



NAVAL POSTGRADUATE SCHOOL

MONTEREY, CALIFORNIA

THESIS

**ENHANCING DISPERSION OF CARBON NANOTUBES
WITHIN METAL MATRIX COMPOSITES**

by

Margaret C. Ruud

June 2023

Thesis Advisor:
Second Reader:

Troy Ansell
Young W. Kwon

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REPORT DOCUMENTATION PAGE			<i>Form Approved OMB No. 0704-0188</i>	
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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June 2023	3. REPORT TYPE AND DATES COVERED Master's thesis	
4. TITLE AND SUBTITLE ENHANCING DISPERSION OF CARBON NANOTUBES WITHIN METAL MATRIX COMPOSITES			5. FUNDING NUMBERS	
6. AUTHOR(S) Margaret C. Ruud				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Postgraduate School Monterey, CA 93943-5000			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) N/A			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES The views expressed in this thesis are those of the author and do not reflect the official policy or position of the Department of Defense or the U.S. Government.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release. Distribution is unlimited.			12b. DISTRIBUTION CODE A	
13. ABSTRACT (maximum 200 words) The dispersion of carbon nanotubes (CNTs) in an aluminum (Al) metal matrix composite (MMC) was explored in this thesis. CNTs have demonstrated strong and lightweight properties, making them a promising candidate for composite development in maritime, aeronautical, and aerospace industries. Different methods for combining CNTs with Al powder were tested including high energy ball milling (HEBM), cryomilling, and wet chemistry methods. The powders were analyzed via scanning electron microscopy (SEM) to determine which method maximizes CNT dispersion while minimizing breakage or agglomerations. It was found that wet chemistry ultrasonication in acetone created a powder composite with the smallest CNT agglomerations. The HEBM at 1 to 2 ball to powder ratio (BPR) was the next best dispersion technique. The powders that demonstrate adequate dispersion were selected for cold spray onto 6061 aluminum alloy substrate bars. Cold spray has the distinct advantage of deformation at low temperatures avoiding the heat-induced defects inherent in welding. Composite powders of 1, 2, and 3 vol% CNT for the HEBM and the acetone dispersion techniques were mixed and cold sprayed. The cold-sprayed formulations were tested for corrosion and wear resistance. The deposition efficiency of these coatings, especially for the ultrasonicated powders, was extremely low and requires further parameter optimization to obtain usable mechanical performance results.				
14. SUBJECT TERMS cold spray, carbon nanotube, CNT, composite, metal matrix composite			15. NUMBER OF PAGES 81	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UU	

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18

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**ENHANCING DISPERSION OF CARBON NANOTUBES
WITHIN METAL MATRIX COMPOSITES**

Margaret C. Ruud
Lieutenant, United States Navy
BS, United States Naval Academy, 2018

Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

from the

**NAVAL POSTGRADUATE SCHOOL
June 2023**

Approved by: Troy Ansell
Advisor

Young W. Kwon
Second Reader

Brian S. Bingham
Chair, Department of Mechanical and Aerospace Engineering

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ABSTRACT

The dispersion of carbon nanotubes (CNTs) in an aluminum (Al) metal matrix composite (MMC) was explored in this thesis. CNTs have demonstrated strong and lightweight properties, making them a promising candidate for composite development in maritime, aeronautical, and aerospace industries. Different methods for combining CNTs with Al powder were tested including high energy ball milling (HEBM), cryomilling, and wet chemistry methods. The powders were analyzed via scanning electron microscopy (SEM) to determine which method maximizes CNT dispersion while minimizing breakage or agglomerations. It was found that wet chemistry ultrasonication in acetone created a powder composite with the smallest CNT agglomerations. The HEBM at 1 to 2 ball to powder ratio (BPR) was the next best dispersion technique. The powders that demonstrate adequate dispersion were selected for cold spray onto 6061 aluminum alloy substrate bars. Cold spray has the distinct advantage of deformation at low temperatures avoiding the heat-induced defects inherent in welding. Composite powders of 1, 2, and 3 vol% CNT for the HEBM and the acetone dispersion techniques were mixed and cold sprayed. The cold-sprayed formulations were tested for corrosion and wear resistance. The deposition efficiency of these coatings, especially for the ultrasonicated powders, was extremely low and requires further parameter optimization to obtain usable mechanical performance results.

