when the stainless steels contain a significant amount of submicron or nanometric pores. The Gibson-Ashby models are not accurate for the samples containing submicron pores, either.
- SS316 with submicron pores exhibited both a higher yield strength and a higher specific yield strength than the counterpart with large pore sizes, even when the grain diameter of the counterparts is finer. The mechanism of the significant strengthening was attributed to local stiffening and the formation of precipitates adjacent to the pores.

In summary, incorporating submicron pores led to improved yield strength and strength to weight ratio compared to the fully dense counterparts. The stainless steels with submicron pores exhibited a yield strength of 482MPa, compressive strength of ~1.4GPa at a strain of 0.3 without fracture, and a specific yield strength of 67.7 MPa·cm<sup>3</sup>/g, which is greater than the annealed Al7075 (Al-Zn-Mg-Cu) alloy, a material ubiquitous in the aerospace industry. These findings indicate potential new directions for future design of cost-effective lightweight structural materials via control of the pore size and distribution.

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## CHAPTER 4 Effect of Powder Morphology on the Microstructure and Mechanical Property Gradients in Stainless Steels Induced by Thermal Gradients in Spark Plasma Sintering

While chapter 3 focused on the effect of powder particle size on the characteristics of pores formed during sintering, and how the pore distribution affected the mechanical properties of the sintered parts, this chapter focuses on the impact powder morphology has on thermal gradients. Thermal gradients during SPS lead to microstructural and property gradients in the sintered parts. To elucidate the effect of starting powder morphology on these gradients, the present work investigated location-specific microstructure and mechanical properties of austenitic stainless steels fabricated via SPS of unsymmetrical powder compacts by paring three types of powders: spherical, plate-like and flakey. Local mechanical properties as a function of radial distance from the center of the sample were investigated via microhardness tests, nanoindentation, and nanoscratch. Radially graded microstructure (porosity and grain size) resulting from the thermal gradients in SPS led to gradients in local microhardness ( $\Delta H = 120\text{--}150$  MPa) and Young's modulus ( $\Delta E = 30\text{--}65$  GPa), yielding higher wear resistance at the sample surface and higher elastic modulus at the sample center, suggesting that higher powder morphology aspect ratios lead to larger thermal gradients.

### 4.1 Introduction

Spark plasma sintering (SPS) is extensively studied because of its capability of densifying a variety of materials at relatively low temperatures in a short amount of time, on the order of several minutes, compared to other traditional sintering techniques like hot pressing[1–4] . Materials fabricated via SPS often exhibit superior mechanical and functional properties mainly due to the ultrafine or nanoscale grain structure resulting from limited grain growth and increased surface diffusivity[5–10]. The feedstock powder for SPS can have a broad range of

sizes and different morphologies. Thermal gradients were reported in both the tools and the samples during SPS, leading to inhomogeneity in the microstructure[11–13]. The thermal gradients result from the geometries and dimensions of the dies and punches, rapid heating rates, the composition and initial density of the powder compact, the electrical conductivity of the materials constituting the sample, and the pulsed current input[14–16]. Radial temperature differences are commonly attributed to different current distributions and radiative heat loss [17]. Giuntini *et al.* showed that thermal and electrical current gradients could be minimized by optimizing tooling[18]. Nevertheless, it is important to note that thermal gradients are not necessarily undesirable. Rather, thermal gradients are beneficial for design of heterogeneous and anisotropic microstructural features, including but not limited to porosity, grain size, precipitates and second phase particles, which consequently dictate the mechanical properties and performance of materials. While some previous work studied the impact of the powder size on the densification behavior during SPS [19–21], the effects of powder morphology on the densification behavior and thermal gradients remain unclear. Therefore, the present work aimed to elucidate how varied powder morphologies affect the thermal gradients in SPS and the consequent gradients in microstructure and mechanical properties of the sintered parts.

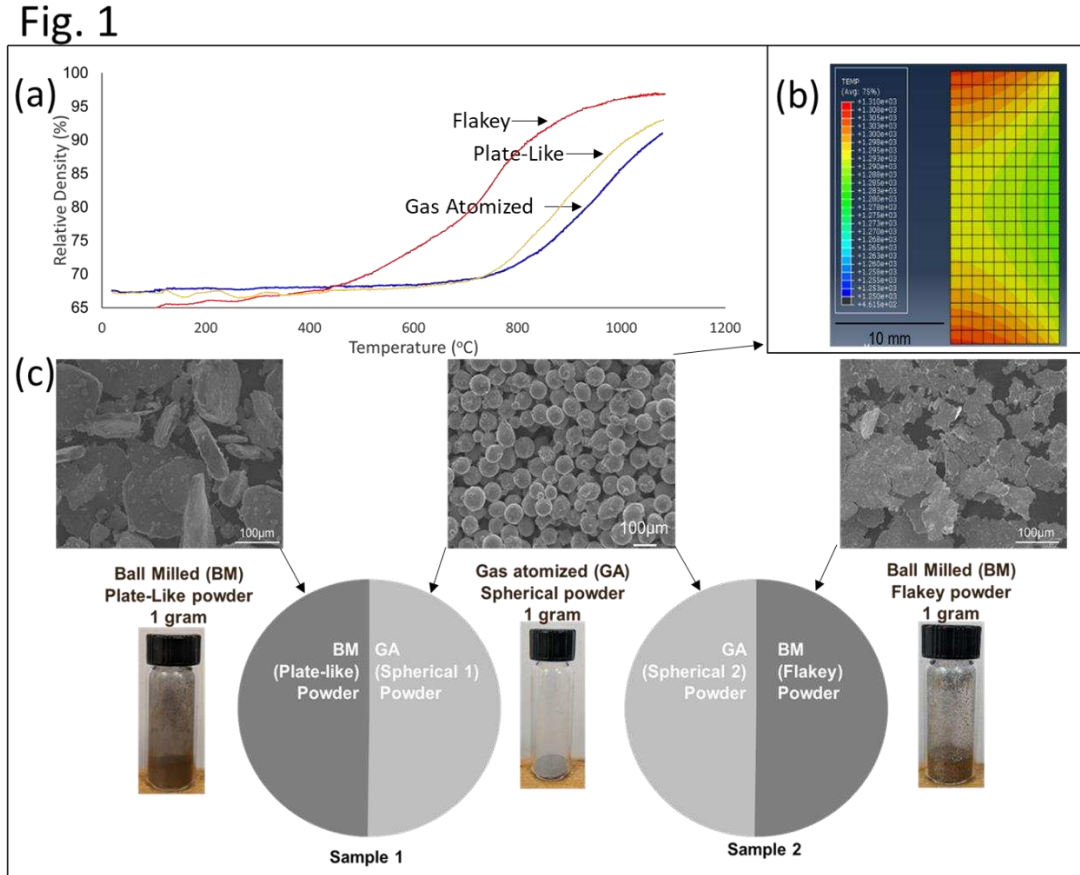
## 4.2 Materials and Methods

### 4.2.1 Starting Powders and SPS Process

316L stainless steel was selected as the model material to study the effect of powder morphology due to its ubiquity in many industries such as the automotive, naval, and defense. Three types of powder with different morphologies were used in this study: spherical powder (commercial gas atomized powder), flakey powder, and plate-like powder. The latter two powders were obtained by ball milling of the gas atomized (GA) powder with and without stearic acid, respectively. The

main difference between the ball milled (BM) powders is the increased thickness of the powder which was milled without steric acid (Fig. 4.1a). The three types of powders showed distinct densification behavior during SPS (Fig. 4.1a). For an identical sintering condition (150°C/min from 25 °C to 1100 °C), the flakey powder achieved the highest relative density out of the three. In other words, the sintering temperature required to achieve the same relative density follows the order of  $T_{\text{flakey}} < T_{\text{plate-like}} < T_{\text{spherical}}$ . Finite element modeling (FEM) result (Fig. 4.1b) showed that a 20 °C radial temperature difference was present in a 10-mm-radius steel sample when the powder arrangement is symmetric. This temperature difference increases as the sample size scales up. To investigate the effect of powder morphology with minimal concerns of miscellaneous discrepancies between nominally identical SPS runs, a strategic arrangement of the powder compact was designed to pair the three types of powders to intentionally achieve asymmetry (Fig. 4.1c). The spherical powder was paired with plate-like powder in Sample 1, and it was paired with flakey powder in Sample 2. Hence, the comparison between the half-disk consisting of spherical powder and the other half sample composed of BM powder, plate-like or flakey, will provide direct insight into the effect of powder morphology on local microstructure and mechanical properties of the sintered parts. The comparison between spherical 1 and spherical 2 will elucidate the effect of irregular powder morphology on the electrical and thermal gradients on the other half of the sample consisting of identical GA powders. The GA powder being used as a control enables direct comparison, without concern with slight differences between starting grain and powder size that is inevitable between the two BM powders. In order to maintain the division between the two powder morphology halves, each BM powder half was first loaded and cold pressed independently against half of a punch to form a half circle powder compact. The top of the BM powder compact was then covered by a half punch the GA powder

was then added, and the entire powder compact was cold pressed at a pressure of 30 MPa for 15 minutes in a ~20 mm-inner-diameter graphite die to enhance particle-particle contact and maintain a consistent powder height. Then the powder compacts were sintered in SPS at 1100°C for 2 minutes with a constant pressure of 20 MPa and a heating rate of 100°C/min.



**Figure 4.1:** (a) Densification curves of the three types of powder; (b) FEM of temperature distribution in a 10-mm-radius stainless-steel sample assuming spherical powder; (c) Powder morphologies (SEM images) and strategic sample construction.

#### 4.2.2 Microstructural Characterization and Mechanical Testing

The overall density of each sample was determined using Archimedes method. Local microstructure and mechanical properties of the samples were investigated at radial distances of 2, 4, and 6 mm from the center. Scanning electron microscopy (SEM) was used to characterize

pore distribution and grain size. For porosity, the cross-section of the samples was mechanically polished to a finishing step of 50-nm alumina suspension. For grain size, the samples were electrochemical polished with a 10 vol% oxalic acid in deionized water in 30 second increments until grain boundaries were revealed in optical microscopy. The average grain size was determined by the average intercept method using 81 lines per location.

Microrhardness was measured by Vickers indentation with 3 indents per location using a load of 9.8N. Nanoindentation was performed using a Berkovich probe with a normal force of 5 mN to make 100 nano-indents per location. To avoid the effect of strain fields from previous indents, nano-indents were spaced 50 $\mu$ m apart and micro-indents were spaced >250 $\mu$ m. Local Young's modulus determined from the nanoindentation was used to study the compliance gradients in the sample. The role of powder particle-particle boundaries was investigated by nanoscratch using a conical probe, which provides constant surface area regardless of the scratch orientation. Nine scratches were performed at each location. Plastic deformation depth profiles were used to compare local wear resistances, where larger plastic deformation depth corresponds to lower wear resistance. Normalized lateral force profiles during scratch were correlated to changes in local microstructure.

## 4.3 Results & Discussion

### 4.3.1 Microstructure

The overall relative density of sample 1 and sample 2 was 95.8% and 98.1%, respectively, indicating that both samples reached the final stage of sintering[22]. All regions demonstrated a porosity gradient regardless of powder morphology: the relative density decreased, and the pore size increased as the location moved from the radial center to the edge of the samples, as shown

in the representative microstructure in Fig. 4.2a. This phenomenon resulted from the thermal gradients during SPS [23–26]. The powder morphology affected the severity of porosity gradient, with the flakey powder giving rise to the smallest pore gradient. Fine micropores (submicron to 2 $\mu$ m) were observed at prior particle-particle boundaries in both half-disk samples made from BM powders, while few fine micropores were observed in those made from spherical powder (Fig. 4.2b). However, the half-disk samples composed of spherical powder exhibited higher porosity and larger pores than the counterparts of flakey and plate-like powder (S1 and S2). Local overheating was reported at the particle-particle contacts in spherical powders due to high current concentrations, promoting neck formation and growth at those particle-particle contacts[27,28]. Residual pores were present between these necks. Plate-like and flakey powder compacts provided larger contacting areas with multiple locations for neck formation than the spherical powder, leading to smaller micropores.

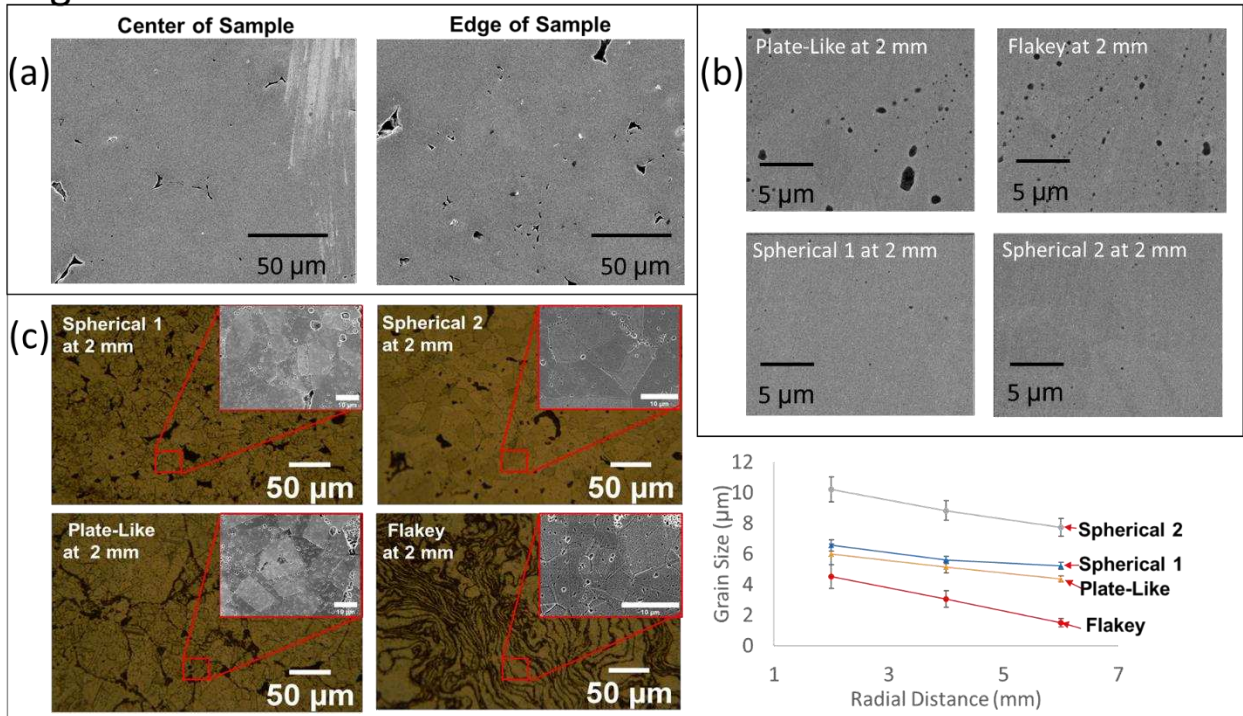
All the half-disk samples also exhibited grain size gradients, with the largest grain sizes present at the disk center and the smallest at the disk edge (Fig. 4.2c). The half disk sample made from flakey powder exhibited the largest grain size gradient, indicating the largest thermal gradient occurred during SPS (Table 1). The half disk made from spherical 2 powder, which was paired with the flakey powder, exhibited the 2<sup>nd</sup> largest grain size gradient, and a larger grain size than the counterpart made from spherical 1 powder, despite that spherical 1 and 2 powders were identical GA powders. This suggested the electrical current path during SPS was influenced by the asymmetric arrangement of the starting powders. A larger fraction of the total electrical current passed through the spherical 2 powder compact in comparison to the spherical 1 powder compact as the flakey powder compact has a higher resistance resulting from the higher contact resistance due to a higher number of powder-powder boundaries than those in the plate-like

powder compact for the same volume. As a result, the half disk of spherical 2 powder compact gained higher thermal energy during SPS than the spherical 1 counterpart though the SPS parameters were set the same, giving rise to the larger grain size in spherical 2.

**Table 4.1:** Summary of gradients in grain size and mechanical properties.

| Powder      | Gradients                                     |                      |                               |                                      |
|-------------|-----------------------------------------------|----------------------|-------------------------------|--------------------------------------|
| Morphology  | Grain Diameter<br>( $\mu\text{m}/\text{mm}$ ) | Hardness<br>(MPa/mm) | Young's Modulus E<br>(GPa/mm) | Plastic Deformation<br>Depth (nm/mm) |
| Spherical 1 | 0.33                                          | 30.8                 | 16.3                          | 4.3                                  |
| Spherical 2 | 0.61                                          | 34.3                 | 11.0                          | 11.6                                 |
| Flakey      | 0.75                                          | 36.5                 | 8.2                           | 2.2                                  |
| Plate -Like | 0.4                                           | 32.0                 | 10.7                          | 3.3                                  |

**Fig. 2**



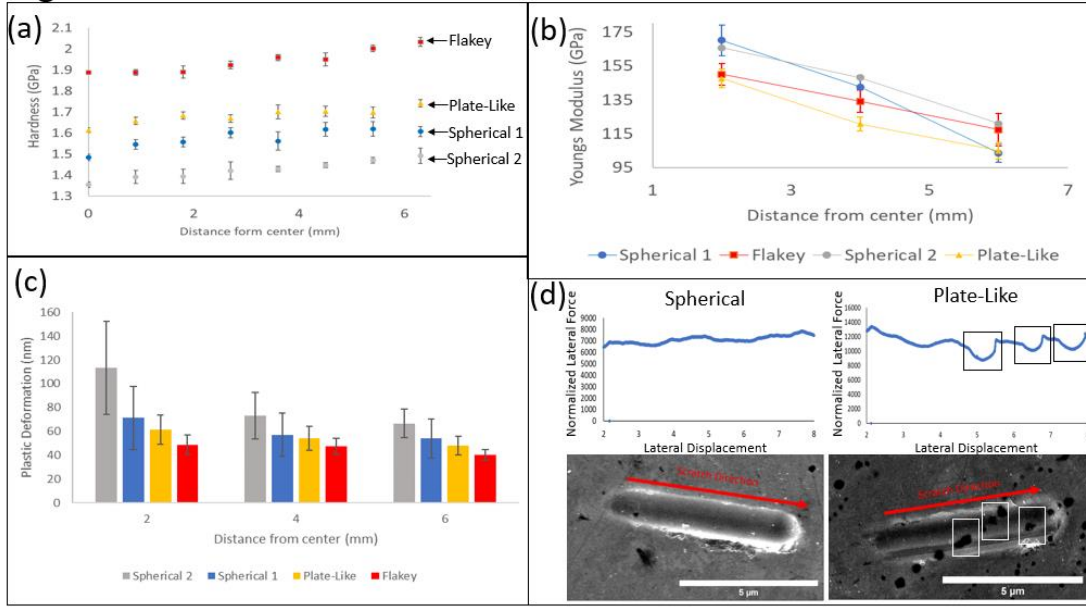
**Figure 4.2:** (a) Porosity gradient shown in spherical 2 region; (b) Micro-pores in the regions made from BM powders at prior particle-particle interfaces compared to relatively pore-free

microstructure in the regions made from GA powder; (c) SEM/optical images of etched samples; and (d) grain size as a function of radial distance from the sample center.

#### 4.3.2 Mechanical Properties

The gradients in microhardness, Young's modulus  $E$ , and plastic deformation depth were provided in Table 1. Fig. 4.3a showed that the microhardness increased as the location moved from radial center to the edge, which was attributed to the grain size gradients described above. In contrast, the Young's modulus decreased with increasing radial distance from the disk center (Fig. 4.3b), which was correlated to the pore gradients discussed above. Powder with a shape of a higher aspect ratio (i.e., flakey) showed a smaller gradient in  $E$ , indicating a smaller change in local porosity, as lower amount of energy is required for the powder compact with a larger particle surface area to achieve densification (Fig. 4.1a). This can be explained by the smaller mean diffusional distance required for powders with higher aspect ratios [29]. Additionally, it is well known that the primary driving force for sintering is the reduction of surface energy caused by the solid-vapor boundary. Therefore, the particle with the highest surface area to volume ratio also requires the least energy for densification as is demonstrated in Fig. 4.1a. The difference in  $E$  gradient between spherical 2 and spherical 1 is attributed to the difference in electrical current density that passed through the powder compact as discussed previously.

Fig. 3



**Figure 4.3:** Mechanical properties for all four half-disk samples made from flakey (red), plate-like (yellow), spherical 1 (blue), and spherical 2 (gray) powders. (a) Microhardness testing, (b) Young's modulus determined from nanoindentation, (c) plastic deformation

Fig. 4.3c shows the plastic deformation depth increased with increasing radial distance from the disk center for all four half-disk samples, suggesting higher wear resistance at the surface which is desirable for structural applications. The gradient in wear resistance arose from the grain size gradients. Overall speaking, the regions made from BM powders showed higher wear resistance than the paired counterparts made from GA powder, due to the finer grain size in BM powders. Additionally, the region made from spherical 2 powder exhibited the largest gradient in plastic deformation depth. Fig. 4.3d displays the normalized lateral force profiles as a function of scratch length. A few concaves (the boxed areas in Fig. 4.3d) were observed in the scratch curve for the region made from plate-like powder, which corresponded to micropores present at the prior powder particle-particle interface, as demonstrated in the SEM images. Such concaves were not present in the scratch data for the spherical counterpart. It is also worth noting that the

normalized lateral force showed continuity for the whole scratch length, indicating a ductile deformation manner despite of the presence of the porosity[30].

#### 4.4 Summary

In conclusion, this work investigated the effect of powder morphology on the microstructure and mechanical property gradients in stainless steels induced by thermal gradients during SPS. The key findings include: (1) radially graded microstructures (pores and grain size) were achieved due to thermal gradients and varied starting powder morphology; (2) Flakey powder led to smallest grain size, largest grain size gradient, but smallest porosity gradient; (3) Microstructural gradients resulted in gradients of mechanical properties, yielding higher wear resistance at the sample surface and higher elastic modulus at the sample center.

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## CHAPTER 5 Incorporation of the Master Sintering Curve into Finite Element Modeling to Understand Gradients in Spark Plasma Sintering

The previous chapters focus on how the implementation of pores can be useful within inherently heavy alloyed metals. However, the formation of local precipitates makes the understanding of the direct impact of powder morphology on pore characteristics and densification more convoluted. For this reason, commercially pure titanium was used in lieu of stainless steel. This chapter and Ch6 present the research on pure Ti. Additionally, the work in the previous chapters focused on almost solely experimental practices, which motivated the investigation into computational approach to guide the design of experiments and selection of sintering parameters for scaling up. Specifically, in this chapter, the effort focused on incorporating the master sintering curves (MSC) into a thermal-electric (TE) finite element analysis (FEA) model to enable continuous nodal-specific simulation of the sample's thermal and electrical properties during sintering with respect to both relative density and temperature. This combined model is proposed as an alternative to a fully coupled thermal-electric-mechanical model, which is much more computationally costly and difficult to parametrize experimentally. Both MSC and thermal-electric (TE) finite element analysis (FEA) models have been utilized by other researchers to understand the SPS process. The MSC model is typically used to predict the overall relative density of a sample, while the TE FEA model provides useful information on temperature and electrical current distributions during the sintering process. However, both have their distinct flaws. The classical MSC model only predicts the average overall relative density based on average thermal energy, and the TE FEA model only predicts material properties based on temperature. To break through the limits of both models, the MSC model is incorporated into the TE FEA model at a nodal level. This enabled a

detailed understanding of local densification behavior within the entire sample during sintering, as well as taking into account the temperature and relative density dependence of material properties in the FEA model. Three different heating rates were selected for SPS to construct the MSCs, which gave an apparent sintering activation energy of 156.5 kJ/mol by minimizing the mean residual square between the three experiments. Nine additional experiments were used to verify the results of the MSC. The predicted relative densities were compared to the experimental results from sintering, and the scaled-up sample. The microstructure of the sample showed that the location-specific final relative densities at three different locations were within  $\pm 1\%$  deviation from the predicted results by the combined model. Micro computed tomography results exhibited a general trend of decreasing relative density as the location moved radially from the sample's center to the sample's surface, which agreed with the simulation results using the combined model.

