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Titanium-6Aluminum-4Vanadium For Functionally Graded Orthopedic Implant Applications

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Kyle Daniel Crosby, PhD
University of Connecticut, 2013

Rising costs of health care are attributed to an increasing number of medical procedures with great complexity and costly instrumentation. Novel materials and devices must be developed to reduce the time, economic cost, and physical pain associated with invasive orthopedic surgery. As well the lifetime of components must be extended to meet the needs of a population with an increasing life expectancy. To prolong the lifetime of an implant device, components should closely mimic the naturally occurring biological structure they are replacing in terms of both mechanical and biological function in order to assimilate undetected in the human body. Studies on orthopedic implant materials are herein investigated to determine the feasibility of functionally graded metallic-ceramic composite components that show improved load bearing capability while simultaneously enhancing biological activity necessary to avoid pain and/or device failure. Powder metallurgy studies are conducted using the titanium alloy (Ti-6Al-4V), which has shown great promise in orthopedic implant applications due to its high strength, lightweight, and biocompatible properties. Development of functionally graded titanium-hydroxyapatite components require the co-sintering temperature for the composite to be lowered below the onset of detrimental reactionary products. Powder processing and sintering is used to drive the Ti-HA co-sintering temperature below 1000°C, such that the beneficial mechanical and biological attributes of each constituent are preserved. X-ray diffraction, optical microscopy, and electron microscopy are used to monitor the phase purity, crystal structure, microstructure, particle morphology, particle size and relative density as they relate to the powder processing and sintering phenomena necessary for solid freeform fabrication.
Titanium-6Al-4V for Functionally Graded Orthopedic Implant Applications

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APPROVAL PAGE

Doctor of Philosophy Dissertation

Titanium-6Al-4V for Functionally Graded Orthopedic Implant Applications

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1. Introduction

1.1. Biomedical implants

Currently, there is a significant need to improve biomedical implant device performance because of the growing elderly population. This demographic will inevitably require our nation to provide more health care resources than ever before because persons 65 years and older make up 13% (~40 million people) of the US population\(^1\), many of whom utilize one or more medical device to maintain their quality of life. The necessity for improvements in biomedical implant device technology are driven by the economic cost of highly sophisticated surgical instrumentation and rapidly evolving biomaterials, as well as the physical dangers associated with the invasive nature of implant surgery. Secondary factors that also drive up the cost of biomedical device implantation include the high cost of medical malpractice insurance which the surgeon passes on to the patient, and the loss of wages incurred by the patient during the procedure and subsequent rehabilitation period.

A biomedical implant by definition is an artificial device that is implemented in the human body to repair or replace a naturally occurring biological component that is damaged or has failed catastrophically\(^2\). A biomedical implant device, as it is most universally defined, is a component intended to restore form and function to a native biological system that has otherwise been damaged or diseased beyond the natural repair capability of the living organism. Even after a biomedical implant device is successfully installed in the human body the patient is not yet free from harm because there exist a number of short term and long term complications that illicit immediate
response. While the implant device is intended to last for at least 20 years in service, many patients (~10%) experience a failure much sooner than expected.

The major shortcomings of orthopedic implant devices include implant loosening, implant fracture, implant dislocation, implant infection and/or patient related device rejection. Three common sources of systematic failure include osteolysis (i.e. bone resorption) caused by wear debris, stress-shielding caused by differential elastic moduli between the implant component and the native biological structure, and micro-motion of the implant caused by geometrical design flaws or implantation procedural flaws. In cases where an implant device has fractured, loosened from its intended implantation site, or been rejected by the patient’s immune system, a secondary surgery is required to repair or replace the defective component.

The primary, as well as any remedial surgery is accompanied by prolonged pain, discomfort, and/or infection at the implant site which can take months to rehabilitate even under optimal conditions. Loss of wages and a negative physical impact to the patient’s quality of life can accompany a prolonged rehabilitation period, such that for the greater good of the entire population a shift in biomedical implant technology is an obligation of the modern engineer. By enhancing the mechanical properties of the implant device itself and also by improving the mechanical/chemical stability of the device at the desired implantation site, the patient can avoid multiple surgeries and/or the negative side effects associated with implant failure. Device lifespan and bioactivity have drastically improved since the inception of artificial biological components through the use of novel materials systems and fabrication techniques however, there is still a desire to further enhance the mechanical properties and biological performance of a biomedical implant component such that the device meets or exceeds the performance of the missing or damaged natural biological structure for the entire lifetime of the
patient. In this way the component will have no discernible negative effect on the natural biological system into which it is installed, thus optimization of an implant device has been achieved.

1.1.1. Evolution of biomaterials

Biomaterials are a class of materials that are developed based on interactions between naturally occurring cells/tissues/organs and their artificial counterparts. The biomaterials industry has accounted for $28 billion in gross sales as of 2010\(^6\), with an expected increase in the upcoming decades. Biomedical grade materials for implant device fabrication include metallic, ceramic, and polymeric based materials. Among these material classes there are various biological responses that dictate the end usability of a specific biomaterial including bioinert, bioactive, and biodegradable properties respectively\(^7\).

Bioinert materials are those that do not react directly with the native biological system and thus result in minimal interaction with the patient’s immune or foreign body response mechanism. Bioactive materials are those which do directly stimulate a reaction with the native biological system to augment tissue repair and speed up the healing process. Biodegradable materials are those that react with the native biological system by gradually dissolving as the natural biological structure rebuilds itself allowing for direct replacement of the artificial implant material with a newly grown natural biological structure. Bioinert metallic components are the most common for load bearing applications where appreciable mechanical strength and toughness are required, bioactive ceramic components are utilized to promote enhanced bioactivity at the implant-biological interface when mechanical properties are secondary, and
biodegradable polymeric components are utilized as temporary scaffolds which are slowly dissolved and expelled by the body as the natural biological component rebuilds itself.

A comparison of the mechanical properties of various natural and synthetic biomaterials is presented in Figure 1.1, which shows a plot of fracture toughness versus elastic modulus. Take note the location of titanium, hydroxyapatite, and natural cortical bone-l (i.e. longitudinal strength) which reference the materials that are of particular interest for load bearing femoral stem components as per the objective of this study. Although the elastic modulus matching for these three materials is less than ideal, there are specific properties of each material that can be exploited to promote accelerated healing and improved quality of life for a patient in need of a total hip replacement.

Widely used metallic biomaterials include stainless steel alloys (e.g. 316L), cobalt-chromium alloys (e.g. CoCrMn), and titanium alloys (e.g. Ti-6Al-4V) which have appreciable mechanical strength and are therefore best suited to replace hard tissue. Stainless steel components have recently been replaced with lower elastic modulus materials in order to alleviate the stress shielding phenomenon (i.e. a cause of implant failure that will be explained in greater detail in the following sections). While cobalt chromium alloys display the necessary mechanical properties for load bearing implant applications, chromium ion (Cr$^{3+}$) exposure results in DNA mutation and eventually cancer after prolonged use. Titanium alloys are much lower density and thus much lighter than stainless steel components, as well they show very low rates of corrosion decomposition in a body fluid environment thus they can be expected to remain mechanically robust over decades of service due in part to their tendency for passivation. Studies have also shown that even if there is a release of titanium ions into the body fluid from wear debris, the toxicity of those ions is much less than for other
metal ions and no appreciable negative foreign body response is experienced, thus titanium based biomedical components are among the most bioinert metallic materials.

Ceramic biomaterials including porcelain (e.g. \( \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \)), hydroxyapatite (e.g. \( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \)), and alumina (e.g. \( \text{Al}_2\text{O}_3 \)) based materials more closely mimic natural biological structures in terms of chemical composition as compared to their metallic counterparts, which is the reason for their longterm stability in vivo. Compositional homogeneity at the interface between the implant component and the natural biological structure allows for augmented tissue formation which in turn leads to enhanced mechanical properties at the implant device-biological system interface.

Purely ceramic implant components are hindered by the fact that they have very low mechanical strength based on Griffith’s criterion (i.e. finite number of small but critical flaws are inherent in all ceramics), and thus they exhibit very high failure rates when utilized for load bearing applications. Ceramics are particularly poor under tensile loading because they do not plastically deform prior to fracture due to the nature of their atomic bonding (i.e. strong, directional ionic or covalent bonding rather than shared, non-directional metallic bonding), thus pure ceramic components should not be used for structural implants.

Polymeric biomaterials including polymethylmethacrylate (e.g. \((\text{C}_5\text{O}_2\text{H}_8)_n\)), ultra high molecular weight polyethylene (e.g. \((\text{C}_2\text{H}_4)_n\)), and polyetheretherketone (e.g. \((\text{OC}_6\text{H}_4 \text{OC}_6\text{H}_4 \text{OC}_6\text{H}_4)_n\)) are useful for a number of applications because they can decompose by design while in service. Sterilization of biomedical components is done prior to implantation in order to eliminate bacteria as necessary for preventing infection and/or rejection by the patient’s immune system. In the case of polymeric materials electromagnetic radiation is used to sterilize the component because polymers are generally susceptible to decomposition during chemical or thermal sterilization.
polymeric materials contain catalysts to promote polymerization (i.e. the process necessary to form solid engineering materials from gaseous or liquid molecules) as well as other stabilizing agents (i.e. additives necessary to provide mechanical strength to the long carbon-carbon chains), they are greatly affected by the irradiation treatments used for sterilization. Irradiation sterilization can cause various changes in the chemical, mechanical and biological properties of the precursor polymeric materials such that the long-term toxicological effects must be considered. While many lightly to moderately irradiated polymeric biomaterials are readily excreted by the human body with no appreciable biological interaction, some heavily irradiated polymers lead to gas evolution in vivo, double bond formation, and/or free radical formation which can alter the mechanical, biological and even cosmetic properties of the implant material and biological system for the worse. Therefore the limitations of polymeric biomaterials include high levels of free radicals in heavily cross linked materials (i.e. crosslinking is necessary to improve the mechanical properties of polymers because the crosslinks act as pinning points that block polymer chain realignment to the applied stress direction) which are known to be carcinogenic in nature, issues related to high wear rates, and issues related to poor mechanical bonding of polymers to biological structures.

1.1.2. Evolution of biomedical device design

Advances in biomedical implant device technology include modifications to the surface structure of the implant (e.g. intentional porosity) and/or the application of a bioactive constituent (e.g. hydroxyapatite thin coating), see Figure 1.2(a) and Figure 1.2(b) respectively. Surface structure alterations focus on fabrication of an implant device with a porous network that allows for interpenetrating
bone growth, thereby mechanically interlocking the implant and native bone without the need for a bone cement to achieve stable fixation. The enhanced mechanical interlocking provided by porous surface structured components allows for more uniform stress transfer across the bone-implant interface, thus aseptic loosening issues attributed to cemented implants can also be prevented. The use of porous surface structured components is done so at the cost of a significant reduction in the mechanical integrity of the implant itself due to the stress concentrating nature of crack tips and sharp protrusions which form the porous geometry.

Currently, many implant components are held in their intended location with polymeric bone cement that bonds the metallic implant to the organic bone material. While bone cement is effective in anchoring the implant device, wear debris associated with failure of the cement over time, along with a magnified stress shielding effect due to the rigid nature of the fixation make cement-less implants the preferred approach. For cement-less devices a bioactive ceramic material is often incorporated as a thin coating on a metallic substrate. Metallic components with a thin bioceramic coating often show spallation of the coating from the substrate due to differential mechanical properties, differential thermal expansivities, and/or differential corrosion mechanisms. When the bioceramic coating separates from the metallic substrate the implant fixation is severely compromised, which is a situation that inevitably leads to an additional remedial surgery to repair or replace the faulty component.

The goal of this research is to make use of the advantages of both a porous surface structure and a bioactive chemistry by using a functionally graded material (FGM) approach. The FGM design intended for femoral stem hip implant components will have a pure metallic core region to provide load bearing mechanical strength, while a compositionally graded bioactive ceramic porous surface structure will enhance implant-
bone mechanical interlocking and provide improved cell bioactivity for enhanced interfacial bonding. The FGM component will be prepared using a layer-by-layer 3-dimensional printing technique which is a type of solid freeform fabrication (SFF) capable of producing complex geometries from a powder feedstock. The details of this novel FGM femoral stem component design are explained in greater depth in Chapter 3.

1.1.3. The total hip replacement

The total hip replacement is a device composed of a femoral stem component, a femoral head component, and an acetabular cup component as shown in Figure 1.3\textsuperscript{23}. The total hip replacement is a procedure that affects more than two hundred thousand patients annually in the United States alone\textsuperscript{24}. The specifics of the total hip replacement include some particularly alarming details concerning open wound infection, painkiller addiction and overwhelming health care costs. In particular, the total hip replacement involves a large incision along the outer thigh to access the hip joint and femoral head, see Figure 1.4\textsuperscript{25}. This incision exposes many large arteries, veins, and nerves which are susceptible to damage during and after the operation and therefore should be protected from additional exposure by avoiding a secondary remedial surgery at a later time.

The conventional sizing method employed to date involves overlaying a femoral stem template on an x-ray image of the damaged hip joint and femur prior to surgery, see Figure 1.5(a) and Figure 1.5(b) respectively\textsuperscript{26}. The surgeon then selects a standard sized component based on the femur length and diameter, making any final adjustments to the geometry during the actual implantation procedure in real time which is less than an ideal approach. Many total hip replacements require intentional breaking of the femur and/or removal of any damaged or weakened bone material in order to mold and seat
the artificial femoral stem and acetabular cup components of the implant device. Femoral stem and acetabular cup seating must be done in vivo because the size and geometry of these natural structures are unique to each patient, which makes the total operation duration an important parameter to minimize in the future in order to reduce physical dangers and lessen economic costs of the procedure. This method could easily be replaced with a better “true fit” method using the layer-by-layer 3-dimensional printing process because the SFF component can be uniquely fabricated for each patient, rather than relying on modification of a standard sized component during the operation in an attempt to make the fit merely as good as possible.

During the total hip replacement procedure the patient’s lower body is numbed using a strong spinal epidural to block nerve signals below the waist. Additionally, a strong local anesthetic which helps to lessen bleeding at the operation site is used to numb the hip and upper leg region. The duration of a conventional total hip replacement surgery is approximately 2 hours from the first incision until the wound is sown shut. Post surgery, the patient often relies on morphine to control pain during the recovery and rehabilitation period, which can last for weeks or months depending on the specific individual. While morphine is effective at suppressing physical pain as the patient requires, the side effects associated with prolonged narcotic use include seizures, confusion, severe weakness, and insomnia. Even short term narcotic use can lead to high rates of chemical addiction and a high cost of medication, which can be lessened by promoting accelerated healing through improved mechanical properties of the device as well as increased bioactivity at the implantation site by using a FGM design via SFF.

Malfunctions of the total hip implant are characterized by the specific mode of failure and the resulting biological response that is automatically initiated by the patient’s immune system. The ball and socket portion (e.g. acetabular cup) of the implant device
has many issues associated with high rates of material wear, rapid fatigue of an 
actuating component in a corrosive body fluid environment, and/or decomposition of the 
component due to oxidation. Wear debris resulting from friction in the ball and socket 
portion stimulate cytokine and activated macrophage production. Formation of these 
biological agents is accompanied by inflammation, apoptosis (i.e. programmed cell 
death), necrosis (i.e. premature cell death), and osteoporosis (i.e. bone resorption) 
which contribute to weakening of the bone and eventually lead to systematic failure of 
the implant device\textsuperscript{27}. Because the mechanical property requirements for the actuating 
acetabular cup component are much different than that of a static load bearing 
component such as the femoral stem, the acetabular cup is typically fabricated using a 
dramatically different material class (i.e. high hardness, low wear rate, high density 
material = low toughness, heavy and brittle) and thus only the issues related to the 
femoral stem component (i.e. high yield strength, high toughness, low density material = 
lightweight and ductile) are of interest for this study.

The malfunctions of the femoral stem include fracture of the component itself due 
to compositional or geometrical impurities in the component which do not directly 
stimulate a biological immune response. The other issues that do cause a direct 
biological response include loosening of the stem due poor mechanical interlocking at 
the implant-biological interface which results in bone resorption, and/or decomposition of 
the component which leads to metal ion toxicity. Metal ion dissolution from metallic hip 
implant components resulting from mechanical forces (i.e. friction) or chemical forces 
(i.e. corrosion) may lead to excessive concentrations of otherwise harmless essential 
elements in the bloodstream\textsuperscript{28}. The specific effect of metal ions in the body is not clear; 
however, an increase in any chemical element beyond the normal amount can lead to 
cancer (i.e. beyond a threshold dosage some carcinogenic/mutagenic effects occur),
poisoning (i.e. beyond a threshold dosage some toxic effects occur) or chronic inflammation (i.e. high concentrations can lead metal sensitization effects) of biological entities.

For these reasons, design alterations to both the component material system and component geometry must be realized to lower the frequency of device failures, reduce biological side effects, and minimize risky secondary remedial surgeries. The specific objective of this research is focused on improving the mechanical properties of the femoral stem component itself, as well as improving the mechanical properties at the interface between the implant and native biological structure. The specific properties to be modified are addressed in Chapter 3.

1.2. Titanium-6Aluminum-4Vanadium details

1.2.1. Properties

The modern chemical name titanium, given by Martin Heinrich Klaproth after isolation by William Gregor in 1791, is derived from the Greek word *titanos* which references the advantageous mechanical, electrochemical and visual properties of the material being characteristic “of the gods”. Titanium based alloys have shown great performance as biomedical implant materials because of their excellent corrosion resistance in body fluid environments and their lightweight but high strength characteristics which make them particularly useful for skeletal repairs\(^29\). Grade 5 titanium (e.g. Ti-6Al-4V) is an alloy composed of 6 wt% aluminum, 4 wt% vanadium and the balance titanium mixed in solid solution. The ternary phase diagram is given in
Figure 1.6, where the Ti-6Al-4V composition is indicated by the intersection of binary tie lines.

The Ti-6Al-4V alloy has a two phase $\alpha$-$\beta$ composition which undergoes the allotropic transformation from $\alpha$ hexagonal close packed (HCP) structure to $\beta$ body centered cubic (BCC) structure at $980^\circ$C. The room temperature $\alpha$ phase HCP crystal structure has lattice parameters of $a = 2.95 \, \text{Å}$ and $c = 4.68 \, \text{Å}$ resulting in $c/a$ ratio of 1.586, while the high temperature $\beta$ phase (BCC) crystal structure has a lattice parameter of $3.32 \, \text{Å}$ as shown in the ball and stick models in Figure 1.7. The presence of a two phase $\alpha$-$\beta$ composition, achieved by addition of the alloying elements shown in Figure 1.8, results in a lower modulus of elasticity in Ti-6Al-4V than in that of a pure $\alpha$ HCP titanium component. The reduced modulus, achieved via vanadium $\beta$ stabilization, more closely replicates the modulus of natural biological structures such as bone, proving Ti-6Al-4V’s advantage over pure $\alpha$ HCP titanium in orthopedic implant applications.

A lower elastic modulus alloy is more effective at avoiding the stress shielding phenomenon because it has mechanical properties more closely matched to that of the native human bone which it is replacing. Stress shielding is the process by which native bone deteriorates from being under worked in the area immediately surrounding the implant device. The native bone degenerates much like that of a patient with severe osteoporosis due to the fact that the implant is significantly stronger and more rigid than the native bone, thus the full weight of the body is carried by the implant rather than requiring the surrounding bone to actively participate in supporting weight during locomotion. As a result, the native bone weakens and deteriorates over time until implant fixation has been compromised from a lack of mechanical integrity at the bone-implant interface (i.e. implant loosening occurs), thus materials with a modulus of
elasticity close to that of the natural biological structure they are replacing are preferred (i.e. Ti-6Al-4V preferred over pure Ti).

The lightweight character of Ti-6Al-4V is derived from its low molar density as compared to typical structural materials. The atomic radii of the solvent metal titanium, and the solute atoms of aluminum and vanadium are 176 pm, 118 pm, and 171 pm respectively\textsuperscript{34} giving molar volumes of 10.64 cm\textsuperscript{3}, 10.00 cm\textsuperscript{3}, 8.32 and cm\textsuperscript{3} respectively\textsuperscript{35}. The molar mass of titanium, aluminum, and vanadium are 47.87 g/mol, 26.98 g/mol, 50.94 g/mol respectively\textsuperscript{36}, giving molar densities of and 4.5 g/cm\textsuperscript{3}, 2.7 g/cm\textsuperscript{3}, 6.1 and g/cm\textsuperscript{3} respectively. A molar density of 4.45 g/cm\textsuperscript{3} for Ti-6Al-4V is calculated using the rule of mixtures given in Equation (1),

\[ D_{\text{alloy}} = D_{Ti}M_{Ti} + D_{Al}M_{Al} + D_{V}M_{V} \] (1)

where \( D \) is the density, \( M \) is the mass, and the subscripts alloy, Ti, Al, and V refer to the chemical constituents of the alloy and elements respectively\textsuperscript{14}. The molar density of Ti-6Al-4V is much less than typical structural biomedical components such as 316L stainless steel and Co-28Cr-6Mo which have a molar densities of 7.9 g/cm\textsuperscript{3} and 8.3 g/cm\textsuperscript{3} respectively\textsuperscript{37}, thus Ti-6Al-4V components are much lighter than their biomedical alloy counterparts with comparable mechanical strength.

Another important factor to note is that Ti-6Al-4V has the added benefit of a slightly lower raw material cost than pure titanium because a portion of the titanium has been replaced by aluminum, which itself is a more abundant and thus less expensive raw material. The raw mineral commodity cost per metric ton given for the chemical constituents are as follows; titanium ($10,300/tonne), aluminum ($2,640/tonne), and vanadium ($14,630/tonne)\textsuperscript{38}. Using a rule of mixtures calculation of the same form as
shown in Equation (1), it can be shown that pure titanium ($10,300/tonne) is more expensive than the grade 5 alloy Ti-6Al-4V ($10,014/tonne) such that industrial scale usage of the alpha-beta alloy will result in savings for the manufacturer.

1.2.2. Processing

Titanium-6Al-4V components are fabricated using various traditional metal working processes as well as some more contemporary laser based or freeform processes. Traditional casting is used to fabricate a component directly or to create bar, sheet, or ingot feedstock for use in downstream consumer component fabrication. Cast components show appreciable mechanical strength, however, the processing defects associated with casting mold interactions and cooling from a melt in the ambient atmosphere lead to a lower mechanical strength than predicted by inherent atomic structure. Some of the mechanical properties can be enhanced through the application of a post casting heat treatment, but there is a limit to the improvement which also has an additional cost associated with the process. Casting itself requires maintaining a continuous melt pool which is an expensive manufacturing overhead cost due to the high cost of energy in the United States ($0.08/kWh – $0.17/kWh)\textsuperscript{39}, thus alternative processing techniques must be investigated to lower the manufacturing cost for orthopedic implant devices.

Forging is a solid state processing technique capable of improving the mechanical properties of as cast components through the application of a compressive strain field at the surface and subsurface regions of the component. Forging can be simply described as a macroscopic hammering process that results in a high dislocation defect density in the microscopic surface region. The dislocations and accompanying
strain fields hinder subsequent dislocation mobility which actively blocks crack propagation through the bulk, thus resulting in the improved mechanical strength. This type of post casting mechanical treatment is effective at enhancing the mechanical properties of a component but it is done so at the expense of a reduction in net shape control (i.e. not capable of tight geometrical tolerances) and an increase in economic cost associated with an additional processing step.

While a machining process often allows for the best combination of geometrical tolerance control and retention of mechanical properties for the final product, the specific material properties of the machined component must be evaluated prior to drawing this conclusion. Machining of Ti-6Al-4V components is possible using diamond tipped machining tools; however the high wear rate and thus high cost of said machining tools can be cost prohibitive. The high material hardness of Ti-6Al-4V is also prohibitive because tight geometrical tolerance is difficult when machining high hardness materials because they tend to experience brittle fracture due to uncontrolled crack propagation, and therefore geometrical accuracy is difficult to maintain.

Novel processing methods for the production of Ti-6Al-4V components include SFF powder fabrication techniques wherein the final geometrical tolerance is determined by the dimensions of the powder feedstock and the dimensions of the SFF extrusion tip used to deliver the powder slurry. SFF techniques also have the added benefit of allowing for densification of the component in the solid state (i.e. sintering), which requires less energy consumption than traditional casting and heat treating techniques, thus the economic benefit of SFF is also realized. Sintering of SFF components can be achieved using basic radiant thermal heating, microwave heating, electrical joule heating, or site specific laser based heating methods which allow for greater retention of mechanical and chemical properties than in traditional casting techniques. Currently
however, SFF techniques are hindered by the overall component macroscopic
dimensional limitations (i.e. small components are possible with commercially available
SFF instrumentation, but larger components require larger SFF printing machines that
are currently not yet commercially abundant) and by the manufacturing throughput
capabilities of layer-by-layer printing and sintering processes to date because the layer-
by-layer slurry delivery and subsequent sintering processes require longer time than
traditional casting until improved software control and sintering are realized.

1.2.3. Applications

Some common applications for Ti-6Al-4V materials include aerospace
components, see Figure 1.9\textsuperscript{40}, because Ti-6Al-4V has a high melting temperature (i.e.
maintains its inherent mechanical strength in the combustor and exhaust regions of jet
turbine), low density (i.e. allows for increased fuel efficiency and reduced operational
cost when used for aircraft skin), and good corrosion resistance (i.e. does not
decompose under high temperature oxygen rich combustion conditions). Titanium-6Al-
4V is also utilized in sporting goods such as golf club heads and bicycle frames where
maximum component strength must be balanced with minimal weight, see Figure
1.10(a)\textsuperscript{41} – Figure 1.10(b)\textsuperscript{42} respectively. In this manner the component is able to provide
optimum performance and enhanced user functionality in applications where the human
body provides all of the energy.

Biomedical applications, in which a natural biological system is directly in contact
with a manmade device, require the component to be fabricated from a biologically
stable material such as Ti-6Al-4V. From simple cosmetic components such as earrings,
Figure 1.11\textsuperscript{43}, to complex implant devices such as dental anchors, Figure 1.12\textsuperscript{44}, Ti-6Al-
4V proves it medal (pun intended) time and again due to its low specific gravity and excellent corrosion resistance in an acidic body fluid environment. While there exist countless other applications for Ti-6Al-4V materials, the overwhelming majority of its applications lies within the aerospace and biomedical fields where it's most advantageous properties (i.e. strong, light, and inert) can be exploited for the benefit of the human race.

