Microstructural analysis of the failure mechanisms of carbon nanofibers and inorganic fullerene-type tungsten disulfide

Cook, Jamie E.

Monterey, California: Naval Postgraduate School

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MICROSTRUCTURAL ANALYSIS OF THE FAILURE MECHANISMS OF CARBON NANOFIBERS AND INORGANIC FULERENE-TYPE TUNGSTEN DISULFIDE

by

Jamie E. Cook

December 2013

Thesis Advisor: Claudia Luhrs
Second Reader: Garth Hobson

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### Title and Subtitle
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### Author(s)
Jamie E. Cook

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CNF produced from nickel showed agglomeration from all testing methods but no evidence of fiber breakage or delamination. IF-WS$_2$ failure modes observed were related, primarily, to the transition between 3D and 2D polymorphs, with subsequent agglomeration of the plate-like 2D structure, producing larger particle sizes. The secondary mechanism identified was delamination of IF-WS$_2$, which, in contrast to the former, gave origin to smaller particulates.

The failure modes identified herein were used to re-design the CNF material and test it using the gas gun. CNF with larger diameter distributions were grown from palladium catalyst, producing ultralow density carbon foam. This architecture presented viscoelastic properties that recovered the original shape after unloading, not showing evidence of failure under the gas gun test regime employed.

### Subject Terms
Carbon nanofiber, inorganic fullerene-type tungsten disulfide, gas gun, ultrasound, military rounds, agglomeration, delamination
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Jamie E. Cook
Lieutenant Commander, United States Navy
B.S., Principia College, 2003

Submitted in partial fulfillment of the requirements for the degrees of

MECHANICAL ENGINEER
AND
MASTER OF SCIENCE IN MECHANICAL ENGINEERING

from the

NAVAL POSTGRADUATE SCHOOL
December 2013

Author: Jamie E. Cook

Approved by: Claudia Luhrs
Thesis Advisor

Garth Hobson
Second Reader

Knox Millsaps
Chair, Department of Mechanical and Aerospace Engineering
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LIST OF ACRONYMS AND ABBREVIATIONS

2D two-dimensional
3D three-dimensional
Å Angstroms
Ar argon
BET Brunauer-Emmett-Teller
BABT behind armor blunt trauma
°C Celsius
CNF carbon nanofibers
CVD chemical vapor deposition
DSC differential scanning calorimeter/calorimetry
EDS energy dispersive x-ray spectroscopy
g gram
GPa gigapascal
He helium
Hg mercury
Hz Hertz
IF inorganic fullerene
J Joule
keV kiloelectron volts
kHz kilohertz
kPa kilopascal
kV kilovolts
kW kilowatts
LED light emitting diode
m meter
m² square meter
m³ cubic meter
mA milliamperes
MFC mass flow controller
mg milligram
<table>
<thead>
<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>min</td>
<td>minute</td>
</tr>
<tr>
<td>ml</td>
<td>milliliter</td>
</tr>
<tr>
<td>mm</td>
<td>millimeter</td>
</tr>
<tr>
<td>µm</td>
<td>micrometer</td>
</tr>
<tr>
<td>MPa</td>
<td>megapascal</td>
</tr>
<tr>
<td>NATO</td>
<td>North Atlantic Treaty Organization</td>
</tr>
<tr>
<td>NAWC</td>
<td>Naval Air Weapons Center</td>
</tr>
<tr>
<td>Ni</td>
<td>nickel</td>
</tr>
<tr>
<td>NPS</td>
<td>Naval Postgraduate School</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer</td>
</tr>
<tr>
<td>N₂</td>
<td>nitrogen gas</td>
</tr>
<tr>
<td>O₂</td>
<td>oxygen gas</td>
</tr>
<tr>
<td>Pd</td>
<td>palladium</td>
</tr>
<tr>
<td>Psig</td>
<td>pounds per square inch gage</td>
</tr>
<tr>
<td>rpm</td>
<td>rotations per minute</td>
</tr>
<tr>
<td>s</td>
<td>second</td>
</tr>
<tr>
<td>sccm</td>
<td>standard cubic centimeter per minute</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope/microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscope/microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analyzer/analysis</td>
</tr>
<tr>
<td>W</td>
<td>Watts</td>
</tr>
<tr>
<td>WO₃</td>
<td>tungsten oxide</td>
</tr>
<tr>
<td>WS₂</td>
<td>tungsten disulfide</td>
</tr>
<tr>
<td>WSL</td>
<td>Weapons Survivability Laboratory</td>
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<td>XRD</td>
<td>x-ray diffraction/diffRACTometer</td>
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ACKNOWLEDGMENTS

First and foremost, I would like to thank my advisor, Dr. Claudia Luhrs. Her constant and unwavering support was a true blessing. I would not have been able to accomplish much over the course of this project without her tireless support and patience.

I would also like to thank our research group including LCDR Chris Daskam, LT Russ Canty, LT Jason Downs, LT Sam Fromille, LT Nick Vilardi and LT Ashley Maxson. Their support and camaraderie was invaluable to me and truly helped me keep a positive attitude throughout. All those silly, fun, and bizarre conversations in Wa-242 will stay with me.

Dr. Garth Hobson and Dr. Sarath Menon also deserve thanks for taking significant time to help me learn the ins and outs of all of the characterization equipment and the use of the gas gun at the Turbopropulsion Lab. Also, sincere thanks to Mr. Chris Clay and Mr. John Gibson for taking significant time to help me operate the shock tube. Without their help, I would probably still be fumbling around trying to figure out that ancient oscilloscope. Both Stevie Rhyans and Dr. Hugo Zea deserve thanks for helping me run all those ultrasound tests and BET analysis experiments. I would also like to thank Ying-Bing Jiang of the University of New Mexico for providing the TEM images of our samples used in the document below. Additionally, I’d like to thank Mr. Lou Roncase and the range staff at the Weapons Survivability Laboratory at NAWC China Lake for their support and assistance during our testing with military rounds.

Lastly, I would like to thank my wife, Cynthia, for her sincere, unending and complete love and support. I put her through a lot during our time at NPS, and she deserves mountains of credit for putting up with me when school had me on my last nerve. Thank you, darling, for being there for me. Without you, I could never reach as far as I have been able.
I. INTRODUCTION

A. OVERVIEW

This manuscript summarizes some of our research group’s efforts to advance the understanding of how structural features at the nanoscale determine the mechanical properties and failure mechanisms of carbon nanofiber (CNF) and inorganic fullerene-type tungsten disulfide IF-WS$_2$ materials meant to be used in personal protection systems. In the past, our group has sought novel ways to synthesize in situ hybrid materials composed of CNF and IF-WS$_2$ nanoparticles with the aim to study their potential applications as personal protection systems. The ultimate goal of our endeavors is to use the lessons learned to develop more effective and lighter materials than the ones currently employed. This thesis seeks to induce CNF and IF-WS$_2$ failure using diverse pressure loading methods. The characterization of the failure modes of these structures will help us to understand them better and ultimately allow us to optimize their design against the failure modes identified.

B. PERSONAL PROTECTION SYSTEMS

Personal protections systems have existed since the advent of warfare. The invention of armor allowed soldier to deflect attacks and thus survive battle. Over the course of time offensive weapons became more and more powerful. As the penetrating power of these weapons became greater and greater, the need for improved armor arose. Leather armor gave way to chain mail, which yielded to metal plate armors. The increased stopping power of these more powerful armors also led to a massive increase in weight and subsequent decrease in mobility. Ultimately, the massive penetrating power of firearms led to the abandonment of personal protection systems since even the heaviest of plate armors could not stop bullets. This began to change in the mid-twentieth century with the discovery of aramid fibers such as Kevlar and Twaron and high performance polyethylene fibers such as Dyneema and Spectra. The most famous of these being Kevlar, first introduced by Dupont in the 1970s. Kevlar has both ballistic and stab-resistant properties [1].
Current ballistic armors consist of a combination of flexible ballistic fabrics and hard removable ceramic or metal plates. The ceramic plates afford higher protection against ballistic threats but add significant weight and provide less flexibility. Soldiers of today, much like their warrior ancestors, are forced to choose between a heavier more protective armor system or a lighter, more flexible system that is less capable of neutralizing incoming ballistic threats.

Though both materials provide ballistic protection to the wearer, they do so in two very different ways. Ceramic plates have extremely high strength and hardness and stop penetrators by relying on these characteristics. Ballistic fabrics, on the other hand, stop incoming threats by dissipating their kinetic energy. As a projectile impacts a ballistic fabric, a stress wave propagates along the fibers. As the wave propagates down the fiber, it transmits energy to the surrounding fibers, dissipating this energy. Additional energy is dissipated through friction between the fibers. This is illustrated in Figure 1.

![Figure 1](image)

Figure 1. Computer simulation of a projectile striking a ballistic fabric from the Army High Performance Computer Research Center. The fabric deforms on impact and ultimately fails when the stress waves reach the fixed ends from [2].

An additional concern on the modern battlefield is behind armor blunt trauma (BABT). Current armor systems do a serviceable job of stopping incoming ballistic threats although at a high flexibility and weight cost to the wearer. Stopping the penetrator, however, is not the only issue. Ballistic threats also have associated pressure
blast waves incident as well. Neutralization of the penetrator itself does not imply that the shockwave has dissipated as well. Thus, an armor system can prevent a penetrator from damaging the wearer, but severe, even fatal, injuries can still occur due to the blunt force trauma suffered [3–5].

C. USE OF NANOMATERIALS

As mentioned above, personal protection systems have evolved through time as an effort to stop penetrators and their effects, BABT included. Better understanding of the mechanisms that allow us to stop a penetrator and dissipate the energy of the impact has led to the development of diverse types of materials, being composites made with nanostructures one of the most significant examples. Nanomaterials, defined as materials with features in the nanometer scale (1 nm=10^{-9} \text{ m}), can be used as filler in personal protection composites (when mixed with polymeric matrices) or as single components of bulk objects. In order to reduce weight of the protective system while improving its performance, our team has proposed the use of a hybrid material composed of CNF and IF-WS\textsubscript{2}. The rationale of such combination of structures derives from their individual properties: carbon nanofibers should act as a resilient but flexible layer, while IF-WS\textsubscript{2}, although brittle, will provide the stiffness and strength. Literature in the field has already proven that IF-WS\textsubscript{2} could stand shockwaves in the order of 25 GPa [6, 7], however, prior to our work, no efforts have been made to combine these two nanostructures. Moreover, the failure modes of the individual structures are not well defined or understood.

1. Carbon Nanofibers and Nanotubes

CNF, and closely related carbon nanotubes (CNT) are nanostructured materials that have some of the highest strength to weight ratios known. CNT are structures composed of graphitic carbon sheets rolled up and connected, forming a tube structure. They range in size from a few nanometers to micron-sized materials depending on the conditions under which these materials are grown. Due to their exceptionally small size, it has been incredibly difficult to assess the mechanical properties of CNT. The Young’s modulus of multi-walled CNT has been experimentally measured at 1.8 TPa [8, 9]. Although individual tubes are typically only several microns in length, they are amenable
to being spun into yarn and woven into ballistic fabric. It has been calculated that a mere six layers of woven nanotube yarn could completely stop a nine mm bullet. A protection system of this type would be only 600 microns in thickness [10]. CNF, while still presenting diameters at the nanometer scale but lacking the empty space of the tubes and not as strong as CNT, have excellent mechanical properties, with a modulus on the order of 800 GPa [9]. While significant research has been done to determine the effects that CNF have when suspended in epoxy matrices [11-18], there is far less research on the mechanical properties of CNF alone. Much of the data to date founds its origin in computer simulations and models [15–17]. Similar to CNT, CNF are formed from stacked graphitic layers that make a solid fiber, as opposed to the rolled, hollow graphite sheets found in CNT. While they do have a lower modulus than CNT, CNF are easier to synthesize since lower temperatures are required for their growth. The size of CNF can be controlled using various operating conditions and precursor materials.

2. Tungsten Disulfide

The discovery of organic fullerene structures brought with it a great deal of interest in this material; for many years it researchers assumed that this structure was unique to carbon. Tenne et al proposed the existence of inorganic fullerene-type materials made of elements other than carbon [19-23]. Among those materials proposed was WS$_2$. In addition to spherical fullerene-type WS$_2$ structures (IF-WS$_2$), other polymorphs were found as well including two-dimensional plate-like structures and nanotubes [24]. The structure of an inorganic fullerene sphere can be likened to a hollow onion: numerous loosely bonded concentric layers form around a hollow core.