### 5.1. Introduction

Spark plasma sintering (SPS), commonly known as field assisted sintering technology (FAST), is an efficient consolidation process to produce metallic and ceramic bulk materials because of its capability to sinter powders at a lower temperature with shorter holding time, compared to other sintering technologies like hot press. SPS utilizes Joule heating with or without a uniaxial mechanical pressure to achieve high heating rates (typically  $>100^{\circ}\text{C}/\text{min}$ ), by applying a pulsed electric current to a punch/die set that encloses the feedstock powder compact. The die and punches are often made of graphite. One attractive benefit of SPS is that it can restrict grain growth of the material during sintering, and thus improve the mechanical and functional properties of the final products [1–3]. However, electrical current gradients and radiative heat loss from the die's outer wall cause thermal gradients in both the sample and the die.

Subsequently, these thermal gradients give rise to gradients in both mechanical and functional properties of the final materials[4–8]. Despite that research efforts have been devoted to minimizing thermal gradients for the purpose of improving homogeneity in materials, it is relatively unknown how to utilize and control the thermal gradients to develop graded microstructure for graded properties and functions. To better understand and utilize the thermal gradients, it is imperative to implement modeling and integrate the modeling with experiments to investigate the spatial and temporal distributions of electric current and temperature in the powder compact during sintering, and how the evolution is dependent on the changes in material properties relating to temperature and the relative density of the powder compact.

In general, master sintering curves (MSC) are used to estimate how the overall average relative density of the powder compact changes during sintering, which was originally developed by Su and Johnson [9] for pressure-less sintering. It is assumed in the MSC model that the microstructure evolution is only a function of the relative density of the material being sintered, and the densification process is dominated by one mechanism based on atomic diffusion. The MSC model was later modified by An and Johnson to include pressure assisted sintering [10]. Although the MSC model has shown high levels of consistency with experimental results [11–14], it is typically assumed that the sample has a uniform relative density. The potential gradients in relative density resulting from the thermal gradients during sintering were overlooked in previous work using the MSC method for SPS. To understand and predict gradients during the SPS process, many researchers turned to numerical methods to simulate the entirety of the process via finite element method (FEM). Initially, FEM was implemented via thermal-electrical (TE) modeling to simulate the electric current and temperature distributions during SPS [15–17]. Despite that the changes in material property as a function of temperature were considered in

previous TE FEM, these models did not consider strains or changes in material properties caused by the densification during sintering, which can cause large discrepancies between the model and experimental work [18]. To account for the previously overlooked parameters, thermal-electrical-mechanical fully coupled models were developed by incorporating creep for the mechanical part of the model [19–21]. Thermal-electrical-mechanical models are effective for predicting electric current and temperature profiles in the samples that are sintered with large pressure gradients or large strains. However, many studies on SPS do not fall under either of these two situations. In addition, it requires a tremendous amount of experimental work to construct the thermal-electrical-mechanical models, such as the use of hot isostatic pressing or hot pressing to determine creep parameters (e.g., creep activation energy), making the development of these models difficult and time-consuming [22–24]. Large strain rates achieved in SPS due to high heating rates, as well as the presence of thermal gradients, also make it a big challenge to obtain accurate measurements of creep strains. While Maniere et al. showed the feasibility of parameterizing creep in SPS, it still requires many lengthy experiments with precise strain-rate measurements. Moreover, thermal-electrical-mechanical models are more computationally expensive than a TE model [25].

To enhance the scientific understanding of the gradients in SPS so that the thermal gradients can be utilized for functionally graded materials, it is in demand to develop a modeling method with improved efficiency and accuracy. To fulfill this need, the present work investigated how a TE model can be modified to retain high levels of accuracy by taking into account the material property dependence on both temperature and relative density. The ultimate goal is to implement the modified model to predict thermal gradient distribution in the materials during sintering, and subsequently guide experimental design to manipulate the thermal gradients for different

desirable microstructures, e.g., minimizing the gradients if homogeneity is favorable, or increasing the gradients for specific locations if heterogeneous microstructure is desired for graded properties. It was hypothesized a combination of the MSC and TE models, both relatively easily accessible, could be an alternative to the complex and computationally expensive thermal-electrical-mechanical fully coupled model when strains and pressure gradients within the sample are small or negligible. The hypothesis is supported by the fact that MSC can predict relative density based on local thermal history, which can be supplied by the TE FEA model given initial material properties. Then the thermal history is calculated at each time step to update the relative density at each point of integration based on the MSC. To develop this MSC-TE FEA combined model, a three-step strategy is proposed in the present work: (1) estimation of the apparent sintering activation energy for a specific powder, using a set of lab-scale small diameter samples, sintered at three differing heating rates, to construct the MSC; (2) Verification of MSC via sintering of additional samples, the data from which were not used for the initial construction of MSC; and (3) Incorporation of the MSC model at a nodal level, using the MSC to update material relative density and allowing material properties to evolve according to both local temperatures and relative density in a TE FEM. To develop and validate the MSC-TEFE combined model, pure titanium (Ti) was selected as the material for experimental work as it is the base of Ti alloys that have ubiquitous importance in aerospace and defense applications. Starting with pure Ti in lieu of complex Ti alloys also enables efficient simulations to incorporate MSC into the TE FEA, with mitigation of the concern of secondary phases. Finally, the location-specific relative density distribution predicted by the MSC-integrated FEM is compared to the experimental characterization of a scaled-up Ti sample sintered by SPS to verify the accuracy of the combined model.

## 5.2. Materials and Methods

### 5.2.1 Modeling Procedure: Construction and Verification of the Master Sintering Curve

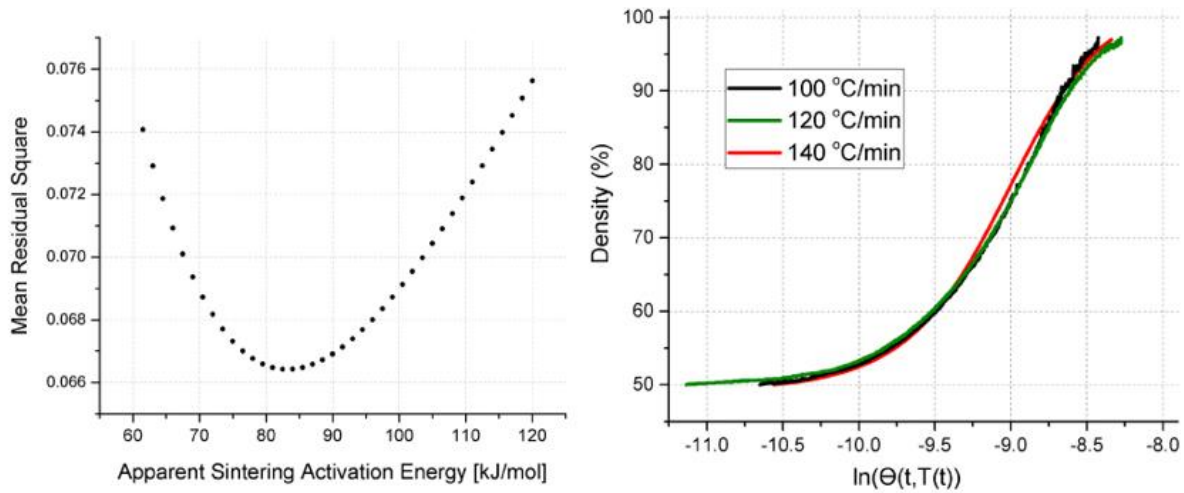
First, master sintering curves (MSC) are constructed to accurately assess the relative density at incremental steps during the FEA process within the TE model instead of creating a fully coupled thermal-electrical-mechanical model. Detailed information on the origin and background of the master sintering curve can be found in the article by Su and Johnson[9]. Basically MSC shows the densification behavior of a material with respect to sintering time and temperature, which is expressed as

$$\text{EQ(5.1)} \quad \phi(\rho) = \Theta(t, T) = \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt$$

Where  $\phi(\rho)$ ,  $\Theta(t, T)$ ,  $t$ ,  $T$ ,  $Q$ ,  $R$ , and  $dt$  are the densification parameter, the work of sintering, time, temperature, the apparent sintering activation energy, the gas constant, and the incremental change in time. If a specific powder is sintered with multiple different heating schedules, and the dominant mass transport remains constant, then the plot of relative density against the work of sintering for the various heating schedules should converge to construct an MSC. However, to define the master sintering curve from multiple sintering programs, the apparent sintering activation energy  $Q_{MSC}$  must be determined first. This term is computed by minimizing the mean residual square (MRS) between the sets of data according to EQ (5.2), which was completed using MATLAB in this study:

$$\text{EQ(5.2)} \quad MRS = \sqrt{\left(\frac{1}{\rho_f - \rho_g}\right) \int_{\rho_g}^{\rho_f} \sum_{i=1}^N \frac{\left(\frac{\Theta_i}{\Theta_{avg}} - 1\right)^2}{N} d\rho}$$

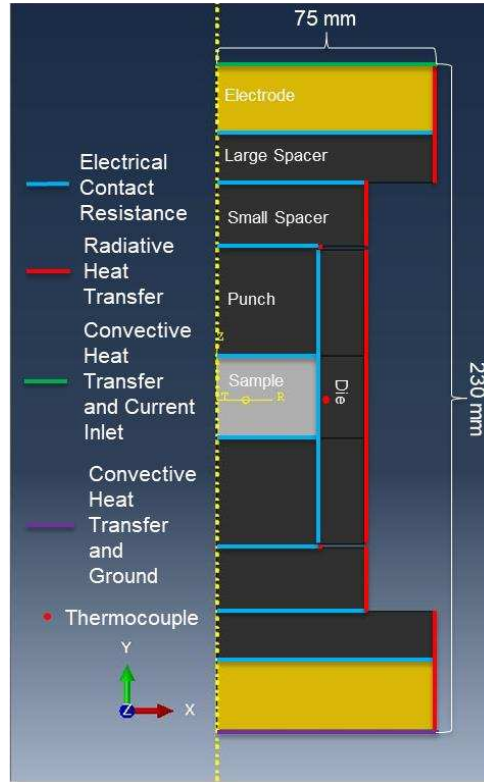
Where  $\rho_f, \rho_g, N, \frac{\theta_i}{\theta_{avg}}$ , and  $d\rho$  are the final density, green body density, number of heating programs, ratio of that single heating program's  $\Theta$  compared to the  $\Theta$  at that density for the other programs, and the incremental change in relative density. Once a range of apparent activation energies are calculated, the minimum value of is found, as shown in Fig. 5.1a. Then all the densification curves converge on a single curve, as shown in Fig. 5.1b[26]. Fig. 5.1 displays typical output graphs from the calculation of the MSC. After MSC are determined for a given powder, the densification behavior, i.e., evolution of relative density as a function of time (t) or temperature (T), can be predicted for arbitrary heating schedules. The thermal work for a node is summed, according to equation EQ(5.1), then the total thermal work is matched to the MSC, which provide the prediction of the relative density value. The procedure to predict density from an MSC is summarized as three steps: (1) create an arbitrary heating schedule as a function of time,  $T_{arb}(t)$ ; (2) Calculate the thermal work  $\Theta_{arb}(t, T)$  for this arbitrary heating schedule; and (3) Match  $\Theta_{arb}(t, T)$  to the values from  $\Theta_{MSC}(t, T)$  determined from the experimentally collected data to predict relative density. In other words, the index where  $\Theta_{arb}(t, T) = \Theta_{MSC}(t, T)$  is where  $\rho_{arb} = \rho_{MSC}$ .



**Figure 5.1:** (a) Example of how the apparent sintering activation energy, is determined by minimizing the mean residual square (MRS); (b) a typical example of a MSC. [26]

### 5.2.2 Modeling Procedure: Material Properties and Geometry in FEM

Thermal-electric FEA modeling was performed via ABQQAUS software. A 4-node quadrilateral element was chosen with a mesh size of 2 mm and time increment of 1 second. Further reduction of mesh size or time increment showed negligible changes. The SPS process was modeled as Z-axis-symmetric (shown in Fig. 5.2), which is typically used for FEM of SPS [27]. The Z-axis-symmetric setup also saves the computation time and cost required per simulation. Material properties for the tooling parts made of graphite, such as spacers, punches, and the die, were all modeled with the dependence on temperature. The Inconel electrode electrical and thermal properties, which is constantly being cooled by chilled water were treated as constants during the simulation. The electrical conductivities of the graphite tooling were measured from 293K to 1293K in the SPS. All temperature dependent material property equations used within this model can be found in Appendix C-1 [28–32], with a diagram of the FEA geometry shown in Fig. 5.2.



**Figure 5.2:** FEM geometry, inclusive of boundary conditions and overall system dimensions

In terms of material properties (e.g., thermal conductivity and electrical conductivity) for the sample, both temperature and density dependence were considered by using a user defined field (USDFLD) subroutine. This subroutine allows the user to create a field equation based upon other known local variables, in the case of this work it allows us to define density and material properties reliant on density based upon local thermal energy and time. First, the nodal temperatures and times were loaded into the subroutine. After each time increment was completed, these values were added to a state variable with the time and temperature profiles of all previous steps. Then, the changes in material properties as a function of temperature were determined. This was followed by a calculation of the work of sintering, which is described in the previous section, the value was then matched to the MSC to determine the appropriate relative density at each nodal location. This key step differentiates this model from a traditional

TE model that usually neglects the effect of changes in relative density of the sample during sintering. The temperature-dependent material properties, including electrical conductivity, thermal conductivity, relative density, and heat capacity, were then modified by using the effective medium approximations ( EQ 5. 3 – 5.6) below to create material property dependence on both relative density and temperature[33] :

$$\text{EQ(5.3)} \quad \sigma_{Porous} = \sigma_{Dense} \cdot \left(1 - \frac{3}{2}\theta\right)$$

$$\text{EQ(5.4)} \quad \kappa_{Porous} = \kappa_{Dense} \left(1 - \frac{3}{2}\theta\right)$$

$$\text{EQ(5.5)} \quad \rho_{Porous} = \rho_{Dense}(1 - \theta)$$

$$\text{EQ(5.6)} \quad C_{p\ Porous} = C_{p\ Dense}(1 - \theta)$$

Where  $\sigma_{porous}$ ,  $\sigma_{dense}$ ,  $\theta$ ,  $\kappa_{porous}$ ,  $\kappa_{Dense}$ ,  $\rho_{porous}$ ,  $\rho_{dense}$ ,  $C_{p\ porous}$ , and  $C_{p\ Dense}$  are the electrical conductivity of the porous material, electrical conductivity of the bulk material, volume fraction porosity, thermal conductivity of the porous material, thermal conductivity of the porous material, thermal conductivity of the bulk material, density of the porous material, density of the bulk material, heat capacity of the porous material, and heat capacity of the bulk material, respectively.

### 5.2.3 Modeling Procedure: Thermal-Electrical Governing Equations

Section 5.2.3 to 5.2.5 describe the governing equations, boundary conditions, and initial conditions used to establish the thermal-electric FEA with the incorporation of the master sintering curve using ABAQUS commercial FEA software. The governing equation for this thermal electric model is [34]:

$$\text{EQ(5.7)} \quad \int_V \frac{\partial \delta \phi}{\partial x} \cdot \sigma^E \cdot \frac{\partial \phi}{\partial x} dV = \int_S \delta \phi J dS + \int_V \delta \phi r_c dV;$$

And the amount of electrical energy dissipated into a conductive material via Joule's law is:

$$\text{EQ(5.8)} \quad P_{ec} = \mathbf{J} \cdot \mathbf{E} = \frac{\partial \phi}{\partial x} * \sigma^E \cdot \frac{\partial \phi}{\partial x}$$

Where  $V, \phi, x, \sigma^E, S, J, r_c$ , and  $E$  are volume, electric potential, distance, electrical conductivity matrix, surface area, current density per unit area, internal volumetric current source per unit volume, and the field intensity respectively.

#### 5.2.4 Modeling Procedure: Thermal Boundary and Initial Conditions

In this model, it is assumed that all components started with an initial condition of temperature at 293K. During the simulation, most of the heat loss through the graphite tooling is removed by water cooled Inconel electrodes within the SPS, which is modeled as a convective heat flux:

$$\text{EQ(5.9)} \quad Q_{conv} = hA\Delta T$$

Where  $h, A$ , and  $\Delta T$  are the heat transfer coefficient, contact area, and difference in temperature between electrode surface and water cooling at 293K. The heat transfer coefficient between the electrode and cooling water used is set to 880 W/m-K, based on another research group using a similar SPS machine[25]. Significant heat loss also results from the tooling's vertical walls to the inner SPS chamber walls, which is radiation heat transfer and modeled by the Stefan-Boltzmann equation:

$$\text{EQ(5.10)} \quad Q_{rad} = \epsilon A \xi (T_1^4 - T_2^4)$$

Where  $\epsilon, A, \xi, T_1$ , and  $T_2$  are the material emissivity, radiating area, the Stefan-Boltzmann constant, the radiating surface temperature, and the absorbing surface temperature which is assumed to be 293 K. This study used 0.8 for the graphite emissivity, and an emissivity of 0.67 for Inconel, based on literature data [25]. The thermal contact resistance was not considered in this model, as Wei et al. have demonstrated this to be negligible [35].

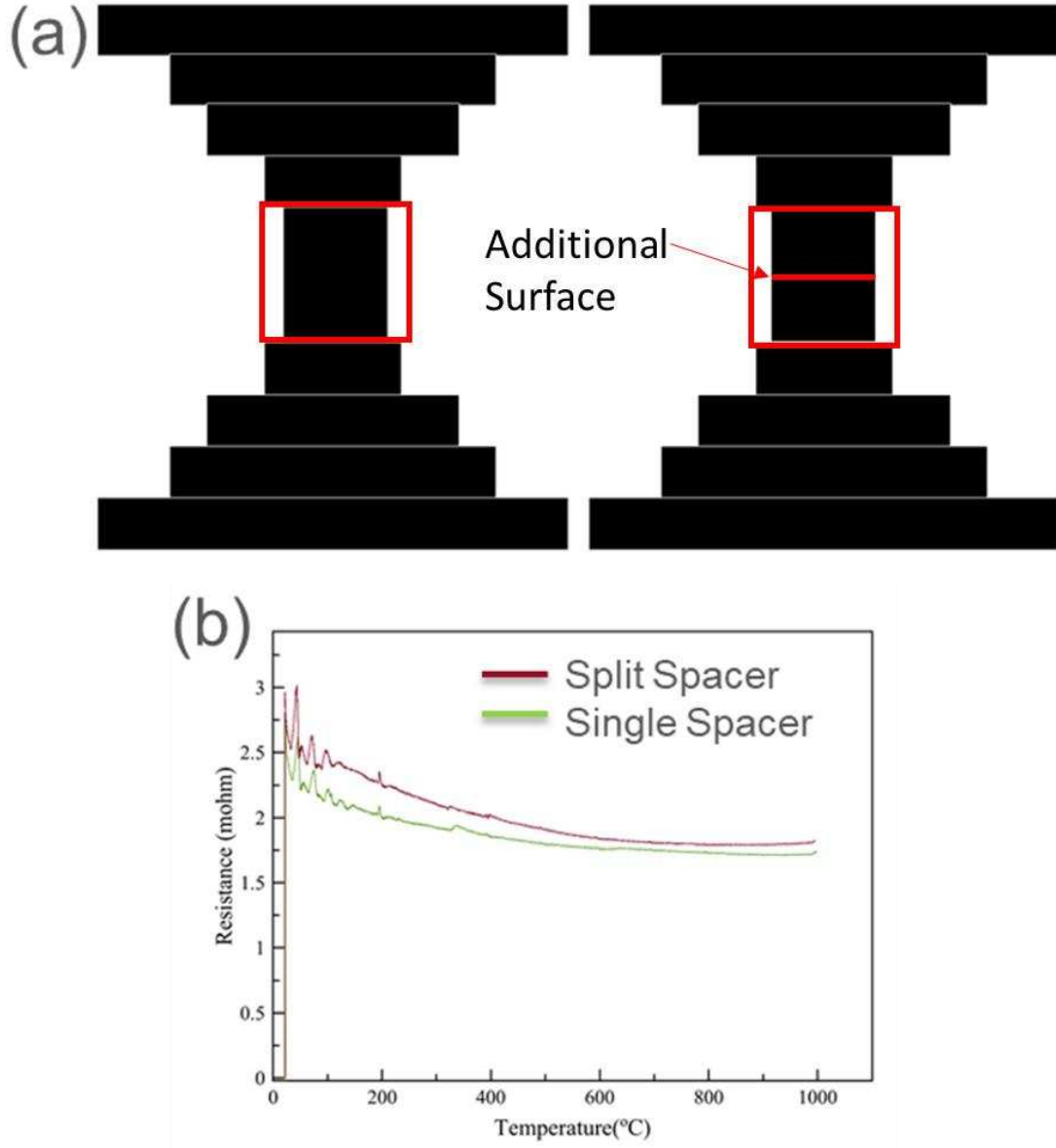
### 5.2.5 Modeling Procedure: Electrical Boundary Conditions

A potential of zero was applied at the lower electrode to simulate ground status during the entirety of the simulation. Additionally, an ABAQUS UAMP subroutine was used to simulate current density moving into the system at the upper electrode. The UAMP subroutine allowed for the simulation of a PD (proportional derivative) controller, incrementally correcting the current density flowing into the system to closely follow a thermal program based on the nodal temperature of the simulated thermocouple shown in Fig. 5.2. The numerical values of  $K_p$  and  $K_d$  are autotuned by the SPS based on the cooling and heating of a specific tooling set. The current density controlled by the simulated thermocouple is described as [26]:

$$\text{EQ(5.11)} \quad I_t = I_{t-1} + K_p \cdot T_{Diff} + K_d \cdot \frac{d}{dt} \cdot T_{Diff}$$

Where  $I_{t-1}$  and  $T_{Diff}$  are the current density at the previous time increment and the temperature differential between the assigned heating schedule and the nodal temperature of the simulated thermocouple.

Electrical contact resistances were also considered in this model. The horizontal contact resistances were measured with two different experiments. The first incorporated a single spacer placed between larger graphite spacers, and the second incorporated split spacers, each of which are half the height of the initial spacer (Fig. 5.3a).



