Microstructural Engineering of Titanium-Cellulose Nanocrystals Alloys via Mechanical Alloying and Powder Processing

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ACADEMIC ABSTRACT

Titanium been used industrially for nearly a century. Ever since it was first reduced to its elemental form, concerted efforts have been made to improve the material and to reduce the cost of production. In this thesis, titanium is mechanically alloyed with cellulose nanocrystals followed by powder consolidation and sintering to form a solid titanium metal matrix composite. Cellulose nanocrystals (CNCs) were chosen as the particle reinforcement as they are a widely abundant and natural material. Additionally, the nanocrystals can be derived from waste materials such as pistachio shells. This offers a unique advantage to act as a green process to enhance the mechanical properties of the titanium as well as to reduce to cost of production.

Vibrational milling using a SPEX 8000M mill was used to mechanically alloy titanium powder with varying concentrations of CNCs. Additionally, the milling time was varied. This process showed that varying the concentrations of CNCs between 0.5% - 2% by weight did not noticeably alter the microstructural or mechanical properties of the materials. Conversely, changing the milling time from 0.5 hours to 5 hours proved to greatly alter the microstructural and mechanical properties of the titanium matrix metal composites. Further increasing the milling time to 10 and 25 hours caused the materials to become exceedingly brittle thus, the majority of experiments focused on samples milled between 0.5 hours and 5 hours. The hardness values for the Ti-1%CNC materials increased from 325-450-600-800 for the samples milled for 0.5, 1, 2, and 5 hours respectively. The other concentrations used were found to yield similar values and trends. SEM micrographs showed that small precipitates had formed within the grains except materials milled at 5 hours, which showed the production of very coarse particles at the grain boundaries.

Similarly, an attrition mill was used to mechanically alloy titanium with varying CNC concentrations. Milling time was also varied. The powders were consolidated, sintered and characterized. It was found that increasing CNC content at low milling times caused a reduction in hardness. The X-ray diffractograms also showed a trend in that the diffraction patterns shifted to the lower angle with increasing CNC concentration, thereby suggesting that the increase in CNC content facilitated the removal of oxygen atoms housed within the interstitial sites. The oxygen was observed to diffuse and precipitate platelet titanium dioxide particles. These particles were found to be located within the titanium grains and coarsened with milling time. Generally, increasing the milling time to 15 hours was found precipitate particles at the grain boundaries as well as to excessively dissolve oxygen into the titanium lattice leading to embrittlement. The materials milled for 5 hours showed the best increase in strength while maintaining good ductility.

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GENERAL AUDIANCE ABSTRACT

Titanium has only been used industrially since the early 1940's thanks in large to the modern advances to reduce titanium ore to its elemental state. Titanium gained much interest as a structural material because of its corrosion resistance and its exceptional strength for a lightweight metal, making the material ideal for medical and aerospace applications. Pure titanium was found to be soft and had poor wear resistance, therefore, efforts were made to create titanium alloys which mitigated these weaknesses. Often titanium is alloyed with costly and toxic elements to enhance its strength properties, making it dangerous to use in the medical field.

One way to enhance the strength properties of titanium without the addition of these harmful alloying elements is to create a titanium composite by adding strong inert particles to a titanium matrix. One method to create titanium metal matrix composites is to violently mix titanium powder with the reinforcement material, through a process called mechanically alloying. Following the mixing process the powder is then compacted and heated to form a solid part through a process called sintering. While these powder processing methods are known and viable for forming titanium metal matrix composites, some of the reinforcement materials can be expensive.

In this thesis, cellulose nanocrystals (CNCs) will be added as reinforcement to titanium by means of two mechanical alloying processes, vibratory milling (shaking) and attrition milling (stirring). CNCs can be derived from plant matter which is widely abundant and inexpensive. The viability of CNCs to be used as a reinforcement material, as well as the mechanical alloying processes were investigated to determine the effect on the titanium strength properties. The powder processing steps were found to cause the CNCs to react with the surrounding titanium matrix which caused beneficial oxides to form as the reinforcement materials. In general, it was found that vibratory milling caused the final titanium metal matrix composite to be hard and brittle. Attrition milling was found to be more favorable as some materials were observed to be strong yet ductile.

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Dedicated To:

First and Foremost, I give thanks to the Almighty God. For it was him who put me on this planet and blessed me with the skills that I possess. The most value lesson that can may learned is that through him I can do all things (Philippians 4:13).

To my mother Cindy Angle. You taught me to be strong and to persevere, and you instilled into me a value system that has helped me to succeed. You believed in me when no one else did. Your unwavering faith in me helped me to have confidence that I could accomplish anything I set my mind to.

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List of Acronyms

Al- Aluminum

CIP- Cold Isostatic Press

CNCs- Cellulose Nanocrystals

CNT- Carbon Nanotubes

EDS- Energy Dispersive Spectroscopy

FIB- Focused Ion Beam

HIP- Hot Isostatic Press

ICP-MS- Inductively Coupled Plasma- Mass Spectroscopy

MA- Mechanical Alloying

MMC- Metal Matrix Composite

SEM- Scanning Electron Microscopy

SLS- Selective Laser Sintering

SPS- Spark Plasma Sintering

TEM- Transmission Electron Microscopy

Ti- Titanium

Ti-6Al-4V- Titanium with 6% Aluminum and 4% Vanadium

TiB- Titanium Boride

TiB_2- Titanium Diboride

TiC- Titanium Carbide

TiN- Titanium Nitride

TiO- Titanium Oxide

TiO_2- Titanium Dioxide

Ti-MMC- Titanium Metal Matrix Composite

V- Vanadium

XPS- X-ray Photoelectron Spectroscopy

XRF- X-ray Fluorescence Spectroscopy

XRD- X-ray Diffraction

1. Introduction

Titanium, which was discovered centuries ago, has only been used industrially since the early 1940's thanks in large to the modern advances to reduce titanium ore to its elemental state. This modern process of reduction is known as the Kroll's Process[1]. Quickly after the development of this process, titanium gained much interest as a structural material due to its high specific strength and corrosion resistance[2]. It was observed however that commercially pure titanium was soft and had poor wear resistance due to its low elastic modulus. Therefore, efforts were made create titanium alloys which mitigated these weaknesses. This led to development of Ti-6Al-4V in the early 1950's which is still the most widely used alloy of titanium today[3].

The development of Ti-6Al-4V greatly expanded on the strength properties of titanium in which the compressive and tensile strengths doubled that of commercially pure titanium. Though this alloy greatly improved its strength properties, thereby increasing its industrial use, it did not greatly improve it wear properties. Additionally, this alloy utilized vanadium, which increases the cost of the alloy and was later determined to be a cytotoxin. Therefore, this alloy must be excluded from biomedical applications and certain automotive and aerospace applications in which wear resistance is an issue.

It was conveniently at this time that research had begun in the field of metal matrix composites. The first titanium metal matrix composite was developed in the 1960's in which boron fibers were incorporated into a titanium matrix[4]. It was observed that the strength and the wear properties of the material had improved. However, this material was anisotropic and the cost to fabricate these materials made this material cost prohibitive. In the 1980's research

had begun to create particle reinforced titanium metal matrix composites by mixing boron and titanium powder followed by compaction and sintering. It was observed that these parts could be made more economically, and the mechanical behavior was now isotropic. A new challenge presented itself to homogenously disperse the particles evenly in the matrix[5].

In the 1990's researchers began to mechanically alloy ceramic particles such as titanium boride and titanium carbide with titanium powder to disperse the particles evenly in the bulk matrix. It was found that this method of dispersion was effective yet introduced new challenges[5]. The high energy of this technique provided a cataclysmic scenario in which oxygen could easily dissolve into the titanium matrix, embrittling the material. Also, typical process control agents (PCAs) which were used for other metals employed the used of hydrocarbons and fatty acids[6]. Researchers fear that this would further contaminate the titanium matrix with interstitial elements. Lastly, scalability to process industrial batches of titanium powder now posed to be problematic[7].

Starting in the 1990's and early 2000's research exploded to effectively mechanically alloy titanium to develop cost effective titanium alloys and metal matrix composites. This led to discoveries such as high strength carbon nanotube reinforced titanium, nanogranular titanium, and oxygen scavenging PCAs[8, 9]. Although research over the last 20 years has greatly expanded the knowledge in the field, questions remain unanswered or speculated.

Previous articles dispute or support the use conventional hydrocarbon PCAs which argue that they will contaminate the titanium matrix by dissolving carbon and oxygen into the interstitial sites of the titanium lattice[6, 10]. Other researches have used hydrocarbon PCAs with

titanium and reported little to no problems using them[10, 11]. In this thesis Cellulose nanocrystals, a hydrocarbon material, will be mechanically alloyed to evaluate its effect on the titanium matrix.

Additionally, previous articles which use carbon nanotubes to reinforce a titanium matrix state that the use of a nano-material will affect the dislocation movement within the matrix[8]. This thesis will attempt to experimentally demonstrate the effect of using a nano-material to reinforce a titanium matrix which has not yet been shown. Also, unlike carbon nanotubes, the use cellulose nanocrystals may prove to be much more cost effective, which is a very desirable characteristic when considering the expense of titanium[12, 13].

2. Background

2.1 Titanium

Titanium is the 22nd element on the periodic table and its name is derived from the Titans who were the fathers of gods in Greek mythology. The element was first discovered in the late 18th century when William Gregor postulated that the mineral ilmenite ($FeTiO_3$) was likely composed of not only iron but a metal of unknown origins. Shortly thereafter Martin Klaproth suspected that rutile was also comprised of titanium and is credited with naming the material[4].

The discovery of the existence of titanium was not quickly followed with the isolation of the material in its elemental form as the metal was observed to quickly react with oxygen and nitrogen present in the atmosphere. Early attempts of reducing titanium ore using titanium tetrachloride (TiO_4) yielded minimal success as the metal was notably brittle due to the high oxygen and nitrogen content. The first ductile high purity titanium was developed in 1910 by

Mathew Hunter using what is now known as the Hunter Process[14]. This process involved reacting titanium tetrachloride and molten sodium in an argon atmosphere to produce elemental titanium and sodium chloride (Equation 1). The products would undergo an acid wash to remove the sodium chloride.

$$TiCl_4 + 4Na_{(l)} \rightarrow Ti + 4NaCl \quad (1)$$

While this process proved to be useful in the production of elemental titanium, it also proved to be costly. While the production of elemental titanium was in its infancy other scientists worked to improve the reduction process. In the late 1930's William Kroll developed the Kroll process which utilized molten magnesium as opposed to molten sodium (Equation 2)[15].

$$TiCl_4 + 2Mg_{(l)} \rightarrow Ti + 2MgCl_2 \quad (2)$$

The Kroll process replaced the Hunter process as the most efficient method to produce commercial pure titanium and is currently the predominant method of reduction today. Although the Kroll process indeed reduced the cost of reducing titanium to its elemental form, it remains to be expensive as the production of titanium dioxide and other organic synthetic processes competes for the supply of titanium tetrachloride. Research into alternative reduction methods is ongoing such as the electrochemical reduction of titanium dioxide[16].

2.2 Titanium Alloys

Shortly after the birth of the Kroll process, the world began to take notice of the useful properties exhibited by titanium. The high specific strength and corrosion resistance material quickly became applied in many military and industrial applications as the second world war

ended and the cold war era started[4]. This exacerbated the need for a high temperature, high strength, lightweight, ductile materials. Titanium alloys were subsequently researched and led to the discover of Ti-6Al-4V in the 1950's[17].

Ti-6Al-4V is the most widely used alloy of titanium today as it greatly improved the mechanical properties as compared to the commercially pure titanium. The key to the success of this alloy its ability to retain both alpha (HCP) and beta (BCC) phases. Titanium alloys are generally divided into three classes, alpha alloys, beta alloys and alpha + beta alloys. Titanium alpha alloys, such as commercially pure titanium, tend to maintain better corrosion resistance and ductility over beta alloys which exhibit superior strength. The combination of the two, alpha +beta alloys (Ti-6Al-4V), provide a great compromise between physical and mechanical properties. The production of stronger alloys ultimately led to the introduction of titanium into to aerospace field and the eventual production of innovative aircraft such as the SR-71 [4]. While a vast improvement in mechanical properties was noted, the Ti-6Al-4V alloy still maintained some weaknesses, such as poor wear resistance and shear strength[18-20]. It was observed that the essential alloying element of vanadium could be leached into the body when used as a structural implant. In recent years it was discovered that patients exposed to vanadium had increased chances of developing Alzheimer's disease. This necessitates the need for alternative alloys or other methods of strengthening for biomedical applications.

2.3 Metal Matrix Composites (MMC)

The ever growing need to increase strength and reduce weight introduces a new class of materials, metal matrix composites. Composites themselves have been in existence since time immemorial[21]. Nature produces some of the best composites still used today, i.e. wood[22].

Synthetic composites have been produced for thousands of years with early examples including adding straw to mud brick to enhance the structural integrity of early building materials. Even the use of metal matrix composites has been recorded in history for thousands of years, created by hammering and forging dissimilar metals together to create armor[21]. It wasn't until 60 years ago that modern metal matrix composites were developed by adding continuous Boron fibers to an aluminum matrix[21]. The area of continuously reinforced metal matrix composites was pioneered in the late 1950's and 1960's, and were extensively researched in the 1970's and 1980's. It was observed that there was as adjustment in focus in the 1980's to discontinuous or particulate reinforced metal matrix composites. Particulate reinforced metal matrix composites differ from continuous fibers as they can be randomized in the metal matrix to reinforce the material isotropically. Metal Matrix composites generally created to reinforce the mechanical properties of the metal matrix. In this case, high strength ceramic reinforcements are typically added to the metal matrix to enhance the mechanical properties. Other physical properties may be augmented as well. One such example is the addition of carbon nanotubes to metal matrices to improve thermal conductivity and Yttria stabilized zirconia to control thermal coefficient of expansion.

2.4 Titanium Metal Matrix Composites (Ti-MMC)

The history of titanium metal matrix composites (Ti-MMC) shares a similar timeline to the history of metal matrix composites. The first titanium metal matrix composite was developed by adding continuous boron fibers to a titanium matrix (Figure 1)[23]. The results showed a marked increase in the Young's modulus and other mechanically properties. The major disadvantage was

that boron reinforcement fibers were expensive, and adding these to titanium makes the material cost prohibitive[4].

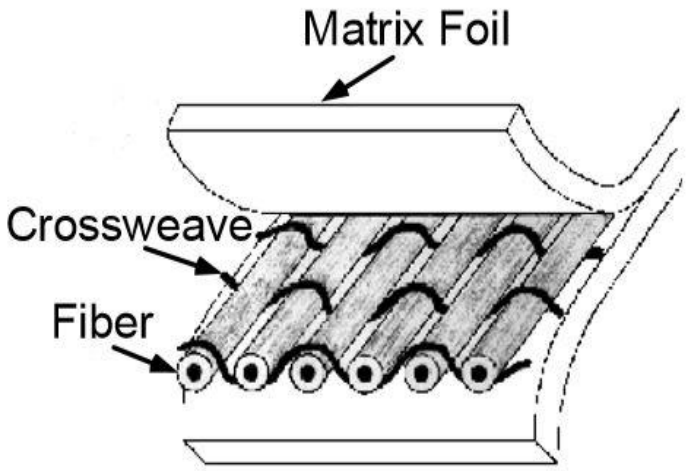

Figure 1. Schematic for Boron Fiber Reinforced Ti-MMC. Image reproduced with permission [24].

A research opportunity for a less expensive Ti-MMC was now available. A particulate reinforced titanium was developed in the 1980's by reinforcing the titanium matrix with titanium boride whiskers[25]. The results indicated the successful fabrication of a cost-effective isotropic Ti-MMC. A key attribute of this Ti-MMC was that the Ti/TiB composite mitigated a major weakness in titanium materials, poor wear resistance. Consequently, the Ti/TiB composite found major uses in the aerospace and automotive industries which became especially important in engine components[26]. These parts could now be made of titanium in areas where metal could grind on itself, thusly reducing the weight of the vehicle. Because of the success of forming this Ti-MMC, an explosion of research began on forming Ti-MMCs using other reinforcing materials

to further enhance mechanical and physical properties, such as: titanium carbide, carbon nanotubes, titanium nitride, silicon carbide[27-29].

2.5 Cellulose Nanocrystals (CNCs)

In this thesis, we investigate the production of TI-MMC's as well as the strengthening mechanisms associate with reinforcing Titanium with Cellulose nanocrystals (CNC's). The research field of the usage of cellulose nanocrystals as a reinforcement material is still in its infancy. Cellulose nanocrystals are a desirable additive as cellulose its self is widely abundant, renewable, and relatively inexpensive to isolate.

Cellulose is polymeric network which is found in plant sources such as wood and cotton, which are the most common sources of CNCs. The polymeric network is comprised of both crystalline and amorphous regions. To isolate the crystalline region the cellulose typically undergoes an acid hydrolysis step in which the acid attacks the amorphous regions and leaves the nanocrystals intact. For polymeric reinforcement the acid hydrolysis step is important as it can lead to functionalization of the polymer which may alter certain properties[30]. The versatility of this material has led to abundance of research to create polymer matrix composites, to prevent blood from clotting and even creating conductive polymers. Cellulose nanocrystals have even shown to resist thermal degradation up to 300^{o}C[30]. However typical powder processing temperatures for titanium exceed 1000^{o}C. Additionally, the Cellulose structure is comprised largely of carbon, oxygen and hydrogen atoms. The high reactivity of these elements with titanium have been extensively researched and are well understood. It is hypothesized that the cellulose nanocrystals, will degrade during sintering and react with the titanium matrix to form a composite through in-situ powder metallurgy which involve reacting the contents during

processing. The effects of this process are unknown using CNCs, and the benefits or detriments have not yet been evaluated.

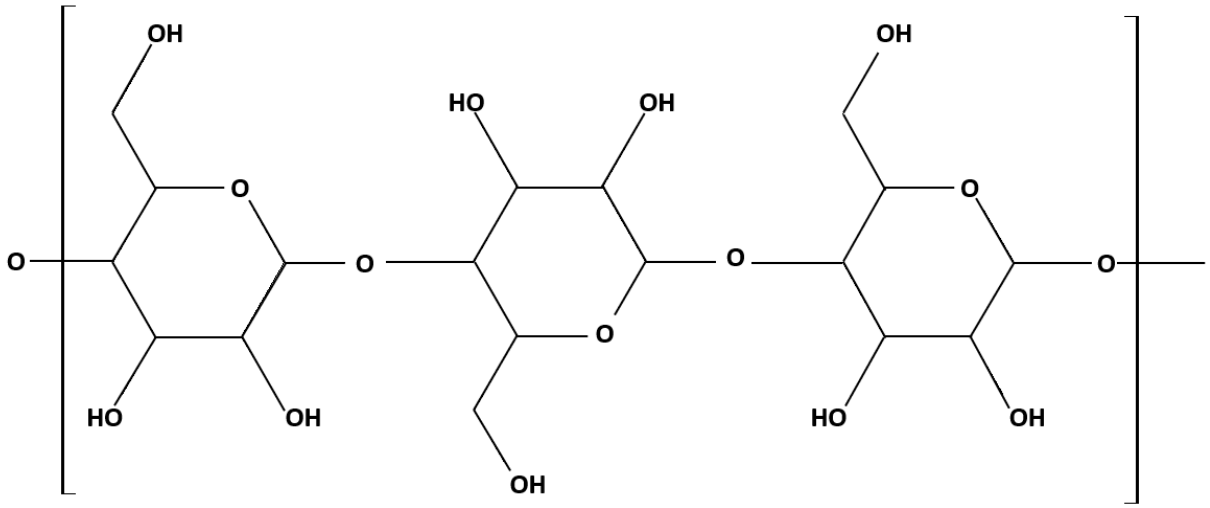

Figure 2. Polymeric Structure of Cellulose Nanocrystals.

A major advantage of using cellulose nanocrystals is the fact that the material is nano sized. Articles have shown that larger particle reinforcements are harder to evenly disperse and tend to agglomerate in metal matrices, which becomes a structural hindrance rather a reinforcement. Therefore, the smaller particle size CNCs are advantageous. Agglomerations have been reported with carbon nanotubes due to the Vander Waals attractive forces, which has been mitigated in some cases through mechanical alloying[8]. It is possible that if the phenomenon is observed with CNCs that they may be functionalized to prevent agglomeration. Commonly CNCs are derived from wood and cotton which has competing uses. Isolation of cellulose nanocrystals from waste products i.e. corn husks, pistachio shells is a topic of current research which could further lower the cost of this material[31].

2.6 Mechanical Alloying (MA)

Mechanical alloying (MA) is a common powder metallurgical technique that is utilized as a dry homogenization technique. It was originally developed in the late 1966 by INCO to fabricate oxide dispersion strengthened nickel super alloys. The technique involves blending two or more powders and using a high energy ball mill to repeatedly weld and fracture the powder components. Depending on which milling technique is employed the powder is either impacted or sheared between the milling media. A major benefit to MA is the capability to create homogenous mixtures as well as several non-equilibrium phases, such as supersaturated alloys and amorphous phases. These results can often create unique physical and mechanical properties unattainable by conventional metallurgical processes.

While the MA has several benefits, challenges also exist which may outweigh the benefits of the process. Unintentional chemical reactions and milling media contamination exist as common detriments to mechanical alloying. The kinetic energy of the balls causes inevitable fracturing of the milling media which can contaminate powders. The milling environment may also pose to contaminate the powders as the high surface area, clean fractured surfaces, and the energetic process create a cataclysmic scenario for oxidation. It is for this reason that the selection of milling equipment and milling conditions is of utmost importance.

The milling media is the material used to grind of the powders. Typical milling media used are stainless steel and tungsten carbide. In certain cases, in which contamination from these materials should be avoided, other less common materials such as alumina, silicon carbide or zirconia are used. Tungsten carbide is the densest, hardest, and most energetic milling media used. This provides an advantage in that milling times can often be lowered due to energy is

generates. However, the brittleness of tungsten carbide allows for the potential for contamination when milling for extended periods of time. While contamination is still a possibility when milling with stainless steel media, the potential is lower and is therefore a good compromise between energy and contamination.

