

**INVESTIGATION OF CARBON NANOTUBE DISPERSIONS IN
ZIRCONIA FOR IMPROVEMENT OF MECHANICAL PROPERTIES**

An Undergraduate Research Scholars Thesis

by

DANIEL OLIVIER LEWIS

Submitted to the Undergraduate Research Scholars program at
Texas A&M University
in partial fulfillment of the requirements for the designation as an

UNDERGRADUATE RESEARCH SCHOLAR

Approved by Research Advisor:

Dr. Mathew Kuttolamadom

May 2018

Major: Manufacturing & Mechanical Engineering Technology

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ABSTRACT

Investigation of Carbon Nanotube Dispersions in Zirconia for Improvement of Mechanical Properties

Daniel Olivier Lewis
Department of Engineering Technology & Industrial Distribution
Texas A&M University

Research Advisor: Dr. Mathew Kuttolamadom
Department of Engineering Technology & Industrial Distribution
Department of Material Science & Engineering
Texas A&M University

The overarching goal of this project is to investigate the effects of adding various carbon nanotube (CNT) dispersions to Zirconium Oxide, on its mechanical properties. For this, first it will be investigated on how to uniformly disperse different CNTs in Zirconium Oxide powder to create Spark Plasma Sintered (SPS) composite specimens. Then the impact of CNT length, diameter, and weight fraction on its role as a reinforcement material in sintered Zirconia will be investigated, from a toughness improvement standpoint. The addition of CNT is expected to increase the toughness of the Zirconia composite by hindering crack propagation by acting as a randomly oriented crack propagation suppressor. Also, since CNTs are similar to graphite powder (a dry lubricant), the frictional coefficient and wear rates are expected to be lower. The sintered specimens will be characterized using electron microscopy and elemental analysis. Its mechanical performance will be evaluated through micro-hardness, nano-indentation, bending, and impact tests, and the results compared with those of pure Zirconia to quantify mechanical performance.

NOMENCLATURE

| | |
|------------------|---|
| CNT | Carbon Nanotubes |
| COOH | Carboxyl Functional Group |
| EDX | Energy-Dispersive X-ray Spectroscopy |
| HIP | Hot Isostatic Pressing |
| MWCNT | Multi-Wall Carbon Nanotubes |
| SEM | Scanning Electron Microscope |
| SPS | Spark Plasma Sintering |
| ZrO ₂ | Zirconium Dioxide, also known as Zirconia |
| MSDS | Material Safety Data Sheet |

CHAPTER I

INTRODUCTION

Project Objectives

The overarching goal of this project is to investigate the effects of different carbon nanotube (CNT) dispersions in Zirconium Oxide on its mechanical properties. Specific objectives include:

- (i) To investigate how to uniformly disperse different CNT configurations, and successfully fabricate Zirconium Oxide composite specimens via Spark Plasma Sintering (SPS),
- (ii) To determine the impact of CNT length, diameter, and weight fraction on its role as a reinforcement material in sintered Zirconia, specifically for compression and toughness.

Introduction

Ceramics have attributes that make them ideal for use in environments that require very high melting temperature, compressive loading, hardness, or corrosion resistance. However, other traits that limit their use include very low tensile strength, impact resistance, machinability, and severe crack propagation due to high hardness [1]. An area in which ceramics excel is use in bearings. Their very high hardness and compressive loading capabilities make them desirable, as bearing balls are always in contact with the inner and outer races and as such impact loading is minimized. Most ceramic bearings have balls made of Zirconium Dioxide (ZrO_2), also known as Zirconia. As well as having high hardness, Zirconia is among the toughest of ceramics; toughness being a material's ability to absorb energy without fracturing.

Toughening of ceramics has long been an area of research as ceramics have many potential uses due to their unique properties and ability to withstand certain harsh environments. One method of toughening ceramic is to incorporate reinforcing materials that compensate for its

deficiencies. When this is done the material is known as a composite and consists of a reinforcement suspended in a matrix. An example of this is reinforced concrete, a ceramic matrix composite. The ceramic, cement, acts as the matrix and the metal rebar acts as the reinforcement. The concrete contributes the ability to withstand large compressive forces and corrosive environments. The rebar adds tensile strength that the cement lacks and keeps the concrete together if it does crack. The end result is a material that has properties which are superior to either of the individual components.

While Zirconia is very tough for a ceramic, it still suffers from low toughness relative to materials such as metals and plastics [1]. This is because high-hardness materials tend to be brittle; once a crack forms it takes very little energy to propagate it. Adding high tensile strength reinforcement to a brittle ceramic is well known to increase its toughness.

The highest tensile strength of any currently known material is that of Carbon Nanotubes (CNT). These consist of sp^2 bonded carbon atoms in a tubular orientation. “The Young’s modulus of the best nanotubes can be as high as 1000GPa, approximately five times higher than steel, while their tensile strength can be up to 63GPa, around 50 times higher than steel.” [2] They are also among the best thermal conductors along the tube lengths, and act as thermal insulators across the tubes. Unfortunately, CNT have not seen as much use as is expected, mainly due to the fact that they are very short even with high aspect ratios. However, despite their short length and difficulty of use, they have shown promise as a reinforcement for a large range of materials including plastics, metals, and ceramics [3].

Hypotheses

The reinforcements to be used in the Zirconia composite are Multi-Wall Carbon Nanotubes (MWCNTs). As stated in Carbon Nanotube Science, “These molecular-scale carbon tubes are the stiffest and strongest fibers known.” [2]. When used as a randomly oriented reinforcement they would likely increase the toughness of the Zirconia matrix composite. If the matrix-reinforcement bond interface is strong enough, the tensile capabilities of the nanotubes could hinder or possibly even prevent the propagation of cracks that form. Since CNT have excellent thermal conductivity, they may also help the composite distribute heat more evenly. This would result in more uniform heat dissipation throughout the material, which would help reduce internal stress due to uneven thermal expansion. This may further assist in the prevention of crack initiation, possibly increasing the composite’s toughness.

It is also hypothesized that the use of functionalized CNTs (those that contain surface charge, allowing them to repel each other in an aqueous solution) will allow for their better dispersion. Further, by using an SPS approach, the CNT exposure time to heat is expected to be minimum, resulting in a low-porosity high-density composite with evenly distributed, intact CNTs. This should result in an increase in toughness and wear resistance, leading to a superior composite version of Zirconia.

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

Increasing the Toughness of Ceramics

Ceramics are typically known to have high hardness as well as excellent corrosion resistance and compressive load bearing abilities. However, they tend to be very brittle, which results in severe crack propagation when deformation of the material occurs. This crack propagation causes them to have very poor resistance to impact loading and in turn low values of toughness when compared to metals and polymers. With advancements in technology and demand for materials with better properties, the toughening of ceramics has long been an area of interest in the scientific community.

Control over the microstructure of a ceramic is one of the key elements of producing a material with desirable properties. Many different sintering strategies exist due to this need. They range from the simple baking of clay in an oven to advanced HIP (Hot Isostatic Pressing) and SPS (Spark Plasma Sintering) methods. Precise regulation of the sintering process allows for high levels of control in the product's microstructure.

Sintering Methods for Ceramics

A common sintering method for fabricating high-grade ceramics is Hot Isostatic Pressing (HIP). This procedure is known to result in near-theoretical maximum densities of ceramics, but is difficult to perform on powders. This method of sintering involves exposing a material to high pressure and temperature in an inert atmosphere. A sealed chamber with the material to be sintered is typically evacuated and filled with argon, after which heating coils increase the

temperature in the chamber, and the pressure rises as temperature increases in the system. After a soak time at peak temperature and pressure the material is cooled at a controlled rate. Soak times can last for several hours in HIP.

When dealing with a powder, special means must be taken as exposure to high pressure atmosphere alone will not assist in the compaction of porous material. In this situation the powder must be transferred to a metal canister which is then evacuated and filled with an inert gas before being sealed. The canister is then placed into the HIP and normal procedures are followed. Compaction of the material occurs via deformation of the canister under high temperatures and pressure.

As ceramics are usually produced from fine powders the canister route must be taken when dealing with powdered ceramics. However, due to the immense heat required for the sintering of engineering grade ceramics, there are a limited amount of metals which can be used to create the canister. The metal used to create the capsule must be able to withstand temperatures that exceed the sintering temperature while being malleable enough to deform without cracking or bursting. In this study the HIP method was considered and a suitable material for the canister was found to be an alloy known as grade 5 Titanium, composed of Titanium, Aluminum, and Vanadium. However, due to the cost and difficulty associated with the manufacturing of this canister a different process was chosen as the sintering method for this study.

SPS (Spark Plasma Sintering) is another method of sintering which is known to result in near-theoretical densities achievable of the produced material. When pure Zirconia was sintered using spark plasma sintering, a near theoretical density was reported when exposed to 1200⁰C at 50MPa for 8 minutes [4]. Unlike HIP sintering, there is no need to design a canister and

sintering happens much more quickly. This method utilizes low voltage, high amperage current to resistance heat the material. Powder is loaded into a graphite die and plugs are inserted on both ends. The die is placed into the SPS machine and the material is subject to uniaxial pressure as current is applied. Due to the rapid heating of the SPS method, sintering times are much shorter than HIP with soak times being in minutes instead of hours. This is especially beneficial when working with materials which are sensitive to heat and more likely to experience thermal breakdown.