**Figure 5.3:** (a) Single and split spacer experiments (b) resistance measurements from each respective experiment

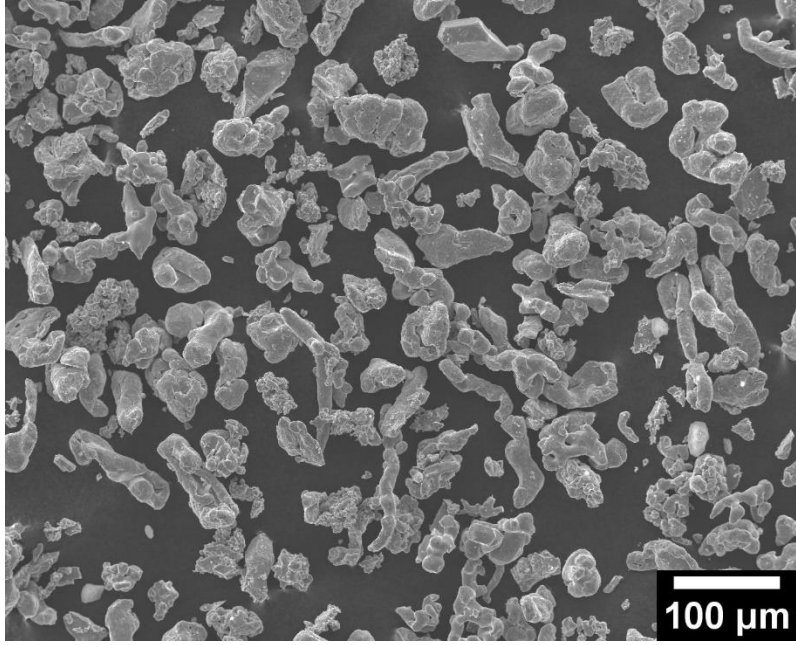
In each experiment, the heating rate was 100K/min to achieve a final temperature of 1273K. The difference in total resistance between the two experiments is attributed to the contact resistance of the additional surface. Values of the calculated horizontal contact resistance and vertical contact resistance at a pressure of 20 MPa [35] can be found in Appendix C-2. The contact resistance with respect to temperature can then be described using the following equation:

$$\text{EQ(5.12)} \quad \rho_c = A_c R_c(T)$$

Where  $\rho_c$ ,  $A_c$ ,  $R_c(T)$  are resistivity at the contact, area of the contact, and the resistance of the contact with respect to temperature.

#### 5.2.6 Experimental Procedure: Starting Powders and SPS Process

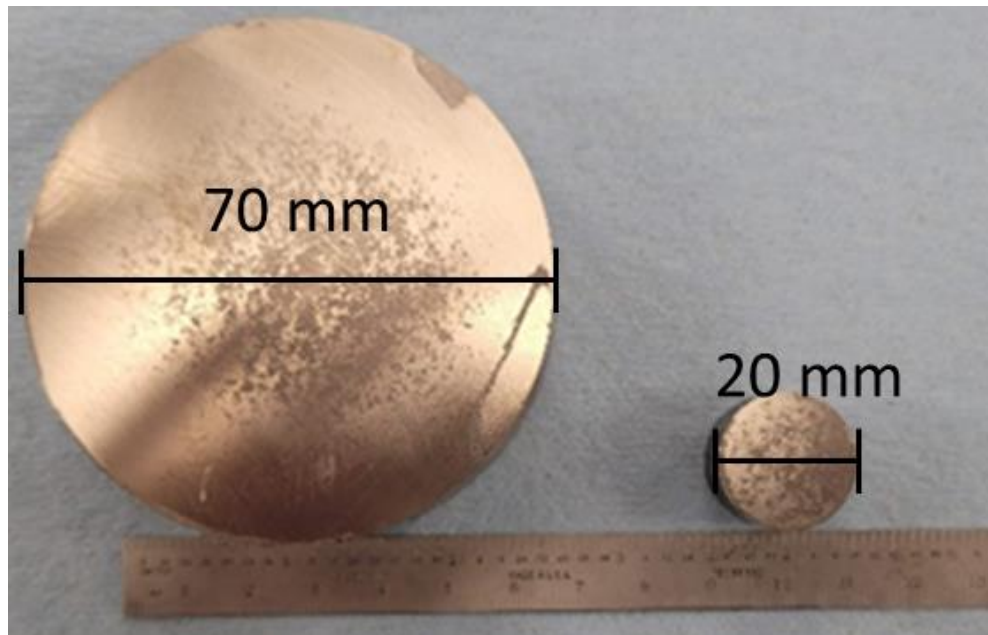
The material used in this study was commercial pure Ti powder produced via the Kroll's process with a -325 mesh size ( $< 44 \mu\text{m}$ ) and 99.5% purity (O<0.28%, C<0.09%, H<0.03%), purchased from Alfa Aesar. The starting morphology of the powder is irregular in nature as shown in Fig. 4.



**Figure 5.4:** SEM image of commercially pure titanium -325 mesh

One set of lab-scale disk-shape samples (diameter  $\sim 20 \text{ mm}$ ) was sintered at three different heating rates to construct the MSC, while another set of (9 additional) lab-scale samples were sintered to verify the MSC. And a scaled-up sample (70 mm diameter) was sintered and characterized to verify the accuracy of the combined MSC and FEA model. Fig. 5.5 shows a

representative image of both the 20-mm lab-scale and the 70- mm mid-scale samples. All samples started with a powder compact (green body) packed via a cold press with a pressure of 40 MPa to ensure initial powder particle-particle contact. During SPS, a constant pressure of 20 MPa was applied. Three different heating rates were used to sinter the set of samples for constructing MSC: 75, 100, and 150 K/min, to achieve a final temperature of 1273K without any holding time. The set of samples used to verify the MSC (called the “challenge series”) were sintered using the same graphite die with the same amount of feedstock powder. The heating rates, holding time, and final temperature were varied to verify the MSC model, provided in Table 1. Lastly, the 70 mm diameter sample was sintered by a simple heating step at a rate of 100K/min to achieve a final temperature of 1073K, without any holding time. The sample was then cooled to the ambient temperature in the SPS chamber.



**Figure 5.5:** 70 mm sample and 20 mm representative samples

**Table 5.1:** Sintering conditions used for the challenge series

| Sample # | Heating Rate (K/min) | Final Temperature (K) | Holding Time (min) | Relative Density (%) |
|----------|----------------------|-----------------------|--------------------|----------------------|
| 1        | 75                   | 973                   | 0                  | 79                   |
| 2        | 75                   | 1023                  | 0                  | 85                   |
| 3        | 75                   | 1073                  | 0                  | 87                   |
| 4        | 100                  | 973                   | 0                  | 79                   |
| 5        | 100                  | 1023                  | 0                  | 85                   |
| 6        | 100                  | 1073                  | 0                  | 86                   |
| 7        | 150                  | 953                   | 2                  | 80                   |
| 8        | 150                  | 1053                  | 2                  | 87                   |
| 9        | 150                  | 1153                  | 2                  | 93                   |

#### 5.2.7 Experimental Procedure: Microstructural Characterization

To determine the average final density of all 20 mm samples, Archimedes method was used. The density of the larger sample (70 mm diameter) was determined via geometric means. Local microstructure of the 70 mm sample was investigated via scanning electron microscopy (SEM); the SEM used in this study was a JEOL-JSM-5800 FESEM which was operated at 15 kV.

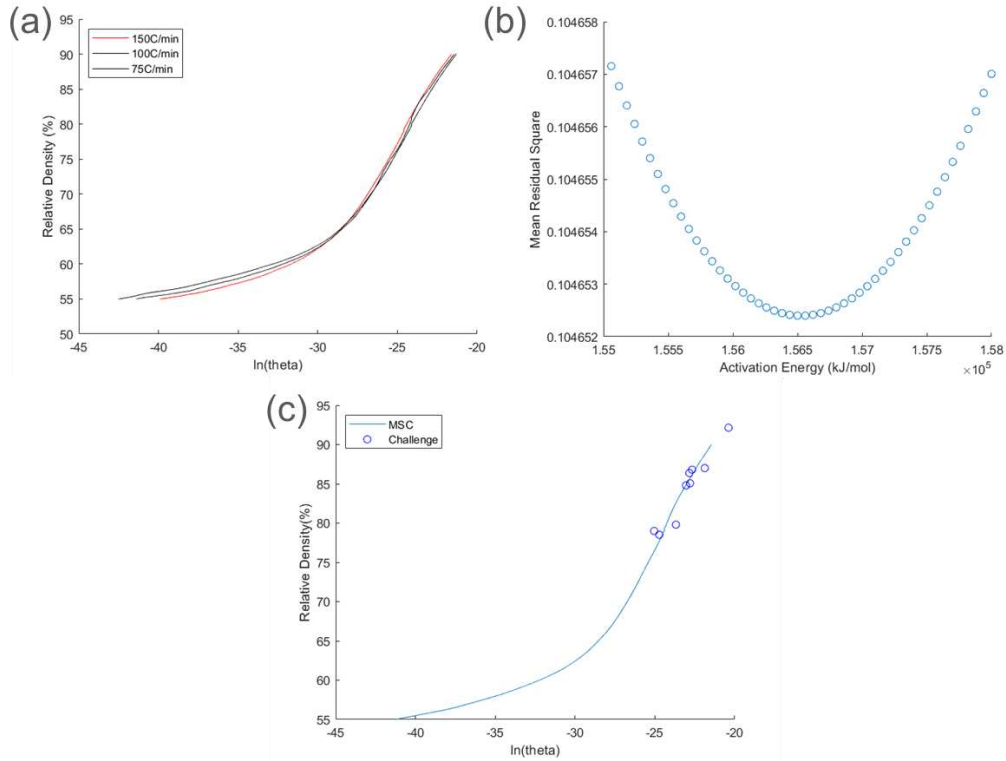
Particularly, three locations were selected as regions of interest (ROI), as they correspond to hot, intermediate, and relatively cold zones in the sample predicted by the FEA model. To prepare the sample for SEM characterization, its cross-section was mechanically polished to a finishing step of 50-nm diamond and then 50-nm colloidal silica with 30 vol% hydrogen peroxide to remove any surface damage from the polishing process. Image J software was implemented to assess the average volume porosity, and average ferret diameter at each position with nine images used per location. Edge detection, filling, and threshold processes were implemented to detect the pores in each image. This was followed by particle analysis with the exclusion of any features smaller than  $10 \mu\text{m}^2$  to avoid noise being counted as porosity. A radial cross section was then cut from the 70 mm sample, to assess the distribution of pores using X-ray Micro-CT (Scanco micro-CT

80), with a nominal resolution of 10  $\mu\text{m}$ . Five different radial distances were analyzed: at 30 mm, 22.5mm, 15mm, 7.5mm, and 0 mm from the sample center. A standard volume was then taken from the rendering with dimensions of 0.1x1.5x1.5 mm (radial-x-y) as depicted in Fig. 5.10a to assess the porosity in that volume. The radio density of each voxel known as the Hounsfield unit within the 3-D rendering is used to describe the absorption of the radio wave at each distinguishable location. To quantify the porosity in the 3-D rendering, a Hounsfield unit of -1000 was used, which is associated with the radiodensity of air [36].

### 5.3. Results and Discussion

#### 5.3.1 Master Sintering Curve

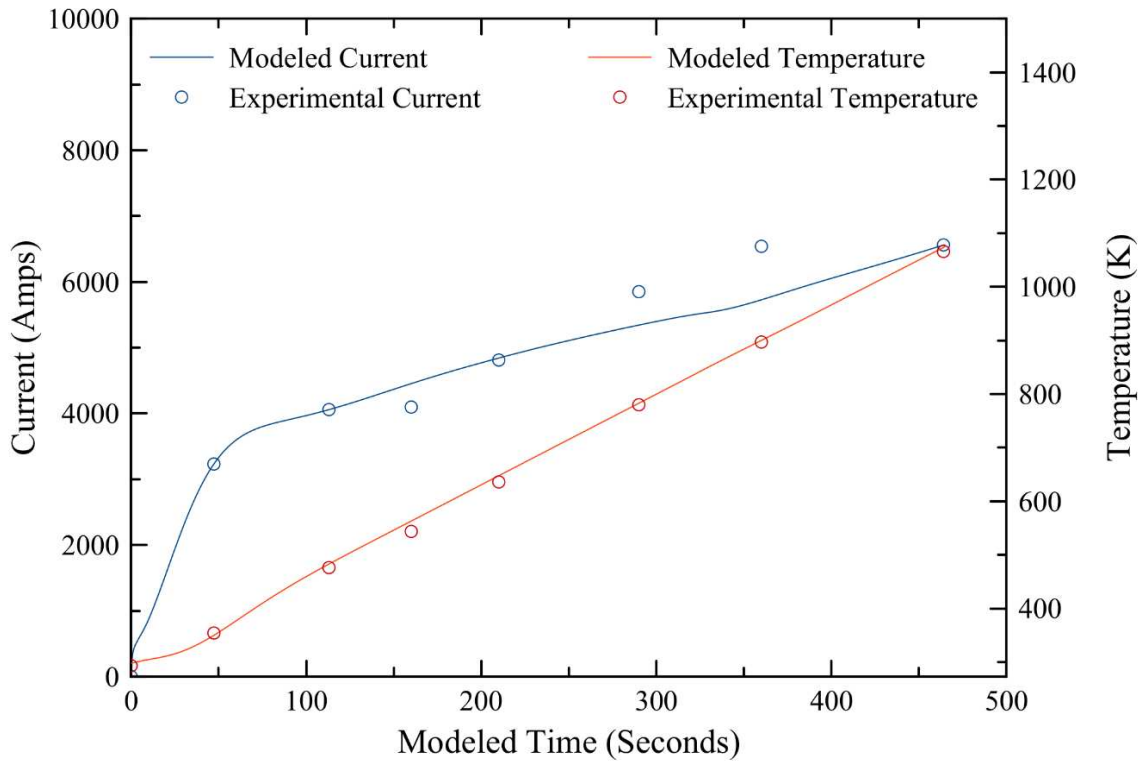
The master sintering curve results ( Fig. 5.6a) show that all three samples from the three differing heating rates converge to a single curve. The MRS among the three different heating rates reaches a minimum at 156.5 kJ/Mol (Fig. 5.6b). These results are consistent with the work by Koppers et al., who reported that the activation sintering energy was around 160 kJ/mol for gas atomized (GA) commercially pure (CP)-Ti powder [37]. Another study by Qian et al. reported a comparable activation energy, 184 kJ/mol, for GA CP-Ti powders [38]. Additionally, the results from the challenge series of samples depicted in Fig. 5.6c also agree well with the master sintering curve, which validated the overall MSC model.



**Figure 5. 6:** (a) Relative density vs. sintering work for the CP-Ti powder (b) MRS of the three different heating rates (c) MSC vs challenge series.

### 5.3.2 Electrical-Thermal FEM Combined with the MSC

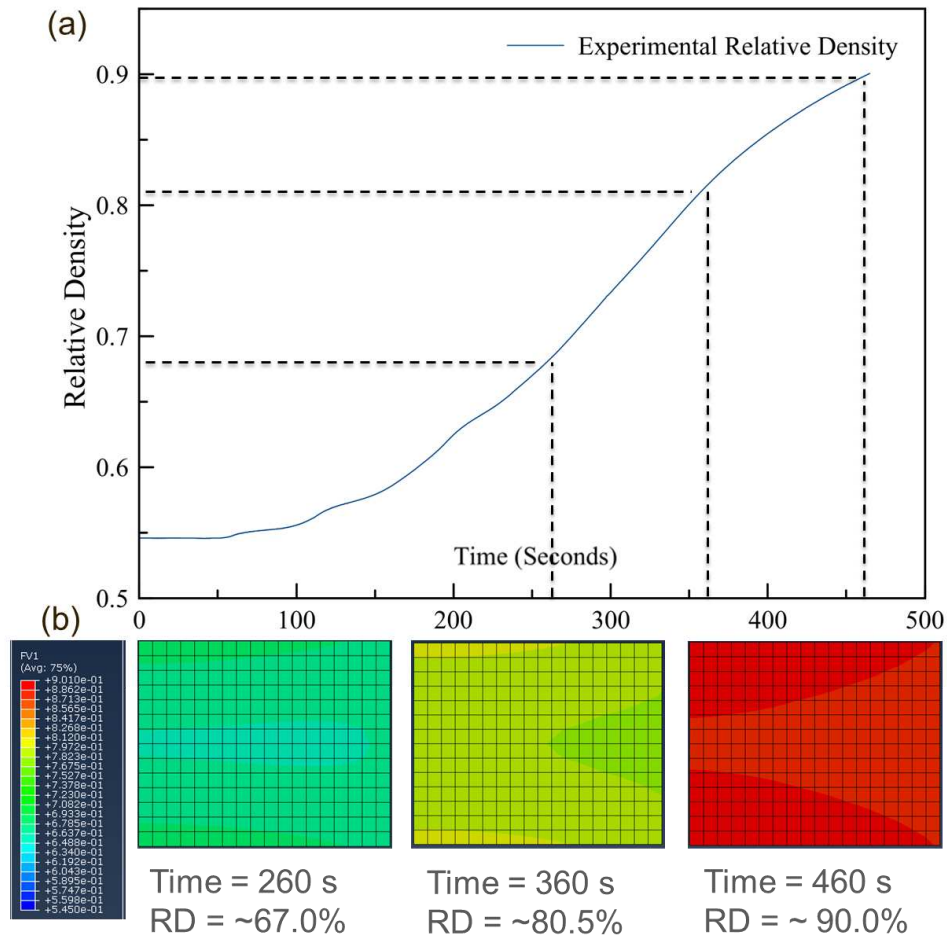
Fig. 5.7 shows the comparison of electrical current and temperatures between the modeling results and experimental measurements as a function of heating time, obtained from the sintering of the 70-mm diameter sample. The temperature data shows a high degree of consistency between the modeling and experimental data. While experimental data for the electric current also exhibit general agreement with the modeling result, there is some level of incongruency in the time range of 300 to 400 seconds, which was considered acceptable compared to other studies [39].



**Figure 5.7:** Comparison of temperature and electrical current between modeled results (lines) and experimental data (circles)

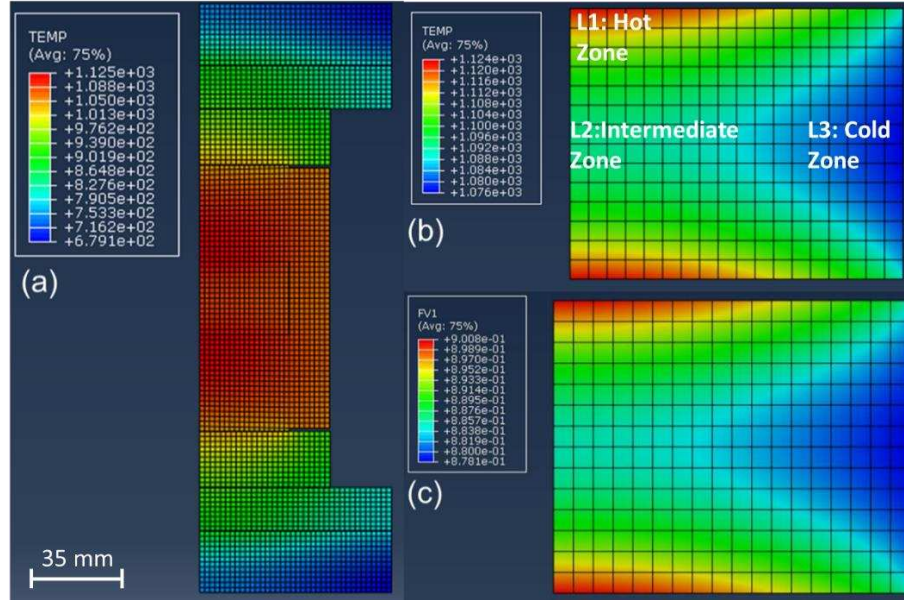
The relative density determined experimentally using the displacement data is presented in Fig. 5.8a. The final relative density of the sample was at approximately 90.8% after the sintering. The relative density reached 68.0%, 81.0%, and 90.5%, at 260, 360, and 460 seconds, respectively. It is worth noting that the purpose of the present work was not to make fully dense materials via SPS. Rather, the heating schedules were selected to intentionally avoid reaching the 3<sup>rd</sup> stage of sintering so that pores can be used as a microstructural feature to reflect the thermal gradients present during the sintering process. Fig. 5.8b shows the relative density distribution in the sample and the corresponding average overall relative density simulated by the combined MSC-FEA model, which gave an average relative density of approximately 67.0%, 80.5%, and 90.0%,

with respect to the previously mentioned times. The very small discrepancy ( $<1.5\%$ ) validated the effectiveness of incorporating MSC into the FEA to accurately predict the relative densities and the evolution of thermal-electrical properties as a function of temperature and the relative density. It is also important to note that the modeling result (Fig. 5.8b) showed differences in location-specific relative densities (the different color/contrast between the center location and the radial edge locations for a given time). This gradient in relative density is to be further discussed in section 5.3.3.



**Figure 5. 8:** (a) Experimental relative density data determined by sample displacement. (b) FEA simulated sample relative density using the MSC at three distinct times.

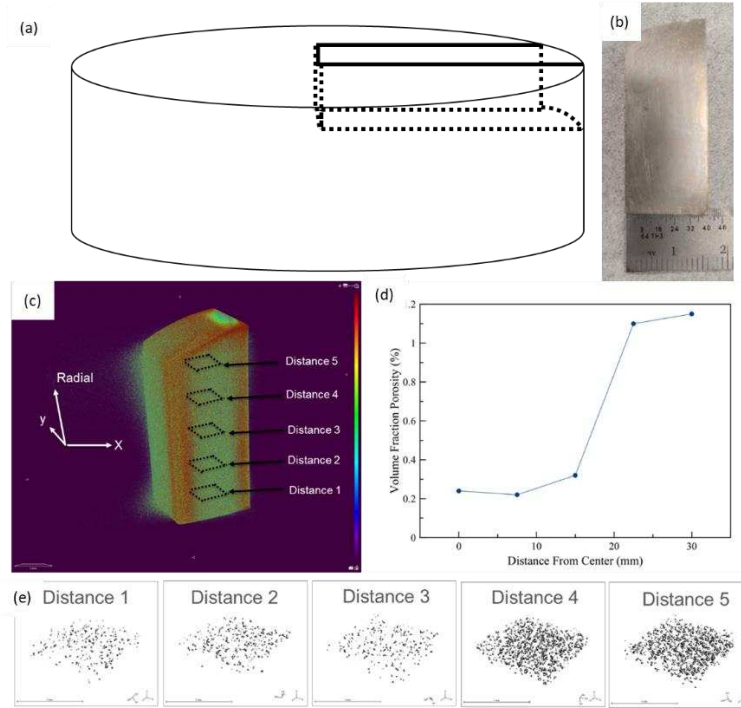
Fig. 5.9a displays the thermal gradients in the entire system at the end of the simulation, corresponding to the last second of the sintering experimentally, showing higher temperatures towards the center of the SPS column, and lower temperatures towards the edge. When we focused on the temperature distribution in the sample, the highest temperature occurred at the radial center of top (location 1) and bottom surface of the sample, while the radial edge represented the coldest regions (location 3), and the region corresponding to both Z-axis middle and radial center (location 2) represented an intermediate hot zone, as shown in Fig. 5.9b. This local temperature changing trend is in general agreement with many SPS FEA studies, which reported that electrically conductive samples experienced higher temperatures at the center than the sample edge [40–42]. Higher temperatures at the center indicated that more thermal energy was provided to these local regions, which eventually led to higher relative density at this region. The distribution of relative densities is present in Fig. 5.9c, which shows a higher density towards the sample center and lower density towards the edge. The highest temperature and maximum relative density are located at the top center and bottom center of the sample, which are attributed to the additional Joule heating produced by the electrical contact resistances at the punch-sample interface [35]. A maximum temperature difference of ~50 K was observed, which gave rise to a maximum relative density difference of ~2.3%. The maximum temperature gradient along the Z-axis, 2.4 K/mm, occurred at the center; and the maximum radial temperature gradient, 1.1 K/mm, occurred at the surface of the sample.