1.3. Hydroxyapatite details

One of the most common ceramic materials utilized for improved bioactivity of orthopedic implant components is the compound hydroxyapatite \( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \) referred to as HA, which shows great corrosion resistance in the human body due to the inert nature of its mineral phases. HA is particularly effective because it has a chemical composition that is nearly identical to that of the load bearing phase of natural cortical bone, which is mainly calcium phosphate. A diagram of the human femur is shown in Figure 1.13\(^{45} \), wherein the load bearing portion of the skeletal structure is identified as the dense, compact, cortical bone. HA serves to aid in the formation of the crystalline lattice type structure in bone, which in turn provides the structural integrity desired of load bearing components such as the human femur. Natural bone calcium phosphate, like HA, is relatively strong under compressive loads but fails catastrophically under tension or torsion loading due to the inherent brittle nature of ceramic materials, thus pure HA structural components are not practical. Natural bone instead has a secondary phase made of collagen (i.e. a naturally elastic protein phase) that provides fracture toughness to the skeletal system through a composite strengthening mechanism, thus
HA components should likewise utilize a secondary composite strengthening mechanism through the application of a metallic phase such as Ti-6Al-4V.

HA can be produced naturally within the human body or synthesized using precipitation, sol-gel, hydrothermal, emulsion, or deposition techniques as outlined by Nayak. The existence of HA within and on the surface of natural bone facilitates osseointegration, the process responsible for a coherent interface between an implant material and the natural bone material which ideally should be free of scar tissue, cartilage, or ligament fibers which could interfere with the mechanical and biological functions of the implant component. Osteoblast (i.e. mononucleate cells responsible for bone formation) attachment and proliferation on the surface of an implant material is a standard method of osseointegration analysis that is vital for evaluation of the biocompatibility of a given implant material system. The inherently poor mechanical properties of HA mandate that they be used in conjunction with a mechanically robust phase such as a metallic Ti-6Al-4V, however fabrication of a composite component of this type has its own flaws as compared to a single phase component. Details of the benefits and drawbacks of such a device will be discussed in greater depth in Chapter 3.
2. Research Motivation

2.1. Contemporary implant flaws

Biomedical implant device failure in femoral stem components can be described by the issues that plague the implant component itself as well as those that plague the interface between the implant component and biological structure. Implant component failure is an issue readily attributed to the processing of said device. Femoral stem biomedical implant components derive their load bearing capability from a metallic phase which is often fabricated through a traditional casting process. Because of the nature of the melting and pouring processes in casting, the resulting component is susceptible to high levels of physical and compositional contamination.

Physical contamination involves residual porosity in the final component which may result from impurities or trapped gas bubbles in the parent melt. The existence of porosity depreciates the mechanical strength of a component because it reduces the cross sectional area available to carry the applied load, which in turn increases the applied stress the component must withstand. As well, voids act as stress concentration sites which allow for crack propagation in the component at a lower applied stress level and should therefore be avoided in the final product. Chemical contamination from casting often includes metal carbide formation due to interactions between the melt and the casting crucible (i.e. crucible is often high carbon steel or cast iron), and/or metal oxide formation due to interactions between the melt and the casting atmosphere (i.e. ambient air). Carbide and/or oxide phases have inherently low toughness as well as poor physical bonding with the rest of the metallic mass that comprises the bulk of the component and should therefore be avoided in the final product. An in vivo example of
implant component failure of a femoral stem is shown in Figure 2.1(a)\textsuperscript{47}, which is a result that demands immediate replacement surgery. In order to avoid issues associated with chemical contamination and stress concentration, powder metallurgy sintering should be used to fabricate the component via an SFF technique which allows for fully dense metallic components with a high level of compositional purity such that the aforementioned modes of failure are suppressed accordingly.

The second major flaw in femoral stem implant components is a failure at the implant-biological interface, described as implant loosening which results from poor adhesion of the implant device to the native biological structure. When there is a lack of mechanical or chemical interlocking at the implant-biological structure interface, the implant can rotate, vibrate, and pull completely out of the intended implantation site. An in vivo example of implant system failure is shown in Figure 2.1(b)\textsuperscript{47}, wherein the dark region on the interior of the femur indicates a hollow space (i.e. air does not absorb x-rays so it appears dark, while bone and metallic implant do absorb x-rays so they appear bright white) resulting from a separation of the implant device and the native bone. Again, this is a diagnosis that would inevitably lead to an immediate remedial surgery to replace the faulty component.

In order to avoid implant loosening components with a porous surface structure and bioactive surface chemistry must be utilized, with the added caveat that the mechanical strength of the component itself must not be compromised. In order to stimulate improved cell adhesion and promote appreciable bone ingrowth while maintaining the load bearing mechanical strength of the underlying metallic substrate, a FGM composite Ti-6Al-4V + HA component with a tailored cross sectional composition must be fabricated. Using this novel FGM device design, next generation biomedical implant materials with improved performance are possible.
3. Research Objective

3.1. Next generation functionally graded (FGM) orthopedic implant device

Design considerations for next generation components should utilize the beneficial material properties of more than one constituent; that is composite components should be developed to maximize orthopedic implant device performance. In the case of the total hip replacement, the femoral stem component is commonly made from a metallic substrate with a thin bioceramic coating as described previously. The major flaw of such a laminated composite device has been described in terms of separation of the coating due to dissimilar properties between the constituents (i.e. spallation). While a variety of techniques for bioceramic coating on a metallic substrate have been investigated (e.g. plasma spraying\textsuperscript{48}, sputter coating\textsuperscript{49}, sol-gel processing\textsuperscript{50}, electrophoretic deposition\textsuperscript{51}, and hot isostatic pressing\textsuperscript{52}), no one technique has been shown to produce a coating that is free of cracks, pores, secondary phases, and/or residual stresses that lead to premature failure of the device. Issues related to metal ion dissolution (i.e. toxicity) and elastic modulus mismatch (i.e. stress shielding) of the underlying metallic substrate were also discussed in previous sections of this report as they pertain to the metal alloys commonly used in orthopedic implant applications.

Therefore the ultimate goal of this research is to produce Ti-6-Al-4V and HA powder feedstock for layer-by-layer SFF of a composite orthopedic implant device that has a bioinert load bearing metallic core, coupled with a bioactive surface functional ceramic constituent using a FGM approach. By using a FGM implant design the patient will be more able to avoid spallation, metal ion dissolution into the bloodstream, and/or bone loss side effects related to stress shielding. The specific intention of this project is
to use powder metallurgy to develop a FGM femoral stem with a gradual change in the composition (i.e. a gradual change in the mechanical/biological properties) from the core to the surface region of the component. The composition will be controlled such that there exists a 100 vol% high strength metallic core region (e.g. Ti-6Al-4V), with a mechanically weaker but much more bioactive surface region that consists of only 60 vol% high strength metal (e.g. Ti-6Al-4V) and the balance 40 vol% being a bioactive ceramic (e.g. HA) constituent. By shifting from a design that uses a thin bioceramic coating on a metallic substrate with a distinct interface, to one where the composition is gradually transitioned from a metallic core region to a bioceramic rich surface region without an abrupt interface, the mechanical properties, biological properties, and lifespan of the component are expected to improve drastically.

An image of a current titanium femoral stem\textsuperscript{53} is shown in Figure 3.1(a), while a schematic of the intended FGM composite component cross sections are shown in Figure 3.1(b) and Figure 3.1(c)\textsuperscript{54} respectively. The composition gradient is represented by a color coded scale wherein the metallic constituent Ti-6Al-4V is represented by the white region at the core of the cross section and the bioceramic constituent HA is represented by the orange region at the surface of the cross section. The cross section will have many layers of intermediate Ti-6Al-4V + HA composition represented by the purple, blue, green, and yellow regions such that the predicted mechanical and biological properties shown in Figure 3.2 may be achieved.

Metal ion dissolution from the metallic core region should be less pronounced when using a FGM design because there will be less Ti-6Al-4V volume present in the FGM component as compared to a completely metallic component. Additionally, due to the fact that surface will be 40 vol% HA rather than 100 vol% Ti-6Al-4V, less Ti-6Al-4V surface area will be exposed to the body fluid environment and thus fewer harmful metal
ions should be released in the patient over the lifetime of the implant due to corrosion. Because the stress transfer through a FGM component is more uniform than across a distinct interface as in the case of thin HA coated metallic substrates, fewer wear debris particles should be generated and thus fewer metal ions produced. Even if the metal ions released by the implant are not toxic or carcinogenic in nature, they have been shown to cause biological tissue inflammation which can potentially complicate healing and should therefore be avoided. One negative implication of a FGM component fabricated from Ti-6Al-4V + HA rather than from Ti-6Al-4V alone is that a portion of the Ti-6Al-4V volume is directly replaced with a much higher cost raw material HA (i.e. ~$300/kg for Ti-6Al-4V PREP powder replaced by ~$7,500/kg for high purity wet synthesized HA powder based on cost of commercially available precursor chemicals).

Therefore, even though there is an advantage gained in terms of a reduction in cost and pain associated with implant failure and remedial surgery, the manufacturing scale production cost for Ti-6Al-4V + HA composites components must be considered.

The expected improvements in implant device/system performance lie in the fact that a powder metallurgy processed FGM component design allows for more uniform stress distribution (i.e. smaller difference between discrete compositional layers), enhanced bonding of the bioceramic and metallic constituents (i.e. Ti-6Al-4V and HA are interpenetrating rather than distinct layers) and enhanced surface bioactivity (i.e. improved mechanical bonding to the native biological structure), thus implant fracture and bioceramic spallation will be suppressed accordingly. The improved stress transfer across the implant-native biological structure interface in turn allows for the use of a metallic constituent with a greater elastic modulus mismatch from that of the natural bone, without an exacerbated stress shielding effect. Thus, Ti-6Al-4V is appropriate for orthopedic implant components even though it has an elastic modulus significantly
greater than cortical bone (e.g. $E_{\text{Ti-6Al-4V}} \approx 110$ GPa\(^8\) while $E_{\text{bone}} \approx 20-30$ GPa\(^8\)) because of the unique nature of the FGM composite fabrication approach.

The key barrier to development of FGM implants using Ti-6Al-4V + HA is decomposition of the parent constituents which results in formation of oxide and phosphate phases. Powder processing of commercial Ti-6Al-4V along with in house synthesis of HA nanorod powder provide the feedstock that will eventually be used for slurry mixing and layer-by-layer FGM fabrication, however simultaneous coalescence and densification (i.e. co-sintering) of these two materials is known to lead to many disastrous reactionary products. While titanium becomes passivated at temperatures above 450°C in air, HA decomposition begins at 900°C in air, thus processing of the individual constituents indicates that the co-sintering conditions should eliminate oxygen exposure and minimize temperature accordingly\(^{56}\). Passivation of the titanium constituent leads to the formation of TiO\(_2\), which at high temperature (i.e. $>1000^\circ$C) can in turn react with HA to form CaTiO\(_3\) as shown in Equation (2)\(^{57}\),

$$Ca_{10}(PO_4)_6(OH)_2 + TiO_2 = 3Ca_3(PO_4)_2 + CaTiO_3 + H_2O \quad (2)$$

both of which have negligible mechanical strength as compared to metallic Ti-6Al-4V and should therefore be avoided in load bearing implant applications. Decomposition of the HA phase occurs via the chemical reactions shown in Equation (3) and Equation (4) when co-sintering is done at 1100°C\(^{57}\).

$$Ca_{10}(PO_4)_6(OH)_2 = 2Ca_3(PO_4)_2 + Ca_4P_2O_9 + H_2O \quad (3)$$

$$Ca_{10}(PO_4)_6(OH)_2 = 3Ca_3(PO_4)_2 + CaO + H_2O \quad (4)$$
Titanium oxide, titanium carbide, calcium oxide, and tricalcium phosphate phases are the possible products from reactions between the parent materials and the reaction products from Equations (2), (3) and (4). Previous studies indicate that the detrimental reactionary products can be suppressed by co-sintering below 1000°C\textsuperscript{58}, thus sintering of the individual constituents (e.g. Ti-6Al-4V or HA) below this threshold temperature must be demonstrated prior to slurry mixing and co-sintering studies. If each constituent can be sintered to a fully dense (i.e. mechanically stable) body at a temperature below 1000°C on their own, then there is an opportunity to utilize these materials in a composite body through a singular powder consolidation and densification process. Therefore, the specific focus of this project is to develop a powder feedstock suitable for SFF that allows for a reduction in the sintering temperature necessary to produce a fully dense Ti-6Al-4V or HA body below 1000°C through various powder processing and sintering techniques. Because sintering of the HA constituent below 1000°C has already been demonstrated by Wang et al.\textsuperscript{59} the efforts for this report will attend to reducing the sintering temperature of Ti-6Al-4V powder compacts through powder processing and sintering modifications.

The powder feedstock requirements of Ti-6Al-4V for fabrication of a FGM device include; small particles capable of forming a stable slurry with pseudoplastic viscosity for SFF printing (i.e. larger spherical particles tend to settle whereas smaller particles with a higher surface roughness are capable of being suspended), small particles that are capable of flowing through a SFF nozzle in significant numbers simultaneously without clogging the tip (i.e. particles should be ~1/10 diameter of the extrusion tip because a sufficient number of particles need to be delivered point-by-point during printing to ensure a high density mechanically robust FGM component), small grain structure and
high defect density particles capable of sufficient mass transport during sintering at temperatures below the onset of Ti-6Al-4V and/or HA decomposition (i.e. necessary to avoid decomposition of the component during densification), and small particles that allow for intricate control during SFF printing of a surface topography that is on the appropriate size scale for osteoblast adhesion and proliferation (i.e. proper surface roughness allows for a higher number of cells to attach and multiply when the suitable size channels exist for body fluid flow of nutrients and proteins to the implant surface during healing). With these considerations in hand, powder processing of commercially available Ti-6Al-4V is carried out to achieve the objectives of a reduction in particle size and a reduction in grain size for improved SFF printing and co-sintering capability necessary for the development of a FGM composite Ti-6Al-4V + HA femoral stem component.
4. Materials and Methods

4.1. Powder processing

Commercial PREP titanium-6aluminum-4vanadium powder is purchased and used without any pretreatment (Advanced Specialty Metals, Nashua, NH). The commercial PREP Ti-6Al-4V powder is identified by the manufacturer as -60+325 mesh, indicating particles between 45 µm - 250 µm. The as received Ti-6Al-4V powder is produced using the plasma rotating electrode process (PREP); wherein a bar of the pure cast alloy is spun along its longitudinal axis while one end is heated to the melting temperature\textsuperscript{60}, see Figure 4.1(a)\textsuperscript{61}. Highly uniform spherical particles solidify from their molten droplet state as they are spun off the rotating Ti-6Al-4V anode, see Figure 4.1(b). The resulting powder product has a high degree of geometrical and compositional purity due to a final separation and filtration process, see Figure 4.1(c). Because the PREP process involves cooling from a molten state in ambient air the resulting highly spherical particles, shown in Figure 4.1\textsuperscript{62}, have a well adhered thin oxide layer on their surface due to passivation.

In order to reduce the particle size of the PREP Ti-6Al-4V powder and to introduce defects which will help to increase the driving force for densification during sintering, ball milling is applied. Attritor style ball milling is performed using a modified Szegvari attritor, see Figure 4.2\textsuperscript{63}, which is effective in preventing the formation of a dead zone and thus produces uniform milling products\textsuperscript{64}. The canister of the attritor and the grinding balls (e.g. 6.4 mm in diameter) are made of stainless steel. The ball-to-powder weight ratio is 60:1, the milling speed is 600 rpm, and the milling time is 24 or 72 hours depending on the specific experiment, see Table 4.1. The milling temperature is
$20^\circ$C, achieved by water cooling around the canister with a flowing rate of 770 ml/min. The milling atmosphere is maintained under positive pressure ultrahigh-purity argon (99.999%), while loading and collecting of the Ti-6Al-4V powder in done a sealed glovebox also under UHP argon, see Figure 4.3.$^65$

After experiencing many difficulties in obtaining a sample that is easily collectable (i.e. loose powder) and free of oxidation using the attritor style ball milling apparatus, the choice is made to switch to SPEX ball milling which is a very high energy, shaking style apparatus. Because of severe cold welding on the interior of the attritor it is also apparent that some type of process control agent (PCA) is necessary moving forward. To further avoid the issues related to particle aggregation, agglomeration, and cold welding, stearic acid is applied at a loading of 1 wt% per 1 hour of milling time such that a SPEX milling duration of 4 hours utilizes 4 wt% stearic acid PCA.

Volumetric limitations based purely on the size of the standard SPEX milling vial forces smaller batches (e.g. 4 – 5 g) of Ti-6Al-4V powder to be prepared as compared to the amount that can be prepared in the attritor style mill (e.g. 10 – 12 g). Because SPEX milling is a higher kinetic energy collision process, shorter milling durations (e.g. 1 – 5 hr) are capable of producing powders comparable to those produced using much longer milling durations (3 – 72 hr) in the attritor style mill. Because of the shorter milling times, a greater variety of sample conditions are investigated with SPEX milling than are investigated with attritor milling, see Table 4.2. The higher kinetic energy of the grinding media in SPEX milling causes more localized heating in the powder charge because there is no water cooling jacket for temperature control in the SPEX apparatus. Because of a lack of temperature control, SPEX milling is limited to shorter increments of the total duration (i.e. milling durations listed in Table 4.2 are applied with 15 minutes of cooling at room temperature between each segment as indicated by the + symbol, such that for
a SPEX milling duration of 4 hours, 4 one hour milling intervals with 15 minutes of cooling between leads to a total processing time of 5 hours).

While the milling media charge ratio in attritor milling is 60:1, the milling media charge ratio in SPEX milling is lowered first to 40:1 (e.g. sample 110406 in Table 4.2) and eventually to 10:1 (e.g. all other samples in Table 4.2) to allow for a larger sample volume yield per milling cycle with less heating. The 40:1 charge ratio involves the use of only two large 12.7 mm stainless steel grinding balls, while the latter 10:1 charge ratio is first applied with only two large 12.7 mm balls plus four small 6.35 mm balls (e.g. samples 110422 and 110503 in Table 4.2), but later the 10:1 is applied via four large 12.7 mm balls plus eight small 6.35 mm balls (e.g. samples 110510, 110516, 110525, 110527, 110602, 110607 in Table 4.2). Samples with varying degrees of cold welding are collected by lightly scraping the powder from the walls of the vial using a stainless steel spatula. Previous attritor style ball milling experiments with no PCA, 1 wt% stearic acid, or 2 wt% stearic acid lead to an extreme degree of cold welding which cause the rotating shaft of the attritor mill to seize and the powder to be oxidized. Therefore SPEX milling of Ti-6Al-4V with less than 2 wt% stearic acid was not investigated in this portion of the study.

High energy shaker style SPEX ball milling is applied for particle and grain size refinement of Ti-6Al-4V during the remainder of the powder processing experiments. The SPEX milling vial is fabricated in house from stainless steel, with an o-ring sealed threaded cap for atmosphere control, see Figure 4.4. The as received PREP Ti-6Al-4V powder loading and SPEX milled powder collection are done under UHP argon (99.999%) in a sealed glovebox to prevent oxidation of the powder charge during the milling process. Issues associated with oxidation are effectively mitigated using the SPEX type ball mill because the vial is o-ring sealed with no moving internal components.
(i.e. no rotating shaft to seize due to cold welding), thus sample yield is more consistent and free from oxidation. The milling vial is loaded into the SPEX instrument at approximately a 45° and clamped into place at the top and bottom. During milling the instrument shakes the milling vial axially along its vertical axis while simultaneously rotating the vial around its center of mass as indicated by the two arrows in Figure 4.4.

4.2. Pellet pressing and sealing

In order to produce a solid body representative of the desired femoral stem component, a green body must first be formed by a powder consolidation technique. For radiant heat tube furnace sintering experiments uniaxial pressing of Ti-6Al-4V powders is done using a 1/2” hardened steel die to form the green body, see Figure 4.5. Initial green body pressing was done at either 840 MPa or 700 MPa but was later reduced to 300 MPa for the remainder of the samples once pellet delamination was observed. In the case of the as received PREP Ti-6Al-4V powder a polymer binder, polyethylene glycol (PEG 10,000g), is applied at 5 wt% of the Ti-6Al-4V powder loading by dissolving in a few drops of ethanol to produce a solid pellet capable of being handled for sintering experiments. The approximate density of a green body is calculated from the direct caliper volume measurement and the direct digital balance mass measurement. The relative density prior to sintering is calculated by dividing the approximate green density by the theoretical density of Ti-6Al-4V from the rule of mixtures calculation.

Powder consolidation for microwave sintering (MWS) experiments is achieved via a two step pressing technique wherein the powder is first pelletized via uniaxial pressing at 670 MPa, followed by isostatic pressing via a liquid medium at 690 MPa to further increase the green density, see Figure 4.6. In the case of spark plasma sintering
(SPS), the instrument itself doubles as a pressing die and a furnace chamber, thus powder consolidation in SPS is achieved by directly loading powder into the SPS unit as will be described in the following section. Because the SPS densification mechanism relies on a closed electrical circuit, intimate contact between the sample and the upper and lower punches of the furnace chamber is critical. To maintain intimate contact with the upper and lower punches, the instrument is programmed to apply a uniaxial pressure of 50 MPa prior to sample heating to form the green body and establish a closed electrical circuit loop. A constant pressure of 50 MPa is maintained throughout the sintering process while the sample height decreases (i.e. void and pore elimination reduces volume) by allowing the upper punch to travel down the furnace chamber.

In order to alleviate issues associated with high temperature oxidation of the Ti-6Al-4V pellet, all RHS experiments are done in an inert UHP argon atmosphere. To further protect the sample from oxidation at high temperature, green body pellets are sealed in high temperature quartz tubing with tantalum foil which is evacuated to less than 12 mtorr (<1.2*10^{-3} torr) prior to necking the ends closed, see Figure 4.7. The quartz tubing seen in Figure 4.7 has an outer diameter of 19 mm with an inner diameter of 17 mm, thus sealing requires necking closed a 17 mm span with only 1 mm of wall thickness which can be a very problematic endeavor. While sealing of the larger quartz tubing is possible, many breakages due to thinning of the tube wall initiated a change in the quartz tube design.

The modified quartz tube geometry utilized for later activation energy studies is fabricated by David King of the University of Connecticut Biotechnologies Glass Blowing Service as shown in Figure 4.8. The new design utilizes quartz tubing of two different diameters being joined together prior to evacuation in order to allow for easier sealing of the pellets with fewer tube breakages. A piece of the 17 mm tube is first closed off at one
end with a round bottom and then joined to a piece of the 3 mm tube. The Ti-6Al-4V green pellet and tantalum foil oxygen getter are inserted before closing off at the other end with a round bottom. The advantage gained is that final sealing of the evacuated tube is much easier with the smaller diameter tube because there is double the wall thickness available to neck closed a gap that less than 1/5 the span of that of the pervious design (i.e. the small tube has an inner diameter of only 2 mm versus the 17 mm inner diameter of the larger tube). The extra volume available to bridge the gap between the inner tube walls leads to quicker and easier sealing with a lower frequency of tube breakages, thus proper atmosphere control is easier to attain.

For RHS experiments a quartz tube sealed Ti-6Al-4V pellet is placed directly in the alumina tube furnace and sintering will be carried out as normal. Initially two uniaxially samples were placed in the tube, those being sample 110525 and 110527 from Table 4.1. Note that the disk prepared from sample 110525, Figure 4.7(right), is wrapped in tantalum foil prior to evacuating and sealing the quartz tube with the knowledge that the tantalum foil will act as an oxygen getter to even further protect the sample from oxidation at high temperature while the disk prepared from sample 110527, Figure 4.7(left), is sealed without additional protection. All subsequent RHS samples are sealed individually with tantalum foil wrapping prior to sintering. In the case of microwave sintering the pellet is heated under positive argon pressure with no additional protection, while the spark plasma sintering is done under vacuum with no additional protection.

As per the ultimate objective of this project, composite Ti-6Al-4V + HA bodies are prepared to investigate the effectiveness of SPEX ball milling and/or alternate sintering methods in the suppression of the high temperature reaction between Ti-6Al-4V and HA constituents. Composite compositions are prepared using mixtures of Ti-6Al-4V + HA with varying volume fraction of HA loading. The precursor powders utilized for this
portion are the 4hr/4wt% SPEX milled Ti-6Al-4V powder and the wet synthesis produced
HA powder respectively. The two materials are blended to a uniform mixture by low
speed tumbling milling of the specific composition for 2 hours using stainless steel
grinding balls at a charge ratio of 10:1 of the total powder loading. The composite green
body pellet is prepared using the specific method required for the specific sintering
technique according to the protocols established earlier in this section.

4.3. Ti-6Al-4V pellet sintering

While powder processing and RHS processing are conducted in house, alternate
consolidation and densification methods of MWS and SPS are also employed to
determine the best processing method for FGM composite Ti-6Al-4V + HA component
fabrication below the threshold temperature for the onset of Ti-6Al-4V and HA
decomposition (i.e. T<1000°C). Powders of the same starting condition (e.g. as received
PREP Ti-6Al-4V powder, 4hr/4wt% SPEX milled Ti-6Al-4V powder, and the wet
synthesis HA powder) were sent to two different institutions to investigate alternate
consolidation and densification methods.

4.3.1. Radiant heat tube furnace sintering (RHS)

Experimental parameters for RHS are programmed directly into the furnace
temperature controller (Eurotherm 2440, Ashburn, VA) which manages voltage and
current output to the tube furnace (CM Furnace, Bloomfield, NJ) heating elements.
Furnace temperature calibration was conducted using a K-type thermocouple which is
inserted into the hot zone of the alumina tube throughout the duration of a typical heating
and cooling cycle. The calibration curve used for all RHS heating is shown in Figure 4.9, wherein the desired dwell temperature is input for the x variable and the necessary furnace controller set temperature y is calculated. An example of a tube furnace sintering temperature profiles are seen in Figure 4.10, wherein the dwell time is held constant at 2 hours and the heating and cooling rates are 5°C/min for all RHS experiments. The two profiles shown in Figure 4.10 represent the two dwell temperatures investigated during RHS sintering experiments, those being 1100°C and 1250°C respectively.

The green body 4hr/4wt% Ti-6Al-4V pellet sealed in quartz tubing under vacuum is placed into the furnace hot zone as shown in the schematic in Figure 4.11. After the sample is inserted into the furnace tube, both ends of the alumina tube are capped with stainless steel flanges fitted with vacuum and inert gas connections. Silicone o-ring sealing is achieved at both ends of the alumina tube using a compression type fitting that is tightened at room temperature prior to heating. An inert gas atmosphere is maintained by evacuating and backfilling the furnace chamber at least five times with UHP argon prior to heating. The inert gas is allowed to flow continuously to maintain a 3 psi positive pressure UHP argon atmosphere during the heating, sintering and cooling stages until the programmed sintering run has reached completion.