Creating Ceramic Composites

Control over sintering will only be able to improve a ceramic to the point of its material limits as a pure substance. Another approach to obtaining ceramics with superior toughness is to incorporate them into a composite. Composites consist of a matrix and reinforcements. The reinforcement is suspended in the matrix with the intent of acquiring a material with properties which are characteristic of both the matrix and reinforcement. Many different forms of reinforcement exist, but in most cases the reinforcement is fibrous (and/or particulate) in some fashion. These fibers may be randomly oriented in the matrix to achieve isotropic properties or aligned to obtain orthotropic properties. In the case of this study the CNTs will act as a randomly oriented fibrous reinforcement.

Parameters which are critical to the resultant properties of a composite are the independent properties of both the matrix and reinforcement, the ratio of matrix to reinforcement, the bond interface strength of the matrix and reinforcement, and the dispersion of the reinforcement throughout the matrix. The matrix to reinforcement ratio is typically brought as low as possible, as more reinforcement tends to correlate with more desirable mechanical

properties. The bond interface between a matrix and reinforcement plays a crucial role to the result. If the interface is not strong enough the reinforcement material will not be able to contribute its properties to the composite. In this case the reinforcement will slip within the matrix leading to an inability for the matrix to transfer load through the reinforcement.

Effects of Adding CNTs to Zirconia

The addition of CNTs to a Zirconia matrix is expected to significantly alter many of the mechanical properties of the composite in comparison to those of pure Zirconia. The interface between the Zirconia and CNTs is intended to be closely studied as it is an important factor in the resulting properties. Due to the excessively low coefficient of friction shown by CNTs, the composite is expected to have frictional properties that differ from those of pure Zirconia.

Bond Reinforcement Interface

When similar silicon carbide-CNT composites were made by hot isostatic pressing, there was an increase in fracture toughness of 10% compared to normal SiC [5]. On studying microstructures of Zirconia-CNT composites, it was found that Zirconia was prone to nucleate on and around the nanotubes [6], leading to the potential for strong interface bonds. Perhaps certain CNT lengths or diameters as well as functionalization may affect bond strengths.

Since the functionalization process impacts the outermost shells of the CNTs there is a possibility that the modification will affect the matrix-reinforcement bond interface. It is theorized that the functionalization may increase the bond interface strength as it causes abnormalities on the nanotube exteriors which may assist in preventing slip. If the bond interface is strong enough the result should be a mitigation of crack propagation in the composite. As

severe crack propagation in ceramics is of major concern due to the detrimental effects on toughness, the reduction of crack propagation is a primary target when attempting to increase toughness.

Coefficient of Friction

One expected result of using CNTs in the composite is an impact on the frictional properties of the material. CNTs are chemically similar to graphite and as such are expected to have lubricating effects similar to those of graphite, which is commonly used as a highly heat resistant, dry lubricant. A study conducted on Zirconia with CNT dispersions found that inclusion of Nanotubes at 2% by weight substantially decreased the wear rate for nano/macro scratches [2]. Reduced wear rates would be beneficial to the ceramic as it would extend service time in its applications. One study showed that samples of the composite displayed the lowest coefficient of friction at 6% weight fraction of nanotubes [7].

Health Risks

It should be mentioned that CNTs pose potential health risks to those exposed to them. Despite CNTs having been used for several decades, the risks posed by CNTs are still not well understood. Due to their size they easily propagate and remain suspended in the air. Upon examination of the MSDS included with the purchase of the CNTs it can be found that “Inhalation is the most common route of exposure to airborne particles in the workplace. Inhalation may lead to the formation of lung Granulomas or possibly Mesothelioma.” [8]. The handling instructions state that a fume hood should be used to prevent exposure. This study

utilizes a sealed glovebox under a vacuum to protect the user as well as minimizing the risk of the CNTs becoming airborne.

Fabricating CNT and ZrO₂ Composites

There are a large range of process options to select from when working with ceramic composites including sintering methods, sintering parameters, material selection and composition, and dispersion techniques. It is not always known or obvious which steps to take to achieve the desired material outcomes.

On considering methods to fabricate CNT-Zirconia composites, one used a deposition technique to create composite layers [9], thus proving that the CNTs are able to survive the sintering process. A major concern in the sintering stage of the composite is the degradation of the nanotubes due to heat exposure. Because of this, SPS is often chosen to sinter composites containing CNTs due to the minimal amount of time the specimen is exposed to peak temperatures. One study showed that examination of a CNT-Zirconia composite via high resolution transmission electron microscopy revealed the effectiveness of SPS in the fabrication of near theoretical density composites without notable oxidation or damaging effects on the integrity or structure of the CNTs [10].

Because pure Zirconia undergoes a phase change from tetragonal to monoclinic as it cools it experiences a large change in volume. To counteract this, Zirconia can be stabilized by doping with Ytria. This stabilizes the crystalline structure and allows it to retain its tetragonal form after cooling, resulting in an increase in strength versus pure Zirconia [11].

Weight Fraction of CNTs

The percent composition of CNTs in the composite varied between studies but did not typically go above 6% by weight. One study found that a CNT composition of above 9% became undesirable due to agglomeration and kinking of the nanotubes. Agglomeration of nanotubes, especially at the grain boundaries, tended to decrease the mechanical properties of the composite. As the weight fraction of CNTs rises it becomes increasingly difficult to obtain a composite with near-theoretical density. High amounts of reinforcements can sometimes interfere with the ability to create a fully dense product, as is noted in most attempts at creating a ceramic composite with CNTs [5-7, 9, 10, 12-14]. As the weight fraction rises increasing temperatures and pressures are required to obtain the same level of densification. CNTs are known to

Sintering Time, Temperature, and Pressure

To obtain full densification the correct combination of time, temperature and pressure must be used. However, excess exposure to elevated temperatures and pressures will have a profound impact on the microstructure of the resulting composite. If the soak time is too long or the temperature is too high the results are an increase in the average grain size of the Zirconia, which is associated with a decrease in toughness. However, if the pressure, temperature, or soak time are too low the composite will not reach the desired level of densification, which is also strongly correlates with a decrease in material toughness.

A study that used SPS to create a CNT-Zirconia composite with 6.3% CNTs by weight [12] reported a slightly lower fracture toughness. However, a separate study by Mazaheri that also used the SPS process to create a CNT-Zirconia composite reported an increase in fracture toughness of over 30% [13]. The study with the increase in toughness showed numerous

variations between both techniques and materials chosen. For example, the Mazaheri study used a lower CNT weight percentage as well as significantly higher axial pressure of 50MPa versus 20MPa during the SPS runs. This demonstrates that the method of fabrication as well as the process parameters are critical to the resulting mechanical properties.

Required soak time to reach peak density varied wildly according to the starting grain size, sintering temperature, and weight fraction. As such it is difficult to determine the precise time needed for full densification based on other parameters. One study stated that “Throughout all the SPS cycle it was possible to measure the height variation of the powder body precisely and instantaneously. Knowing the instantaneous variation of the sample height, one can calculate the instantaneous relative density” [13]. This information will be extremely useful in determining the density of the material as it can actively be monitored and determined when additional soak time will no longer provide benefits in density.

The temperatures used in various other experiments [7, 12-15] seems to imply that the temperature required for full densification correlates strongly with the weight fraction of CNTs used. Low weight fraction composites, ranging from 0.5-3.0% CNTs by weight, were typically able to achieve near-theoretical density with temperatures between 1200-1250 °C. When the weight fraction was increased past 3.0% temperatures were elevated to 1250-1350 °C to acquire the same density.

Sintering pressure was examined from multiple studies [7, 12-14] using pressures ranging between 36-100 MPA and the relationship between final density and sintering pressure appears to imply that higher sintering pressures correlated with higher densities. One issue that arises from this is the fragility of the graphite die used in the SPS process. Discussion with the operator of the SPS machine at Texas A&M University’s MDC2 material development and

characterization laboratory revealed that the die was somewhat fragile and prone to cracking or breaking under high loads. Exertion of pressures approaching the capacity of the SPS machine should be done so with care as not to damage the die used.

Dispersion of CNTs

One of the difficulties of using CNTs as a composite component is obtaining proper dispersion of the CNTs throughout the composite. Although their material properties lead to high expectations their size and geometry have limited their use. As other studies have found, “A homogeneous distribution of CNTs on the ceramic grain boundaries is essential to improve mechanical properties. However, as previously reported in several studies, CNTs have been found to be highly aggregated into bundles due to Van der Waals attraction.” [13]. This is the main reason for the choice of functionalized nanotubes, as the repulsion due to surface will hopefully diminish the attractive Van der Walls force.

Due to this difficulty, a common approach is to use a colloidal processing method. This technique involves suspending the CNT and matrix components in a medium in order to ensure uniformity. Two methods of dispersion in colloidal processing are commonly used, electrostatic and polymeric mechanisms [16]. Electrostatic methods involve the utilization of particle charges, as is performed in this study. Polymeric methods use polymers to stabilize a mixture prior to sintering. This second method was considered, but decided against due to the uncertainty of residual contamination after polymer binder burnout. When dispersion methods of other studies were examined it was found that a study which used a chemical dispersant [15] displayed lower fracture toughness than a study which utilized the electrostatic mechanism [12]. However, it is difficult to determine how much of this impact was due to the dispersion method alone, as many

variables differ or are unstated between experiments. An example of good CNT dispersions can be seen in Figure 1 below, obtained from the Thostenson study [5].