D. FAILURE MECHANISMS

When studying engineering materials, it is commonly recognized that their failure modes fall into one of three general failure mechanisms: fracture, fatigue, and creep. Failure, when related to a personal protection system, is regarded as an undesirable condition; it is therefore critical to understand how the underlying causes of these mechanisms in order to prevent their occurrence or to use that knowledge to design against it.
1. Fracture

Fracture occurs when a material separates into two or more pieces as a result of an imposed static stress (meaning it is not constant or only slowly changing with time) and at a temperature that is low relative to the melting point of the material. Fracture can be characterized as ductile or brittle. Ductile fracture is preceded by some plastic deformation where brittle fracture occurs with little or no plastic deformation. When ceramics and polymers fracture it is usually through brittle fracture. Cracks form at stress concentrators like notches and sharp flaws in the material. When an applied tensile stress at one of these stress concentrators exceeds the critical value, cracks form and propagate. When the crack propagates sufficiently through the material, the material fails [25]. Knowing the maximum stress that can be found at a crack tip and the stress needed for crack propagation, engineers can compute the maximum allowable flaw length or be aware of the maximum working stress to prevent this failure mode [26, 27] as seen in Equations 1 and 2 [28].

\[
\sigma_c = \frac{K_{Ic}}{\sqrt{\pi a}} \quad Eqn(1)
\]

\[
a_c = \frac{1}{\pi \left( \frac{K_{Ic}}{\sigma Y} \right)^2} \quad Eqn(2)
\]

Where \(\sigma_c\) is critical stress, \(K_{Ic}\) is the fracture toughness, \(Y\) is a dimensionless parameter dependent on crack and specimen geometry, \(a\) is the flaw size and \(a_c\) is the maximum allowable flaw size for a given stress level.

2. Fatigue

Fatigue failure occurs in materials that are subjected to cyclic loads over an extended period of time. This type of failure is associated with stresses that are considerably lower than the yield strength of the material under static load. Fatigue failure has three distinct steps: a) a crack is initiated at a high stress concentration point, b) the crack propagates incrementally with each subsequent cycle, and c) rapid failure the material when the crack has reached critical size. In polymers, fatigue behavior is quite sensitive to loading frequency, which is not the case in metals. When polymers are
cycled at high loads or frequencies this can cause localized heating, which can lead to material failure due to softening as opposed to typical fatigue processes [28].

3. Creep

Deformation can occur when a material exposed to a static stress at elevated temperatures. This is called creep. There are three stages of creep. The first is primary, or transient, creep where strain rate of the material decreases over time due to strain hardening. The second is called steady-state creep since the strain rate is constant over time. The third stage, called tertiary creep sees an acceleration of the strain rate and subsequent failure, often termed rupture. This is the creep failure mechanism for ceramics, though the elevated temperatures required are usually significantly higher than for metals. Creep in polymers is called viscoelastic creep. In polymers, creep can occur even at room temperature and at stresses below the material’s yield strength [28].

E. THESIS OUTLINE AND OBJECTIVES

As discussed in the overview above, the objective of this research was to determine the failure mechanisms of CNF and IF-WS₂ in an effort to design against these modes. Chapter II outlines the synthesis and preparation of the materials tested during this study. It also provides some detail on the characterization methods used to investigate the failure modes of these materials. These characterization methods include scanning electron microscopy, transmission electron microscopy, powder x-ray diffraction, BET surface area analysis, and energy dispersive x-ray spectroscopy. Chapter III discusses in detail the test methods chosen to induce failure in the materials, which include gas gun, ultrasound treatment, and impact with military rounds. Chapter IV is an in-depth discussion of the results seen from the testing methods used. An analysis of the failure modes discovered is included. Chapter V discusses the results of our re-designed CNF material into an ultralow density carbon foam that demonstrates viscoelastic properties, which are ideal in a material intended to absorb energy. Chapter VI summarizes our conclusions and presents our recommendations for continuing research efforts.
II. MATERIALS SYNTHESIS AND CHARACTERIZATION

A. OVERVIEW

This chapter discusses the methods used to synthesize the materials investigated for this project along with the various methods used to characterize those materials. For the synthesis of carbon nanofibers (CNF) nickel (Ni) was initially used as a catalyst because it is inexpensive, abundant, and very well documented as a CNF precursor [29]. The use of Ni as a catalyst led to the production of CNF that macroscopically looked like black millimeter-scale conglomerates. Later in our study we shifted to the use of palladium (Pd) to grow CNF because a parallel research effort performed in our research group showed that the use of Pd as a CNF precursor promotes the production of novel interwoven foam-like structures of CNF, which maintain their integrity during cycling compression tests. Such ultralow density foam-like structures showed the ability to recover their shape after the application of small loads (several hundred Newtons) along with viscoelastic behavior, an ideal characteristic for shock dissipation. Inorganic fullerene-type tungsten disulfide (IF-WS$_2$) used for the tests described in Chapter III was purchased commercially and prepared as necessary for experimentation as discussed below.

In order to characterize individual CNF or IF-WS2 materials or their composites before and after testing them, several methods were employed. These methods included scanning electron microscopy, energy dispersive spectroscopy, transmission electron microscopy, x-ray diffraction, and surface area analysis via Brunauer-Emmett-Teller gas adsorption. The mechanical properties were studied using an Instron single column testing frame, model 5942.

B. MATERIALS SYNTHESIS

1. Nickel-based Carbon Nanofibers

CNF were grown using Sigma-Aldrich nickel nanopowder <100 nm 99.9 percent as a catalyst. For each growth experiment approximately 100 mg of nanoparticles were
weighed and placed in a ceramic crucible. The ceramic crucible was then inserted into a quartz tube and placed in a Lindberg Blue M 80 kW tubular furnace as shown in Figure 2.

Figure 2. Lindberg Blue M 80kW tubular furnace used for CNF synthesis.

The quartz tube was positioned in such a way so as to ensure that the center of the ceramic crucible containing the nanopowder was placed directly over the furnace’s thermocouple. Each end of the quartz tube was sealed using an ultratorr connection. The inlet was connected to the gas lines controlled by a mass flow system and the exhaust side directed to a fume hood. Nitrogen gas flow was initiated for 20 minutes at 300 sccm to displace the air atmosphere in the tube. ‘tAfter completing the nitrogen purge, the furnace was set to a temperature of 350 ºC. Once at the appropriate temperature, a flow of two percent argon/98 percent hydrogen at 20 sccm was added to the nitrogen flow to scavenge any remaining oxygen in the tube’s atmosphere. This step also reduced any possible traces of nickel oxide that the nickel particles might contain on their surface, to
elemental nickel. The Ar/H$_2$ purge was maintained for 30 minutes. Upon completion of
the reducing step, Ar/H$_2$ was stopped and nitrogen gas flow reduced to 30 sccm. Growth
was initiated by starting the flow of ethylene (used as the fuel—source of carbon—for the
fiber growth) at 15 sccm and oxygen at 5 sccm. The oxygen flow was incremented by
five sccm up to a final flow of 20 sccm over a period of 15 min. The gases used were
Praxair Ultra-high Purity. The flow rate of all gases was controlled by MKS Alta Digital
Mass Flow Controllers and an MKS 647c Multi-gas Controller shown in Figure 3.

![MKS 647c Multi-gas Controller and Alta digital mass flow controllers used for precision control of gas flow rates.]

After the growth initiation step, the furnace temperature was increased to 550 °C
and growth continued for 90 minutes. It should be noted that the growth phase length
could be changed as necessary to obtain the desired yield from the experiment. Typical
growth phase duration range was between 60 and 90 minutes. After completion of the
growth step, the flows of oxygen and ethylene were stopped and the furnace was turned
off. Nitrogen flow was maintained during the growth step and left until the sample had
cooled sufficiently to be handled. Small fans were turned on to assist in cooling the tube.
When the tube was cool it was disconnected and the resulting CNF were collected and
stored for use.
2. Palladium-based Carbon Nanofibers

CNF were also grown using palladium nanoparticles (Sigma-Aldrich <1 µm 99.9 percent) as a catalyst. For each experiment 20 mg of nanopowder was weighed out and placed in a metal boat made of 304 stainless steel depicted in Figure 4.

![Metal boat manufactured from 304 Stainless Steel used for synthesis of CNF from Palladium. The assembly was fabricated at NPS from [30].](image)

The nanopowder was arranged in the boat in several straight lines running along its length. The top of the boat was then screwed on rendering it airtight. The boat was inserted inside a quartz tube and placed in a Linderg Blue M 80 kW tubular furnace. The tube was positioned to ensure that the middle of the boat was directly atop the furnace’s thermocouple. The metal tubes were then attached to the mass flow controllers and exhaust hose lines. Nitrogen flow was initiated at 100 sccm to purge the atmosphere inside the boat. The furnace was then set to 550 °C and the purge continued while the system heated up to the temperature setpoint. Growth was initiated by starting the flow of ethylene at 15 sccm and oxygen at five sccm. The oxygen flow was incremented by five sccm to a final flow of 20 sccm over a period of 10 min. After increasing the oxygen flow to the final rate, growth continued for the desired amount of time, which was generally between two and three hours. After completion of the growth step, ethylene and oxygen flows were stopped and the furnace was turned off while nitrogen flow...
remained active and the boat allowed to cool to room temperature with the assistance of small fans aimed at the quartz tube. When the tube was sufficiently cool the boat was disconnected from the flow controllers and exhaust. The metal sample boat was then opened and the CNF were collected and stored for use.

3. Tungsten Disulfide Preparation

Commercially-manufactured inorganic fullerene-type tungsten disulfide (IF-WS$_2$) was obtained in the form of commercial lubricant Nanolub (ApNano Materials Inc, Israel), for use in experimentation. During characterization of a sample using the scanning electron microscope (SEM) the presence of an unknown foreign substance was detected on the surface of the particles. It was not known whether this material would have any substantive effects on our research so a method of cleaning the IF-WS$_2$ was formulated in order to prevent any effects this substance might have.

Assuming an organic nature of the substance, an attempt to remove it was initially undertaken through heat treatment in a Netzsch STA449 F3 thermogravimetric analyzer/differential scanning calorimeter (TGA/DSC). Sample preparation for analysis consisted of weighing a small amount of IF-WS$_2$ and placing it in a ceramic crucible and on top of the microbalance located in the TGA instrument. The sample was heated from 30 °C to 900 °C at a rate of 5 °C/min under inert atmosphere. After cooling, the sample was recovered and analyzed in a Philips 1830 analytical X-Ray diffractometer (XRD) to check if the crystalline or chemical structure of the tungsten disulfide had been affected by the heat treatment. An analysis between 2θ values of 5–70 degrees showed the presence of tungsten oxide (WO$_3$) in the heat-treated IF-WS$_2$ sample. Based on the undesired oxidation of the material being investigated for this project the heat-treatment method of potential cleaning was abandoned.

The alternative cleaning procedure involved the use of ethanol to dissolve the unidentified material. IF-WS$_2$ particles were placed in a beaker. The amount to be cleaned was dependent on how much material was needed for experimentation. A few ml of ethanol were then added to the beaker. The mixture was then placed on a stirring plate with a magnetic bar and the mixture was stirred for one hour in order to dissolve the
substance on the IF-WS$_2$. The mixture was then separated into an even number of centrifuge vials and placed in a centrifuge. The type of centrifuge used was an Eppendorf Model 5418 shown in Figure 5. The centrifuge was run at 4000 rpm for three minutes.

![Eppendorf Centrifuge Model 5418](image)

Figure 5. Eppendorf Centrifuge Model 5418 used during procedures to clean tungsten disulfide.

After completion the precipitated IF-WS$_2$ was removed from the vials and separated from the supernatant, placed in a small sample bottle, and placed into a desiccator under vacuum overnight. After confirming the removal of the substance by observing the microstructure of the sample produced by SEM, and determining that the sulfide preserved its characteristics without oxidizing, the resulting dry IF-WS$_2$ was used for experimentation.
C. CHARACTERIZATION METHODS

The materials being investigated needed to be characterized through different methods, first to determine their microstructural characteristics as prepared, and second to determine the effects that insulting the samples using gas gun tests, ultrasonic wave treatment, and military rounds had on the IF-WS$_2$ and CNF microstructures. The characterization methods employed included scanning electron microscopy, energy dispersive spectroscopy, transmission electron microscopy, x-ray diffraction, and surface area analysis.

1. Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a characterization method that uses a beam of electrons to obtain a high-resolution micrograph of an object. The microscope forms an electron beam that is accelerated toward the sample by the application of a positive electric potential. Apertures and magnetic lenses are then used to focus the beam. When the beam hits the sample, some electrons are backscattered and secondary electrons are ejected. Detectors collect the electrons and convert them into the micrographs displayed on the screen. Secondary electrons are electrons ejected from the atoms near the surface of the sample due to the interaction of the incident electron beam with the sample. These secondary electrons are of a lower energy state than backscattered electrons (which are produced by elastic collisions with sample nuclei) and contain valuable information about the topography of the sample’s surface. SEM is advantageous to study particulates of a specific size and shape, since it produces extremely high-resolution images when compared to optical microscopy techniques. Thus, it can effectively display images of objects that are on the nanoscale such as the materials being investigated for this project [31].

A Zeiss Neon 40 High Resolution SEM, shown in Figure 6, was used to collect micrographs of each material tested. The samples were prepared by placing a small amount of the sample onto a clean surface and then placing double-sided carbon tape on an aluminum specimen stub and pressing the stub lightly onto test material. Compressed air was then blown on the sample to remove any excess material from the specimen stub.
Any samples prepared were then placed under vacuum overnight in preparation for use in the SEM the following day. A potential of 10 or 20 kV was used for these samples. Particle size distributions were determined using Image J software [32]. Findings from this characterization method are discussed in detail in the Results section.