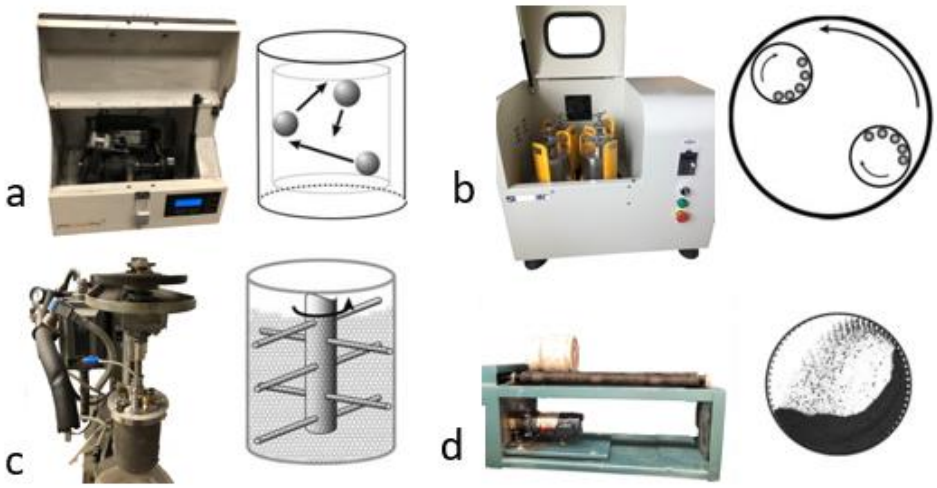

Figure 3. Various Milling Techniques and the Respective Diagrams of Operations. A. Vibratory (Spex) mill B. Planetary Mill, C. Attrition Mill, D. Tumbler Mill. Cartoons reproduced with permission[7].

Another challenge with MA of metal powders is cold welding. Ductile metal powders will tend to weld as opposed to fracture which leads to an inhomogeneous material as well as to large particle sizes which facilitate porosity during powder compaction and sintering. To mitigate this phenomenon, a process control agent (PCA) is used and typically these are organic solvents or fatty acids. Solvents such as ethanol are used and are later evaporated to remove the PCA post processing. Solid PCAs such as stearic acid can be removed either by gentle heating of the powder or removal with a solvent post processing.

Figure 4. Batch Comparison of Milling Techniques. From left to right: vibratory milling vial, a planetary ball milling vial, and an attritor milling vessel. The containers shown are laboratory scale with larger containers existing for each.

Common types of high energy milling equipment are vibratory ball mills (SPEX mills), attrition ball mills, and planetary ball mills. Each come with its own benefits and challenges. Vibratory ball mills use a sealed vial, either stainless steel or tungsten carbide, in which the milling balls and powders are vigorously shaken to cause the milling ball to collide catching the powder between the milling media. Generally, a low ball to powder ratio is used to ensure high kinetic energy of the milling media. This technique is the most energetic of the milling techniques described in this thesis and is subject to heating of the powder. Another drawback is that the powder must be between the balls during collisional event for MA to occur. The probability of this event is relatively low as compared to other techniques. Typically, the milling vessels are smaller, and the generation of large batch quantities is difficult.

Planetary ball mills are the most common types of high energy milling equipment employed. The powders and the milling media are added to a sealed vessel which is placed into the machine. The machine then orbits centrifugally while the milling containers are rotating, similarly to how the earth orbits the sun while rotating around the equator. Gravity holds the contents to the bottom of the milling vessel and the milling media applies a shear force to the powder. As gravity is constantly pulling the contents to the bottom of the container, a high probability of ball to powder interaction exists. The sealed container allows for a variety of milling environments to be used ranging from low pressure inert environments (vacuum), to reactive gases. This technique is considered to have medium scalability, yielding powder loads greater than vibratory mills but less than attrition mills[7].

Attrition mills offer the largest scalability of the listed milling techniques which has the capability of mill several kilograms of powder at a time. Similarly, to planetary ball milling the contents are added to a vessel in which gravity holds the contents at the bottom of the vessel. An impeller is used to spin the powder and milling media. As the impeller is an external source of rotation it is impossible to attrition mill powders in a closed system. Therefore, carrier gases such as argon are used to prevent oxidation. As the milling vessel is stationary, this provides advantages over the other milling techniques listed. Typically, the milling vessels are incased in a water-cooling jacket to prevent the powders from heating. In addition to carrier gasses, the milling process can take place in cryogenic liquids which can refine microstructures and augments the milling environment purity.

2.7 Mechanical Alloying of Titanium

Contamination control especially important for titanium which readily absorbs oxygen and nitrogen from the atmosphere. It is for this reason that the production of usable MA titanium powders was fabricated 30 years after nickel, iron and aluminum alloys. It has been reported that even the purest gases and extensive purging of the milling environment contains sufficient levels of oxygen and nitrogen to react with the titanium powders. Controlling gaseous contamination of titanium powders remains to be an issue even today. Processes involving milling in vacuum, the addition of Yttria oxygen scavengers, and cryogenic milling of powder have all been developed as methods to mitigate these challenges[10].

The most common forms of equipment used to mechanically alloy titanium are planetary ball milling and attrition milling. These techniques are known for having good mixing properties and decedent scalability of product. In addition to scalability, it has been observed that an FCC non-equilibrium phase, intermetallics and other complex ceramics can be generated through mechanically alloying titanium[32, 33]. Post milling handling of titanium is a topic of debate. Some authors state the after milling an oxide barrier forms on the surface of the particles which prevents further oxidation of the powder, while others choose to ensure that titanium powder is kept under a constant blanket of argon. As much of the research described in this thesis is based on the mechanically alloying aspect of titanium, the following literature review chapter describes research in this field in greater detail.

2.8 Powder Consolidation

The Kroll process when complete produces a porous titanium powder often called “titanium sponge”. To consolidate the titanium powder into a continuous titanium ingot the

powder is melted in a process called vacuum arc melting[34]. Due to titanium's high affinity to oxygen and nitrogen at elevated temperatures it is impossible to melt titanium in the presence of these gases[35]. Even inert Argon environments are not pure enough to prevent oxidation, therefore the vacuum environment is imperative[36]. The titanium powder is added to a graphite crucible which has a high current applied. The current heats the material past its melting point where it is cast into molds, typically rods bars or sheets. Titanium is mostly fabricated in this manner, but this technique has flaws[37]. Firstly, as it is a casting technique, typically parts cannot be fabricated to near net shapes. Therefore, machining is required, which causes waste and further expense. Efforts to fabricate Ti-MMC using vacuum arc melting have shown that achieving homogenous distribution of particles is difficult.

Alternative methods of consolidation typically involve compaction under pressure and sintering. Sintering is a process in which a powder material is coalesced and subsequently heated to allow atoms from neighboring particles to fuse[38]. The atoms can diffuse in the process allowing for densification of materials. Typical sintering temperatures are kept %20-%30 below the melting temperature, with higher temperatures leading to denser products[39]. Sintering provides advantages over vacuum arc melting as there is greater control over the microstructure. Sintering has shown to produce homogenous microstructure, limit grain growth and produce near net shape parts[39].

Furnace selection is important when considering sintering. Many metals can be sintered at elevated temperature while the furnace is purged with an inert gas. The powders can be further reduced by introducing a small flow of hydrogen to extract oxygen. Inert gas

environments may not be sufficient to prevent titanium from oxidizing during sintering therefore a vacuum furnace is typically used where the titanium powder is heated in high vacuum[35].

Uniaxial pressing is a basic form of powder compaction (Figure 5). Metallic powder is added to the barrel of a compaction die, pistons are then used to apply a uniaxial compaction force on the powder. This technique requires the material to ductile so that the metal will cold weld. The compaction die is typically made from a large amount of stainless steel in comparison to the size of the compact it yields[39]. Therefore, the production of large components with this method is difficult.

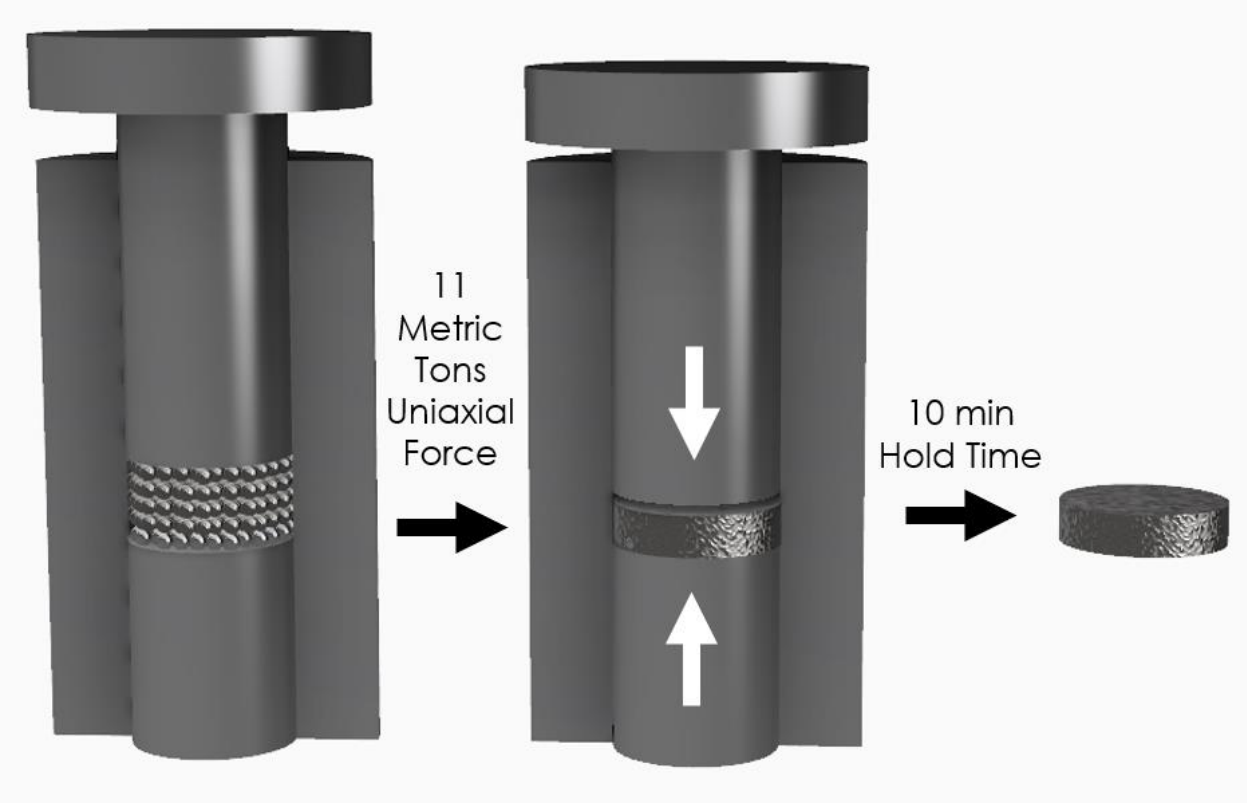

Figure 5. Schematic for the Uniaxial Compaction of Samples.

Powders can be cold isostatically pressed (CIP) in which a powder is added to a rubber mold and submerged in a room temperature water bath. The water bath is pressurized which applies an isostatic compressive force on the mold[39, 40]. The powder molds can be any shape and therefore a near net shape green compact can be formed. Similarly, powders can be hot isostatically pressed (HIP)(Figure 6) in which a heated argon gas can be used to compress powders at temperatures exceeding 1000^{o}C. Instead of a rubber mold, copper molds or stainless-steel molds are typically used. The HIP process holds an advantage over CIP in that the powders are sintered during the compaction process which leads to denser products, however it is notably more expensive[39].

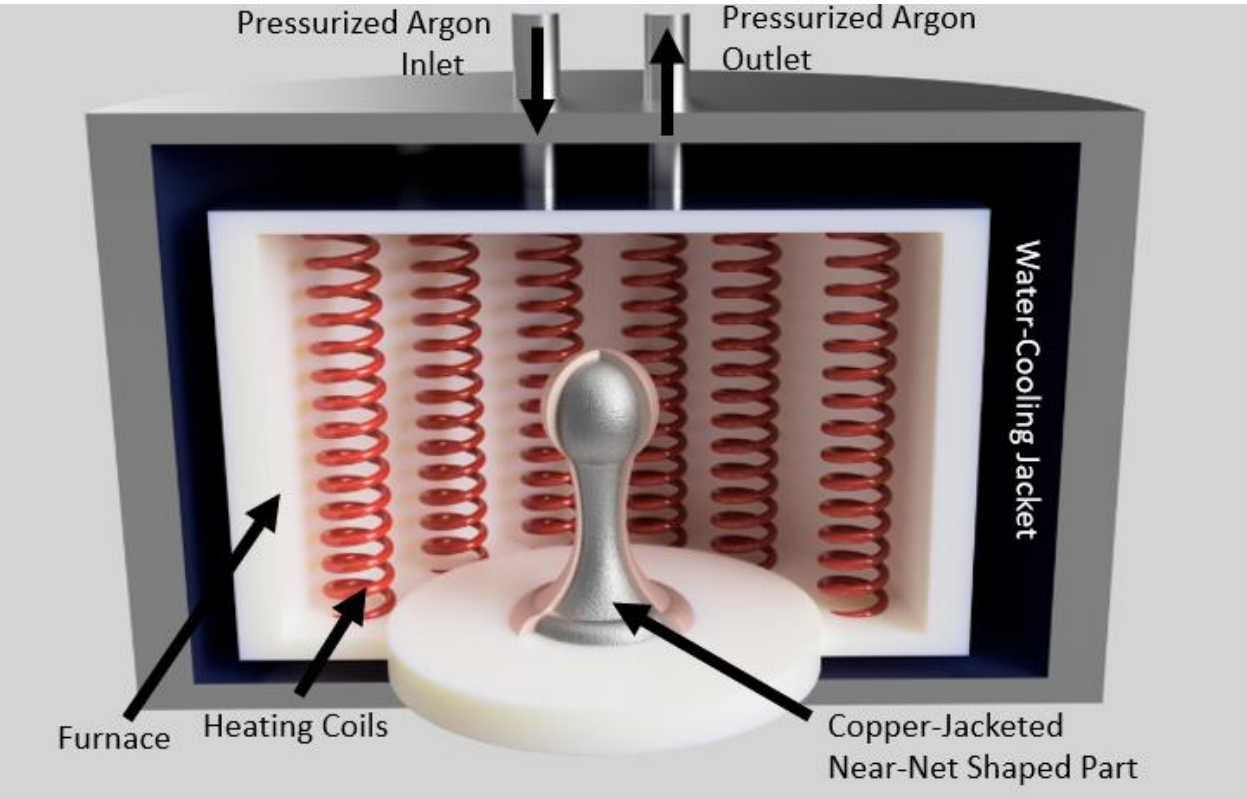

Figure 6. Schematic for a Hot Isostatic Press.

Spark Plasma Sintering (SPS) is a consolidation technique in which a uniaxial pressure is applied to a powder in the presence of an applied DC current to heat and sinter the material. This process offers many advantages which are unattainable by other methods[39]. This process can take place in vacuum which minimizes contamination for materials such as titanium. Additionally, SPS is unique in that the ramp rates are very fast, and the dwell time are very short for this process[9]. The uniaxial pressure allows for full densification of the material to be achieved at much lower temperature than other techniques. This allows for the potential to limit grain growth and recrystallization of materials which lead to strengthening. Non-equilibrium phases are more likely to be present as the rapid sintering process and low sintering temperatures may prevent phase transformations. There are currently size limitations to the production of SPS titanium parts. The majority of SPS work has been relate to research however efforts are being made to produce large ingots of SPS titanium. A 250mm, 5kg billet of SPS titanium has been fabricated (Figure 7), thereby proving the potential for scalability[41].

Titanium powder is relatively dull and tends not to be reflective. These properties make titanium a viable candidate for selective laser melting (SLM)(Figure 8)[42]. The SLM process is an additive manufacturing technique which involves placing the titanium into the powder bed and scanning a high energy laser over the powder bed to selectively melt areas of interest. After a pass is completed the powder bed is lowered and an additional layer of titanium powder is deposited over the original scan. Another pass is made to melt the new layer of deposited titanium.

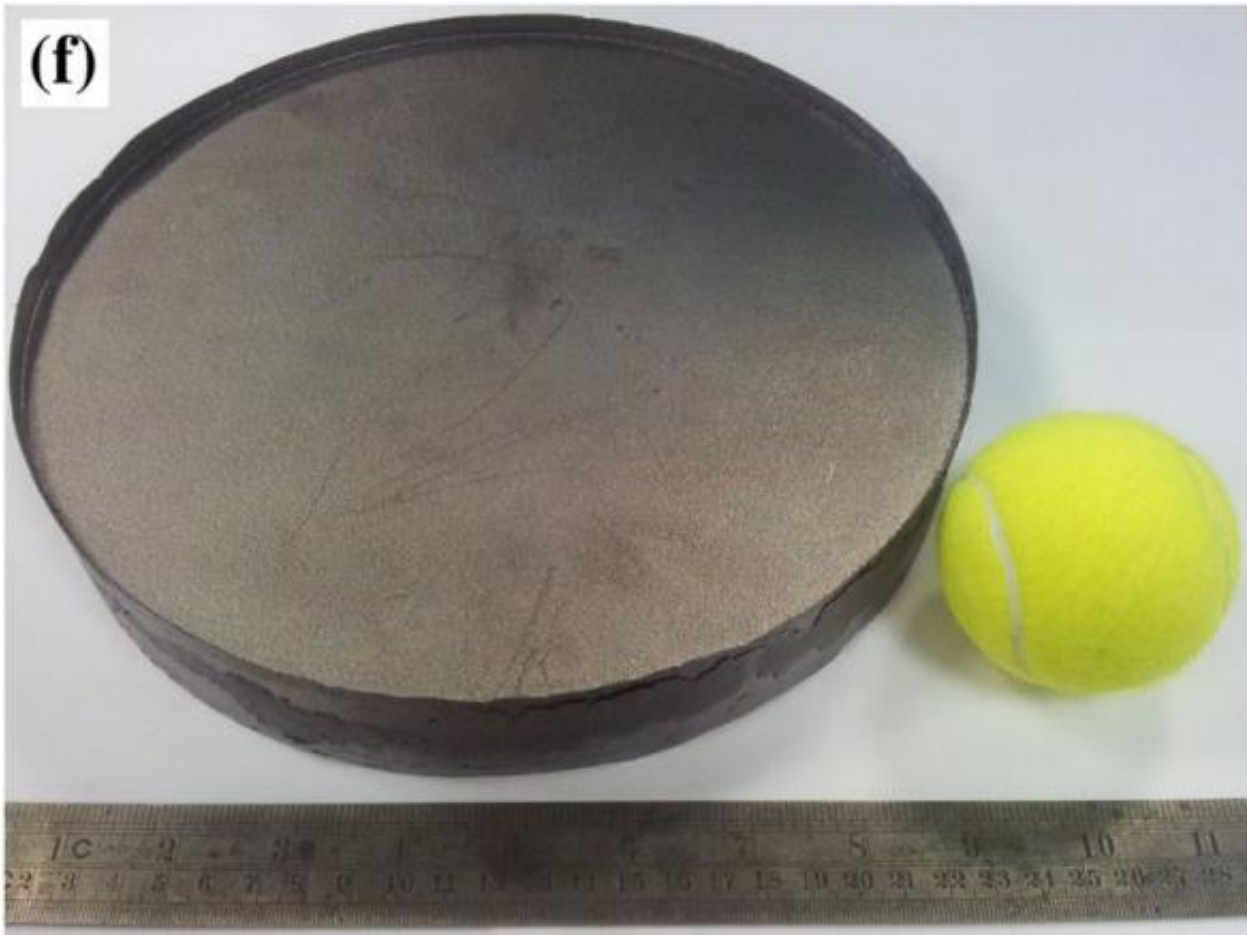

Figure 7. Bulk Titanium Billet Produced by Spark Plasma Sintering. The author states the billet is 250mm in diameter which weighs 5kg, Weston et al [41]. Image reproduced with permission.

This process is continued until the desired 3D geometric shape is produced. The ability to 3D print titanium allows for the creation of complex geometric shapes which are otherwise unattainable. Other benefits include creation of very near net shapes, low powder waste which makes the process economical[39, 42]. However, the titanium particle needs to be spherical to achieve densification. Production of spherical powders can be expensive which subverts the economic benefits of this technique.

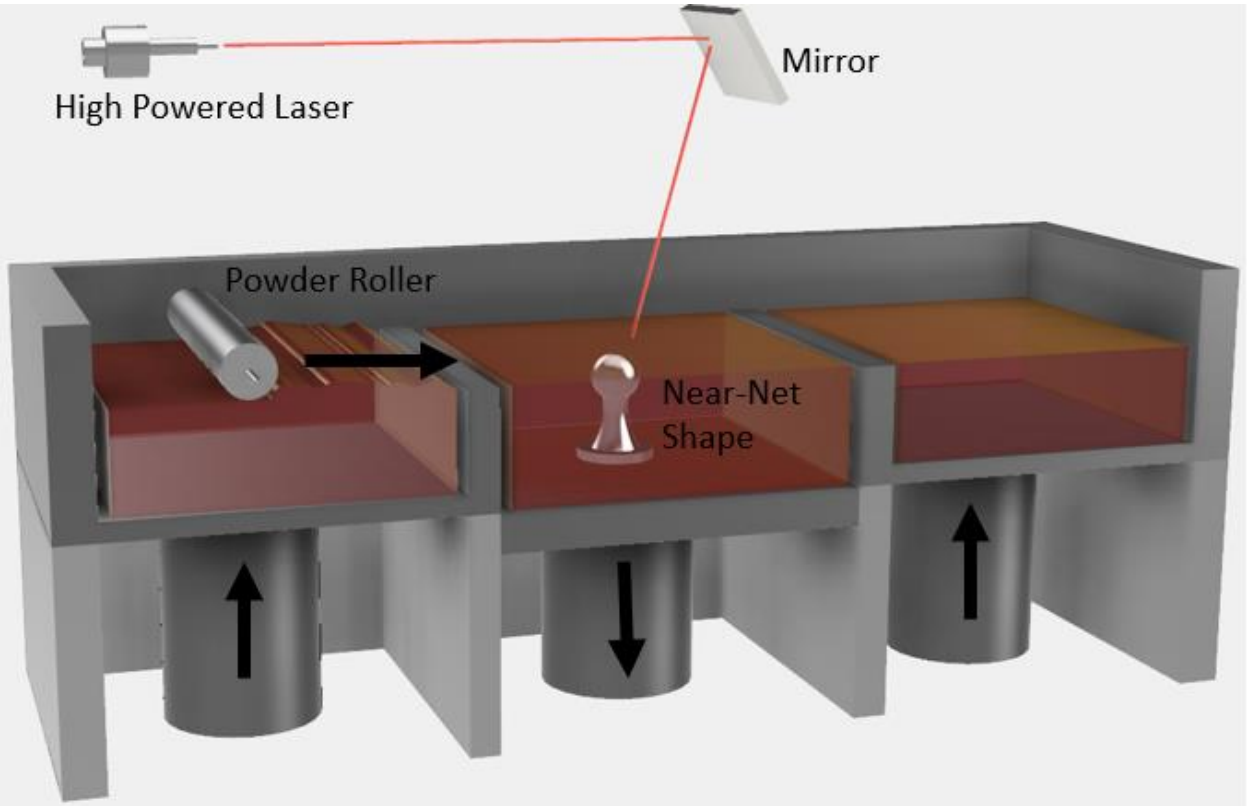

Figure 8. SLM Manufacturing Process. A powder roller pushes powder from the feed stock which is evenly deposited in the powder bed. A high power laser is directed toward a mirror which rasters the beam toward the powder bed. The beam is scanned across selective regions in which sintering is desired. This process is repeated for multiple layers until a 3D part is attained.