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LIST OF ACRONYMS AND ABBREVIATIONS

Al	aluminum
AS	as sprayed
BPR	ball to powder ratio
CNT	carbon nanotube
CS	cold spray
DOD	Department of Defense
HAZ	heat affected zone
HEBM	high energy ball milling
MM	metal matrix
MMC	metal matrix composite
MWCNT	multi wall carbon nanotube
NAD	non-available days
OM	optical microscopy
PLA	polylactic acid
PVA	polyvinyl alcohol
SDBS	sodium dodecyl benzene sulfate
SEM	scanning electron microscope
SFC	salt fog chamber
SS	stainless steel
SWCNT	single wall carbon nanotube
US	ultrasonicated
WD	working distance
XRD	x-ray diffraction

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ACKNOWLEDGMENTS

I would like to start by expressing my deepest gratitude to Dr. Andy Nieto, my original thesis advisor. Dr. Nieto's guidance and support were invaluable to me during the early stages of my research. His passing was a great loss, and I will always remember him as a brilliant academic and mentor.

I would also like to thank Dr. Troy Ansell for taking over as my thesis advisor after Dr. Nieto's death. Dr. Ansell's expertise, patience, and encouragement were instrumental in helping me complete this work. I am grateful for his willingness to step in and support me during this challenging time.

Finally, I want to thank my husband, Brendan, for his unwavering love and support throughout my graduate studies. Brendan's encouragement, understanding, and patience helped me stay focused and motivated, even during the most stressful times. I am incredibly grateful for his presence in my life.

To all those who have supported me during this journey, I offer my heartfelt thanks.

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I. INTRODUCTION

A. MOTIVATION FOR ALUMINUM COMPOSITE COLD SPRAY COATINGS

Naval forces are operating in a corrosion-rich environment, which is constantly degrading metals with coastal salty and humid air [1], [2]. Corrosion issues cost the United States Department of Defense (DOD) \$20 billion annually and are the cause of 10% of non-available days (NAD) of DOD assets [3]. It is the cause of 31% of NAD for Naval Aviation [3]. Aluminum (Al) is primarily used in aviation because of its light weight and high specific strength [1]. It would be ideal to improve the corrosion and wear resistance to save money and increase operational readiness.

Aluminum cold spray (CS) composite coatings present a promising solution for meeting various requirements. These coatings offer superior corrosion resistance compared to bulk aluminum [4]. Carbon nanotubes (CNT) are a particularly appealing reinforcement material due to their exceptional mechanical, thermal, and electrical properties, as well as their low coefficient of thermal expansion and density [5]–[8]. CNTs have an electrical conductivity of around 10^3 S/cm and a thermal conductivity twice that of diamond (the well-known polymorph of carbon), around $1900 \text{ W m}^{-1} \text{ K}^{-1}$ [9], [10]. Moreover, CNTs exhibit a modulus of elasticity greater than 1 TPa and are 10–100 times stronger than steel [9]. For context, the elastic modulus of common structural steel is around 200 GPa, about 20% the theoretical value of CNTs. These enhanced properties include a high tensile strength and a high strength-to-weight ratio making it a prime candidate as a reinforcer for Al CS coatings [7]. However, there is a considerable lack of research on CS coatings of Al with CNT reinforcements. The use of cold-sprayed Al-CNT powder offers a potential solution for creating robust, lightweight, and corrosion-resistant coatings. Cold spray is an optimal fabrication technique, as it operates at lower temperatures, thereby protecting the properties and microstructure of the Al from secondary phase formation and the CNTs from oxidation and thermal degradation. It is also more energy-efficient and portable, making it an ideal choice for on-station operational repairs [11]–[14].