![Zeiss Neon 40 High Resolution scanning electron microscope used for characterization of CNF and IF- WS₂.](image)

### 2. Transmission Electron Microscopy

Transmission electron microscopy (TEM) is similar to SEM regarding the use of a high energy electron beam to obtain images of samples with very high resolution. Unlike the SEM, which uses the secondary electrons to produce an image, the TEM uses electrons that pass through the sample to obtain images of the internal structure of the samples. As such, very thin samples (on the order of several hundred Angstroms) are required in order to have enough electrons pass through to successfully make an image of the material. TEM also uses higher energy electron beams than SEM [31]. TEM was used to analyze IF-WS₂ samples after treatment with the gas gun, ultrasound, and military
rounds as well as an untreated sample. TEM characterization was performed on a JEOL 2010 high-resolution transmission electron microscope (HRTEM) equipped with an energy dispersive spectroscopy (EDS) analysis detector.

3. **X-Ray Powder Diffraction**

X-ray powder diffraction (XRD) is a technique that determines the crystalline structure of material. It is also commonly used to determine the composition of a material, however this is not inherent to the process and only accomplished by comparing the crystallographic data obtained from a given sample to an existing database of spectra from known crystalline material compositions. The general process consists of directing a beam of electrons to collide on a metal source inside an x-ray tube. In the tube, electrons in the target material are knocked from the inner shells. As these electrons de-excite to their base state, x-rays are produced. The x-rays generated are then filtered to subtract the undesired portion of the spectra and produce a monochromatic beam, which is then directed toward the sample. These x-rays are diffracted by the sample at specific angles based on the crystallographic orientation and according to the Bragg law, which describes the condition needed for constructive interaction of the diffracted waves, and a diffraction pattern to appear. A detector counts the number of x-rays received at each incidence angle (2θ). The diffraction peaks and the angle at which they occurred are then used to determine the orientation of the crystallographic planes in the material, which can then identify the type of crystal lattice present and its dimensions along with the composition of the sample (assuming a database of known compositions is available) [31].

The XRD used for this project was a Philips 1830 analytical x-ray, shown in Figure 7. The tube contained a copper source whose x-rays had a primary wavelength (called the K-alpha) of 1.5418 Å. The 2θ angle range was set from 5–70 degrees. The step size for each measurement was 0.020 degrees with a dwell time at each step of one second. Each sample was placed in a low background silicon sample holder. This sample holder was manufactured in such a way so as to have no crystallographic planes
in the standard operating range of the XRD and thus provides no influence on the data output. The electrical current and voltage were set at 30 mA and 35 kV respectively.

![Philips1830 analytical x-ray](image)

Figure 7. Philips1830 analytical x-ray

4. Surface Area Analysis

Surface area measurements were performed in order to compare the values of surface area of untreated samples with those of samples treated by ultrasonic waves. The instrument used for surface area analysis was a Quantachrome NOVA 4200e surface area and pore analyzer (Figure 8) that uses the BET gas adsorption principle. BET stands for Brunauer-Emmett-Teller who were the researchers who pioneered this technique. The process utilizes the adsorption of gases onto the surface of a material to determine its surface area, assuming that a monolayer of the adsorbates forms on the surface of said material. In this instance, Nitrogen was used as the gas adsorbate. The key equation used in this technique is as follows in Equation 3 [33]:

$$\frac{1}{W \left( \frac{P_0}{P} - 1 \right)} = \frac{1}{W_mC} + \frac{C - 1}{W_mC} \frac{P}{P_0} \quad Eqn(3)$$
Where $W$ is the weight of the gas adsorbed at relative pressure $P/P_0$, $W_m$ is the weight of adsorbate constituting a monolayer of surface coverage, and $C$ is the BET constant.

The material to be tested was weighted, the test cell was weighted, and then both the cell and material were weighted together. The test cell with sample was then placed in the left-hand side of the instrument and secured tightly. The sample was allowed to degas under vacuum for 10 minutes at room temperature, followed by 30 minutes at 100 °C and then two and half hours at 300 °C. Nitrogen was then selected to backfill the sample. To conduct the BET analysis, the sample was cooled using liquid nitrogen and nitrogen gas was dosed to the cell containing the sample. Partial pressures at diverse temperatures are taken and absorption/desorption isothermal graphs generated.

![Quantachrome NOVA 4200e BET surface area analyzer.](image)

Figure 8. Quantachrome NOVA 4200e BET surface area analyzer.

5. Energy Dispersive X-Ray Spectroscopy

Energy dispersive x-ray spectroscopy (EDS) is a characterization method that utilizes a high energy beam of electrons to produce characteristic x-rays to determine the nature of a sample. To stimulate the emission of characteristic x-rays from a specimen, a
high-energy beam of electrons is focused into the solid material under study. The incident beam excites an electron in an inner shell, knocking it out of the shell while creating an electron hole where the electron was. A second electron in the atom, from a higher energy shell, fills the hole while an x-ray is produced to compensate for the energy difference between the higher-energy shell and the new lower-energy shell. A detector counts the number of x-rays emitted from the sample and their energy level. By compiling the spectrum of how many x-rays are detected at each energy level, the composition of the sample in question can be determined. There are some limitations in method in that the characteristic energy levels of x-rays from some materials can overlap each other leading to potential ambiguity, yet this is still an effective method at determining a material’s makeup [34]. For this project, EDS was used on the samples insulted by the testing methods along with an untreated sample to determine whether the samples had oxidized under shock pressures. The EDS detector was used in conjunction with the SEM and TEM described above.
III. TESTING METHODS

This chapter discusses the different testing methods used on the materials described in Chapter II. The rationale behind these tests was to produce the materials failure and study the microstructural characteristics of the materials post mortem, with the intention of determining which mechanisms were responsible for the material breakdown to be able to design against it. The methods included gas gun testing, ultrasound treatment, and insult with military rounds. The procedures used for each method, including operational principles, sample preparation, and procedural methods are described in detail below.

A. GAS GUN PROCEDURES

A gas gun, or shock tube, apparatus located at the Naval Postgraduate School’s (NPS) Turbopropulsion Laboratory was used for testing the effects of pressure loads on the test materials. The system uses a pressurized driver section and evacuated driven section separated by a pair of diaphragms to create a supersonic wave that propagates along the tube and impinges on a test holder at the end of the device. Pressure transducers located along the tube allow for monitoring of the shock and measuring its strength (pressure sensors 1, 2 and 3 in Figure 9). The apparatus at NPS was built by a previous NPS student. Figure 9 illustrates the specific setup of the gas gun and detailed theory can be found in [35].
1. Sample Preparation

The materials investigated for this project were dispersed as backing of Kevlar sheets for use in shock tube experimentation. This was done in order to contain the materials as they were synthesized or obtained in powder form and thus would not conform to the test holder in the gas gun apparatus. Additionally, without such containment, the shock wave incident on the test material would have most likely spread the powder inside of the tube.

To prepare a gas gun sample, JPS Composite Materials Kevlar fabric pieces (two each per shock test) were cut to 1.75 inches square. Next, 100 mg of the test material were placed in a beaker. Approximately 3–5 ml of solvent was added to the beaker, which was then placed in a Branson ultrasonic model 2510R-MTH sonicator, as shown in Figure 10, for one minute.
Figure 10. Branson Ultrasonic Model 2510R-MTH sonicator for use in sample mixing and preparation.

One Kevlar piece was placed on a flat surface with four glass slides arranged on top to provide a one inch square hole. The test material-solvent mixture was then poured slowly, as a paste, onto the Kevlar fabric into the one inch hole. The Kevlar fabric was then allowed to dry overnight, sufficient time for the solvent to evaporate. When loading the sample into the gas gun test holder, a bare piece of Kevlar was placed over the fabric that had the test material on it in order to prevent spreading of the sample into the tube when the shock wave impinged upon it.

Samples utilizing palladium-grown CNF were prepared in a different manner. When Pd-based CNF were grown in the metal boat designed for that procedure, the fibers grew together to form a cohesive foam-like substance as opposed to the agglomerate and powder-like CNF formed from nickel. As such, there was no need for Kevlar fabric pieces to contain the fibers as they were essentially one unit. A piece of Pd-grown CNF was cut to approximately 0.75” square. A piece of thin clear cellulose acetate was then cut to about 1.75” square. The clear plastic is an analog to the top piece of Kevlar in preparation of powder-like samples; the plastic holds the Pd-grown CNF test sample onto the vertical gas gun sample holder.
2. **Heat Treatment of Copper Diaphragms**

Copper diaphragms (shown in Figure 11) were part of the gas gun inner components, as such, were meant to fail under pressure and free the compressed gas, creating the shock wave that will interact with the sample material. Copper diaphragms were prepared by an annealing process: once machined to the needed shape and size, the copper sheets were placed in a Lindberg Blue M 4.88 kW 12,000 ºC furnace. The diaphragms were placed flat with the scoring up. Ceramic separators were used to ensure that diaphragms do not touch each other. Up to four diaphragms fit in each furnace. The furnace was set to 600 ºC and turned on for four hours. The furnace was then turned off and the annealed diaphragms were allowed to cool in the furnace for 24 hours.

![Figure 11. Diaphragms used in the shock tube. The diaphragm on the left has not received the heat treatment. The diaphragm on the right has been heat treated.](image)

3. **Gas Gun Operation**

The material to be tested was attached to the holder and bolted onto the end section and the pressure transducer cable is connected. An image of the test holder with a sample loaded inside it can be found in Figure 12.
Figure 12. Sample test holder unit for shock tube. A Kevlar sample is loaded into the holder. The metal piece securing the sample to the holder was manufactured at NPS.

An oscilloscope was used for data collection. The shock tube was then loaded with two heat-treated copper diaphragms 0.025 inches thick scored to a depth of 0.013 inches. The four rubber O-rings were then inspected for excess dirt and grease that are removed if necessary. O-rings were then placed back in their respective grooves. The sections were then sealed with four bolts to assure the apparatus is airtight. Vacuum was then drawn to an absolute pressure of approximately 2 mm Hg in the driven section through the use of a roughing pump. When this was complete, carbon dioxide was added in a controlled manner until atmosphere in the driven section is at 25 mm Hg. The vacuum gauge was isolated and then disconnected to prevent damage to it during creation of the pressure event. The driver section was then loaded with either Nitrogen or Helium (depending on the desired Mach number) to 720 psig. When the pressure gauge reached 350 psig, the mid-section was isolated. The shock tube was then fired by opening the firing valve. As pressurized gas entered the diaphragm section the pressure differential
across the second diaphragm causes it to burst creating a supersonic wave through the 
driven section. The subsequent drop in pressure in the diaphragm section caused the first 
diaphragm to burst and the formation of a second, faster wave. The second wave 
overtook the first and the two coalesced into a single supersonic wave that traveled along 
the driven section and to the sample holder [35]. A more detailed description of the 
procedure can be found in Appendix C.

B. ULTRASOUND TREATMENT PROCEDURES

Analogous to subjecting the samples to a gas gun insult, samples were treated as 
dry powders or in solvents in an ultrasonic horn. The ultrasonic tester used for this 
procedure was a Sonomechanics 1200 W ultrasonic liquid processor shown in Figure 13. 
The equipment consists of a generator that provides electric signal input to the 
piezoelectric transducer, a water-cooled barbell horn and a protective enclosure. The 
generator produces a constant frequency of 20 kHz, but the amplitude of said frequency 
can be varied. The transducer functions by taking electric energy from the generator and 
converting it to mechanical energy in the form of high frequency ultrasonic vibrations. 
This energy conversion is completed by the piezoelectric transducer [36].

Figure 13. Sonomechanics 1200 W ultrasonic liquid processor.
The ultrasonic horn was used to test both CNF and WS$_2$ in dry and wet environments. Samples were taken from CNF samples synthesized in the laboratory or from batches of IF-WS$_2$ cleaned in the manner described in Section II.A.3. Hybrid CNF/WS$_2$ were also tested. The procedure began when a sample was then placed in a beaker. If a liquid sample was used, the bell horn was verified to be covered in liquid by no more than 65 mm. If a dry sample was used, the beaker opening was covered with Parafilm to ensure the powder did not leave the beaker upon initiation of the ultrasonic frequency signal. Sample setup in both environments is illustrated in Figure 14.

Figure 14. Ultrasound test setup with sample in liquid (left) and sample in dry atmosphere (right).
The door to the enclosure was then shut and ice was placed in the water bath to cool the ultrasonic transducer during operation. Prior to starting the instrument, all connections in the instrument were verified to be in place including power, grounding wire, remote controller, ultrasound output to transducer, water input and submersible pump power. Additionally, ear protection was donned prior to turning on the instrument. The water pump was then turned on by connecting its power plug to the wall outlet. The generator was then powered on. The “Test” key was then pressed and held and the screen verified to display proper conditions. After the system test was complete, any needed adjustments were made for the upcoming experiment. The actual material testing was started by adjusting the amplitude to be used and pressing the remote start button. After the desired run time passed, the experiment was stopped by pressing the button on the remote or pressing the “Offline” key on the generator. The various testing conditions are summarized in Table 1. CNF and IF-WS₂ were also mixed in a proportion of approximately 8:1 by weight.