**Figure 5.9:** FEA simulation of the 70-mm-diameter Ti sample at the end of SPS: (a) temperature distribution of the entire system, (b) temperature distribution in the sample, and (c) relative density distribution in the sample.

### 5.3.3 Microstructure Results

Fig. 5.10c is the 3-D rendering results of a specimen cut from the 70-mm diameter sample obtained via micro-CT. It provides the information on the volume fraction of pores detectable at the resolution of the Micro-CT. The volume fraction porosity ranged from approximately 0.2% to 1.1%, as shown in Fig. 5.10d. These low values for porosity were attributed to the limited resolution of the micro-CT, which makes the pores having a size below 10 $\mu$ m not detectable. Slices from the 3D scanning results were taken at radial distances of 0, 7.5, 15, 22.5 and 30 mm from the sample center for further analysis to reveal the relative density gradients. It was observed that the porosity was higher at the locations having larger distances from the sample center, which agrees with the results predicted by the FEA model shown in Fig. 5.9c.



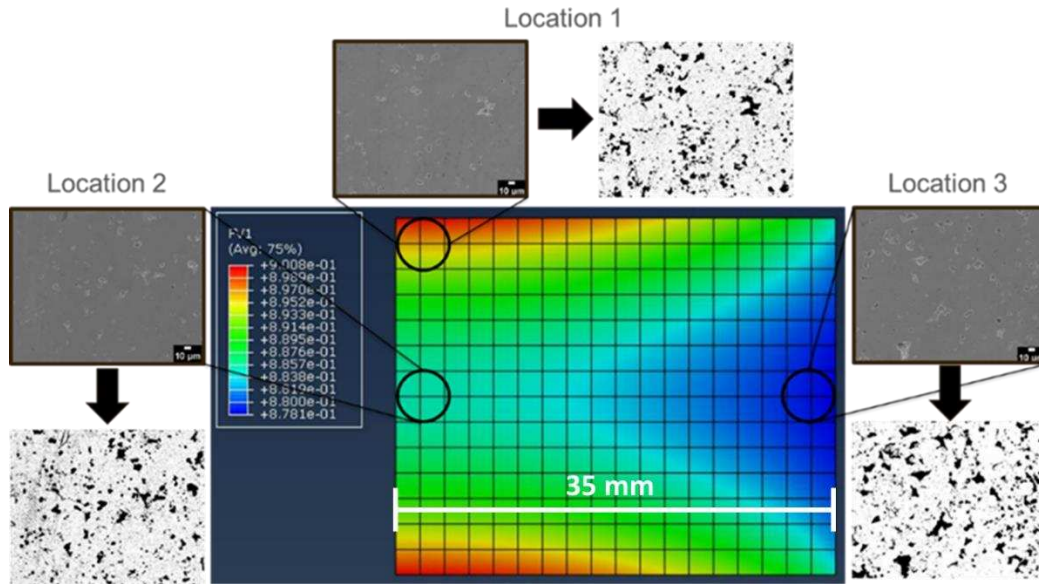
**Figure 5.10:** (a) A schematic of where the micro-CT specimen was cut from the 70 mm diameter Ti sample; (b) a photo of the specimen for micro-CT; (c) 3-D rendering of radial sample from micro-CT (d) volume fraction of porosity vs radial distance identified by Micro-CT (e) 3-D renderings of pores around each respective distance

To ensure fine pores (size < 10  $\mu\text{m}$ ) are also included, the 70 mm Ti sample was also characterized by SEM. Representative micrographs from the three ROIs are provided in Fig. 5.11. Many micro-sized pores that were not detected by the micro-CT, were observed in SEM. Locations 1-3 referred to in Table 5.2, corresponding to the hottest, intermediate hot, and cold regions as marked in Fig. 5.9, exhibited lowest porosity, medium porosity, and highest porosity, respectively. The characteristics of those micron-sized pores obtained from Image J analysis of SEM graphs are provided in Table 5.2, in comparison to the volume fraction porosity results obtained from FEA. It is also observed that the pore size increases as the location moves from the radial center of the sample to the sample edge, which is consistent with the micro-CT results. The porosity predicted from the MSC-TE FEA combined model only showed a  $\sim 1\%$  deviation

from the results determined experimentally. Therefore, the feasibility of incorporating MSC to TE FEA to improve the modeling efficiency and accuracy is well verified.

**Table 5.2:** Image J analysis and FEA porosity results

| Location<br>(#) | Average Image J Ferret<br>Diameter ( $\mu\text{m}$ ) | Average Image J Volume<br>Fraction Porosity (%) | FEA Volume Fraction<br>Porosity (%) |
|-----------------|------------------------------------------------------|-------------------------------------------------|-------------------------------------|
| 1               | $9.8 \pm 0.2$                                        | $9.8 \pm 0.6$                                   | 10.1                                |
| 2               | $11.5 \pm 0.4$                                       | $10.4 \pm 0.9$                                  | 11.2                                |
| 3               | $12.2 \pm 0.5$                                       | $11.6 \pm 1.3$                                  | 12.2                                |



**Figure 5.11:** The final relative density distribution predicted by FEA (middle of the image), compared with the experimental result - representative SEM images taken at each marked location.

#### 5.4. Summary

In this study, the MSC was successfully incorporated to thermal-electric FEM to provide an efficient method to assess and predict thermal gradients that occur in the materials being sintered during spark plasma sintering, considering the changes in material properties as a function of both temperature and relative density during sintering, and finally predict the

location-specific relative density in the final sintered product. This MSC-TE FEM combined model is an alternative to a thermal-electric-mechanical fully coupled FEM that is computationally expensive and requires lengthy experiments for parameterization. It was verified by experimental results that the combined model developed in the present work has a high degree of accuracy while maintaining the ability to update thermal-electric properties based on the perceived changes in relative density. The key findings are summarized as follows: (1) Commercial pure Ti has an apparent activation energy of 156.5 kJ/mol for sintering via SPS; (2) The MSC-TE FEM combined modelling result revealed that the pure Ti powder compact underwent thermal gradients during SPS, with the highest temperature at the radial centers of the bottom and top surface, an intermediate temperature at the Z-axial middle and radial center location, and the lowest temperature at radial edges. A maximum temperature difference of ~50 K was observed for a 70-mm diameter sample, which gave rise to a maximum relative density difference of ~2.3%; (3) Micro-CT and SEM experimental data validated the accuracy of the modeled work, with analysis depicting that the location-specific relative densities are within 1% deviation from the predicted results by the MSC-TE FEM combined model. Pores/relative density distribution was selected as the microstructural features to reflect the gradients that occur in SPS. Additional work focusing on grain size gradients is in progress, which will be published in a separate article. Gradients in relative density and/or grain size can be utilized to generate gradients in properties such as hardness, strength, and ductility for functionally graded materials. The scope of the present work focused on the development and verification of the methodology to incorporate MSC into FEM. Although the present work focused on the use of the combined model for sintering of a metal via SPS, it is anticipated that the methodology developed here is

also feasible for ceramic systems to account for the changes in thermal-electrical properties as a function of densification status.

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## CHAPTER 6 Impact of Powder Morphology on Densification Gradients within Spark Plasma Sintering

Chapter 5 laid the groundwork for modeling the densification behavior of a metal powder with the combination of FEA and the MSC models; but the effect of powder morphology was not included. In this chapter, the combined model is used to predict the relative density distributions in pure Ti samples that were sintered using different starting powder morphologies. To investigate the effect of powder morphology, three types of pure Ti powders were used: as-received gas atomized powder, 1.5 hrs ball milled powder, and 2.5 hrs ball milled powder, which exhibit spherical, cuboidal, and plate-like shape, respectively. First, the apparent activation energies of sintering for the three different powder morphologies were calculated by sintering lab-scale (diameter ~ 20mm) samples with five different heating rates. Subsequently, the MSC/TE FEM combined model was applied to predict the relative density distribution for mid-scale (diameter ~ 66 mm) samples. Simulation results show that the powder morphology that has a larger activation energy for sintering exhibits a larger maximal difference in local relative density during the sintering, which is also verified experimentally. This phenomenon is attributed to the onset of densification occurring at lower temperatures due to higher powder surface area to volume ratio and higher surface activity of the ball milled powder. Additionally, the powders that were ball milled for a longer time has a smaller temperature range for the second stage of sintering. The 2<sup>nd</sup> sintering stage typically exhibits a high rate of densification, which results in the largest gradient in relative density out of the three sintering stages. When the temperature range for the second stage of sintering is altered by the different powder morphologies, the gradients in thermal and relative densities of the samples are varied accordingly. This study

further addresses the vital role that powder morphology plays in the microstructural gradients in spark plasma sintering.

## 6.1. Introduction

Powder characteristics are the way in which we describe the morphology, size, and distribution of powders. Many of the applications that use powdered metals are methods of additive manufacturing or molding some of the most popular additive manufacturing techniques include powder bed fusion, direct energy deposition, and binder jetting which require specific powder characteristics for the process to work effectively. Within these processes powder characteristics are generally of concern, because the powders must have the ability to be easily spread for powder bed and binder jetting purposes[1–5]; and in the case of direct energy deposition the powders must have high flowability in order to avoid clogging and have a consistent flow of powder to the substrate[6–8]. These restrictions generally lead to powders with a small size distributions and spherical shape. This has led to most powders being produced and researched to be predominately spherical in morphology. Powders with these characteristics are almost exclusively produced via gas atomization, which is an energy intensive way of making powder[9]. However, some studies have recently shown that a more environmentally sustainable method, and one which is far less energy intensive is the ball milling of metal scrap to useable powder[9–15]. The drawback being this can lead to undesirable morphologies and sizes for additive manufacturing.

In general, this is not a concern for molding processes such as hot isostatic pressing, hot pressing, and spark plasma sintering (SPS) because the powder is added to a reusable die directly and then sintered. Making these manufacturing techniques potentially a key in a more environmentally friendly future. Also, in the case of spark plasma sintering this can be paired with high heating rates and pressure which allow for the retention of fine grain structure which

can be achieved by ball milling metallic powders[16, 17]. This has led to studies that pair ball milling and spark plasma sintering for improved mechanical and functional properties in comparison to their gas atomized counterparts [18–20]. However, SPS does come with its own set of challenges. The joule heating which allows for high heating rates also creates electrical gradients within the die and sample, additionally radiative heat is constantly lost from the die's outer wall. Both of these factors contribute to significant thermal gradients that occur in the sample and die[21–23]. These thermal gradients then give rise to heterogeneity within the microstructure, leading to gradients in both functional and mechanical properties[13, 24]. This has led to a large research effort in trying to minimize the thermal gradient to improve the homogeneity within the sintered samples, which is almost exclusively done by modifying the tooling used within spark plasma sintering [25]. However, limited research has been conducted on how powder characteristics directly impact the densification behavior and resultant microstructure during the spark plasma sintering process.

Recently some research groups have investigated a few powder characteristics and how they affect the materials sintered via SPS. Such as Deng et al, who found with increasing powder size, there was an increase in the thermal energy which was required in order to enter subsequent sintering stages due to the additional energy barrier for diffusion[26]. Additionally, studies such as Bake et al have investigated the impact of particle size on phase formation finding the reduction of powder size allows for the more rapid formation of a targeted phase[27]. Similarly, studies have been conducted on how powder distributions impact the sintering process[28, 29]. However, the impact of powder morphology specifically on densification, grain growth, and their respective gradients that occur during the SPS process is still relatively unknown.

To further our scientific understanding of how the functional and mechanical gradients can be controlled and utilized within the SPS process, it is necessary to understand how powder morphology can directly impact the homogeneity and microstructure of the sintered material. To answer this question, this study uses ball milling of powders to change their starting morphology, and then utilizes both simulation and experimental methods to understand their densification behavior and final microstructure. The goal of this research is to identify how morphology can be used as an additional parameter which can be tuned, and further assist in controlling property gradients of materials consolidated via SPS. The impact of powder morphology is investigated within this study via three different commercially pure titanium (CP-Ti) powders including an as received spherical gas atomized powder, a cuboidal 1.5 hour ball milled powder, and a plate-like 2.5 hour ball milled powder. The activation energy of each powder is then identified using small (20 mm) samples, and this parameter is used within a combined master sintering curve and thermal electric finite element analysis (MSC-TE FEA) model as established the previous chapter to simulate the temporal and spatial evolution of densification behavior of the different powders. The simulations are then experimentally verified with scaled up (66 mm) samples. The impact of different starting powder morphologies on microstructural gradients is then experimentally explored within the scaled-up samples by identifying gradients in relative density and grain diameter with respect to regions of interest (ROI) within the scaled-up sample.

## 6.2. Materials and Methods

### 6.2.1 Modeling Procedure

A brief summary of the modeling procedure is given within this chapter including a short overview of the MSC, FEA governing equations, boundary/initial conditions and material

properties. A more robust and detailed version of the procedure can be found in the previous chapter.

### 6.2.2 Modeling Procedure: Construction of the Master Sintering Curve

The master sintering curve (MSC) in short is a way of estimating the average relative density of a sintered material based upon the thermal work done to the system. It relies upon a single dominant form of densification occurring regardless of heating rate. This allows for a single curve to be constructed from multiple sintering runs at different heating rates based upon the thermal energy in relationship to relative density. This relationship between relative density and thermal energy was first discovered by Su and Johnson and is expressed as [30]:

$$\text{EQ(6.1)} \quad \phi(\rho) = \Theta(t, T) = \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt$$

Where  $\phi(\rho)$ ,  $\Theta(t, T)$ ,  $t$ ,  $T$ ,  $Q$ ,  $R$ , and  $dt$  are the densification parameter, the work of sintering, time, temperature, the apparent sintering activation energy, the gas constant, and the incremental change in time. However, to define the master sintering curve from the multiple heating runs the apparent sintering activation energy ( $Q_{msc}$ ) must be determined. This term is calculated by minimizing the mean residual square (MRS) between the data sets of each individual sintering run as described in EQ (6.2):

$$\text{EQ(6.2)} \quad MRS = \sqrt{\left(\frac{1}{\rho_f - \rho_g}\right) \int_{\rho_g}^{\rho_f} \sum_{i=1}^N \frac{\left(\frac{\Theta_i}{\Theta_{avg}} - 1\right)^2}{N} d\rho}$$

Where  $\rho_f$ ,  $\rho_g$ ,  $N$ ,  $\frac{\Theta_i}{\Theta_{avg}}$ , and  $d\rho$  are the final density, green body density, number of heating programs, ratio of that single heating program's  $\Theta$  compared to the  $\Theta$  at that density for the other programs, and the incremental change in relative density. Once, the  $Q_{msc}$  has been determined

then the densification behavior can easily be predicted via the use of EQ (6.1) and matching the calculated  $\phi(\rho)$  to the  $\phi(\rho)$  found on the MSC. This allows for the estimation of density with respect to thermal energy a value which can be calculated within the thermal-electric FEA model described in the next section.

### 6.2.3 Modeling Procedure: Thermal-Electric Model

The thermal-electric simulation of the spark plasma sintering process is based upon the ability to accurately portray the heating that occurs due to the resistance of electrical current, known as “Joule heating”. The governing equation used to describe the electrical field within the system at any given spatial or temporal point is a combination of the maxwell’s equation for conservation of charge and Ohm’s law [31]:

$$\text{EQ(6.3)} \quad \int_V \frac{\partial \delta \phi}{\partial x} \cdot \sigma^E \cdot \frac{\partial \phi}{\partial x} dV = \int_S \delta \phi J dS + \int_V \delta \phi r_c dV;$$

While the amount of electrical energy dissipated into a conductive material is described by Joule’s law:

$$\text{EQ(6.4)} \quad P_{ec} = \mathbf{J} \cdot \mathbf{E} = \frac{\partial \phi}{\partial x} * \sigma^E \cdot \frac{\partial \phi}{\partial x}$$

Where  $V, \phi, x, \sigma^E, S, J, r_c$ , and  $E$  are volume, electric potential, distance, electrical conductivity matrix, surface area, current density per unit area, internal volumetric current source per unit volume, and the field intensity respectively. The respective change in temperature with relationship to the dissipated energy can then be described by the following equation:

$$\text{EQ(6.5)} \quad P_{ec} = \rho V c_p \Delta T$$

Where  $\rho, V, c_p$ , and  $\Delta T$  are the local density, volume, heat capacity, and change in temperature of the material.

### 6.2.4 Modeling Procedure: Boundary and Initial Conditions

Within this section the thermal and electrical initial and boundary conditions used in this study are described. First, we must consider the conditions of the environment prior to the start of the simulation which includes an initial temperature 273 K, and no electrical charge within the entire system. Additionally, a potential of zero is held at one electrode to establish ground during the extent of the simulation. Once these conditions are set a current is applied to the top of the electrode to simulate the electric field present during sintering. The current is controlled by a simulated PD (proportional derivative) controller, which corrects the current at each time interval to approximate a specific thermal program specified by the user. This is performed using the following equation for the PD controller:

$$\text{EQ(6.6)} \quad I_t = I_{t-1} + K_p \cdot T_{Diff} + K_d \cdot \frac{d}{dt} \cdot T_{Diff}$$

Where  $I_t$ ,  $I_{t-1}$ ,  $K_p / K_d$ , and  $T_{Diff}$  represent the current density at the current time interval, the current density at the previous time interval, numerical optimized parameters, and the difference in temperature between the program and simulation for a given point.

Boundary conditions were also considered for electrical contact resistances at both vertical and horizontal surfaces within this model with respect to average temperature of the surface. This calculated by the following equation:

$$\text{EQ(6.7)} \quad \rho_c = A_c R_c(T)$$

Where  $\rho_c$ ,  $A_c$ ,  $R_c(T)$  are resistivity at the contact, area of the contact, and the resistance of the contact with respect to temperature the values of which can be found in our previous work.

Thermal contact resistances were not considered within this model, as they have previously been shown to be negligible[32].

Additionally, the thermal energy lost during the sintering process must be considered. This is done in two ways, the first is convective heat lost from the water-cooled electrodes described as:

$$\text{EQ(6.8)} \quad Q_{conv} = hA\Delta T$$

Where  $h$ ,  $A$ , and  $\Delta T$  are the heat transfer coefficient, contact area, and difference in temperature between electrode surface and water cooling at 293K. The heat transfer coefficient between the electrode and cooling water used is set to 880 W/m-K, this value is based on another research group using a similar SPS machine [33]. The second major form of heat loss which is considered is radiation from the vertical faces of the die, spacers, and electrodes which is estimated based on the Stefan-Boltzmann equation:

$$\text{EQ(6.9)} \quad Q_{rad} = \epsilon A \xi (T_1^4 - T_2^4)$$

Where  $\epsilon$ ,  $A$ ,  $\xi$ ,  $T_1$ , and  $T_2$  are the material emissivity, radiating area, the Stefan-Boltzmann constant, the radiating surface temperature, and the absorbing surface temperature which is assumed to be 293 K. This study used 0.8 for the graphite emissivity, and an emissivity of 0.67 for the electrodes made of Inconel, based on literature data [33].

### 6.2.5 Modeling Procedure: Material Properties

In this study material properties were considered in relationship to both temperature and relative density described by the effective medium approximations below:

$$\text{EQ(6.10)} \quad \sigma_{Porous} = \sigma_{Dense} \cdot \left(1 - \frac{3}{2}\theta\right)$$

$$\text{EQ(6.11)} \quad \kappa_{Porous} = \kappa_{Dense} \left(1 - \frac{3}{2}\theta\right)$$

$$\text{EQ(6.12)} \quad \rho_{Porous} = \rho_{Dense}(1 - \theta)$$

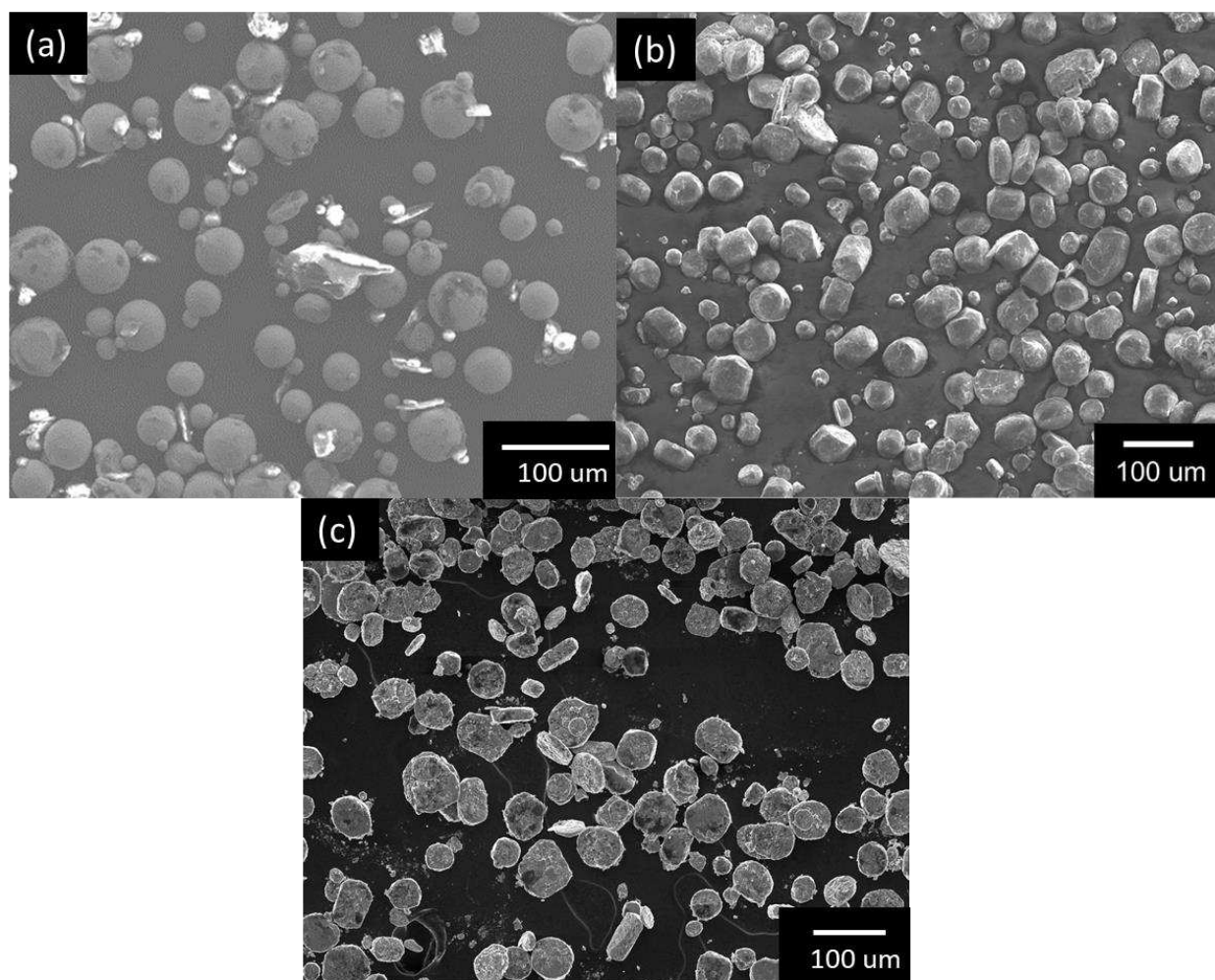
$$\text{EQ(6.13)} \quad C_{p_{\text{porous}}} = C_{p_{\text{dense}}} (1 - \theta)$$

Where  $\sigma_{\text{porous}}$ ,  $\sigma_{\text{dense}}$ ,  $\theta$ ,  $\kappa_{\text{porous}}$ ,  $\kappa_{\text{dense}}$ ,  $\rho_{\text{porous}}$ ,  $\rho_{\text{dense}}$ ,  $C_{p_{\text{porous}}}$ , and  $C_{p_{\text{dense}}}$  are the electrical conductivity of the porous material, electrical conductivity of the bulk material, volume fraction porosity, thermal conductivity of the porous material, thermal conductivity of the porous material, thermal conductivity of the bulk material, density of the porous material, density of the bulk material, heat capacity of the porous material, and heat capacity of the bulk material, respectively. The specific material property relationship with temperature can be found in the appendix, while the density is determined by directly calculating the location specific theta value previously described in EQ(6.1), and then matching it to the known MSC for the given powder. The material property values are updated after each time interval, with relationship to density and temperature.