Chapter 3 Literature Review

3.1 Mechanical Alloying of Titanium Based Materials

Nearly 30 years after oxygen dispersed nickel super-alloys were fabricated using mechanical alloying, scientists began using this technique on titanium and its alloys. With the growing interest to develop high strength light weight titanium materials, the mechanical alloying of titanium became a research focus starting in the 1990's. A list of early mechanical alloying projects were compiled and published detailing advances of mechanically alloying titanium as of 1996[43]. The authors state that a clear advantage of alloying titanium was the ability to create ultra-lightweight titanium alloys by alloying titanium and magnesium. The equilibrium solubility limit for magnesium in a titanium matrix is less than 2%. However, it was reported that compositions of up to 9% magnesium can be dissolved via mechanical alloying. Additionally, fabricating Ti-MMCs is of interest due to the ability to potentially increase the wear properties. When fabricating particulate reinforced MMCs, it is difficult to evenly disperse the reinforcement into the metal matrix. In the Mid-1990s Titanium was first milled with elemental boron to create a particulate reinforced TiB/Ti-6Al-4V MMC. The milling process dispersed boron particles and through heat treatments locally reacted the boron with the surrounding titanium matrix to form a composite. The results indicated that the reinforcement was homogenous with augmented mechanical properties of the titanium component.

The authors suggest that the greatest difficulty to overcome when milling titanium was controlling contamination. Contamination can result from either the milling media or the milling environment, and the more time the powder is milled the higher the potential for the

contamination. Contamination from the milling media comes from the fracturing of the milling media, which is subsequently alloyed with the titanium powder. It has been observed that iron can segregate to the grain boundaries which can embrittle the material. More importantly, oxygen and nitrogen can contaminate the powder in the milling process. It is suggested that great care is taken to ensure that the seals of the milling equipment are tight, and that the milling environment is inert. Residual oxygen, nitrogen and water vapor will always adhere to the surfaces of the milling media; therefore the charge ratio of the milling media must be considered. A high ball to powder ratio will inherently increase the surface area of the milling media and therefore lead to increased contamination. Mechanical alloying usually enlists a process control agent (PCA) to prevent materials from cold welding to the milling media. As PCA's are usually organic, a strong concern exists that appreciable oxygen and carbon contamination will occur. Previous experiments showed that stearic acid has been used to create Ti-Mg alloys[43]. However, it was inconclusive whether contamination came from the PCA or the milling environment.

3.2 Production of Titanium Particulate Metal Matrix Composite by Mechanical Milling

Prior to mechanical alloying of titanium, the milling of aluminum had already been established as a viable method to produce aluminum metal matrix composites with commercial success. The automotive and aerospace industries found the Al MMCs had improved stiffness, strength, fatigue and creep properties, all of which desirable characteristics. The downfall with Al MMCs was that the materials are not temperature resistant, therefore researching Ti MMCs

was a worthwhile investment. In 1999, a paper was drafted pioneering the incorporation of a particulate reinforcement into a titanium matrix by mechanical milling[44]. This paper investigated the incorporation of 10 vol.-% TiB, 6.4vol.-% TiB_2, and 2 vol.-% elemental boron reinforcement of titanium via mechanical milling.

Due to the newness of this topic at the time, much of the milling information was proprietary and was not found in the publication. For example, the specific milling equipment used was not described and the milling times were all related to the shortest milling time instead of the actual elapsed time of the experiment. The set-up indicated that the milling took place in an inert argon environment. The powders were subsequently hot isostatically pressed (HIP) for consolidation and sintering.

The results indicated that there was some uptake in oxygen content with a minimal uptake in nitrogen content. The oxygen content was found to triple at a milling time denoted as 4T. The authors attributed the uptake of oxygen to oxygen adherence of the milling surfaces and not the purity of the milling environment. As the powders were repeatedly welded and fractured, clean unoxidized titanium was exposed and was then available to react with any oxygen present. Cold welding was noted during the process which ultimately led to powder low yield. SEM of the microstructures showed that the distribution of the particles was found to be inhomogeneous.

The article showed that the Ti-MMC could be formed by mechanical milling but admitted that several challenges must first be overcome. As titanium is a ductile powder, cold-welding to the milling media is likely. General powder metallurgical principles suggest the use

of PCAs to prevent cold welding. The most commonly used PCAs are hydrocarbons such as ethanol and stearic acid. The fear is that these materials will add unwanted interstitial contamination to the titanium matrix and cause embrittlement of the material. The authors did offer cryogenic milling as alternative to using PCAs but suggested its use would make any titanium material formed cost prohibitive. The poor distribution of the particulate reinforcement was attributed to the particle size of the starting materials (~250µm Ti, and >45µm for the reinforcement). The authors noted that the materials with the smallest particle size appeared to be the most homogenous. The size of these particles coupled with the cold welding challenges likely prevented the formation of a homogenous product. The authors suggested that increasing the milling time could also improve the homogeneity of the materials. It is likely that the increase in milling time would also further exacerbate the uptake in oxygen content, leading to embrittlement of the materials.

3.3 Mechanical Characteristics and Preparation of Carbon Nanotube Fiber-Reinforced Ti Composite

Once viable methods of creating Ti-MMCs had been established, many researchers began to experiment with different reinforcement materials. A Ti-MMC reinforced with carbon nanotubes (CNTs) was fabricated by mechanically mixing titanium and CNTs with subsequent sintering of the powder[45]. CNTs are a tubular fullerene structure which is noted for having extraordinary electronic and mechanical properties. Due to its tubular structure, CNTs inherently have a high aspect ratio which is typically a very good property for particle reinforcement. Carbon nanotubes are unique in that while they maintain an exceptionally high Young's modulus, they

also deform plastically, which indicates that their use will not sacrifice ductility. This study compares the microstructural and mechanical properties to other carbon based Ti-MMCs.

Very little information was detailed for the fabrication of the composite. The authors stated that the carbon nanotubes were mechanically mixed with the titanium for 5 hours as excessive mixing was estimated to cause structural damage to the CNTs. Following the mixing process, the powders were compacted in a carbon die then hot pressed for two hours at 1208K at 30MPa in vacuum. The CNTs used were noted to contain up to 40% of other graphitic allotropes. The volume fraction of CNTs used was 20%

X-ray Diffraction (XRD) was performed and it was found that TiC had formed following powder consolidation. Transmission Electron Microscopy (TEM) was subsequently performed and it was found that the CNTs remained intact. As the powder was only 60% CNT the likely source of TiC particle formation was from the other graphitic content. The relative density of the compact was reported to be 95.8% compared to 98.6% for pure titanium. The mechanical properties were determined by Vickers hardness and ultrasonic spectrum microscopy which was used to estimate the Young's modulus of the compacts. The increase of hardness was determined to be substantial as the Vickers hardness was stated to be 1216 HV. It was observed that large error was present in the data and was attributed to the porosity of the compact. The Young's Modulus was reported to be 198GPa, which was a solid increase in stiffness. The authors suggested that aside from the obvious structural reinforcement due to the CNT properties, it was likely that the nanotubes blocked the migration of dislocations which further strengthened the materials.

There is no doubt that the addition of CNTs augments the mechanical properties of titanium. In an article reviewing fabrication of Ti-CNT MMCs [8], the authors suggested that high energy ball milling was a widely accepted and efficient way to disperse CNTs evenly within a titanium matrix. Research has shown however that milling for longer than 2 hours substantially shortens the length of the CNTs which lose effectiveness as reinforcements[8]. The review article also calls for the use of a PCA to ensure homogenization. When considering the effectiveness of a composite one must evaluate the interface between the reinforcement and the matrix. It was observed that the CNT interface will react with the surrounding Ti matrix to form titanium carbide. Another article which used TiC as reinforcement showed good interfacial bonding between titanium and TiC[46]. Therefore, this reaction is thought to help the bonding properties between titanium and the CNTs. The fragility of the CNTs during the milling process makes the use of this material as a reinforcement difficult. Historically the production of carbon nanotubes is expensive and therefore may make a commercial product cost prohibitive. However, in 2012 a process was patented to rapidly and economically produce CNTs[47].

3.4 Nanocrystalline titanium powders by high energy attrition milling

Many challenges arise with milling titanium such as the prevention of cold welding and oxygen contamination. PCAs, such as stearic acid, are commonly used for other materials, yet most publications regarding the use of such PCAs suggest that their use will be detrimental to the ductility of the titanium matrix. In order to evaluate the effect of alternative PCAs, titanium powder was in an attrition mill with calcium and magnesium to reduce the particle and crystallite size of titanium powder[11]. The titanium powder was milled in a Svegari attritor mill using a

1:10 charge ratio with a milling speed of 450 RPM. The milling environment was high purity argon, and 2.5% stearic acid was used as a PCA. The milling vessel was water-cooled to prevent excessive heating of the powder. Milling times ranged from 0-75 hours. The authors state that the attritor was specifically designed such that the argon carrier gas flowed through the impeller to introduce the gas at the bottom of the milling vessel. This extra precaution was taken to prevent oxygen take-up during the milling process. As contamination control was paramount, the contamination levels of the powder were monitored.

Inductively Coupled Plasma (ICP) was performed on the milled powders to determine the quantity of contamination for each milling time. ICP is often used to quantify metal content. Therefore, only contamination from the milling media was considered. It was observed that the contamination from the milling media increased as a function of milling time. Dynamic Thermal Analysis (DTA) was performed on the powders to determine the effect of milling on the crystallographic transition temperature. It was observed the $\alpha \rightarrow \beta$ phase transition temperature decreased as a function of milling time with the minimum crystal transition temperature reported as 562^{o}C for powders milled for 75 hours. Minimum particle size was obtained after the powders were milled from 15-30 hours after which the particle size was stabilized. The crystallite size was determined to be approximately 10nm for powders milled for 30-75 hours. XRD showed the that intensity of oxide peaks increased with respect to milling time, but exact quantities were not listed.

The authors showed that attrition milling can effectively reduce the particle size, crystallite size, and $\alpha \rightarrow \beta$ phase transition temperature. While this information was shown for the powders post processing, no data was presented which demonstrated how compaction and

sintering affected these properties, or if these properties could be retained after sintering. This left an opening for research to be performed on sintered materials to determine both the microstructural and mechanical properties.

3.5 Mechanical Alloying of Titanium

As titanium is inherently susceptible to oxygen and nitrogen contamination, alternative PCAs have been researched to determine the effectiveness on cold welding reduction, the prevention of nitrogen and oxygen uptake, and the effect on microstructural and mechanical properties. A publication compiling a wide-ranging examination into the various processing control agents used for titanium was written [6]. Many researchers disagree on the use of organic PCAs as these materials pose to embrittle titanium matrices through interstitial strengthening. The author therefore studies the use of magnesium, calcium and other metallic compounds as PCAs for titanium.

Titanium powder was mechanically alloyed with the magnesium, calcium, MgY and CrY utilizing a Fritsch Pulverisette planetary ball milling apparatus. The setup utilized a ball to powder ratio of 10:1 with a milling speed of 450 RPM, pausing every 2 minutes to ensure the powder remained cool. The milling environments were both vacuum and argon. Post processing, powders were removed from the milling vials and stored simply in bottles exposed to air. The powders were spark plasma sintered (SPS) to form cylindrical test specimens for SEM, three-point bending and tensile testing.

The author noted that the processing agents did not have a clear effect on the oxygen or nitrogen uptake in the process. This could be due to powders being milled in a low-pressure argon

environment, which may have depleted the availability of gaseous contamination. With the respect to reduction of cold welding, all types of the PCAs used proved viable. Porosity was observed when the Mg and MgY PCAs were in use. Recovery was reported to be the best for the titanium powder milled with 5% calcium, yielding recovery values over 90% regardless of milling time. Additionally, calcium proved to produce other beneficial properties such as a homogenous microstructure, refined grainsize and increased tensile strength properties. A yield stress of 627 MPa and an elongation of 17% was reported, showing that the increase of strength was nearly double that of commercially pure titanium without sacrificing ductility. The author attributes the success of the calcium PCA being due to it having a higher melting point boiling point, vapor pressure, and solubility in titanium. These properties show that calcium PCA is much more stable than the magnesium PCA at elevated temperature, which is an important factor when considering sintering.

The author stated that the use of hydrocarbon containing PCAs should be avoided due to the high reactivity of hydrogen, carbon, nitrogen, and oxygen. While it is well understood that titanium is highly reactive to these elements, the statement that hydrocarbon PCAs should not be used was not referenced and to knowledge has not been fully evaluated. Additionally, the author utilized a maximum milling time of two hours, which is relatively short for mechanical alloying. While it was noted that the PCAs did not change oxygen adsorption, it is unknown whether or not this fact stays true at longer milling times. It was apparent that the PCAs have a positive effect on grain refinement and subsequent mechanical properties.

3.6 High-Performance, Low-Cost Titanium Metal Matrix Composites

Metal matrix composites can be formed by two milling methods: ex-situ and in-situ powder metallurgy. In the case of ex-situ powder metallurgy, the two materials are inert and therefore are simply mixed together prior to compaction and sintering. In the case of in-situ powder metallurgy the two materials are not necessarily inert and may chemically react at some point in the powder metallurgical process. Often, the reactions take place during the sintering process. Creation of a particle reinforced Ti-MMC by intentionally reacting the particulate reinforcement with the titanium matrix was investigated [48]. The aim of the experiment was to mechanically alloy titanium with carbon black, subsequently sintering the materials to create a titanium carbide/titanium metal matrix composite. High energy ball milling techniques have been noted to have sufficient energy to cause materials to react. Titanium has unique difficulties associated with powder metallurgy, largely revolving around its affinity to oxygen. The authors state that in-situ does tend to introduce more oxygen into the matrix. However, it has been reported to be difficult to homogenously disperse particle reinforcement using the ex-situ method.

The authors mechanically alloyed titanium powder with 3% carbon black using a Fritsch Pulverisette planetary ball milling apparatus. An alpha alloy (Ti-5Sn-3C) and a beta alloy (Ti-13Cr-5Sn-3C) were investigated. Calcium was researched as a viable processing agent in Zadra et. [6] and was used as the PCA in this experiment. The setup utilized a ball- o powder ratio of 20:1 with a milling speed of 500 RPM, milled for 80 minutes. No pausing steps were noted. The milling environment was described as low vacuum. Post processing, powders were removed from the

milling vials and simply stored in bottles exposed to air. The powders were spark plasma sintered at various temperatures to form cylindrical test specimens for SEM, three-point bending, and tensile testing. XRD was performed to identify the presence of titanium carbide, and high temperature carrier gas extraction was used to monitor the oxygen and nitrogen content.

The process yield was noted to be above 95% with the oxygen and nitrogen content remained below 0.4% and 0.05% respectively. The importance of the 0.4% and the 0.05% oxygen and nitrogen contents is that values exceeding these limits are thought to lead to embrittlement of the titanium matrices. The XRD confirmed that the carbon black had reacted with the titanium matrix, causing the formation of titanium carbides in the matrix. The SEM results showed that the particles could be evenly dispersed in the matrix. A coarsening effect was observed, positively correlating sintering temperature and particle size. An increase in mechanical properties was also noted, yielding ultimate tensile strengths of approximately 1200 MPa at a substantial sacrifice to ductility. The minimum tensile elongation was reported to be 3% and the maximum tensile elongation shown was 5%.

The authors did show success in forming a carbide reinforced Ti-MMC, yet the authors stated that they felt that additional carbon black could be used to further reinforce the titanium matrix. The SEM images started to show particle saturation as particles began to concentrate at the grain boundaries and were shown in Figure 9. The authors briefly acknowledge this fact but fail to discuss whether this adversely affects the structural integrity of the material. Also, pits were observed in an SEM micrograph but were not discussed. The authors reported that the materials had a maximum flexural elongation of 17%, but this data was not shown in the article.

It is thought that if the authors had limited the amount of carbon black used, the particles may not have concentrated at the grain boundaries, improving the ductility of the material.

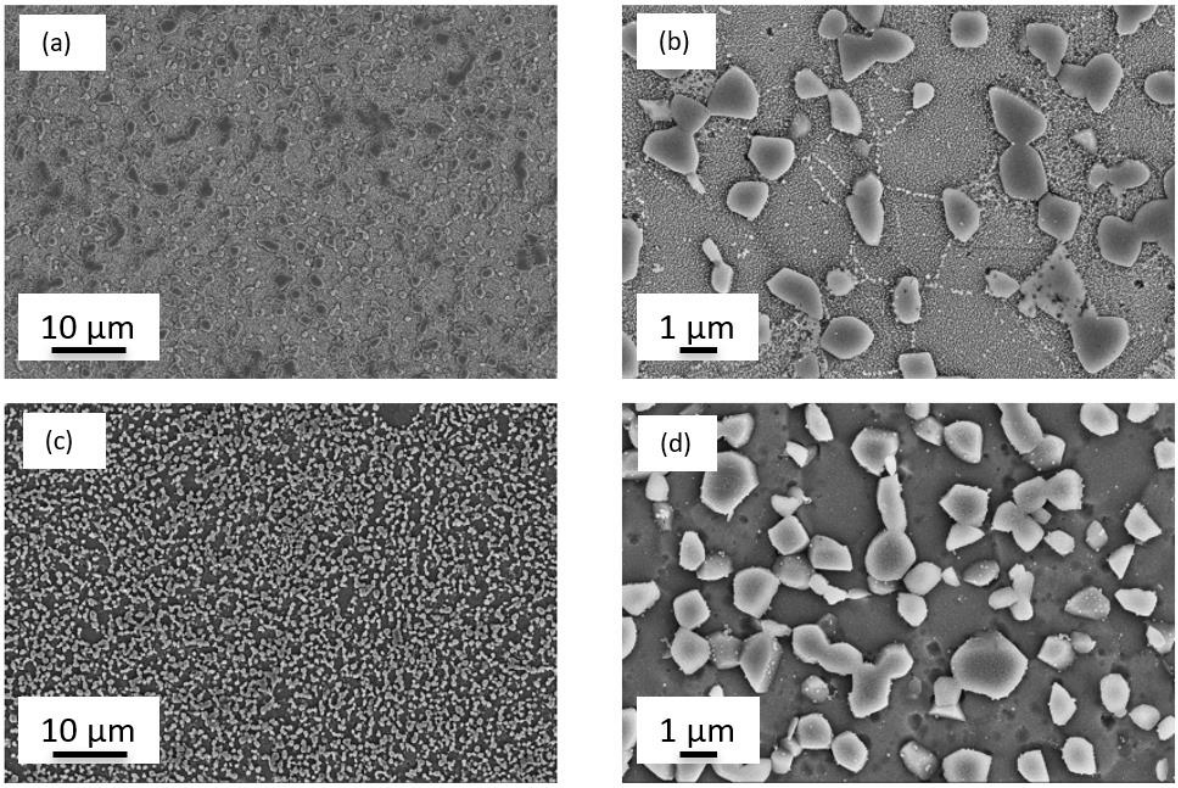

Figure 9. SEM of TiC/Ti-MMC via Attrition Milling/Sintering. Images from Zadra et. al. 2014. Particle formation is observed. (a) Mechanically alloyed Ti-5Sn-3C powder sintered at 1050°C/ 1 min, Kroll's reagent. (b) Mechanically alloyed Ti-5Sn-3C powder sintered at 1150°C/ 1 min, Kroll's reagent. Concentration of particles at the grain boundary is observed. (c) Mechanically alloyed Ti-13Cr-5Sn-3C powder sintered at 1050°C/ 1 min, Kroll's reagent. (d) Ti-13Cr-5Sn-3C powder sintered at 1150°C/ 1 min, Kroll's reagent. Etch pits are observed in the matrix. Image reproduced with permission.

3.7 Cryogenic Milling of Titanium.

Cryogenic milling of titanium was suggested as an alternative to traditional PCAs to reduce interstitial contamination as well as prevent cold welding [49]. 20 years later Kozlik et. al. [10] examined the feasibility and the effect of milling titanium powder in varying cryogenic atmospheres[10]. The two cryogenic fluids chosen for this experiment were liquid nitrogen and

liquid argon. Titanium has an immense affinity to interstitial gases such as oxygen and nitrogen. Milling for extended time intervals in a gaseous argon environment has shown an inevitable take-up in nitrogen and oxygen content. Additionally, for aluminum alloys cryogenic milling has shown to reduce to crystallite size to the order of tens of nanometers. High energy ball milling has shown the ability in previous studies to enhance the mechanical properties through grain refinement and the Hall-Petch relation[50]. The refinement of crystallite size is aided by the reduction of particle size. Cryogenic milling was originally thought to diminish the ductility of the powders and allow for reduction of particle size.

Commercially pure titanium (CP Ti) was cryogenically milled using a Svegari attrition mill. The milling time, speed, and charge ratio were dependent on the milling media used. For the WC media the conditions were 3.25h, 650RPM, and CR 32:1 for milling time, milling speed, and charge ratio respectively. For the SS media the conditions were 4h, 700RPM, and CR 16:1 for milling time, milling speed, and charge ratio respectively. The increase in time and speed were to account for the use of SS media being less energetic to that of the WC media. The resultant powders were analyzed to determine particle size, oxygen/nitrogen content, grain size, and micro hardness of the powders.

The use of liquid nitrogen was determined to be detrimental to the experiment as significant uptake in nitrogen was reported. It was hypothesized that the cryogenic temperatures of the milling process would inhibit any chemical reactions or dissolution of nitrogen into the matrix. However, the results suggest that this was fallacious. Therefore, the need for the more expensive liquid argon was justified. The uptake in oxygen and nitrogen was kept below 0.6% for all experiments. It was observed that the use of WC media exacerbated the uptake in oxygen

content. Additionally, contamination from fractured WC milling media was reported. The particle size reduction was not reported for titanium powder milled in liquid argon. Particle size reduction was observed for the powders milled in liquid nitrogen which is attributed to the embrittlement of the titanium powder via nitrogen contamination. In fact, cold welding was reported for the powder milled in liquid argon and substantiated the use of a PCA. The authors used stearic acid to mitigate the cold welding. Cryogenic milling of the titanium powder exhibited an ultra-fine grain structure with typical grain sizes reported around 100nm.