4.3.2. Microwave sintering (MWS)

One batch of samples is investigated by Dr. Ashraf Imam at the Naval Research Laboratory in Washington D.C. for MWS studies. Pellets are prepared using the same starting powders as described previously with the following compositions; pure as received PREP Ti-6Al-4V, pure 4hr/4wt% SPEX milled Ti-6Al-4V, pure wet synthesized HA, 4hr/4wt% SPEX milled Ti-6Al-4V (90 vol%) + wet synthesized HA (10 vol%)
composite, and 4hr/4wt% SPEX milled Ti-6Al-4V (75 vol%) + wet synthesized HA (25 vol%) composite respectively. The MWS instrumental parameters include rapid heating to the desired dwell temperature of either 1250°C or 900°C depending on the specific experiment. Pellets that were sintered at 1250°C were held at temperature for a dwell time of 30 minutes, while those sintered at 900°C were held at temperature for a dwell time of 1 hour. The microwave sintering was performed under inert atmosphere by evacuating and backfilling the furnace chamber with argon prior to heating.

A schematic diagram of the microwave sintering setup and the resulting temperature profile experienced by the pellet are shown in Figure 4.12. The MWS instrument is essentially a modified box furnace with a microwave radiation source connected via line of sight to the green body. The microwave radiation is produced in a 2.45 GHz industrial microwave generator (Cober Electronics Model S6F, Stratford, CT) and transported to the heating chamber via an S-Band waveguide.

4.3.3. Spark plasma sintering (SPS)

Powders of the same starting condition as those investigated by RHS and MWS are also sent to Dr. Claude Estournes at Université Paul Sabatier in Toulouse France for SPS studies. Pellets are prepared using the same starting powders as described previously with the following compositions; pure as received PREP Ti-6Al-4V, pure 4hr/4wt% SPEX milled Ti-6Al-4V, pure wet synthesized HA, 4hr/4wt% SPEX milled Ti-6Al-4V (90 vol%) + wet synthesized HA (10 vol%) composite, and 4hr/4wt% SPEX milled Ti-6Al-4V (75 vol%) + wet synthesized HA (25 vol%) composite respectively. Because the SPS sintering chamber is also the uniaxial pressing die, green body pellets are prepared by directly loading the powder into the 8 mm diameter graphite die chamber,
which is shown schematically in Figure 4.13 along with the resulting temperature profile within the pellet during heating.

A uniaxial pressure of 50 MPa is applied at room temperature and held constant throughout the heating and cooling stages. Immediately after the 50 MPa preloading the sample chamber is heated to the desired dwell temperature. The dwell temperature and dwell time is 1000°C and 3 minutes respectively, with one additional 4hr/4wt% SPEX milled Ti-6Al-4V sample that is sintered at 600°C for 5 minutes. The 600°C SPS sample is fabricated to show proof of concept that “very low temperature” (i.e. T<<1000°C) sintering using SPS is possible.

4.4. Characterization methodologies

Material properties of the ball milled powders and sintered pellets including particle size, particle morphology, grain size, crystallite size, chemical/phase composition, sintered pellet density, and sintered pellet mechanical properties are characterized through various techniques including scanning electron microscopy (SEM), optical microscopy, transmission electron microscopy (TEM), x-ray diffraction (XRD), energy dispersive x-ray spectrometry (EDS), x-ray photoelectron spectroscopy (XPS), thermogravimetric mass spectrometry (TGA), hardness testing, and compression testing. Details of sample preparation and instrument operation for each of the characterization techniques will be described, with the data extracted therein presented in Chapter 5 of this report. Quantitative and qualitative scrutiny of the results appears in Chapter 6 of this report to provide the justification for the use of each of these characterization techniques.
The average particle size of the as received PREP Ti-6Al-4V powder and ball milled Ti-6Al-4V powders are measured directly using SEM analysis in secondary electron imaging mode (FEI Electroscan ESEM 2020, Hillsboro, OR and JEOL JSM-6335F/JSM-6330F, Tokyo, Japan). SEM sample preparation for powder particle size involves dry dropping of the specific powder on a double sided adhesive copper tape which is attached to a standard SEM stub. Because Ti-6Al-4V is metallic and therefore conductive, there is no need to sputter coat the sample prior to imaging, thus average particle size measurement is quick and easy to achieve. Particle size evaluation simply requires the user to record a series of images for each sample at different locations on the SEM stub to obtain an accurate description for the average particle size. SEM image processing entails superimposing a line of unknown length along a particle diameter on each particle of interest. The length of the line in pixels is displayed by using the automatic line measure function in the ImageJ software (NIH, Bethesda, MD). After the diameter of many particles is displayed in the Results Window, another line is superimposed on the scale bar for that SEM image such that the magnification calibration factor is known. The pixel length of the particle diameter is then converted to a physical length scale based on the magnification calibration factor so that the average particle size as a function of milling condition can be determined.

The average crystallite size of ball milled powders is measured directly using TEM analysis (FEI Tecnai Spirit Twin, Hillsboro, OR). TEM sample preparation for powder particle crystallite size is equally simplistic to powder particle size via SEM in that the specific Ti-6Al-4V powder is dropped onto a lacy carbon on copper standard TEM sample grid with no additional processing. In this case however the powder dropping is done in a liquid suspension, which is prepared by ultrasonicating a small volume of Ti-6Al-4V powder in ethanol for 15 minutes to effectively disperse the powder
particles in the liquid. Dispersion by ultrasonicating aids in preventing agglomeration and/or stacking of the powder particles on the surface of the TEM sample grid. Effective dispersion is necessary to ensure that there are a significant number of particles spread out in a single layer such that the TEM beam can pass completely through their thickness (i.e. TEM can only image that which is electron transparent) to create the particle projection at the CCD camera image detector. Particle size can be confirmed in the TEM using bright field imaging mode, while the crystallite size can be directly observed by switching to dark field mode wherein single crystal domains appear as bright spots within each powder particle.

Chemical composition, crystallite size, and crystal structure changes are monitored using XRD analysis throughout the various processing stages. Attritor milled Ti-6Al-4V powder XRD analysis is carried out using a D8 Advance diffractometer (Bruker, Karlsruhe, Germany) with CuKα radiation (λ = 1.54 Å) with a scan range from 20° - 90° 2θ, a step size of 0.02°/step, and a holding time of 0.25 sec/step. SPEX milled Ti-6Al-4V powder and RHS, MWS and SPS sintered Ti-6Al-4V pellet XRD analysis is carried out using a D2 Phaser desktop diffractometer (Bruker, Karlsruhe, Germany) with CuKα radiation (λ = 1.54 Å) with a scan range of 2θ from 20-90°, a step size of 0.02°/step, and a holding time of 0.25 sec/step. Each SPEX milled powder and sintered pellet Ti-6Al-4V sample is scanned twice by selecting the loop function in the Bruker XRD Commander software (i.e. repeats scan range and sums x-ray counts of both passes) such that the constructive peak intensity becomes more pronounced compared to the background (i.e. Bremstralung radiation) intensity.

The XRD spectra is processed using Bruker XRD Analysis software to account for uniform shifts in the spectra due to sample loading offset which results from differences in sample height (i.e. sample must be on the same plane as the incident x-
rays to be detected at the proper angle \(2\theta\). Accurate shifting of the spectra is accomplished based on the position of the three most intense peaks given in the Powder Diffraction File (PDF) standard database for the known elements identifiable in the scan (i.e. titanium PDF peak positions). After the uniform shifting is accounted for, the spectrum is again modified to remove the \(K_{\alpha2}\) radiation using a Bruker XRD Analysis software function. The preprogrammed function converts the spectrum to a plot based on a monochromatic incident radiation which allows for more accurate data analysis during calculation of crystallite size values from peak broadening.

Confirmation of chemical analysis is done using EDS analysis which is carried out in conjunction with SEM analysis because the EDS detector (Thermo Fisher Scientific, Waltham, MA) is a component of the SEM instrumentation itself. While the SEM imaging detectors allow for visual representation based on electron signals from the sample, EDS is designed to collect x-ray signals from the sample as it responds to the incident electron beam. The x-ray signal emitted from the sample is characteristic of the chemical species and energy level transition that generated the electromagnetic wave, thus the chemical composition from the interaction volume is determined with great precision. The EDS analysis is utilized to monitor any powder contamination after milling and/or pellet contamination after sintering.

Additional chemical analysis is conducted to determine the surface chemistry of the Ti-6Al-4V powder particles before and after ball milling using XPS which is effective at measuring near surface composition and surface contamination. The XPS analysis of as received and ball milled powders is carried out using a Phi Multiprobe XPS system (Perkin Elmer 5300, Waltham, MA) wherein the untreated powder is inserted directly into the sample chamber and bombarded with x-ray radiation while the electron emission energy from the sample is recorded. TGA analysis (TA Instruments TGA Q-500, New
Castle, DE) is used to confirm the chemical stability of the ball milled Ti-6Al-4V powders as a function of temperature, a property that will have a considerable impact during sintering studies.

Once the powder processing effects have been extensively studied, sintering of the green bodies into solid pellets is carried out using the various sintering conditions described above. Once a sintered body is collected from the furnace a number of characterization tools are utilized to determine sample quality. Sample preparation for relative density measurement via SEM is done using a low speed rotary cutoff saw (Allied TechCut 4, Rancho Dominguez, CA) with a diamond blade spinning at 350 rpm to cross section the sintered pellet, revealing the internal pore structure for analysis. The sintered pellet is cross sectioned along the cylinder diameter with the aid of a low speed cutting lubricant (Allied High Tech Products Low Speed Cutting Fluid, Rancho Dominguez, CA) such that two half moon disks are created from each pellet. The cross sectional face of one half of the sintered pellet is ground to a 1200 grit roughness using either silicon carbide grinding paper or a diamond resin grinding disk (Struers Inc., Cleveland, OH), and then polished to a 0.05 μm colloidal silica finish (Sturbridge Metallurgical Services Inc., Sturbridge, MA) on a MD-Nap cloth pad (Struers Inc., Cleveland, OH). Once again because the sintered pellet is metallic Ti-6Al-4V there is no need to sputter coat the sample prior to imaging, however because the sample is polished using a ceramic suspension the pellet must be ultrasonically cleaned to remove any polishing compound which may result in charging during imaging. SEM inspection of the relative porosity of a sintered body at various locations is carried out using a low magnification which is most representative of the average density of the entire sample.

ImageJ analysis software allows for the SEM image to be converted to a binary (i.e. black and white) image that can be analyzed pixel by pixel to determine the area
fraction of solid Ti-6Al-4V (i.e. white pixels) versus the area fraction of porosity (i.e. black pixels) for calculation of the relative density of the sintered pellets. The area fraction of solid is multiplied by the theoretical density of Ti-6Al-4V (e.g. 4.45 g/cm$^3$) to determine the real sample density. There is a source of error using this ImageJ method to quantify density due to the fact that the final pixel counting is dependent upon the threshold delineation between black and white pixels set by the user, however because the initial image is 1280x1024 pixels (i.e. >1.3 million pixels total) the actual error is minimal due to the large statistical data set acquired for each area fraction measurement. After the half pellet is imaged for density calculation, the sample is examined using XRD with the experimental parameters described previously to determine phase purity, crystallite size, and monitor the formation of any new phases that may have occurred during the sintering process.

Evaluation of microstructures through direct observation requires the sintered Ti-6Al-4V pellet to be ground, polished and etched to reveal the underlying details. The underlying microstructure may be revealed by a chemical or thermal etching process. Because thermal etching may result in a modification of the true grain structure due to grain growth at elevated temperature, a chemical etchant was chosen to examine the precursor powders and sintered pellets. Alternatively a commercial Ti-6Al-4V cast sheet metal (President Titanium, Hanson, MA) sample is thermally etched to confirm the predicted grain growth at elevated temperature. The as received PREP and ball milled Ti-6Al-4V powders are chemically etched after they have been cross sectioned and polished by embedding many particles in plastic mounting resin using a hot mounting press. Sintered Ti-6Al-4V pellet SEM sample preparation has already accounted for the grinding and polishing to a 0.05 µm finish, thus the etching process can be carried out without any further sample preparation after imaging for density calculation. The etchant
chosen for this study is Kroll’s Reagent which is a mixture of 0.5 mL hydrofluoric acid (HF) + 1.5 mL nitric acid (HNO₃) + 23 mL water (H₂O). The etchant solution is measured and mixed in a plastic graduated vial as required for handling of hydrofluoric acid. The etchant is applied to the surface of the Ti-6Al-4V by swabbing with a Q-tip for 5 seconds up to a minute depending on the nature of the sample (i.e. swabbing is done until the sample surface changes from shiny to cloudy).

The Ti-6Al-4V is selectively dissolved until the grain boundary areas and/or secondary phases are recessed enough to create sufficient contrast to resolve the microstructure during imaging. The etched samples are imaged using optical microscopy (Nikon Metaphot, Brighton, MI) to observe the structure that is not discernible to the naked eye. Optical images are evaluated for grain size by superimposing lines of arbitrary pixel length on the image and counting the number of grain boundary intersections per unit length. The pixel length is converted to a physical length in microns based on the magnification calibration factor deduced from the scale bar associated with each specific microscope image. From the conversion to a physical length scale an average grain size is calculated for each sample condition.

4.5. Activation energy calculation

Tracking of Ti-6Al-4V pellet density as a function of sintering ramp rate and quench temperature allows for calculation of the sintering activation energy (Qₘₐₜ) using various data analysis methods. As per the RHS sintering methodology described above, green body pellets are made by uniaxial pressing 4hr/4wt% SPEX milled Ti-6Al-4V powder at 300 MPa, followed by sealing fused quartz tubing under a vacuum of less than 12 mtor prior to heating in the alumina tube furnace. Three ramp rates of 4°C/min,
8°C/min, and 16°C/min and five quench temperatures of 900°C, 1000°C, 1100°C, 1200°C, 1300°C are utilized to calculate a value for activation energy based on relative density measurement of the sintered pellet after different heating conditions. Ramp rates during heating are restricted by the Eurotherm programmable furnace temperature controller and the quench temperature is regulated by removing the quartz tube sealed sample from the alumina furnace tube and dropping it immediately into a room temperature water bath. Because the pellet is sealed under vacuum the quartz tube initially floats and thus a hammer is used to break the quartz against the wall of the quench bucket, allowing the 4hr/4wt% Ti-6Al-4V pellet to rapidly cool as it sinks to the bottom of the water bath, resulting in the temperature profiles seen in Figure 4.14.

The data is first analyzed using the MSC method described by Shao et. al\textsuperscript{66}, which indicates the average sintering activation energy of a material. This approach does not take into account changes in the activation energy due to a shift in the rate limiting diffusion mechanism (i.e. grain boundary diffusion control vs. lattice diffusion) at different stages of densification, but rather utilizes an average of the overall activation energy independent of the particular mass transport mechanism. Analysis of the relative density allows for calculation of the 4hr/4wt% Ti-6Al-4V sintering activation energy based on the mean residual squares fitting method. A second MSC method described by Pouchly et al.\textsuperscript{67}, who also provides software (Density MSC, BRNO University of Technology, Czech Republic) for the data analysis, is used to determine the activation energy based on the mean perpendicular curves distance fitting method. In this portion of the study $Q_{sinter}$ is calculated for only the 4hr/4wt% SPEX milled Ti-6Al-4V powder for comparison to values in the literature on thermodynamic properties of Ti-6Al-4V bodies.

Validation of the activation energy calculation is done with the aid of a dilatometer during experiments conducted by Dr Satyanarayana Emani at the Illinois
Institute of Technology (IIT). A vacuum tube furnace dilatometer is used to measure shrinkage as a function of sintering temperature with constant heating rates of 4°C/min, 8°C/min, and 16°C/min respectively. The mean residual squares fitting method from Shao et al. is used to determine the average sintering activation energy of 4hr/4wt% SPEX milled Ti-6Al-4V powder. Additional analysis of the activation energy values derived via MSC is done using the constant heating rate (CHR) method described by Wang and Raj. In this case the CHR method allows for differentiation of the activation energy during different stages of sintering based on the specific rate limiting diffusion mechanism that is dominant at a given temperature. The specifics of the activation energy calculations will be divulged in Chapter 6.

4.6. Mechanical property evaluation

Mechanical property evaluation is conducted using hardness testing and uniaxial compression testing to determine sintered Ti-6Al-4V pellet resistance to plastic deformation under an applied compressive stress (i.e. the type of stress experienced by a femoral stem in the total hip replacement). The mechanical properties of sintered Ti-6Al-4V pellets are first measured by Vickers hardness testing using a universal hardness testing instrument (DuraVision 20, Emco-Test, Kuchl, Austria). Vickers hardness testing in this case utilizes a diamond pyramid indenter tip and a 10 kg load applied for 30 seconds as shown by the schematic in Figure 4.15. Because the sintered sample geometry is established by the uniaxial pressing die which is used to form the green body, the top and bottom surface of the sintered pellets are inherently flat and smooth but may require some light grinding and polishing to establish clean parallel surfaces prior to testing.
Compression testing involves the use of a universal mechanical test instrument (Tinius Olsen, Willow Grove, PA) operated in compression mode wherein the upper crosshead travels down the vertical axis to apply a uniaxial load on a test specimen, see Figure 4.16. Dynamic compression and/or fatigue testing was not investigated in this study due to lack of test specimens remaining after activation energy density measurements (i.e. pellets were sectioned into half disks which no longer makes them a valid standard test geometry) and also due to the time constraints imposed by typical fatigue testing (i.e. usually requires more than a million cycles). Although higher strain rate compression may occur in the femoral stem during running or jumping locomotion, only compression testing with a low strain rate is conducted in this study to mimic stationary standing and the walking form of locomotion.

Compression testing by ASTM International (formerly American Society of Testing and Materials) calls for a test specimen that has a cylindrical geometry with a ½” diameter and a height of 1” or greater, however due to a lack of 4hr/4wt% SPEX milled Ti-6Al-4V powder remaining after sintering and activation energy studies the compression test specimen is limited to a diameter of ½” and a height of only ¼” for this study. The experimental parameters include the use of a cross head speed of 1 mm/min until the test specimen stress drops 40% below its maximum value. Compression testing is done with the use of hardened steel upper and lower flat platens that have been lubricated with hydrocarbon grease to allow for lateral expansion of the test specimen during loading, while the data is recorded as a plot of the load versus position.
5. Experimental Results

5.1. Powder characteristics

An SEM image of the particle morphology and particle size of the as received PREP Ti-6Al-4V powder is shown in Figure 5.1. In this image take note of the presence of a thin oxide layer encapsulating the surface of the highly spherical particles. SEM images representative of the particle morphology and particle size of the attritor ball milling conditions are shown in Figure 5.2 and Figure 5.3. XRD spectra of as received PREP Ti-6Al-4V and attritor milled Ti-6Al-4V powders are shown in Figure 5.4. Surface chemistry analysis using XPS yields the plots shown in Figure 5.5 and Figure 5.6 for the as received PREP Ti-6Al-4V and 24 hour attritor milled Ti-6Al-4V powder respectively. Likewise particle diameter and powder morphology as a function of SPEX milling duration are shown visually in the SEM images Figure 5.7 – Figure 5.16, while their corresponding XRD spectra are shown in Figure 5.17.

Quantitative analysis including average particle diameter from SEM image analysis and average crystallite size of the Ti\textsubscript{\textit{101}} reflection from XRD analysis are presented in Table 5.1 for the attritor milled samples and in Table 5.2 for the SPEX milled samples respectively. The trend of a change in both particle size and crystallite size as a function of milling duration is shown in Figure 5.18 and Figure 5.19, while the trend of a change in both particle size and crystallite size as a function of stearic acid PCA concentration is shown in Figure 5.20 and Figure 5.21. Visual microstructure analysis of the SPEX milled Ti-6Al-4V powder via TEM is utilized to confirm the creation of nanostructured micron sized particles prior to sintering, see Figure 5.22(a) which
shows a micron sized particle in bright field imaging and Figure 5.22(b) which shows nanosized single crystal domains as bright white spots in dark field imaging.

Optical micrographs of Ti-6Al-4V samples after Kroll’s Reagent etching are presented in Figure 5.23 – Figure 5.25, which show the microstructure of the commercial as cast Ti-6Al-4V sheet metal, the as received PREP Ti-6Al-4V powder, and the 4hr/4wt% SPEX milled Ti-6Al-4V powder respectively. The trend of grain growth at elevated temperature in a piece of commercial as cast Ti-6Al-4V sheet metal exposed to 1250°C for 2 hours inside of the RHS alumina tube furnace results in the grain structure shown in Figure 5.26.

5.2. Green body characteristics

Consolidation of powders into solid pellets results in drastically different green body characteristics pertaining to the powder particle morphology and pressing conditions for the specific pellet. Some general trends are witnessed during consolidation of the various powders via uniaxial pressing including pellet crumbling, pellet “accordioning”, and pellet delamination effects. Pellet crumbling occurs when pressing of the as received PREP Ti-6Al-4V powder is done without a polymer binder additive, resulting in a pile of loose powder upon removal of the sample from the die cavity. Pellet “accordioning” is identified as an expansion of the green body pellet along the axis of the applied uniaxial pressure when the load is removed, resulting in a low green density. Pellet delamination occurs in pellets that are uniaxial pressed at 840 MPa and 700 MPa, but does not occur when pressed at the lower 300 MPa pressure. Pellets that exhibit a delaminated green body are not useful for sintering studies because each layer will coalesce independent of the others, resulting in layer-by-layer separation of the
subsequent sintered body. The green density of pressed pellets is derived based on
geometrical measurements of the mass and volume using an electronic balance and dial caliper respectively.

5.3. Sintered Ti-6Al-4V pellet characteristics

5.3.1. Radiant heat tube furnace sintered (RHS) pellet characteristics

RHS experiments yield a variety of results depending on the starting powder characteristics as well as the sintering condition specific to each sample. Evidence of the onset of sintering is shown in Figure 5.27, wherein neck formation and pore elimination is clearly seen in an as received PREP Ti-6Al-4V pellet after 2 hours of RHS at 1300°C. The polished cross section of as received PREP Ti-6Al-4V pellets after 2 hours of RHS at 1100°C and 1250°C are shown in Figure 5.28 and Figure 5.29 respectively. Results for sintering of the SPEX milled powders are shown in Figure 5.30 – Figure 5.33 for the 1hr/4wt% SPEX milled Ti-6Al-4V powder and 4hr/4wt% SPEX milled Ti-6Al-4V powder pellets after 2 hours of RHS at 1100°C and 1250°C respectively.

5.3.2. Microwave sintered (MWS) pellet characteristics

The SEM images that appear in Figure 5.34 and 5.35 are the polished cross section of 4hr/4wt% SPEX milled Ti-6Al-4V pellets sintered using MWS at 900°C and 1250°C respectively. The MWS processed pellets show a gradient in porosity form the outer surface to the core region. The outer surface region of all MWS samples remains highly porous even though the interior region of all the MWS samples indicates a much
higher and more uniform density, see Figure 5.36. The gradient in porosity generated via MWS will be discussed in greater detail in the Chapter 6 in terms of how to account for this phenomenon when designing a MWS processing method.

5.3.3. Spark plasma sintered (SPS) pellet characteristics

Densification characteristics for the SPS processed samples are listed in Table 5.3 as derived from the displacement versus temperature plot seen in Figure 5.37. The relative density via Image J pore area fraction analysis is done using the SEM images that appear in Figure 5.38 and Figure 5.39 for the as received PREP Ti-6Al-4V and 4hr/4wt% SPEX milled Ti-6Al-4V respectively. An SEM image showing proof of concept for “very low temperature” SPS processing of 4hr/4wt% SPEX milled Ti-6Al-4V is seen in Figure 5.40.

The XRD spectra for each of the RHS, MWS, and SPS processed samples described in Chapter 5.3 are shown in Figure 5.41. Optical microscopy of the RHS, MWS, and SPS processed samples are shown in Figure 5.42 after Kroll’s Reagent chemical etching, and the quantitative grain size analysis is shown in Table 5.4.

5.4. Composite Ti-6Al-4V + HA bodies

Sintering of the wet synthesized HA using RHS has already been established by Wang et al., thus sintering of HA via MWS and SPS is attempted in conjunction with composite Ti-6Al-4V + HA processing. MWS sintering of HA is possible however metallographic preparation was not attempted due to delamination of the pellet which
made grinding and polishing a futile effort. Therefore, only the SPS processed HA sample is imaged in this study, see Figure 5.43.

RHS of Ti-6Al-4V + HA composites at 1250°C for 2 hours results in a body that has many large cracks and pores as seen in Figure 5.44 and Figure 5.45 for the Ti-6Al-4V (75 vol%) + as synth. HA (25 vol%) and 4hr/4wt% SPEX milled Ti-6Al-4V (50 vol%) + as synth. HA (50 vol%) pellets respectively. MWS processing of Ti-6Al-4V + HA composite bodies exhibit similar results including a large volume fraction of porosity and low mechanical strength due to incomplete sintering and/or adverse reactionary products. Images of the MWS composite pellets are not recorded because metallographic preparation is not possible due to the pellets crumbling during cross sectioning and grinding which results in a pile of loose powder. The only co-sintering method attempted in this study that generates a fully dense composite Ti-6Al-4V + HA body is SPS, done at 1000°C for 3 minutes. The SPS bodies are shown in Figure 5.46 and Figure 5.47 for the 4hr/4wt% SPEX milled Ti-6Al-4V (90 vol%) + as synth. HA (10 vol%) and 4hr/4wt% SPEX milled Ti-6Al-4V (75 vol%) + as synth. HA (25 vol%) pellets respectively. Quantitative analysis of the relative density for all composite Ti-6Al-4V + HA co-sintering conditions appears in Table 5.5.

5.5. Sintering activation energy data

RHS diffusion activation energy (Q_{sinter}) is calculated from the relative density measurement of 4hr/4wt% SPEX milled Ti-6Al-4V pellets sintered using three different ramp rates and five different quench temperatures. The resulting pellets are shown visually in the SEM images in Figure 5.48 – Figure 5.63, while the corresponding XRD spectra for each sample appear in Figure 5.64. Relative density via ImageJ pore area

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fraction analysis for each of the activation energy samples processed in house appears in Table 5.6. The relative density value of each pellet as a function of sintering ramp rate and sintering quench temperature, as plotted in Figure 5.65, is used for subsequent activation energy calculations. The value for $Q_{\text{sinter}}$ that shows the best correlation to the mean residual squares fitting described by Shao et al. for the MSC method is shown in Figure 5.66, while the value for $Q_{\text{sinter}}$ that shows the best correlation to the mean perpendicular distance fitting described by Pouchly et al. for the MSC method is shown in Figure 5.67.

Pellet shrinkage as a function of temperature and relative density as a function of temperature from dilatometer measurements are shown in Figure 5.68 for the 4°C/min, 8°C/min and 16°C/min heating rates respectively. Calculation of $Q_{\text{sinter}}$ using the MSC method from Shao et al. is shown in Figure 5.69 for the 4hr/4wt% SPEX milled Ti-6Al-4V powder. Calculation of $Q_{\text{sinter}}$ using the MSC method with the Density MSC software provided by Pouchly et al. is shown in Figure 5.70. Calculation of $Q_{\text{sinter}}$ using the CHR method from Wang et al. is shown in Figure 5.71.