#### 6.2.6 Experimental Procedure: Starting Powders and Ball Milling Process

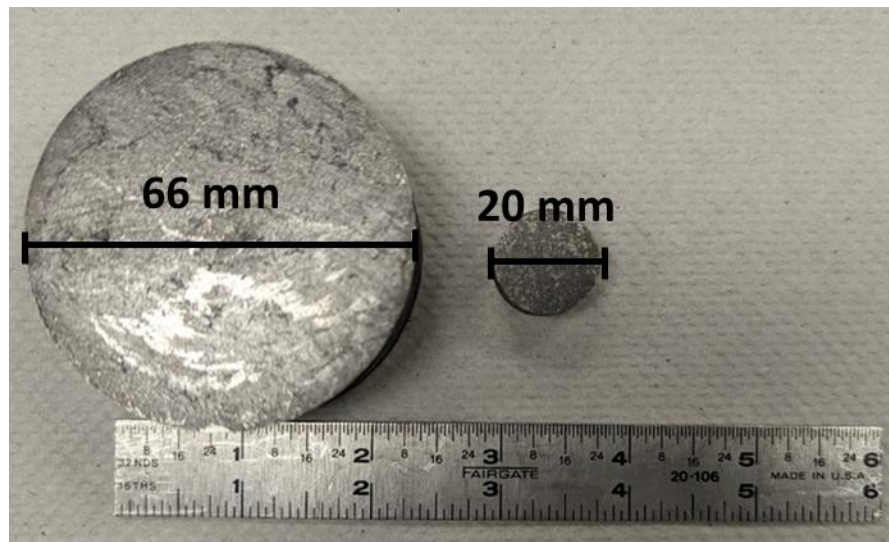
Commercially pure titanium was selected as the model material, due to it being the base for Ti alloys which are ubiquitous within many transportation industries and are becoming more popular each year. The choice of pure Ti instead of one of its popular alloys also excluded the concern of an intermetallic secondary phase. The powder used in this study was commercially produced by AP&C (a GE Additive company) via gas atomization (GA) with a range of  $20 \mu\text{m} < x < 63 \mu\text{m}$ , an oxygen content up to 0.18 At%, and a reported starting apparent density of  $2.56 \text{ g/cm}^3$ . The starting morphology of the GA powder is spherical in nature as shown in Fig. 6.1a. The other two powders were obtained by ball milling the GA titanium powder with 3wt% steric acid for 1.5 hrs (shown in Fig. 6.1b) and 2.5 hrs (shown in Fig. 6.1c) in an argon environment. The starting gas atomized powder has a spherical morphology. After 1.5 hours of ball milling the powder morphology changes into a more cuboidal morphology as the powder is impacted on all

edges. Finally, after 2.5 hours the powder appears plate like, with the thickness of the powder is much smaller in comparison to the diameter of the powder. High energy ball milling was conducted in a Across International PQ-NO4 planetary ball mill. All milling media and jars were made of 304 stainless steel, with ball diameters of 6 mm. The ball: powder ratio used within this study was 10:1. Post ball milling, the powders were rinsed three times with 200 proof ethanol to remove any steric acid from the powder surface. Then, powders were dried at 80°C on a hot plate to remove any residual ethanol.



**Figure 6.1:** (a) GA powder (b) BM powder for 1.5 hrs (c) BM powder for 2.5 hrs

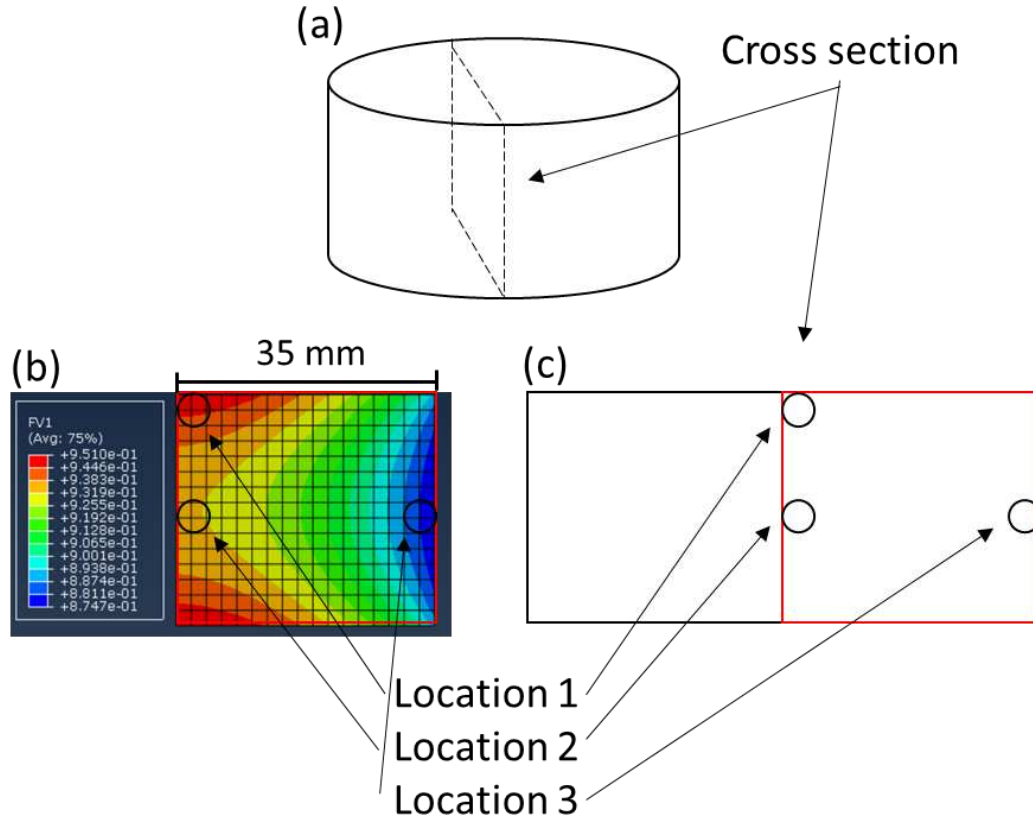
A set of five 20 mm diameter samples were then sintered using the SPS for each powder. Heating rates used included 50 K/min, 75 K/min, 100 K/min, 125 K/min, and 150 K/min up to a final temperature of 1273 K. All samples were green packed with a pressure of 40 MPa to ensure initial powder contact, and a constant pressure of 20 MPa was applied during sintering. These samples were all used to construct the master sintering curve, with the minimum of the mean residual square identifying the activation energy of sintering for the given powder. Then, the 66 mm diameter samples were sintered by a simple heating step at a rate of 100K/min to achieve a final temperature of 1073K, without a thermal hold. This final temperature choice was guided ABAQUS simulations using the MSC/TE FEA model, which showed around 800°C, a maximum difference in porosity should be present in the GA powder sample slightly under 8%, which is discussed further in section 6.3.2. After sintering, the samples were then allowed to cool in the SPS chamber under vacuum. A representative image of both a 20 mm and 66 mm gas atomized sample can be found in Fig. 6.2.



**Figure 6.2:** 66mm and 20 mm sample sintered from GA powders

### 6.2.7 Experimental Procedure: Microstructural Characterization

To determine the average final density of all 20 mm samples, Archimedes method was used. While the larger 66 mm sample's density was determined via geometric means. Local microstructure of each 66 mm sample was investigated at three ROI as marked on Fig. 6.3 which correspond to the hot (location 1), intermediate (location 2), and relatively cold (location 3) zones predicted by the combined model. Imaging was conducted via scanning electron microscopy (SEM), this study used a JOEL-JSM-5800 FESEM which was operated at 15 kV. For SEM preparation of the 66 mm sample, its cross-section was mechanically polished to a finishing step of 50-nm diamond and then 50-nm colloidal silica with 30 vol% hydrogen peroxide to remove any surface damage from the polishing process. After imaging, Image J software was implemented to assess the average volume porosity via 10 images for each location. Edge detection, filling, and threshold processes were implemented to detect the pores within each image. This was followed by particle analysis with the exclusion of any features smaller than  $10\ \mu\text{m}^2$  to avoid noise being counted as porosity. Additionally, EBSD (electron backscatter diffraction) was implemented to understand local grain structure at ROIs, this was performed within the JOEL-JSM-5800 FESEM at 25 kV. A step size of 1 micron was used and points were only considered with a confidence interval of 0.1 or greater with over 500 grain diameters measured at each ROI. Grain diameters which were under 4 microns were not considered, as the step size should be at least  $\frac{1}{4}$  of the measured grain diameter(Mingard et al., 2007).



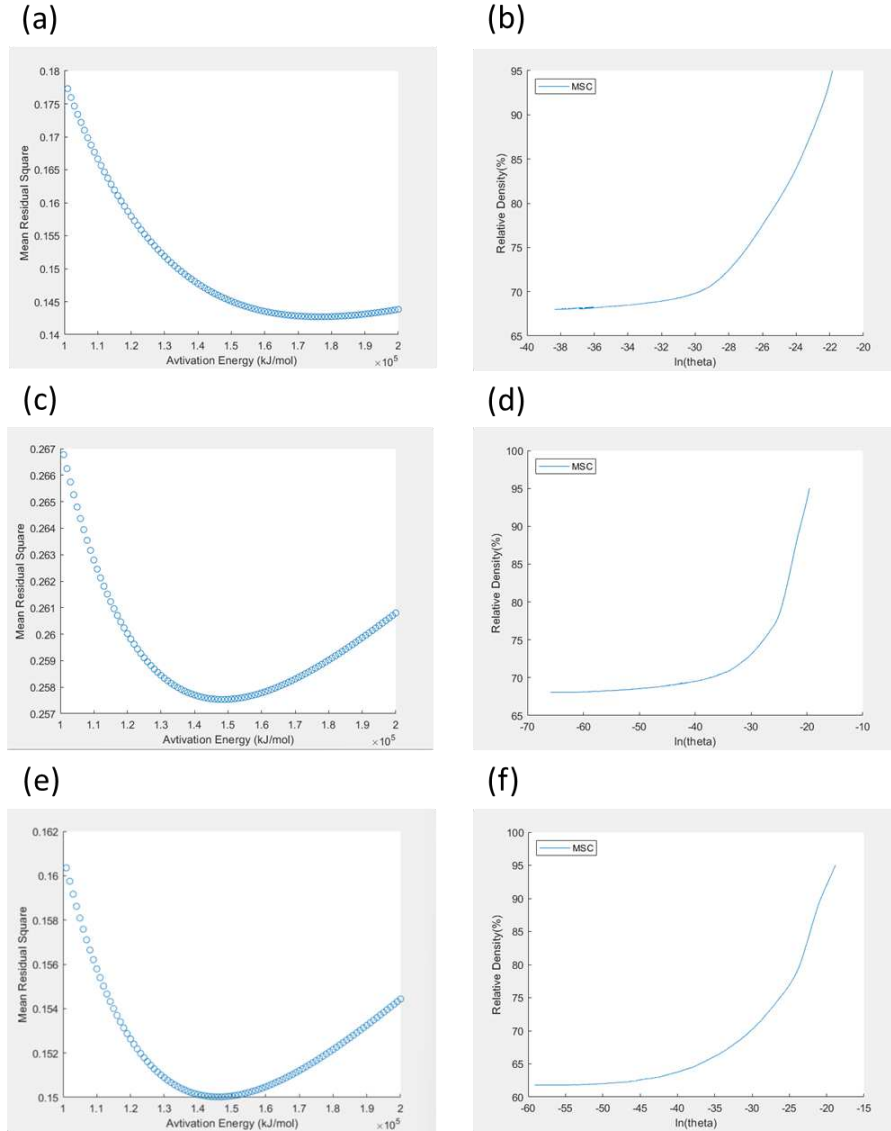
**Figure 6. 3:** (a) Shows the cross section taken from the center of the 66 mm sample, (b) simulated half cross section with ROIs locations 1-3 marked, (c) cross section with ROIs locations 1-3 marked

## 6.3 Results and Discussion

### 6.3.1 Master Sintering Curve

The master sintering curve results are detailed in Fig. 6.4, the MRS for the gas atomized powder between the five differing heating rates comes to a minimum at 170 kJ/Mol (Fig. 6.4a), while the BM powders activation energies were identified as 148 kJ (Fig. 6.4c) and 146 kJ/mol (Fig. 6.4e) for 1.5 hrs and 2.5 hrs, respectively. The limited change in activation energy between 1.5 and 2.5 hrs indicates that ball milling the gas atomized powder for more than 1.5 hrs did not greatly reduce the activation energy, and this can likely be attributed to limited additional deformation of the powder particles or limited additional grain refinement. The activation energy

identified for the GA powder of 170 kJ/Mol is in good agreement with Koppers et al. and Qian et al. who recorded activation energies of 160 kJ/mol and 184 kJ/mol, respectively[35, 36]. A recent study by Kozlik et al found cryomilling of Ti powder, which is a process that increases the activity of the powder surface even further than high energy ball milling due to the additional reduction in grain size to have an activation energy of 115 kJ/mol[37]. This means the 148 kJ/mol and 146 kJ/mol found in this study for ball milled titanium are in good agreement with current literature. When comparing the master sintering curves in Fig. 6.4 b, d, and f it becomes apparent that higher levels of densification are predicted to occur at lower thermal energy levels for powders that have been ball milled longer. This is due to the increase in surface area that occurs from ball milling, and the higher activity at the surface of the powder due to plastic deformation and reduction of grain size[38]. Both attributes lower the energy required for diffusion at said surfaces and aid in densification of the powders during the first stage of sintering, therefore lowering the overall activation energy of the powder. It should also be noted that this increased densification of the ball milled powder in the first stage of sintering also limits the range of thermal energy in which the second stage of sintering occurs within the powder. Meaning with higher ball milling times the powder experiences the second stage of sintering at later stages of densification. This is important to note, as the second stage of sintering is later identified as the timeframe in which the largest pore gradients emerge within the sample during sintering.

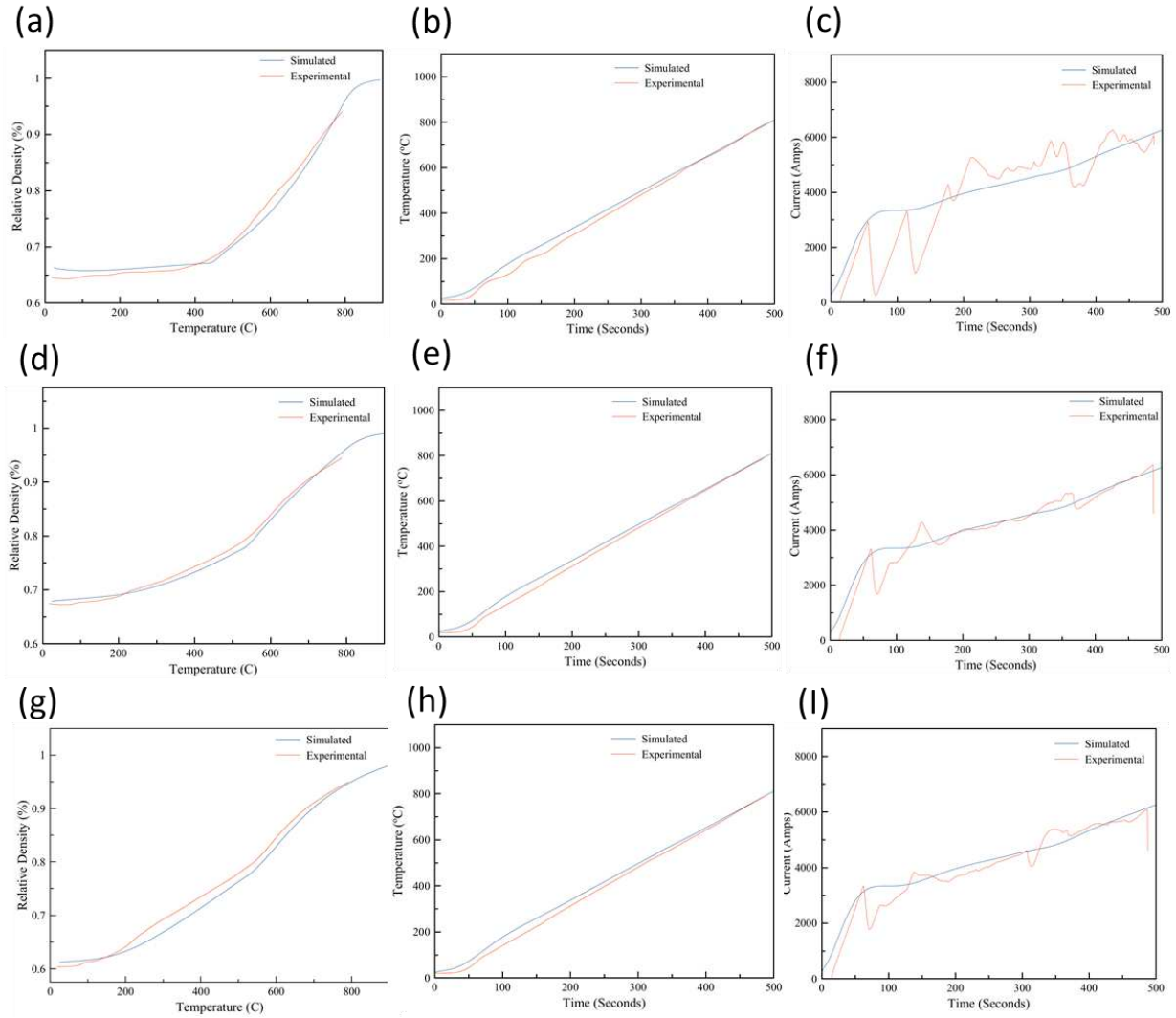


**Figure 6.4:** (a), (c), and (e): Identification of activation energy by minimization of mean residual square for GA, 1.5 hrs BM, and 2.5 hrs BM, respectively (b),(d), and (f) Master sintering curves for GA, 1.5 hrs BM, 2.5 hrs BM powders, respectively

### 6.3.2 Experimental and Simulation Comparisons

The average electrical current for both experimental and modeled results of the 66 mm diameter sample during the sintering process are shown in Fig. 6.5 (c, f, and i). The trend between experimental and simulated average electrical current show general agreement. However, in Fig 6.5 c, it is observed that the experimental current exhibits large swings, this is a due to the large

nature of the tooling and is considered acceptable for this experiment because we do not observe a large difference between the simulated and experimental temperatures as shown in Fig. 6.5b. In fact, temperature data Fig. 6.5 (b, e, and h) shows a high degree of accuracy between all the modeled and experimental systems, with limited error throughout the entirety of the process. Lastly, the average relative density of the sample in the simulation and experimental Fig. 6.5(a, d, and g) show a high degree of agreement, with an error between the two being less than 2% relative density during the entire process. The experimental relative density when the thermocouple reached 1073 K was found to be 93.1%, 94.5%, and 95.0%, while the simulation predicted 94.0%, 95.5%, and 94.7% for the GA, 1.5 hrs BM, and 2.5 hrs, BM powders, respectively. Meaning the final predicted density was less than 1% different in comparison to the experimental, which showcases the high degree of accuracy while using this combined model.

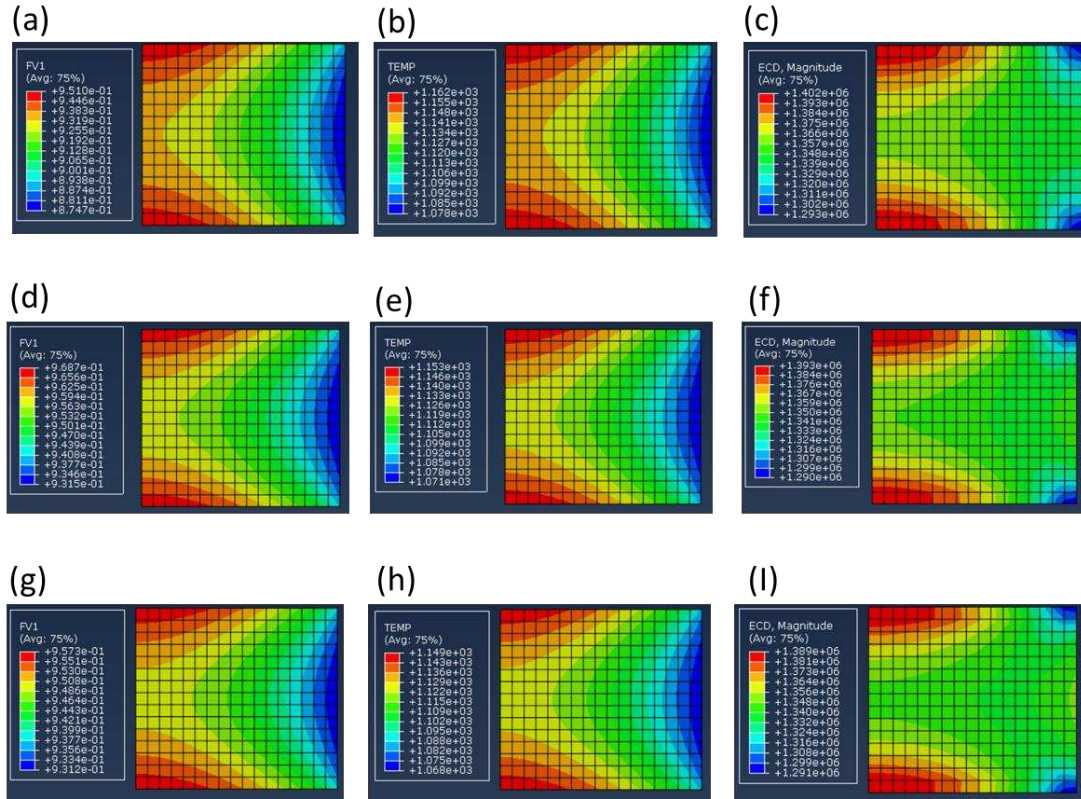


**Figure 6.5:** (a, d, and g) Compare relative density results for both the experiment and simulation, (b, e, and h) compare simulated and experimental results for temperature, (c, f, and I) compare simulated and experimental results for current (a-c) Being from GA, (d-f) BM 1.5 hrs, and (g-i) BM 2.5 hrs powder experiments

The final simulated relative density, temperature, and current density distributions are shown in Fig. 6.6, with GA being represented in Fig 6.6(a-c), 1.5 hrs BM (d-f), and 2.5 hrs BM (g-i).