It was determined that the powder milled in liquid argon for 4 hours using stearic acid and stainless milling media yielded the best results in terms of contamination and ductility. As such, this powder was selected to be further studied in a separate article to determine the effects of SPS sintering on the microstructure Kozlik, et.al. 2017 [9]. The powder was handled simply in air after milling. 8 wt. % Stearic Acid was used as a PCA and was removed by rinsing the powder with ethanol after milling. Sintering temperature was varied from 600^{o}C to 850^{o}C using a 100^{o}C/min ramp rate and a 3-minute dwell time. Cooling rate was not controlled but approximated at 200^{o}C/min. The goal of the study was to determine the extent of recrystallization as a function of sintering temperature and to characterize the phases present.

The microstructure of the sintered compacts was examined using scanning electron microscopy with electron back scatter diffraction (SEM-EBSD). These results showed the formation of an FCC phase at all sintering temperatures. The FCC phase was only recently discovered and not much is known about this phase. It is hypothesized that the FCC phase would increase the ductility of the material due to the increased number of slip planes in this crystal structure. It was observed that at 650^{o}C to 750^{o}C, a bimodal distribution of large grains and ultra-

fine grains existed (Figure 10). Current conjecture suggests that this microstructure will make the material behave like a composite, with the ultra-fine grains reinforcing the larger ones. Through the Hall Petch relation, the ultra-fine grains should in fact strengthen the material. Sintering at 850^{o}C was noted to lose its bimodality as substantial recrystallization was observed. XRD and SEM-EBSD was performed and later confirmed that the darker regions in the micrographs were the FCC phase (Figure 11). The residual porosity of the materials were determined from the micrographs and were observed to be 1.62%, 1.62%, 0.11% for the samples sintered at 650^{o}C, 750^{o}C, 850^{o}C respectively. The authors then correlated these numbers to a decrease in hardness. However, numerical values for Vickers' microhardness were not reported.

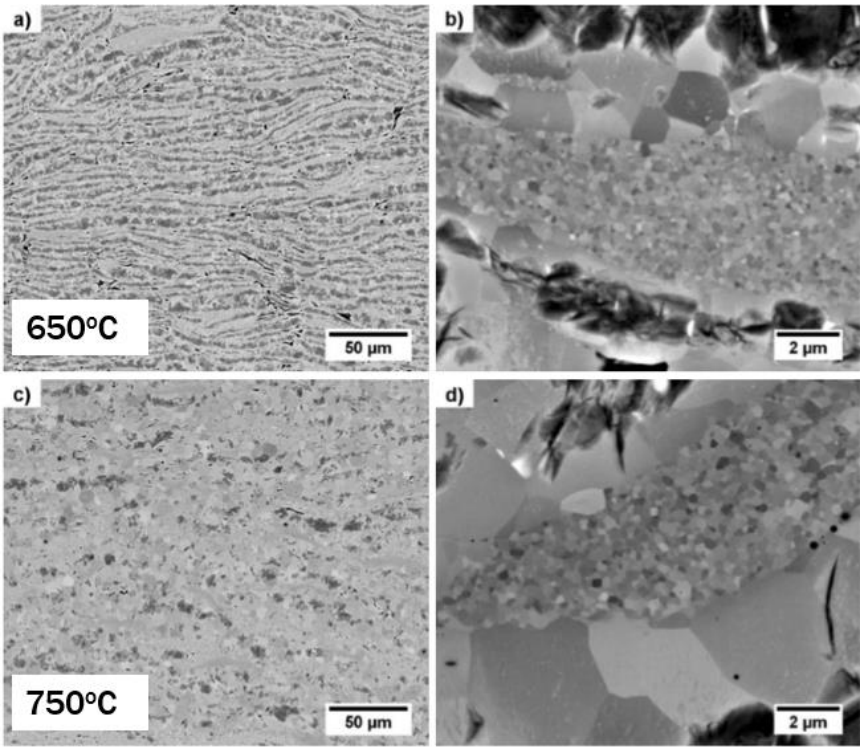

Figure 10. Nano-Crystalline Microstructure of Ti Via Cryo-Attrition Milling. The above image shows liquid Ar Cryomilled powder which had been SPS sintered at various temperatures: a) and b) at 650^{o}C, c) and d) at 750^{o}C. Images b) and d) show a bimodal microstructure in which ultra-fine grains and larger grains are present. Additionally, the darker regions in the micrograph is an FCC phase which was later confirmed by SEM-EBSD. Image reproduced with permission.

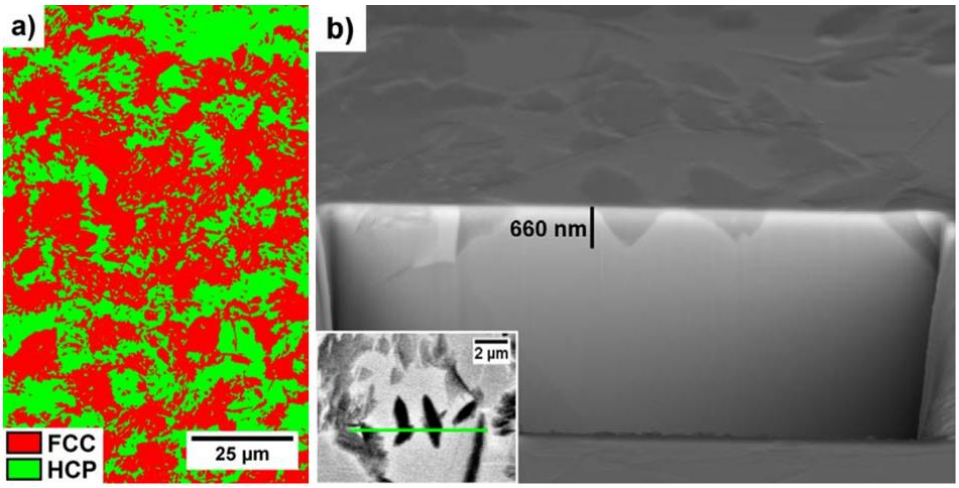

Figure 11. SEM-EBSD Revealing FCC Grains in Titanium. a) EBSD phase map of titanium spark plasma sintered at 850°C. b) Cross-section containing FCC lamellae. The above data suggests that a large portion (60%) of a meta-stable FCC phase is retained in the microstructure. Image reproduced with permission.

The authors developed a milling procedure which prevented the interstitial contamination of titanium powder. Very interesting results were generated such as the retention of ultra-fine grains after sintering. The retention of this microstructure is due largely to the tremendously quick heating ramp rates and opportunity to sinter for short periods of time. The feasibility of producing commercially viable parts using SPS sintering is still in question as these machines are generally used for laboratory purposes. Additionally, the cost of using liquid argon as a PCA may prove to be cost prohibitive. It should be noted that the authors showed that stearic acid could be used as a PCA, which has been speculated to be destructive to ball milling of titanium. The existence of an FCC metastable phase is unique to this process and future mechanical tests may prove this phase enhances its mechanical properties.

3.8 Summary of Previous Work/ Research Needs

There are undoubtedly great advances that have been made with titanium, especially in the last 30 years. However, a need for continued research still exists. Cost to produce titanium parts remains 20 times higher than that of carbon steel and 4 times higher that stainless steel[51]. Reduction of titanium cost is feasible as titanium is the ninth most abundant materials in the earth crusts, yet due to its affinity to oxygen, commercially pure titanium remains expensive. Alternative methods have been researched, yet they have not been widely implemented as a commercial process. Commercially pure titanium is generally soft, and it is often alloyed to enhance its mechanical properties. Many titanium alloys employ toxic elements, such as vanadium, which render the material unusable in biomedical fields. Also, once titanium parts have been created, they often undergo machining to achieve its net shape, which leads to loss of material. Reclaiming the titanium scrap must undergo additional processing which also increases the price of titanium materials.

The above literature[6, 8-10, 43, 45, 48] introduces powder metallurgy of titanium which helps to mitigate the cost of fabricating titanium parts as the process can create, titanium alloys and Ti-MMCs of enhanced mechanical properties at near net shapes. While mechanically alloying titanium can be an attractive process, it also has many challenges which are commonly addressed in the literature. Mechanically alloying is a process which inherently causes titanium to oxidize. Zadra et.al [6, 48] and Kozlik et.al. 2018 [9, 10] use calcium as a PCA and cryogenic milling respectively to reduce oxygen contamination. The calcium PCA proved as it minimized cold welding and kept the oxygen content below 0.23%. However, the effectiveness of this PCA's

oxygen scavenging properties is unknown for higher milling times. Cryogenic milling produced the best results for preventing oxygen contamination, as well as produced a unique FCC phase and nanograins. As liquid argon is relatively expensive, this makes this process cost prohibitive for producing industrial parts.

Titanium tends to cold weld during the milling process which necessitates the need for a PCA. PCA type for titanium is a topic that is disputed in the field. Many authors suggest that organic PCAs, such as ethanol or stearic acid should not be used, while other authors have used such PCAs with minimal negative effect. Therefore, the need to further examine the effectiveness of organic PCAs is still desired.

Mechanical alloying allows for the blending of powders to create particulate reinforced metal matrix composites. The benefit of particulate reinforced Ti-MMCs are that the mechanical properties can be greatly enhanced without a substantial increase in cost. The research performed in the above literatures successfully create many Ti-MMCs of beneficial mechanical properties. However, one must consider cost when also considering the feasibility of reinforcement for industrial use. Table 1 shows a comparison of the mechanical properties of titanium materials, and Ti-MMCs. Table 2 shows the relative cost of each additive as well as the strengthening efficiency in terms of cost. The strengthening efficiency is calculated in terms of cost divided by either the tensile strength or the compression strength, depending of which value is available.

Table 1. Comparison of Literary Ti-MMC Mechanical Properties. Included at the bottom of the table is comparison data from the Ti-2CNC-5A material from chapter 5 in this thesis.

Materials	*Vickers Hardness*	*Modulus of Elasticity (GPa)*	*Compressive Strength (MPa)*	*Tensile Strength (MPa)*	*Maximum Ductility %*
5% TiB Ti-MMC[52]	375-400	180-200	1500	---	15
20% TiC Ti-MMC[52]	475-500	180-190	1600	---	10
0.34% CNT Ti-MMC[8, 27]	950-100	200-250	---	700	30
5% Graphite Ti-MMC[48]	350-400	130	---	1200	17
Ti Grade 2[53]	145	110	---	344	20
Ti-6Al-4V	349	114	1080	950	14
Ti-2CNC-5A Ti-MMC	410	130	1697	---	19

Table 2. Comparison of Material Costs. A cost/strength calculation has been performed to determine the feasibility of using CNCs as an additive.

Materials	*Compressive Strength (MPa)*	*Tensile Strength (MPa)*	*Additive Cost (USD/gram)*	*Product cost (USD/in^3)*	*Cost/Strength (USD/GPa)*
5% TiB Ti-MMC[52]	1500	---	$1.00[54]	---	$4.78
20% TiC Ti-MMC[52]	1600	---	$88.80[55]	---	$6.50
0.34% CNT Ti-MMC[8, 27]	---	700	$1000[13]	---	$15.61
5% Graphite Ti-MMC[48]	---	1200	$0.66[56]	---	$5.97
Ti Grade 2[53]	---	344	---	$7.50[57]	21.80
Ti-6Al-4V	1080	950	---	$27.50[57]	25.46
Ti-2CNC-5A Ti-MMC	1697	---	$0.99[58]	---	$4.37

The aim of this work was to create a cost-effective Ti-MMC which also has competitive mechanical and microstructural properties available in the literature. It was shown in Table 2 that the Ti-2CNC-5A Ti-MMC can be fabricated efficiently compared to other Ti-MMCs reported in the literature. CNCs are beneficial in that they are naturally occurrent and abundant. CNCs are innately organic and could be either problematic or beneficial to a titanium matrix, thus evaluating the effectiveness of this compound is necessary. Lastly, the strengthening mechanism associated with creating the Ti/CNC MMCs will be explained in the subsequent experimental chapters.

Chapter 4.

Processing Effects and the Characterization of Titanium Mechanically Alloyed with Cellulose Nanocrystals.

4.1 Abstract

Titanium powder was mechanically alloyed via high energy ball milling with ethanol and cellulose nanocrystals (CNCs) to increase the strength and hardness of titanium without the addition of toxic alloying elements such as vanadium. The mechanically alloyed materials were compacted and sintered at 1200^{o}C for one hour and subsequently characterized using SEM, TEM, XRD, XPS, and Vickers hardness characterization techniques. The results indicated that milling titanium in the presence of ethanol and CNCs increased and stabilized the dislocation density of the system which played a major role in strengthening the material. The dislocation density of microstructure was studied as a function of milling time and process control agents (PCA) used. Particle formation was evident and likely advantageous in samples milled up to two hours. The strengthening mechanism can be explained microstructurally by increasing the dislocation density, reducing the grain size, and forming a metal matrix composite by the precipitation of ceramic particles.

4.2 Introduction

Titanium and its alloys are very useful materials which are used primarily as a result of the materials' high strength, low density, and high corrosion resistance. Due to these desirable mechanical and physical properties, titanium and its alloys are often used in the aerospace, automotive, and biomedical fields. To further augment its mechanical properties, titanium is

typically alloyed with vanadium and aluminum with subsequent heat treatments to create beta and alpha-beta alloys[59]. Vanadium is a known cytotoxin and has also been linked to the development of Alzheimer's, rendering these alloys unusable in the biomedical fields[59] [60]. Even with the enhanced mechanical properties that alloying titanium offers, it is known that titanium alloys have tribological weaknesses such as unfavorable wear resistance and poor shear strength[61]. To mitigate these weaknesses of titanium alloys they are often reinforced with a ceramic to create metal matrix composites[59].

Cellulose nanocrystals (CNC's) have recently gained attention as polymer additives due to its high rigidity. Cellulose nanocrystals are also natural, abundant, and are toxicologically innocuous[62]. Additionally it has been shown that the material can be made thermally stable when used in polymer matrices[63], but the material will degrade at metal processing temperatures. Hence, it is not surprising why this material has gone unnoticed as a potential additive in the metals industry. However, we hypothesize that the degradation of the material may influence the reactions needed to transform and create unique microstructural features.

The strengthening mechanisms using cellulose nanocrystals as a particulate reinforcement is evaluated in this paper. The intentional addition of interstitial elements increases the strain of the crystal lattice, thereby increasing the dislocation density of the titanium matrix[64]. As dislocations have a repulsive nature in materials, increasing the dislocation density will increase the difficulty of further deforming the material[65]. This phenomenon can be directly observed via microscopic analysis following the use of an etchant solution to make the dislocations visible. As the dislocations are energetic sites, the etchant solution preferentially removes material at a higher rate than areas without dislocations,

resulting in etch pits. Etchant solutions are typically specific to a material are chosen based off of the corrosion behavior of that material. In other systems, such as gallium nitride, distinctive hexagonal etch pits have been observed [66]. It is suggested that this is the spiral growth etch pit pattern of screw dislocations [64]. Typically, sintering and heat treatments performed on milled metals will have an annealing effect which allows for a reduction in dislocation density. The reactive nature of titanium with the cellulose nanocrystals will precipitate small nano-sized particles. It has been shown that the precipitation of these small particles prevents dislocations from gliding even at elevated temperatures, as is the case for oxide dispersion strengthened materials [67, 68]. It has been speculated that nanoparticles dispersed within a titanium matrix will also have this effect for titanium[45]. S. Naka et al [69] has observed that the dislocation velocities in titanium are relatively low. Providing that the cooling rate is not sufficiently slow, the strengthening effect was predicted to remain after sintering.

Powder metallurgy is an economically attractive process due to its ability to form parts with little waste as well as for allowing for physical properties to be custom engineered[70]. Mechanical alloying is a powder metallurgical preparation technique which utilizes kinetically energetic balls to impact the material, causing repeated welding and fracturing of the material. The energy of the system, which is important for engineering the physical properties, can be controlled by choosing the milling media and the length of milling time. A major result is the formation of a supersaturated solid solution which can be used to further precipitate reinforcement particles[71].

In this chapter, the physical and microstructural properties of Ti-CNCs MMC are examined and analyzed as a function of CNCs concentration as well as milling time. Various characterization techniques were employed to study and understand these properties and to determine which combination of processes fabricated the superior material. Hardness, particle size, calorimetric, and microstructural properties are characterized. The results explain the production of nanocomposite features found because of milling, pressing, and the sintering Ti-MMC.

4.3 Material Preparation

Commercially pure titanium powder (Atlantic Equipment Engineers, 99.7% ~325 mesh) and Cellulose Nano-Crystals (CNCs) (USDA Forest Products Laboratory; obtained as a freeze dried solid, 0.85 wt % sulfur), were used as the starting materials. The titanium and CNC powders were combined, and the materials were mixed via high energy ball milling. The CNC powder was added in the amounts of 0.5% and 1% by weight. For the remainder of this paper the nomenclature for these two compositions will be Ti-0.5 CNC and Ti-1.0 CNC respectively. Tungsten carbide was chosen to be the milling media. The powder and milling media were combined and milled using a charge ratio of 2.5 which yielded 12.9 grams of material per batch. Ethanol was added in the amount of 1.25mL to the contents to act as a lubricant and minimize welding in the vial and ball surfaces. The contents of the milling vials were added in a glove box purged with argon. The oxygen content of the glove box environment was monitored using an oxygen sensor. The milling vessels were then sealed in the glove box to inhibit the formation of oxides and nitrides. The milling was performed using a SPEX 8000M high energy ball mill with milling times varied from 1 hour to 25 hours, agitated at 20 Hz. The milled materials were compacted in a 0.5 inch (diameter) stainless steel die press. Approximately 1 gram of material was added to the barrel of the die.

The material was compacted at 11 metric tons and held for 10 minutes. The compacts were then placed in a ceramic crucible, pre-cleaned by sand-blasting and loaded into a tube furnace. The furnace was heated to 1200°C at a ramp rate of 5°C/min while flowing argon through the furnace at 40 mL/min. The sintering temperature was 1200°C held for 1 hour. The samples were then furnace cooled back to ambient. Figure 12 below shows a schematic of the preparation process.

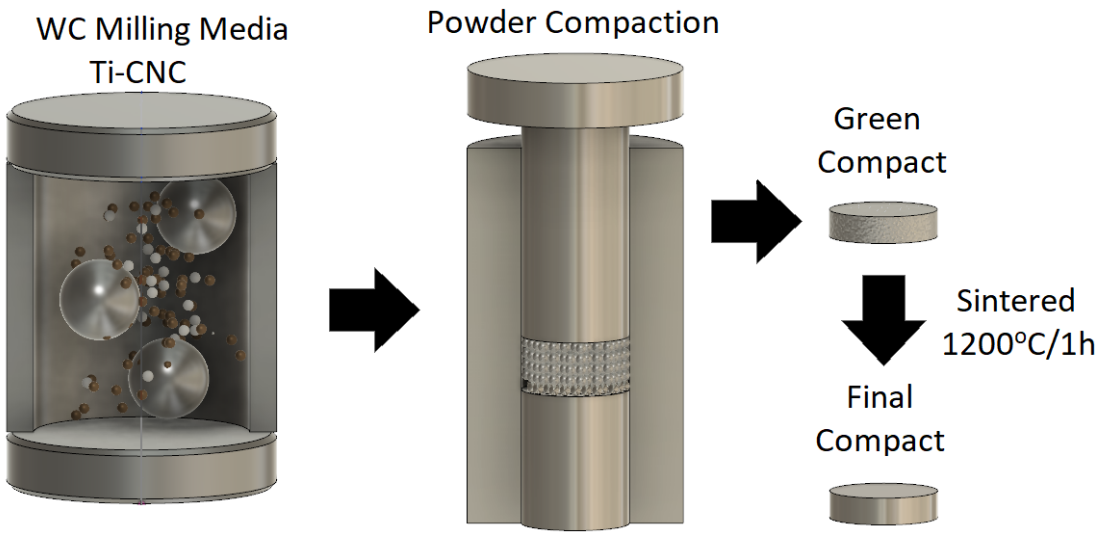

Figure 12. SPEX Milling and Sintering Schematic. The titanium and CNC powders were combined and milled, which created a mixture of the two materials. The mechanically alloyed powders were then uniaxially pressed at 850 MPa. The resultant green compact was sintered at 1200°C for 1 hour. The naming convention details the matrix, the CNC content, the lubricant used, and the time in hours. i.e.: (Ti-1.0CNC-EtOH-1h).

4.4 Characterization

X-Ray Diffraction (XRD) was performed on the milled powder samples and the sintered compacts using a PANalytical X'pert PW3040 Powder Diffractometer. The compact samples were ground to a final smoothness of 600 grit using silicon carbide paper. X-Rays were generated by applying an acceleration energy of 45kV and 40 amps to a copper source. The specimens were

placed in holders which were rotated at 60Hz while the diffraction pattern was analyzed stepwise from 10^{o} to 95^{o} angular rotations (2θ).

Following XRD, the sintered compacts were cross-sectioned and mounted in a conductive phenolic resin using an encapsulating hot press. The operational parameters for the hot press was 150^{o}C and 3000 psi for 20 minutes. The mounted samples were grinded and polished to a 0.05µm finish using silicon carbide grinding paper and alumina powder suspension respectively. The polished samples were immersed in an aqueous 5% (vol. %) hydrofluoric acid and a 3.5% (vol. %) nitric acid etching solution for 10 seconds at ambient temperature.

The etched samples were loaded into an SEM and attached to the platen with copper conductive tape. SEM imaging was performed using an FEI Environmental SEM while varying the accelerating voltages between 10kV and 20kV. Everhart-Thornley and backscatter electron detectors were used to acquire SEM images.

The sintered compacts were polished to a 0.05µm finish similarly to the SEM preparation. Indentations were made using a Phase II 900-398 Macro Vickers Hardness Tester utilizing a pyramidal diamond indenter with 136^{o} angled faces. Using an indentation load of 29.4 N and a dwell time of 15 seconds, indentions were made on the compact. Five indentations were made on each compact except the Ti-1.0 CNC-25H compact which was noted to be especially porous. Indentations were made on the centerline of the cross-sections to avoid surface hardening effects from sintering (Appendix A).

The materials which were previously prepared for SEM analysis were furthermore prepared for TEM analysis. Focused ion beam (FIB) was used to extract a portion of the sample

and was attached to a copper grid. The extracted material was thinned below 100nm to achieve electron transparency. The grid was then transferred to a JEOL 2100 TEM and analyzed utilizing an accelerating voltage of 200kV. Transmission electron micrographs were acquired as well as the resulting diffraction patterns.

The hydrogen, carbon, oxygen and nitrogen content of the titanium compacts were analyzed using the carrier hot gas extraction method (HCNO analysis). Approximately 3 grams of sample were heated in a furnace to degrade the H,C,N,O which were dissolved in the titanium. A flow of argon was used to carry the removed gasses to be detected and quantified.