5.6. Mechanical property data

Vickers hardness from as received PREP Ti-6Al-4V and 4hr/4wt% SPEX milled Ti-6Al-4V pellets sintered via RHS, MWS, and SPS is shown in Figure 5.72. The fracture surface of an RHS sintered 4hr/4wt% SPEX milled Ti-6Al-4V pellet is shown in the stereoscopic optical image seen in Figure 5.73. Low strain rate compression data of a RHS sintered 4hr/4wt% SPEX milled Ti-6Al-4V pellet is shown in the stress-strain plot seen in Figure 5.74, while the resulting crack formation is shown in the SEM image in Figure 5.75.
6. Discussion and Analysis

6.1. Powder processing analysis

Ball milling of Ti-6Al-4V is useful for production of a feedstock ideally suited for powder metallurgy FGM component fabrication via SFF. The objective of this study is to produce a composite Ti-6Al-4V + HA femoral stem using a SFF printing approach similar to the one outlined by Xu et al. Milling of metals can result in ultrafine particles with nanometer scale grain structures that show enhanced sintering properties due to shorter diffusion distances and enhanced thermodynamic driving force respectively. Milling is also useful for production of metal powders with modified particle geometry as required for obtaining the optimal rheology for SFF slurry extrusion as well as optimal powder consolidation during green body preparation (i.e. proper powder suspension is necessary to achieve a stable slurry, proper slurry flow through a nozzle is necessary to achieve uniform slurry delivery, minimum nozzle size is necessary to achieve precise geometrical control, and proper slurry wetting layer-by-layer is necessary to achieve maximum green density for ease of sintering to a fully dense final component).

Mechanical forces within the ball milling container include impact (i.e. instantaneous striking of particles), attrition (i.e. production of wear debris through rubbing of particles), shear (i.e. cutting or cleaving of particles) and compression (i.e. crushing or squeezing of particles) which result in compaction of trapped particles, particle size reduction, agglomeration of fractured particles, and eventually release of a powder agglomerate back to the powder charge. The relative impact energy at a ball milling media collision site is plotted as a function of position in Figure 6.1(a), while the continuous processes of trapping, refinement and agglomerate release are shown in
Figure 6.1(b). The difference in particle response during the early stages of milling is shown in Figure 6.1(c) for brittle and ductile materials respectively. Milling of brittle materials results in fracture and particle refinement within the early moments of milling, while milling of ductile materials typically result in plastic deformation without any appreciable particle refinement for prolonged durations.

During the initial stage of milling, Figure 6.1(a), powder particles are compacted between two milling surfaces (e.g. two milling media or milling media and container wall). As the two milling surfaces move closer together, Figure 6.2(b), the powder compact density at the collision site increases due to friction between powder particles and due to friction between the powder particles and the milling surfaces. While some particle sliding occurs to allow for a further increase in powder compact density, some initial fracture and particle refinement also occurs depending on the nature of the powder. The general trend in particle geometry evolution during milling of metal powders include a change from smooth spherical particles to smooth flattened “pancake” particles, followed by formation of roughened flake particles which eventually fracture to form rough surfaced equiaxed particles with a smaller average diameter than the starting powder.

During the later stages of compaction, particle geometry has a significant implication on energy transfer and overall milling efficiency. Smooth spherical particles will slide easily past one another, converting much of the kinetic impact energy into a radial displacement of particles prior to collision rather than transmitting energy into the particles to induce fracture through direct mechanical stress transfer. If the powder particles are large flakes or irregularly shaped they entangle such that a majority of the impact energy is transferred to the powder charge in the form of direct mechanical stress transfer. Continued stress transfer during milling of ductile metal powders results in a work hardening effect with increasing defect concentration, until brittle fracture begins to
dominate. The final stages of compaction involve particle fracture and a further increase in the powder compact density as small previously refined particles slide into the pores between larger not yet refined particles. Sliding of the small particles into voids causes the larger particles to experience the highest stresses during collisions until they too are fractured into smaller entities.

Chemical and mechanical interactions within the milling container are dictated by the type of loading/milling atmosphere (e.g. vacuum, gasesous, or liquid) and the specific milling conditions (e.g. milling media charge ratio, milling media material, and milling duration). A progression of defects in the powder charge must occur to induce particle size reduction including facial, volume and edge flaws. Generation of a facial flaw, due to repeated collision by the milling media, will occur prior to the generation of an internal flaw which could be in the form of a vacancy or interstitial lattice defect. The internal volume flaw in turn generates an edge flaw that contains a large number of line defects which become the site of a new fracture surface when the milling media impact energy is sufficient. The limit to which a specific material can be refined is determined largely by the following factors; work hardening effects in the refined particles, increasing cohesion between increasingly smaller particles, excessive clearance between milling media surfaces, coating of milling media surfaces by refined particles that act as a cushion during impacts, surface roughness of the grinding media, bridging of large particles that protects smaller particles during impact, increasing apparent viscosity as particle refinement occurs, and/or decreasing internal friction of powder slurry.

Two different types of milling were investigated for particle and grain refinement of a commercially available PREP Ti-6Al-4V powder feedstock for improved SFF production of FGM components, specifically attrition and high energy vibratory SPEX milling. While attrition is capable of producing fine uniform powder products, cold welding
on the interior of the milling canister repeatedly lead to the milling propeller becoming jammed. Repeated jamming of the propeller lead to bending of the shaft and/or tearing of the o-ring shaft seals, such that the powder charge is exposed to atmospheric oxygen which results in high levels of contamination in the product. Along with cold welding issues, difficulties in powder loading and handling of the bulky attritor canister in an inert atmosphere glovebox (i.e. required for titanium materials that readily passivate) lead to a change from the attritor mill to a simple SPEX type vibratory ball mill. Because the SPEX milling canister has no moving internal parts, issues related to oxidation during milling due to jamming of the propeller shaft can be avoided altogether. Also because the SPEX milling canister is much smaller than the attritor canister, issues with powder loading and handling in the glovebox are also alleviated.

Another difference between the two milling methods involves the size and number of milling media applied to the powder charge. The gap between the bottom of the attritor propeller and the milling canister effectively limits the minimum size of the milling media that can be used without jamming the shaft, while the gap between the sides of the propeller branches and the walls of the milling canister effectively limits the maximum size of the milling media that can be used without also jamming the shaft. In the SPEX mill the lack of an internal rotating propeller affords the user the option to apply a range of milling media sizes. While larger milling media is desired for refinement of large particles, smaller milling media is required for fine grinding such that a combination of both large and small media is ideal. SPEX milling allowed for the use of just four 12.7mm diameter balls plus eight 6.4mm diameter balls (i.e. 12 total milling media) to achieve similar refinement as in attritor milling that required more than 100 of identical 6.4mm diameter balls. Because the attritor mill utilized only one size of milling media and because it exhibits lower average kinetic impact energy than SPEX milling,
the milling duration required to achieve refinement was 72 hours in the attritor mill as compared to only 4 hours in the SPEX mill.

In the case of Ti-6Al-4V powder processing, careful consideration of the processing atmosphere is necessary to avoid contamination of the final product. The as received PREP Ti-6Al-4V powder is produced in the plasma state in ambient atmosphere and therefore experiences oxygen passivation. Passivation is a process in which an oxygen atom occupies an interstitial titanium lattice site to form an oxide scale through an anodic metal dissolution process. Spontaneous formation of a stable oxide scale on the surface of the Ti-6Al-4V powder particle lowers the overall free energy of the particle because the oxide species has a much lower chemical potential energy of reaction with oxygen species in the atmosphere as compared to the metallic titanium species. Passivation is detrimental to atomic transport of the metallic species (i.e. Ti, Al, V) during the sintering process because of the lower rate of atomic diffusion of metallic species through an oxide layer due to the higher chemical bond strength in the oxide as compared to the pure metal. Passivation is accelerated at high temperature when the alloy experiences the alpha-beta phase transformation from the hexagonal close packed (HCP) structure to the body centered cubic (BCC) structure at 883°C. The accelerated passivation is due to the larger interstitial vacancy site available in the BCC lattice as compared to the HCP lattice, thus powder processing should be done entirely in the alpha phase temperature regime under inert atmosphere to minimize the extent of oxide formation.

By powder processing under inert argon atmosphere, the formation of any new oxide scale is suppressed, while repeated fracture of powder particles introduces a large area fraction of fresh oxide free Ti-6Al-4V surface. Proper surface chemistry of the powder will affect the green body mechanical strength because clean metal surfaces
allow for better mechanical interlocking than oxide surfaces which tend to be smooth and brittle. Proper Ti-6Al-4V surface chemistry also ensures optimal mass transport kinetics across the interparticle neck boundary during sintering, thus suppression of surface passivation effects is critical. Evidence of a reduction in area fraction of titanium oxide is shown via XPS analysis wherein the oxygen concentration highlighted in yellow on Figure 5.5 has decreased from ~53 atomic percent in the as received PREP Ti-6Al-4V powder, to only ~37 atomic percent after twenty four hours of attritor style ball milling as seen in Figure 5.6. The trend of an increasing fraction of fresh metallic Ti-6Al-4V surface area is expected to be consistent for the entirety of ball milling conditions investigated in this study (i.e. both attritor and SPEX style, all PCA concentrations, and for all milling durations) because inert gas atmospheric protection is maintained for all milling conditions.

Particle morphology during ball milling is scrutinized via SEM analysis to determine the optimal particle morphology for green body preparation and density maximization. The SEM image seen in Figure 5.2 shows a flattened flake-like morphology after 24 hours of attritor ball milling. Direct measurement of the average particle diameter shows that the Ti-6Al-4V particle size has increased from ~110 µm to ~250 µm due to spreading in the directions orthogonal to the direction of the milling media collision (i.e. thickness is reduced but length and width are increased). The goal of a reduction in particle diameter via ball milling has not yet been met after 24 hours therefore a longer ball milling duration is investigated. After 72 hours of ball milling the as received PREP Ti-6Al-4V powder has successfully been refined to an average diameter of only 5 µm while simultaneously resulting in more uniform equiaxed powder morphology seen in Figure 5.3. In the case of SPEX ball milling an equiaxed morphology with ~25 µm average diameter is achieved after just 4 hours of milling.
An increase in the average particle diameter after 24 hours of attritor style ball milling or 1 hour of SPEX style ball milling indicates incomplete processing (i.e. the particles have been severely plastically deformed but not fractured into smaller entities). After 72 hours of attritor style ball milling or 4 hours of SPEX style ball milling the Ti-6Al-4V particles are much smaller with faceted edges, indicating brittle fracture has occurred. A schematic of the Ti-6Al-4V particle size/geometry as a function of SPEX milling duration is seen in Figure 6.2. Similarly a schematic of the Ti-6Al-4V particle size/geometry as a function of SPEX milling PCA concentration is shown in Figure 6.3 for comparison.

SPEX ball milling energetic analysis has been studied previously to determine the magnitude of the energy imparted to the powder charge as a function of the milling media charge ratio. Collisions of the grinding media with each other and with the walls of the milling vial are assumed to be purely elastic in nature (i.e. deformation of the balls and/or vial walls is considered to be negligible because the vial and grinding media are both made of stainless steel). The motion of the SPEX milling apparatus is shown in Figure 6.4\(^1\), while the grinding media collision modes are shown in Figure 6.5\(^2\). Quantification of the kinetic energy present in the SPEX milling process is useful for predicting the mechanism by which particle refinement is achieved. The kinetic energy of the milling media is calculated using the relationship shown in Equation (5),

\[
K.E. = \frac{1}{2}mv^2
\]  

where \(m\) is the mass of the milling media and \(v\) is the impact velocity of the milling media\(^2\). The SPEX milling condition utilized for the creation of nanostructured powders for sintering and activation energy studies (e.g. 4hr/4wt% SPEX milled Ti-6Al-4V)
involves four large stainless steel balls each with a mass of 7.78 g and eight small stainless steel balls each with a mass of 0.95 g. The milling media velocity is taken from a previous study by Concas et al.\textsuperscript{71}, wherein the average velocity of a ball is given as 4.186 m/sec. The calculated kinetic energy for this specific SPEX milling condition is 0.339 J total with 0.0682 J/large ball and 0.00832 J/small ball, which is much less than the 20 J Charpy impact energy\textsuperscript{73} given for Ti-6Al-4V in the literature. Therefore particle refinement must undoubtedly proceed via defect pileup and cold working mechanisms rather than via a fracture event induced by a single collision.

Deformation mechanics of Ti-6Al-4V during ball milling may involve twinning of the powder particles prior to fracture. It has been established that materials with an HCP crystal structure have a tendency to form \{10\overline{1}2\} twins during deformation in order to accommodate large strains along the c-axis of the unit cell without fracture\textsuperscript{74}, giving titanium alloys their simultaneous high yield strength and considerable toughness. While the twinning effect is prominent in pure α-phase HCP titanium it can be suppressed by the addition of both aluminum and vanadium, although for different reasons. Addition of aluminum in the Ti-6Al-4V alloy initiates slip on the pyramidal planes prior to twinning while addition of vanadium increases the β-phase BCC volume fraction which itself has a multitude of possible slip systems that accommodate a fraction of the strain energy prior to twinning in the α-phase HCP volume\textsuperscript{75}. Grain boundary sliding likely also plays a role in deformation of Ti-6Al-4V during ball milling because a large grain boundary area fraction is present in the heavily deformed SPEX milled powder, thus a portion of the incident strain energy should be consumed by translation of neighboring grains. Some parameters accounting for particle agglomeration and cold welding are not treated in this analysis and thus all ball collisions with the Ti-6Al-4V are considered to induce fracture
and refinement only, although aggregation, agglomeration, and cold welding do in fact occur experimentally.

While a number of defects are introduced into the particle with each collision, those defects do not result in the creation of a new interface until critical threshold is attained. As the milling process continues the concentration of defects increases as point defects congregate to form a line defect, line defects congregate to form a crack, and eventually the crack propagates through the entire particle thus fracturing it into two separate entities. This phenomenon is explained in great detail by Shaw et al.\(^7_6\) who investigated the effects of PCA concentration on cold welding, cold working, and particle/grain refinement. The delicate balance between cold welding and work hardening must be achieved because an increase in PCA concentration decreases cold welding and work hardening while an increase in milling duration leads to more extensive work hardening and eventually results in brittle fracture and particle size reduction. In the case of Ti-6Al-4V with attritor milling the threshold for cold work induced brittle fracture is not seen until \(~72\) hours of milling, while in SPEX milling the threshold for cold work induced brittle fracture of Ti-6Al-4V is achieved after \(~4\) hours of milling.

Stearic acid in particular has a molecular formula of C\(_{18}\)H\(_{36}\)O\(_2\) with a structure consisting of a hydrophilic polar (O-OH) head group as shown in Figure 6.6\(^7_7\). The presence of stearic acid during ball milling results in adsorption of the PCA on the Ti-6Al-4V surface, see Figure 6.7\(^7_8\). Adsorption occurs as the hydrophilic head of the stearic acid molecule becomes bonded to the surface of the metallic Ti-6Al-4V powder particle, lowering the surface free energy of the powder charge by creating a uniform monolayer around each particle. The hydrophobic tail of the stearic acid molecule is left dangling freely from the Ti-6Al-4V surface, creating a "like charge" state around each powder particle. When multiple stearic acid coated Ti-6Al-4V particles with a "like charge" come
into intimate contact (i.e. such as being trapped between milling media or between the walls of the milling container) they repel each prior to being cold welded. Stearic acid prevents the Ti-6Al-4V particles from directly interacting with each other and/or the milling media and thus powder processing yield is increased while particle refinement and grain refinement are perpetuated at a decreased rate as compared to dry milling with no PCA. The establishment of a physical barrier as well as an electrostatic barrier on the surface of each Ti-6Al-4V particle helps to mitigate aggregation, agglomeration, and cold welding effects as shown schematically in Figure 6.8.

There are various issues associated with the use of a PCA during powder processing including carbon and oxygen contamination that can lead to carbide and oxide formation uniformly throughout the powder charge because ball milling is effective at creating homogeneous mixtures on the nanoscale. Because some of the stearic acid will decompose due to a local temperature rise at the milling media collision site, a portion of the stearic acid chemical species (i.e. C, H, O) will be trapped in the powder charge through adsorption on the surface and inclusion in the bulk due to repeated fracture and cold welding. While hydrogen and oxygen are released in the gaseous phase, carbon is released in the solid phase. The free carbon present in the powder charge at this point is either amorphous in nature or at a concentration that is below the detection limit of XRD analysis because only a few of the spectra in Figure 5.17 show reflections attributed to pure carbon. Although the exact reason for carbon reflections appearing in some spectra while not in others is not know, it may have some dependence on the ratio of PCA concentration to milling duration where higher PCA concentrations with shorter milling durations allow for the retention of large concentrations of crystalline free carbon. Solid state carbon present in the powder
charge after ball milling may lead to carbide formation during sintering to the detriment of the pellet density, pellet chemistry, and subsequent mechanical properties.

While carbon inclusion has a negative effect for load bearing composite Ti-6Al-4V + HA FGM femoral stem components, the formation of TiC at temperatures as low as 1000°C during this study is a result that may unintentionally be beneficial for alternate applications. Because TiC formation is demonstrated at a temperature much lower than typical direct reaction between Ti and C (1900-2900°C) or carbothermal reduction of TiO$_2$ (1500°C), this side effect may actually be of great importance. The root cause of low temperature TiC formation in this case is due to nanoscale mechanical alloying of titanium and carbon by inclusion of the free carbon generated from decomposition of stearic acid at the local ball milling collision site. Nanoscale mechanical alloying results in shorter diffusion distances and a greater titanium-carbon interfacial area fraction than commercial macroscale TiC formation processes, thus the lower formation temperature is achieved.

With increasing PCA concentration there is also a reduction in milling efficiency due to the lubricating nature of stearic acid. While a significant concentration of PCA is necessary to mitigate cold welding effects, any excess PCA will act as a solid lubricant resulting in a powder charge consisting of large flakes rather than small equiaxed particles. The creation of many large flake-like particles is a result of the majority of the kinetic energy from the milling media being used to overcome the friction force between bodies rather than being used to overcome the fracture strength of the powder charge. When the friction force is much lower than the fracture strength, the Ti-6Al-4V particles will plastically deform into flakes which can slide easily between the milling media without further size reduction. Also important to powder processing is the size and polarity of the specific PCA molecule, which determine its effectiveness as a particle size
reduction agent by altering the deformation and fracture pathways during milling. Therefore, the choice of PCA molecule, the loading concentration, and its consumption during milling are important parameters to monitor in order to achieve particle refinement with a high powder yield and minimal contamination.

XRD analysis used to monitor phase purity and crystallite size as a function of all attritor and SPEX milling conditions reveals some positive and negative trends. Titanium reflections are identified using an indexed powder diffraction standard (PDF # 44-1294) and the spectra shown in Figure 6.9\textsuperscript{82}. In addition to monitoring phases, XRD was also used to estimate the crystallite size via peak broadening through the use of the Scherrer formula shown in Equation (6),

\[
\beta_g = \frac{k\lambda}{\cos \theta D}
\]  

(6)

where \(\beta_g\) is the full width half maximum peak breadth (FWHM), \(k\) is a shape factor constant, \(\lambda\) is the x-ray wavelength (\(\text{Cu}\text{K}_\alpha = 1.541\ \text{Å}\)), \(D\) is the mean size of the ordered domain (i.e. crystallite size), and \(\theta\) is the Bragg angle\textsuperscript{83}. The average crystallite size of the two major Ti-6Al-4V reflections corresponding to the (101) and (002) planes respectively, are derived from the XRD spectra in Figure 5.4, Figure 5.17, and Figure 5.41. The method used to determine the FWHM from a given XRD spectra (i.e. the unknown value necessary to calculate the average crystallite size of the Ti\text{[101]} and Ti\text{[002]} reflections) is described for the MATLAB curve fitting tool using the step by step process as follows:

1) In Microsoft Excel – open the .UXD data file which contains the raw XRD (Intensity vs. 2 Theta) data
2) In the MATLAB Command Window – type **cftool** and press enter to open the curve fitting window

3) In the MATLAB Workspace Window – click the new variable icon to open a new data set, rename the variable **data** and press enter

4) Double click on **data** to open the Variable Editor Window

5) Copy and paste the Excel spreadsheet data text into the Variable Editor Window

6) In the Command Window – type **dataX = data(:,1);** to generate the x-variable data set for curve fitting

7) In the Command Window – type **dataY = data(:,2);** to generate the y-variable data set for curve fitting

8) In the Curve Fitting Window – click on the Data tab to open the variable selection window and select **dataX** and **dataY** variables to be plotted

9) Examine the spectra for peak(s) desired to be fit

10) Crop the data sets to view only the desired peak(s) in the Command Window – type **dataX = data(start 2θ data point number:end 2θ data point number,1);** to generate the x-variable data set for curve fitting and type **dataY = data(start 2θ data point number:end 2θ data point number,2);** to generate the y-variable data set for curve fitting

11) In the Curve Fitting Window – click on the Data tab to open the variable selection window and select **dataX** and **dataY** variables to be plotted

12) In the Curve Fitting Window – click on the Fitting tab to open the Fit Editor Window

13) Examine the spectra again and determine the number of peaks to be simultaneously fitted

14) In the Command Window – type **lorentzEqn (#of peaks)** to generate the curve fitting equation for low angle crystallite size analysis which appears in the general form of \( y=mx+b \) where \( c \) is the peak center Bragg angle, \( i \) is the peak intensity from the background, and \( w \) is the FWHM of the peak.

15) Open the Fit Editor Window – Select New Fit → Custom Equation → General Equation

16) Copy and paste the curve fitting equation from step 14) in the General Equation box

17) Use the Curve Fitting Window spectra to choose starting values for the peak center position in 2θ, peak intensity from the background in arbitrary units, and peak breadth in 2θ

18) Click Apply tab to fit the spectra using the boundary conditions set in 17)

19) Examine the output to determine the correlation \( (R^2) \) of the curve fitting equation to the actual XRD spectra

20) Open the Curve Fitting tab and iteratively adjust the starting and ending values for each variable until the correlation is a maximum (i.e. ideally \( R^2 = 1 \))

21) Output the data to the workspace – click Save to Workspace tab

22) Output the curve fitting results with additional significant figures in the Command Window – type **coeffvalues (fittedmodel1)** to display the values for peak center position in 2θ, peak intensity from the background in arbitrary units, and peak breadth in 2θ

23) Insert the values obtained via MATLAB curve fitting into Equation (6) to calculate the mean crystallite size for the Ti\(_{(101)}\) and Ti\(_{(002)}\) reflections respectively
A screengrab of the MATLAB software command window is shown in Figure 6.10, wherein each step from the method above is shown via the red numbers overlayed on the image. Similarly an example of the curve fitting module is shown in Figure 6.11, wherein the purple markers are the raw data points and the red curve is the best fit line based on the specific curve fitting equation utilized for the analysis.

In the case of attritor milling, the XRD spectra for the 24 hr and 72 hr milled Ti-6Al-4V show a large broad hump due to very small sample volume available for characterization after sintering density experiments. The lack of crystalline Ti-6Al-4V sample volume allowed the amorphous plastic sample holder to contribute to the signal rather than being drowned out as background radiation, making crystallite size calculations via MATLAB difficult. Subsequent SPEX milled Ti-6Al-4V XRD analysis utilized a larger sample volume to obtain a better signal to noise ratio for each spectra, allowing for more accurate crystallite size analysis. A schematic of the trend in average crystallite size of the Ti-6Al-4V (101) and (002) reflections is shown as a function of SPEX milling duration in Figure 6.12 and as a function of SPEX milling PCA concentration in Figure 6.13.

TEM confirmation of the crystallite size calculation from XRD analysis, by name requires the sample to be electron transparent (i.e. allows the transmission of electrons through its entire thickness to create an image from the projection of the internal structure of the sample), thus only crystallites in Ti-6Al-4V powder particles that are less than ~200 nm in thickness will be resolved. Direct comparison between the as received PREP Ti-6Al-4V powder and the SPEX milled Ti-6Al-4V powder is not possible because the as received PREP particles are not electron transparent due to their appreciable thickness (i.e. ~110 µm average particle diameter) and high atomic number (i.e. Ti = 22). Because of this only the crystallite size of the 4hr/4wt% SPEX milled Ti-6Al-4V powder
can be confirmed through direct visual observation for comparison to the crystallite size obtained via XRD analysis, however the overall trend of a reduction in crystallite size due to an increase in defect concentration during the milling process is confirmed in Figure 5.22. Imaging in bright field mode allows for the observation of the particle size and particle geometry, see Figure 5.22(a), while the dark field imaging mode allows for direct observation of the individual single crystal domains (i.e. crystallites) within each powder particle, see Figure 5.22(b). Note that the individual single crystal domains of the dark field image in Figure 5.22(b) are indeed much smaller than the 100 nm scale bar that appears on the image and can therefore be considered a nanostructured powder.

Comparison of the grain size before and after SPEX ball milling also yields important results for the subsequent sintering studies because of the drastically altered grain structure and increased grain boundary area fraction in each powder particle. The 4hr/4wt% SPEX milled Ti-6Al-4V powder seen in Figure 5.25 has a microstructure that has been severely cold worked, indicated by a large grain boundary area fraction and highly irregular grain morphology as compared to the grain boundary area fraction and grain morphology seen in the as received PREP Ti-6Al-4V powder seen in Figure 5.24. The 4hr/4wt% SPEX milled Ti-6Al-4V seen in Figure 5.25 shows signs of repeated plastic deformation, fracture, and cold welding of the powder particles indicated by the elongated, lamellar grains seen throughout the particle where relatively equiaxed grains once existed in the as received PREP state. The trend of severe plastic deformation (i.e. ductile particle flattening), cold work induced fracture (i.e. brittle particle breaking), and thermally induced fusion (i.e. cold welding) of the powder particles witnessed macroscopically via SEM particle size analysis is paralleled directly by the grain structure witnessed microscopically via optical investigation of the etched samples.
Prediction of the effect of high temperature exposure during sintering is done using a piece of commercial as cast Ti6-Al-4V sheet metal to monitor grain growth as a function of temperature. During high temperature exposure the as cast sheet metal sample experiences thermal etching and thus the grain structure can be examined without Kroll’s Reagent chemical etching immediately after removing the plate from the RHS furnace. A comparison between the as received sheet metal grain structure revealed by Kroll’s Reagent chemical etching in Figure 5.23 and the thermally etched as received sheet metal grain structure in Figure 5.26 does not provide a direct quantitative correlation for grain growth as a function of temperature in the powder compacts, rather it simply provides qualitative justification for the expectation of an increase in grain size with increasing temperature. Because of the grain growth witnessed in the sheet Ti-6Al-4V sample during thermal etching, the same trend of increasing grain size with increasing temperature can be expected to occur during sintering of the powder compacts when exposed to similar dwell temperature and dwell time conditions, however the exact nature of the grain growth in the powder compacts will be slightly different due to the competing atomic mass transport mechanism which also occurs to lower the free energy of the system.