When comparing relative densities, it quickly becomes apparent that GA has a much large density gradient than both BM powders at the final 1073 K temperature. The GA powder has an estimated 7.6% difference, between the highest density area and lowest density area. By

comparison the 1.5 hr BM sample has less than half of the density difference at 3.6%, and the 2.5 hr BM sample even less with only around 2.5%. When comparing temperature gradients within the sample at this time we observe only slight differences with a maximum temperature difference of 84°C, 82°C, and 81°C for the GA, 1.5 hr BM, and 2.5 hr BM powders, respectively. Similarly, the electric current density distribution also appears to be quite similar between the three powder systems. This indicates that the final temperature gradient is not the key in predicting the porosity gradient that occurs during the sintering process.

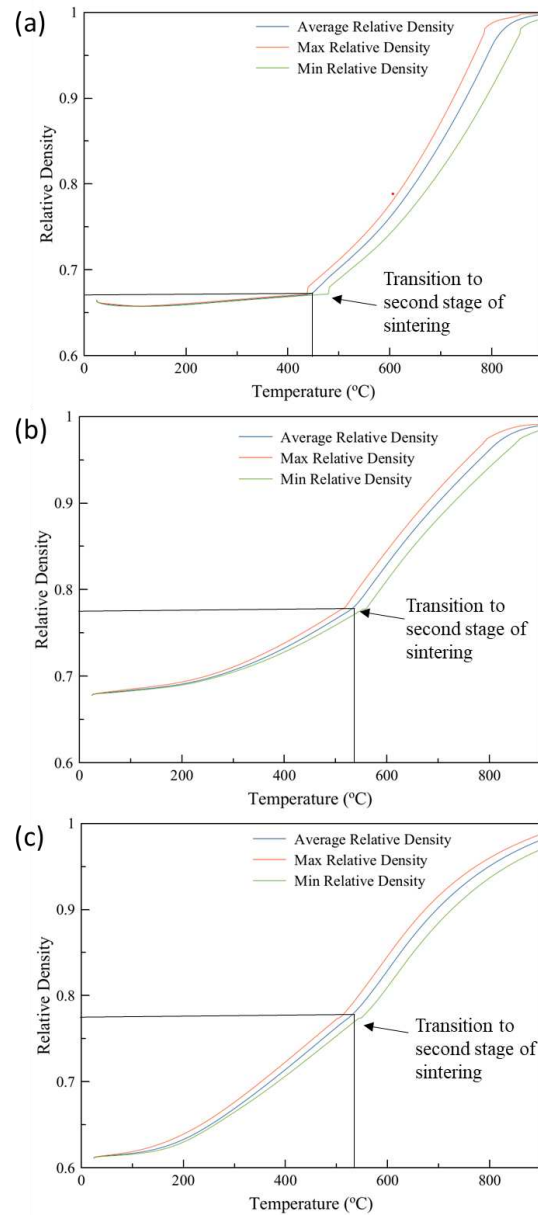


**Figure 6.6:** (a, d, and g) Show relative density results for the simulated sample when the simulated thermal couple reads 1073 K, (b, e, and h) show temperature results for the simulated sample when the simulated thermal couple reads 1073 K, and (c, f, and I) show electric current density results for the simulated sample when the simulated thermal couple reads 1073 K (a-c) Being from GA , (d-f) BM 1.5 hrs, and (g-i) BM 2.5 hrs powder experiments

To further investigate the key mechanisms that allow for the creation of pore gradients, the maximum, minimum and average simulated densities were plotted against temperature at the

simulated thermocouple for each simulation as shown in Fig. 6.7 (a-c), with Fig. 6.7 a representing the GA powder, Fig 6.7 b the 1.5 hr BM powder, and Fig 6.7 c the 2.5 hr BM powder. Fig 6.7 a, demonstrates what appears to be a standard sintering curve, with minimal densification occurring in the first and last stage of sintering, and a sudden sharp increase in densification at the transition from the first to second stage. However, Fig 6.7 b and c demonstrate very different sintering behavior, with both simulated samples showing a large amount of densification occurring in the first stage of sintering due to the additional surface area and higher surface activity as previously discussed. Additionally, the transition temperature from the first stage of sintering to the second stage of sintering for both BM samples is around 530°C, much higher than the transition observed for the GA powder around 450°C. The BM samples also enter the second stage of sintering with higher relative densities around 77-78% while the GA powder enters the second stage of sintering with an approximate relative density of 67%. Meaning, a much larger percentage of pores are within the GA powder when entering the second stage of sintering and a higher amount of densification occurs during this stage. This leads to a larger slope in the second stage of sintering around  $8.1(10^{-4})$  (% RD/°C), vs the BM powders with slopes of  $6.1(10^{-4})$  and  $5.8(10^{-4})$  for the 1.5hr and 2.5 hr BM powders, respectively. Meaning, the same thermal gradient within the three samples will produce the largest density gradient in the GA powder, followed by the 1.5 hr BM powder, and the smallest gradient in the 2.5 hr BM powder during the second stage of sintering. Therefore, it appears there are two key factors when considering the occurrence of porosity gradients within samples during spark plasma sintering, the slope of densification, and the thermal gradient when densification occurs. Both lead to the conclusion that if a powder has a lower activation energy, which in turn causes more densification at lower temperatures when thermal gradients are smaller; then the overall

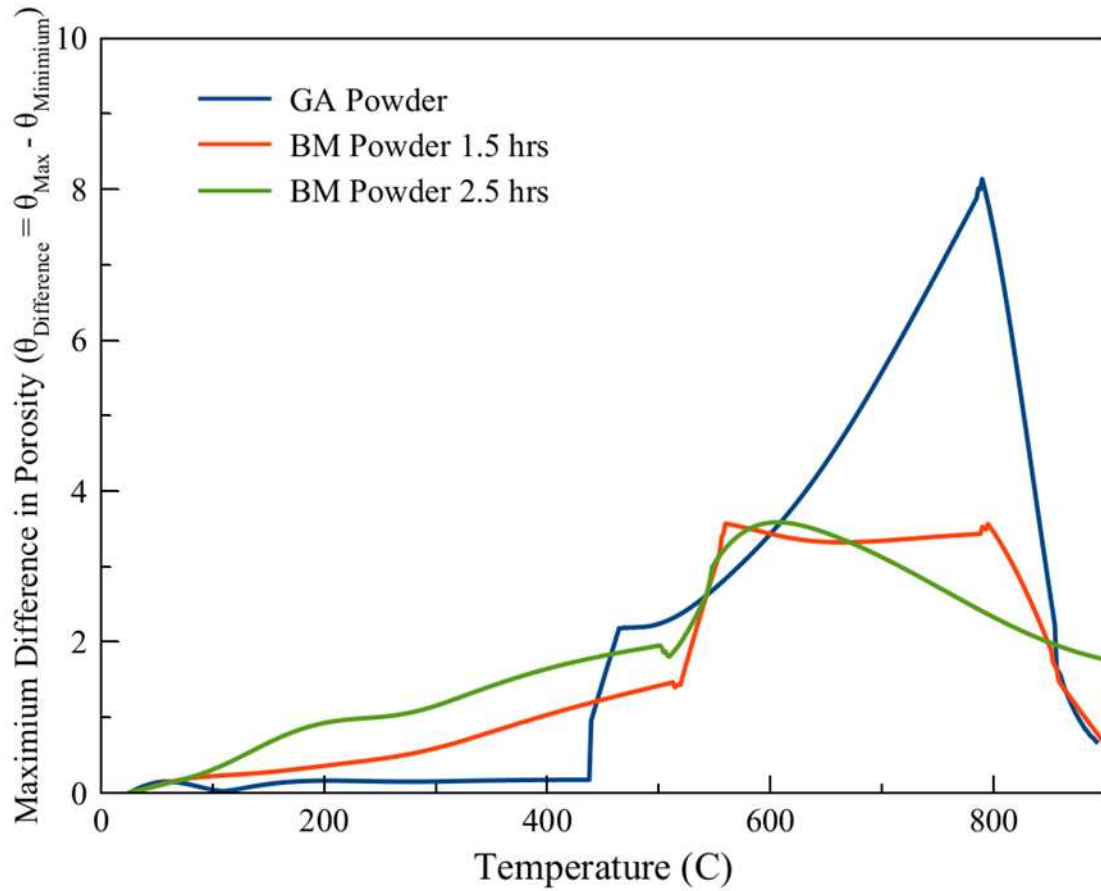
porosity gradient will also be smaller in turn and lead to higher homogeneity during the sintering process.



**Figure 6.7:** Maximum, minimum, and average simulated relative densities vs simulated thermocouple temperature for (a) GA powder, (b) BM 1.5 hrs powder, and (c) BM 2.5 hrs powder

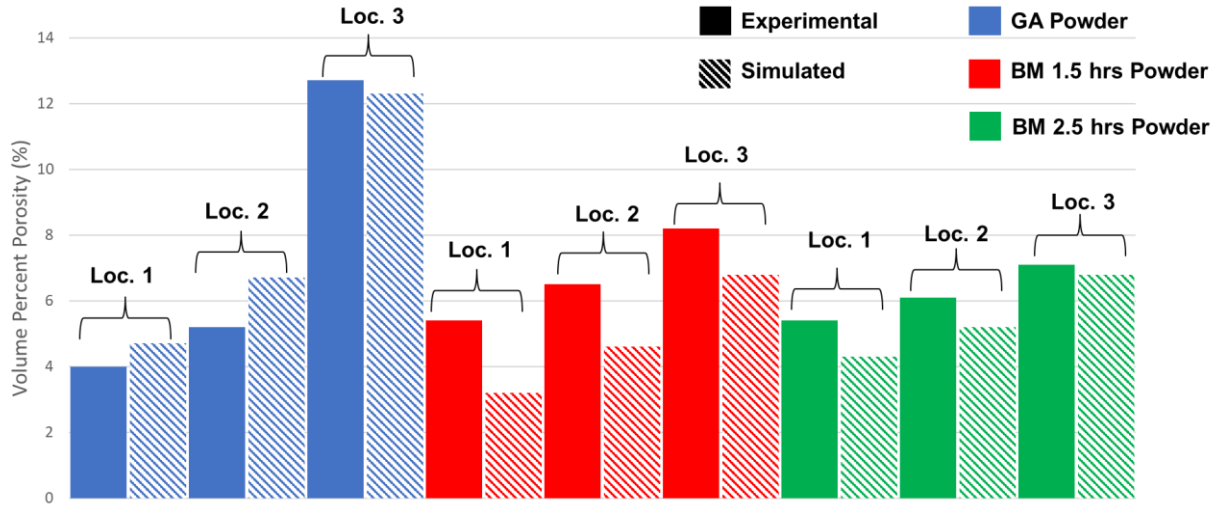
This is further examined and verified by plotting the difference between the maximum and minimum relative densities of each sample during the simulated sintering process shown in Fig

6.8. In this figure the longer time spent in the second stage of sintering and larger slope during the second stage of sintering leads to a predicted much larger porosity gradient during the sintering process for the GA powder. Interestingly, we also observe that the 2.5 BM powder more gradually enters the third stage of sintering in comparison to the other two powders, leading to a slightly higher porosity gradient after around 860°C.



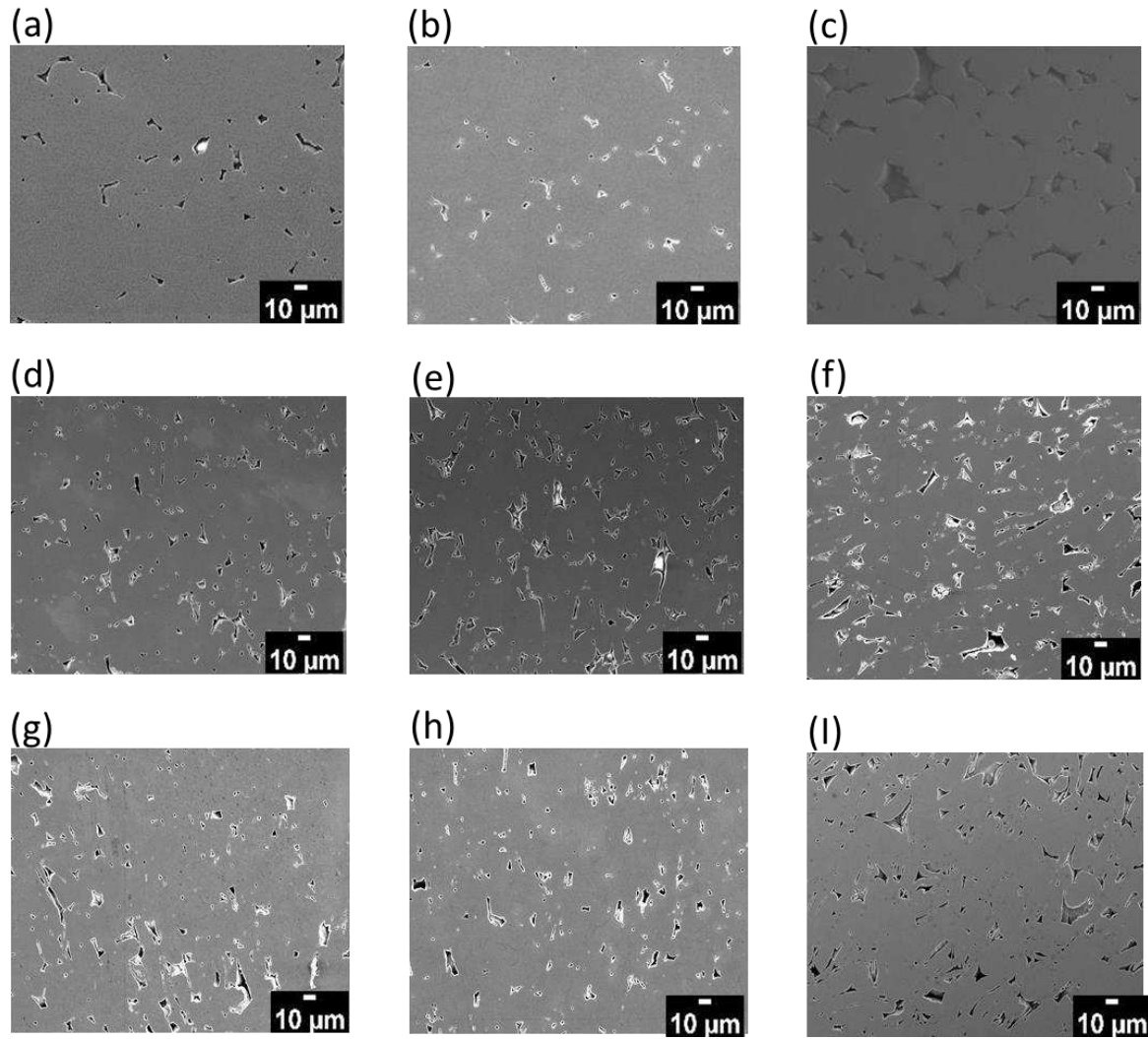
**Figure 6.8:** Simulated maximum difference in porosity vs the temperature at the simulated thermocouple.

SEM results further confirm the general trends shown in the model, with Fig. 6.9 below, showing the average volume fraction porosity determined from 10 SEM images analyzed using image J and the simulated volume fraction porosity determined by the simulation. A representative of each location is shown in Fig. 6.10.



**Figure 6.9:** Simulated volume fraction porosity vs experimental volume fraction porosity

The maximum discrepancy between the image J analysis and predicted volume fraction porosity via FEA is around than 2.2% volume fraction porosity. Additionally, the maximum difference in porosity predicted for each sample is around 7.6%, 3.6%, and 2.5%, SEM analysis identified the maximum difference as 8.7%, 2.8%, and 1.7% meaning that the general trend identified by the FEA model is verified. The error between the model and the experimental results are minimal meaning it could be used as an excellent tool for guiding research and experimental design.

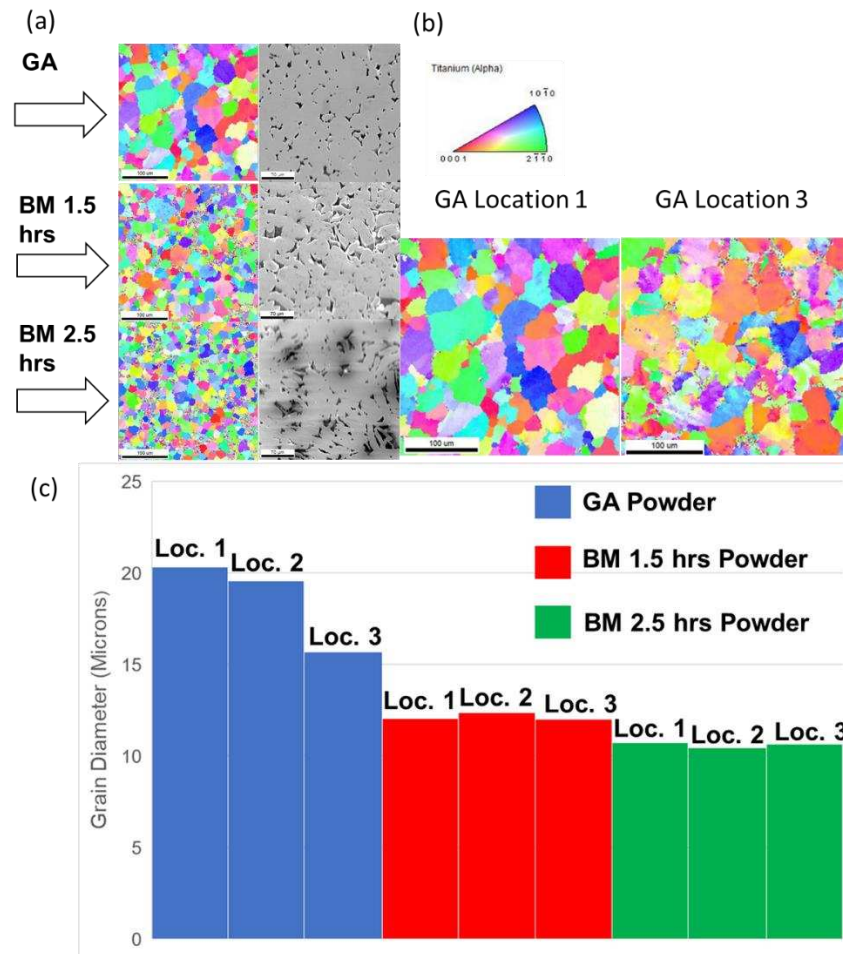


**Figure 6. 10:** The first column shows all location 1 photos, the second column showing all location 2 photos, and the third column shows all location 3 (a-c) show photos from the GA powder sample, (d-f) show photos from the 1.5 hr BM powder sample, and (g-i) show photos from 2.5 hr BM powder sample

### 6.3.3 EBSD

In addition to mapping porosity at ROIs grain diameter was also carefully inspected. EBSD results shown in Fig. 6.11c indicate that the average final grain size was finer for powders that were ball milled longer, which agrees with current literature [39–42]. However, it was discovered that the ball milled powder's grain size distribution was fairly homogenous, whereas

the gas atomized powders showed a heterogeneous distribution of grains. This heterogeneity can be seen in Fig 6.11b which compares the ROIs location 1 and location 3 for the 66 mm GA powder sample. This heterogeneity of the grain structure is attributed to the more gradual sintering that occurs within the 2<sup>nd</sup> stage of sintering for the ball milled powders in comparison to the GA powders, leading to a more uniform entrance of all ROIs into the third stage of sintering where grain growth occurs.



**Figure 6.11:** (a) EBSD and corresponding SEM maps of the 66 mm samples each at the ROI location 1 (b) EBSD maps for GA's ROIs locations 1 and 3 (c) plot of average grain diameter from EBSD results for each ROI of the 66 mm samples

#### 6.4 Summary

This work studied the impact of powder morphology on local densification, grain size and their respective gradients that occur during the SPS process. Key findings from this study include: (1)

Activation energies of 170 kJ/mol, 148 kJ/mol, and 146 kJ/mol were identified for gas atomized spherical, 1.5 hour ball milled cuboidal; and 2.5 hour ball milled plate like CP-Ti powders, respectively; (2) the combined model was able to accurately predict the relative density of all large 66 mm samples within 2% error during the entirety of the sintering process ; (3) the simulated densification maps indicated that additional ball milling allowed for smaller porosity gradients during the sintering process. The smaller porosity gradients were associated with the lower activation energy due to larger powder surface areas and higher powder surface activities from plastic deformation/grain refinement. This led to more densification for ball milled powders during the first stage of sintering when thermal gradients are small, in comparison to the later stages of sintering when thermal gradients are larger. (4) Grain growth is found to be more homogenous in ball milled powders in compared to their gas atomized counterparts. This is attributed to the more gradual sintering that occurs within the 2<sup>nd</sup> stage of sintering for the ball milled powders in comparison to the GA powders, leading to a more uniform entrance of all ROIs into the third stage of sintering where grain growth occurs. While this work focused on the ball milling of titanium powder, metallic powders that can be ball milled with higher sintering temperatures should reap even larger benefits since higher temperatures implies larger thermal gradients in the powder and tooling. Overall, this study demonstrates that powder morphology is a key aspect of sintering, specifically in relationship to porosity and grain growth and should be carefully considered when designing experimentation using the SPS process.

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## CHAPTER 7 Conclusion and Future Work

Light weight structural materials are in demand and will continue to grow in popularity for the foreseeable future for their use in transportation, aerospace, and defense, among other industries. Currently, fully dense materials dominate these industries, using metals and alloys which are intrinsically lightweight. However, these materials can be extremely expensive and have high energy costs to produce. Therefore, it is important to explore the possibility of including porosity within inherently heavy alloys to increase the available selection of materials that can be used for lightweight applications. Additionally, the impact of powder morphology has been greatly overlooked in the spark plasma sintering community. But, with the recent trends of using non spherical powder produced by ball milling it is important for additional research to understand the larger implications and benefits of using powder with a wide range of characteristics; specifically, when these powders may be more economically and environmentally viable.

Within this study, we have successfully shown that porosity can be beneficial in terms of increasing the specific strength of an alloy. This was demonstrated in 316 L stainless steel, one of the most commonly used alloys in many industries, inclusive of the one listed above. Pore size was found to be key in facilitating precipitation events surrounding the pore, which is credited as the reason for the increase in specific strength. Decreasing pore size was identified as leading to higher diffusional driving forces allowing for the precipitation event to occur adjacent to the pore surface. While larger pores did not facilitate the necessary driving forces to allow for the precipitation event to occur. This study also investigated how powder morphology impacts

microstructure, finding that powders with larger starting surface areas and higher surface activity lead to materials with smaller pore gradients and larger grain size gradients.