4.5 Results and Discussions

It was found that there was a correlation between the milling time and the hardness of the materials (Figure 13). The results also suggested that milling time was the dominant factor which determined the hardness of the material; the effect of composition was negligible. The hardness values for each specimen were found to range from 400 to 800HV, increasing in value with milling time. Typically, high strength titanium alloys such as Ti-6Al-4V (Grade 5) exhibit hardness values below 350HV [72]. To better understand the strengthening mechanisms of the materials, other characterization techniques were employed (HCNO analysis, XRD, SEM, TEM).

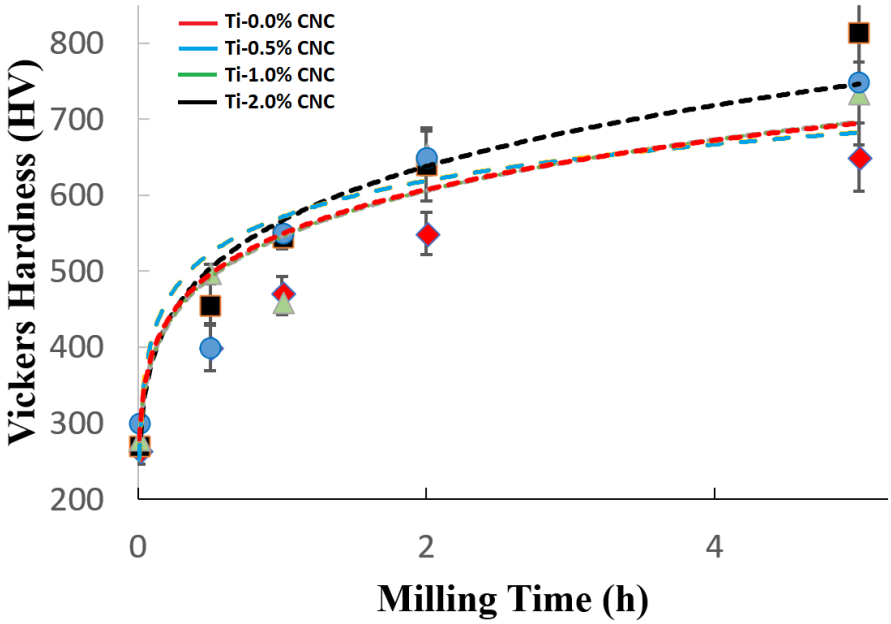

Figure 13. Hardness Trends with Respect to Milling Time and CNC Concentration. The indentions were made in the center of the cross-sections of the compacts. The results indicate that the hardness of these materials is largely dependent on milling time.

The carrier gas hot extraction method was utilized to determine the hydrogen, carbon, nitrogen, and oxygen content of the processed materials (Table 3). The results indicated that even without the CNCs, oxygen was present post processing. Further increasing the milling time exacerbates the take-up in oxygen. This suggested that the milling environment was largely responsible for the increase in oxygen content. Although milling vials were prepared and sealed in an argon environment, the glove box was found to contain roughly one percent oxygen. This suggested that this purity of the milling environment was adequate to react with the titanium powder during the milling process. It was noted that the nitrogen content was negligible for all specimens which were milled below five hours. The carbon content was also noted to increase with milling time. The fact that a finite concentration of CNCs was added to the milling vial

suggests that the ethanol PCA was incorporated into the titanium matrix. It was observed that at lower milling times the powder was slightly moist after milling. Post-processing, the residual ethanol was evaporated off, making the carbon content less for these milling times.

Table 3. HCNO Content for SPEX Milled Samples. Results show that carbon and oxygen content increases with milling time. Concentrations of nitrogen below 5 hours of milling are negligible.

	Elemental Content (Wt.%)			
Sample	**Carbon**	**Oxygen**	**Nitrogen**	**Hydrogen**
Ti-0CNC-1h	0.32	1.95	0.01	0.02
Ti-1CNC-0.5h	0.30	1.26	0.01	0.00
Ti-1CNC-1h	0.61	1.55	0.01	0.00
Ti-1CNC-2h	1.16	2.52	0.01	0.00
Ti-1CNC-5h	2.26	4.30	0.08	0.00

The XRD spectra for the materials are shown in Figure 14. The XRD performed on the milled powders showed that the precipitation of titanium ceramics coincided with increased milling time. The formation of an unknown titanium ceramic (TiO, TiN) appears to become especially noticeable after 10 hours milling time and as the sample reaches 25 hours, the titanium ceramic signal suppresses that of the titanium. It was important to note that substantial peak overlaps exist for titanium oxides and nitrides which made identifying these individual compounds virtually impossible. As titanium is highly reactive, the increased surface area allowed for additional sites for the titanium to react, thereby increasing the ceramic content. Additionally, peak broadening was especially evident as milling time reached 10 hours. This was attributed to the distortion of the crystal lattice, which was a consequence of the repeated collisions in the milling process. The results from the sintered specimens showed that the peaks had sharpened.

The sintering process allowed for recovery and recrystallizing which reduced the residual strain on the lattice, thus sharpening the peaks. Additionally, the interstitial elements likely diffused to lower energy interstitial sites which led to less deviation of the lattice parameter and sharpening of peaks. The sharpening of peaks showed that the formation of the titanium ceramic had developed after 5 hours milling time. The signal from the CNCs was not observed. It was also important to note that the alpha titanium peaks shifted to lower angles as milling times were increased, indicating that interstitials had dissolved into the crystallographic matrices thereby increasing the lattice parameter. The appearance of the Ti-1.0CNC-EtOH-25h was unique as the sintered compact turned to a dull brown color as opposed to a metallic appearance. XPS was performed on the Ti-1.0CNC-EtOH-25h compact and it was determined that elevated levels of nitrogen were present (Figure 14). The data indicates the titanium, oxygen, and nitrogen were the dominant elements. Note that tungsten peaks were present in the data but were excluded from the quantitative data as it was a known contaminant from the milling media.

Using SEM, one very apparent observation in the milled and sintered samples was the presence of hexagonal etch pits. The etch pits are formed as a result of the Kroll's reagent preferentially removing material at high energy sites resulting from screw dislocations. Although present in lower quantities within the unmilled titanium powder, it was unmistakably evident that the milling process further increases the quantity of the screw dislocations (Figure 15). The density of the dislocations was further augmented by the addition of ethanol and CNCs. Increasing the dislocation density substantially lead to the even distribution of dislocation in the titanium matrix. Milling the titanium powder with both ethanol and CNCs increased the

dislocation density of the material by an order of magnitude. This increase of dislocations was thought to be a predominate factor which increases the hardness of these materials.

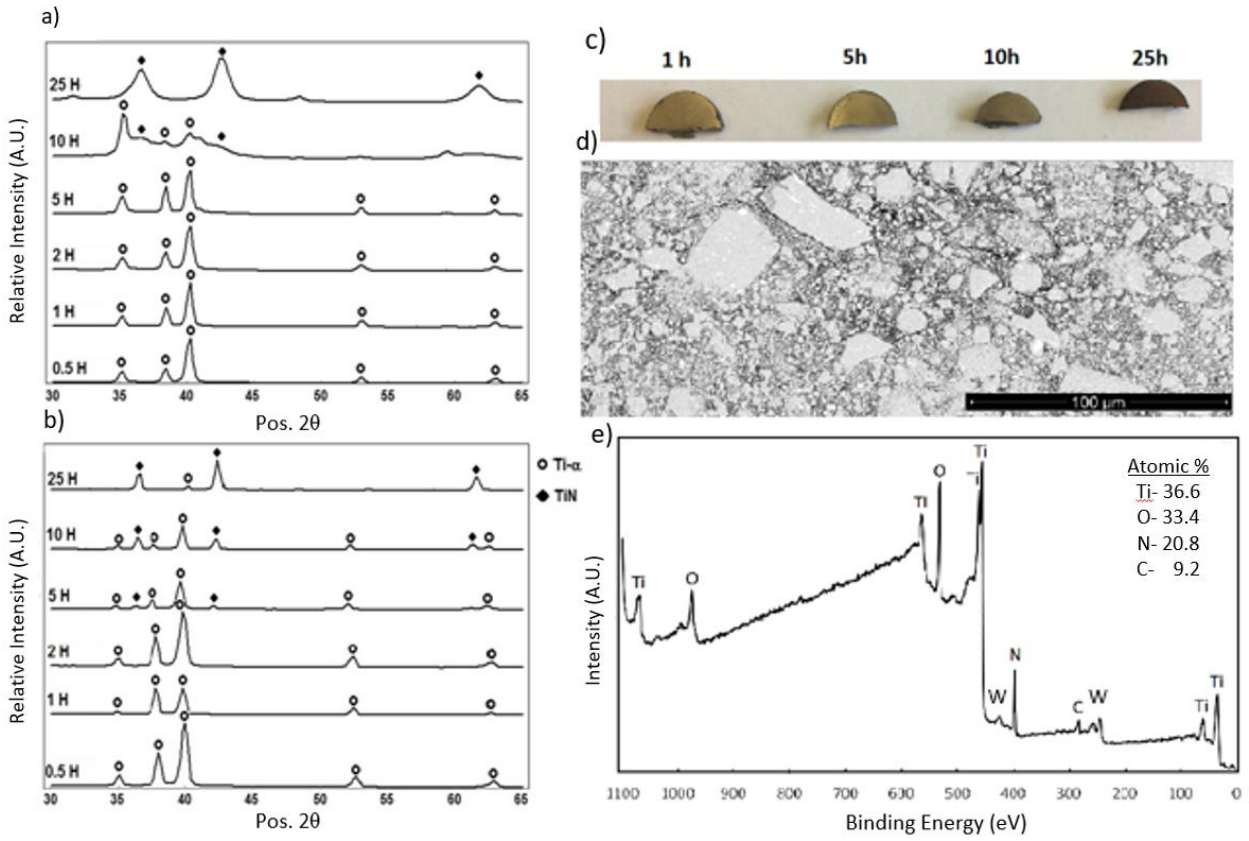

Figure 14. XRD Diffractograms/Discoloration of Ti-1CNC-25h/XPS Results. a) The X-Ray Diffractograms of Ti-1.0CNC-EtOH powders are shown and are representative on the Ti-0.5CNC-EtOH material. The data represents the effect of the crystal structure and composition as a result of the time milled. The data suggests that the inert milling environment was impure, leading to formation of titanium ceramics solely from the milling process. As the milling time is increased the material is largely converted to titanium nitride. b) The Ti-1.0CNC-EtOH-1h compacts were also analyzed. The materials were ground to remove possible surface artifacts. As expected, sharpening of the peaks was observed as a result of the heat treatment process. Ti-α peak shift was observed to shift to the left as a function of milling time. Free carbon, which is present as the CNCs degrade, is dissolved into the interstitials. c) A strong discoloration was observed for the Ti-1.0CNC-EtOH-25h compact post-sintering. d) Microscopic inspection of that samples suggest that particle formation is occurring within the matrix. e) XPS was performed on the sintered compacts and it was determined that an anomalous amount of nitrogen was present in the Ti-1.0CNC-EtOH-25h sample, indicating that the powder had nitrided during milling. The tungsten which was detected is also contamination from the milling media.

Once the milling time approaches two hours the presence of the dislocations became less evident likely due to the features becoming infinitesimally small; conversely, particle formation began to become increasingly evident within the grains.

The SEM results also indicate that the microstructure depended greatly on milling time (Figure 16). Increasing milling times of the titanium powders was noted to increase the dislocation density. At 2 hours of milling the etch pits became minuscule making quantifying the dislocation density difficult. Additionally, a coarsening effect of the particle reinforcement was observed and the location of the particles were found within the grains. After five hours milling the particle formation had predominantly began precipitating at the grain boundaries and the particles have substantially coarsened. Energy dispersive spectroscopy was performed on the bulk matrix of this material as well as on the particles which had formed (Figure 17). It was observed that the carbon content increased at the sites where the particles exist. This data coupled with the XRD and HCNO analyses, suggest the precipitation of a complex titanium ceramic (TiC_xO_y). It was noted at this point that the material was at its hardest and beyond five hours milling, the particle formation compromises the integrity of the material, making it brittle and weak as observed by the hardness data.

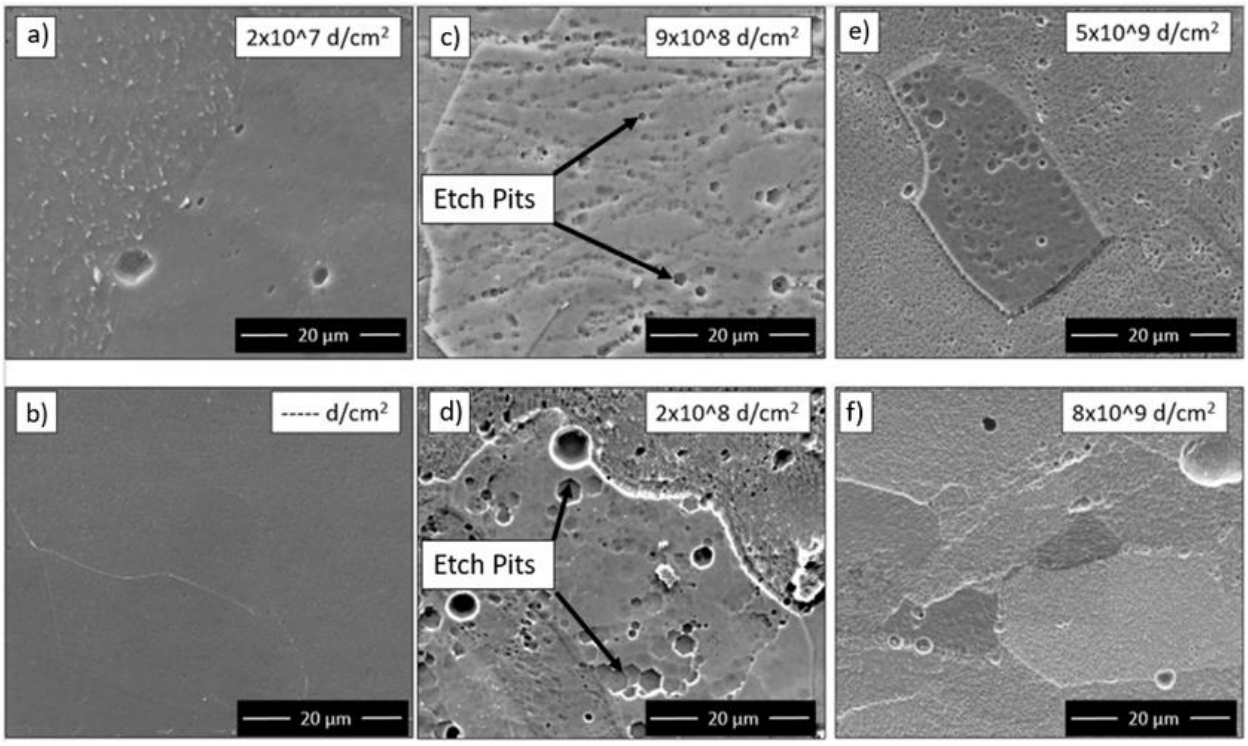

Figure 15. SEM to Show Increasing Presence of Dislocation Density. a) unmilled Ti, b) Wrought Ti, c) Ti milled 1h, d) Ti-1.0-CNC-1h, e) Ti-1.0-EtOH-1h f) Ti-1.0-CNC-EtOH-1h. The dislocation densities of these materials were semi-quantitatively calculated counting the number of etch pits per a determined area. Multiple locations were counted and averaged per sample. Initially the unmilled and wrought titanium a) and b) were analyzed and determined that dislocations were inherently present albeit in small quantities. Once titanium was milled without the addition of other processing agents, the presence of screw dislocations became apparent c). Adding processing agents such as ethanol d) and CNCs e) increased the dislocation density of these materials, though it was observed to be irregular in appearance. The use of both ethanol and CNCs with the titanium powder showed that dislocation density increased and becomes very consistent and controllable f). As a result, the hardness of this material was found to be at its highest with the when both ethanol and CNCs.

Using SEM-FIB, a lift-out was performed on the Ti-1.0 CNC-EtOH-1h compact. The location of the lift-out was performed where the dislocations were prominent as well as where particles were observed. The TEM analysis showed faceted particles located within the titanium matrix suggesting that particles were initially forming within grains. Very small dark features were observed within the titanium matrix which is hypothesized to be dislocations.

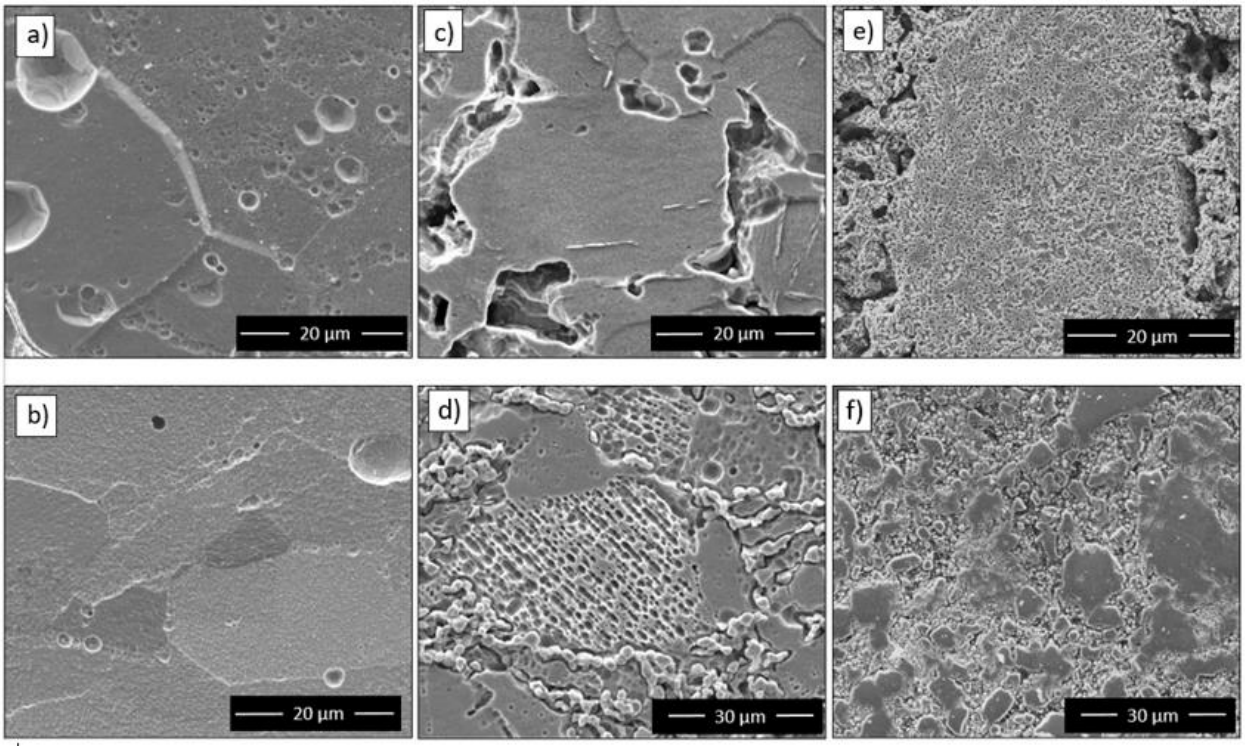

Figure 16. SEM to Show Changes in Microstructure with Respect to Milling Time. a) Ti-10.-CNC-EtOH-0.5h, b) Ti-10.-CNC-EtOH-1h, c) Ti-1.0-CNC-EtOH-2h, d) Ti-1.0-CNC-EtOH-5h, e) Ti-1.0-CNC-EtOH-1h f) Ti-1.0-CNC-EtOH-25h. As milling time increases the dislocation density also increases. However, this phenomenon is no longer observed after 2 hours of milling which is attributed to the dislocation feature becoming infinitesimally small. At 5 hours of milling, the presence of coarsened particles becomes apparent, which are housed at the grain boundaries. Increasing the milling time further leads to a much larger number of particles which compromises the integrity of the material.

Additionally, diffraction mode was used to gain understanding to identify of the particles observed. The diffraction data suggests that the majority of the signal was a result of alpha titanium. Small signals neighboring the alpha titanium signal were observed. Given that the d-spacing of alpha titanium and its ceramic counter parts are similar, it was difficult to identify the exact species of the composite material.

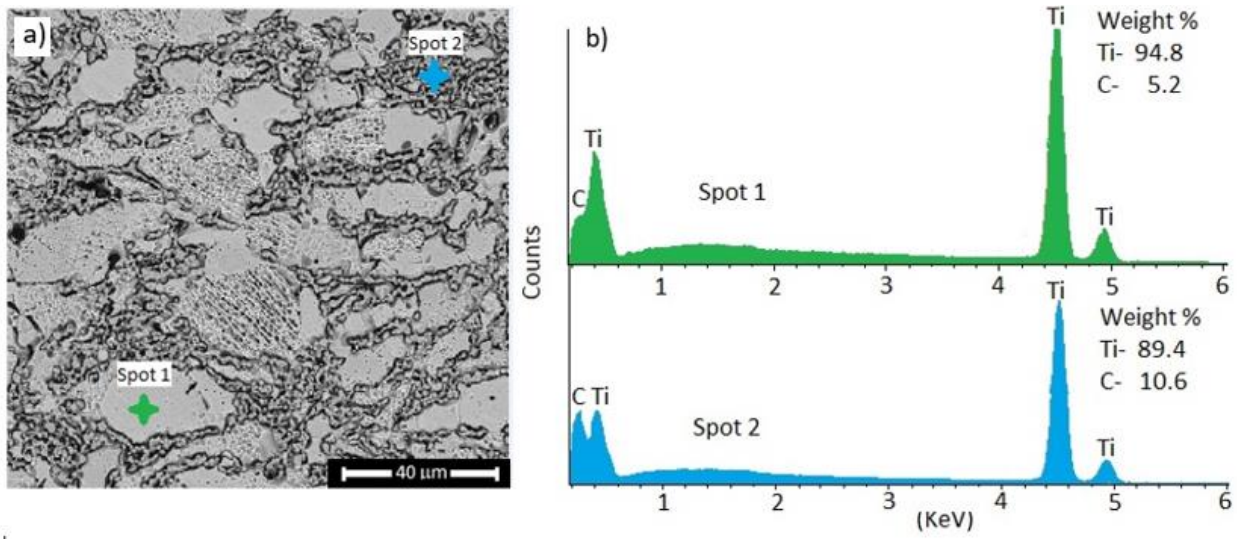

Figure 17. SEM-EDS of Particles from Ti-1CNC-5h. a) SEM image showing locations where EDS was performed. b) EDS Spectra which correlate to the spots shown on the SEM image. The results indicated in increase in carbon content where particles were concentrated.