6.2. Sintering analysis

In general the sintering process is used to create a solid body of macroscopic proportions from a powder feedstock with has the same chemical composition only on a much smaller size scale. Because the sintering process is done completely in the solid state, there are no melting and recrystallization effects but rather just atomic diffusion and surface energy effects that provide for particle coalescence and green body
densification. Details of the sintering process as a function of starting powder and green body condition will be discussed as they pertain to density optimization of the final product.

In general the driving force for sintering involves a reduction in the overall free energy of the green body through atomic diffusion from regions of higher free energy to regions of lower free energy. The gradient in driving force is established by the difference in surface free energy at the solid-vapor interface ($\Gamma_{SV}$) and the surface free energy of the solid-solid interface ($\Gamma_{SS}$). Physically this relationship manifests between regions of porosity (i.e. $\Gamma_{SV}$) and regions of solid Ti-6Al-4V (i.e. $\Gamma_{SS}$) where the particle-particle contact exists, known as the interparticle neck boundary region. The overall free energy of the system is reduced as atomic mass is transported from the higher energy pore region to the lower energy interparticle neck region when sufficient input energy is available in the form of heat. During atomic transport the overall volume fraction of solid-vapor interface is reduced, while the overall volume fraction of solid-solid interface is increased. The interparticle neck region has a lower surface free energy than that of the atoms in the pore region because the atoms at the interparticle neck region are bonded to other Ti-6Al-4V atoms uniformly in a three dimensional network. At the pore region a solid particle will have a portion of dangling or nonuniform bonds due to the free surface state adjacent to it, which has no atomic mass with which to interact and therefore results in a higher surface energy state than for atoms in the bulk.

A schematic of the initial driving force for sintering of the green compact is shown in Figure 6.14, wherein the sphere model represents the sintering process as it proceeds with temperature and/or time and the radius of the pore and radius of the solid Ti-6Al-4V particle are given by $r$ and $a$ respectively. Shrinkage is predicted using the relationship given in Equation (7),

68
where \( c \) is the equilibrium vacancy concentration under a curved surface, \( c_0 \) is the equilibrium vacancy concentration under a flat surface, \( \gamma \) is the surface free energy per unit area, \( V_m \) is the molar volume, \( R \) is the gas constant, \( T \) is the temperature, \( a \) is the radius of curvature of the solid Ti-6Al-4V particle, and \( r \) is the radius of curvature of the pore neck region between the solid Ti-6Al-4V particles. As per the notation used to describe the green body pore-particle interface, the surface of a solid Ti-6Al-4V particle has a convex positive curvature while the curvature of a neighboring pore will be concave and negative. From Equation (7) the equilibrium vacancy concentration under the concave curved neck region during sintering will be greater than that of a convex particle surface region. Thus, mass transport from the convex pore region to the concave interparticle neck region will proceed as the system lowers its overall free energy through a reduction in the overall entropy of the system according to Equation (8),

\[
\Delta G = \Delta H - T \Delta S
\]

where \( \Delta G \) is the change in Gibbs free energy of the system, \( \Delta H \) is the change in enthalpy of the system, \( T \) is the temperature, and \( \Delta S \) is the change in entropy of the system. The change in disorder of the system, \( \Delta S \), is positive when the concentration of defects (e.g. vacancies and pores) is reduced. When \( \Delta S \) is positive the overall free energy of the system, \( G \), is reduced as atomic transport from the Ti-6Al-4V particle surface to the
interparticle neck region eliminates atomic vacancies and eventually microscopic and macroscopic pores.

A more detailed description of the mass transport process during sintering involves a discussion of the concept of diffusion. Diffusion is defined as the thermally activated movement of atoms through a crystalline lattice in a solid which results in a net transport of mass from one location to another\textsuperscript{86}. While the movement of atoms in a solid is much slower than that of atoms in a liquid or a gas, the net flux of atomic diffusion increases with increasing temperature due to an increase in the amplitude of atomic vibrations within the crystal lattice. Although atomic diffusion is present at all nonzero temperatures, the extent of atomic flux is highly dependent on temperature and thus diffusion of Ti-6Al-4V at low temperatures (i.e. $T<900^\circ$C) is negligible. The driving force for diffusion within a solid is a concentration gradient based on disorder within the system that leads to areas of higher concentration and areas of lower concentration that have different values of free energy. As per the vacancy and pore concentration conditions described by the green body description, atomic transport during sintering is driven by the gradient in vacancies between the bulk Ti-6Al-4V particle with an infinite radius of curvature, and the pore region with finite concave curvature. Diffusion flux in essence plays the role of reducing the overall free energy of the system through a change in the green body surface geometry and internal pore structure, as well as through a reduction in lattice vacancy concentration.

Mass transport during diffusion is limited by the type of gradient, type of defect present, and the concentration of such defects which creates a chemical potential gradient at different locations in the system. Mass transport in general can be described by Fick’s first and second laws which are given in Equation (9) and Equation (10) for steady state and non-steady state conditions respectively,
where \( J \) is the diffusion flux (i.e. number of atoms per unit area per unit time) for steady state conditions, \( D \) is the diffusion coefficient, \( C \) is the concentration. For the specific case of atomic diffusion to the interparticle neck region during sintering, the diffusion flux can be described by the relationship known as Herring’s equation seen in Equation (11),

\[
J_a = -\frac{D}{\Omega_a k_B T} \nabla (\mu_a - \mu_v)
\]

where \( J_a \) is the diffusion flux at the interparticle neck region, \( D \) is the diffusion coefficient, \( \Omega_a \) is the atomic volume, \( k_B \) is the Boltzmann’s constant, \( T \) is the temperature, and \( \nabla (\mu_a - \mu_v) \) is the chemical potential gradient established by the difference in curvature between the solid Ti-6Al-4V particle and pore regions of the green body.85

The dominant modes of diffusion in solids are vaporization followed by solidification (path #4), surface diffusion (path #3), grain boundary diffusion (path #2), and lattice based bulk diffusion (path #1) as seen in the schematic in Figure 6.15. Vaporization and solidification does not occur during sintering because the process is carried out below the melting point of the material, thus this pathway can be ignored for the present study. Surface diffusion during sintering does not actively participate in the densification process because surface diffusion merely causes coarsening of the interparticle neck boundary region without a reduction in the pore volume that exists.
between particles. Grain boundary and lattice diffusion both participate in the densification process because both mechanisms result in coarsening of the interparticle neck boundary region while simultaneously causing the pore volume to be eliminated as the particle centers of two contacting particles move closer together. Typically, grain boundaries serve as pipelines for atomic transport to the interparticle neck region while the bulk lattice serves as the source of atomic mass and the interparticle neck region serves as the sink for atomic deposition. Ideally, grain boundary rate limiting diffusion kinetics during sintering are preferred over lattice diffusion rate limiting kinetics because of the higher atomic mobility in the disordered grain boundary region as compared to the highly ordered lattice. In the case of Ti-6Al-4V sintering the rate limiting diffusing species is atomic titanium which has the largest ionic radii of the possible diffusing species (e.g. Ti, Al, V), thus its transport from the bulk lattice to the interparticle neck boundary region will require the most energy input for mobility.

The sintering process itself can be broken down into three basic stages wherein each can be described by the particular dominating mass transport and geometry reconstruction phenomena. During the initial stage of sintering (i.e. up to approximately a 10% increase in density) particles within the green body undergo a geometric rearrangement to lower their free energy by transforming the curved particle surfaces in contact at the interparticle neck region to a flat interparticle neck interface that has a lower free energy. An interparticle neck region with a negative curvature is established in this stage as the powder particles first join together physically. Shrinkage of the green body related to the interparticle neck growth during the early stages of sintering is described by Equation (12),
\[
\frac{\Delta L}{L_0} = \left(\frac{x}{D}\right)^2
\]

where \(\Delta L/L_0\) is the shrinkage, \(x\) is the neck diameter, and \(D\) is the particle diameter\(^{87}\).

Following the initial particle surface geometry reconstruction, the intermediate stage of sintering (i.e. up to approximately 90\% relative density) proceeds with appreciable neck growth and interconnected pore formation as mass is transported from the interparticle boundary area to the neck region as governed by Equation (13),

\[
\frac{x^6}{D} = B_0 \exp\left(-\frac{Q_{gb}}{RT}\right) \frac{t}{D^4}
\]

where \(x\) is the neck diameter, \(D\) is the particle diameter, \(B_0\) is a constant related to interparticle boundary width, surface energy and atomic volume, \(Q_{gb}\) is the grain boundary activation energy diffusion, \(R\) is the gas constant, \(T\) is temperature, and \(t\) is time\(^{87}\). During the intermediate stage of sintering the particle surface geometry reconstruction continues to flatten the curved interparticle neck interface, effectively bringing the particle centers closer together and thus increasing the density of the green compact. Some negative effects are also likely during the intermediate stage of sintering including particle coarsening which occurs at the detriment of sintering kinetics (i.e. coarsening reduces the free energy of the system and thus reduces the driving force for mass transport) and also grain growth which can reduce the mechanical strength of the final product. Typically, the densification rate decreases with increasing interparticle neck size due to coarsening effects and thus the final stage of sintering takes over. During the final stage of sintering the interconnected network of pores become isolated islands of porosity dispersed throughout the powder compact. For most materials under
reasonable sintering temperature and time conditions (i.e. \( T = 0.9T_m \) and \( t = 2 \) hrs respectively) the final compact will reach a relative density greater than 92%, but longer time sintering or a post sintering treatment such as hot isostatic pressing (i.e. pressure assisted sintering) are required to reach 100% theoretical density.

Investigation of different sintering techniques for densification of 4hr/4wt% SPEX milled Ti-6Al-4V powder reveals differences in the final component density related to the interaction mechanism of the specific energy source responsible for the atomic diffusion. Radiant heat sintering, done in the alumina tube furnace, involves the application of thermal phonon energy to the green body that causes heat to penetrate from the outer surface of the body to the interior of the body in a direct heat transfer mechanism defined by the thermal conductivity of the solid\(^{88}\). The applied phonon energy causes atoms in the lattice of the Ti-6Al-4V particles to vibrate with greater amplitude and frequency until their energy is greater than the interatomic bond strength, at which point they are able to break bonds and move throughout the solid from point to point in the opposite direction to the motion of atomic vacancies. Because the application of heat is based on the thermal conductivity, the diffusion process from the surface to the core region is time dependent and thus thermal equilibrium must be attained to ensure homogeneous diffusion throughout the body. The prolonged time for thermal equilibrium in RHS is done at the cost of a reduction in mechanical strength due to grain growth effects. RHS processing is shown to be capable of producing a fully dense final component when sintering of the 4hr/4wt% SPEX milled Ti-6Al-4V powder is done under strict vacuum control, however the high temperature requirements (i.e. >1000°C) for this method are not suitable for production of mechanically robust Ti-6Al-4V + HA composites.
Microwave sintering utilizes the particle-pore dipole structure present in the green body to generate eddy currents on the surface of the Ti-6Al-4V particles which causes heat generation that supplies the energy for atomic diffusion\textsuperscript{89}. Because the green body is highly porous, the microwave radiation is able to penetrate to the interior regions of the pellet causing a higher temperature on the inside of the green body where the dipole volume is greatest. Because of a lower dipole volume on the surface of the green pellet and also because of the thermal heat sink of the surrounding furnace chamber, heat flows from the center of the green pellet outward in MWS, thus a higher final density is achieved at the core than in the surface of the body. MWS processing has been shown to produce highly dense components using the 4hr/4wt\% SPEX milled Ti-6Al-4V powder, however issues related to a gradient in porosity remaining in the final component make this method not suitable for retention of tight geometrical tolerances required for SFF femoral stem components.

Heat generation in SPS is derived from the intrinsic joule effect which is a method of resistive heating in conducting materials. As electric current passes through a conducting material, the amount of heat released is given by the proportional relationship between current and resistance shown in Equation (14)

$$Q \propto I^2 R$$  \hspace{1cm} (14)

where $Q$ is the heat released, $I$ is the current, and $R$ is the resistance of the material\textsuperscript{90}. The pulsed electrical current utilized in SPS results in concentration of current density at the contact point between Ti-6Al-4V particles, thus a very large increase in the local temperature is possible\textsuperscript{91}. The rapid and extreme rise in local temperature leads to high rates of atomic diffusion at the interparticle neck region which in turn results in rapid
densification without appreciable grain growth, thus the final component offers better mechanical strength than RHS or MWS processing. Because the SPS process relies on electric current flow through the green body, physical contact between the instrument die and workpiece must be maintained throughout the heating by the application of a 50 MPa uniaxial pressure in the furnace chamber. The applied pressure throughout the heating process may help to promote physical particle rearrangement, the breakdown of agglomerates, as well as inducing creep-like high temperature plastic deformation which all act to enhance the densification efficiency. Other non-thermal factors include enhanced defect mobility, point defect generation and electromigration effects that result from the applied electrical current, which also aid in the enhanced densification efficiency although the exact nature of atomic mobility in SPS is still not clear from the literature. The SPS process is shown to be the method best suited for production of highly dense components using the 4hr/4wt% SPEX milled Ti-6Al-4V powder, however like MWS it too has issues related to net shape control of the final product due to the applied mechanical force during heating. The rapid heating and high rate of atomic diffusion at the interparticle neck region resulting from the intrinsic joule heating mechanism in SPS does provide the foundation for low temperature processing (i.e. <1000°C) necessary for co-sintering of Ti-6Al-4V + HA composite FGM bodies, however low pressure techniques must be explored to allow for net shape retention specific to the individual total hip replacement patient.

Initial uniaxial pressing is done at the maximum pressure possible that does not result in permanent plastic deformation to the upper and lower platens of the press or the destruction of the powder compact with the intention of creating a green body with maximum relative density prior to sintering. Maximum green body density allows for maximum final component density, while allowing for sintering at a lower temperature or
a shorter time because fewer number and smaller size pores are present in the body. After discovery of delamination issues related to excess friction along the die walls, a lower uniaxial pressure of 300 MPa was used for the remainder of the experiments.

Detailed analysis of the die wall friction forces and the gradient in density within the resulting pellet are shown schematically in Figure 6.16. The relative density gradient, indicated by the numbered zones in Figure 6.16(b) and Figure 6.16(c), shows the underlying mechanism responsible for the layer-by-layer separation of distinct layers within the green compact. Green bodies that have a gradient in density prior to sintering will delaminate as each layer of different density sinters independent of the other surrounding layers.

Crumbling of the as received PREP Ti-6Al-4V green body pellets is a result of a very low surface roughness of the spherical particles and also because of the passivated oxide surface layer that inherently encases each particle. The lack of surface roughness (i.e. very small contact surface area for mechanical interlocking between particles) coupled with an oxide interfacial condition (i.e. smooth brittle ceramic oxide phase means no plastic deformation for mechanical interlocking of particle surfaces), leads to negligible green body mechanical strength. For increased green body strength, powder particles should ideally have a high surface roughness and allow for ductile deformation under the applied uniaxial load. Because the as received PREP Ti-6Al-4V powder is neither rough nor ductile under a 300 MPa load (i.e. Ti-6Al-4V compressive yield strength = 970 MPa), a binder additive must be applied. Mixing the as received PREP Ti-6Al-4V powder with PEG binder results in the metal particles being encased with PEG ligands that interact to provide van der Waals bonding between the particles in the green body. Although van der Waals bonding is a very weak type of bonding, it is sufficient to allow for handling of the as received PREP Ti-6Al-4V green bodies for sintering studies.
without crumbling. A schematic representation of the root cause of pellet crumbling is shown in Figure 6.17(a), while the PEG binder coated condition for green body preservation is shown in Figure 6.17(b). The ideal powder condition for appreciable green body strength without a binder is shown in Figure 6.17(c), which represents the mechanical interlocking mechanism that is active in the 4hr/4wt% SPEX milled Ti-6Al-4V powder compacts due to the higher surface roughness of the milled powders.

Green body "accordioning" is witnessed in uniaxial pressing of the 1hr/4wt% SPEX milled Ti-6Al-4V powders which have an enlarged, flat, plate-like morphology. When the 1hr/4wt% SPEX milled powder is consolidated via uniaxial pressing, many of the individual particles that are parallel to the applied load fold under the 300 MPa pressure. Once the uniaxial die punch is removed to extract the green body, the pellet expands along the uniaxial pressing axis as the folded plate-like particles return to their preloading unfolded geometry. Because the 300 MPa pressure is not sufficient to cause permanent plastic deformation, the elastic deformation that causes the particles to fold and compress is completely relieved when the load is removed.

The average green density of equiaxed 4hr/4wt% SPEX milled Ti-6Al-4V powder samples pressed at 300 MPa is approximately 55.6%, while the average green density of all other Ti-6Al-4V powders is lower due to inefficient particle packing and particle folding as shown in Figure 6.18(a) and Figure 6.18(b). Because of the particle folding and unfolding there exists a large volume fraction of empty space within the green body after uniaxial pressing, thus the relative density of the 1hr/4wt% SPEX milled Ti-6Al-4V green body is actually lower than both the as received PREP Ti-6Al-4V green body and 4hr/4wt% SPEX milled Ti-6Al-4V green body. The additional number and additional volume of voids leads to poor sintering results because the kinetics of void elimination are dictated by the diffusion distance required for transport of Ti-6Al-4V to the
interparticle neck region adjacent to each void. As the total pore volume and individual pore size increase, the diffusion distance and thus diffusion time for Ti-6Al-4V transport increase accordingly. If the pores are interconnected and exposed to the free surface of the pellet, sintering may not reach completion but rather result in a change in the pellet geometry without densification (i.e. surface diffusion mechanism does not contribute to void elimination but rather just surface geometry homogenization).

The change in particle morphology as a function of SPEX milling condition has important implications concerning slurry preparation and slurry extrusion for SFF layer-by-layer printing that will be used to construct the FGM component. Prediction of the SFF properties based on results of the 4hr/4wt% SPEX milled powder properties are as follows. Stable slurry preparation requires the powder feedstock to have a small particle size with appreciable surface roughness, while maximum consolidation of the extruded slurry is dependent on the particle morphology and subsequent packing efficiency\(^95\). The increased particle size and flake-like geometry of the 1hr/4wt% SPEX milled Ti-6Al-4V powder results in poor packing efficiency during consolidation, as well it would likely show poor slurry suspension characteristics because the smooth surface state of the commercial PREP Ti-6Al-4V is preserved after short milling times which will allow particles to settle in the SFF hopper. The large flake-like morphology may also cause clogging of the SFF extrusion nozzle due to tangling of the particles in the slurry, causing inconsistent geometrical control during printing and thus poor dimensional precision of the final component.

The refined particle size and increased surface roughness of the 4hr/4wt% SPEX milled Ti-6Al-4V powder on the other hand, reduces the mass of the individual particles and increases their surface area which will allow for better slurry preparation and consolidation. Because of an increased surface area, the 4hr/4wt% SPEX milled Ti-6Al-
4V powder will have a greater slurry surfactant interaction that will allow them to overcome the force of gravity that causes PREP Ti-6Al-4V particles to settle under the same surfactant concentration slurry conditions. Slurry extrusion will also be more reliable with the 4hr/4wt% SPEX milled Ti-6Al-4V powders because they have a spherical geometry with similar flow characteristics to the as received PREP Ti-6Al-4V powder, however the smaller particle size will allow them to be extruded through a smaller extrusion nozzle at a lower extrusion pressure for a greater green body packing efficiency. The use of a smaller extrusion nozzle and lower extrusion pressure allow for greater dimensional precision during printing of the FGM component, thus better net shape control and a surface condition more closely matching the natural biological structure required for FGM Ti-6Al-4V + HA femoral stem components is possible.

Relative density of a Ti-6Al-4V body is given by Equation (15),

\[
D_{relative} = \frac{M_{green}}{\frac{V_{green}}{4.45}}
\]  

(15)

where \( D \) is the density, \( M \) is the mass, and \( V \) is the volume, while the theoretical density of the alloy calculated previously from the rule of mixtures is 4.45 g/cm\(^3\). Area fraction determination of porosity in the sintered body for calculation of relative and absolute density requires the grayscale SEM image of the polished cross section of as sintered pellets to be analyzed using the ImageJ program functions as follows:

1) Click FILE → Open → filename.tif (open SEM image in ImageJ window)
2) Click Rectangular selections box
3) Click on image and drag open a box to select the area on the image from which to measure area fraction
4) Hold CTRL+SHIFT+X (Crop off scale bar, image details and irrelevant pixels)
5) Hold CTRL+SHIFT+S (Smooth image by removing blurry or outlier pixels)
6) Click Process → Find Edges (Trace edges of the features such as pores based on difference in contrast)
7) Click Process → Binary → Make Binary (Convert grayscale image to black and white image)
8) Click Process → Binary → Close- (Close any open loops in the binary image)
9) Click Process → Binary → Fill Holes (Fill closed loops in the binary image)
10) CTRL+M (Measure defined variables including area fraction of black pixels and displays data in Results window table)

A screenshot of the area fraction determination method is shown in Figure 6.19, with the corresponding step overlaid in red numbers on the image. Take note that the scale bar, image details, and image border are cropped from the image prior to area fraction measurement such that those pixels do not contribute to the measurement. Also note that during cutting to reveal the pellet cross section a low speed cutting lubricant composed of ~75% propylene glycol with the balance water is utilized to remove cut debris, cool the sample to prevent phase transformations during sample preparation, and cool the blade to prolong blade lifetime all while providing a smooth consistent surface for pore area fraction analysis. Because this protocol relies on image contrast on a pixel by pixel basis, only single phase materials with a consistent image contrast throughout can be analyzed accurately via this ImageJ pore area fraction method.

Initial RHS studies confirm that mass transport and particle coalescence are certainly impeded by oxidation during the sintering process if the sintering atmosphere is not carefully controlled. While the passivated layer on the surface of the PREP Ti-6Al-4V powder can be broken apart using the ball milling protocols established in the earlier stages of this project, high temperature oxidation of the 4hr/4wt% SPEX milled Ti-6Al-4V is an issue that continues to plague powder metallurgy fabrication. Because the RHS furnace utilized in this study is composed of an alumina tube with steel flanges for inert gas and vacuum connections, the sealing between these interfaces is not ideal (i.e. not vacuum tight). Although high temperature silicone o-rings are used to seal the steel
flanges using a compression type fitting, overtightening of the fitting can result in fracture of the alumina tube thus tightening is only done until the screws are finger tight. Even if the o-ring sealing is confirmed at room temperature prior to heating, continual evacuation of the tube during the heating, sintering, and cooling stages inevitably leads to some amount of oxygen exposure due to differential thermal expansion at the alumina tube-steel flange interface. Any oxygen that is drawn into the evacuated sample chamber will migrate to the Ti-6Al-4V pellet, especially at high temperature when the titanium has a high oxygen affinity in the BCC phase regime. If the SPEX milled particles become oxidized prior to particle coalescence then the oxide layer will effectively prevent intimate Ti-6Al-4V to Ti-6Al-4V particle contact, thus preventing sintering from proceeding to completion (i.e. 100% dense final product is not possible).

Comparison of Figure 5.28 and Figure 5.29 to Figure 5.32 and Figure 5.33 shows that SPEX ball milling does indeed provide for enhanced sintering capability due to the smaller particles and higher defect concentration of the SPEX milled powders compared to the commercial PREP powder. The smaller particles generated by 4hr/4wt% SPEX milling offer better packing during green body consolidation and offer shorter diffusion distances during sintering which allow for a higher final density when sintered at the same temperature as the PREP Ti-6Al-4V powder. Comparison of the SEM images in Figure 5.30 and Figure 5.31 to those in Figure 5.32 and Figure 5.33 show that the irregular morphology of the 1hr/4wt% SPEX milled Ti-6Al-4V particles result in poor packing and thus a lower density in the sintered body as compared to that of the 4hr/4wt% SPEX milled Ti-6Al-4V samples. Also evident from these images is that a higher sintering temperature of 1250°C results in a lower pore area fraction (i.e. higher density) than for samples sintered at 1100°C due to the greater thermal energy available for mass transport at the higher dwell temperature. From Table 5.6 it is clear
that sintering of 4hr/4wt% SPEX milled Ti-6Al-4V powders at or below 900°C does not result in any appreciable sintering because the relative density of those samples is not significantly greater than that of the initial green body. This is further evidenced by the lack of particle necking in the SEM images of those samples sintered at 900°C that show the rough surface state remaining on each of the discrete powder particles rather than a smooth surface state that is generated to lower the surface free energy of the particles during the early stages of sintering, see Figure 5.58.

The higher MWS dwell temperature of 1250°C results in a slightly higher density as compared to the 1100°C MWS sample, although both temperatures resulted in a large volume fraction of porosity in the outer regions of the pellet due to the nature of the heat generation responsible for mass transport. Heat generation in MWS is basically opposite to that of RHS, therefore the MWS process is capable of generating a highly dense core region but in general it lacks the ability to effectively generate a highly dense outer region. Design considerations of the sample geometry must include a significant machining tolerance (i.e. green component must be designed to have considerable excess volume by uniformly increasing the component dimensions) for MWS processed components at the cost of an extra processing step and a reduction in geometrical tolerance because machining of high hardness materials such as Ti-6Al-4V results in high wear rates of diamond tipped cutting tools and also uncontrolled brittle fracture which may ruin the geometrical tolerance of the final product. Excess volume for machining purposes is not necessary for RHS because the porosity is more uniform throughout the component.

For SPS processing, excess volume for machining purposes is not necessary because SPS has the added benefit of being a pressure assisted sintering technique wherein the heat generation is uniform throughout the workpiece and the applied
uniaxial pressure ensures uniform densification for the entire component. The uniaxial pressure preloading is indicated by the initial displacement prior to the onset of heating shown by a vertical jump in displacement below 100°C in Figure 5.37, which is merely a physical reduction in the volume of the sample due to particle rearrangement without atomic diffusion. The horizontal line that comes next refers to heating of the sample without displacement of the die punch, thus sintering has not yet occurred. The point at which the die punch displacement curve transitions from a horizontal line to an upward slope indicates the onset of pellet densification via atomic diffusion. In other words, the positive displacement of the punch indicates a reduction in sample height and thus a reduction in sample volume, which is the same as an increase in sample density because the sample mass remains constant throughout the heating. Once the die punch displacement reaches a final horizontal plateau, the sintering process is said to be fully completed because there is no additional reduction in volume with increasing temperature.

Examination of the 1000°C SPS processed Ti-6Al-4V samples show a very high, very uniform density throughout the pellet which indicates the possibility of a mechanically robust component that rivals traditional cast components. The “very low temperature” 600°C SPS processed Ti-6Al-4V sample exhibits a slightly lower density than those sintered at 1000°C, however there is clear evidence of significant densification (i.e. D>95%) at a temperature well below the threshold for the onset of detrimental reactionary products in Ti-6Al-4V + HA composites. Also note the dwell times associated with SPS processing which are mere minutes of heating as compared to the hours of heating required in RHS, MWS and/or casting techniques. Both MWS and SPS processing methods also offer the added benefit of no appreciable grain growth during sintering as seen in the grain size data in Table 5.4, which will allow for the retention of a
higher mechanical strength of the final component as compared to RHS and cast components which do show some extent of grain growth in the final processed state. Demonstration of a fully dense HA body via SPS is shown in Figure 5.43 for confirmation that SPS is capable of densification in insulating ceramic bodies, not just conductive metallic Ti-6Al-4V bodies which is important for co-sintering of Ti-6Al-4V + HA.