Additionally, a model was then proposed within this study combining the master sintering curve and thermal electric finite element analysis methods to better understand the densification behavior of powder during the spark plasma sintering process. The master sintering curve was identified at a small scale (20 mm die), this minimized the thermal gradient to less than 20°C between the thermal couple. This minimization allowed for the master sintering curve approximation to be used with other tooling sets. The combined model allowed for identification of potential gradients in densification, we then identified gas atomized powders with higher activation energy also had significantly larger density gradients in comparison to ball milled powders with lower activation energies. This means, the ball milling increased the homogeneity in terms of porosity of the powder during the sintering process. This was a key parameter, that could be used to improve future manufacturing processes. The remainder of this chapter will describe suggestions for future work and proposals for how this work could potentially be done.

#### 7.1 Suggestions for Future Work

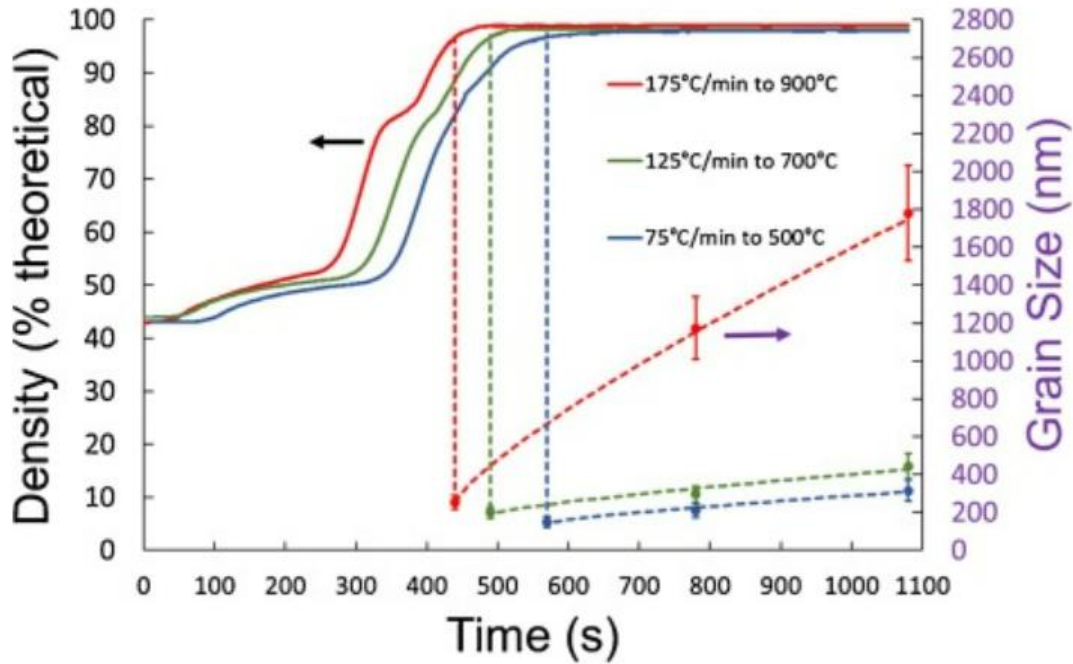
There are a few directions in which immediate future work could be done which would help build upon the foundation from this dissertation. The first being a continuation of chapter 2's work. While it was identified that smaller pores did allow for the creation of fine precipitates which subsequently increased the specific yield strength, the critical pore size and critical driving force for this to occur is still unknown. From a purely experimental perspective this would be daunting work, which would require many experiments to create an empirical relationship. However, if a general model could be constructed or identified to help identify the critical pore size and critical driving force, pores could become an important strengthening microstructure which facilitates the precipitation events in alloys.

Another route would be to add grain size growth trajectory within the presently proposed model. This would help guide researchers even further in understanding the spark plasma sintering process, and further aid in predicting mechanical property gradients such as hardness, strength, and elastic modulus. Additionally, it would facilitate a need in allowing researchers to predict gradients in grain size which are impactful not only to mechanical properties but also functional properties.

A final suggestion would be creating a better understanding between pore characteristics and its impact on thermal and electrical conductivities. The general medium approximation used within this work is commonly used as a first order approximation, however it only considers the impact of total volume fraction porosity on the conductivities and not the characteristics of the pore. In reality, the interaction of the porous medium is more convoluted. With the interaction between phonons and electrons with the porous material depending upon the number of scattering events in the medium and the distribution of the scattering events. These scattering events heavily depend on the shape, size, and distribution of the pores within the material. If a general framework could be conceived relating these characteristics to the conductivities a more accurate model could be created and help researchers further deduce the impact of powder morphology on sintering.

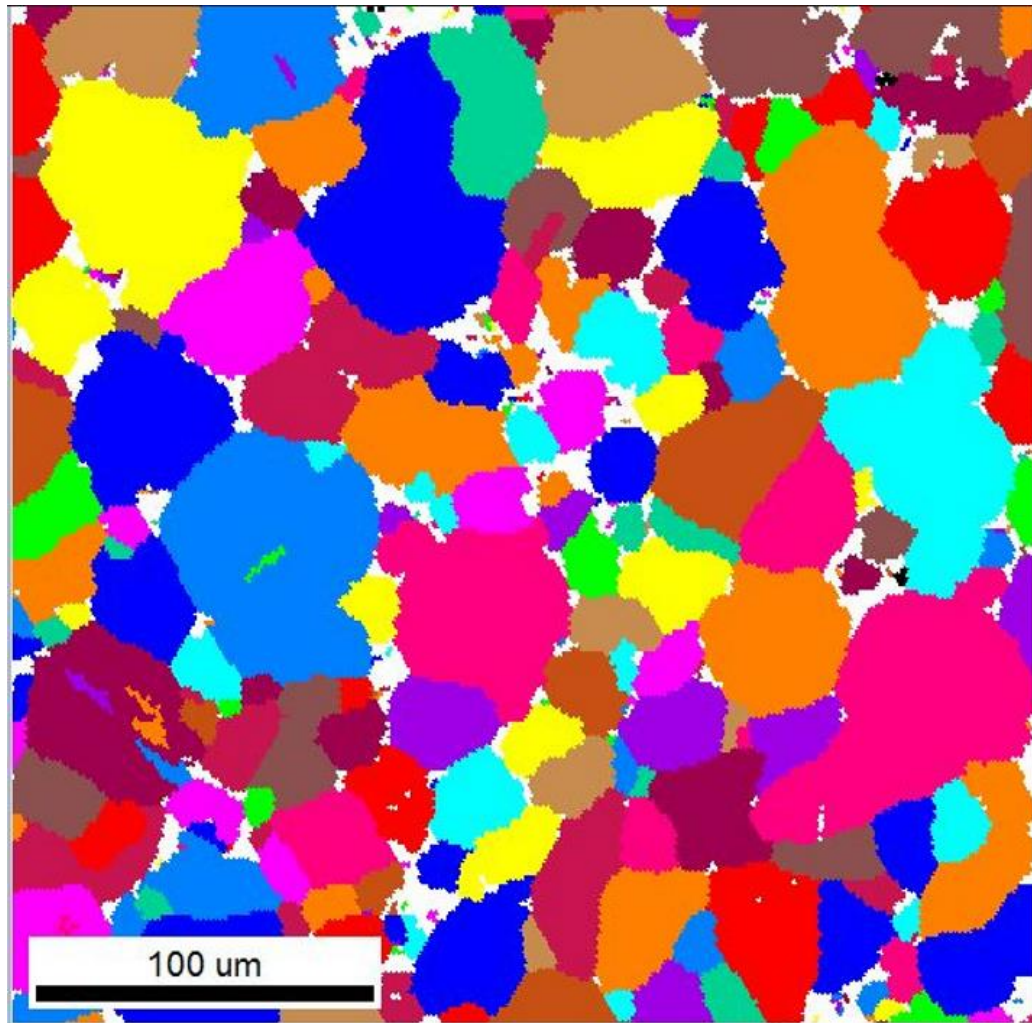
It is well established that grain size can have a large impact on both functional and mechanical properties[1–4]. While the present combined model has shown good accuracy between experimental and simulated density, to be more useful in terms of predicting mechanical/functional properties based on SPS simulations the grain size also needs to be estimated. However, unlike densification where the master sintering curve can be constructed based solely on thermal history, the heating rate has been shown to be critical to grain growth

projections within the SPS[5, 6]. In order to accurately predict grain growth, grain trajectory mapping is needed this is shown in the figure below by Cramer et al[7].



**Figure 7.1:** Grain growth trajectory of ZnO, with differing heating rates.

Therefore, it is necessary to know the maximum average heating rate and minimum average heating rate that a sample is exposed to during sintering, this can be predicted by the combined model previously discussed. Then, sintering experiments must be performed to map the expected grain growth with heating rates reflective of the maximum and minimum average heating rates predicted by the model in addition to the average heating rates in between. This should be done with a small-scale sample to minimize thermal gradients, similar to the methods used for identifying the MSC. Samples should then be cross-sectioned and electron backscatter diffraction should be performed with hundreds to thousands of grains diameters being recorded per sample.



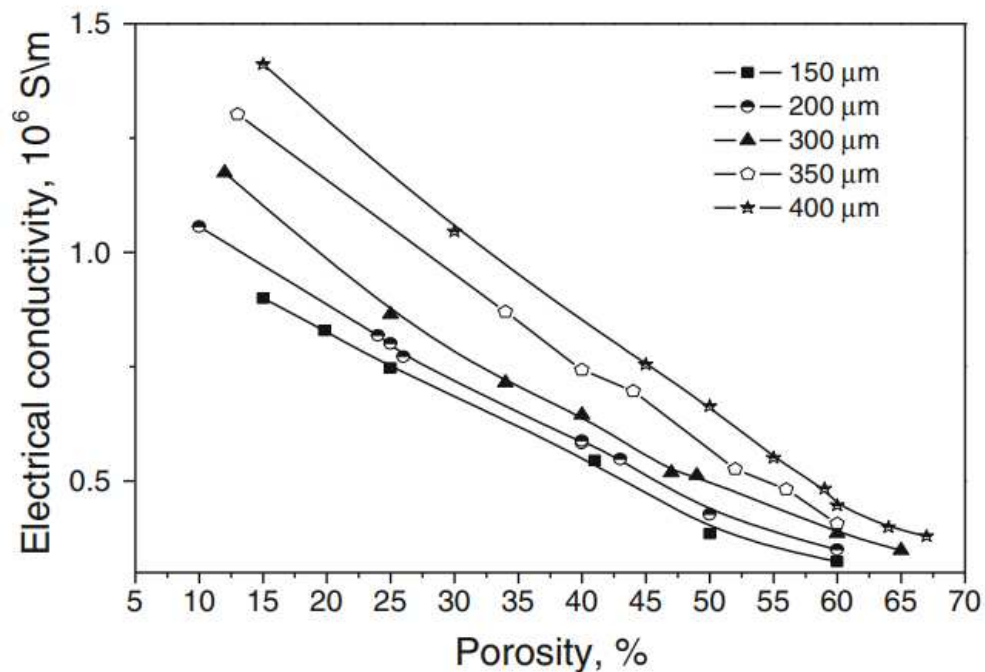
**Figure 7.2:** Example of EBSD image with unique grains from CP-Ti sample

Once grain size analysis has been completed a 3-D surface can be constructed to predict grain size based on average heating rate and time, similar to how density was mapped based on thermal history in chapter 5 and chapter 6. Grain size could now be estimated based on its location upon the mapped surface. This could further be added to an ABAQUS subroutine which when called would estimate grain size based on location specific heating rate and time allowing for at least a first order approximation of grain size based on sample location for a specific powder. This would further help researchers reduce iterative methods to produce and tailor

functionally graded materials and optimize sintering parameters, tooling, and powder characteristic choices when creating FGMs.

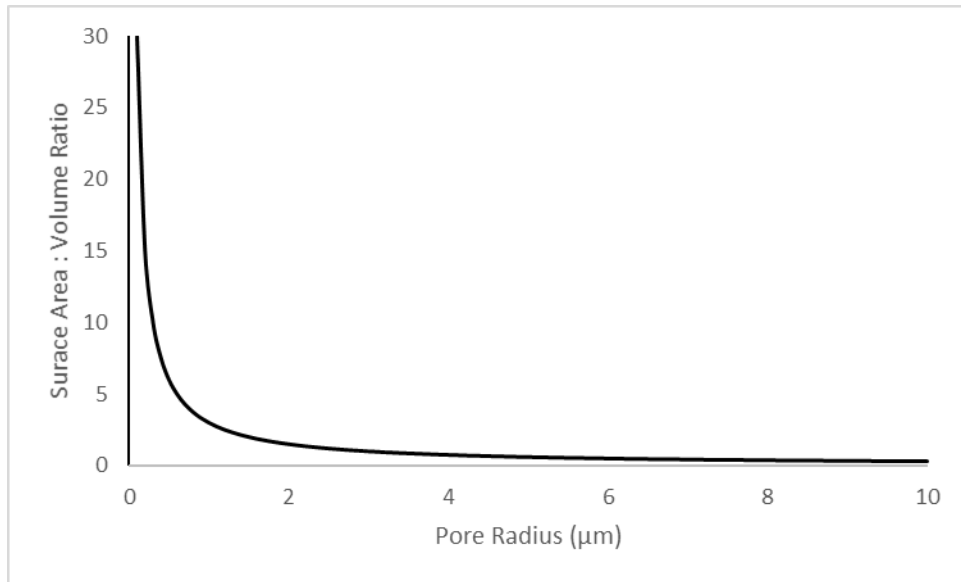
#### 7.12 Pore Characterization for Material Conductivity Estimation

Within the combined model used in my work the assumption has been made that the medium approximation theorem can be used within a first order degree of accuracy to predict electrical conductivity, thermal conductivity, density, and heat capacity as described in chapter 5. When reviewing the results between our experiment and model of chapter 5 and 6 we can with some certainty say that does appear to be the case, or that any discrepancy appeared to have a minor impact on the combined model. However, studies such as the one completed by Lu et al[8] who studied the effect of pore size on electrical conductivity in CP-Ti have shown that decreasing pore size decreases electrical conductivity and similar results have been shown for both energy absorption[9] and thermal conductivity[10].



**Figure 7.3:** Figure by Lu et al, demonstrating the decrease in electrical conductivity with decrease in pore size

This phenomenon has been attributed to the increased scattering sites of phonons and electrons with respect to decreasing pore size as they travel through the material due to a thermal or electrical gradient. The increased number of scattering sites occurs because of the increased amount of total pore surface area. The relationship becomes evident when we plot the surface area: volume ratio with respect to pore radius if a spherical pore is assumed between 100 nm and 10  $\mu\text{m}$ .



**Figure 7.4:** Surface area: volume ratio with respect to spherical pore radius

However, pores are generally not truly spherical and are better approximated as ellipsoids, meaning the radii are not equivalent in all three Cartesian directions. As the radii become more dissimilar the surface area to volumetric ratio also increases, indicating more scattering sites are present and conductivity should decrease. Therefore, I propose a relationship could be established between pore surface area and thermal/electrical conductivity this could be used to amend the medium approximation theorem by considering the area where phonon/electron scattering occurs. Which could be accomplished by sintering samples with differing particle size ranges, each range having a fine particle size distribution, assured by the implementation of sieving.

Samples would then be sintered to approximately the same density via the MSC for each powder distribution. Then micro-CT could be utilized to approximate the size/shape of the pores and confirm average density, assuming coarse enough powder is used to produce large pores which are easily detected. The electrical and thermal conductivity could be subsequently tested and plotted vs the calculated surface area. This correction could be directly implemented into models to consider the impact of pore surface area on thermal and electrical gradients caused by changes in conductivity during sintering. This would further help researchers predict a material's functional and mechanical properties when creating FGMs and limit need for trial-and-error methodology, specifically if very fine powders are used which produce finer pore structures.

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## Appendices

A-1



Image A1: Radial sample used for micro-CT

B-1

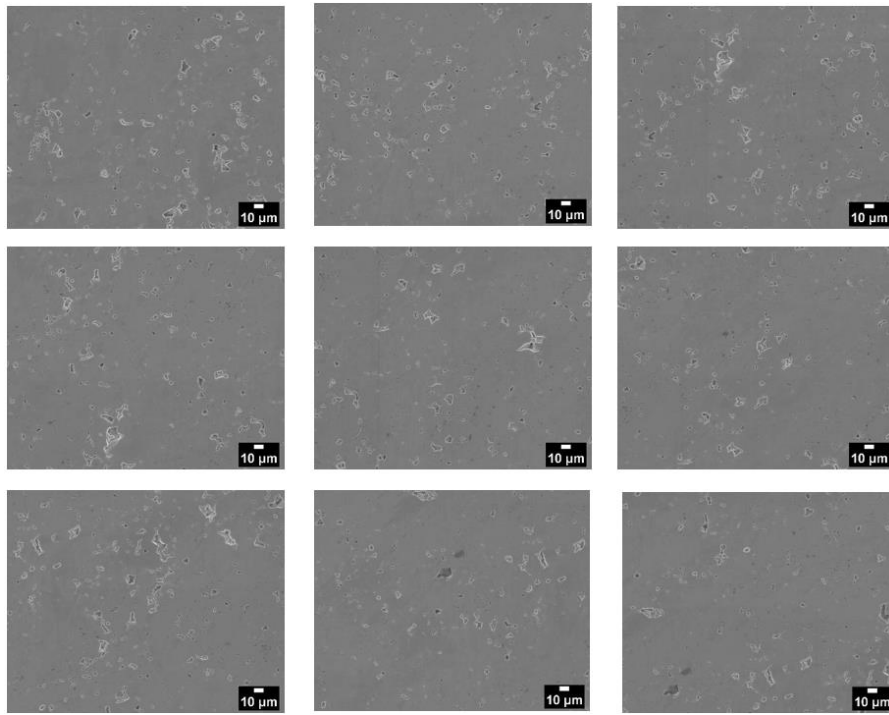


Image B1: Additional images from 70 mm sample location 1

B-2

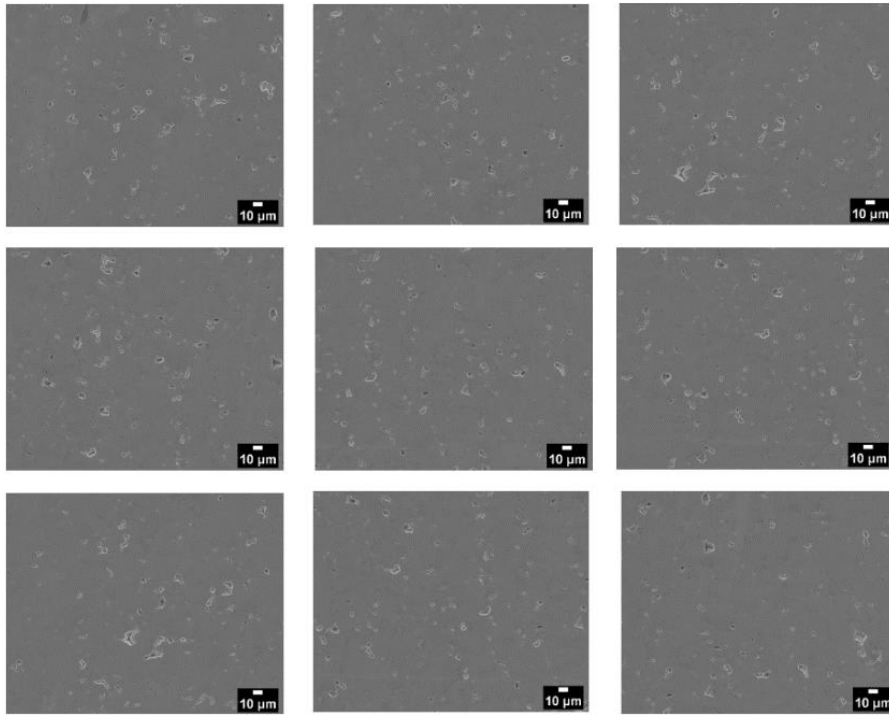


Image B-2: Additional images from 70 mm sample location 2

B-3

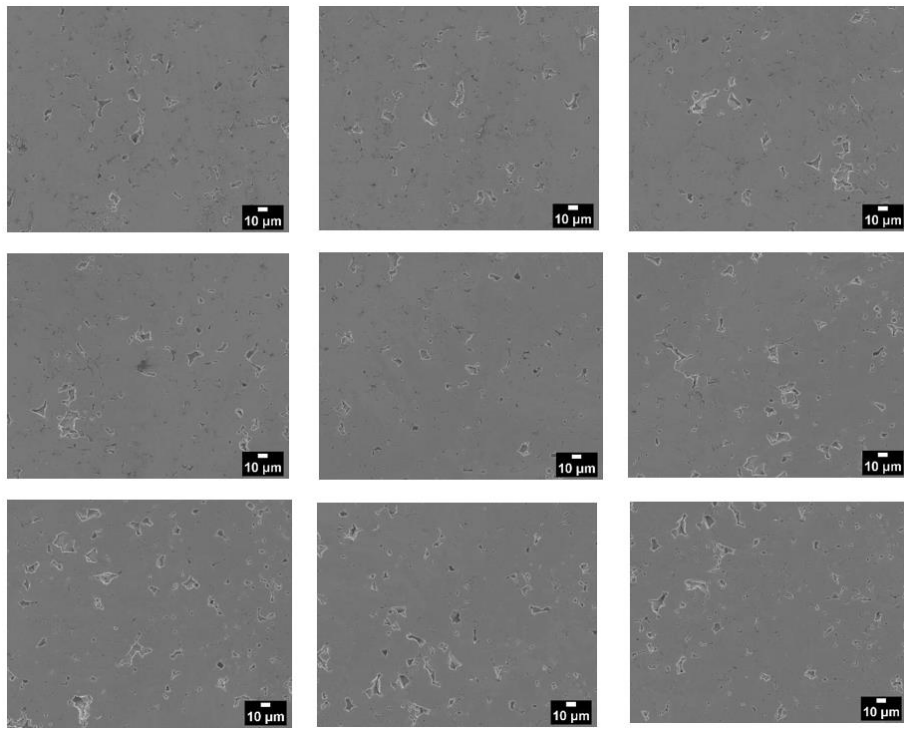


Image B-3: Additional images from 70 mm location 3

Thermal-Electrical Properties (T = Temperature in Kelvin)

| Properties                           | Ar-14                                       | Ar-12                                  | Titanium                                                             | Inconel |
|--------------------------------------|---------------------------------------------|----------------------------------------|----------------------------------------------------------------------|---------|
| <b>Electrical Conductivity (S/m)</b> | $-0.0002T^3 + 0.4876T^2 - 280.77T + 101730$ | $2E-18T^3 - 5E-15T^2 + 12.81T + 15216$ | $-0.0022T^3 + 5.6407T^2 - 4851.2T + 1.77E6$                          | 800000  |
| <b>Thermal Conductivity (W/m-K)</b>  | $5E-20T^3 + 2E-05T^2 - 0.0784T + 143.25$    |                                        | $-3.61E-14T^5 + 1.88E-10T^4 - 3.66E-7T^3 + 3.38E-4T^2 - 0.146T + 43$ | 11.4    |
| <b>Specific Heat (J/K-kg)</b>        | $1E-05T^3 - 0.0226T^2 + 16.536T - 2598.8$   |                                        | $-2E-7T^3 + 0.0005T^2 - 0.0578T + 224.13$                            | 435     |
| <b>Density (Kg/m<sup>3</sup>)</b>    | $7E-19T^3 - 2E-15T^2 - 0.0141T + 1900.1$    |                                        | $4510/(1+(8.5E-6*(T-273)))$                                          | 8190    |