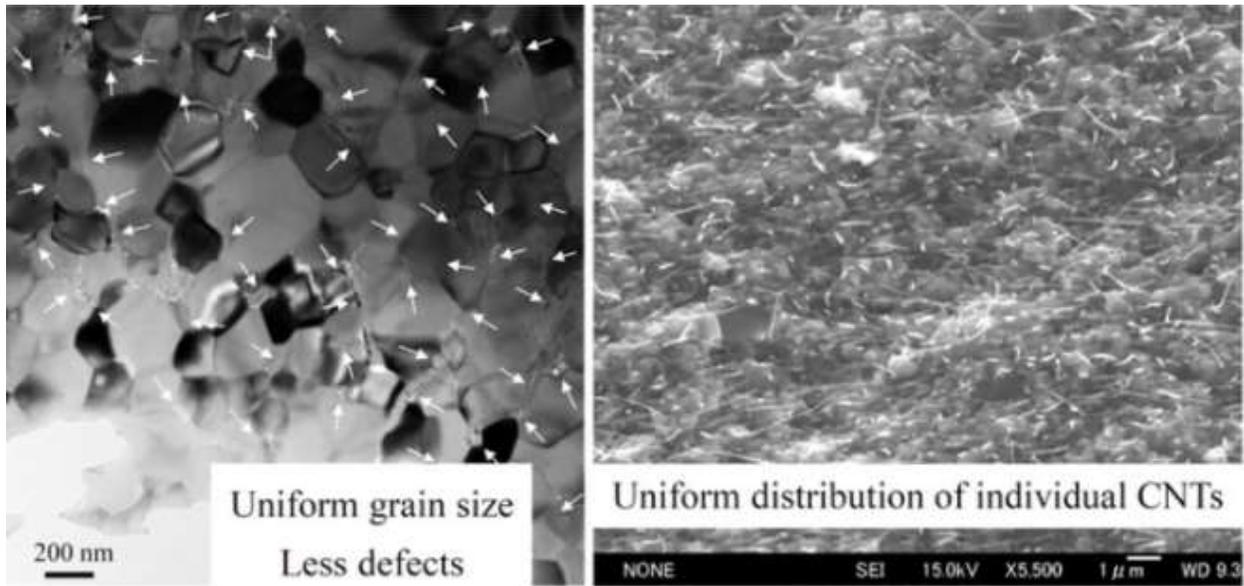


Figure 1. Demonstration of uniform CNT distribution in a ceramic matrix.

Functionalized CNTs have been chosen for this study to ease in the dispersion of CNTs. Functionalization leads to a surface charge, which allows even dispersion of the nanotubes [14]. This attaches COOH groups to the walls and ends of the nanotubes. This allows the nanotubes to be easily dispersed in an aqueous solution, such as de-ionized water, without the need for a dispersant additive. One report on a failed attempt to produce a mechanically superior CNT-Zirconia composite showed notable differences in the fabrication process in comparison to the Mazaheri study. The method of dispersing the nanotubes used was a diluted solution of sodium dodecyl sulfate in which untreated nanotubes were added, the suspension was then vigorously mechanically stirred [15].

CHAPTER III

MATERIALS AND METHODS

Materials

Creation of the composite includes forming controlled samples of CNTs dispersed in Zirconium Oxide ceramic. Two lengths of nanotubes are used to investigate how the length impacts the strength of the matrix-reinforcement bond interface or dispersion characteristics. Once the length which most impacts composite toughness is determined, more samples are created using that length to find the reinforcement to matrix ratio which provides the greatest increase in toughness. Interactions between nanotubes and Zirconia as well as changes to both materials during sintering are critical to the resultant properties and the sintering parameters required for full densification.

Required Materials

This study utilizes Zirconia powder doped with 3mol% Ytria, or Yttrium Oxide. The addition of Ytria prevents undesirable crystal structure transition between tetragonal, monoclinic, and cubic structures by stabilizing the tetragonal structure formed during sintering. Stress transformation initiated by stress concentration can cause the stabilized tetragonal crystal state to revert to monoclinic. This stress transformation is desirable as it results in compressive stress due to the change in volume caused by the change in crystal structure. This transformation has been known to assist in preventing the propagation of cracks, resulting in a higher overall toughness. The average particle size of the Zirconia is 30-60nm. Due to the very high aspect ratios of the nanotubes this particle size is small enough for the powder to compact around the

nanotubes. The Zirconia powder is also small enough to stay suspended in water for long periods of time without settling, making it possible to maintain a homogenous mixture while drying.

General properties of Zirconia can be seen below in Table 1, obtained from the Shirooyeh study [17] which examined mechanical properties of Zirconia.

Table 1. Mechanical Properties of Zirconia Variants

| Property | ZrO ₂ | 3YSZ | La ₂ Zr ₂ O ₇ | BaZrO ₃ |
|--|----------------------------|----------------------------|--|----------------------------|
| T_m (K) | 2973 [55] | 2973 [60] | 2573 [60] | 2963 [60] |
| D_{th} (m ² .s ⁻¹) (1273 K) | 0.43x10 ⁻⁶ [56] | 0.58x10 ⁻⁶ [50] | 0.54x10 ⁻⁶ [50] | 1.25x10 ⁻⁶ [50] |
| k (W.m ⁻¹ .K ⁻¹) (1273 K) | 2.17 [57] | 2.12 [50] | 1.56 [50] | 3.42 [50] |
| E (GPa) | 21 (1373 K) [58] | - | 175 (293 K) [61] | 181 (293 K) [61] |
| α (K ⁻¹) (293-1273 K) | 15.3x10 ⁻⁶ [59] | 11.5x10 ⁻⁶ [50] | 9.1x10 ⁻⁶ [50] | 8.1x10 ⁻⁶ [50] |
| C_p (J.g ⁻¹ .K ⁻¹) | - | 0.64 [50] | 0.49 [50] | 0.45 [50] |
| ν | 0.25 [58] | - | - | - |

Symbols : T_m , melting point; D_{th} , thermal diffusivity; k , thermal conductivity; E , Young's modulus; α , coefficient of thermal expansion; C_p , heat capacity; ν , Poisson's number.

Two types of nanotubes are used. Both are multiwall functionalized with outer diameters of 50-80nm, and inner diameters of 5-10nm. The lengths of the tubes are 0.5-2um and 10-20um. This leaves length as the only variable in the nanotubes and allows the impact of length to be more easily determined.

Carbon Nanotubes used consist of over 95% with less than 1.5% ash and 0.5-1.0% functional content by weight. Outer diameters are specified as greater than 50nm with 0.5-2.0um and 10-20um lengths. Packaging of the nanotubes with specifications can be seen on the following page in Figure 2.

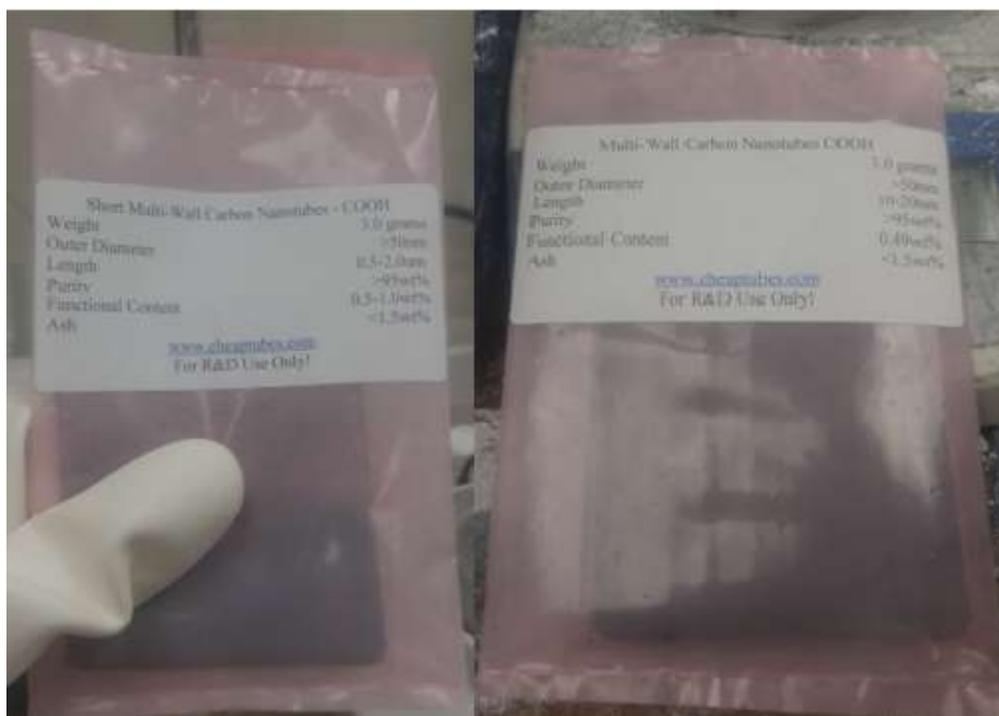


Figure 2. Packaging for short (Left) and long (Right) Carbon Nanotubes.

Safety Precautions

Carbon Nanotubes pose potential health risks due to their size and difficulty to detect. To prevent accidental exposure, this study utilizes a sealed glove box under vacuum to prepare samples. A scale and hot plate have been placed into the glove box and the location of the power cable entry sealed with silicone. A vane type vacuum air pump is attached to a hose which connects to a gas nozzle on the glovebox. The hose is filled with filter paper to provide additional filtration for evacuated air. The purpose of maintaining a vacuum in the glovebox is to mitigate the likelihood of CNTs becoming airborne by removing air, making the nanotubes' density relative to the contained atmosphere higher. This minimizes the buoyant force on the nanotubes and makes it more difficult for turbulence in the air to pick them up and suspend them. The established working area is shown in figure 3 below.