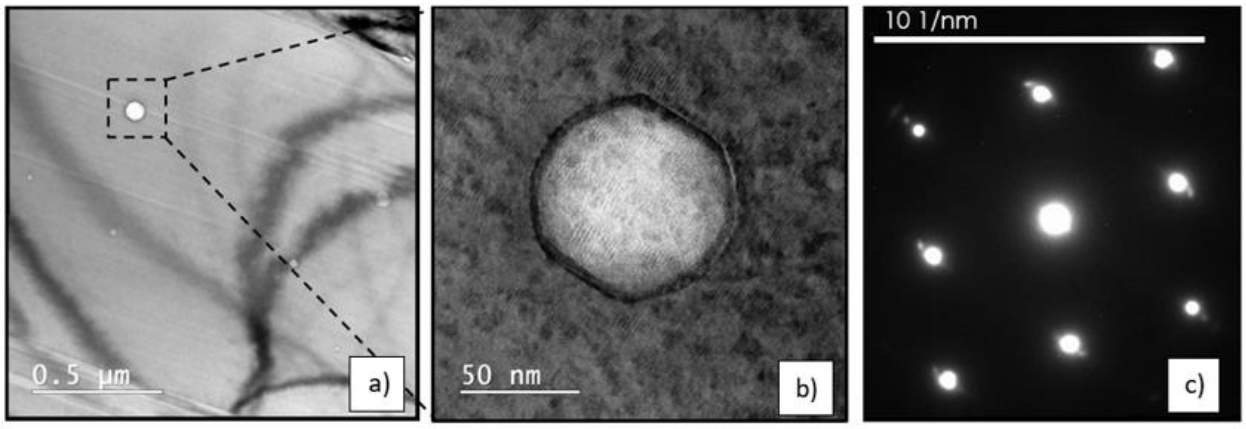

Figure 18. TEM Image of Ti-1CNC-EtOH-1h Sintered at 1200°C for 1 hour. a) The micrograph shows the presences of particles distributed within the matrix. b) Additionally, a dark speckled pattern is observed likely due to the presence of dislocations. c) The acquisition of a diffraction pattern to identify the particles was attempted. Another phase is present in the diffraction pattern. However, due to overlaps and similarities between titanium and its ceramic compounds, the exact identity remains unknown.

Overall, increasing the CNC concentration from 0.5% to 2.0% did not appear to substantially alter the results of the experiment. The hardness results suggest that the primary mechanism of strengthening was the milling process itself. The addition of processing agents such as ethanol and CNCs increased the dislocation density and appeared to evenly disperse these features which made the material homogeneous. It was observed that just milling titanium with 1% CNCs in the presence of ethanol was sufficient to increase the Vickers hardness from 264 HV to 497 HV, which was notably higher than that of Ti-6Al-4V (~350 HV). Varying the content of CNCs concentration did not prove to be advantageous as the microstructure and the hardness of these materials were found to be similar. In fact, it was likely that the addition of excessive CNCs may increase the likeliness of particle growth at grain boundaries which would compromise the integrity of the material.

The sintering process did not appear to have a strong annealing effect. As powders were heated and the CNCs begin to degrade, the free carbon present in the material was to repose in the interstitial sites of the Ti-α crystal lattice as well as to react with the surrounding titanium matrix to precipitate nano-sized complex ceramic particles. Typically heating a material will decrease the dislocation density of a material. However, the precipitation of small ceramic particles and the slow dislocation velocity of titanium is likely responsible for the retention of dislocations in the matrix. This phenomenon is also observed in oxide dispersion strengthened steels and nickel super alloys. In addition to the mixing of the CNCs, the titanium grains and particle sizes were refined as a function of milling time. The materials were milled in an 'inert' argon atmosphere, yet sufficient oxygen was found to be present to react with the titanium to form titanium oxides, as well as to dissolve into interstitial sites of the Ti-α matrix.

4.6 Summary to Chapter 4

Titanium/CNCs metal matrix composites were created by employing mechanical alloying and powder metallurgical methods. The materials were compacted and sintered at 1200^{o}C for one hour. Both the powders and the sintered compacts were subsequently characterized using SEM, XRD, TEM, XPS, and Vickers hardness characterization techniques. The identification of the particulate reinforcement has not yet been made as diffraction patterns are very similar between titanium ceramic compounds. The TEM results indicated that particle precipitation occurred mostly within the grains at lower milling times. Generally, increasing CNC composition did not significantly affect the hardness of the materials. Milling time was found to be a crucial element to the evolution of the precipitate of ceramic particles as well as the dominant factor in altering the microstructural and mechanical properties of the material. This is determined to be a result of the cold work performed on the powders during the milling process. The cold work introduces dislocations into the titanium matrix which are not substantially removed during the sintering process. Milling times below 2 hours favored material with high dislocation density without the particle precipitation at the grain boundaries. Materials milled for greater than 5 hours were found to be exceedingly brittle due to the excessive formation of titanium ceramics from the milling process, thusly compromising the integrity of the material. The hardness of the sintered materials was determined to be superior to alloys sold commercially, ranging from approximately 400 HV to 800 HV for the Ti-0.5 CNC material milled for 0.5 and 5 hours respectively.

4.7 Acknowledgements

I would like to thank Virginia Tech and the Materials Science and Engineering department for the allowed access to equipment, making this work possible. I would also like to thank Mr. Hesham Elmkharram and Mr. Manuel Umanzor for lending expertise in X-Ray Diffraction characterization and for assisting in the creation of unmilled titanium samples. Gratitude is also expressly given to Dr. William Reynolds who provided additional guidance. Finally, I would like to express gratitude to Honeywell and the National Security Campus for providing funding without which none of this would be possible.

Chapter 5.

Attrition Milling of Titanium and Cellulose Nanocrystals to Fabricate Titanium Metal Matrix Composites Reinforced with Titanium Dioxide

5.1 Abstract

Commercially pure titanium powder was mechanically alloyed with cellulose nanocrystals (CNCs) to create a titanium metal matrix composite (Ti-MMC) via attrition milling. The processed powders were compacted in a cold isostatic press in which the powders were held at 300 MPa pressure for 10 minutes. The milling time and the CNC concentration were varied to determine their effect. Subsequently the green compacts were vacuum sintered at 1300^{o}C for 1 hour. Following the processing steps, the microstructural and mechanical properties of the sintered compacts were characterized using SEM, XRD, Vickers macro hardness, and compression testing. SEM micrographs showed that a ceramic reinforcement had precipitated, and its coarsening effect was correlated to milling time. XRD and SEM-EDS identified the ceramic particles as TiO_2. Additionally, the XRD results suggest that oxygen contamination, likely from the milling environment, was evident. At five hours milling, the hardness of the compacts decreased as a function of CNC concentration, indicating that the CNCs facilitated the removal of oxygen from the interstitial sites of the titanium lattice. The compressive properties showed that the compressive strength was higher than that of Ti-6Al-4V, which is often considered the gold standard for titanium materials. The oxygen scavenging effect of the CNCs proved that the Ti-5%CNC material that was milled for five hours could maintain good ductility while making the material stronger than Ti-6Al-4V. Milling materials up to 15 hours began to coarsen the particles

into high aspect ratio reinforcement plate-like particles. However, materials were observed to be brittle at this milling time, suggesting that sufficient oxygen had dissolved interstitially, thus embrittling the material.

5.2 Introduction

Titanium and its alloys are versatile materials that are used primarily because of the materials' high strength, low density, and high corrosion resistance [27, 51]. Despite these very favorable characteristics, titanium is known to have poor mechanical wear behavior [27]. This limitation is often mitigated by reinforcing titanium with a hard ceramic to create a metal matrix composite [73]. Titanium metal matrix composites were first developed in the late 1960's by reinforcing the titanium matrix with boron filaments [23]. This discovery showed that the Young's modulus of titanium parts could be greatly improved [4]. The disadvantage was that this method of reinforcement was expensive and led to anisotropy in the parts[44]. To mitigate these disadvantages, particulate reinforced titanium metal matrix composites were developed by adding titanium boride to titanium matrices [43]. These new composites demonstrated improved wear resistance, isotropic behavior, and an increase of strength properties. Later efforts to form particulate reinforced Ti-MMC allowed for isotropic parts and reduction in cost. Ti-MMCs reinforced with materials such as TiB, TiC, SiC, and carbon nanotubes (CNTs), have been fabricated with much success and additional efforts to further create cost effective Ti-MMCs are still being made [2, 8, 27, 28, 52, 74]. In this paper, alternative strengthening mechanisms will be investigated using a carbon-based additive for particle reinforcement.

Materials used as reinforcements for titanium-based composites have been researched and are detailed below. Wire reinforcement of titanium has been performed. Zhang et al [60] created a Ti-MMC using a wire with the composition of Ti-36Nb-2Ta-3Zr-0.350 and added the material to commercially pure titanium. The results showed a substantial increase in strength while maintaining good ductility. It was reported that grain size reduction in conjunction with the wire additive were the strengthening methods. It was not reported that mechanical alloying of the materials or high energy ball milling was performed; these could have led to more grain refinement, thereby enhanced the results. Research has also been done forming a Ti-MMC using graphite and carbon nanotubes [27]. The results showed improvement in the mechanical properties when using both carbon nanotubes and graphite reinforcements, but less auspicious results were generated for the graphite reinforced material. The carbon nanotubes showed promising results as the strength was enhanced and good ductility was maintained.

Ti-MMCs can be fabricated by employing ex-situ or in-situ powder metallurgical techniques [2, 6]. Ex-situ powder metallurgy involves the mixing of the powder components to disperse the reinforcement followed by powder consolidation and sintering. In this case the powders are non-reactive, and the reinforcement is already in its final form. In-situ powder metallurgy differs in that the reinforcement will react at some point during processing to create a different particulate component. Zadra et. al. 2014 [48] demonstrated an example of this technique whereby the authors formed a TiC/Ti-MMC by dispersing graphite into a titanium matrix. The authors suggested that through in-situ powder metallurgy greater homogenization of the reinforcement material can be achieved. Typically, carbon has low solubility in titanium.

Titanium carbide (TiC) is precipitated once the carbon content exceeds the maximum solubility limit of 0.08% by weight [59]. One major concern when using carbon-based materials is that carbon has ability to diffuse into the interstitial sites of the crystal lattice. It is well understood that carbon, oxygen, and nitrogen can diffuse into the interstitial sites leading to the strengthening of the material [24, 75, 76]. Excessive dissolution of these interstitial elements can lead to embrittlement. In this paper, in-situ powder metallurgy will be used to reinforce titanium with cellulose nanocrystals (CNCs).

Cellulose is a polymeric compound which is found abundantly in nature [77, 78]. Cellulose is comprised of amorphous and crystalline regions. An acid hydrolysis process can be used to remove the amorphous regions of the material, leaving behind cellulose nanocrystals (CNCs) [63, 79]. Currently, some the largest sources of CNCs are wood and cotton, which have obvious competing uses. Therefore, research to isolate CNCs from waste material, such as pistachio shells, is ongoing which should help to increase its availability and limit cost [31]. The crystals are rigid, strong and have high aspect ratios, making them an ideal reinforcement material for polymer matrix composites. Although studies have shown that CNCs can resist thermal degradation up to 300^{o}C [63], this material cannot withstand the temperatures needed for metal processing. The lack of thermodynamic stability is of interest as the material may react with titanium to create a composite through the means of in-situ powder metallurgy.

Nano materials, such as carbon nanotubes have shown a tendency to agglomerate because of Van der Waals attractive forces [8]. To achieve homogenization as a metal matrix composite, the materials are often mechanically alloyed. Attrition milling is a mechanically

alloying technique in which an impeller is rotated to agitate the milling media and the powders resulting in repeated welding and fracturing of the powders. As all the contents in this system are held to the bottom of the tank by gravity, a high probability of ball to powder interactions exists which results in good mixability. Risks to dissolve oxygen inherently exist when milling titanium, therefore it is essential that the milling environment is kept inert[10].

The principles of in-situ powder metallurgy are employed to fabricate TiO_2/Ti-MMC by attrition milling Ti/CNCs followed by powder compaction and subsequent sintering. The fabrication of the TiO_2/Ti-MMC is hypothesized to follow the mechanism provided in Figure 19. The physical and microstructural properties of TiO_2/Ti-MMC will be examined and analyzed as a function of CNC concentration as well as milling time. Various characterization techniques were employed to study and understand these properties and to determine which combination of these processes fabricates materials with exceptional properties. The results explain the role of the nanocellulose in the production of nanocomposite features as well as its effect on the ductility parts.

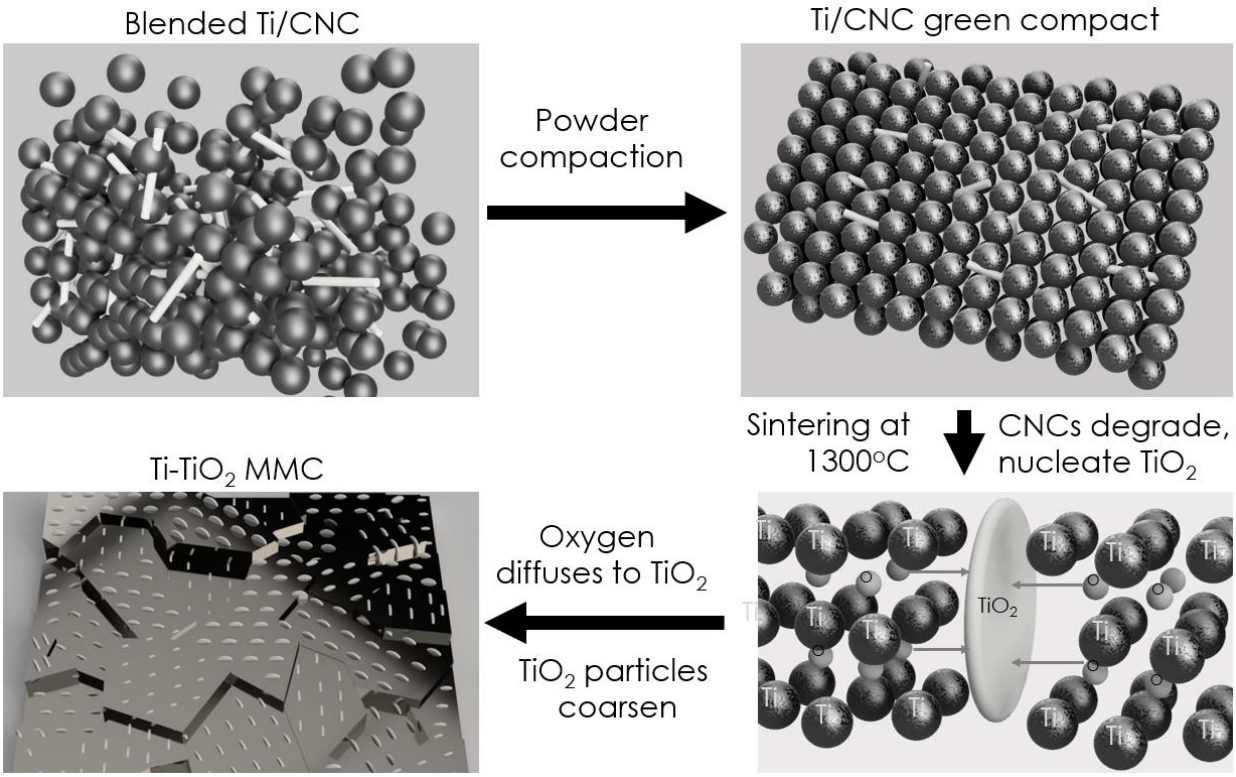

Figure 19. TiO_2/Ti-MMC Fabrication Mechanism via Attrition Milling Titanium and Cellulose Nanocrystals.

5.3 Material Preparation

Commercially pure titanium powder (Atlantic Equipment Engineers, 99.7% ~325 mesh) and cellulose nano-crystals (CNC) (USDA Forest Products Laboratory; obtained as a freeze dried solid, 0.85 wt % sulfur), were used as the starting components. The two materials were then attrition milled using a Union Process Svegari Attrition Mill (Model 01HDT). The milling canister and milling media were both 440C Stainless steel. The blend was combined and milled using a charge ratio of 20:1 which yielded 56 grams of material per batch. Ethanol was added in the amount of 6mL to the contents to act as a lubricant and prevent the material from cold welding. The milling tank was encompassed by a cooling jacket to prevent excessive heating of the sample

during the milling process. A constant flow of 40 SCFH of Argon was used to minimize the formation of oxides and nitrides. Milling times varied from 5 hours to 15 hours while the concentrations of CNCs ranged from 0%-5% by weight. The milled materials were compacted using a cold isostatic press (CIP) utilizing a 0.5 inch diameter butadiene mold. The CIP process was executed using a hold pressure of 300 MPa for 10 minutes. The compacts were then sintered in a vacuum furnace at 1300°C for 1 hour using a ramp rate of 5°C/min. Figure 20 below shows a schematic of the preparation process.

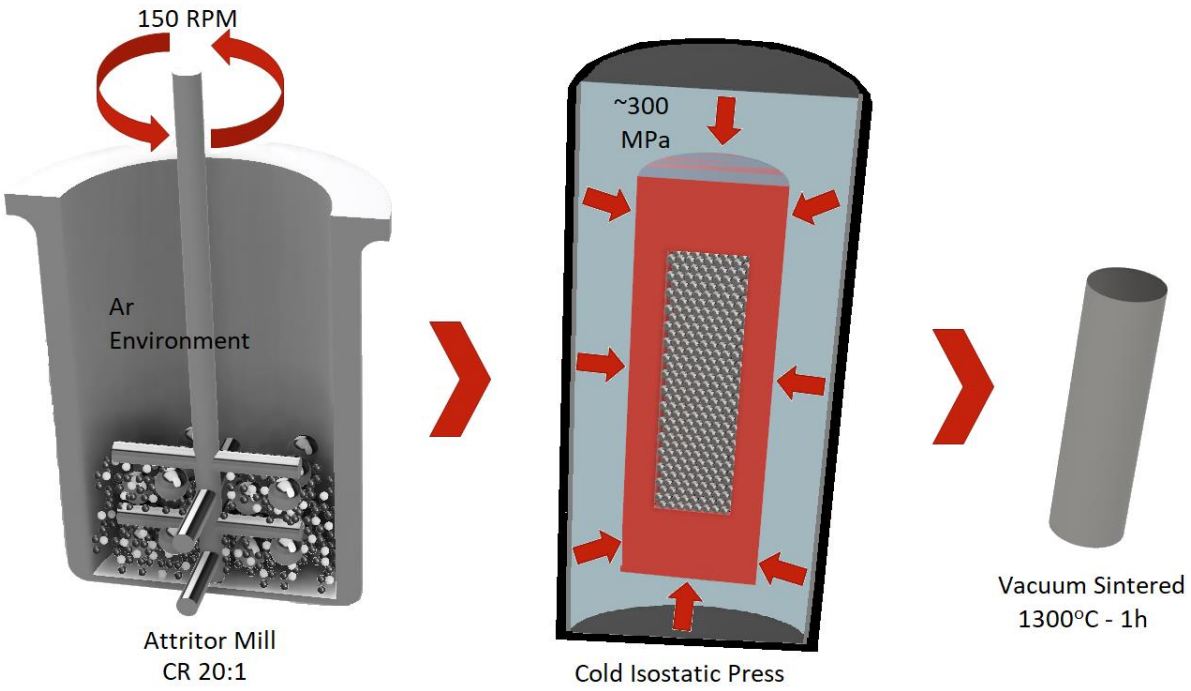

Figure 20. Schematic for milling, consolidation, and sintering of titanium powder.

5.4 Characterization

X-Ray Diffraction (XRD) was performed on the sintered compacts using a PANalytical X'pert PW3040 Powder Diffractometer. The compact samples were ground to a final smoothness

of 600 grit using silicon carbide paper. X-Rays were generated by using an acceleration energy of 45 KV and 40 amps were used to excite the copper source. The specimen holders were rotated at 60Hz while the diffraction pattern was analyzed stepwise from 25^{o} to 60^{o} angular rotations (2θ).

The sintered compacts were cross-sectioned and mounted in a hot press. The operational temperature and pressure for the hot press was 150^{o}C and 3000 psi respectively for 20 minutes. The mounted samples were grinded and polished to a 0.05µm finish. The polished samples were etched with an aqueous 5% (vol. %) hydrofluoric acid and a 3.5% (vol %) nitric acid solution.

The etched samples were mounted into the SEM and attached to the platen with copper conductive tape. SEM imaging was performed using an FEI Environmental SEM while varying the accelerating voltages between 10kV and 20kV. An Everhart-Thornley secondary electron detectors were used to acquire SEM images. At times chemical composition of certain regions within the microstructure was ascertained. A Bruker Silicon Drift Energy Dispersive Spectroscopy detector (EDS) was used to acquire these results during the SEM analysis.

The sintered compacts were re-polished to a 0.05µm finish. Indentations were made using a Phase II 900-398 Macro Vickers Hardness Tester with a pyramidal diamond indenter with 136^{o} angled faces. Using an indentation load of 29.4 N and a dwell time of 15 seconds, five indentions were made on each compact.

Sintered compacts were grinded and ultra-sonicated to remove any surface contaminates which may be present. The cleaned samples were analyzed in a Thermo Fisher Niton XLT3 X-ray fluorescence spectrometer (XRF) to determine the chemical composition of the specimens. The

samples were analyzed using the General Metals calibration mode utilizing a dwell time of 90 seconds. The XRF results were verified using ICP-MS. Approximately 200mg of material was digested in 3mL of 10% HF heated to 180^{o}C. The volume of the solution was reduced to approximately 1mL. 2mL of concentrated HNO_3 was added to the solution and deionized water was added to give a final volume of 5mL. The solutions were subsequently diluted 200 fold with 2% HNO_3. The diluted solutions were analyzed by an Agilent 7900 ICP-MS. Limited external standards were available therefore a calibration curve was created for iron to verify the results.

5.5 Results and Discussions

The sintered compacts were characterized to determine their physical and microstructural properties. After five hours milling, an iron-rich region was observed to have precipitated at the grain boundaries, which is a result of contamination from the milling process (Figure 21). EDS was performed on the iron-rich regions and it was found to be roughly 8% by weight iron in these regions with lesser amounts of chromium and nickel being detected (Table 4). To determine the amount of iron needed to precipitate the iron-rich phase, XRF was employed to determine the chemical compositions of each sample. ICP-MS was also performed on the samples to verify the iron content (Table 5). It was determined that roughly 0.1% by weight was enough iron to segregate and precipitate this phase at the grain boundaries. The low iron content needed to precipitate this phase suggests this effect is inevitable when milling with ferrous media. The iron contamination does not substantially alter the mechanical properties of the materials. However, previous researchers have shown that the corrosion resistance is

undesirably affected[80]. In corrosive environments, these iron-rich regions will etch much faster than the bulk matrix, thereby leading to the embrittlement of the material[81].