Electrical Conductivity at Interfaces (T = Temperature in Kelvin)

|                                      | <b>Horizontal Contact Conductance</b>                                            | <b>Vertical Contact Conductance</b>                                   |
|--------------------------------------|----------------------------------------------------------------------------------|-----------------------------------------------------------------------|
| <b>Electrical Conductivity (S/m)</b> | $7\text{E-}15\text{T}^3 + 2\text{E-}11\text{T}^2 + 41099\text{T} - 8\text{E+}06$ | $4\text{E-}05\text{T}^3 - 0.0012\text{T}^2 + 166.65\text{T} + 501094$ |

## D-1

### Main Error Reduction Code

```
%Alexander Preston 1/26/2021
clc
close all
clearvars -except time time2 temp temp2 dens dens2 cooling trial1 trial2 trial3 trial4
trial5 trial6 trial7 trial8 trial9 trial10 trial11 trial12

n = 100; % number of iterations between min and max Q_msc
Qmax = 200*10^3; % max activation energy%
Qmin = 100*10^3 ; % min activation energy
N = size (dens,2);
maxD = 95; %Max density for all curves
minD = 61.8 % Min density for all curves
minT = 300 + 273; % Minimum Temperature for Second Stage of Sintering (Used to
calculate contribution to cooling)
%challenge = [79,-25.1767; 84.8, -24.0808; 86.8, -22.5887; 78.51, -24.7207 ; 85.069,
-22.8009; 86.3702, -22.8418; 79.8,-23.6814; 87, -21.8772; 92.15, -20.3876]

lowT_theta = zeros(n,1);
MRS=zeros(n,1);

for loop = 1:n
    Q(loop) = Qmin+((Qmax-Qmin)/n)*loop;
    for i = 1:N
        [reldens, theta, lowT_theta(loop)] = MSC(Q(loop), minD, maxD, minT, dens(:,i),
time(:,i), temp(:,i) + 273);
        theta = log(theta);
        data(i) = struct('D', reldens, 'T', theta);
    end

    [MRS(loop), avg_theta, sum_theta_error] = MRS_MSC_FUNCTION(data,minD,maxD);

    %Generate MSC
    if loop ==1 %compare the error from (Qloop) to the saved valuee best Q_msc
        msc_curve(:,1) = avg_theta; %initial value of theta value at the best Q_msc
        msc_curve(:,2) = data(1).D; % density of reference data set
        weighted_err=sum_theta_error; %average theta value at thcurve
    elseif MRS(loop) < MRS(loop-1)
        msc_curve(:,1) = avg_theta; %average theta value at the best Q_msc
        weighted_err = sum_theta_error; %weighted error sum
    end
end

[~,idx] = min(MRS);
Q_msc=Q(idx);

dTdt = 50:25:150;

gmisc = zeros(size(msc_curve,1),4);
gmisc_data(length(dTdt)) = struct ('theta', [], 'dens',[],
'time',[], 'temp',[], 'adj_dens',[]);

for i = 1:length(dTdt)
    Tf = 1000 +273;
    Ts = 0 +273;
```

```

t_hold = 0; %mins
t_ramp = (Tf-Ts)/dTdt(i); %mins
t_study = (t_ramp+t_hold)*60;
gtemp(1) = Ts;
gtime = linspace(0,t_study, 5000);
for j = 2:5000
    gtemp(j) = dTdt(i)/60*gtime(j)+gtemp(1);
    if gtemp(j) >= Tf
        gtemp(j) = Tf;
    end
end

[gmsc,intr_gmsc] = generate_densityMSC(msc_curve, Q_msc, minT, gtime, gtemp,
cooling);
gmsc_data(i).time=gmsc(:,3);
gmsc_data(i).temp=gmsc(:,4)-273;
gmsc_data(i).theta=gmsc(:,1);
gmsc_data(i).dens=gmsc(:,2);

%intr_gmsc_data(i).time=intr_gmsc(:,1);
%intr_gmsc_data(i).temp=intr_gmsc(:,2)-273;
%intr_gmsc_data(i).dens=intr_gmsc(:,3);
end
%Create a MSC based on the middle heating rate density data
[Average_MSC] = MIDDLE_THETA_INTEGRAL(Q_msc,time(:,3),temp(:,3)+273.15,dens(:,3));
figure(1)
hold on
plot(data(1).T,data(1).D,'-r')
plot(data(2).T,data(2).D,'-k')
plot(data(3).T,data(3).D,'-y')
plot(data(4).T,data(4).D,'-b')
%plot(data(5).T,data(5).D,'-g')
legend({'50C/min','75C/min','100C/min','125C/min'},'location','northwest')
xlabel('ln(theta)')
ylabel('Relative Density (%)')
hold off

figure(2)
hold on
plot(Q,MRS,'o')
%plot(gmsc_data(i).time(:),gmsc_data(i).dens(:),'.');
%scatter
xlabel('Activation Energy (kJ/mol)')
ylabel('Mean Residual Square')
hold off

figure(3)
hold on
plot(gmsc(:,1),gmsc(:,2));
plot(Average_MSC(:,1),Average_MSC(:,4))
%plot(challenge(:,2),challenge(:,1),'bo')
xlabel('ln(theta)')
ylabel('Relative Density(%)')
legend({'MSC'},'location','northwest')
hold off

```

## Adjusts MSC Based on Cooling Data

```

function[gmsc, adj_gmsc] = generate_densityMSC(msc_data,Q_msc,minT,time,temp,cooling)
%msc_data is nx2 MSC matrix. Column #1 is log(theta) Column#2 is density
% generate_densityMSC() returns generated master sintering curve data
%"gmsc" data in an nx4 matrix: [ theta, density, time, temp]
n = length(msc_data); %number of elements in MSC
theta_start = msc_data(1,1); %starting log(theta) value of MSC

integral_theta = THETA_INTEGRAL(Q_msc, time, temp);
log_integral_theta=log(integral_theta);

%Low temperature theta contribution
[~, idx_T_low] = min(abs(temp-minT));
[~,idx_MSC_start]=min(abs(log_integral_theta-theta_start));

lowT_MSC_temp = temp(idx_T_low:idx_MSC_start);
lowT_MSC_time = time(idx_T_low:idx_MSC_start);

lowT_theta = THETA_INTEGRAL(Q_msc,lowT_MSC_time,lowT_MSC_temp);
lowT_theta = lowT_theta(end);
%Create the MSC curve

[~,idx_MSC_stop] = min(abs(log_integral_theta-msc_data(n,1)));

%build gmsc time and temperature columns:
gmsc(:,3) = linspace (time(idx_MSC_start), time(idx_MSC_stop),n);
gmsc(:,4) =
interp1(time(idx_MSC_start:idx_MSC_stop),temp(idx_MSC_start:idx_MSC_stop),gmsc(:,3));

%Build over the applicable density range with low T theta contribution
gmsc(:,1) = log(THETA_INTEGRAL(Q_msc, gmsc(:,3), gmsc(:,4))+lowT_theta);

%Fit density from this gmsc theta to the MSC theta
for i = 1:n
    [~,idx] = min(abs(gmsc(i,1)-msc_data(:,1)));
    gmsc(i,2) = msc_data(idx,2);
end

adj_dens = zeros (size(msc_data,1),1);
adj_theta=zeros(size(msc_data,1),1);

for i = 1:size(msc_data,1)
    idx_theta_interrupt=i;
    Tmsc=exp(msc_data(idx_theta_interrupt,1)); %theta at which to interrupt heating
    [~,idx_T_low]=min(abs(cooling(:,2)-minT));%index to inerrupt heating schedule
    [~,hT_idx_interrupt] = min(abs(integral_theta-Tmsc));
    hT = integral_theta(hT_idx_interrupt);

    [~,cool_idx_start]=min(abs(temp(hT_idx_interrupt)-cooling(:,2)));
    %index matching interrupt temperature
    t_cool=cooling(cool_idx_start:idx_T_low,1)+time(hT_idx_interrupt)-cool_idx_start;
    cT = THETA_INTEGRAL(Q_msc,t_cool,cooling(cool_idx_start:idx_T_low,2));
    cT=cT(end);

    adj_theta(i) = (log(cT+hT)); %total theta value for heating and cooling

```

```

        [~,idx] = min(abs(msc_data(:,1)-adj_theta(i))); %index where adjust theta matches
MSC
        adj_dens(i) = msc_data(idx,2);
    end

    adj_gmsc(:,1)=adj_dens;
    adj_gmsc(:,3)=adj_theta;
end

```

## Creation of MSC Based on Middle Heating Rate Code

```

function [ Middle_MSC] = MIDDLE_THETA_INTEGRAL( Q, time, temp, dens)
%calculate _theta_FCN calculate and return theta integral
% time should be in seconds, temperature should be in kelvin, Q should be
% in J/mol K

n = length(temp);
eta = zeros(n,1);
integral_theta = zeros(n,1);
log_theta = zeros(n,1);
integral_theta(1) = 0;
log_theta(1) = -inf;

for i = 1:n
    eta (i) = 1/(temp(i))*exp(-Q/(8.314*(temp(i))));
    if i ~=1
        integral_theta(i)=integral_theta(i-1)+((eta(i-1)+eta(i))/2)*((time(i)-time(i-1)));
        log_theta(i)= log(integral_theta(i));
    end
end
Middle_MSC = [log_theta,time,temp,dens];
end

```

## Calculation of Mean Residual Square Between Heating Rates

```

function [MRS_sum, avg_theta, sum_theta_error] = MRS_MSC_FUNCTION(data,minD,maxD)
%input data structure of the heating scheules with density
%This section calculates the MRS between heating schedules length of 1st
%data struct
%Must have the shortest of all the sintering schedules the function
%returns the total MRS and the average theta at each density

maxD = maxD/100;
minD = minD/100;
N = size(data,2); % number of heating schedules
theta_mat=zeros(size(data(1).D,1),N);
theta_error=zeros(size(data(1).D,1),N);

for row=1:size(data(1).D,1) %length of the first density struct vector
    theta_mat(row,1)=data(1).T(row);
    for col = 2:N
        [~,idx_dens_match]= min(abs(data(col).D-data(1).D(row)));
        theta_mat(row,col)=data(col).T(idx_dens_match);
    end
end
% difference of each theta value from the average theta value at that
% density
avg_theta = mean(theta_mat, 2);

for col=1:N
    theta_error(:,col)=(theta_mat(:,col)./avg_theta-1).^2/N;
end

if theta_error == NaN
    then theta_error = 1
end
sum_theta_error = sum(theta_error,2); % add together weighted errors
Trial = sum_theta_error;
New = data(1).D;
Trial1 = Trial(6:end,:);
New1 = New(6:end,:);
whatarethose = trapz(New1,Trial1);
MRS_sum = sqrt(1/(maxD-minD)*whatarethose);

```

## Creation of MSC Data Based on Input Sampling Run Data

```

function [MSC_dens,summed_theta,lowT_theta] = MSC(Q,minD,maxD,minT,dens,time,temp)
%time in seconds
%temperature in Kelvin

for i = 1:length(dens)
    if dens(i) >= minD && dens(i) ~=0 %nothing occurs
    elseif dens(i) ~=0
        idx_dens_start = i; %find the last density under minD limit
    end
    if dens(i) >= maxD && dens(i) ~=0;
        idx_dens_stop=i %find the first dens over maxD limit
        break;
    end
end
end

%%Low temperature conttribution to the sum
[~,idx_Tt_start] = min(abs(temp(1:idx_dens_start)-minT));

lowT_MSC_temp=temp(idx_Tt_start:idx_dens_start);
lowT_MSC_time=time(idx_Tt_start:idx_dens_start);

lowT_theta = THETA_INTEGRAL(Q,lowT_MSC_time, lowT_MSC_temp);
lowT_theta = lowT_theta(end); %integral sum
%if lowT_theta <= 0
%    lowT_theta = 1E-4
%end
%%%%% Low temp end %%%%%

MSC_dens = dens(idx_dens_start:idx_dens_stop);
MSC_temp = temp(idx_dens_start:idx_dens_stop);
MSC_time = time(idx_dens_start:idx_dens_stop);

summed_theta = THETA_INTEGRAL(Q,MSC_time,MSC_temp) +lowT_theta;

return

```

## Example Fortran Code Used to Run Simulated PID and Update Relative Density

```

SUBROUTINE USDFLD(FIELD,STATEV,PNEWDT,DIRECT,T,CELENT,
1 TIME,DTIME,CMNAME,ORNAME,NFIELD,NSTATV,NOEL,NPT,LAYER,
2 KSPT,KSTEP,KINC,NDI,NSHR,COORD,JMAC,JMATYP,MATLAYO,LACCFLA)
C
C   INCLUDE 'ABA_PARAM.INC'
C
C   CHARACTER*80 CMNAME,ORNAME
C   CHARACTER*3 FLGRAY(15)
C   DIMENSION FIELD(NFIELD),STATEV(NSTATV),DIRECT(3,3),
1 T(3,3),TIME(2)
C   DIMENSION ARRAY(15),JARRAY(15),JMAC(*),JMATYP(*),COORD(*)
C   REAL :: NT, Q, R, Theta, RD, W, tim, dtim
C   REAL :: CpT, CpD, EcT, EcD, TcT, TcD, DT, DD
C   REAL :: P1, P2, Calcs
C   CALL GETVRM('TEMP',ARRAY,JARRAY,FLGRAY,JRCD,JMAC,JMATYP,MATLAYO,LACCFLA)
C   NT = ARRAY(1)
C   Everything above is standard ABAQUS USDFLD code, everything below is what I added
C   in order to approximate the MSC solution and define material properties based on
C   both temperature and density
C   STATEV(1) = NT
C   tim = TIME(1)
C   dtim = DTIME
C   Q = 146000
C   R = 8.314
C   Statev(1) is nodal temperature and statev(2) is MSC Theta term
C   If (tim <= 0) then
C       STATEV(2) = 0
C       RD = 0.611
C   Else
C       STATEV(2)=STATEV(2)+((1/STATEV(1)))*exp((-Q)/(R*STATEV(1)))*dtim
C   endif
C   open(3,file='C:\PIDtxts\StateEVs.txt',position='append')
C   write(3,*) STATEV(1), STATEV(2)
C   close(3)
C   Theta = LOG(STATEV(2))
C   STATEV(3) = Theta
C   Piecewise polynomials, used in order to better approximate all sections of MSC
C   P1 = 9.423140E-6*Theta**4 + 2.280238E-3*Theta**3 + 2.068676E-1*Theta**2 +
8.374887*Theta + 1.895095E+02
C   P2 = 5.014505E-3*Theta**4 + 3.930528E-1*Theta**3 + 1.131117E+1*Theta**2 +
1.439778E+2*Theta + 7.898862E+02
C   If (Theta <= -25) then
C       Calcs = P1/100
C   elseif (Theta <= -17.1 .AND. Theta > -25) then
C       Calcs = P2/100
C   else
C       Calcs = .987
C   end if
C   RD = Calcs
C   FIELD(1) = RD

```

```

Pores = (1-RD)
W = STATEV(1)
DT = 4510/(1+(8.5E-6*(W-273)))
CpT = (-2E-7*(W)**3 + 0.0005*(W)**2 - 0.0578*(W) + 224.13)*3.75
EcT = ((-0.0022*(W)**3 + 5.6407*(W)**2 - 4851.2*W + 1.77E6))*1.43
TcT=(-3.61E-14*W**5+1.88E-10*W**4-3.66E-7*W**3+3.38E-4*W**2-0.146*(W+43))/2
CpD = CpT*(1-Pores)
EcD = EcT * (1 - (3/2)*Pores)
TcD = TcT * (1 - (3/2)*Pores)
DD = DT * (1-Pores)
FIELD(2) = CpD
FIELD(3) = EcD
FIELD(4) = TcD
FIELD(5) = DD
RETURN
END

SUBROUTINE UAMP(
*   ampName, time, ampValueOld, dt, nProps, props, nSvars,
*   svars, lFlagsInfo,
*   nSensor, sensorValues, sensorNames, jSensorLookUpTable,
*   AmpValueNew,
*   lFlagsDefine,
*   AmpDerivative, AmpSecDerivative, AmpIncIntegral,
*   AmpDoubleIntegral)
C
  INCLUDE 'ABA_PARAM.INC'
C   time indices
  parameter (iStepTime      = 1,
*            iTotalTime     = 2,
*            nTime          = 2)
C   flags passed in for information
  parameter (iInitialization = 1,
*            iRegularInc     = 2,
*            iCuts           = 3,
*            ikStep          = 4,
*            nFlagsInfo      = 4)
C   optional flags to be defined
  parameter (iComputeDeriv   = 1,
*            iComputeSecDeriv = 2,
*            iComputeInteg    = 3,
*            iComputeDoubleInteg = 4,
*            iStopAnalysis    = 5,
*            iConcludeStep    = 6,
*            nFlagsDefine     = 6)
  dimension time(nTime), lFlagsInfo(nFlagsInfo),
*            lFlagsDefine(nFlagsDefine)
  dimension jSensorLookUpTable(*)
  dimension sensorValues(nSensor), svars(nSvars), props(nProps)
  character*80 sensorNames(nSensor)
  character*80 ampName
C   Everything after this line I defined everything above is taken from abaqus base
C   code for the subroutine UAMP
  REAL, Dimension(600000) :: a, b, c, e
  REAL :: P, I, D, Integr, Deriv, Current, tim, T1, T, TD, OldCurrent
  integer :: ierr, w, j, k
  Real :: trapz, Pgain, Igain, Dgain, Ptemp, stemp, timst
  Real :: pptemp, pstemp, ptimst

```

```

        tim = time(iTotalTime)
C      Call timestring at interval n which is the max interval which gives us the current
total step time in scalar form (this could be more efficient just not great at coding in
fortran)
C      T = Temperature from sensor in CAE File from ABAQUS names are transfered as all
capitals in fortran files
        T = GetSensorValue('THERMOCOUPLE',jSensorLookUpTable,sensorValues)
C      T1 = The Program Temperature (What you want the thermocouple temp to be simulated
at) Keep in Kelvin
        T1 = 298.15 + (tim/585)*975
C      The TD is the temperature difference between the thermocouple and the programmed
temperature at this specific point in the simulation
        TD = T1-T
C      This opens a text file that will be used to record Programed Temperature, Simulated
Temperature, Difference in temperature and Simulated Time
        open(1,file='C:\PIDtxts\PID.txt',position='append')
        write (1,'(F14.8,"",F14.8,"",F14.8,"",F14.8)') T1, T, TD, tim
        close(1)
C      Find the PID and give sensor new value assuming as long as this is the seond
increment or greater
        if (tim >= 0.1 .AND. T1 <= 473.15) then
            P = (1.4)
            I = (13.6)
            D = (34)
        elseif (T1 > 473.15 .AND. T1 <= 673.15) then
            P = (1.4)
            I = (13.6)
            D = (34)
        elseif (T1 > 673.15 .AND. T1 <= 773.15) then
            P = (1.4)
            I = (13.6)
            D = (34)
        elseif (T1 > 773.15 .AND. T1 <= 873.15) then
            P = (1.4)
            I = (13.6)
            D = (34)
        elseif (T1 > 873.15 .AND. T1 <= 973.15) then
            P = (1.4)
            I = (13.6)
            D = (34)
        elseif (T1 > 973.15 .AND. T1 <=1073.15) then
            P = (1.4)
            I = (13.6)
            D = (34)
        elseif (T1 >1073.15 .AND. T1 <=1173.15) then
            P = (1.4)
            I = (13.6)
            D = (34)
        elseif (T1>1173.15) then
            P = (1.4)
            I = (13.6)
            D = (34)
        endif
        open(3,file='C:\PIDtxts\PIDValues.txt',position='append')
        write(3,*) P, I, D
        close(3)
        if (tim >= 0.1) then
            w = 0

```

```

C    Retrieve both programed and simulated temperature and time data from each increment
within the siulation
    open(1, file = 'C:\PIDtxts\PID.txt',iostat=ierr)
    open(5, file = 'C:\PIDtxts\ierr.txt')
    write(5,*) ierr
    write(5,*) w
C    Find the length of the array in the text file length = n
    do
        read(1,*,iostat=ierr)
        if (ierr<0) then
            exit
        else
            w = w +1
            j = w -1
        end if
        write(5,*) w
    end do
    close(5)
    close(1)
    open(4,file='C:\PIDtxts\n.txt')
    write(4,*) w
    close(4)
    open(1, file = 'C:\PIDtxts\PID.txt',iostat=ierr)
    do k = 1, w
C    a = vector of programed temperature, b = vector of simulated temperature, c =
temperature difference, and d= time
        read (1,*) a(k), b(k), c(k), e(k)
    end do
    close(1)
    Ptemp = a(w)
    Stemp = b(w)
    timst= e(w)
C    j is the number of trapazoids used for integration
    open(1, file = 'C:\PIDtxts\PID.txt',iostat=ierr)
    do k = 1, j
C    a = vector of programed temperature, b = vector of simulated temperature, c =
temperature difference, and d= time
        read (1,*) a(k), b(k), c(k), e(k)
    end do
    close(1)
    Pptemp = a(j)
    Pstemp = b(j)
    Ptimst = e(j)
    Integr = 0
    do k = 1, j
        trapz((((Ptemp-stemp)))+(Pptemp-pstemp))/2)*(timst-ptimst)
        Integr = Integr + trapz
    end do
C    Use PIDs found via SPS Autotuning run which matches your CAE file and Setup your
testing (Again Keep in Kelvin)
C    Derivative of the temperature with respect to time
    Deriv = ((ptemp-stemp)-(pptemp-pstemp))/(timst-ptimst)
    diff1 = (ptemp-stemp)
    diff2 = (pptemp-pstemp)
    diff3 = (timst-ptimst)
    open(5,file='C:\PIDtxts\vals.txt')
    write(5,*) TD,Deriv, diff1, diff2, diff3
    close(5)

```

```

C    Get Old amp Value
      OldCurrent = ampValueOld
C    The equation below is specific to the SPS and the relationship between current and
temperature
      Current = OldCurrent + (P*TD + D*Deriv)
    endif
    Pgain = P*TD
C    Igain = I*Integr
    Dgain = D*Deriv
    open(6,file='C:\PIDtxts\valValues.txt',position='append')
    write(6,*) stemp, ptemp, w, j
    close(6)
    if (tim < 0.1) then
      Current = 0
    endif
    if (Current <= 0) then
      Current = 0
    endif
    if (Current >= 10000000) then
      Current = 10000000
    endif
    AmpValueNew = Current
    open(2,file='C:\PIDtxts\EndValues.txt',position='append')
    write(2,*) Current
    close(2)
    RETURN
  END

```