Figure 3. Glovebox, vacuum pump, scale, and hot plate.

Materials brought into the glovebox are only opened once everything required is placed inside, the glove box is sealed, and a vacuum is established. Once the preparation is complete the materials are returned to their containers and sealed. The glovebox is left under vacuum for one hour. It is then re-pressurized and allowed to sit for an additional hour. This ensures that any airborne nanotubes have precipitated out of the air. The samples are then transferred to the graphite die of the SPS machine. After drying, the samples no longer pose a large risk of diffusing nanotubes into the air. The length of the nanotubes is significantly greater than the matrix powder and the nanotubes are contained in the mixture.

Methodology

The steps taken during the creation of the composite have large impacts on the resultant properties. Identical materials in the same proportions can be used and minor changes in the processing or sintering parameters can result in large variations between samples. Powder preparation, sintering, and processing are done with groups of samples to ensure that the samples undergo virtually identical processing.

Powder Preparation

Due to the need to disperse the reinforcement evenly throughout the composite, the nanotubes used are COOH functionalized. Suspension of dispersed nanotubes in distilled water allows the addition of Zirconia powder while maintaining the nanotube dispersion.

A beaker is filled with 50 mL of water and activated nanotubes are slowly added to the distilled water. The mixture should be vigorously stirred to facilitate nanotube dispersion. A magnetic stir is used if available. Once the nanotubes have been added the Zirconia powder is slowly added while continuing to stir. The ratio of nanotubes to Zirconia is determined by the weight fraction used. Due to the average particle size of the Zirconia being in the nanometer range there are no issues with the powder settling over the short processing period, resulting in an even emulsion. An image of the mixtures in preparation can be seen on the next page in Figures 4 and 5.



Figure 4. Mixture containing Zirconia powder before addition of CNTs.



Figure 5. Mixture containing Zirconia powder and 4% CNTs by weight, excluding water.

The intended resulting specimen is the diameter of the die, 4 cm, and roughly 1 cm tall. With a peak theoretical density of 6.1 g/cm^3 and a volume of 12.57 cm^3 each puck shaped specimen will require approximately 76 g of Zirconia powder.

Once the nanotubes and Zirconia powder are suspended the beaker is placed onto a hot plate and heated until the contents are a semi-viscous slurry. The mixture is then transferred from the beaker to a specially designed container shown on the next page in Figure 6. This container consists of a stainless-steel rod and a similar tube with an inner diameter marginally smaller than that of the SPS die. The rod is machined to produce a slip fit with the tube to allow for axial

compression while drying. The mixture is completely dried in this container while being frequently uniaxially pressed by the steel rod.



Figure 6. Steel tube and rod for powder drying.

However, because of a tenacious film formed by the carbon nanotubes when they are added to water, drying of samples containing carbon nanotubes requires crushing the mixture into a powder form while heating to allow for drying. This is accomplished by transferring the mixture to a pestle and mortar when it becomes too viscous to stir and heating the mortar while crushing the mixture until the powder is dry.

The graphite die used in the SPS machine, shown on the next page in in Figure 7, has an inner diameter of 40 mm, which is identical to the stainless steel tube used to dry the mixture. Once the die is obtained a graphite ram is inserted and the prepared powder is placed into the die. A circular graphite sheet is placed on top of the powder and the next powder type is loaded onto it. Uniaxial force is occasionally applied to the graphite rams to compress the powder. Once the

die is nearly full the graphite plug is placed into the top of the die. There are approximately 65mm of usable height in the die. Figure 8 displays the graphite die prepared for filling. Graphite foil is placed in the die to prevent fusion of the material to the die.



Figure 7. Graphite SPS die and plugs (Rams)



Figure 8. Sample powders ready to be loaded into the prepared die.

Spark Plasma Sintering

The method of sintering the composite is SPS, as it offers the ability to create high density, low porosity ceramics as well as providing the least exposure time to high temperatures during sintering. This will minimize the risk of damaging or oxidizing the nanotubes as they are known to degrade over time when exposed to high levels heat. For the purpose of experimenting economically each SPS run consists of three types of composites, each separated by a sheet of graphite. Once the materials are assembled, the SPS machine is reserved, and the powder mixture is prepared and dried the sintering process is started.

Figure 9 below shows a graphic illustration of the SPS process parameters to be used for this experiment. The bold line denotes temperature and the thin line denotes pressure. A force of 75 MPa will be applied to the die. The sample will be heated at a rate of $75^{\circ}\text{C}/\text{min}$ to a temperature of 1300°C and held for 8 minutes. The cooling rate can be equivalent to the heating rate until 500°C , at which point the composite can be furnace cooled.

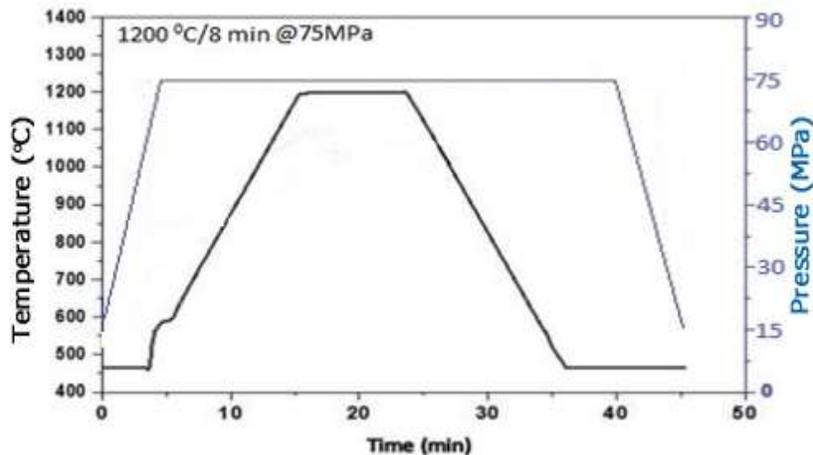


Figure 9. The SPS curve to be used on the composite. The upper line denotes pressure and the bottom line denotes temperature.

Once the machine has been programmed, the graphite die loaded with the composites can be inserted into the SPS machine. The rate and percentage of densification can be accurately monitored by watching the height of the plugs as there is a direct correlation between the compression distance and sample density. The SPS machine used can be below in figure 10.



Figure 10. Spark Plasma Sintering machine at Texas A&M MDC2 lab.

Spark Plasma Sintering heats the sample by resistance heating induced by current flow. Up to 10,000 Amps can be applied to the material in the die and brought to a temperature of over 1900⁰C. Samples in this study are brought to 1300⁰C. The interior of the SPS furnace can be seen on the next page in Figure 11.



Figure 11. Interior of SPS furnace with a thermocouple made of graphite fabric covering the die.

Post Sintering Processing

Once sintering is complete the graphite die is removed and the sintered material is extracted. At this stage the composites are fused together at the graphite sheet separators. After separating the composites along the graphite sheets, they are cleaned of any remaining fused graphite. Grinding and polishing the surfaces of the composite are then conducted. An image of samples of Zirconia and Zirconia with CNTs after separation and light grinding can be seen on the next page in Figure 12.



Figure 12. Pure Zirconia (Left) and Zirconia with added short CNTs (Right). Residual graphite from the SPS process can be seen on both samples. This must be ground away before testing. Samples are roughly 40mm in diameter and vary in thickness from 7mm to 9mm.

Small sections were cut from each of the three samples and placed in epoxy for ease of polishing. Figure 13 below demonstrates the section size relative to the samples and Figure 14 on the next page shows unpolished samples suspended in epoxy. Three sections were placed into the same epoxy disk to expedite polishing and testing of samples.



Figure 13. Small section cut from sample using a diamond cutting disk.

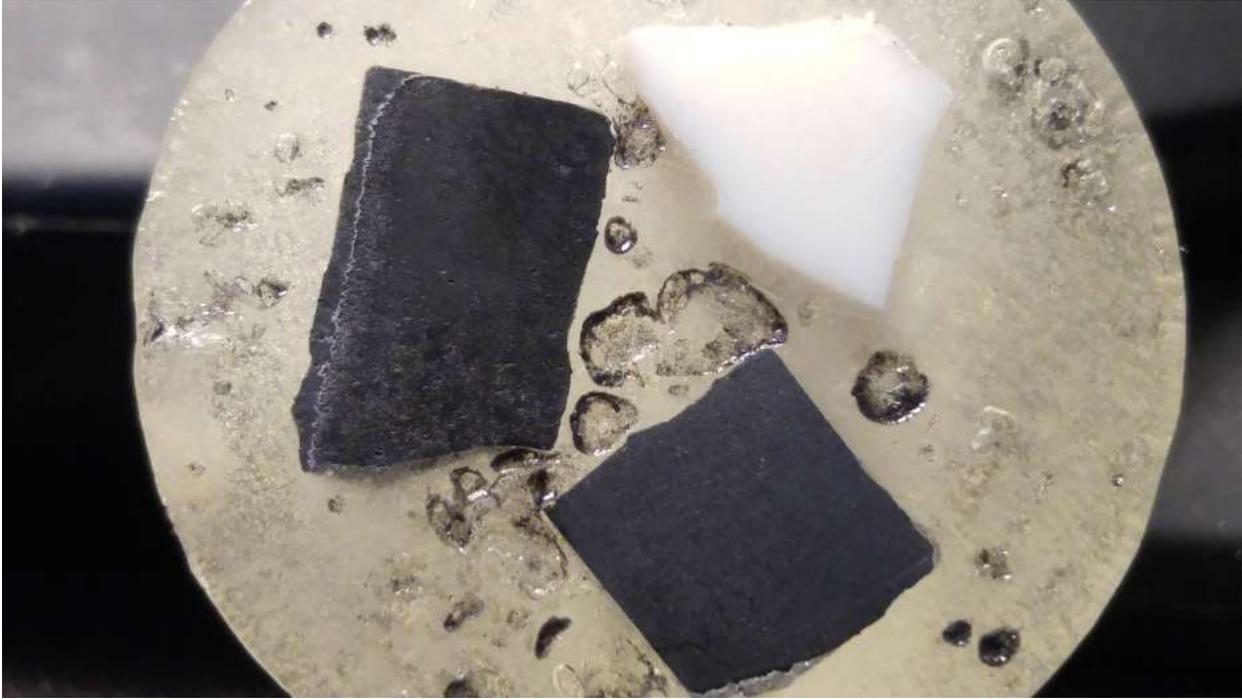


Figure 14. Unpolished samples suspended in Epoxy. Disk is 25mm in diameter.