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>State</th>
<th>Amplitude (%)</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Solid</td>
<td>20</td>
<td>WS₂</td>
</tr>
<tr>
<td>1</td>
<td>Liquid</td>
<td>100</td>
<td>CNF</td>
</tr>
<tr>
<td>2</td>
<td>Solid</td>
<td>60</td>
<td>WS₂</td>
</tr>
<tr>
<td>2</td>
<td>Solid</td>
<td>20</td>
<td>CNF</td>
</tr>
<tr>
<td>2</td>
<td>Solid</td>
<td>100</td>
<td>Mix</td>
</tr>
<tr>
<td>2</td>
<td>Liquid</td>
<td>60</td>
<td>WS₂</td>
</tr>
<tr>
<td>2</td>
<td>Liquid</td>
<td>20</td>
<td>CNF</td>
</tr>
<tr>
<td>3</td>
<td>Solid</td>
<td>100</td>
<td>WS₂</td>
</tr>
<tr>
<td>3</td>
<td>Solid</td>
<td>60</td>
<td>CNF</td>
</tr>
<tr>
<td>3</td>
<td>Solid</td>
<td>20</td>
<td>Mix</td>
</tr>
<tr>
<td>3</td>
<td>Liquid</td>
<td>20</td>
<td>WS₂</td>
</tr>
<tr>
<td>3</td>
<td>Liquid</td>
<td>100</td>
<td>CNF</td>
</tr>
</tbody>
</table>

Table 1. Summary of ultrasound treatment conditions.

C. MILITARY ROUNDS TESTING PROCEDURES

Testing of samples using military rounds was conducted at the U.S. Navy’s Weapons Survivability Laboratory (WSL) located at Naval Air Weapons Center (NAWC) China Lake. This testing was conducted to determine the effects that projectiles have on the materials tested.
1. Sample Preparation

Twelve samples were prepared for testing with military rounds. Each test sample consisted of 10 layers of JPS Composite Materials Kevlar fabric inserted into a nylon pouch to contain the fabric layers. The Kevlar was cut into 7.75” square pieces in order for 10 layers to fit into the 8” square nylon pouch. A number of the Kevlar layers in each sample were treated with CNF, WS₂ or some combination thereof. Table 2 summarizes the configuration of the 12 samples tested.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>No. of Treated Layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfidized CNF in epoxy</td>
<td>1</td>
</tr>
<tr>
<td>CNF with low-load WS₂ in epoxy</td>
<td>1</td>
</tr>
<tr>
<td>CNF with mid-load WS₂ in epoxy</td>
<td>1</td>
</tr>
<tr>
<td>Half-layer WS₂ with half-layer CNF in epoxy</td>
<td>1</td>
</tr>
<tr>
<td>Epoxy with no test material loaded</td>
<td>1</td>
</tr>
<tr>
<td>CNF in epoxy</td>
<td>1</td>
</tr>
<tr>
<td>CNF in epoxy</td>
<td>3</td>
</tr>
<tr>
<td>WS₂</td>
<td>1</td>
</tr>
<tr>
<td>WS₂ in epoxy</td>
<td>1</td>
</tr>
<tr>
<td>CNF</td>
<td>1</td>
</tr>
<tr>
<td>CNF</td>
<td>3</td>
</tr>
<tr>
<td>Kevlar only</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2. Military rounds testing geometries

We used two basic preparation procedures for the materials to be tested: suspending the test material in an epoxy matrix and laying the test material directly onto Kevlar fabric sheets.

The process of preparing the samples placed directly on the Kevlar fabric was similar to the process for preparing samples for the shock tube. Approximately 0.5 g of sample was weighed and placed in a beaker. 15–20 ml of ethanol was added to the beaker. The beaker was then placed in a Branson ultrasonic model 2510R-MTH sonicator and the sample sonicated for one minute in order to disperse the particles into the solvent to form a paste. The Kevlar piece to be treated was placed on a large glass slide and taped down to prevent movement of the piece. The fabric was taped in such a way as to leave a 6” square area for the test material to be placed on the fabric. The 6”
square area was a requirement of the facility conducting the testing with military rounds. The paste material mixture was then slowly poured onto the surface of the fabric. A spreading knife was then passed over the sample to ensure as even a distribution of test material over the fabric as possible. The sample was then allowed to dry overnight. When the sample was dry, the treated layer along with the appropriate amount of untreated layers was placed in a nylon pouch. The sample was then ready for testing.

For the samples dispersed in epoxy matrix, Strues SpeciFix-20 consisting of a resin and curing agent were used. The epoxy was loaded with one percent weight of the material to be tested. The test material was weighted. For these samples, approximately 0.5 g was used for each Kevlar layer to be treated. The amount of total epoxy (resin plus curing agent) was found by multiplying the amount of test material by 100 and then multiplying by the ratio 31/35.75. The total amount of epoxy was divided by 6.1 to find the appropriate amount of curing agent to be used. This number was multiplied by 5.1 to obtain the correct amount of resin to be used. Put another way, the ratio of resin to curing agent is 5.1:1. A clean beaker was used for mixing the materials (cleaning was verified by wiping the inside with a paper towel or kimwipe to ensure removal of any dust or foreign material that may have collected in the beaker while stored). The resin was measured out using the syringe found in SpeciFix-20 kit. The test material was added to the resin and hand stirred using a small wooden rod for two minutes. The mixture was then placed in a Branson ultrasonic model 2510R-MTH sonicator for three minutes. The appropriate amount of curing agent was then measured using a micropipette and added to the mixture in the beaker. The whole mixture was then hand-stirred with the wooden rod for two minutes and then placed in the sonicator for three minutes. The complete epoxy mixture was then allowed to partially cure for approximately 30 minutes. The Kevlar fabric to be treated was taped onto a large glass slide with a six inch square area in the middle for the epoxy. The epoxy was then poured onto the Kevlar. A spreading knife was passed over the treated fabric to ensure an even distribution of epoxy over the fabric. The spreading knife was then dismantled and cleaned thoroughly to prevent any epoxy
from curing on the knife and rendering it unusable. The treated Kevlar fabric layer was then allowed to cure overnight. An illustration of fabric treatment with Kevlar can be found in Figure 15.

![Kevlar fabric with epoxy layer spread on it (center), Beaker used to mix epoxy resin (left), Spreading knife used to evenly spread epoxy onto Kevlar fabric (right).](image)

Figure 15. Kevlar fabric with epoxy layer spread on it (center), Beaker used to mix epoxy resin (left), Spreading knife used to evenly spread epoxy onto Kevlar fabric (right).

2. **Military Rounds Testing Operation**

The test range used for this experimentation at NAWC WSL is located in an underground bunker in order to more readily control the environment and protect the equipment. The rounds used were 7.62 mm NATO ball rounds, which is a standard round used for testing, an example of which is depicted in Figure 16.
A single round was fired at each of the samples. The testing equipment used consisted of following items: a specialized test rig used to fire the rounds at the test materials; clay heated to approximately 38 °C to simulate the temperature of a human body; a high-speed camera to record the interaction of the military round with the sample; impact sensors to determine at what time the round reached specific distances in front of and behind the sample (used to determine initial round velocity and residual velocity after impact); humidity, temperature, and pressure sensors to read the environmental conditions. This experimental setup is shown in Figure 17.
Figure 17. Military rounds test setup showing clay backing and nylon pouch holding Kevlar sheets.

The actual tests were carried out by range personnel employed at WSL. The clay backing was mounted in a support frame and the test material was taped to the front of the clay. Range personnel conducted appropriate equipment and safety checks and cleared the range. Environmental conditions (temperature, pressure, humidity) were recorded. A designated range worker loaded the test round and prepared the test rig for firing. The range was then cleared once again and the range safety officer gave the order to fire. The average weight of the rounds was 123.79 g and the average weight of the powder in each round was 26.05 g. Upon firing, high speed video captured the impact of the round on the test material and range staff recorded data provided by the equipment. The sample was then retrieved and replaced with the next test sample for the following test.
IV. RESULTS AND DISCUSSION

A. OVERVIEW

This chapter summarizes the results of our experimental efforts and discusses the failure mechanisms identified for nanostructured CNF and IF-WS₂ particulates. We start the Chapter by describing the microstructural features that CNF and IF-WS₂ present as prepared, to then compare those with the characteristics observed in postmortem analysis of the samples when insulted by diverse methods. As described in previous chapters, shock waves produced by a gas gun, ultrasonic treatment in dry and wet environments and impact with military rounds were the chosen approaches to induce the materials’ failure. This section of the manuscript also attempts to correlate the observed postmortem sample characteristics with known failure mechanisms observed in other materials or with recent published work for similar carbon fibers and WS₂ structures. Moreover, the findings regarding the failure modes identified herein were used to re-design the CNF material and test it using the gas gun. The new carbon fiber architecture could be described as carbon foam that presents viscoelastic properties under compression cycles. The optimization of the carbon nanostructure that gave origin to the foam not only rendered an ultralow density material, but also a sample that did not fail under the gas gun experimental conditions employed.

B. SYNTHESIS AND CHARACTERIZATION OF CARBON NANOFIBERS AND IF-WS₂ AS PREPARED

1. Carbon Nanofiber (CNF) Generation from Nickel Precursor

Carbon nanotube and nanofiber growth requires the use of a carbon source, a catalyst and elevated temperatures. Metal nanoparticles, including iron, nickel, palladium, manganese, cobalt, molybdenum, vanadium, copper and their mixtures, are commonly used as catalysts [37, 38]. One of the most commonly used approaches to achieve the carbon nanofiber structure is to employ chemical vapor deposition (CVD). The CVD technique can be described as the creation of a solid product on a surface as the result of vapor-phase chemical reactions in a high temperature gas in close proximity to the
surface. CVD methods and their derivatives are very attractive to generate carbon nanotubes and nanofibers because they can be easily scaled up and produce high quality structures with fewer or no carbonaceous impurities when compared to other methods [39, 40]. For this research, we used a method reported before in the literature [29], a variation of thermal CVD, employing nickel as the catalyst. As explained in the experimental methods chapter, the technique uses a flow reactor and a furnace for the thermal decomposition of the carbon source compound, ethylene. The selection of nickel as catalyst was done for several reasons, including the fact that nickel is prevalent and inexpensive and the process for growing CNF from nickel catalyst is well documented. Other nanoparticles, such as iron, tend to be extremely reactive in the size regime we wanted to investigate and thus extreme care would be required when handling these particles, leading us away from using such particles as a catalyst.

The commercial nickel catalyst used for this procedure is designated as <100 nm particle size (99.9 percent), which should lead, on average, to CNF of diameter in the 100 nm range and less, and image of which can be found in Figure 18. When growing carbon nanostructures by thermal CVD on a catalyst, the CNF diameters are often found to be dependent on the particle size [41], providing reason to explore the size distributions of same.

The nickel nanoparticle distributions were determined by the use of SEM. It was found that the vast majority of the particles were in fact on the order of 100 nm, although a few micron size particles were also encountered [42]. Image J software was used to determine the statistical distribution of the particle sizes, shown in Figure 19. It has been found that catalyst particles smaller than approximately 20 nm render nanotubes (hollow interior), while larger particle sizes produce fiber structures (solid interior).
Figure 18. SEM micrograph of nickel nanoparticles taken at 25k magnification. Note the large number of small nanoscale particle and the existence of a micron size particle from [42].

Figure 19. Size distribution of nickel nanoparticles showed a bimodal distribution: the majority of the particles have an average 60–90 nm size range. A small number of particles present sizes larger than 240 nm.

CNF yields were fairly consistent across growth runs, but were heavily dependent on the length of the growth phase in the procedure. The length of this step varied from 60–90 minutes, with 90 minutes being used most often to maximize the yield for a given
growth run. Starting with approximately 100 mg of catalyst yields between 1.5–2 g of CNF for a 90-minute growth step. The macroscopic aspect of the product is presented in Figure 20.

Figure 20. CNF grown from nickel nanoparticle catalyst. On the macroscale, the material is quite brittle and forms a powdery substance.

SEM was used to characterize the particles and verify that, on the nanoscale, the results of the growth process were in fact fibers. These micrographs (Figures 21, 22, and 23) are important in comparing the fibers before and after testing to determine the effects of each testing method.

Figure 21. SEM micrograph of CNF grown from nickel catalyst.

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The majority of the product was recognized as carbon fibers of diverse diameters. The nanofibers tend to grow in small clumps with an appreciable amount of interweaving and clustering together. It also appears that in addition to fibers there are also some other structures that are not fiber-like in nature, but globular or even amorphous, as seen in Figure 23. The globular and amorphous structures are most likely areas where carbon deposition began around the catalyst but did not continue in a fiber-like manner. That there is some variation in the architecture of the nanomaterials present is not surprising, however the key result is that in fact the greater part of the metal catalyst particles form CNF. In addition to characterizing the synthesized materials with SEM, Image J software was also used to determine the size distribution of the fibers present. 100 randomly chosen fibers were selected from the micrographs and their diameters
determined with the software. As seen in the size distribution (Figure 24) of the catalyst nanoparticles, the majority (60 percent) of the fibers lie in the 30–120 nm diameter range.