It was observed that the HF solution dissolved the titanium matrix without dissolving the ceramic reinforcement. These particles were found to be suspended in solution. The solution was then centrifuged and decanted to remove the acid. The particles were subsequently rinsed with deionized water and ethanol. The material was heated to evaporated the ethanol. The particles were analyzed by SEM-EDS yielding a chemical composition of 64 at.% and 36 at.% of oxygen and titanium respectively (Table 4). These results suggest that the particle reinforcement is titanium dioxide. Titanium dioxide has an elastic modulus of 293 GPa compared to 105 GPa for commercially pure titanium[53, 82]. Using the equation below, which accounts for the shape of the particles, the higher value of titanium dioxide suggests that it will mechanically reinforce the titanium matrix.[22].

$$(1) \quad \sigma_c = \sigma_m V_r \left(1 + \frac{(L+t)}{4L}\right) + \sigma_m (1 - V_r)$$

Where:

$$\sigma_c = Yield\ s\text{trength of the composite}$$

$$\sigma_m = \text{ Yield stress of the matrix}$$

$$L = \text{Particle length perpendicular to applied load}$$

$$t = \text{Particle length parllel to applied load}$$

$$V_r = \text{ Volume fraction of reinforcement}$$

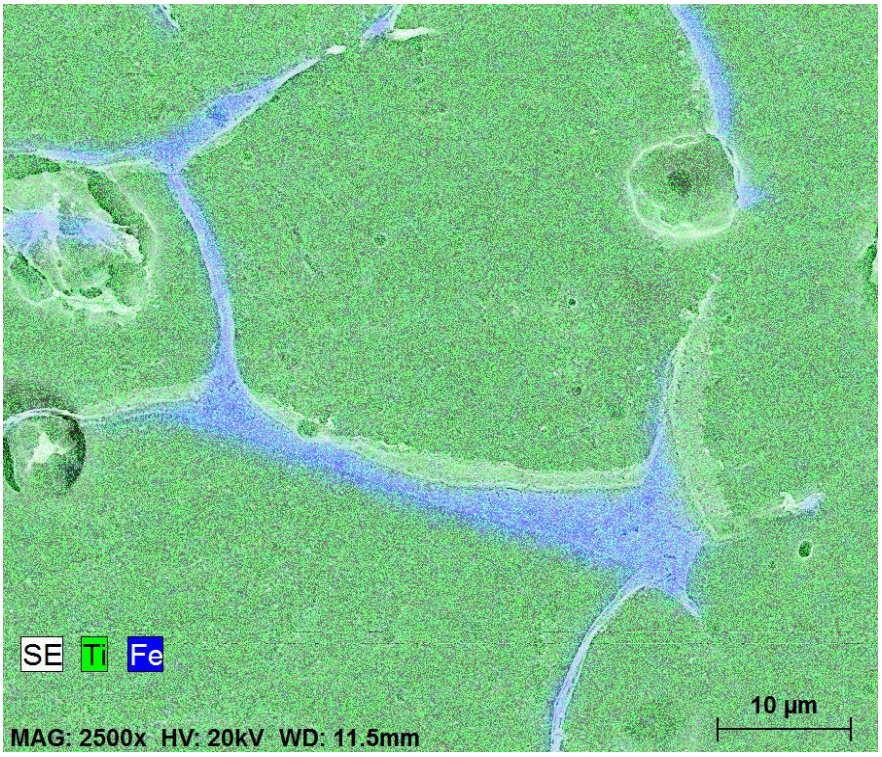

Figure 21. EDS Elemental Map of Ti-5CNC-5A to Show Iron Segregation. Iron-rich regions are denoted in blue; Titanium rich regions are denoted in green.

Table 4. EDS Data Performed on Iron Rich Phases and Particle Reinforcement. Quantative EDS data performed on an iron-rich region of Ti-5CNC attrition milled for 5 hours and on the ceramic reinforcement remaining after ICP digestion.

	Iron-Rich Phase (wt. %)	*Ceramic Reinforcement (at. %)*
Titanium	89.9	36.2
Oxygen	---	63.8
Iron	7.71	---
Nickel	1.94	---
Chromium	0.43	---

--- indicates value is below detection limit

Table 5. XRF/ICP Data for Attrition Milled Samples.

	Elements										
Samples	**Ti**	**Fe**	**Si**	**Cr**	**Cu**	**Zr**	**Sn**	**Ni**	**Co**	**Mo**	**Fe[A]**
Ti-1CNC-5A	99.76	0.165	---	---	---	0.009	---	---	---	---	0.035
Ti-1CNC-10A	99.37	0.261	---	---	---	0.009	---	---	---	---	0.154
Ti-1CNC-15A	99.84	0.066	---	---	---	0.009	---	---	0.012	---	0.051
Ti-2CNC-5A	99.71	0.157	---	0.036	0.009	0.007	---	---	---	0.004	0.272
Ti-2CNC-10A	99.50	0.181	---	---	0.007	0.010	---	---	---	0.003	0.095
Ti-2CNC-15A	99.76	0.065	---	---	0.007	---	0.011	---	---	---	0.049
Ti-5CNC-5A	99.87	0.017	0.105	---	---	---	---	---	---	---	0.017
Ti-5CNC-10A	99.42	0.131	---	---	0.010	---	0.008	0.016	---	---	0.110
Ti-5CNC-15A	99.56	0.048	0.100	---	---	---	0.007	---	---	---	0.031

--- indicates value is below detection limit

[A] Values obtained via ICP-MS

The samples milled without CNCs showed minimal precipitation of TiO_2 particles except for the Ti-0CNC sample milled for 15 hours. Though particles precipitation was evident for this sample it was observed to be smaller and irregular compared to samples milled with CNCs. Sample Ti-5CNC-5A was observed to have precipitated very fine particles within the grains (Figure 24). Increasing the milling time to 10 hours moderated the porosity and homogenization issues observed at the lower milling times. Further increasing the milling time to 15 hours showed TiO_2 precipitation for all concentrations of CNCs. The particles precipitated in the titanium control samples were noted to be smaller, equiaxed and inhomogenously distributed within the microstructure. The Ti-1CNC-15A showed small precipitates distributed within the grains (Figures 22, 23). Increasing the concentration to 2% demonstrated a coarsening effect on the precipitates. The shape of the precipitates was noted to be plate-like or elongated. The plate-like structure suggests that the particles have a high aspect ratio and will structurally reinforce the materials

[83]. The platelets aligned along a plane, which suggests that the growth of these particles is dependent on crystallographic orientation of grains. Further increasing the concentration of CNCs to 5% showed that the particles were beginning to precipitate at the grain boundaries, which will compromise the overall integrity of the material. Figures 22-24 show the SEM micrographs which illustrate these properties.

XRD was performed additionally on the polished surfaces of the sintered compacts (Figure 25). Initially XRD was performed on the attrition milled commercially pure titanium compacts. Peak shifts to the lower angle were observed and coincided with milling time. Magnified diffractograms can be seen in Figure 25 to view this phenomenon. The peak shift observed for the control samples suggest the oxygen is dissolving into the interstitial sites of the titanium during the milling process. The oxygen dissolving into the interstitial sites causes the d-spacing of the titanium lattice to expand. This can be explained by Bragg's law which is shown below. Bragg's Law shows an inverse proportionality between the d-spacing (d) of the matrix and angle (θ) of the X-Rays[84].

$$(2)\ \text{Braggs Law:}\quad \frac{1}{d} = \frac{2sin\theta}{n\lambda}$$

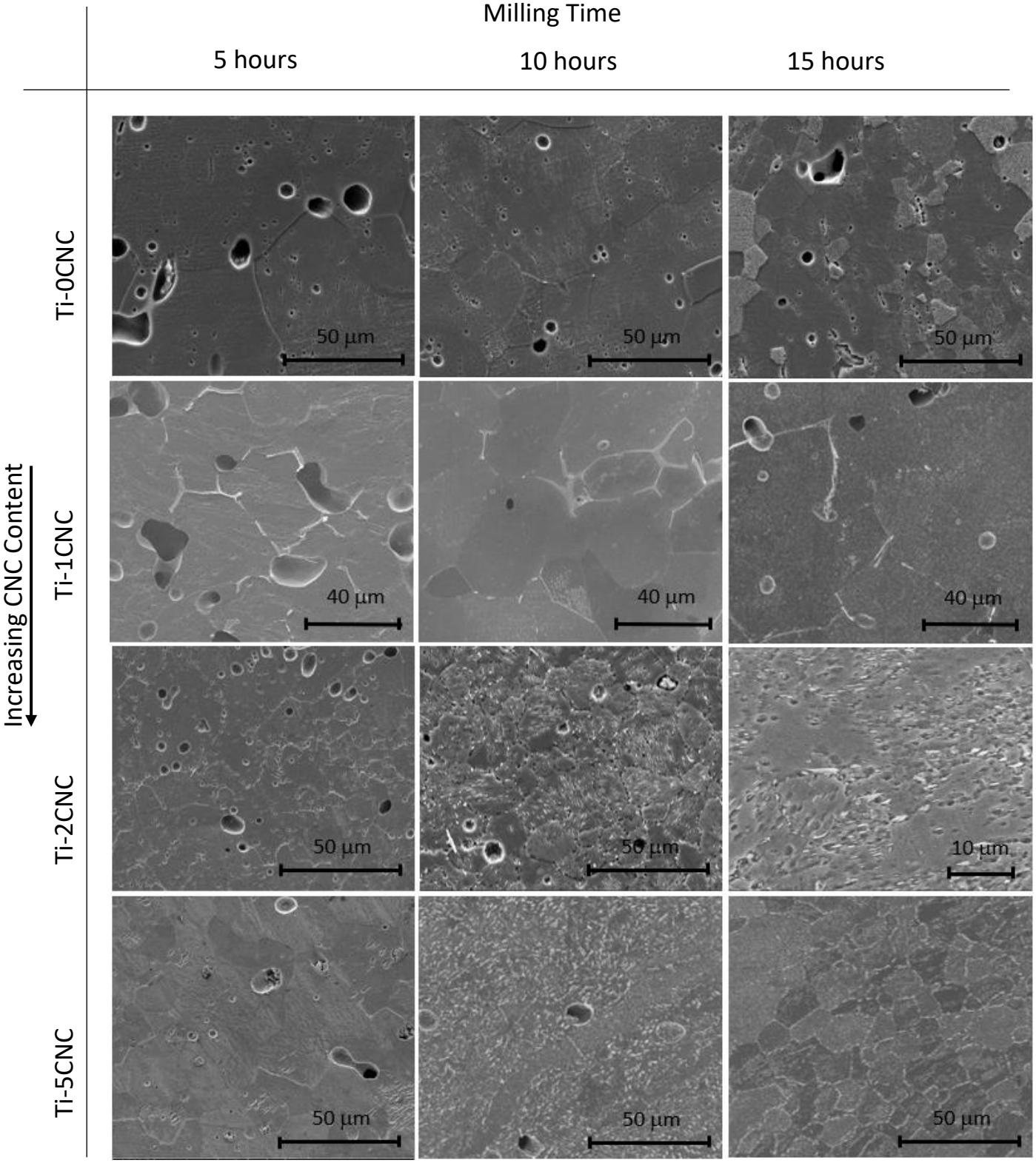

Figure 22. SEM to Show Microstructure of All Samples (Low Mag). The micrographs show an increase of reinforcement in which the volume fraction of this material is proportional to milling time. Increasing the composition also appears to increase the volume fraction. Increasing to 5%CNC at high milling times shows precipitating particles at the grain boundaries.

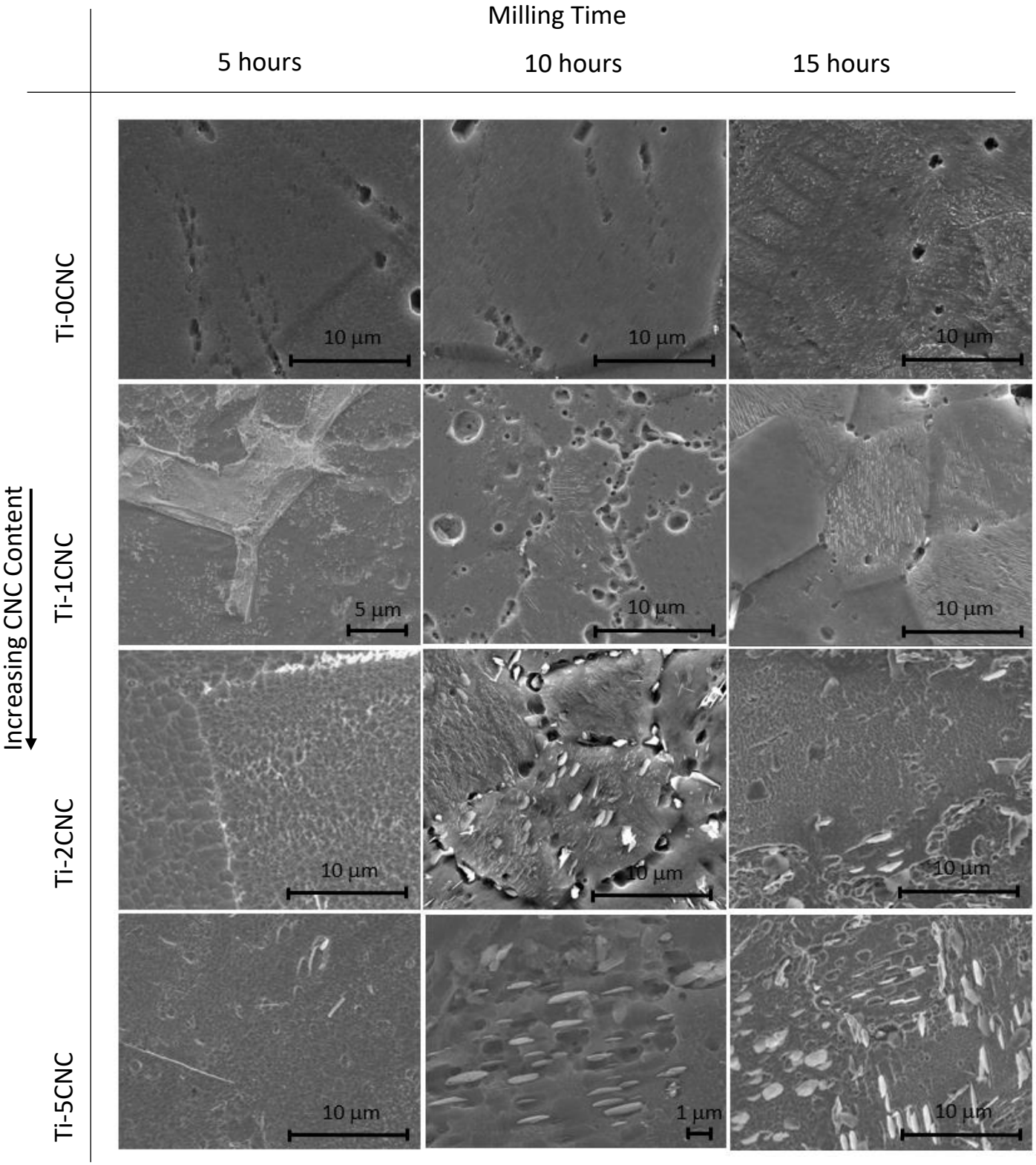

Figure 23. SEM to Show Microstructure of All Samples (High Mag). These micrographs illuminate the plate-like structure of the composite reinforcement. Note that etch pits are can also be observed in these samples.

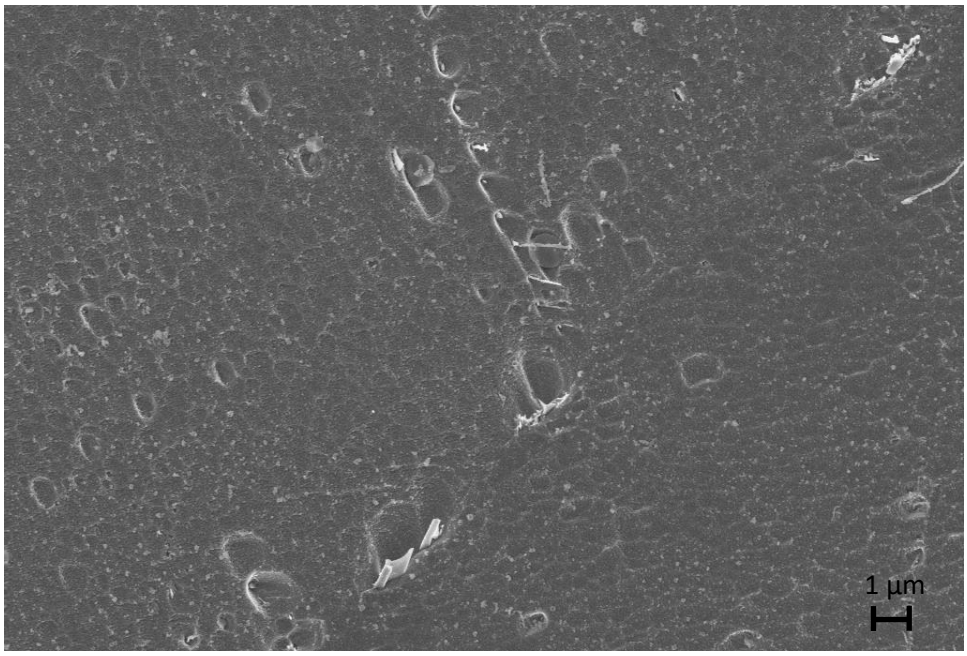

Figure 24. High Magnification SEM micrograph of Ti-5CNC-5A to Show Presence of Nano-Particles. A homogenous dispersion of very fine particles is observed.

Milling with CNCs present causes the diffractogram to initially shift further to the lower angle. However, the diffractograms shift to the right by increasing the CNC concentration and keeping the milling time constant. This phenomenon suggests that increasing the CNC concentration facilitates the removal of oxygen from the titanium interstitial sites. Additionally, the XRD data showed that the intensity of the peak at 38^{o} is intensified by increasing both the milling time and concentration of CNCs. Using Panalytical High Score, this peak was identified to be an overlap of the [002] alpha titanium and [101] titanium dioxide crystallographic planes. These results confirm the increasing volume fraction of ceramic reinforcement observed in the SEM micrographs as well as the titanium dioxide identified via SEM-EDS.

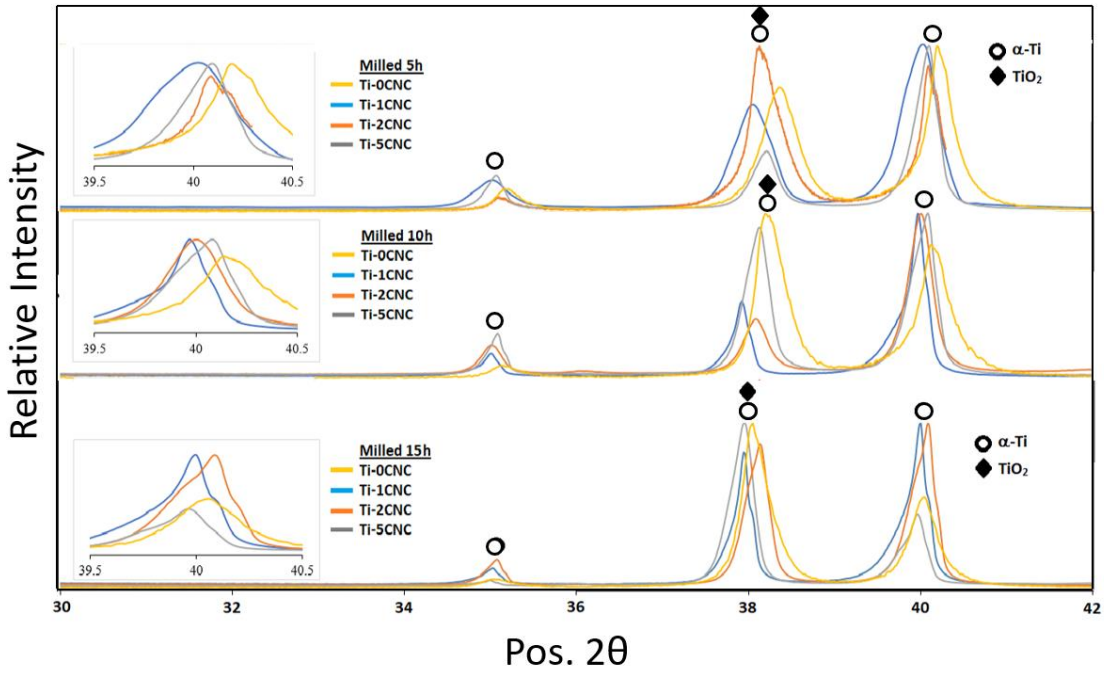

Figure 25. XRD of All Attrition Milled/Sintered Samples. Image shows XRD diffractograms of materials which have been attrition milled and vacuum sintered at 1300°C. It is apparent from the diffractograms that varying milling times cause the peaks to shift to a lower angle, which is an indication of oxygen atoms dissolving into the lattice. The inserts on the plots show a zoomed plot of the peak at 40°, which better illustrate the peak shifts. Another observation is that in all cases materials with 5%CNC tend to have a larger peak around 38° (2θ). The analysis software (Panalytical Highscore) identified this peak as TiO_2. It should be noted that the TiO_2 peak overlaps with signal from alpha titanium.

Vickers hardness was performed on the sintered compacts to evaluate the effects of processing on the mechanical properties of the materials. It was observed that there was a positive correlation between milling time and hardness (Table 6). The Ti-2CNC alloy when milled for 5 hours demonstrated an anomaly as it was especially hard. The hardness value was observed to decrease as a function of CNC concentration for samples milled for 5 and 10 hours which indicates the CNCs are increasing the ductility of the materials. It is hypothesized that the CNCs are reducing the interstitial oxygen content during sintering, thus showing a reduction in

hardness. Increasing the milling time to 15 hours shows that the hardness decreases from 1%CNC to 2%CNC but increases again at 5%CNC. The availability for the CNCs to scavenge oxygen is increased for the 2%CNC. However, increasing to 5%CNC caused excessive particle precipitation at the grain boundaries, which embrittled the material.