CHAPTER IV

RESULTS AND ANALYSES

Characterization of Samples

Due to the brittle nature of ceramics, they are significantly more difficult to mechanically characterize than Metals and Polymers. Hardness tests are performed on a micro-indenter and a hardness value is determined by measuring the resultant indent with respect to the applied load. Any samples which have been hardness tested should be re-polished to remove surface damage caused by indentation. ASTM standard C1421 [18] denotes procedures to prepare samples for flexural and fracture toughness tests and states that during finishing “No less than 0.06 mm per face shall be removed during the final finishing phase, and at a rate of not more than 0.002 mm per pass”. This ensures that residual stresses on the surface are minimized to prevent errors. This Fracture toughness is determined by analysis of fracture after breaking the sample. Flexural Strength is determined by force required to break a sample with respect to its size. Tribological performance can be characterized with a pin on disk Tribometer, and the surface profile analyzed with a 3D surface profilometer or interferometer.

Polishing of Samples

Many of the mechanical tests performed on ceramics must be done with samples which are machined to high degrees of accuracy. Flexural and fracture toughness specimen must have perpendicular faces and a small chamfer as well as being ground along the axis of the bar. Testing conditions are more stringent than those of metals and polymers due to the brittle nature of ceramics. Ceramic toughness is highly dependent on geometry, as areas of stress

concentration, even in the micro range, can cause cracks to initiate. Cracks made by micro-indentation must be removed by polishing before samples are used for the pre-cracked beam method, discussed in the section on fracture toughness.

Several steps must be used to polish samples to required specifications for testing. The highest quality of surface finish is required for nanoindentation. A standard guide for polishing of structural ceramics can be found in ASM Handbook Volume 9: Metallography and Microstructures [19], which denotes Zirconia (ZrO_2) as a structural ceramic and gives a general procedure for polishing, shown below in Table 2.

Table 2. Standard preparation conditions for structural ceramics

| Process | Base | Diamond grade, μm | Lubricant | Speed, rpm | Pressure(a) | | Time, min |
|----------------|---------------------------|------------------------------|---------------|------------|-------------|-----|------------|
| | | | | | N | lbf | |
| Grinding | Diamond disk | 65 | Water | 300 | ~180 | ~40 | Until flat |
| | Diamond disk | 20 | Water | 300 | ~180 | ~40 | 5–10 |
| Fine grinding | Composite disk | 6 | Alcohol-based | 300 | ~100 | ~23 | 5–15 |
| Polishing | Pellon cloth | 6 | Alcohol-based | 150 | ~150 | ~34 | 15–120 |
| | Hard synthetic cloth | 3 | Alcohol-based | 150 | ~120 | ~27 | 15–120 |
| | Hard silk cloth | 1 | Alcohol-based | 150 | ~90 | ~20 | 5–10 |
| Fine polishing | Short napped, fiber cloth | Silicon dioxide suspension | | 150 | ~50 | ~11 | 0.5–5 |

This table should be used as a rough guide only, and parameters will need to be adjusted according to the preparation requirements of specific ceramic samples. (a) Pressure specification for a sample holder with six 25 mm (1 in.) diam specimens

Nanoindentation will require a higher degree of polishing than is produced by the procedure above. However it should suffice for tribological testing such as scratch tests. The facility which contains the nanoindenter used, the Texas A&M Materials Characterization Facility, includes polishing amenities for final polishing before indentation. Figure 15 on the next page shows the three sample pieces after polishing.

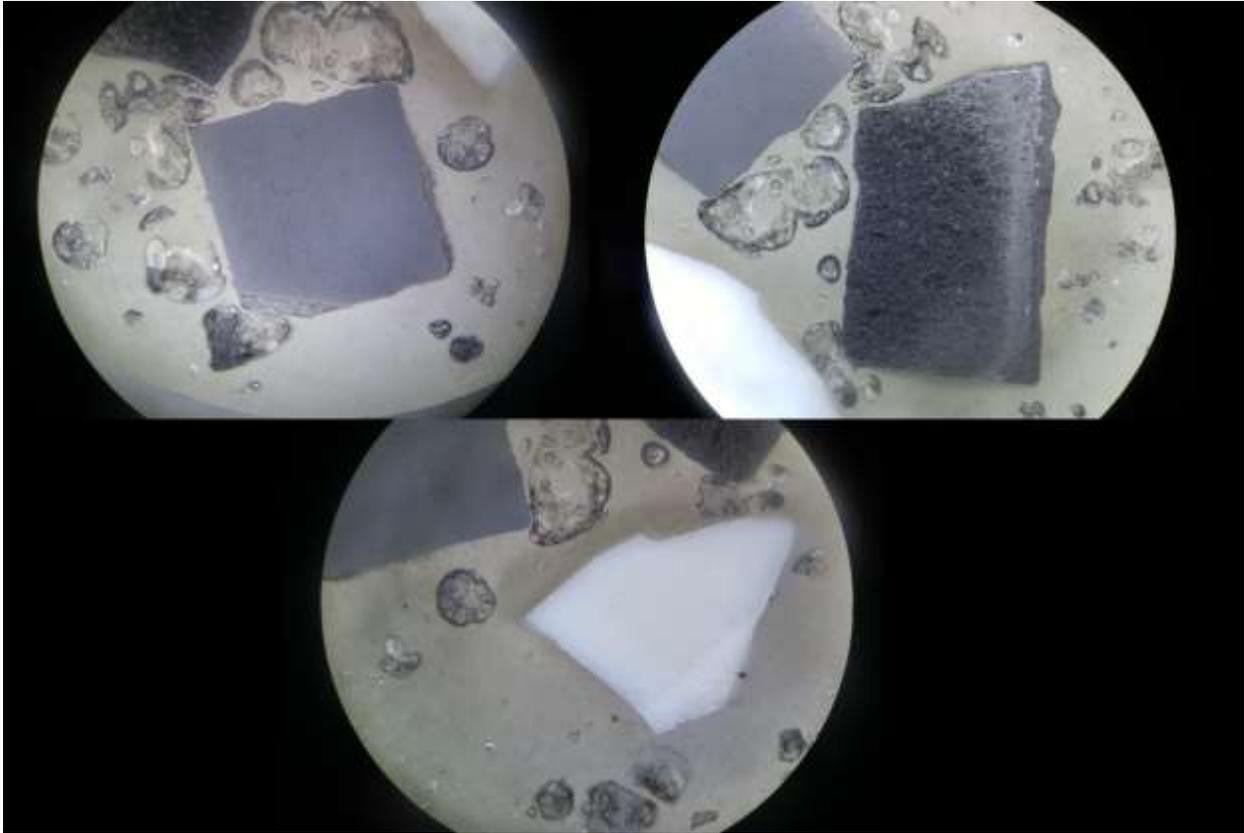


Figure 15. Zirconia (Bottom), Zirconia with short CNTs (Top Right), and Zirconia with long CNTs (Top Left) after polishing. The samples with short CNTs displays some degree of visible porosity. It can also be seen that graphite from the SPS penetrates the outside of the short CNTs sample and fills the porosity. This area is avoided for mechanical testing.

Fracture Toughness

The procedure to determine fracture toughness is denoted by ASTM C1421 [18]. Several variations are available and this study utilizes the precracked beam (pb) method. The precracked beam method was chosen because it is suitable for a three-point bend test and enables the use of smaller samples than other methods. As SPS samples have a diameter of 40mm and a height of about 6mm small samples must be used to maximize the number of samples.

The apparent toughness of ceramics is largely a factor of geometry, which makes it difficult to obtain reliable information on the actual fracture toughness. Locations where stress concentrations occur result in a susceptibility to unwanted cracking during testing. Samples that

do not display stable primary cracks which are no more than 5 degrees from perpendicular to any of the faces are considered to be invalid samples. Testing standards recommend having as many samples as possible to account for errors in testing and invalid samples. The samples must be machined to the requirements shown on the next page in Figure 16. A small chamfer is placed on the sample to remove the sharp edge as this region will contain microcracks. This is most important on the side of the beam which will be in tension during testing. All finishing processes must be performed along the axis of the beam to ensure that microcracks due to finishing don't propagate and effect the resulting toughness calculations or produce an invalid sample.