![Ni-CNF Size Distribution (as prepared)](image)

Figure 24. Size distribution of untreated CNF grown with Nickel catalyst. There is a bimodal distribution with the primary mode centered around the 60–90 nm size range and the second mode roughly around the 240–270 nm range.

The CNF grown from nickel appear to have a distribution similar to that of the nickel nanoparticles. The distribution of the fibers does skew higher with more outliers in the higher diameter ranges. This is due to the fact that when the fibers grow, nickel nanoparticles in close proximity sinter, generating larger nickel agglomerates that later on in the process promote the existence of a larger diameter fiber.

2. **Inorganic Fullerene Tungsten Disulfide (IF-WS₂)**

WS₂ compounds belong to Group VI family of transition metal dichalcogenides. Tungsten disulfide exists in different polymorphs, the most commonly occurring being a plate-like crystal structure. It also exists, however, as nanotubes and as fullerene-like arrangements, all shown in Figure 25. From the latter structure, similar to a carbon fullerene but consisting only from tungsten and sulfur atoms, is where the name inorganic fullerene comes from. The acronym IF-WS₂ refers only to this last structural type. IF-
WS$_2$ is spheroidal in nature consisting of a hollow core with many concentric layers. IF-WS$_2$ is available commercially; however it can also be synthesized in our labs at NPS.

Previous research by our group has demonstrated several different methods of producing IF-WS$_2$, however each individual production run was time consuming or had low yields. Such research demonstrated that the IF-WS$_2$ grown in our labs is more spherical than commercially purchased particles [43]. While particles of a more spheroidal nature would be desirable, the time commitment required to produce enough yield for experimentation was considered impractical at this time. An investigation of the failure mechanisms of these particles is recommended for future work. For the purposes of this project, commercially available IF-WS$_2$ was purchased (Nanolub, Israel) for use in experimentation. As mentioned in Section II.A.3, an unknown material was discovered covering the WS$_2$ while conducting SEM research (Figure 26). The material itself was vaporized by the electron beam as it passed over the sample. Thus, it is unlikely the material has a significant impact on the material properties of the IF-WS$_2$; however, its presence alone was undesirable because if it did have any effects, they would be indistinguishable from the properties of the IF-WS$_2$.

![Figure 25](image.png)

Figure 25. Microstructures of WS2 polymorphs, a) plate-like from [44] b) nanotube from [23] and c) inorganic fullerene from [43].
Due to the presence of this material, the cleaning procedure discussed in section II.A.3 was developed. The initial procedure attempted to heat treat the IF-WS$_2$, however this particular treatment caused the IF-WS$_2$ to oxidize and was thus abandoned.

The XRD pattern presented in Figure 27 shows that the volatile components leaving the IF-WS2 structure reacted with it and promoted its oxidation. The main peaks of WO$_3$ are clearly identified as the dominant phase in the pattern.
Figure 27. XRD spectrum of heat-treated IF-WS₂ sample. Note the distinct tungsten oxide (WO₃) peaks in the middle of the spectrum.

At the macroscopic level, the IF-WS₂ cleaned using solvent is no different than that given no cleaning treatment (Figure 28), which differs from the heat-treated material that had some particles that were tan-colored in addition to the regular gray-black particles found in the ethanol-treated and untreated samples. By XRD the clean IF-WS₂ sample pattern only showed the expected WS₂ peaks with no extra oxide reflections. As with the CNF, Image J was used to determine the particle size distribution of the untreated particles from images collected by scanning electron microscopy (SEM). The distribution shows a roughly Gaussian spread centered in the 100–150 nm range as depicted in Figure 29. Transmission electron micrographs were taken in order to compare interplanar spacing before and after treatments (Figure 30).
Figure 28.    Commercially purchased IF-WS₂ both untreated (left) and treated with ethanol (right). The two are indistinguishable at the macroscopic level.

Figure 29.    Particle size distribution of untreated IF-WS₂. There is a Gaussian distribution centered on the 120–150 nm diameter range.
Figure 30. TEM image of untreated IF-WS$_2$ particle. The hollow core is clearly seen surrounded by concentric semi-spherical layers. Image in the right corresponds to the area above the scale enlarged.

C. TREATMENT OF SAMPLES USING A GAS GUN TO PRODUCE A PRESSURE LOAD

The gas gun tube was used to insult nickel-grown CNF and IF-WS$_2$ on separate occasions. Both helium and nitrogen were used as the driving gases. Nitrogen was used at first, and then helium was used for the remainder of the experiments because it generated significantly higher pressure loads.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Channel Gage Pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Kevlar (N2)</td>
<td>52.60</td>
</tr>
<tr>
<td>CNF #1 (N2)</td>
<td>52.67</td>
</tr>
<tr>
<td>CNF #2 (N2)</td>
<td>55.01</td>
</tr>
<tr>
<td>No sample (He)</td>
<td>186.83</td>
</tr>
<tr>
<td>Kevlar (He)</td>
<td>200.82</td>
</tr>
<tr>
<td>CNF #1 (He)</td>
<td>203.92</td>
</tr>
<tr>
<td>CNF #2 (He)</td>
<td>220.75</td>
</tr>
<tr>
<td>CNF #3 (He)</td>
<td>202.61</td>
</tr>
<tr>
<td>WS2 #1 (He)</td>
<td>198.00</td>
</tr>
<tr>
<td>WS2 #2 (He)</td>
<td>174.21</td>
</tr>
<tr>
<td>WS2 #3 (He)</td>
<td>201.86</td>
</tr>
</tbody>
</table>

Table 3. Gas gun channel pressures for each test run.
Figure 31. Gas gun pressure from each channel along the tube. Each channel is further along the tube with the final transducer located after the supersonic wave has interacted with the test material.
Figure 32. Normalized pressure increase from transducer channel three to four. This illustrates the rise in pressure from the middle of the tube to the end after the pressure load has passed through the test sample. The higher the shock pressure at the end of the tube, the less energy the material has absorbed.

Table 3 and Figure 31 show the pressure profile along the tube for each experiment conducted. The final pressure data was normalized by taking the pressure rise from transducer channel three to four (Figure 32). This is a good indicator of the pressure reduction effects that each material tested has removing the statistical variation between each test run at the middle of the gas gun. The ultimate goal of this research was to determine failure modes of the materials so the data above is illustrative but not required to determine the area of interest of this study. The data includes runs using nothing in the sample holder, Kevlar only, CNF on Kevlar, and IF-WS$_2$ on Kevlar. From this data, there is an interesting trend showing distinct pressure effects from experiment to experiment. We expected that the experiments with nothing in the sample holder would have the highest pressure since there is no material dissipating it, as was later corroborated by the data.

Regarding IF-WS$_2$, the average pressure reduction for samples of IF-WS$_2$ encased in Kevlar are the largest, indicating that from all the materials tested, this is the one that
presents higher absorption. This result is in agreement with published data that indicates the shock absorption characteristics that hollow core nanoparticulates of dichalcogenides can present [6, 7].

It is worth noting that not every experiment is conducted at exactly 700 psig driving pressure, 350 psig intermediate pressure and 25 mm Hg driven pressure, nor were the atmospheric conditions the same for every gas gun shot, so there are variations between each experimental run other than the changing of the material being experimented upon. Data was normalized in order to strictly compare the performance of the different materials using the readings of the pressure reductions in sensor 3.

The size distribution of the IF-WS$_2$ particles post gas gun treatment, that is, the postmortem analysis, shows an interesting trend (Figure 33). The range of particle sizes appears to be more spread out in the particles insulted by the gas gun pressure load, skewing more towards both, smaller sizes and larger particles when compared to the untreated particles. This shows that the supersonic waves dramatically change the microstructure. There is evidence, by analyzing the electron microscopy images of the sample, that larger particulates exist (Figure 34). There are some particles that look to be compressed or flattened as a result of the gas gun pressure load. This mechanism could be described as agglomeration or possibly sintering.
Figure 33. IF-WS₂ size distribution of untreated particles and particles insulted by gas gun pressure loading. The larger number of high-diameter particles and lower-diameter particles supports both delamination and agglomeration as failure modes.

Moreover, the TEM image (Figure 35) depicts another failure mode of tungsten disulfide particles. There is a very clear fracture split at the surface layers of one of the particles. Several of the concentric layers have broken and are shearing away from the rest of the particle. This would be a precursor to the complete delamination and shedding.
of surface layers. This finding supports the particle size distribution data, where smaller particle sizes were identified, indicating that some of the particles broke/delaminated. This result is consistent with other studies regarding IF-WS₂ failure modes [6, 7].

Figure 35. TEM image of IF-WS₂ particles insulted by gas gun pressure load. Note the fracture in the upper portion of the particle in the center of the figure.

Moreover, some of the walls of the IF-WS₂ nanoparticles after impact seem to have a smaller number of layers. This mechanism, agglomeration and delamination combined, suggests that the particles initially compressed as they were impacted by the supersonic wave, and then follow one of the two processes: a) bond breakage from the less stable IF-WS₂ to give origin to the plate-like WS₂, generating flat sheets and b) selective bond breakage for only a few of the external layers, creating smaller particles and more plate-like particulates from the delaminated portion. Figure 36 illustrates this proposed sequence of events.
Regarding the effects of gas gun shock treatment on the carbon nanofiber samples observed in the scanning electron microscope images taken from the postmortem: we detected numerous sections of the sample where the space in between fibers has decrease considerably. Significant fiber agglomeration is evident. The fibers seem to compress due to the pressure and then subsequently do not return to their original shape resulting in flatter fibers. No evidence of fiber breakage was encountered in the SEM figures.

Figure 37. SEM micrograph of untreated CNF (left) and CNF insulted by gas gun pressure loading (right) taken at 25k magnification. Note the agglomeration of fibers in the figure of CNF insulted by gas gun.
Figure 38. SEM micrograph of untreated CNF (left) and CNF insulted by gas gun pressure loading (right) taken at 10k magnification. Note the agglomeration and flattening of fibers insulted by gas gun. Also note the lack of open space in the insulted fibers.

From these observations it is clear that the CNF sample made from nickel does not regain its shape as will be expected from Hookean materials with a spring like mechanism. Figures 37 and 38 show that the new fiber diameters, after the impact, reach values in the order of hundredths of nm and a more flattened structure. All carbon allotropes are solids under normal conditions with graphite being the most stable form. They are chemically resistant and require high temperature to react. Our hypothesis for the observed changes is that the local temperatures and pressure at the instant of the impact should have been enough to open the fibrous structure up and create the most stable extended graphite structure.

D. TREATMENT OF SAMPLES USING AN ULTRASONIC HORN PROCESSOR

When studying mechanisms for materials failure it is common to classify the modes by which the material can fail as: i) fracture, based on the existence of imperfections, such as internal and surface cracks, their radius of curvature and the level of stress that can be concentrated at the crack tip, ii) fatigue, which looks at materials failure under cyclic loads at diverse amplitudes, and iii) creep, which in most materials refers to failure as a function of temperature. The gas gun experiments presented above intended to help us understand how the fibers, in the absence of a polymeric matrix, and a ceramic nanoparticle, IF-WS$_2$, fail under pressure loading conditions. The objective of
the ultrasonic treatments presented in this section was to promote material failure under cyclic stress. The experiments were conducted directly in the powder-like samples as prepared, dry, and dispersed in a solvent.

The Sonomechanics processor employed outputs up to 500 W of acoustic power into the processed substances and operates at a frequency of approximately 20 kHz. The processor consisted of a 500 W ultrasonic generator, a water cooled transducer, and a converging horn. Constant ultrasonic vibration amplitude was always maintained, regardless of the power draw, which was automatically adjusted to compensate for variable loading conditions. The amplitude level can be adjusted from 20–100 percent (up to 107 microns). The processor used had a conventional horn, whose cavitation zone was limited, with a 2.7 mm output tip diameter. The horn is shown in Figure 39.

![Ultrasonic horn processor employed to treat CNF and IF-WS2 particulates. Left: Components of the Barbell horn adapted to the transducer. Right: Red section of the horn represents the output tip that gets immersed in liquid or is in closer contact with powder sample [36].](image)

The ultrasonic treatment tests were conducted according to an experimental design, which helped us select only a few combinations of amplitude and treatment time per material so we could determine the effects of the treatment with the minimum number of experimental runs.

Liquids exposed to high-intensity ultrasound undergo ultrasonic cavitation, which produces violently and asymmetrically imploding bubbles and causes micro-jets that create extreme mechanical shear forces. These forces are responsible for the well-known
ability of ultrasound to tremendously facilitate many physical and chemical processes. Ultrasonic amplitudes on the order of 100 microns (peak-to-peak) are commonly necessary in order to take full advantage of this effect. At low amplitudes (below about 50 microns), the intensity of ultrasonic cavitation is insufficient for many processes, such as the ones involving nanoparticulates (nano-crystallization, nano-emulsification, deagglomeration, extraction), as well as many others. In order to produce sufficient cavitation intensity, ultrasonic transducers (converters) are equipped with high-gain acoustic horns (sonotrodes, waveguide radiators, probes), which amplify the vibration amplitudes generated by the transducers and deliver the ultrasonic energy to working liquids [45–47].