1. Applications

CS is an additive manufacturing technique. It does not require a vacuum or high heat to deposit a coating [11]. Handheld application of CS would be ideal in a forward operating environment to make quick repairs without pulling off station. It provides a method to repair corroded parts, which is a common issue in the Navy due to operating in a highly corrosive environment [15]. It could potentially be a replacement for some welding applications, which would prevent issues of heat affected zones (HAZ) that often degrade mechanical properties and increase corrosion potential of joined metals. It could even be a replacement for hull and component painting. Cold spray is of serious interest to the aerospace industry as it provides a process to dimensionally restore and protect components with a strong lightweight coating [12]. Aviation primarily uses Al alloys for fuselages and a large problem is crack growth which could be mitigated by using on-site cold spray guns to repair and prevent crack growth and prevent crevice and pitting corrosion [4]. Its portability and low operating temperatures make it a valuable and versatile tool. Cold spray, specifically CS of Al metal matrix composites (MMC), requires more research to properly leverage.

2. Properties of CNT Composites and Al CS Coatings

Many nanoparticles have impressive strength and other mechanical and thermal properties but have not been explored as a reinforcement particle in metals due to the high heat processing required and the difficulty of homogenous dispersion. CNTs have been used as a reinforcement in polymer composites due to the lower temperatures and ease of processing polymers [16], [17]. The results of polymer CNT composites have been remarkable with significant increases in tensile strength and tensile modulus [9],[18], [19].

B. THESIS OBJECTIVES

The goal of this thesis is to find an effective and efficient method to disperse CNTs within Al powder, then create CS coatings from this powder and test material properties to compare to a control CS coating of pure Al powder. Ideally, model a dispersion method to manufacture on a large scale. The dispersion is key to maximize the strength properties of

CNTs as a reinforcement in the CS coating. Wet chemistry and mechanical mixing dispersion will be compared by testing the material properties, including corrosion resistance, wear resistance, and micro hardness of the coatings. A microstructural analysis will be conducted to locate CNTs in the coating and how they affected the coating. Included in the comparison will be the feasibility of scaling the dispersion method.

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II. REVIEW OF THE STATE OF THE ART

A. COLD SPRAY

Cold spray (CS) is a solid-state additive manufacturing process utilizing a high-speed gas to accelerate micron-size powder particles at a substrate to deposit a coating [11]. This process is beneficial for retaining microstructure, mechanical and chemical properties of the feedstock, as well as protecting oxygen sensitive materials like Al because of the low amount of heat transfer into the feedstock powder particles and substrate [13], [14]. Figure 1 depicts the equipment and process of CS. The powder feedstock is comprised of either irregular or spherical particles around 15–45 μm in diameter [12], [20]. An inert compressed gas is used to accelerate the powder, usually nitrogen or helium to prevent chemical reactions [12]–[14]. Helium has been found to give denser coatings because of its low molecular weight it can reach higher velocities [12], [21], [22]. However, Nitrogen is preferred due to its significantly lower cost and availability [12]. The gas and powder are heated to augment flow and plasticity but always below the melting point of the powder [11], [13]. The converging diverging de Laval nozzle accelerates the particles to impact velocities around 200–1200 m/s [11], [23], [24].

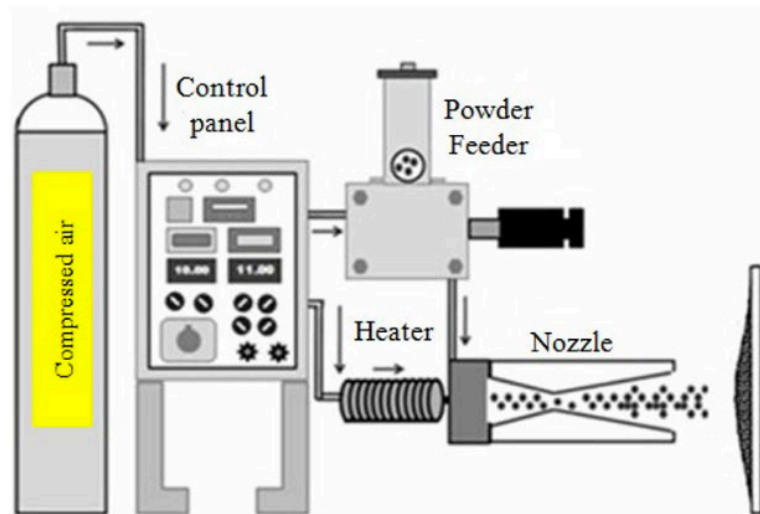


Figure 1. Low pressure CS equipment schematic. Source: [25].