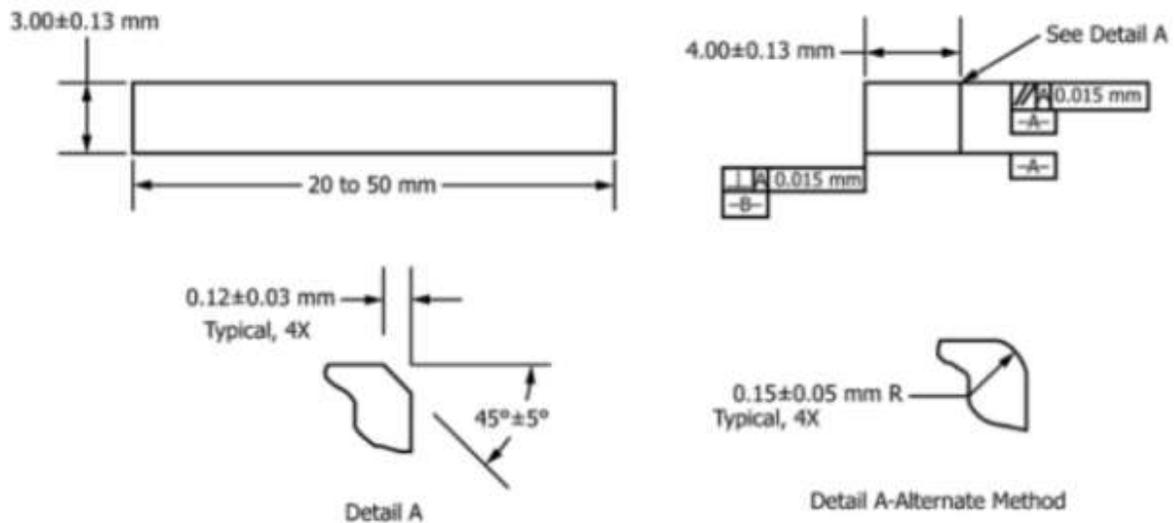


Figure 16. Requirements for Fracture Toughness Samples. [18]

Precracking of the beam is achieved by placing numerous indentations along the center of the sample to assist in the initiation of a stable crack. Alternatively, a small notch may be created in the guidance of the crack. Specifications for placing a precrack on the beam are shown in Figure 17 on the following page.



Figure 17. (a) specifications for notching option (b) Specifications for indentation option (Note that a Vickers indenter is used with axes pointing to the edge of the sample.). [18]

Once samples have been fabricated they are placed in a bending fixture and broken. The crack is then analyzed and parameters of the crack used to determine the stress present at the time of the crack. This data is then used to calculate the fracture toughness. The testing fixture required to break samples, as determined by ASTM standards, can be seen in detail below in Figures 18 and 19.

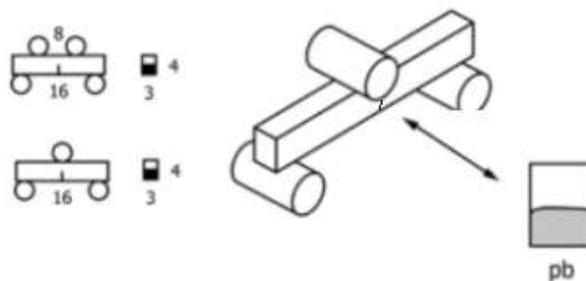


Figure 18. General fixture requirements, in mm, for precracked beam (pb) method. [18]

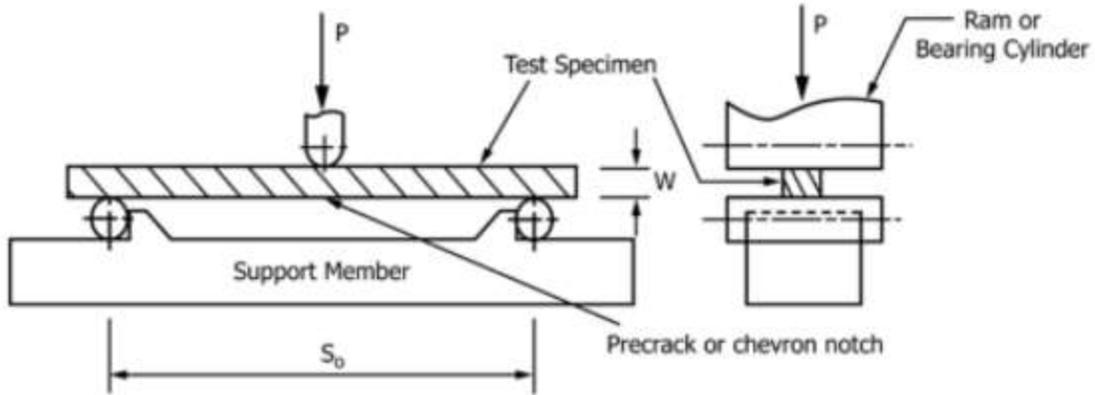


Figure 19. Detailed fixture requirements for precracked beam (pb) method. The width (W) is equal to 4mm and the outer span (S_o) between the rollers is 16mm. Rollers on the bottom should be free to articulate. [18]

Flexural Strength

Flexural strength determination is performed similar to that of fracture toughness and parameters are denoted by ASTM standard C1611 [20]. Sample preparation is similar to that of C1421, but with slightly varying dimensions for the smallest specimen. Sample specifications are shown below in Figure 20.



Figure 20. Flexural strength specimen standard dimensions. Detail A denotes two methods of reducing stress concentrations on tensile edges by using a fillet or chamfer.

The beam is placed into the bending fixture and the force required to break the beam is used to calculate the flexural strength. The formula used for the three-point bend test is as follows. $S = \frac{3 PL}{2 bd^2}$ in which P is break force, L is the span between the outer rollers, b is the specimen width, and d is the specimen thickness. Fixture requirements are shown below in Figure 21.

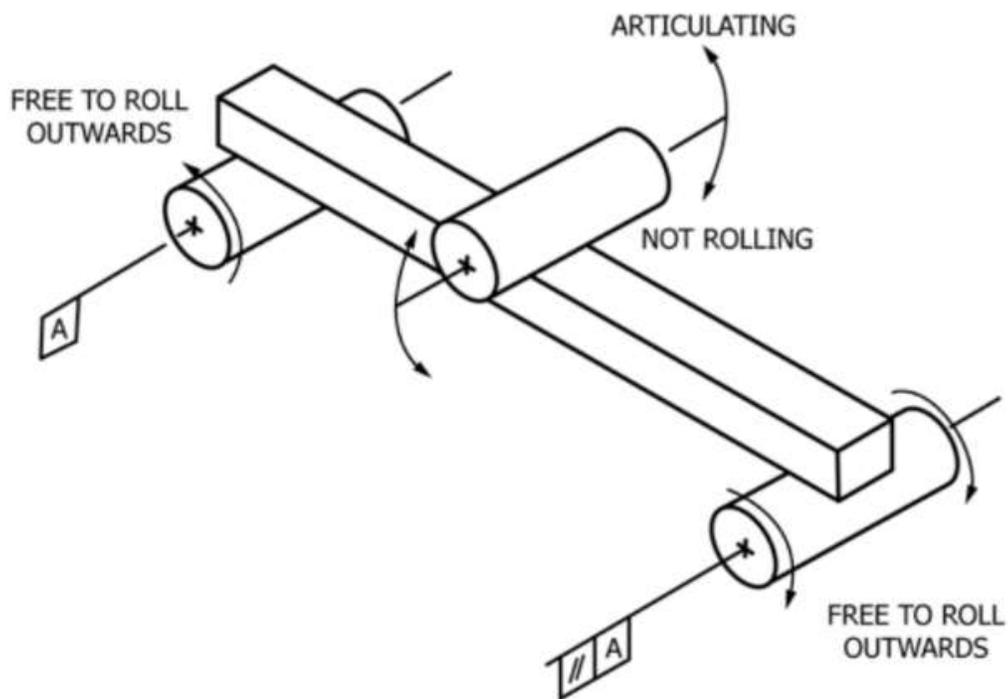


Figure 21. Bending fixture schematic with requirements. [20]

Hardness

Due to the lack of plastic deformation and ease of crack propagation resulting from the hardness of ceramics, microindentations must be made and analyzed to properly assess the hardness of the ceramic.

Microindentation hardness tests were performed on samples using a Vickers hardness test with a 2kg load. The two diameters of the resulting indentations were measured and used to determine hardness. The fixture and device used as well as images of the surfaces are shown below and on the following page in Figures 22 and 23.

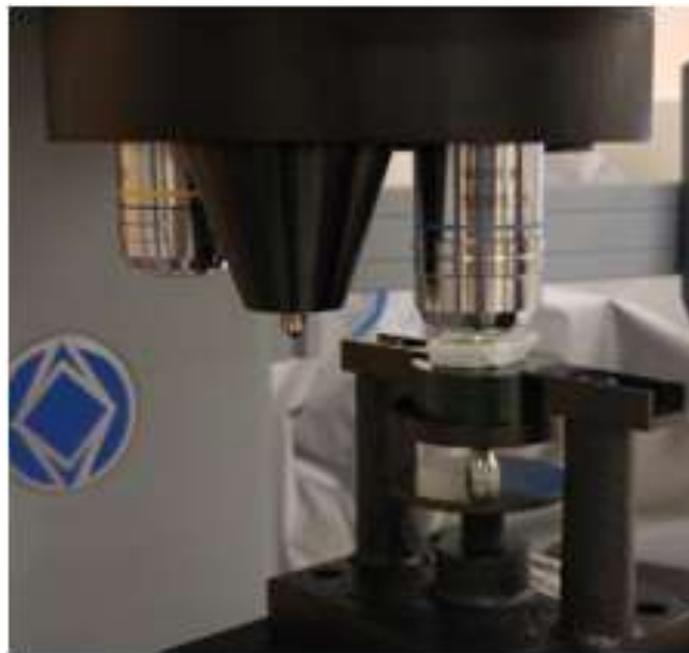


Figure 22. Fixture and device used for hardness testing.