The effect of this cyclic treatment in the CNF samples was observed by SEM analysis of the postmortem samples (Figure 40). The first characteristic that can be identified is related to the amount of empty space in between fibers, which is clearly less than the one observed in the samples prior to the test. Individual fibers were still easily distinguishable. The sample never reached the extreme agglomeration seen for gas gun experiments.

Since agglomeration is a parameter difficult to measure, we relate it to the exposed or accessible surface of the material. The most common method to determine the amount of the sample surface that is accessible is the BET approach, which allows nitrogen molecules to be absorbed in the material to determine how much of the material surface can be covered with them using a range of temperatures and collecting information of the partial pressures registered by the instrument.
Figure 40. SEM micrograph of untreated fibers (left) and fibers insulted by ultrasonic horn (right) both taken at 25k magnitude. Treatment regime for insulted fibers was 100 percent amplitude for three hours. Note the agglomeration and significantly lower empty space in between the insulted fibers.

The surface area of the untreated samples were measured and then compared with the ones of samples tested under the ultrasonic conditions at diverse amplitudes and times, as observed in Figures 41 and 46.

Figure 41. Surface area of CNF as determined from BET analysis. The surface area goes down as both amplitude and time are increased.

The size distribution of tungsten disulfide insulted by ultrasonic waves shows the presence of much smaller particles than that of the untreated sample (Figure 42). As
previously discussed for gas gun results, this observation could be correlated to layer shedding and delamination as the failure mode with this type of testing. The TEM micrograph in Figure 45 shows some delamination of surface layers, which is consistent with the size distribution interpretation. The BET analysis, however, shows a significant decrease in surface area as the amplitude of ultrasonic treatment is increased, which points to agglomeration and sintering taking place when the particles are insulted by ultrasonic waves. It is likely that such mechanism dominates in this case, since the overall surface area consistently diminishes despite the fact that delamination and breakage of particles will increase the BET m²/g number. As seen in the gas gun results and as will be demonstrated in that for the military rounds, both of these failure modes are likely present. The SEM investigation also supports the presence of sintering and agglomeration as many particles appear to mold together (Figure 43).

![WS2 Particle Size Distribution](image)

**Figure 42.** Size distribution of IF-WS₂ particles both untreated and insulted by ultrasonic waves. The increased number of low-diameter particles supports delamination as a failure mode, while the increased number of high-diameter particles supports agglomeration as a second failure mode.
Figure 43. SEM micrograph of untreated WS$_2$ particles (left) and WS$_2$ particles insulted by ultrasonic waves (right) taken at 50k magnification. Treatment regime was dry atmosphere at 100 percent amplitude for three hours. Some particles have flattened, losing the 3D characteristics of IF-WS$_2$ and agglomerated, as evident in the section marked by the arrow of the right-hand figure.

Dry treatments seem to be less impactful in the samples’ microstructures than the ones performed using solvents. Figure 44 shows how a sample treated in liquid media shows a much larger number of particulates with 2D layer or plate-like characteristics, definitively confirming the failure mode proposed. Dry treatment produced surface area reductions of about 45 percent of the original surface area, while liquid experiments reduce it by a larger amount, close to 70 percent of the original value.
Figure 44. SEM micrographs taken at 10k magnification of untreated IF-WS$_2$ particles (left) and IF-WS$_2$ particles insulted by ultrasonic horn (right). Treatment regime was liquid atmosphere at 20 percent amplitude for three hours. There is evidence of agglomeration and there are clearly larger particles. The entire frame is also more compressed.

Figure 45. TEM micrograph of IF-WS$_2$ particles insulted by ultrasonic waves. Note the partial delamination of surface layers of particles in the center of the figure.
The two previous sets of studies have already helped understand some of the possible failure mechanisms for both the CNF and IF-WS$_2$, however there was interest in identifying the microstructural characteristics of the samples under a more dramatic impact event such as that from military standard NATO rounds.

### E. TREATMENT OF SAMPLES WITH IMPACT BY MILITARY ROUNDS

Military rounds were used to insult various configurations of test materials as detailed below. There was some variation in the initial velocity of each test but they are close to each other. The expected outcome of these tests was the generation of samples that could be studied postmortem and correlated with the initial findings. The only parameter that could be measured during the tests, not without considerable variation due to not using the same plywood backing material after each consecutive test, was the residual velocity after the round had passed through the test sample, clay backing, and plywood stabilizer. The percent reduction in velocity can be found in Figure 47. In two of the tests this measurement was not recorded, however it was obtained for the rest of the tests. Due to the fact that only one sample of each configuration was tested it is difficult to say if any variations in the residual velocity are due to the differences in the test sample or statistical variations. For instance, the sample with one layer of CNF laid
directly on the Kevlar has a lower residual velocity than the sample with three layers of CNF, which seem to be counterintuitive since the sample with more of the test sample should slow the round down more, however the initial velocity of the one-layer CNF sample is lower than the initial velocity of the three-layer CNF sample. It is interesting to note that the sample with one layer of WS2 laid directly on the Kevlar sheet has the lowest residual velocity at 299.68 m/s, which would seem to be consistent with the fact that WS2 has high shock absorption characteristics. It does, however, need to be noted that after the fifth test run was completed, the plywood stabilizer located on the back of the clay backing was changed, which caused an associated drop in residual velocity in subsequent test runs so that was a contributing factor as well. The set of samples tested by this procedure is listed in Table 4.

<table>
<thead>
<tr>
<th>Shot Description</th>
<th>Initial Velocity (m/s)</th>
<th>Residual Velocity (m/s)</th>
<th>Humidity (%)</th>
<th>Temp (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kevlar only</td>
<td>782.10</td>
<td>506.04</td>
<td>13.60</td>
<td>27.61</td>
</tr>
<tr>
<td>1-layer bare CNF</td>
<td>776.98</td>
<td>389.27</td>
<td>13.10</td>
<td>26.89</td>
</tr>
<tr>
<td>3-layer bare CNF</td>
<td>782.79</td>
<td>408.03</td>
<td>13.20</td>
<td>26.50</td>
</tr>
<tr>
<td>Bare WS2</td>
<td>779.05</td>
<td>299.68</td>
<td>13.90</td>
<td>25.89</td>
</tr>
<tr>
<td>Epoxy only</td>
<td>785.90</td>
<td>378.17</td>
<td>14.60</td>
<td>25.56</td>
</tr>
<tr>
<td>1-layer CNF in epoxy</td>
<td>788.21</td>
<td>446.33</td>
<td>12.30</td>
<td>27.28</td>
</tr>
<tr>
<td>3-layer CNF in epoxy</td>
<td>780.41</td>
<td>317.24</td>
<td>14.80</td>
<td>25.89</td>
</tr>
<tr>
<td>WS2 in epoxy</td>
<td>786.11</td>
<td>541.17</td>
<td>14.80</td>
<td>24.94</td>
</tr>
<tr>
<td>CNF w/ WS2 (low load) in epoxy</td>
<td>786.24</td>
<td>686.41</td>
<td>16.80</td>
<td>24.11</td>
</tr>
<tr>
<td>CNF w/ WS2 (mid load) in epoxy</td>
<td>789.94</td>
<td>NA</td>
<td>17.40</td>
<td>24.72</td>
</tr>
<tr>
<td>Sulfidized CNF in epoxy</td>
<td>783.54</td>
<td>NA</td>
<td>16.80</td>
<td>24.17</td>
</tr>
<tr>
<td>Dual layer WS2 and CNF in epoxy</td>
<td>779.56</td>
<td>572.50</td>
<td>16.20</td>
<td>24.50</td>
</tr>
</tbody>
</table>

Table 4. Data from military rounds testing.
Figure 47. Reduction in velocity by samples insulted by military rounds. IF-WS$_2$ has the highest reduction, however there is significant variation between samples.

The SEM micrographs in Figures 48 and 49 show fibers that were taken both near the hole made by the military round and away from the military round. It is clear that the first two situations show larger effects on the fiber microstructure. The figures have similar characteristics as the ones observed by previous methods: agglomeration and decrease of interfiber spacing.
Figure 48. SEM micrograph of untreated CNF (left) and CNF from sample with one layer treated with fibers (right) taken at 25k magnification. The fibers were taken from near hole made by the military round. Note the agglomeration and compressing of fibers in the right-hand figure.

Figure 49. SEM micrograph of untreated fibers (left) and fibers taken from the second layer of the sample with three layers treated with CNF (right) taken at 25k magnification. The fibers were obtained from near the hole made by the military round. Note the significant agglomeration in the far right of the right-hand figure.

Figure 50 shows that the individual fibers have become a carbon conglomerate. Similar to the structures observed by impact melting and materials subject to high pressures, micron size agglomerates dominate the microstructure.
Figure 50. SEM micrograph of untreated CNF (left) and fibers taken from the first layer of the sample with three layers treated with CNF (right) taken at 25k magnification. The fibers were taken from a distance away from the hole made by the military round. Note the agglomeration and compression in the right-hand figure is much less than in previous cases, the individual fibers are still easily distinguished.

The size distribution of the IF-WS$_2$ particles insulted by military rounds has two points we would like to emphasize. The distribution itself supports two different failure modes: layer shedding and agglomeration or sintering. This is illustrated by the fact that there are more particles in the smaller size bins in the sample insulted by military rounds, which would support layer shedding. When the particles shed layers, they become smaller so if this is in fact occurring, the sample insulted by a pressure load should have smaller particles in it, which is illustrated in Figure 51. Additionally, there are more particles in the larger size bins, which would indicate that bonds in the 3D structure of the nanoparticles are being broken and larger more stable 2D plate-like WS$_2$ are being formed. Evidence of both of these failure modes are also supported in the SEM and TEM micrographs.
Figure 51. Particle size distribution of untreated IF-WS$_2$ and IF-WS$_2$ insulted by military rounds. The increased number of low-diameter particles supports delamination as a failure mode; the increased number of high-diameter particles supports bond breakage and generation of 2D WS$_2$ as a second failure mode.

Figure 52. SEM micrograph at 50k magnification of untreated IF-WS$_2$ (left) and 2D WS$_2$ insulted by military round, taken from near the hole made by the round. Note the characteristics of the layers, similar to those observed in graphitic materials.

The micrographs taken as part of the postmortem analysis of the samples impacted with military rounds gave us proof of the mechanisms proposed. The mechanism observed the most was the generation of micron-size “blocks” of WS$_2$. Figure 52 presents an SEM micrograph with evidence of how the hollow IF-WS$_2$ nanoparticles
collapse and agglomerate in a similar fashion as atoms getting added to an existing substrate during crystal growth. According to the step growth theory of crystal growth, the irreversible incorporation of atoms into the substrate of the \{100\} surface of a cubic crystal happens preferentially at the ledges and kink sites, which have higher energy states given the dangling bonds, when compared to perfectly flat surfaces as indicated in the right section of the figure. As seen in the microstructure of WS\(_2\) after the military round insult, spherical particles behave in a similar way, acquiring a planar structure that gets incorporated in the edges, kinks and steps of the structure. The sections marked as a, b, c and d represent diverse stages of the process: in a) the individual particle is indistinguishable from the block of WS\(_2\) below it, in b) grain boundaries of the individual particle could still be detected, despite being now part of the substrate, in c) two particles have only been added to the edge and kink of a layer, and in d) the particle still preserves a certain curvature and is not yet part of the main agglomerate.

![Step growth theory of crystal growth](image)

Figure 53. Mechanism by which the 3D IF-WS\(_2\) spherical particles form a micron size 2D WS\(_2\) solid and the similarities of the process when compared to crystal step growth theory [48].

The second IF-WS\(_2\) failure mode proposed, also in Figure 53, refers to the particles delamination. Particle size distributions showed, as mentioned before, a particle size distribution after the impact event that suggests the existence of particles smaller than the ones in the sample before treatment. This could only be possible if particles broke or delaminated, creating smaller ones. In Figure 54, we present an SEM
micrograph that captures a particle suffering such process. The region marked by the arrow points to a particle in which the outer layers have been stripped off, leaving behind only the inner section of the particle, with a smaller diameter.

![Figure 54. SEM micrograph of IF-WS$_2$ insulted by military round away from hole at 75k magnification. Note the appearance of a particle that has split open to show layers beneath the surface.](image)

From Figures 55–57, corresponding to TEM images, we can observe that places where two sets of lattice orientations meet (where the IF-WS$_2$ polyhedral particles have edges, corners or sharp angles) is where bond breakage is noted. The discontinuities on the onion-like structure of the IF-WS$_2$ lattice serve as stress concentrators and are the places where the nanomaterial initially breaks. If the breakage only comprises a few of the external layers, the outer sections of the particle seem to delaminate. If the fracture expands further, we seem to be more likely to find particulates where the structure completely flattens. There is a strong indication that, similar to fracture in macroscopic objects, the curvature of the particles plays a large role in the failure of the WS$_2$ material. In traditional fracture mechanics the curvature refers to the crack or void tip; in our study, the curvature will be related to how spherical the nanoparticles are. A perfectly spherical nanoparticle is expected to withstand higher loads since it will lack the stress concentrators that the angular structures seem to provide.
Figure 55. TEM micrograph of IF-WS₂ particles insulted by military rounds. Note the fractured particle and how the layers are starting to shear away from the center of the particle.