Table 6. Vickers Hardness of Attrition Milled Samples as a Function of Milling Time and CNC Content. The data suggests that the predominant factor in the increase of hardness is the processing time. Hardness is found to decrease as a function of CNC concentration for sample milled at 5 and 10 hours

	Milled 5 hrs.	***Milled 10 hrs.***	***Milled 15 hrs.***
Ti-0CNC	493.4 ± 12.3	513.9 ± 15.7	595.4 ± 10.2
Ti-1CNC	406.9 ± 20.7	575.3 ± 21.7	661.2 ± 36.6
Ti-2CNC	410.7 ± 20.2	505.3 ± 12.6	535.3 ± 49.4
Ti-5CNC	334.2 ± 30.6	452.0 ± 44.5	616.6 ± 23.3

To further assess the mechanical properties of the fabricated materials, compression testing was performed on the sintered compacts with the resultant stress strain curves shown in Figure 26. Overall, the samples showed exceptional compressive properties when compared to the theoretical values of commercially pure titanium (Grade 2 Ti) and Ti-6Al-4V (Figure 26). The Ti-5CNC milled for 5 hours retained excellent ductility, as the CNCs behaved as an oxygen scavenger. Additionally, the compressive strength was very good for this sample with the values exceeding that of Ti-6Al-4V. The Ti-2CNC samples showed the highest compressive strength with values averaging near 1572 MPa and 1532 MPa for samples milled at 5 and 15 hours respectively. Ti-1CNC materials were observed to have the lowest strength properties of 967MPa and 145MPa

for samples milled at 5 and 15 hours respectively. Insufficient CNCs to remove interstitial oxygen were determined to be the cause of the excessive brittleness for the Ti-1CNC sample milled for 15 hours.

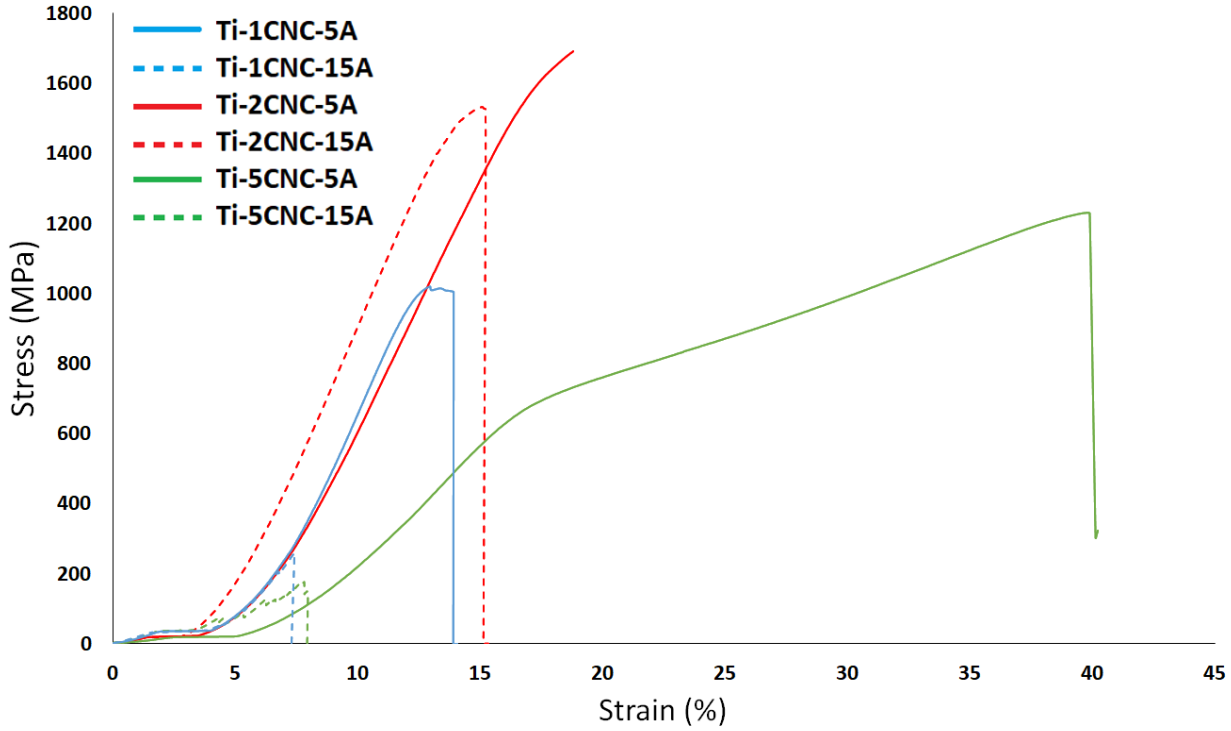

Figure 26. Stress vs. Strain Curves for Attritor Milled Sintered Compacts. The results showed that the most ductile sample is Ti-5CNC milled for five hours. Ti-2CNC compacts showed that the strength did not substantially change with milling time, thereby exhibiting exceptional strength values exceeding the compressive strength of Ti-6Al-4V.

The results indicate that there is a clear correlation between milling time and the coarsening of TiO_2 particles. The XRD results suggest that there is an increase in oxygen content, which not only dissolves interstitially into the titanium crystal lattice, but also facilitates the coarsening effect of the particulate matter. It is hypothesized that the particles act as nucleation

sites to remove and react with oxygen housed in the interstitial sites, which becomes apparent in the experimental data. At 5 hours milling time, the hardness and compression data showed a correlation between CNC content and ductility. It can also be seen that as hardness decreases and the ductility increases.

The parts exceeding 10 hours of milling were noticeably harder, with hardness once again decreasing as a function of CNC content. This suggests that the CNC content once again scavenges the oxygen that has dissolved into the matrix. However, it is likely that the interstitial oxygen content exceeds the recommended value at this point, thereby leading to the embrittlement of the titanium matrix.

At 15 hours milling time a very noticeable particulate material had formed which was observed to be roughly a few micrometers in size. The shape of these particles was observed to be plate-like, having a high aspect ratio. At this milling time, the Ti-5CNC material precipitated excessive TiO_2 particles leading to particle precipitation at the grain boundaries. Because of the particles forming in the grain boundaries, the material was expectedly brittle.

5.6 Summary to Chapter 5

Attrition milling commercially pure titanium showed an inevitable increase in oxygen content due to the milling process. The addition of the CNCs showed improved the ductility of the Ti-MMC by removing the oxygen from the interstitial sites of the titanium lattice. The milling process evenly disperses the CNCs. Upon sintering the CNCs degrade and act as nucleation sites to remove interstitial oxygen. The result is the precipitation and coarsening of

TiO_2 particles, forming a TiO_2/Ti-MMC. Milling materials at 5 hours fabricated the most ductile Ti-MMCs while still greatly improving the strength properties.

5.7 Acknowledgements

The authors would like to acknowledge Mr. David Jarret Wright and Mr. Roberto McAlister Council-Troche for providing the compositional analysis by XRF and ICP-MS. Also, the authors would like to express gratitude to the National Security Campus who funded this project, making this work possible.

Chapter 6. Conclusions and Future Work

6.1 Conclusions

Titanium powder was mechanically alloyed with cellulose nanocrystals using two different milling methods, (vibratory "SPEX" milling and attrition milling). Both techniques effectively incorporated the CNCs into a titanium matrix, yet the strengthening behavior was observed to differ between the two methods.

The titanium powder which was SPEX milled was observed to precipitate nano-sized complex TiC_xO_y Particles. Due to the similarities between titanium ceramics, determining the exact composition of these particles could not be identified. Milling was determined to strongly effect the particle size and shape with little to no contribution to the amount of CNCs used. As a result, milling time was determined to increase the hardness of the material up to five hours of milling. Exceeding five hours of milling caused the samples to become exceedingly brittle in which little testing could be performed on these materials.

Major strengthening mechanisms were observed in the experimental results which were found to harden these materials. First was the dissolution of oxygen into the interstitial sites of the titanium matrix. Interstitial elements, such as oxygen atoms, are fast diffusers which can quickly infiltrate the titanium matrix and settle into the interstitial sites of the crystal lattice. This causes a strain field to be applied to the lattice where the interstitial atoms lie. The strain field inherently increases the energy in this region making dislocation movement difficult. The movement of dislocations is what allows a material to deform. There, the prevention of

dislocation movement leads to the prevention of deformation, which in turn leads to the strengthening of the material.

The experimental results of the materials which where SPEX milled, showed that an additional effect was increasing the dislocation density. The introduction of interstitial elements in addition to the precipitation of nano-sized particles lead to increasing the dislocation density. The titanium powder was extensively deformed in the milling process. It was observed by precipitating the nano-sized particles as well as introducing oxygen as an interstitial element, the dislocations created from the milling process could be retained. Typically heat treatments are used to reduce the internal stress of the crystal lattice. However, it was observed that the sintering process had little effect on decreasing the dislocation density, thereby an increase in hardness and strength was observed.

Previous articles have suggested that by dissolving interstitial elements and precipitating nanoparticles, that an effect on dislocations would be observed. Many books also detail this phenomenon. In this experiment, it was shown that this phenomenon could be directly observed and studied in a titanium matrix. The XRD results showed that the d-spacing of the titanium matrix was increasing by dissolving materials into the interstitial sites, as well as indicated that secondary materials were being precipitated. The effect on the dislocation density could be clearly demonstrated by observing the etch pits resulting from the Kroll's reagent. The dislocation density was noted to increase as a function of the addition of cellulose nanocrystals and ethanol and was further noted to increase as a function of milling time. The TEM results also indicated that nano-particles were precipitated.

Grain size reduction was also observed to contribute to the strengthening effect of these materials. The well know Hall-Petch relation suggests that reducing the grain size leads to the strengthening of materials. SEM micrographs show that the grain size of these materials was reduced as a function of milling time.

The microstructural and mechanical properties of the SPEX milled materials were observed change rapidly as a function of milling time. This suggests a lack of control while utilizing this technique. For instance, the numerous collisions of the milling media inevitably heat the contents of the vial which increases the reactivity of the powder. Additionally, the powders and media were all sealed in an Argon environment, yet the oxygen content was still observed to increase as a function of milling. This necessitated the need for greater control while milling the powders. Therefore, attrition milling of the titanium powders was performed. Attrition milling offers several advantages over vibrational milling. For example, larger sample batches can be created, constant interaction between the milling media and the powders leads to greater mixing, the milling speed can be controlled, and the milling vessel is cooled to prevent reactions during the process.

Attrition milling was performed on titanium powders with varying amounts of CNCs utilizing various milling times. A constant flow of high purity argon gas was used to prevent oxygen contamination and the milling speed was set to 150 RPM. It was observed that at five hours milling time, the CNCs were fully incorporated into the titanium matrix. The sintering process had allowed for the precipitation of nanoparticles which lead to strengthening of the materials. A trend was observed with the five hours milling times which showed that the hardness

decreased as a function of CNC concentration, ultimately leading to greater ductility. The strength of these materials were also observed to be very high as all of the materials were found to have compressive strength values near or exceeding the Ti-6Al-4V alloy.

Increasing the milling time lead to the coarsening of the particulate reinforcement which was observed to become plate-like in shape. Additionally, the samples milled at 15 hours were observed to be brittle except for the Ti-2%CNC material which was found to have excellent compressive strength with values exceeding 1600 Mpa.

The explanation as to why the samples milled for 5 hours appear ductile and the samples milled for 15 hours become brittle are the same. It is hypothesized that at 5 hours milling the CNCs preferentially react with oxygen that was dissolved interstitially in the titanium, which becomes dissolved during milling. During the sintering process, the CNCs, which degrade, react with the neighboring titanium matrix. This new compound likely acts as an oxygen scavenger which leads to coarsening of the particles and depletions of oxygen dissolved into the interstitial sites. This results in the formation of a ductile Ti-MMC. Using a CNC concentration of 1% may not be sufficient material to effectively scavenge oxygen within the matrix. Increasing the CNC concentration to 5% will have a positive effect which can greatly scavenge oxygen, however at 15 hours of milling the concentration of particles becomes excessive, causing the particles to precipitate at the grain boundaries, thereby embrittling the part.

One interesting observation in the attritor milling experiments was how sensitive titanium was to impurities. SEM micrographs of materials milled at 5 hours reveled that iron levels nearing 0.1% by weight was enough of iron to segregate to the grain boundaries creating an iron rich

phase. Earlier experiments in which Al, Si, was detected in amounts less than 0.5% and Zr, Fe, Bi, Sn Cr, Pb were detected below 0.1% studies have shown that this miniscule amount of contamination can greatly affect the hardness of the material (See Appendix A).

Comparatively, the attrition milled samples were clearly more advantageous than the vibratory milled samples. Visually, the particles were evenly dispersed via attrition milling and uniquely precipitated high aspect ratio platelet TiO_2 particles. Numerically, the compressive and hardness properties were clearly better for the attrition milled samples as the compression strength was roughly double that of the vibratory milled samples (Table 7). The cost/strength efficiency ratio was also better for the attrition milled samples. Additionally, compared to other Ti-MMCs available in literature, the mechanical properties for the Ti-CNC attrition milled samples paralleled and slightly exceeded its competitors regarding compressive strength. Additionally, it was shown that Ti-CNC attrition milled samples could cost-effectively enhance the mechanical properties of the titanium matrix (Table 8).

Table 7. Comparison of Literary Ti-MMC Mechanical Data with Experimental Data. Spex milled and Attrition milled samples are listed below.

Materials	*Vickers Hardness*	*Modulus of Elasticity (GPa)*	*Compressive Strength (MPa)*	*Tensile Strength (MPa)*	*Maximum Ductility %*
5% TiB Ti-MMC[52]	375-400	180-200	1500	---	15
20% TiC Ti-MMC[52]	475-500	180-190	1600	---	10
0.34% CNT Ti-MMC[8, 27]	950-1000	200-250	---	700	30
5% Graphite Ti-MMC[48]	350-400	130	---	1200	3
Ti Grade 2[53]	145	110	---	344	20
Ti-6Al-4V	349	114	1080	950	14
Ti-1CNC-0.5S	497.8	---	---	---	---
Ti-1CNC-1S	459.2	45.8	725	---	29
Ti-1CNC-2S	655.3	---	---	---	---
Ti-1CNC-5S	734.7	101	450	---	5
Ti-1CNC-10S	374.7*	---	---	---	---
Ti-1CNC-25S	Material too brittle to test				
Ti-1CNC-5A	406	140	1021	---	14
Ti-1CNC-15A	661	160	260*	---	7.5
Ti-2CNC-5A	410	139	1692	---	19
Ti-2CNC-15A	535	160	1532	---	15
Ti-5CNC-5A	334	52	1230	---	40
Ti-5CNC-15A	616	3.12*	177*	---	8

**Denotes samples which were especially brittle*

Table 8. Comparison of Material Costs with Experimental Data. A cost/strength calculation has been performed to determine the feasibility of using CNCs as an additive. Spex milled and Attrition milled samples are listed below.

Materials	*Compressive Strength (MPa)*	*Tensile Strength (MPa)*	*Additive Cost (USD/gram)*	*Product cost (USD/in^3)*	*Cost/Strength (USD/GPa)*
5% TiB Ti-MMC[52]	1500	---	$1.00[54]	---	$4.78
20% TiC Ti-MMC[52]	1600	---	$88.80[55]	---	$6.50
0.34% CNT Ti-MMC[8, 27]	---	700	$1000[13]	---	$15.61
5% Graphite Ti-MMC[48]	---	1200	$0.66[56]	---	$5.97
Ti Grade 2[53]	---	344	---	$7.50[57]	$21.80
Ti-6Al-4V	1080	950	---	$27.50[57]	$25.46
Ti-1CNC-1S	725	---	$2.50[58]		
Ti-1CNC-5S	450	---	$2.50[58]		
Ti-1CNC-5A	1021	---	$2.50[58]	---	$7.30
Ti-1CNC-15A	260*	---	$2.50[58]	---	$28.65
Ti-2CNC-5A	1692	---	$2.50[58]	---	$4.37
Ti-2CNC-15A	1532	---	$2.50[58]	---	$4.83
Ti-5CNC-5A	1230	---	$2.50[58]	---	$5.89
Ti-5CNC-15A	177*	---	$2.50[58]	---	$40.96

**Denotes samples which were especially brittle*

6.2 Suggested Future Work

The work in this thesis worked to incorporate a natural and abundant material which could lead to cost reduction of fabricating Ti-MMCs in the future. The chapters in this thesis use different milling techniques to create Ti-MMCs. While both milling techniques successfully created Ti-MMCs and new information was gathered on the fabrication and strengthening mechanisms of Ti-MMCs, both techniques also showed that oxygen contamination was evident which was dissolved into the interstitial sites of the titanium lattice. To effectively create a Ti-MMC which could be used industrially the material should contain less than 0.2% oxygen. Therefore, continued work should focus on minimizing oxygen content in these composites. Below are proposed solutions.

6.2.1 Attrition Milling Continued

Attrition milling showed the most promising results of the two milling methods outline in this project. It was observed that milling up to 15 hours showed signs of embrittlement likely a result of oxygen dissolution. Other scientists have proposed methods to achieve minimal oxygen dissolution.

6.2.1.1 Attrition Milling in Liquid Argon

Attrition milling is typically carried out in a high purity argon environment. Due to the high fluidity of gas particles, oxygen will nearly always be present in some level during the milling process, thus oxygen will always be available to react with titanium in the presence of high purity argon. However, milling in liquid argon not only reduces the operating temperatures to prevent

chemical reactions, but greatly concentrates the argon milling environment. Additionally, Kozlik et al [10], has shown that it is possible to form nano grains within the titanium matrix which would further enhance the mechanical properties of the composite.

6.2.1.2 Attrition Milling with Oxygen Scavengers

The experimental results in this thesis suggest that after the CNCs degrade, the resultant material will act as an oxygen scavenger. The results also suggest that this effect is limited as milling up to 15 hours causes the material to dissolve oxygen and become brittle. Milling with other oxygen scavengers may prove to augment the oxygen scavenging effect of the CNCs, leading to increased mechanical properties with little sacrifice to ductility

6.2.1.3 Attrition milling at high RPMs

Compared to previous experiments, the rotational speed of this experiment was low. It is possible that increasing the rotational speed of the attritor could lead to the same production of nano-particles, but with much smaller grain sizes. Through the Hall-Petch relation, the material should have enhanced mechanical properties.

6.2.2 Planetary Ball Milling

Planetary ball milling is one of the most popular forms of milling. As planetary ball milling is absent from this study, these results could be used to provide an additional comparison between techniques. Mechanically, the milling motion is very similar to attrition milling in that the milling media is rotated to apply a shear force on the powder contents. To achieve this, an external force is used to simultaneously orbit and spin the milling containers around a central

point. This action is very similar to how the earth orbits the sun while spinning. Because the force is external, this allows for the milling vial to be sealed while in used. Previous studies have shown success by milling in low pressure argon environments. By pulling a vacuum on the milling vessel the available oxygen left to react with the powder is diminished. It is likely that this milling environment would be the purest between all milling techniques.

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Appendices

Appendix A

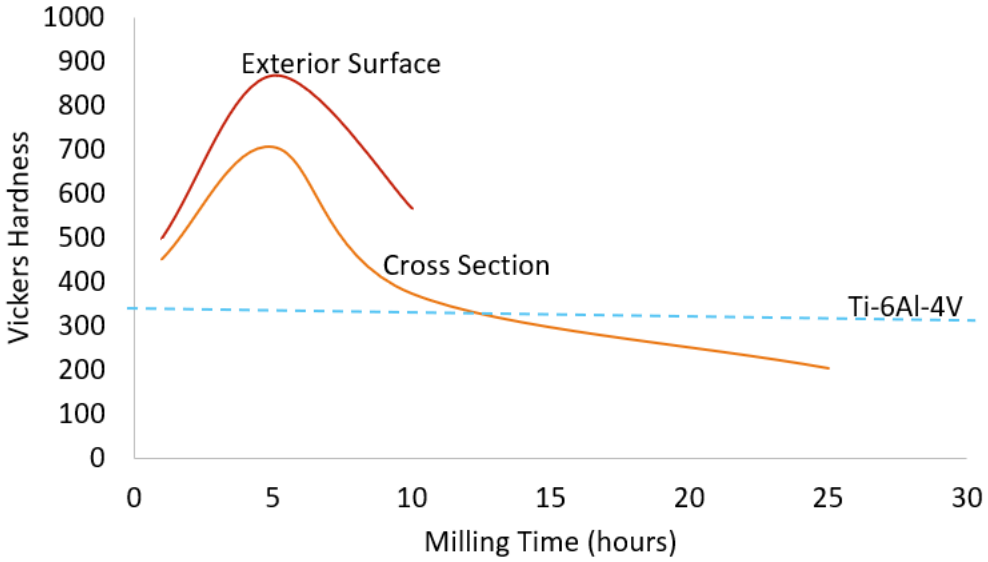

Figure 27. Hardness Comparison Between the Surface and Cross Section. Hardness was performed on the exterior surface and the centerline of cross-sectioned SPEX milled compacts. The exterior surface was found to be harder due to the higher oxygen content and the formation of alpha case at the surface.

Appendix B

Table 9. Attrition Milled XRF and Hardness Data (Contaminated Samples). Contaminated samples are highlighted. Contamination was noted to increase the hardness of the materials.

	Elements										
Samples	**Ti**	**Fe**	**Al**	**Si**	**Bi**	**Cr**	**Cu**	**Pb**	**Zr**	**Sn**	**Hardness**
Ti-1CNC-5A	99.76	0.165		---		---	---		0.009	---	407
Ti-1CNC-10A	99.37	0.261		---		---	---		0.009	---	514
Ti-1CNC-15A	99.84	0.066		---		---	---		0.009	---	595
Ti-2CNC-5A	98.62	0.305	0.592	0.147	0.071	0.07	0.041	0.04	0.037	0.034	568
Ti-2CNC-10A	98.95	0.111	---	0.274	0.051	---	0.022	0.029	0.029	0.021	505
Ti-2CNC-15A	99.76	0.065		---		---	0.007		---	0.011	535
Ti-5CNC-5A	99.87	0.017		0.105		---	---		---	---	334
Ti-5CNC-10A	99.42	0.131		---		---	0.010		---	0.008	452
Ti-5CNC-15A	99.56	0.048		0.100		---	---		---	0.007	617

--- indicates value is below detection limit

[A] Values obtained via ICP-MS

Appendix C

Table 10. Density Data (SPEX and Attrition Milled).

SPEX Milled	*Density*	*Standard Deviation*
Ti-1CNC-0.5s	4.44	0.01
Ti-1CNC-1s	4.40	001
Ti-1CNC-2S	4.50	004
Ti-1CNC-5S	4.61	0.03
Ti-1CNC-10S	4.66	0.03
Ti-1CNC-25S	5.27	0.01
Attrition Milled	**Density**	**Standard Deviation**
Ti-1CNC-5A	4.27	0.10
Ti-1CNC-10A	4.49	0.01
Ti-1CNC-15A	434	0.03
Ti-2CNC-5A	4.43	0.06
Ti-2CNC-10A	4.39	0.03
Ti-2CNC-15A	4.20	0.07
Ti-5CNC-5A	4.26	0.05
Ti-5CNC-10A	4.35	0.04
Ti-5CNC-15A	4.41	0.04