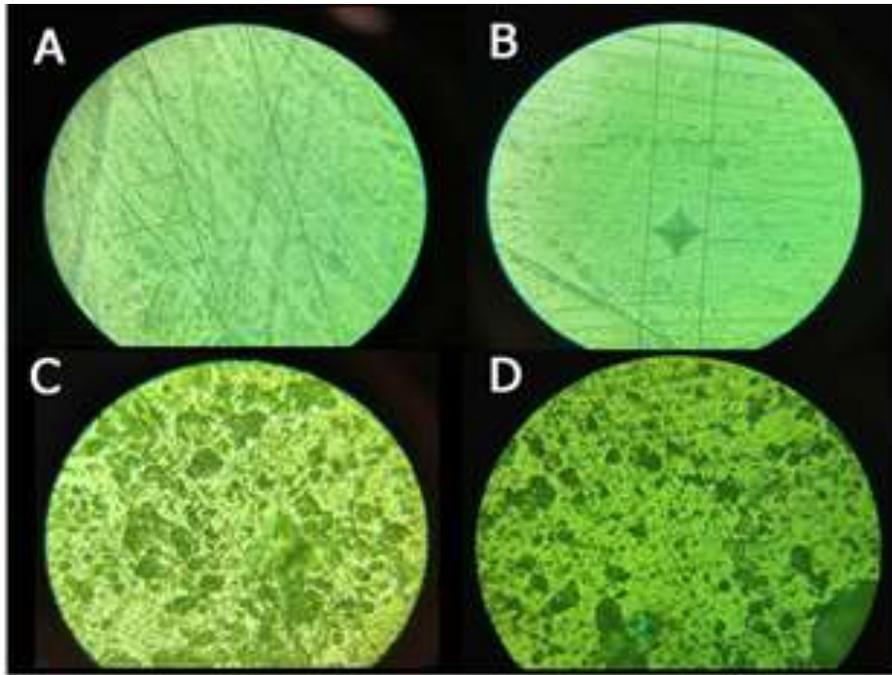


Figure 23.

A.) Surface of pure Zirconia Sample. B.) Indentation on Zirconia sample with diameters 52.66um and 52.74um. C.) Surface of Zirconia sample with 10-20um nanotubes D.) Surface of sample with 0.5-2um nanotubes.

Samples containing nanotubes display porosity which results in a poor surface finish for a hardness test. Due to this rough surface finish, indentations could not reliably be measured on samples containing nanotubes. Lapping will be required to produce a surface finish sufficient for hardness testing of these samples.

Micro hardness tests on the pure Zirconia samples resulted in an average hardness of 1247HV2. This is marginally lower than the standard hardness of Zirconia, which is 1350HV2. This error may be due to the level of surface finish present. Further micro hardness testing will be conducted once lapping of the samples has been completed.

Nanoindentation is another method used to characterize sample properties. Nanoindentation allows for analysis of the hardness and modulus of a material on the nano scale. Measurements may be taken to examine microstructural differences according to region. This

method has been used to measure the hardness of individual grains and may be able to do so on the samples used in this study. Results may not be characteristic of the macroscopic mechanical properties of the composite but may give insight into variations caused by differences in microstructure.

Sixteen indentations were performed per sample. Average values as well as the standard deviations of the resulting measurements can be seen below in Table 3. Force vs displacement curves of the various samples can be seen on the following page in figures 24, 25, and 26.

Table 3. Zirconia nanoindentation data

| | Zirconia | Zirconia + Short CNTs | Zirconia + Long CNTs |
|-------------------------|----------|-----------------------|----------------------|
| Mean Modulus (Gpa) | 193.97 | 187.52 | 175.28 |
| Modulus Std Dev | 11.4 | 21.25 | 47.81 |
| Mean Hardness (Gpa) | 11.65 | 13.42 | 9 |
| Hardness Std Dev | 0.9361 | 2.78 | 2.96 |
| Mean Contact Depth (nm) | 149.16 | 138.66 | 180.15 |
| Contact Depth Std Dev | 6.75 | 17.69 | 33.03 |

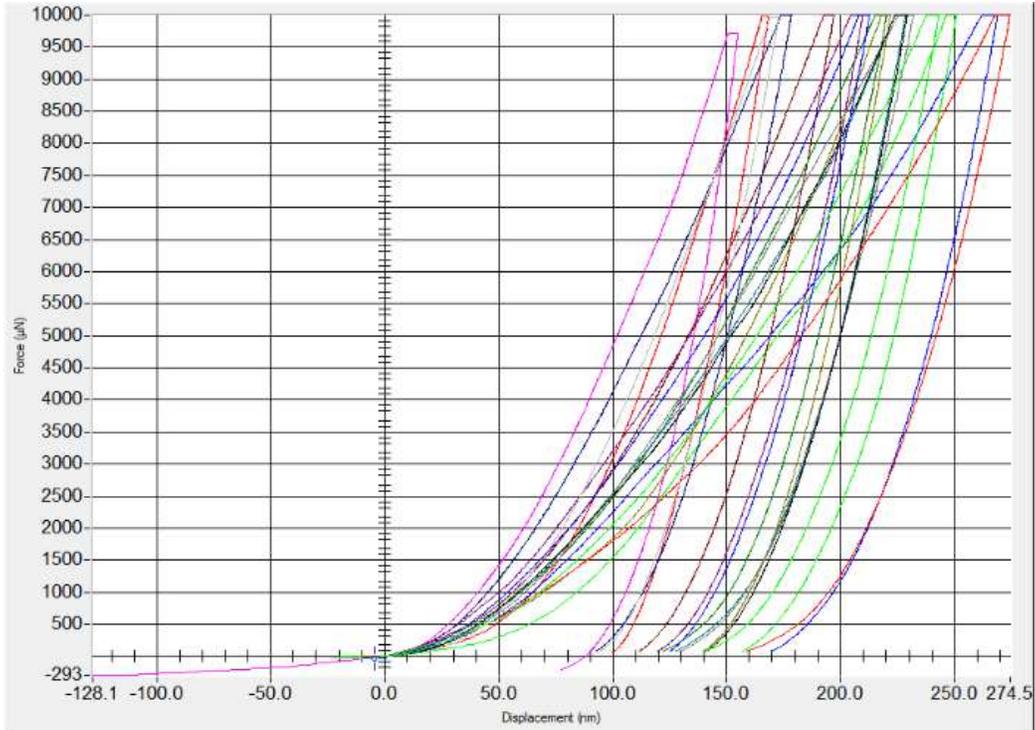


Figure 24. Indentation force vs displacement curves of Zirconia with short CNTs.

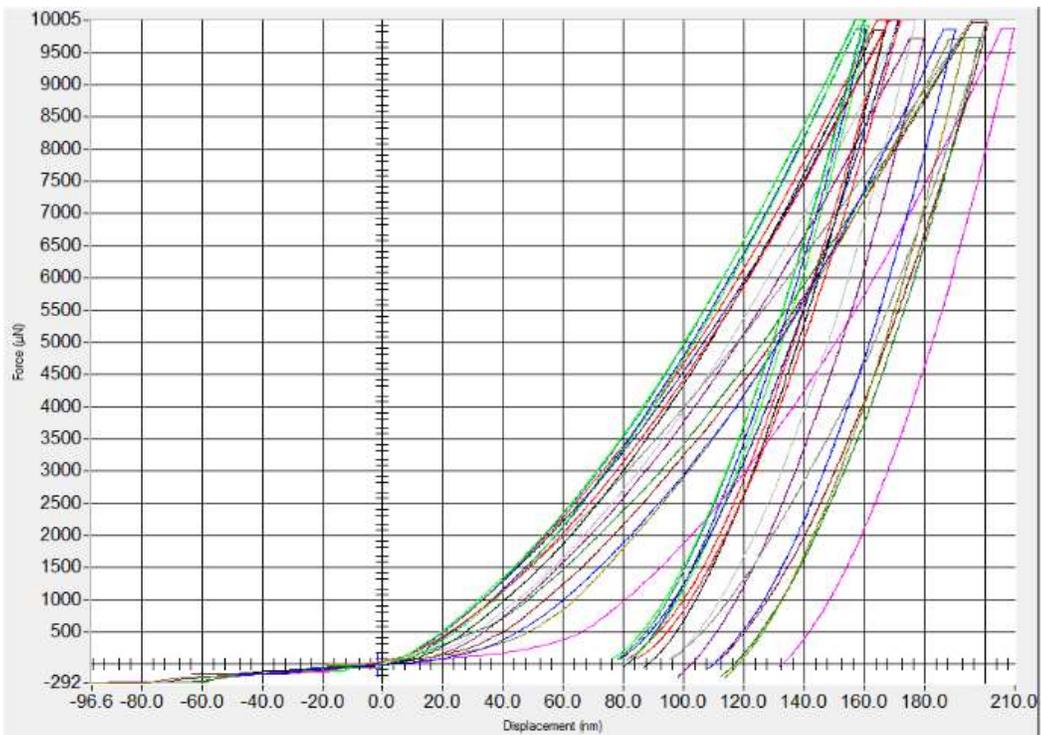


Figure 25. Indentation force vs displacement curves of Zirconia with long CNTs.