Figure 56. TEM image of IF-WS₂ particles insulted by military rounds. Note in the upper portion of the figure the jagged-edged and fractured particles.
Figure 57. TEM image of IF-WS$_2$ particles insulted by military rounds. Note in the bottom right the particle that has fractured and the two particles in the center have lost some of the exterior layers to generate the 2D structure.

F. ENERGY DISPERSIVE SPECTROSCOPY AND XRD ANALYSIS OF IF-WS$_2$ POSTMORTEM SAMPLES

Energy dispersive spectroscopy (EDS) was used to detect the presence of oxygen in the IF-WS$_2$ insulted by all of the various testing methods used for this research. This effort was undertaken in order to demonstrate whether or not the testing methods would cause the particles to oxidize and fundamentally change the chemical structure of the tested IF-WS$_2$ materials. The spectra demonstrate that the IF-WS$_2$ are not being oxidized by the gas gun, ultrasound, and military rounds (Figure 58), in contrast to the heat-treated IF-WS$_2$, which clearly was oxidized by the heating process.
Figure 58. EDS spectra of IF-WS$_2$ particles including untreated as well as samples insulted by gas gun, ultrasound, and military rounds. The peaks are in the same place for all samples showing the presence of tungsten and sulfur. The samples do not have oxygen.

X-ray diffraction (XRD) was used to observe whether the testing on IF-WS$_2$ caused any crystallographic changes in the materials. Specifically, we focused on any peak shifts in the spectrum to see the effect on interplanar spacing of the particles. The presence of the same diffraction peaks in each spectrum shows that the same material is
in each sample (as expected), however a closer look is required to determine the extent of any 2θ shifts in the peaks. When zooming in, a clear peak shift to the left is observed for the insulted samples as seen in Figure 59. Bragg’s law (Equation 4) was used to determine the planar spacing shown in Table 5.

\[ n\lambda = 2dsin\theta \quad Eqn \ (4) \]

Where n is the order of reflection, \( \lambda \) is the wavelength, d is the planar spacing and \( \theta \) is the diffraction angle.

![Offset XRD Spectrum for WS2](image)

**Figure 59.** XRD spectra of untreated and insulted tungsten disulfide. The similarity of the peaks shows that the same material is present in each sample.
Figure 60. XRD pattern focusing in the 31–35 $2\theta$ range. Note the shifts to the left for the Miller index (100) for insulted samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$2\theta$ (deg)</th>
<th>Planar Spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>32.77</td>
<td>0.2733</td>
</tr>
<tr>
<td>Gas Gun</td>
<td>32.67</td>
<td>0.2741</td>
</tr>
<tr>
<td>Ultrasound</td>
<td>32.73</td>
<td>0.2736</td>
</tr>
<tr>
<td>Military Rounds</td>
<td>32.61</td>
<td>0.2746</td>
</tr>
</tbody>
</table>

Table 5. Spacing of (100) plane of IF-WS$_2$ particles both untreated and insulted by the various testing methods.

This shift indicates an expansion of the interplanar spacing, which supports delamination as a failure mode. There is planar expansion in all insulted samples, however it is most pronounced in the sample insulted by military rounds. This matches with expectations in that the military rounds provided the most dramatic impact event of all three test methods therefore the effect on the sample should be highest. In addition to this, we focused on the peak close to 14 degrees (Figure 61) where we note an interesting trend. Like the previous example, the peak from the gas gun and military rounds samples shift to the left indicating an expansion of the planar spacing, but the peak from the
sample treated by ultrasound shifts instead to the right. This also contrasts with other research efforts that found planar spacing compression in the (002) peak from samples treated with very high shock pressures (10–25 GPa) [6, 7]. We should note here that peak shifts are possible due to varying sample heights in an XRD detector, thus a test using a substance with standard peak position, such as silicon, could be conducted to corroborate; time constraints prevent the completion of such here.

Figure 61. XRD pattern focusing in the 12.5–15 degree 2θ range. Note how the gas gun and military rounds peaks shift to the left, yet the ultrasound peak shifts slightly to the right indicating a shrinking of planar spacing. This peak corresponds to the (002) Miller plane.
V. DESIGN AGAINST FAILURE: RESULTS AND DISCUSSION OF PALLADIUM-GROWN CNF MATERIALS AND TESTING

Once it was established that CNF grown from nickel nanoparticles agglomerated after all treatments, we attempted to generate a fibrous structure that contained a larger diameter distribution to promote the fibers to intertwine at larger scales and not solely form agglomerates that will expand over smaller length, thus preventing the powder-like structures seen before. A parallel study in our group achieved such structure using palladium as catalyst and a slight modification in the synthesis protocol. The growth procedure for synthesizing CNF from palladium has significant similarities to that for growing fibers from nickel but the macroscale result is quite different. Both procedures used the same fuel (ethylene) and the growth phase was conducted at the same temperature (550°C). Due to the fact that the Pd nanoparticles were not as reactive to environmental oxygen as nickel, an Ar/H2 reducing step was not required. Less catalyst was used in the Pd procedure (20 mg vice 100 mg) but the growth step was much longer (180 minutes vice 90 minutes). Additionally, a specially designed and enclosed metal boat was used for growing the fibers from Pd whereas a ceramic crucible was used for the Ni procedure. This was used to contain the growth of the Pd fibers into a roughly cube-like structure. The end result of this procedure was a foam-like substance composed of CNF in stark contrast to the powder-like materials resulting from nickel CNF growth (Figure 62).

It is critical to note that following the developed fabrication protocol was extremely important in order obtain the foam-like material. If the atmosphere was incorrectly or incompletely purged or the metal boat is not correctly closed this could result in a contaminated atmosphere, which will produce a powdery and brittle material from this method (Figure 63). This occurred both when the top of the metal boat was improperly tightened and when one of the screws holding the top down was stripped resulting in an improper seal between the base and top of the apparatus. Also it should be noted that after several uses of the metal boat, which require rather severe heating and
cooling cycles, the interface between the base and the top of the boat became warped and required machining to once again ensure a tight and effective seal.

Figure 62. Foam-like material consisting of CNF grown with palladium catalyst.

Figure 63. Material grown from CNF with palladium catalyst without pressure seal being maintained throughout the procedure. The consistency is similar to that of CNF grown from nickel.
As with the nickel-grown CNF, SEM was used to characterize the Pd nanoparticles and fibers; Image J software was used to determine the size distribution of the diameters of the fibers (Figure 65). From the standpoint of looking at the images, there is little qualitative difference between the Pd fibers and Ni fibers (Figure 64).

Figure 64. SEM micrograph of Pd nanoparticles taken at 50k magnification.
Figure 65. Diameter distribution of palladium nanoparticles. It is a bimodal distribution with most particles centered around the 60–90 nm range. Fewer particles are in the higher size bins, but this mode still constitutes a significant number of particles.

Figure 66. SEM micrograph of CNF grown from Pd catalyst with magnification 2.5k.
Figure 67. Size distribution of untreated CNF grown with palladium catalyst.

From the SEM images taken from the palladium growth (an example of which is found in Figure 66) and the CNF diameter distribution presented in Figure 67, we could observe that there is a bimodal particle size distribution. The first section can be described as a Gaussian distribution centered somewhere in the 60–90 nm range, while the second one is less populated in terms of number of fibers, but still significant, showing higher size ranges.

A. GAS GUN

For testing palladium-grown fibers with the gas gun, only helium was used as the driving gas to take advantage of the higher loading pressures. Much the same as with the nickel-grown fibers, the shock pressure at the end of the tube was expected to fall lower than both the Kevlar-only and bare samples and the nickel CNF samples. This expected trend was observed as well. As seen in Table 6 and Figure 68, all of the palladium CNF samples have a lower final shock pressure than the nickel CNF test runs.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Channel Gage Pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No sample (He)</td>
<td>186.83 168.97 1715.92</td>
</tr>
<tr>
<td>Kevlar (He)</td>
<td>200.82 141.33 1742.80</td>
</tr>
<tr>
<td>Ni CNF #1 (He)</td>
<td>203.92 159.11 1589.20</td>
</tr>
<tr>
<td>Ni CNF #2 (He)</td>
<td>220.75 157.73 1564.80</td>
</tr>
<tr>
<td>Ni CNF #3 (He)</td>
<td>202.61 163.18 1691.17</td>
</tr>
<tr>
<td>Pd CNF #1 (He)</td>
<td>202.96 143.46 1512.54</td>
</tr>
<tr>
<td>Pd CNF #2 (He)</td>
<td>207.03 161.25 1561.42</td>
</tr>
<tr>
<td>Pd CNF #3 (He)</td>
<td>189.03 142.09 1504.34</td>
</tr>
</tbody>
</table>

Table 6. Gas gun channel pressures for nickel- and palladium-grown CNF.

![Gas Gun Channel Pressure](image_url)

Figure 68. Gas gun tube pressure from each channel along the tube. Each channel is further along the tube with the final transducer located after the pressure load has interacted with the test material.
Figure 69. Profile of normalized gas gun pressures at transducer four. This illustrates the pressure increase between the middle of the tube and the end of the tube after the supersonic wave has passed through the sample.

As with the previous gas gun data, the final pressures were normalized by taking the pressure rise between transducers three and four in order to remove to the maximum extent possible the statistical variations between test runs (Figure 69); thus, the data provide a good indication of the effects the test materials have on shock dissipation. The aim of this research, as mentioned previously, was to induce failure in the materials and study the resulting microstructural indications.
Figures 70 and 71 above depict SEM images of Pd-grown CNF insulted by gas gun pressure load. The prominent “corkscrewing” of some of the fibers is misleading. Previous research by our group observed this phenomenon in untreated fibers grown from Palladium catalyst as well (Figure 72). Thus, it is unrelated to the gas gun pressure loading treatment. What is interesting, however, is that the level of agglomeration is
either too small to be detected or nonexistent. This contrasts sharply with the observed results of the nickel fibers. This is related the ability of the palladium fibers to be compressed and then subsequently return to their original configuration, or close to it, therefore any agglomerating effects are negated or dramatically reduced. Thus, we can say that the CNF grown using palladium catalyst are an effective method to design against the agglomeration failure mode, specifically for gas gun pressure loading regimes. Figure 73 shows a picture of the sample after testing with the gas gun. On the macroscale it is unchanged as compared to before it was treated.

![TEM image of palladium-grown CNF](image.png)

Figure 72. TEM image of palladium-grown CNF. Note the corkscrew of one of the fibers. This sample was not insulted by any pressure loads.
B. COMPARISON OF TUNGSTEN DISULFIDE AND NICKEL AND PALLADIUM FIBERS

When conducting a direct comparison between the size distribution of the nickel and palladium fibers, it is clear that the palladium fibers, on average, have a larger diameter. Also, there is little evidence of the very small fibers (0–30 nm) being present in the fibers grown from palladium. The fact that the palladium fibers are large allows them to interweave more readily into the macroscale foam-like substance that we see when growing the palladium-based fibers. An interesting feature to note about the fibers grown from Pd is that the structure can be compressed and then will return to its previous configuration when the external pressure is removed. That particular investigation has only been conducted with relatively low external forces and has not yet been subjected to the higher forces and pressures associated with the testing conducted on the nickel fibers (gas gun, ultrasound, military rounds).
Figure 74. SEM micrograph at 50k magnification of Ni nanoparticles (left) and Pd nanoparticles (right). The particles are similar in size, but there is less variation with the Pd particles.

While the images in Figure 74 look very similar, there is some difference between as shown in the analysis done using Image J software. The particle diameter distribution of both types of nanoparticles was analyzed (Figure 75). Both distributions are of a Gaussian nature, however the palladium particles have a higher average size and more particles in the large diameter bins. This is also seen in the SEM micrographs and fiber diameter distributions as illustrated in Figures 76 and 77, respectively.
Figure 75. Diameter distribution of Ni and Pd nanoparticles. Both have a Gaussian distribution, however the Pd particles distribution skews more to the right (higher diameter) than the Ni particles.

Figure 76. SEM micrograph at 10k magnification of nickel-grown CNF (left) and palladium-grown CNF (right). Note how the Pd fibers clearly have a larger average diameter.
We hypothesized that the Pd-grown fibers would have a lower final loading pressure as their ability to compress and return to the original size would help in shock absorption and dissipate some of the shock pressure before it reached the final pressure transducer as compared to the nickel-grown fibers. Our initial investigation seems to bear this out. The average final pressure of the tests conducted using Pd-grown fibers is less than the average final pressure of the tests with Ni-grown fibers (Figure 78); however, these numbers fall within one standard deviation of each other so it is impossible to say with certainty that this is the case. Additionally, the very small sample size warrants further investigation before we can make this claim with confidence, though initial data are promising.