Composite Ti-6Al-4V + HA density evaluation yields drastically different results depending on the green pellet preparation and sintering technique used to co-sinter the sample. The motivation for using all three sintering techniques is simply due to the fact that the interaction of the composite powder mixtures with the specific sintering energy source (i.e. phonon energy in RHS, microwave energy in MWS, and intrinsic resistance joule heating in SPS respectively) is not known prior to experimentation. Consider the RHS processed composite pellet shown in Figure 5.44 which shows a great deal of cracking and porosity which is attributed to the formation of oxide and phosphate phases at elevated temperature. The different phases formed during heating and cooling undergo differential thermal expansion/contraction causing physical separation which results in a low density final product. Also apparent from preliminary RHS processing of composite pellets is the nonuniform distribution of Ti-6Al-4V and HA seen in Figure 5.45. The nonuniform phase distribution results in light and dark contrast regions throughout the sintered pellet which are attributed to Ti-6Al-4V rich regions and HA rich regions respectively.

The root cause of the phase separation is due to incomplete mixing of the constituent powders prior to green pellet pressing because of insufficient mixing time or insufficient mixing media present in the mixing container. Because the constituent powders have different specific gravity (i.e. different density) there needs to be some mixing media (i.e. stainless steel balls) present in the container to promote intimate
blending of the two materials. Without the presence of mixing media during blending the lower specific gravity HA (i.e. 3.16 g/cm$^3$ based on rule of mixtures calculation) will simply migrate to the surface of the powder charge while the higher specific gravity Ti-6Al-4V (i.e. 4.45 g/cm$^3$ based on rule of mixtures calculation) will settle to the bottom of the container with prolonged tumbling. In the case of RHS composite samples the mixing was done for only 30 minutes without the use of any mixing media and thus the sintered sample is not homogeneous.

Recognition of the Ti-6Al-4V + HA mixing issues after RHS processing allowed for changes in the composite powder preparation for MWS and SPS studies including the use a 2 hour mixing time with the application of a 10:1 mixing media charge ratio rather than no media at all. While the composite mixture is prepared as a homogenous blend for MWS and SPS studies, the MWS process does not result in a solid final product whereas the SPS process results in a fully dense final product. The MWS processed pellets crumble when handled and are therefore not analyzed for density calculation due to either a high temperature reaction between Ti-6Al-4V and HA or an unknown issue attributed to the microwave interaction with a composite powder compact.

The SPS processed composite Ti-6Al-4V + HA pellets are capable of being prepared for imaging by grinding and polishing which results in the images that appear in Figure 5.46 and Figure 5.47. The contrast that exists in Figure 5.46 and Figure 5.47 appears to be porosity or cracks based on the contrast seen in the pure Ti-6Al-4V sintering analysis. Examination of the SPS profile in Figure 5.37 however suggests that the bodies are fully dense after sintering because the displacement curve reaches a plateau prior to termination of the heating. Therefore it is concluded that the contrast seen in Figure 5.46 and Figure 5.47 is actually phase contrast between the Ti-6Al-4V
and HA rich regions of the pellet where the Ti-6Al-4V appears lighter than the HA due to Ti-6Al-4V's higher atomic mass (i.e. also known as Z-contrast). Confirmation of Z-contrast is done by evaluating the area fraction of light and dark regions in Figure 5.46 using ImageJ analysis which shows the light regions (i.e. Ti-6Al-4V) to be ~90% and the dark regions (i.e. HA) ~10% of the sample surface area. Likewise in Figure 5.47 the light region is shown to be ~75% and the dark region ~25% of the surface area which again matches the composition of the pellet as given in the caption below the image.

Evaluation of all the sintering conditions from the data in Table 5.5 clearly indicates that SPS is the best method for production of mechanically robust, fully dense components for load bearing applications.

Results from the high energy SPEX milling process can be assessed in terms of their impact on the overall sintering kinetics as a function of the powder condition. A reduction in the average particle diameter from the high energy SPEX milling process results in a substantial reduction in sintering time required for the production of a fully dense final product as shown by the relationship in Equation (16),

\[ x \propto \sqrt{Dt} \quad (16) \]

where \( x \) is the diffusion distance, \( D \) is the diffusion coefficient of the transporting species, and \( t \) is time\(^6\). As per the average particle diameter values listed in Table 5.1, a reduction in particle diameter \( x \) from 110 µm in the commercial PREP Ti-6Al-4V powder to 25 µm in the 4hr/4wt% SPEX milled Ti-6Al-4V powder leads to a reduction in the sintering time by a factor of more than 19. Consequently, the dwell time at a constant temperature required for producing a fully dense body is reduced accordingly. In terms of a manufacturing process this reduction in dwell time leads to higher production rates
and lower economic cost associated with furnace energy consumption per production cycle.

An increase in the overall defect density as a result of high energy SPEX milling is evidenced by an increase in the peak breadth of both low angle and high angle Ti-6Al-4V reflections in the XRD spectra obtained for the 4hr/4wt% SPEX milled Ti-6Al-4V powder in Figure 5.17. The increase in low angle peak breadth indicates the formation of nanograins within micron sized particles, while the increase in high angle peak breadth is attributed to an increase in defect density which has caused the pristine unit cell lattice to expand in order to accommodate interstitial and/or vacancy point defects generated by repeated collisions in the milling vial. When point defects aggregate they form a two dimensional defect known as a dislocation. As the dislocation density increases with increasing milling time, new low angle grain boundaries are formed as single crystal subgrains disintegrate until the dislocation pileup traverses a grain completely and two new grains are formed from what was originally one larger grain.

The creation of a large volume fraction of grain boundaries causes a shift from kinetics that are limited by lattice based diffusion to kinetics that are now limited by grain boundary based diffusion. Because the diffusion coefficient through the bulk lattice of a material is typically two to three orders of magnitude lower than that of the diffusion coefficient of species along a grain boundary, the sintering thermodynamic capability has been altered accordingly. As the grain boundary area fraction continues to increase during the ball milling process, the extent of the shift from lattice diffusion to grain boundary diffusion control is increased such that nearly all atomic transport from the bulk to the interparticle neck region is done through grain boundary pathways rather than through a point by point atomic lattice site jumping mechanism. The higher entropic energy of the disordered grain boundary area as compared to the highly ordered low
entropic energy bulk lattice results in higher atomic mobility at a lower temperature within the grain boundaries based on the driving force of a reduction in the overall Gibbs free energy of the system according to Equation (8).

6.3. Sintering activation energy analysis

Density evaluation of the 4hr/4wt% SPEX milled Ti-6A-4V sintering activation energy samples show bodies that are less than desirable as load bearing structures because they have not reached the high relative density that earlier RHS, MWS, and SPS processing samples were able to achieve. Evidence of this error is seen if the data in Table 5.6 is compared to the data in Table 5.5. Appearance of adverse reactionary products that change the densification and mass transport phenomena in an unintended fashion is confirmed by the formation of prismatic particles seen in Figure 5.63. The geometry of the triangular and pyramidal secondary phases is similar to the carbide phase formation shown by Zhong et al. The appearance of additional peaks in the XRD spectra of the sintering activation energy samples, shown in Figure 5.64, can be used to explain the troubling trends in the results which make quantification of the diffusion activation energy value nearly impossible. Examination of the XRD spectra seen in Figure 5.64(c) that accompanies the SEM image seen in Figure 5.63 confirms the formation of titanium carbide after sintering of 4hr/4wt% SPEX milled Ti-6Al-4V. Further scrutinizing of the XRD spectra shown in Figure 5.64 appears to indicate a possible phase change as a function of sintering quench temperature; however comparison to the spectra shown in Figure 6.20 indicates that the peak evolution is a natural progression for α-phase titanium quenched from the high temperature state due to thermal expansion and crystallization effects. This results in the peaks shifting to a lower angle, and also
results in clear demarcation of individual peaks that were previously convoluted due to
grain boundary scattering in the SPEX milled powder or annealed (i.e. slow cooling from
high temperature to room temperature) state.

The possible sources of contamination during the various stages of activation
energy sample processing, as well as comments to refute/support those claims, include
but may not be limited to the following. During ball milling there may be some small
concentration of oxygen trapped in the milling container during powder loading due to
poor atmosphere control in the glove box. However this can be ruled out if one considers
that the glove box atmosphere is repeatedly evacuated and backfilled with UHP argon,
as well oxygen sensing tablets inside glove box were never reacted thus there is no
indication of oxygen present during powder loading. During ball milling there may be
some oxygen introduced in the Ti-6Al-4V powder charge from the ambient atmosphere
due to leaking of the milling container o-ring seal. However this can be ruled out
because during SPEX milling the threaded lid remains secure and tight for all
experiments due to the nature of the clamping within the SPEX apparatus. During ball
milling iron wear debris may be introduced into the powder charge due to repeated ball
and vial wall collisions. However this can be ruled out because there is no evidence of
iron in the SPEX milled powder XRD spectra. During ball milling free carbon may be
introduced from decomposition of stearic acid followed by inclusion during fracture and
cold welding of the Ti-6Al-4V powder particles. This source of error is the most likely
cause of titanium carbide formation after high temperature sintering of the Ti-6Al-4V
activation energy samples.

The possible sources of contamination during pellet pressing include oxygen
trapped in the internal pores of the green body during uniaxial pressing which is done in
the ambient atmosphere. However gaseous oxygen should be drawn out of the green
body because a vacuum of <12 mtor is attained prior to sealing for in house processing. During pressing there may be carbon introduced due to residue on the uniaxial pressing die from the hydrocarbon oil which is used to prevent oxidation/corrosion of the die when not in use. However this should not be a factor because the die is thoroughly rinsed with acetone prior to powder loading and pressing. During pressing there may be iron contamination from frictional wear debris generated within the pellet pressing die. However this should not result in iron contamination within the interior of the green body nor should the surface experience much of an effect because the die is clean, smooth, and has a tight punch/wall die tolerance maintained by methodical cleaning between pressing of each new pellet and because iron oxide formation is suppressed between uses by coating with hydrocarbon oil thus no contamination is expected from the die itself.

During pellet sealing there may be oxygen remaining inside the quartz tube due to less than ideal evacuation of the tube. However because the tube is only sealed when thermocouple pressure gauge reads less than 12 mtor, the oxygen concentration inside tube should be less than 3.3 ppm\textsuperscript{100} unless leaking occurs. If leaking occurs it is immediately known because vacuum gauge pressure increases rapidly and the pumping creates a whistling sound as air is being drawn through a small pinhole in the tube, thus the sample is not sintered at all but rather discarded as waste. During pellet sealing there may be silica contamination from the quartz wool insulation that is used to protect the Ti-6Al-4V pellet from heat exposure from the oxy-propane torch during sealing. However the melting temperature of quartz is greater than that of the Ti-6Al-4V pellet thus decomposition is not likely while the Ti-6Al-4V remains intact as a solid pellet. During pellet sealing there may also be silica contamination from decomposition of the quartz tube due to overheating with the oxy-propane torch during sealing. However this
is unlikely because even if silica decomposition into a gaseous species does occur, that contamination should be drawn off by the evacuation process. During pellet sealing there could be tantalum contamination due to decomposition of the oxygen getter foil. However this is only possible if the Ti-6Al-4V pellet itself shows signs of melting or decomposition because tantalum has a melting point and a boiling point of 3017°C and 5458°C\textsuperscript{101} respectively, which are both well above the oxy-propane torch temperature capability.

The possible contamination sources during sintering of Ti-6Al-4V include oxygen from the sintering environment. However this issue is avoided in earlier RHS experiments when sealed at the same <12 mtor vacuum pressure with the use of a tantalum foil getter, thus it is not likely in activation energy study samples which are prepared with the same sealing method. During sintering there may be carbon introduced from the RHS sintering tube from residue left behind by previous samples processed in the same tube. However any residue in the furnace tube should not interact with the quartz tube sealed sample because carbon would have to diffuse through the silica glass to gain access to the Ti-6Al-4V pellet.

During quenching of the pellet there may be oxidation resulting from the quenching media which is a tap water bath. However the pellets have already undergone significant sintering such that only closed internal pores are present in most samples thus water will not penetrate to the interior of the pellet. Therefore oxidation is limited to the immediate surface regions that are in contact with the aqueous environment and should not be present in the internal cross section.

During sample preparation for characterization there may be carbon introduced from the low speed cutting fluid used to cross section the sintered pellets. However this process is done at ambient conditions such that the temperature during cutting is far too
low to induce a reaction between Ti-6Al-4V and free carbon in the hydrocarbon fluid. There may be carbon contamination from sample handling with bare hands. However because this too is done in ambient conditions there is no expectation of a reaction between Ti-6Al-4V and carbon at 23°C.

While the activation energy study is expected to yield quantitative evidence for the change in sintering thermodynamics, there are a few interesting qualitative phenomenon to note immediately from the SEM evaluation of the sintered pellets. First, many of the activation energy sintered Ti-6Al-4V pellets cause the SEM sample chamber vacuum to take a significantly longer time than expected to pump down prior to turning on the imaging electron beam. This is most likely due to outgassing of the sample upon insertion in the SEM chamber however the source of the outgassing is quite ambiguous. There are a number of possible sources of the outgassing with one possible cause related to the tube-like features seen in the SEM images shown in Figure 6.21 and Figure 6.22. The geometry of the tube-like features and their location within the internal closed pores of many Ti-6Al-4V activation energy sintered pellets indicates that the features synthesize during the sintering process and remain without decomposing during the grinding, polishing and ultrasonic cleaning processes. While imaging the tube-like features there is charging on the surface of the tubes, indicating that they are some insulating oxide phase rather than a conducting metallic feature.

Further analysis results in the EDS spectra shown in Figure 6.23 which consists of dominant peaks that are of titanium (Ti) and aluminum (Al) signature, while analysis of the tube-like feature itself results in the EDS spectra shown in Figure 6.24 which consists of dominant peaks that are of oxygen (O), carbon (C), and sodium (Na) signature. The root source of such a feature has not been identified to date, however because the Ti-6Al-4V PREP starting powder is highly pure and very stable at room
temperature, see the TGA profile in Figure 6.25, the contaminant must have reacted with something in the 4hr/4wt% SPEX milled powder at elevated temperature during sintering. The TGA profile indicates that there is no decomposition of the Ti-6Al-4V itself during heating, but rather a weight gain most likely attributed to oxidation at elevated temperature which causes the profile to trend upward, thus the tube-like feature is undoubtedly attributed to an external source of contamination.

Of the samples processed for activation energy studies, only the 900°C sintered pellets are treated entirely in the alpha phase and thus there is negligible sintering achieved after heating to the desired quench temperature. For all other sintering conditions the pellet will undergo the alpha to beta phase transformation, which occurs at 980°C, resulting in a reduction in both lattice diffusion activation energy and grain boundary diffusion activation energy with no change to the atomic volume\textsuperscript{102}. The reduction in activation energy from the HCP phase to the BCC phase occurs because of the larger interstitial site in the BCC lattice that can accommodate movement of the Ti chemical species with a lower energy input. Increased Ti atomic mobility through the BCC lattice as compared to Ti mobility in the more restrictive HCP lattice leads to an improvement in sintering kinetics. Therefore, sintering of Ti-6Al-4V in the beta phase results in a reduction in the sintering time required to produce a fully dense component independent of the thermal energy available for increased atomic vibration amplitude based mobility.

Due to the large area fraction of grain boundaries in the nanostructured 4hr/4wt% SPEX milled Ti-6Al-4V powders used for the activation energy study, it is expected that the atomic transport will proceed by a grain boundary diffusion limiting mechanism. The relative density from SEM analysis for each of the activation energy samples is plotted as a function of both constant heating rate and quench temperature to determine if a
single dominant diffusion mechanism is responsible for consolidation and pore elimination in the 4hr/4wt% SPEX milled Ti-6Al-4V pellets. If a singular mechanism is dominant then a master sintering curve (MSC) can be generated to describe the rate limiting diffusion mechanism which is independent of the heating profile and grain growth at elevated temperature. This relationship is described using Equation (17)

$$
\phi(\rho) = \theta(t, T(t)) = \int_0^t \exp \left( \frac{-Q}{RT} \right) dt
$$

(17)

where $Q$ is the apparent activation energy for sintering, $R$ is the gas constant, $T$ is the absolute temperature, and $t$ is the time\textsuperscript{66}. This method is useful for generating a standard sintering curve that can be used to predict the final sintered density of a material for any sintering time-temperature conditions. The MSC is generated by iteratively choosing values above and below the value for activation energy, $Q$, given in the literature for grain boundary self diffusion in titanium until all three heating rate curves lie on the same best fit line. The chosen value for $Q$ is inserted into Equation (17) and the resulting value of $\theta$ is then plotted vs. the relative density ($\rho$) values obtained for each constant heating rate (e.g. 4, 8, and 16°C/min). The process is repeated by iteration of $Q$ above and below the value given in the literature until all three constant heating rate $\rho$ vs. $\theta$ master sintering curves converge to a single curve (i.e. the equation used to describe the best fit line of all three constant heating rate curves is simultaneously correct for all three). The value given in the literature for grain boundary self diffusion in $\alpha$-titanium is $Q = 187$ kJ/mol\textsuperscript{103}, which is a reasonable approximation considering Ti-6Al-4V is 90% $\alpha$-titanium thus this value is used as the starting point for iteration.

Application of the method described by Shao et al. is shown in the plots that appear in Figure 5.66, where the plots corresponding to $Q = 25$ kJ/mol, $Q = 500$kJ/mol
and $Q = 125 \text{ kJ/mol}$ show differences in statistical deviation from a singular best fit curve. It can be seen through visual analysis of the plots that the lowest value of 25 kJ/mol inserted for $Q$ into Equation (17) results in the data from each of the three heating rates being described by drastically different best fit lines. Visual inspection of the highest value of 500 kJ/mol inserted for $Q$ into Equation (17) shows that there is still some deviation in the data from a singular best fit line which is indicated by the gap between the 4C/min and 8C/min data points. Although the value of 125 kJ/mol inserted for $Q$ into Equation (17) does not result in all the data points converging to an identical best fit line, the data does converge to the best possible match for all values of $Q$ attempted in this study. Therefore even though there is a source of significant error (i.e. 8C/min heating rate data points should lie between the 4C/min and 16C/min data points, but due to experimental error and/or contamination they do not) the MSC analysis described by Shao et al. seems to indicate that the 4hr/4wt% SPEX milled Ti-6Al-4V activation energy has been reduced from $\sim 187 \text{ kJ/mol}$ to $\sim 125 \text{ kJ/mol}$ due to the generation of a high defect concentration and a large grain boundary area fraction in the ball milled powder. Although the absolute value for grain boundary activation energy is difficult to ensure due to unintended carbide formation, this method certainly provides a basis for the enhancement in sintering efficiency of the 4hr/4wt% SPEX milled Ti-6Al-4V as compared to the as received PREP Ti-6Al-4V powder which likely exhibits some sintering activation energy value close to that of the value given for bulk $\alpha$-titanium.

Additional analysis of the activation energy was attempted using the method described by Pouchly et al. wherein computer software was provided to do the iteration and best fit curve determination for values of $Q_{\text{sinter}}$ automatically. The plots that appear in Figure 5.67 show the Density MSC calculation for $Q = 300 \text{ kJ/mol}$ and $Q = 130 \text{ kJ/mol}$ respectively, wherein the lowest value of criterium for $Q = 130 \text{ kJ/mol}$ is less than that of
Q = 300 kJ/mol which indicates a curve fitting that is more accurate. Also visual inspection of the value of criterium curve shown to the right indicates that there is no minimum in the mean of residuals for Q = 300 kJ/mol while there does appear to be a minimum in the mean of residuals for Q = 130 kJ/mol which also indicates that the 130 kJ/mol value is likely more accurate given the relative density values obtained from in house activation energy sintering studies. The value obtained from the method described by Pouchly et al. closely matches the best fit value obtained from the method described by Shao et al., thus a sintering activation energy for the 4hr/4wt% SPEX milled Ti-6Al-4V powder is likely in the ~130 kJ/mol range, which is substantially lower than the ~187 kJ/mol value reported in the literature.

Dilatometer measurements during sintering were intended to reveal that the 4hr/4wt% SPEX milled Ti-6Al-4V powder is more suitable for lower temperature densification than the as received PREP Ti-6Al-4V powder according to the shrinkage curves obtained at IIT, however issues related to oxidation of the sample prior to full densification lead to poor results during activation energy calculation. Thermal expansion of the alumina dilatometer rod is subtracted from the raw data prior to plotting of the shrinkage curve as a function of temperature, however none of the samples reach full theoretical density even when heated to temperatures greater than 1300°C, whereas prior RHS sintering results show greater than 99% relative density when sintered at 1250°C. The only discernible difference is the sintering atmosphere which is regulated by sealing pellets under vacuum in quartz tubing for RHS experiments while the dilatometer experiments merely utilize evacuation of the tube furnace itself, thus leakage leading to oxidation of the sample is the likely culprit of less than optimal results.
Plots of shrinkage as a function of temperature and relative density as a function of temperature are shown in Figure 5.68. Conversion of the shrinkage curve to a relative density curve is done using Equation (18)

$$\rho = \frac{\rho_G}{\left(1 - \frac{\Delta L}{L_0}\right)^2} \times \frac{1}{\rho_0} \tag{18}$$

where $\rho_G$ is the green density (i.e. 58% or 2.581 g/cm$^3$), $\Delta L/L_0$ is the shrinkage, and $\rho_0$ is the theoretical density (i.e. 4.45 g/cm$^3$). The MSC method described by Shao et al. is applied to determine the average $Q_{\text{sinter}}$ as described previously using the dilatometer data which is calculated to be $\sim 440$ kJ/mol as seen in Figure 5.69. Inspection of the Density MSC screen grabs shown in Figure 5.70 indicate that the interpretation from the method outlined by Shao et al. is correct because the software provided by Pouchly et al. also leads to $Q = 440$ kJ/mol.

Additionally the CHR method is applied using Equation (19) and Equation (20)

$$\dot{\rho} = \frac{d\rho}{dT} = \frac{dp}{dT} \dot{T} \tag{19}$$

$$\ln \left(T \frac{d\rho}{dT} \right) = \frac{-Q}{RT} + \ln[f(\rho)] + \ln A + n \ln d \tag{20}$$

where $\rho$ is the density, $T$ is temperature, $\dot{\rho}$ is the instantaneous rate of densification, $\dot{T}$ is the heating rate during sintering, $Q$ is the activation energy, $R$ is the gas constant, $f(\rho)$ is a function only of density, $A$ is a material parameter that is insensitive to grain size, $n$ is the grain size power law exponent, and $d$ is the grain size. Analysis of the plots generated from this method are shown in Figure 5.71, wherein the CHR method results in an average value for activation energy over all temperatures of $Q = 383 \pm 60$ kJ/mol.
which is close to the values obtained from the MSC method described by both Shao et al. and Pouchly et al. If the analysis is done so as to determine the change in sintering activation energy at different stages of densification where $\rho = 0.65, \rho = 0.70, \rho = 0.75, \rho = 0.80, \rho = 0.85$, the corresponding values are $Q = 300$ kJ/mol, $Q = 97$ kJ/mol, $Q = 187$ kJ/mol, $Q = 9700$ kJ/mol, and $Q = 156$ kJ/mol respectively. Therefore the CHR method is useful for identifying the change in sintering activation energy as it corresponds to a change from grain boundary controlled diffusion during the early stages of densification to lattice controlled diffusion during the later stage of densification. Physically this can be described by the large interconnected pore volume fraction present during the early and intermediate sintering stages where a large fraction of grain boundary pipelines exist for atomic transport in 3-dimensions which leads to grain boundary diffusion rate limiting kinetics. During the later stages of sintering the pellet has only small isolated pores remaining, thus densification becomes dominated by lattice diffusion rate limiting kinetics through the bulk.

6.4. Mechanical property analysis

Preliminary mechanical property testing was conducted to obtain an assessment of the expected mechanical performance of a component fabricated using the powder processing and sintering methodology established in this study. Alpha-beta type alloys such as Ti-6Al-4V have a particular advantage over single phase alloys or pure metals in that they offer an elastic modulus which more closely matches that of natural skeletal structures. The lower elastic modulus and considerable corrosion resistance in body fluid environments lead to Ti-6Al-4V being the material of choice for composite orthopedic implant studies. Specifically for Ti-6Al-4V the alpha phase has the hexagonal close-
packed (HCP) crystal structure while the beta phase is a body centered cubic (BCC) crystal structure. The BCC beta phase has a lower modulus of elasticity than that of the HCP alpha phase because hexagonal close-packed crystals contain only 12 distinct slip systems while body centered cubic crystals contain up to 48 distinct slip systems\textsuperscript{104}. Because of the greater number of possible slip planes and slip directions in the beta phase, the alpha-beta Ti-6Al-4V alloy has a lower modulus of elasticity than the pure alpha titanium due to the fact that more dislocation slip systems are likely to be aligned with the direction of the applied load (i.e. pure titanium has a higher critical resolved shear stress than alpha-beta Ti-6Al-4V\textsuperscript{105}).

The mechanical properties of discrete Ti-6Al-4V particles are not directly measured due to the size scale difference between the ball milled powder particles and the mechanical testing instrumentation available for this study. Another reason to bypass the mechanical properties of an individual powder particle is that the bulk mechanical properties of a component fabricated using a powder metallurgy process will be limited by the interparticle bond strength rather than by the inherent strength related to the interatomic forces within the Ti-6Al-4V chemical species, thus the bulk mechanical strength of the macroscopic component after sintering are more relevant.

Vickers hardness testing yields a clear trend between the mechanical properties of the sintered pellet and the corresponding sintering conditions. Because hardness is a measure the material resistance to penetration deformation under an applied load, this test reveals a property that can be used to quickly compare different material classes while providing some qualitative quality control analysis with limited component damage. The Vickers hardness (VHN) is calculated using Equation (21),

\begin{equation}
VHN = \frac{1.72P}{L^2} \times 100
\end{equation}
where $P$ is the applied load and $L$ is the length of the indenter impression diagonal, which is measured using an optical microscope that is part of the Vickers test instrument\textsuperscript{105}. Hardness testing in general requires flat parallel surfaces to prevent sample rocking or sliding of the indenter tip across the sample surface which will result in a misleading hardness value that is lower than the true strength of the sample.