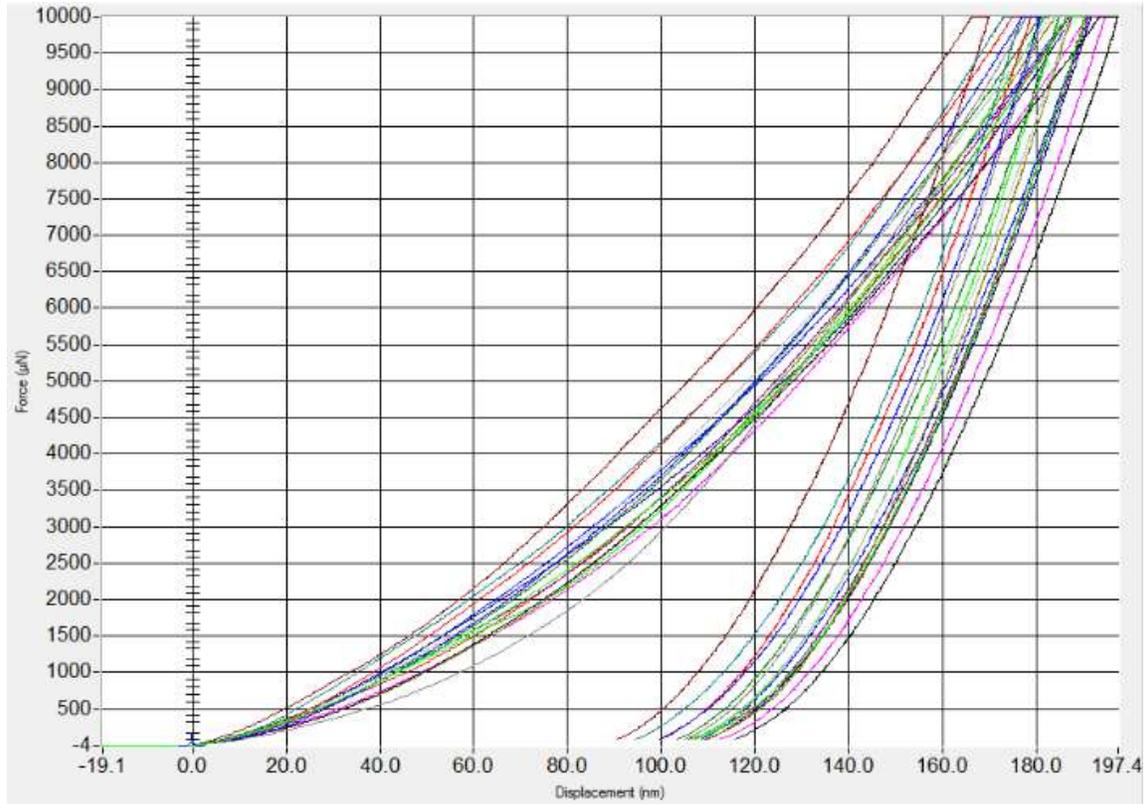


Figure 26. Indentation force vs displacement curves of Zirconia.

Surface Characterization

An Alicona InfiniteFocus G4 Optical 3D Surface Profiler, seen on the following page in Figure 27, was used to depict the surface of the samples. This verified that the long nanotube sample contained higher porosity than the short nanotubes sample. Images of the surfaces of the pure Zirconia and short nanotubes Zirconia can be seen on the following page in Figure 28. Porosity and poor surface finish are seen on the zirconia with nanotubes sample. This porosity made micro hardness testing on the composite too indeterminate to use, as there was no accurate way to denote or measure the indentation.



Figure 27. Alicona InfiniteFocus G4 Optical 3D Surface Profiler
<http://www.alicona.com/products/infinitefocus/>

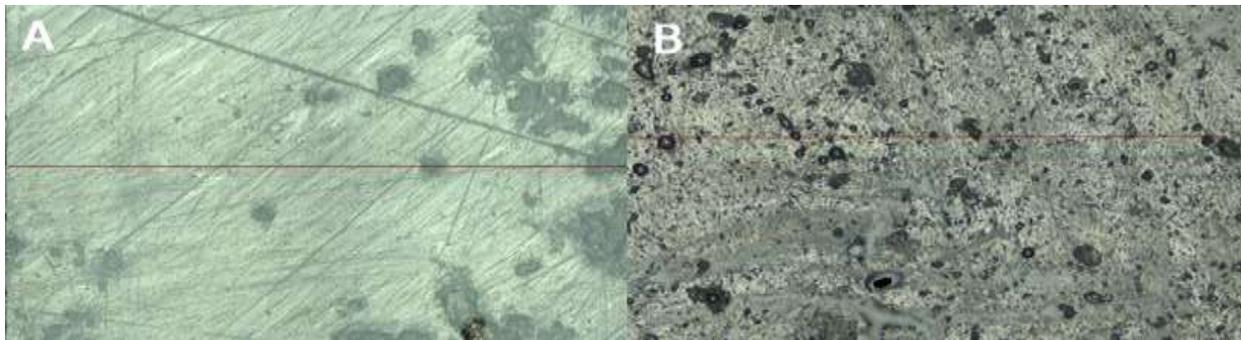


Figure 28.
Surface of pure Zirconia (A) and surface of Zirconia with 0.5-2um nanotubes (B).

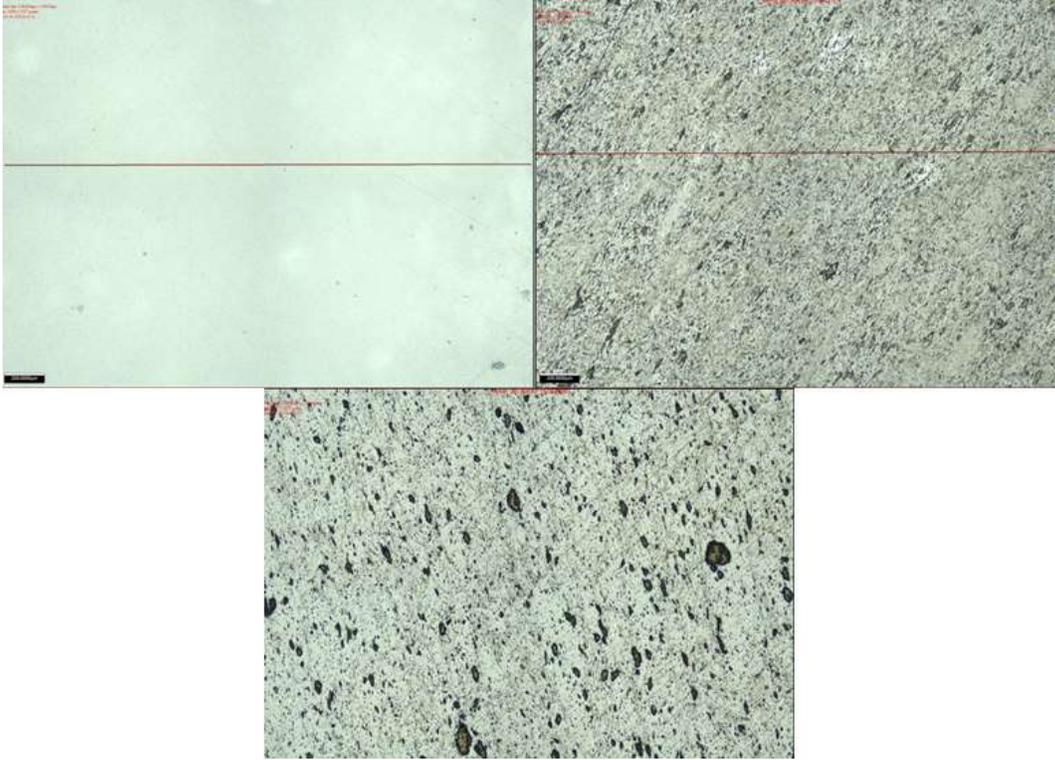


Figure 29. Samples after fine polishing as viewed by Alicona Infinite Focus Machine. Zirconia (Top Left), Zirconia with long CNTs (Top Right), and Zirconia with short CNTs (Bottom).

Results and Discussion

The SPS process required the use of graphite foil to separate the samples from each other and facilitate removal of the samples post-sintering. It was noted on the pure Zirconia sample that the graphite penetrated about 1mm into the surface on one side. The sample was discovered to contain a crack after sintering and split into four pieces upon removal of the graphite foil. A similar, less severe crack was noted in the sample containing the 0.5-2um nanotubes, although this sample did not break along crack upon removal of the foil. The 10-20um nanotubes sample appears to be free of cracks. The formation of cracks, especially across the midpoint of a sample, is known to be a defect associated with SPS.

CHAPTER IV

CONCLUSION

By analyzing the surface of the ground samples it becomes apparent that the addition of Carbon Nanotubes results in the formation of some porosity. The sample containing the longer, 10-20um nanotubes showed a higher density of porosity than the shorter 0.5-2um sample. This may indicate that longer nanotubes are more likely to result in porosity than shorter nanotubes when incorporated in ceramic composites.

With current data the impact of CNTs on the fracture toughness of Zirconia cannot be determined. Further preparation and testing of the samples is required to properly characterize the material properties. Due to the brittle nature of ceramics they are exceptionally difficult to characterize. Small variations in sample geometry, such as the direction of machining, have large impacts on the calculated values for mechanical testing. This is due to the formation of micro cracks, which may rapidly propagate and cause undesired results in testing.

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