Figure 77.  Fiber size distributions of untreated CNF grown from palladium and nickel nanoparticle catalysts.
C. VISCOELASTICITY OF PALLADIUM CARBON NANOFIBERS

1. Behavior of Viscoelastic Materials

Viscoelastic materials are substances that have both viscous and elastic properties when placed under load. Specifically, the material will deform when stressed and then return to its original shape when the load is removed (elastic behavior) but it will take a some finite amount of time to do so (viscous behavior). This behavior can be understood in terms of the form of dynamic testing conducting on this type of material. In dynamic testing, stress or strain is varied cyclically (often sinusoidally) with time and the response to this stimulus is measured at different deformation frequencies. An elastic material, when placed under a sinusoidal stress, will have a sinusoidal strain in phase with the stress (Figure 79) [49].
On the other hand, a viscous material with no elastic component has the highest stress at the point of highest strain rate. In this case, the highest strain rate occurs when the strain itself is zero. Thus, the stress and strain are out of phase by 90 degrees. A viscoelastic material will demonstrate some combination of these two instances (Figure 80) [49].

From a molecular standpoint, then, an appropriate first approximation is that any molecular displacements occurring in phase with the externally applied oscillations would represent energy storage. By contrast, the proportions of displacements that are out of phase represent energy dissipated by the material. When the load is removed, the
stored energy is returned and the dissipated energy is lost. It is the dissipation of energy that makes this type of material worth investigating with regard to personal protection systems. It is common for materials to dissipate energy imparted to them through breakage. Viscoelastic materials, alternatively, dissipate some incident energy as heat and, just as importantly, return to their original shape.

2. Viscoelasticity in CNF Grown From Palladium

The stress-strain testing conducted on palladium CNF grown in our lab show behavior that matches that of viscoelastic materials discussed above. A dynamic testing regime was used to investigate the viscoelastic properties of the CNF. The material was tested in an INSTRON 5942 mechanical testing device. The material was sequentially loaded and unloaded 20 times to check for significant variation in the loading and unloading cycles. The material was constrained so that the area under load did not change with time. This was done at two different frequencies to investigate any differences that arise. Both strain and stress were recorded over the duration of the experiment. A plot of stress versus strain was then created to check the behavior of the material. As can be seen in Figure 81, the stress-strain curve has the same properties as the viscoelastic material detailed above.
Figure 81. Stress-strain curve of CNF grown from palladium catalyst. The frequencies used were 0.035 Hz (fast) and 0.0074 Hz (slow). The profile matches that of a viscoelastic material; the energy absorbed is equal to the area between the load curve and unload curve.

Furthermore, a number of the cycles were investigated in detail to determine what the modulus was, specifically for cycles 3–10. The loading phase of the cycle was plotted up to the maximum strain reached. A linear curve was then fit to this data, the slope of which was the modulus for that cycle. For each successive cycle, the modulus became higher, in other words the material became stiffer. As can be seen in the Figure 82 the rise in stiffness becomes less pronounced over time, approaching a plateau.
The area between the load and unload curve for each cycle represents the energy dissipated during that cycle. In other words, taking the integral of the stress-strain relationship will calculate this energy dissipation. This was done for the tenth cycle of both the fast and slow test runs. To calculate the area difference, the Trapezoidal Rule was implemented in a spreadsheet containing the data first on the load phase and then the unload phase. This calculated the area underneath both curves. The unload area was then subtracted from the load area to obtain the total energy dissipated per unit volume. The high-frequency cycle dissipated 5834 J/m$^3$ and the low-frequency cycle dissipated 168887 J/m$^3$. The trend seen here is that the higher the cycling frequency, the lower the energy absorption capability. From this, we can infer that a dramatic impact event like insult with military rounds will decrease the energy dissipation capacity even further to the quickness with which the material is stressed. Further research is required to determine whether this is the case.

It is worth noting that since the carbon foam (CNF from palladium) studied in Chapter V presents viscoelastic behavior, commonly used criteria to express the measure
of the material resistance to brittle fracture, such as fracture toughness, or to crack propagation, such as critical stress for crack propagation, do not apply and were not calculated.
VI. CONCLUSIONS

A. MILESTONES

In this research, our objective was to determine the failure modes of carbon nanofibers (CNF) and inorganic fullerene-type tungsten disulfide (IF-WS$_2$) using diverse methods of pressure loading including gas gun, ultrasonic treatment, and impact with military rounds. We were able to successfully characterize these failure modes for both materials. Furthermore, we redesigned the CNF using a different catalyst in an attempt to design against the failure modes identified. This effort was successful, although further research into this material is necessary. The failure modes can be summarized as follows:

- Nickel CNF: Agglomeration
- Palladium CNF: None
- IF-WS$_2$: Agglomeration and delamination

We synthesized CNF using nickel and palladium catalyst. The former produced fibers with a bimodal diameter size distribution of fibers with the first, much more abundant mode, ranging from 20–150 nm and the second from 150–300 nm. CNF grown from nickel formed loosely bound, micron-sized, powder-like conglomerates. Nickel-grown CNF showed agglomeration as single failure mode after pressure loading from all three test methods. Analysis using scanning electron microscopy (SEM) showed clear evidence of fibers becoming a single carbonaceous body. Fibers formed compressed agglomerates and micrographs had significantly less empty space between fibers than the micrographs of untreated fibers. Gas gun pressure loading showed the least severe evidence of agglomeration while impact with military rounds had the most significant effects. Treatment with ultrasonic waves demonstrated the material’s response to a cyclic load and had a level of agglomeration somewhere between the gas gun and military rounds.

The palladium-produced fibers showed a bimodal diameter size distribution; the first mode ranged from 30–210 nm and the second from 210–380 nm, the latter size dominating the microstructural features of the sample. In contrast to the powder-like
agglomerates observed in nickel grown fibers, CNF grown from palladium formed an ultralow density carbon foam, which acquired the dimensions of the mold it was grown in and remained as a single macroscopic object. From our electron microscopy observations, the existence of larger diameter fibers seem to be responsible for interconnecting the smaller fibers and maintaining the sample as a highly porous interconnected framework.

The redesigned fibers grown from palladium demonstrated viscoelastic properties when placed under cyclic loading conditions conducted at multiple frequencies; in all instances the material returned to its original shape after loads were removed. We were able to calculate energy dissipation per unit volume numbers from the stress-strain curves developed from the cyclic load tests. The higher frequency test dissipated significantly less energy than the low frequency test (5,834 J/m$^3$ and 16,887 J/m$^3$ respectively) showing that this ability of the material is highly dependent on loading frequency.

Pressure load testing was conducted on the palladium CNF using the gas gun. SEM analysis and macroscopic inspection of fibers insulted by pressure loading showed no discernible difference when compared to untreated fibers. The fact that this material did not fail under the same conditions that caused other materials investigated in this study to fail seems very promising for shock absorption applications and bears further investigation. It is worth noting that since the carbon foam studied here presents viscoelastic behavior, commonly used criteria to express the measure of material’s resistance to brittle fracture, such as fracture toughness, or to crack propagation, such as critical stress, do not apply and were not calculated.

Due to the fact that the main component of this foam is carbon, the new material presents thermal stability at much higher temperatures than other viscoelastic substances, such as polymers, which start decomposing between 200 and 300 ºC in air. According to thermogravimetric analysis data, the new carbon foam is stable up to at least 550 ºC.

WS$_2$ has multiple polymorphs including the spherical inorganic fullerene particles we investigated during this research along with plate-like and tubular forms. We demonstrated that IF-WS$_2$ fails in two ways. The first is related to a shift from the 3D spherical polymorph to the 2D plate-like form. Pressure loads promote bond breakage
and transform some of the particles from their fullerene form to the 2D polymorph. In addition to such morphological change, we observed particle agglomeration by a similar mechanism than the one observed during crystal growth steps, in which particles attach to kinks and edges of the 2D plate like surfaces. To support such observation, postmortem analysis for ultrasonic treated samples showed a reduction in surface area with increasing amplitude of ultrasonic waves, which is a very clear indicator of many smaller particles turning into fewer, larger particles (i.e., agglomeration). The other failure mode we identified for IF-WS₂ was delamination, or layer shedding, which was demonstrated in both SEM and TEM analysis, a result of the breaking of bonds upon absorption of incident energy. When the surface layers of this onion-like structure are impacted by pressure loads, some of the bonds break in response to this stress, and the broken layers are pulled away from the structure. XRD analysis of postmortem specimens showed an increased interplanar distance, consistent with electron microscopy observations. The SEM analysis shows that the failure of IF-WS₂ structures, either by delamination or by the transition from the 3D to the 2D polymorphs, seems to be related to the sharp angles encountered in the cage-like IF-WS₂ structure. Those are the main points where these nanostructures break and act as stress concentrators. Continued investigation of this substance using particles with a more spherical shape is suggested. As with the nickel CNF, the most severe effects were noted in the samples tested via impact with military rounds.

B. FURTHER RESEARCH

We suggest full characterization of the mechanical properties of the new foam and to correlate it with mathematical models that could predict fracture toughness or other indicators of mechanical strength. Time constraints prevented us from testing the new foam by other methods in order to fully explore the potential of this material. The investigation of the Pd CNF should be completed by testing with ultrasound treatment, and, more importantly, impact with military rounds. As well, a correlation of the angles in the IF-WS₂ polyhedral particles with the stress concentration at those points is needed.
APPENDIX A. NICKEL GROWTH PROCEDURE

Flush
- Place 100 mg of nickel nanopowder in ceramic crucible
- Place ceramic crucible inside quartz tube
- Attach gas feed and exhaust tubes to tube ends
- Flush with nitrogen (N2) at 200 SCCM for 20 min
- Turn on furnace, set to 350 °C
- Run argon/hydrogen (Ar/H2) at 20 SCCM for 30 minutes

Growth
- Turn off argon/hydrogen
- Reduce nitrogen (N2) to 30 SCCM
- Run ethylene (C2H4) at 25 SCCM
- Run oxygen (O2) at 5 SCCM
- At 5 minute intervals, increase O2 flow by 5 SCCM increments until at 20 SCCM
- Increase temperature in furnace to 550 °C
- Run for 60–90 minutes depending on desired yield
- Turn off ethylene and oxygen

Cool Down
- Turn off furnace
- Turn on side fans
- Cool to room temperature with 30 SCCM of (N2)
- Turn off (N2) when the sample has reached room temperature
- Turn off side fans
- Remove sample
APPENDIX B.  PALLADIUM (PD POWDER 99.9%) PROCEDURE

**Flush**
- Place 20 mg of palladium powder on the edges and center of the metal rectangular mold.
- Flush with nitrogen (N2) at 100 SCCM
- Turn on furnace and set to 550 °C

**Growth**
- Once it is at 550 °C, turn on Ethylene at 15 SCCM and Oxygen at 5 SCCM for 5 min then 10 SCCM for 5 min then 20 SCCM
- Run for 2 to 3 hours
- Turn off ethylene (C2H4) and oxygen (O2)

**Cool Down**
- Turn off furnace
- Turn on side fans
- Cool to room temperature with 30 SCCM of nitrogen (N2)
- Turn off nitrogen (N2) when the sample has reached room temperature
- Turn off side fans
- Remove sample
APPENDIX C. SHOCK TUBE OPERATING PROCEDURES

A. LOADING DIAPHRAGMS

• Open diaphragm section. Ensure that the center section is always supported properly.
• Remove rubber O-rings (4 total), wipe excess grease/dirt off with rag and coat with thin film of high vacuum grease.
• Replace O-rings and insert diaphragms with the scored side towards the driven section.
• Close diaphragm section and tighten down securely. (Bolts should be started by hands to avoid cross-threading).

B. PREPARING THE DRIVEN SECTION

• Connect the vacuum gauge. (Connector should thread most of the way by hand. Be careful not to cross-thread the connection. Tighten with two wrenches.)
• Turn on the roughing pump.
• Open Valve #1.
• Pull pin from orange handle and PUSH to open the valve. This will start evacuating the section.
• Evacuate the driven section to approximately 2 mm Hg.
• Shut organ handle (pull up), replace the safety pin, and turn off the roughing pump.
• Open CO2 bottle. Ensure discharge pressure is approximately 25 psig.
• Open valve #2.
• Using valve #4 slowly belled in CO2 until the vacuum gauge reads 25 mm Hg. Record time and pressure.
• Close valve #2 and CO2 bottle.
• Close valve #1 and disconnect vacuum gauge.

C. LOADING THE DRIVER SECTION (ensure that the Data Acquisition System is ready)

• Close valve #11 (purge valve) and OPEN Valve #6 (firing valve.)
• Close valve #7, #8, #9, and #10.
• Open nitrogen/helium bottle and set regulator for 800 to 1000 psig (turn “T” clockwise to increase pressure).

• Open valve #7.

• Pressurize the driver section by slowly opening Valve #9 (tap pressure gauge for accurate readings).

• When gauge reads desired pressure for mid-section (section between both diaphragms), close valve #6 and continue filling the driver section to its desired pressure.

• At the desired pressure, close valve #7 and #9, and the Nitrogen/Helium bottle.

• The Shock Tube is now ready for firing.

D. FIRING THE SHOCK TUBE

• Ensure all Data Acquisition System is up and ready, give a three, two, one countdown and fire the shock tube by rapidly opening valve #6. Record firing time and pressure.

• Purge the shock tube by slowly opening valve #11 to a 45º angle.

• Bleed the tube until approximately 50 psig and then open fully.
## APPENDIX D. SUMMARY OF EXPERIMENTS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Characterization</th>
<th>Test</th>
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<tbody>
<tr>
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<td>TEM</td>
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<td>Epoxy</td>
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LIST OF REFERENCES


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