Examination of the data presented in Figure 5.68 reveals that hardness values for the RHS processed activation energy samples increase with increasing sintering temperature due to an increase in relative density of the pellet. As the relative density increases (i.e. inverse of reduction in porosity) with sintering temperature a larger cross sectional area to carry the applied load is established and thus the hardness increases. With increasing sintering temperature also comes a reduction in the number of stress concentration sites (i.e. void elimination) and a change in the geometry of the stress concentration sites (i.e. from sharp crack tips to rounded spherical pores) and thus the hardness increases. The trend of increasing hardness value with increasing processing temperature in RHS is somewhat counterintuitive because in general a material will generally become softer with increasing processing temperature due to grain growth effects which reduce the number of dislocation blocking grain boundary areas through annealing. As the grain size increases with increasing processing temperature the number of grain boundaries decreases and the distance between grain boundaries increases, thus dislocation movement is less restricted as compared to materials with a smaller average grain size. Because the RHS powder metallurgy sintering by definition is a processing method conducted entirely in the solid phase, there are no melting and recrystallization effects, thus the trend of increasing hardness with increasing sintering temperature is less affected by grain size and more reliant on the increase in load.
bearing cross sectional area and the change in pore/crack geometry as described in the
sintering effects section of this report.

The trend of decreasing hardness with increasing temperature predicted by grain
growth effects is however witness in the SPS samples which were processed at 600°C
and 1000°C respectively because the SPS heating mechanism may actually result in
localized melting and recrystallization at the interparticle neck region due to the extreme
concentration of electrical current at the contact point between particles in the powder
compact. The SPS SPEX 600°C sample has a higher hardness than the SPS SPEX
1000°C sample due to the fact that the Ti-6Al-4V pellet experiences more grain growth
at 1000°C as compared to that experienced at 600°C. The grain size effect is also well
pronounced by the difference in hardness shown between the commercial PREP Ti-6Al-
4V and 4hr/4wt% SPEX milled powders which were sintered using the SPS as shown in
Figure 5.68. The 4hr/4wt% SPEX milled Ti-6Al-4V SPS 1000°C shows a higher
hardness than the commercial PREP Ti-6Al-4V SPS 1000°C sample due to the smaller
starting grain size in the SPEX powder. The 4hr/4wt% SPEX milled Ti-6Al-4V feedstock
contains powder particles with many more grain boundaries and thus a much smaller
average grain size as compared to the as received commercial PREP Ti-6Al-4V due to
the defect concentration established by high energy ball milling, a trend that is
maintained after sintering as well. The trend witnessed for the MWS samples is unique
in that the hardness seems to be independent of the sintering temperature, indicating
that the MWS process does not result in appreciable grain growth during heating. This
phenomenon could be exploited in future studies now that the trend has been
established.

From the preliminary compression testing results a few details about the alpha-
beta nature of the Ti-6Al-4V alloy as compared to the single phase nature of pure
titanium materials are revealed. The Ti-6Al-4V alloy contains vanadium as a beta phase stabilizer which allows for better cold working properties at room temperature (i.e. allows for easier forming of the final component geometry), but it also contains aluminum as an alpha phase stabilizer which allows for higher component strength at room temperature. Therefore Ti-6Al-4V has the beneficial properties of a two phase composition that allow it to be utilized in load bearing structures. Uniaxial compression testing requires lubrication of the upper and lower surfaces of the test specimen to allow for radial expansion of the test specimen as it is reduced along its vertical axis. Based on a conservation of volume during plastic deformation, the sample must expand in the orthogonal direction(s) to the loading axis according to the Poisson’s ratio for Ti-6Al-4V. A majority of the applied load will be distributed along a 45° angle through the test specimen as shown in Figure 6.26 thus the lubrication is key to preventing barreling of the sample which skews the mechanical property measurement erroneously. Therefore constraint based strengthening effects due to friction can be considered negligible if the test setup is done properly.

The load versus position plot obtained in the mechanical testing software is converted to a stress versus strain plot using the relationships in Equation (22) and (23) respectively,

\[ \sigma = \frac{P}{A} \]  \hspace{1cm} (22)
\[ \varepsilon = \frac{l_f - l_0}{l_0} \]  \hspace{1cm} (23)

where \( \sigma \) is the stress, \( P \) is the applied load, \( A \) is the cross sectional area, \( \varepsilon \) is the strain, \( l_f \) is the final specimen length, and \( l_0 \) is the initial specimen length\(^{105}\). The stress-strain
curve obtained therein can be analyzed to determine the yield strength (i.e. maximum point on the stress-strain curve) and the elastic modulus (i.e. the linear portion of the stress-stress curve prior to yielding) of the 4hr/4wt% SPEX milled Ti-6Al-4V pellet.

Compression testing results indicate that the extent of sintering of 4hr/4wt% SPEX Ti-6Al-4V bodies at 1250°C is considerable because the pellet remained intact even after the maximum load of the test instrument (e.g. 12,000 lbs, 53379 N) is reached. The sintered Ti-6Al-4V pellet has a cross sectional area of 1.075x10^{-5} m^2, which means that if the load limit of the instrument is reached the pellet must be capable of withstanding a stress greater than ~5000 MPa without catastrophic failure. After inspection of the pellet it is apparent that the pellet has actually cracked, but the crack does not traverse the entire thickness because the two halves remain together as a single pellet. Although the absolute compressive yield strength cannot be determined from this experiment because the stress vs. strain plot does not exhibit a yield point, the elastic modulus of the sample can be determined by fitting the linear elastic portion of the stress vs. strain curve that appears in Figure 5.70. The value obtained from the slope of the elastic region is ~42 GPa, which is lower than the elastic modulus value available for cast Ti-6Al-4V components given in literature, but it is very close to that of natural human cortical bone thus powder metallurgy fabrication of Ti-6Al-4V femoral stem components has great potential for avoiding the stress shielding phenomenon.

While mechanical properties of composite Ti-6Al-4V + HA bodies are not measured directly through tensile, compressive, or 3-point bend testing there are a few conclusions that can be drawn from the underlying microstructure. The Hall-Petch relationship is used to quantify material hardness and thus predict material toughness based on grain boundary strengthening. As a material is work hardened or grain refined through processing, the dislocation density (i.e. grain boundary area) increases such
that future dislocation movement is stymied. Dislocation glide is obstructed when the line defects become entangled within the interior of a grain or when they pileup at the grain boundary because the energy barrier to traverse the highly disordered boundary regions is substantial. By preventing further dislocation propagation, slip failure under an applied stress is effectively blocked. Slip mitigation leads to a greater mechanical strength up to the point at which a critical defect concentration at the grain boundary is reached. At this time the dislocation will expend energy to assume glide on the slip system of a neighboring grain. As the crack propagates the applied load is now being carried by an increasingly smaller cross sectional area such that the applied stress is increasingly larger within the material. This progression inevitably leads to catastrophic failure, thus the mechanical properties of composite Ti-6Al-4V + HA bodies can be predicted based on the mechanical property evaluation of the load bearing metallic phase conducted in this study using the relationship between yield strength and grain size as shown in Equation (24),

$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{D}}$$

(24)

where $\sigma_y$ is the yield stress, $\sigma_0$ is the critical stress for dislocation movement in the material, $k_y$ is the strengthening coefficient of the material, and $D$ is the average grain diameter\textsuperscript{105}. As $D$ becomes smaller, the predicted mechanical strength becomes larger, which is a result exploited by high energy SPEX ball milling and low temperature sintering of Ti-6Al-4V.

Commercially available Ti-6Al-4V sheet metal produced via casting shows a grain size 6 µm of in the as received state. The grain size of the as received PREP
powder is 3.5 µm, while the grain size of the 4hr/4wt% SPEX milled Ti-6Al-4V has been reduced to 1 µm. The grain size reduction witnessed in the 4hr/4wt% SPEX milled Ti-6Al-4V powder leads to an increase in the predicted mechanical strength of a component by a factor of ~2.5 when compared to as cast components and by a factor of ~1.9 when compared to commercial PREP powder fabricated components based solely on the difference in grain size. When the Ti-6Al-4V sheet metal is subjected to 1250°C for 2 hours, (i.e. the temperature and dwell time used for sintering of Ti-6Al-4V powder compacts) the grain size increases to 750 µm due to recrystallization and annealing of casting defects. Grain growth at elevated temperature is inevitable during sintering of the powder compacts however the extent of the grain growth is not as significant for powder metallurgy processed samples because of the smaller starting grain size in the SPEX milled powder feedstocks as compared to the as cast feedstock, and because the sintering process only reaches about <90% of the melting temperature as compared to casting processes which by definition take place completely in the liquid phase. Both the as received and thermally etched commercial sheet metal samples show a much larger average grain diameter than that of the commercial PREP and SPEX milled powders indicating that the yield strength of the SPEX powder sintered bodies should exceed that of an as cast component if the powder sintering process is carried out to completion.

In order to further increase the mechanical strength of a sintered component hot isostatic pressing (HIP) can be applied to the sintered component to achieve full density and maximum component strength. The HIP process uses isostatic gas pressure applied at high temperature to promote internal closed micropore elimination necessary to achieve the final 1-3% in relative density. Realization of a component with full theoretical density will inevitably lead to mechanical properties that are far superior to those with even a single flaw present in the component, thus for applications with extreme
requirements the HIP process is almost always applied. The HIP process can certainly improve the final mechanical properties but it is done so at the high cost required to heat the component to greater than 90% of its melting temperature while simultaneously pumping inert gas into the furnace chamber. The high pressure condition surrounding the sample establishes the pressure gradient between the internal pores and the external atmosphere responsible for the driving force necessary to complete the densification process. Both the electrical energy and compressed gas cylinders consumed during the HIP process are not negligible, thus careful consideration of the benefits to the mechanical properties versus the drawbacks of a higher cost manufacturing process must be analyzed.
7. Future Considerations

7.1. Mechanical & biological properties of Ti-6Al-4V + HA composite

Using the insight gained from SPEX powder processing and SPS of Ti-6Al-4V, preparation of FGM composite Ti-6Al-4V + HA components are possible. While there is still a great deal of work to be done concerning optimization of the powder processing and sintering parameters (i.e. eliminate contamination during ball milling, further reduce particle size, further increase grain boundary area and defect volume, minimize SPS sintering temperature/pressure/dwell time) necessary to produce a fully dense and compositionally pure FGM composite Ti-6Al-4V + HA component, we can address the future considerations of such a composite for femoral stem applications. In order to produce the FGM component via an SFF process the preparation of stable Ti-6Al-4V and HA slurries is necessary including optimization of the solid powder loading, effective dispersion of the particles through proper surfactant concentration and pH, and proper Ti-6Al-4V and HA slurry mixing just prior to extrusion. Likewise the SFF extrusion parameters to be optimized include extrusion nozzle size selection for proper slurry flow and optimal surface roughness of the final implant component, extrusion pressure control for uniform and continuous slurry delivery, and extrusion nozzle lateral velocity control for proper layer-by-layer thickness and wetting, see Figure 7.1. Also the SFF extrusion software must be modified to account for compositional changes within each 2-dimensional layer of the printing process in order to produce compositional changes in 3-dimensions for proper FGM component construction.

After a FGM composite Ti-6Al-4V + HA hip stem is fabricated through a layer-by-layer 3-D printing technique, the component must be made into a functional mechanical
component with proper geometric retention via a low pressure or pressureless SPS technique. If a FGM composite Ti-6Al-4V + HA hip stem with adequate geometric net shape control has been demonstrated the mechanical and biological properties of that component must be quantified to determine the structural integrity and biological surface activity as compared to properties witnessed in traditional metallic components with a thin bioceramic coating. Careful consideration of the inverse relationship between mechanical and biological properties in composite FGM components must be carefully balanced to ensure long term functionality for the end user.

Mechanical property evaluation of Ti-6Al-4V + HA composites should focus on compressive strength, flexural strength, tensile strength, fatigue strength, torsional strength, and elastic modulus determination. A universal mechanical test instrument should be utilized to perform uniaxial compression testing, three point bend testing, uniaxial tensile testing, compression-compression dynamic cyclical testing, and torsion testing. Also a universal hardness tester should be utilized to measure hardness as a function of radial position from the core to the surface of the FGM composite Ti-6Al-4V + HA femoral stem to determine the gradient in mechanical properties as a function of the FGM composition.

Preliminary studies of cell attachment and proliferation on Ti-6Al-4V$^{106}$ and HA$^{107}$ surfaces independently indicate that osteoblast behavior is strongly dependent on surface roughness, thus the surface roughness of a composite Ti-6Al-4V + HA component will undoubtedly be a significant parameter to control during SFF of FGM components. Because cell attachment and spreading are strongly dependent on the size scale of the surface features on which they reside, a range of surface roughness can be represented by scratching the surface of a sintered body with silicon carbide grinding papers of various grit (e.g. 320, 600, 1200) to create surface conditions with various size
scale topographical features as seen in the schematic in Figure 7.2. Biological property evaluation should therefore focus on quantifying osteoblast cell attachment and the kinetics of cell proliferation as a function of radial position from the core to the surface of the femoral stem as well quantify them as a function of the underlying surface roughness of the sintered Ti-6Al-4V + HA composite component. Osteoblast adhesion and cell spreading as a function of the underlying surface roughness of the composite FGM component will be useful information to be fed back to the SFF printing process for further optimization of the layer-by-layer printing process. The surface roughness of the scratched bodies should be quantified using an optical interference profilometer to measure surface roughness of the as sintered bodies as a function of starting Ti-6Al-4V and HA powder condition, SFF extrusion tip diameter, and/or the specific sintering condition utilized to fabricate the composite component.

7.2. Surface functionalization of Ti-6Al-4V + HA implant

Surface functionalization is a logical step in the line of succession for in vivo and full clinical scale component testing. Osteoblast adhesion (i.e. cell physical/chemical bonding), subsequent proliferation (i.e. cell multiplication and spreading), and viability (i.e. cell lifetime) may be tailored by the underlying surface chemistry and surface morphology, however one could envision taking the surface tailoring one step further. The use of an HA rich surface composition in composite FGM femoral stem components addresses the surface chemistry aspect necessary for bone compatibility, however the underlying surface morphology has not been investigated as thoroughly to date. Once the details of the surface morphology have been more thoroughly revealed, the component can be improved even further by functionalizing the component to promote
accelerated healing and/or mitigate inflammation and infection locally at the implantation site rather than through an intravenous, diluted, full body treatment. Local or targeted drug delivery allows for more rapid and more effective interaction at a lower drug dosage, thus the side effects associated with the particular pain reliever or antibiotic are minimized accordingly to the benefit of the patient. A schematic of this idea is shown in Figure 7.3, wherein the composite FGM component would be fabricated via an SFF process with the use of an additional slurry hopper during printing that contains either a pain reliever aerogel, antibiotic aerogel, or growth hormone/protein aerogel that allow for enhanced biological function and minimized pain or infection at the implantation site. Delivery of the functionalized aerogel should be done at the surface of the FGM component where it is readily accessible to the body fluid environment responsible for transport to the surrounding biological system.
8. Conclusions

Powder processing of Ti-6Al-4V biomaterials for SFF production of load bearing composite FGM femoral stem components has lead to many interesting results. Mitigation of cold welding and achievement of increased powder yield during SPEX milling is accomplished by applying 1 wt% stearic acid PCA for every 1 hour of incremental ball milling duration, which allows for increased recovery from 48% to 85% or greater. Generation of many new oxide free metallic surfaces is attained by SPEX milling under a controlled UHP argon environment. Particle refinement from 110 µm to 25 µm is achieved after only 4 hours of SPEX milling of commercial PREP Ti-6Al-4V powder. Likewise, crystallite size refinement from greater than 100 nm to 35 nm is achieved after only 4 hours of SPEX milling of commercial PREP Ti-6Al-4V powder. Cold work induced brittle fracture of commercial PREP Ti-6Al-4V particles during SPEX milling therefore allows for the production of nearly spherical equiaxed particles with a smaller average particle size and smaller average grain size that are more suitable for slurry suspension, slurry extrusion, improved green body consolidation, and enhanced sintering efficiency during SFF or FGM composite Ti-6Al-4V + HA femoral stem components.

The results from Ti-6Al-4V powder processing in turn provide for enhanced densification phenomena during subsequent sintering studies. The particle refinement achieved by 4 hours of SPEX milling results in a reduction in sintering time by a factor of more than 19x based lattice diffusion alone. The reduction in grain size from 3 µm to less than 1 µm provides for shorter diffusion distances from the grain interior to the higher mobility grain boundary regions by a factor of more than 9x based on lattice diffusion alone. More importantly however is the increased grain boundary area fraction and
increased overall defect density in the Ti-6Al-4V powder after just 4 hours of SPEX milling which provide for an increased thermodynamic driving force for densification during sintering. Alterations to the microstructure from a relatively uniform dendritic microstructure with a low fraction of grain boundary area in the commercial PREP Ti-6Al-4V powder, to a chaotic lamellar microstructure with a much greater fraction of grain boundary area after just 4 hours of SPEX milling results in a shift from lattice diffusion control to grain boundary diffusion control. The change in rate limiting thermodynamic mechanism offers a diffusion coefficient for mass transport that is 2-3 orders of magnitude greater in the SPEX milled powder, which is indicated by the reduction in sintering activation energy from ~187 kJ/mol to ~130 kJ/mol.

Investigation of alternate sintering techniques for production of composite Ti-6Al-4V + HA bodies for next generation FGM femoral stem components with enhanced mechanical and biological function yields both positive and negative results. RHS processing allows for retention of complex geometries in macroscale components as required for SFF production of FGM orthopedic implants because there is no restriction to the furnace geometry nor is there application of pressure during heating. RHS however has the drawback of a significant thermal penetration lag time to the interior of the workpiece due to the low thermal conductivity of Ti-6Al-4V, which results in long sintering times of 2 hours or more and high sintering temperatures of 1250°C or more to produce a fully dense component. The requirement of a sintering temperature in excess of 1000°C means that RHS processing is not suitable for composite Ti-6Al-4V + HA co-sintering because adverse reactionary products cannot be avoided.

MWS processing allows for the production of a solid Ti-6Al-4V body using a sintering time of 1 hour at a sintering temperature of just 900°C due to the rapid microwave dipole interaction in the workpiece, however the resulting body shows a
significant gradient in porosity from the core to the surface region. Although the temperature requirement of less than 1000°C for composite Ti-6Al-4V + HA co-sintering is demonstrated in MWS of pure Ti-6Al-4V bodies, the required post sintering machining process to remove the porous surface region results in a loss of complex shape retention thus MWS is not suitable for SFF fabrication of FGM orthopedic implants. Also the results from MWS co-sintering of composite Ti-6Al-4V + HA still do indicate issues related to detrimental reactionary products and/or ineffective heating due to unknown microwave energy interactions in the composite mixture.

The SPS process allows for production of nearly fully dense bodies at temperatures as low as 600°C in a matter of just 5 minutes due to rapid heating by the intrinsic joule effect which causes the pulsed electrical current to be concentrated at the very small surface area contact point at the interparticle boundary neck region. The rapid heating rate and an extreme local temperature rise during SPS results in rapid diffusion and enhanced densification which does allow for composite Ti-6Al-4V + HA co-sintering without adverse reactionary products. However, the applied mechanical pressure throughout heating restricts the geometry of the final component to the specific SPS die/furnace chamber geometry and thus “pressureless” SPS techniques must be investigated to allow for retention of the complex geometry required for SFF production of FGM femoral stem components. The manifestation of these achievements is witnessed in the demonstration of co-sintering of Ti-6Al-4V + HA using 4hr/4wt% SPEX milled Ti-6Al-4V powder feedstock via the SPS processing method that results in a final component that shows high density (i.e. improved mechanical strength) and a retention of compositional purity (i.e. improved bioactivity) as required for next generation FGM femoral stem components.
9. Figures and Tables

The following figures and tables appear in the order in which they are referenced in the body of the text, with the chapter in which it is used specified by the first number of the caption. All tables and figures are cited in the references except for those create by the author for personal use in this dissertation.
Figure 1.1. Mechanical properties of various biomaterials including titanium, hydroxyapatite, and cortical bone. 
Figure 1.2. Contemporary biomedical device design including (a) porous surface structured metallic component\textsuperscript{17} and (b) bioactive ceramic coated metallic components\textsuperscript{18}.
Figure 1.3. Total hip replacement component construction\textsuperscript{23}.
Figure 1.4. Total hip replacement surgical procedure schematic\textsuperscript{25}.
Figure 1.5. Image of (a) a standardized femoral stem sizing template and (b) an example of manual femoral stem templating prior to implantation surgery\textsuperscript{26}. 

\textsuperscript{26}\textit{References are not included in this document.}
Figure 1.6. Titanium-aluminum-vanadium ternary phase diagram\textsuperscript{30}. 

\textsuperscript{30} Reference or citation not provided.
Figure 1.7. Ball and stick schematic of Ti-6Al-4V unit cell for (a) α-HCP crystal structure and (b) β-BCC crystal structure.

Figure 1.8. Titanium phase diagram trends associated with various alloying elements.
Figure 1.9. Aircraft component material usage schematic\(^{40}\).

Figure 1.10. Titanium-6Al-4V sporting goods components such as (a) golf club head\(^{41}\) and (b) bicycle frame\(^{42}\).
Figure 1.11. Titanium-6Al-4V earrings\textsuperscript{43}.

Figure 1.12. Titanium-6Al-4V dental implant anchor screw\textsuperscript{44}.
Figure 1.13. Cross section of human bone.
Figure 2.1. X-ray image of (a) a broken femoral stem, and (b) femoral stem loosening\textsuperscript{50}. 
Figure 3.1. Images of (a) current Ti-6Al-4V hip implant femoral stem\textsuperscript{53}, (b) schematic of a functionally graded hip implant femoral stem\textsuperscript{54}, and (c) schematic of one radial slice of a functionally graded hip implant femoral stem\textsuperscript{54}. 

\textsuperscript{51} 100 vol\% Ti-6Al-4V

\textsuperscript{52} 60 vol\% Ti-6Al-4V + 40 vol\% HA

\textsuperscript{53} Ce 

\textsuperscript{54} Ci
Figure 3.2. Schematic representation of the difference in mechanical and biological properties of (a) the traditional thin bioceramic coated metallic substrate design, and (b) the novel FGM design. *Not to scale.
Figure 4.1. Schematic of (a) – (c) PREP powder production process\textsuperscript{61} and the resulting spherical powder morphology\textsuperscript{62}.
Figure 4.2. Szegvari attritor schematic for attritor ball milling experiments\textsuperscript{63}.

Table 4.1. Attritor milling conditions.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Stearic Acid (wt%)</th>
<th>Charge Ratio</th>
<th>Milling Duration (hr)</th>
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</thead>
<tbody>
<tr>
<td>100122</td>
<td>-</td>
<td>60:1</td>
<td>24</td>
</tr>
<tr>
<td>100312</td>
<td>-</td>
<td>60:1</td>
<td>72 (dry)</td>
</tr>
<tr>
<td>100730</td>
<td>-</td>
<td>60:1</td>
<td>72 (wet)</td>
</tr>
<tr>
<td>101228</td>
<td>-</td>
<td>40:1</td>
<td>48</td>
</tr>
<tr>
<td>110110</td>
<td>2</td>
<td>40:1</td>
<td>48</td>
</tr>
</tbody>
</table>
Figure 4.3. Laboratory glovebox used for loading and collection of ball milled Ti-6Al-4V powders\textsuperscript{65}.
Table 4.2. Ti-6Al-4V SPEX milling conditions.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Stearic Acid (wt%)</th>
<th>Charge Ratio</th>
<th>Milling Duration (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110406</td>
<td>2</td>
<td>40:1</td>
<td>0.5 + 0.5</td>
</tr>
<tr>
<td>110503</td>
<td>2</td>
<td>10:1</td>
<td>1</td>
</tr>
<tr>
<td>110422</td>
<td>2</td>
<td>10:1</td>
<td>1 + 1 + 1 + 1</td>
</tr>
<tr>
<td>110510</td>
<td>3</td>
<td>10:1</td>
<td>1 + 1 + 1 + 1</td>
</tr>
<tr>
<td>110527</td>
<td>4</td>
<td>10:1</td>
<td>1 + 1</td>
</tr>
<tr>
<td>110519</td>
<td>4</td>
<td>10:1</td>
<td>2</td>
</tr>
<tr>
<td>110525</td>
<td>4</td>
<td>10:1</td>
<td>1 + 1 + 1</td>
</tr>
<tr>
<td>110516</td>
<td>4</td>
<td>10:1</td>
<td>1 + 1 + 1 + 1</td>
</tr>
<tr>
<td>110602</td>
<td>4</td>
<td>10:1</td>
<td>1 + 1 + 1 + 1</td>
</tr>
<tr>
<td>110607</td>
<td>5</td>
<td>10:1</td>
<td>1 + 1 + 1 + 1</td>
</tr>
</tbody>
</table>

Figure 4.4. Schematic cross section of SPEX milling vial with shaking directions indicated by the black arrows.
Figure 4.5. Schematic of the uniaxial pressing process used for production of green body pellets for RHS showing (a) powder loading and (b) uniaxial compaction.
Figure 4.6. Schematic of the two step uniaxial and isostatic pressing process used for the production of green body pellets for MWS showing (a) uniaxial pressing and (b) subsequent isostatic pressing.
Figure 4.7. Initial design of high temperature quartz tube sealing of Ti-6Al-4V pellet without tantalum foil wrapping (left) and with tantalum foil wrapping (right) using 17 mm inner diameter tube.

Figure 4.8. Modified design of high temperature quartz tube sealing of Ti-6Al-4V pellet with tantalum foil getter and quartz wool insulation using 3 mm inner diameter tube.
Figure 4.9. RHS alumina tube furnace temperature controller calibration curve.

\[ y = 1.1145x - 81.262 \]
\[ R^2 = 0.9997 \]

Figure 4.10. RHS tube furnace temperature profile showing (a) 1100°C dwell and (b) 1250°C dwell.
Figure 4.11. Schematic of RHS tube furnace setup with resulting pellet temperature profile.

Figure 4.12. Schematic of the microwave sintering instrument setup and the pellet temperature profile resulting from the particle-pore interaction shown to the top right.
Figure 4.13. Schematic of the spark plasma sintering instrument die/chamber and the resulting pellet temperature profile.
Figure 4.14. Temperature profiles for RHS activation energy samples quenched at 900°C, 1000°C, 1100°C, 1200°C, 1300°C, and 1400°C with (a) 4°C/min heating rate, (b) 8°C/min heating rate, and (c) 16°C/min heating rate.

Figure 4.15. Schematic of Vickers hardness test method\textsuperscript{69}.
Figure 4.16. Schematic of uniaxial compression testing method. *Not to scale.
Figure 5.1. SEM image of as received commercial PREP Ti-6Al-4V powder.
Figure 5.2. SEM image of Ti-6Al-4V with 24 hours attritor ball milling.
Figure 5.3. SEM image of Ti-6Al-4V powder with 72 hours attritor ball milling.
Figure 5.4. X-ray diffraction spectra for attritor ball milled samples of (a) as received PREP Ti-6Al-4V powder, (b) Ti-6Al-4V powder with 24 hr attritor ball milling, (c) Ti-6Al-4V with 72 hr attritor ball milling.
Figure 5.5. XPS analysis of the as received Ti 6Al-4V powder.
Figure 5.6. XPS analysis of Ti 6Al-4V with 24 hours ball milling.
Figure 5.7. SEM image of 1hr/2wt% SPEX milled Ti-6Al-4V powder 110406 from Table 4.2.
Figure 5.8. SEM image of 1hr/2wt% SPEX milled Ti-6Al-4V powder 110503 from Table 4.2.
Figure 5.9. SEM image of 4hr/2wt% SPEX milled Ti-6Al-4V powder 110422 from Table 4.2.
Figure 5.10. SEM image of 4hr/3wt% SPEX milled Ti-6Al-4V powder 110510 from Table 4.2.
Figure 5.11. SEM image of 2hr/4wt% SPEX milled Ti-6Al-4V powder 110510 from Table 4.2.
Figure 5.12. SEM image of 2hr/4wt% SPEX milled Ti-6Al-4V powder 110519 from Table 4.2.
Figure 5.13. SEM image of 3hr/4wt% SPEX milled Ti-6Al-4V powder 110525 from Table 4.2.
Figure 5.14. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V powder 110516 from Table 4.2.
Figure 5.15. SEM image of 5hr/4wt% SPEX milled Ti-6Al-4V powder 110602 from Table 4.2.
Figure 5.16. SEM image of 4hr/5wt% SPEX milled Ti-6Al-4V powder 110607 from Table 4.2.
Figure 5.17. X-ray diffraction spectra for each of the SPEX milling conditions described in Table 4.2; (a) 110406 – 1hr/2wt%, (b) 110422 – 4hr/2wt%, (c) 110503 – 1hr/2wt%, (d) 110510 – 4hr/3wt%, (e) 110516 – 4hr/4wt%, (f) 110519 – 2hr/4wt%, (g) 110525 – 3hr/4wt%, (h) 110527 – 2hr/4wt%, (i) 110602 – 5hr/4wt%, (j) 110607 – 4hr/5wt% respectively.
Table 5.1. Ti-6Al-4V attritor milling results.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Milling Duration (hr)</th>
<th>Avg. Particle Size (µm)</th>
<th>Avg. Ti\textsubscript{(101)} Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As rec PREP</td>
<td>0</td>
<td>109±18</td>
<td>102</td>
</tr>
<tr>
<td>100122</td>
<td>24</td>
<td>254±105</td>
<td>54</td>
</tr>
<tr>
<td>100312</td>
<td>72</td>
<td>5±1</td>
<td>6</td>
</tr>
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</table>

Table 5.2. Ti-6Al-4V SPEX milling results.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Stearic Acid (wt%)</th>
<th>Milling Duration (hr)</th>
<th>Approx. Powder Yield (%)</th>
<th>Avg. Particle Size (µm)</th>
<th>Avg. Ti\textsubscript{(101)} Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110406</td>
<td>2</td>
<td>0.5+0.5</td>
<td>97</td>
<td>19±4</td>
<td>50</td>
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<td>110503</td>
<td>2</td>
<td>1</td>
<td>96</td>
<td>55±4</td>
<td>54</td>
</tr>
<tr>
<td>110422</td>
<td>2</td>
<td>1+1+1+1+1</td>
<td>48</td>
<td>41±14</td>
<td>20</td>
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<td>110510</td>
<td>3</td>
<td>1+1+1+1+1</td>
<td>50</td>
<td>31±4</td>
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<td>147±26</td>
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<td>24±2</td>
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<td>110602</td>
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<td>1+1+1+1+1</td>
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<td>19±2</td>
<td>16</td>
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<td>110607</td>
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<td>1+1+1+1+1</td>
<td>90</td>
<td>15±2</td>
<td>30</td>
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Figure 5.18. Average Ti-6Al-4V particle size (via SEM image analysis) as a function of SPEX milling duration.

Figure 5.19. Average crystallite size (via XRD analysis) of Ti-6Al-4V (101) and (002) reflections as a function of SPEX milling duration.
Figure 5.20. Average Ti-6Al-4V particle size (via SEM image analysis) of 4 hour SPEX milled powders as a function of process control agent concentration.

Figure 5.21. Average crystallite size (via XRD analysis) of Ti-6Al-4V (101) and (002) reflections as a function of process control agent concentration.
Figure 5.22. TEM micrographs of 4 hour SPEX milled Ti-6Al-4V powder in (a) bright field imaging mode, and (b) dark field imaging mode respectively.
Figure 5.23. Optical microscope image of commercially available Ti-6Al-4V sheet metal as chemically etched with Kroll’s Reagent.
Figure 5.24. Optical microscope images of as received PREP Ti-6Al-4V powder as chemically etched with Kroll’s Reagent.
Figure 5.25. Optical microscope images of 4wt%/4hr SPEX milled Ti-6Al-4V as chemically etched with Kroll's Reagent.
Figure 5.26. CCD camera image of commercially available Ti-6Al-4V sheet metal thermally etched at 1250°C for 2 hours.
Figure 5.27. SEM image of as received PREP Ti-6Al-4V powder RHS at 1300°C for 2 hours.
Figure 5.28. SEM image of as received PREP Ti-6Al-4V powder RHS at 1100°C for 2 hours.
Figure 5.29. SEM image of as received PREP Ti-6Al-4V powder RHS at 1250°C for 2 hours.
Figure 5.30. SEM image of 1hr/4wt% SPEX milled Ti-6Al-4V powder, RHS at 1100°C for 2 hours.
Figure 5.31. SEM image of 1hr/4wt% SPEX milled Ti-6Al-4V powder, RHS at 1250°C for 2 hours.
Figure 5.32. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V powder, RHS at 1100°C for 2 hours.
Figure 5.33. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V powder, RHS at 1250°C for 2 hours.
Figure 5.34. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V powder MWS at 900°C for 1 hour.
Figure 5.35. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V powder MWS at 1250°C for 30 minutes.
Figure 5.36. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V powder MWS at 1250°C for 30 minutes showing increased porosity at the surface region.
Table 5.3. SPS data recorded during processing.

<table>
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<tr>
<th>Sample ID</th>
<th>Pressure Decrease Temp (°C)</th>
<th>Displace. Onset Temp (°C)</th>
<th>Max Displace. Temp. (°C)</th>
<th>Displace. Plateau Temp. (°C)</th>
</tr>
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<tbody>
<tr>
<td>As Rec PREP Ti-6Al-4V SPS 1000°C</td>
<td>550</td>
<td>620</td>
<td>800</td>
<td>880</td>
</tr>
<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V SPS 1000°C</td>
<td>350</td>
<td>350</td>
<td>600</td>
<td>750</td>
</tr>
<tr>
<td>HA as synth SPS 1000°C</td>
<td>640</td>
<td>640</td>
<td>790</td>
<td>930</td>
</tr>
<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V (90 vol%) + HA (10 vol%) SPS 1000°C</td>
<td>320</td>
<td>350</td>
<td>575</td>
<td>800</td>
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<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V (75 vol%) + HA (25 vol%) SPS 1000°C</td>
<td>380</td>
<td>430</td>
<td>620</td>
<td>920</td>
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<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V SPS 600°C</td>
<td>100 MPa, 5 minutes at 600°C</td>
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Figure 5.37. Spark plasma sintering punch displacement vs. temperature for; (a) as received PREP Ti-6Al-4V, (b) 4hr/4wt% SPEX milled Ti-6Al-4V sintered at 1000°C, (c) as synthesized HA, (d) 4hr/4wt% SPEX milled Ti-6Al-4V (90 vol%) + as synth. HA (10 vol%), and (e) 4hr/4wt% SPEX milled Ti-6Al-4V (75 vol%) + as synth. HA (25 vol%).
Figure 5.38. SEM image of as received PREP Ti-6Al-4V SPS at 1000°C for 3 minutes.
Figure 5.39. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V SPS at 1000°C for 3 minutes.
Figure 5.40. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V SPS at 600°C for 5 minutes.
Figure 5.41. XRD spectra for RHS, MWS, and SPS samples with (a) as rec PREP Ti-6Al-4V RHS at 1100°C for 2 hours, (b) as rec PREP Ti-6Al-4V RHS at 1250°C for 2 hours, (c) 1hr/4wt% SPEX milled Ti-6Al-4V RHS at 1100°C for 2 hours, (d) 1hr/4wt% SPEX milled Ti-6Al-4V RHS at 1250°C for 2 hours, (e) 4hr/4wt% SPEX milled Ti-6Al-4V RHS at 1100°C for 2 hours, (f) 4hr/4wt% SPEX milled Ti-6Al-4V RHS at 1250°C for 2 hours, (g) 4hr/4wt% SPEX milled Ti-6Al-4V MWS at 900°C for 1 hours, (h) 4hr/4wt% SPEX milled Ti-6Al-4V MWS at 1250°C for 30 minutes, (i) as rec PREP Ti-6Al-4V SPS at 1000°C for 3 minutes, (j) 4hr/4wt% SPEX milled Ti-6Al-4V SPS at 1000°C for 3 minutes, and (k) 4hr/4wt% SPEX milled Ti-6Al-4V SPS at 600°C for 5 minutes.
Figure 5.42. Optical microscope images of sintered pellets that have been etched for grain size analysis including (a) as rec PREP Ti-6Al-4V RHS 1250°C – chemical etch, (b) 4hr/4wt% SPEX milled Ti-6Al-4V RHS 1250°C – chemical etch, (c) as rec PREP Ti-6Al-4V SPS 1000°C - chemical etch, (d) 4hr/4wt% SPEX milled Ti-6Al-4V SPS 1000°C - chemical etch, and (e) 4hr/4wt% SPEX milled Ti-6Al-4V MWS 1250°C - chemical etch.

Table 5.4. Grain size analysis of various Ti-6Al-4V bodies.

<table>
<thead>
<tr>
<th>Sample Condition</th>
<th>Grain Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-4V sheet – chemical etch</td>
<td>6±0.5</td>
</tr>
<tr>
<td>Ti-6Al-4V sheet – 1250°C thermal etch</td>
<td>757±7</td>
</tr>
<tr>
<td>As rec PREP Ti-6Al-4V powder</td>
<td>3±0.5</td>
</tr>
<tr>
<td>4hr/4wt% SPEX milled Ti-6Al-4V powder</td>
<td>1±0.1</td>
</tr>
<tr>
<td>As rec PREP Ti-6Al-4V RHS 1250°C – chemical etch</td>
<td>4±0.5</td>
</tr>
<tr>
<td>4hr/4wt% SPEX milled Ti-6Al-4V RHS 1250°C – chemical etch</td>
<td>2±0.1</td>
</tr>
<tr>
<td>As rec PREP Ti-6Al-4V SPS 1000°C - chemical etch</td>
<td>3±1</td>
</tr>
<tr>
<td>4hr/4wt% SPEX milled Ti-6Al-4V SPS 1000°C - chemical etch</td>
<td>1±0.1</td>
</tr>
<tr>
<td>4hr/4wt% SPEX milled Ti-6Al-4V MWS 1250°C - chemical etch</td>
<td>2±0.6</td>
</tr>
</tbody>
</table>
Figure 5.43. SEM image of wet synthesis HA after SPS at 1000°C for 3 minutes.
Figure 5.44. SEM image of composite 4hr/4wt% SPEX milled Ti-6Al-4V (75 vol%) + as synth. HA (25 vol%) after RHS at 1250°C for 2 hours.
Figure 5.45. SEM image of composite 4hr/4wt% SPEX milled Ti-6Al-4V (50 vol%) + as synth. HA (50 vol%) after RHS at 1250°C for 2 hours.
Figure 5.46. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V (90 vol%) + as synth. HA (10 vol%) SPS at 1000°C for 3 minutes.
Figure 5.47. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V (75 vol%) + as synth. HA (25 vol%) SPS at 1000°C for 3 minutes.
Table 5.5. Relative density for Ti-6Al-4V, HA, and Ti-6Al-4V + HA composite pellets prepared via RHS, MWS, and SPS sintering methods.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sample Condition</th>
<th>Relative Density* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As rec Ti-6Al-4V RHS</td>
<td>Tube furnace, 1100°C, 120 min</td>
<td>78</td>
</tr>
<tr>
<td>As rec Ti-6Al-4V RHS</td>
<td>Tube furnace, 1250°C, 120 min</td>
<td>90</td>
</tr>
<tr>
<td>As rec Ti-6Al-4V MWS</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>As rec Ti-6Al-4V SPS</td>
<td>SPS, 1000°C, 3 min</td>
<td>&gt;99</td>
</tr>
<tr>
<td>1hr/4wt% SPEX Ti-6Al-4V RHS</td>
<td>Tube furnace, 1100°C, 120 min</td>
<td>60</td>
</tr>
<tr>
<td>1hr/4wt% SPEX Ti-6Al-4V RHS</td>
<td>Tube furnace, 1250°C, 120 min</td>
<td>75</td>
</tr>
<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V RHS</td>
<td>Tube furnace, 1100°C, 120 min</td>
<td>83</td>
</tr>
<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V RHS</td>
<td>Tube furnace, 1250°C, 120 min</td>
<td>97</td>
</tr>
<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V MWS</td>
<td>Microwave, 900°C, 60 min</td>
<td>95 center, 80 edge</td>
</tr>
<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V MWS</td>
<td>Microwave, 1250°C, 30 min</td>
<td>98 center, 81 edge</td>
</tr>
<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V SPS</td>
<td>SPS, 600°C, 5 min</td>
<td>96</td>
</tr>
<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V SPS</td>
<td>SPS, 1000°C, 3 min</td>
<td>&gt;99</td>
</tr>
<tr>
<td>HA as synth MWS</td>
<td>Microwave, 900°C, 60 min</td>
<td>75**</td>
</tr>
<tr>
<td>HA as synth SPS</td>
<td>SPS, 1000°C, 3 min</td>
<td>&gt;99</td>
</tr>
<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V (90vol%) + HA (10vol%) RHS</td>
<td>Tube furnace, 1250°C, 120 min</td>
<td>60**</td>
</tr>
<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V (90vol%) + HA (10vol%) MWS</td>
<td>Microwave, 900°C, 60 min</td>
<td>60**</td>
</tr>
<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V (90vol%) + HA (10vol%) MWS</td>
<td>Microwave, 1250°C, 30 min</td>
<td>59**</td>
</tr>
<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V (90vol%) + HA (10vol%) SPS</td>
<td>SPS, 1000°C, 3 min</td>
<td>&gt;99</td>
</tr>
<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V (75vol%) + HA (25vol%) RHS</td>
<td>Tube furnace, 1250°C, 120 min</td>
<td>63**</td>
</tr>
<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V (75vol%) + HA (25vol%) MWS</td>
<td>Microwave, 900°C, 60 min</td>
<td>81**</td>
</tr>
<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V (75vol%) + HA (25vol%) MWS</td>
<td>Microwave, 1250°C, 30 min</td>
<td>78**</td>
</tr>
<tr>
<td>4hr/4wt% SPEX Ti-6Al-4V (75vol%) + HA (25vol%) SPS</td>
<td>SPS, 1000°C, 3 min</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

* Relative density value based on rule of mixtures calculated theoretical density for Ti-6Al-4V = 4.45 g/cm³.

**Values based on direct electronic balance mass and caliper volume measurement rather than pore area fraction ImageJ analysis due to inability of metallographic sample preparation.
Figure 5.48. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V sintered with 4°C/min ramp rate and 900°C quench temperature.
Figure 5.49. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V sintered with 4°C/min ramp rate and 1000°C quench temperature.
Figure 5.50. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V sintered with 4°C/min ramp rate and 1100°C quench temperature.
Figure 5.51. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V sintered with 4°C/min ramp rate and 1200°C quench temperature.
Figure 5.52. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V sintered with 4°C/min ramp rate and 1300°C quench temperature.
Figure 5.53. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V sintered with 8°C/min ramp rate and 900°C quench temperature.
Figure 5.54. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V sintered with 8°C/min ramp rate and 1000°C quench temperature.
Figure 5.55. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V sintered with 8°C/min ramp rate and 1100°C quench temperature.
Figure 5.56. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V sintered with 8°C/min ramp rate and 1200°C quench temperature.
Figure 5.57. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V sintered with 8°C/min ramp rate and 1300°C quench temperature.
Figure 5.58. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V sintered with 16°C/min ramp rate and 900°C quench temperature.
Figure 5.59. SEM image of 4hr/4wt% SPEG milled Ti-6Al-4V sintered with 16°C/min ramp rate and 1000°C quench temperature.
Figure 5.60. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V sintered with 16°C/min ramp rate and 1100°C quench temperature.
Figure 5.61. SEM image of 4hr/4wt% SPECT milled Ti-6Al-4V sintered with 16°C/min ramp rate and 1200°C quench temperature.
Figure 5.62. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V sintered with 16°C/min ramp rate and 1300°C quench temperature.
Figure 5.64. SEM image of 4hr/4wt% SPEX milled Ti-6AI-4V sintered during activation energy studies that shows prismatic particle formation.
Figure 5.64. Complete XRD spectra of all 4hr/4wt% SPEX milled Ti-6Al-4V pellet activation energy samples listed in Table 5.6 where (a) 1300°C-4°C/min, (b) 1200°C-4°C/min, (c) 1100°C-4°C/min, (d) 1000°C-4°C/min, (e) 900°C-4°C/min, (f) 1300°C-8°C/min, (g) 1200°C-8°C/min, (h) 1100°C-8°C/min, (i) 1000°C-8°C/min, (j) 900°C-8°C/min, (k) 1300°C-16°C/min, (l) 1200°C-16°C/min, (m) 1100°C-16°C/min, (n) 1000°C-16°C/min, and (o) 900°C-16°C/min.
Table 5.6. RHS condition and resulting pellet density of 4hr/4wt% SPEX milled Ti-6Al-4V diffusion activation energy study.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ramp Rate (°C/min)</th>
<th>Quench Temp (°C)</th>
<th>Relative Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Act Eng #4</td>
<td>4</td>
<td>900</td>
<td>57</td>
</tr>
<tr>
<td>Act Eng #5</td>
<td>4</td>
<td>1000</td>
<td>86</td>
</tr>
<tr>
<td>Act Eng #2</td>
<td>4</td>
<td>1100</td>
<td>93</td>
</tr>
<tr>
<td>Act Eng #1</td>
<td>4</td>
<td>1200</td>
<td>99</td>
</tr>
<tr>
<td>Act Eng #17</td>
<td>4</td>
<td>1300</td>
<td>99</td>
</tr>
<tr>
<td>Act Eng #13</td>
<td>8</td>
<td>900</td>
<td>55</td>
</tr>
<tr>
<td>Act Eng #10</td>
<td>8</td>
<td>1000</td>
<td>54</td>
</tr>
<tr>
<td>Act Eng #9</td>
<td>8</td>
<td>1100</td>
<td>72</td>
</tr>
<tr>
<td>Act Eng #8</td>
<td>8</td>
<td>1200</td>
<td>74</td>
</tr>
<tr>
<td>Act Eng #12</td>
<td>8</td>
<td>1300</td>
<td>99</td>
</tr>
<tr>
<td>Act Eng #14</td>
<td>16</td>
<td>900</td>
<td>58</td>
</tr>
<tr>
<td>Act Eng #11</td>
<td>16</td>
<td>1000</td>
<td>63</td>
</tr>
<tr>
<td>Act Eng #6</td>
<td>16</td>
<td>1100</td>
<td>67</td>
</tr>
<tr>
<td>Act Eng #3</td>
<td>16</td>
<td>1200</td>
<td>89</td>
</tr>
<tr>
<td>Act Eng #16</td>
<td>16</td>
<td>1300</td>
<td>94</td>
</tr>
</tbody>
</table>

Figure 5.65. Relative density vs. quench temperature for samples listed in Table 5.6.
Figure 5.66. Activation energy calculation of 4hr/4wt% SPEX milled Ti-6Al-4V powder using the Mastering Sintering Curve method described by Shao et al. from data collected during in house sintering.
Figure 5.67. Activation energy calculation for 4hr/4wt% SPEX milled Ti-6Al-4V powder using the Mastering Sintering Curve method with the aid of the Density MCS software provided by Pouchly et al. from data collected during in house sintering where (a) \( Q = 50 \) kJ/mol, (b) \( Q = 300 \) kJ/mol, and (c) \( Q = 140 \) kJ/mol.
Figure 5.68. Dilatometer data from sintering of 4hr/4wt% SPEX milled Ti-6Al-4V with (a) shrinkage as a function of temperature, and (b) relative density as a function of temperature.
Figure 5.69. Dilatometer data activation energy calculation of 4hr/4wt% SPEX milled Ti-6Al-4V powder using the Mastering Sintering Curve method described by Shao et al.
Figure 5.70. Dilatometer data activation energy calculation for 4hr/4wt% SPEX milled Ti-6Al-4V powder using the Mastering Sintering Curve method with the aid of the Density MSC software provided by Pouchly et al. where (a) $Q = 50$ kJ/mol, (b) $Q = 700$ kJ/mol, and (c) $Q = 440$ kJ/mol.
Figure 5.71. Dilatometer data activation energy calculation using the Constant Heating Rate (CHR) method from Wang et al. for 4hr/4wt% SPEX milled Ti-6Al-4V powder with (a) derivative of relative density versus temperature, and (b) plot of estimates for Q from CHR method.

\[ Q = 383 \pm 60 \text{ kJ/mol} \]
Figure 5.72. Hardness Vickers (10 kg) vs. temperature for various RHS, MWS, and SPS processed Ti-6Al-4V samples.

Figure 5.73. Stereographic optical microscope image of the fracture surface of Act Eng #1 (4°C/min - 1200°C) from Table 5.6. Surface was created by fracture along the line where three Vickers hardness test indents were made. The Vickers indents are marked with red triangles and corresponding plastic flow bands are marked with red arrows for clarity.
Figure 5.74. Quasi static (1mm/min) compression profile for 4hr/4wt% SPEX Ti-6Al-4V pellet sintered at 1250°C for 2 hr with 5°C/min heating and cooling rate.

Figure 5.75. SEM image of the top surface of a Ti-6Al-4V pellet sintered at 1250°C for 2 hours after quasi static compression testing with resulting microcracks indicated by red arrows.
Figure 6.1. Schematic of milling process including (a) the impact energy within powder compact as a function of milling media position, and (b) trapping, fracture, agglomeration and elastic rebound of milling media at collision site. 

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Figure 6.2. Schematic of relative particle size as a function of SPEX milling duration representing (a) as received PREP Ti-6Al-4V powder, (b) 1hr/4wt% SPEX milled Ti-6Al-4V powder, and (c) 4hr/4wt% SPEX milled Ti-6Al-4V powder.

Figure 6.3. Schematic of relative particle size as a function of process control agent concentration representing (a) as received PREP Ti-6Al-4V powder, (b) 4hr/1wt% SPEX milled Ti-6Al-4V powder, (c) 4hr/2wt% SPEX milled Ti-6Al-4V powder, (d) 4hr/3wt% SPEX milled Ti-6Al-4V powder, and (e) 4hr/4wt% SPEX milled Ti-6Al-4V powder.
Figure 6.4. Schematic of SPEX type milling motion.

Figure 6.5. Collision modes of ball milling media during SPEX milling.
Figure 6.6. Stearic acid molecular structure with polar (O-H) head group indicated in red\textsuperscript{77}.

Figure 6.7. Stearic acid surface adsorption on titanium\textsuperscript{78}.
Figure 6.8. Schematic of stearic acid occlusion on Ti-6Al-4V, indicating the physical and electrostatic barriers that mitigate aggregation, agglomeration and cold welding during ball milling.

Figure 6.9. XRD reflection 2 theta position markers for alpha and beta phases as well as the indexed Ti-6Al-4V spectra.\(^\text{82}\)
Figure 6.10. MATLAB software screenshot showing step by step curve fitting data input method.
6.11. MATLAB curve fitting tool screengrab showing the curve fitting method.
Figure 6.12. Schematic of the relative size of Ti-6Al-4V (101) and (002) XRD reflections as a function of SPEX milling duration representing (a) as received PREP Ti-6Al-4V powder, (b) 1hr/4wt% SPEX milled Ti-6Al-4V powder, and (c) 2hr/4wt% SPEX milled Ti-6Al-4V powder, (d) 3hr/4wt% SPEX milled Ti-6Al-4V powder, and (e) 4hr/4wt% SPEX milled Ti-6Al-4V powder.

Figure 6.13. Schematic of the relative size of Ti-6Al-4V (101) and (002) reflections as a function of process control agent concentration representing (a) 4hr/2wt% SPEX milled Ti-6Al-4V powder, (b) 4hr/3wt% SPEX milled Ti-6Al-4V powder, and (c) 4hr/4wt% SPEX milled Ti-6Al-4V powder.
Figure 6.14. Schematic of the driving force for sintering of a Ti-6Al-4V green body where (a) is the as received PREP powder after uniaxial pressing, (b) is the interparticle necking stage, and (c) is the pore elimination and densification stage.

Figure 6.15. Mass transport diffusion pathways during sintering.
Figure 6.16. Schematic of the (a) finite element model for uniaxial powder pressing, (b) experimentally obtained relative density gradient within the resulting pellet, and (c) finite element model obtained relative density gradient within the resulting pellet. 

1: 0.975  
2: 0.970  
3: 0.984  
4: 0.989  
5: 0.994  
6: 0.999
Figure 6.17. Schematic of (a) the as received PREP Ti-6Al-4V powder surface characteristics that lead to green body crumbling, (b) PEG binder coated condition, and (c) the preferred powder condition for green body strength without a binder.
Figure 6.18. Schematic of green body pellets prepared from (a) as received PREP Ti-6Al-4V powder, (b) 1hr/4wt% SPEX milled Ti-6Al-4V powder, and (c) 4hr/4wt% SPEX milled Ti-6Al-4V powder.
Figure 6.19. Screengrab of ImageJ area fraction analysis method.
Figure 6.20. XRD spectra showing the evolution of the α-titanium as a function of temperature\textsuperscript{99}.
Figure 6.21. SEM image of 4hr/4wt% SPEX milled Ti-6Al-4V pellet as sintered showing tube-like structures indicated by the red arrows.
Figure 6.22. SEM image of 4hr/4wt% SPEX milled T-6Al-4V pellet as sintered with tube-like structures seen at higher magnification.
Figure 6.23. EDS spectra of Ti-6Al-4V region of as sintered pellet shown in Figure 6.19.

Figure 6.24. EDS spectra of tube-like feature seen in Figure 6.19.

Figure 6.25. TGA profile of 4hr/4wt% SPEX milled Ti-6Al-4V powder.

Figure 6.26. Schematic of conservation of volume and barreling effect during compression testing\textsuperscript{105}.  

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Figure 7.1. Schematic of SFF printing process parameters that need to be optimized for FGM Ti-6Al-4V + HA component fabrication.
Figure 7.2. Schematic diagram showing sample preparation method used for analysis of the effect of surface roughness on osteoblast adhesion and spreading on the surface of sintered pellets.

Figure 7.3. Schematic representation of a FGM femoral stem surface functionalization. *Not to scale.
10. References


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