The kinetic energy of the particle is converted into plastic deformation energy and heat upon impact [20]. The plastic deformation causes a high strain rate, thermal softening and adiabatic shear instability, which results in mechanical interlocking and metallurgical bonding of the feedstock powder to the substrate leaving a coating [11]. The high kinetic energy allows the particle to penetrate the substrate, breaking any oxide film on the surface. This creates contact between subsequent particles and the substrate, a necessity for metallurgical bonding [13], [14]. Successful bonding relies on exceeding the particles critical velocity which is dependent upon thermomechanical properties of the feedstock and substrate [23], [24]. If a particle is moving slower than the critical velocity it will either erode the substrate or rebound off, at or above critical velocity the particles will adhere to the substrate [13], [24]. The ideal situation is of soft feedstock on soft substrate, shown in Figure 2. The particle deforming and jetting into the substrate offers better adhesion to the substrate [20]. The exact mechanism of the bonding of CS interface is still under debate but it is clear that there is an optimum temperature and velocity required for effective bonding of the feedstock onto the substrate [20].

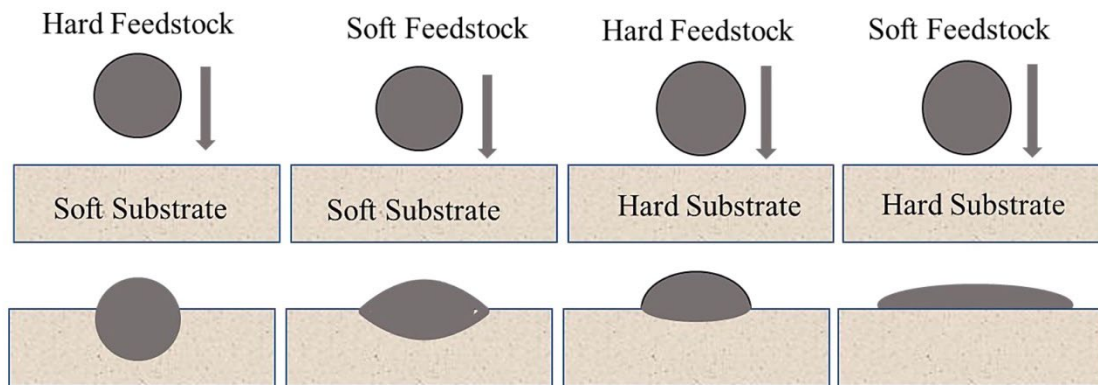


Figure 2. Schematic of different particle-substrate behaviors. Source: [20].

Spray parameters like temperature, and pressure effect bonding, adhesion, and deposition efficiency. Deposition efficiency is the ratio of the coating mass to the mass of powder sprayed onto the substrate [25]. Increasing the temperature of the gas increases the velocity of the gas and particles. This also increases the temperature of the particles which

softens them leading to more deformation at impact [20]. Increasing the pressure also increases the impact velocity [20]. These increases lead to improved bonding and adhesion and increased deposition efficiency [26].

B. CARBON NANOTUBES

There are two types of CNTs single walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT). MWCNTs have concentric tubes versus SWCNT only have one tube wall [7]. From this point forward MWCNTs will be referred to as CNTs. CNTs obtain their incredible material strength because they are built upon the carbon-carbon bond which is the strongest bond in nature [27]. The tensile strength of CNTs has been measured from 11–63 GPa, making it one of the strongest materials known to man [7]. Its unmatched strength matched with its low density makes it the ultimate fiber for composites [7]. Carbon covalently bonds with other carbon atoms. In a covalent bond atomic orbitals overlap, and they share electrons in a molecular orbit [28]. Carbon has six electrons, two in the first shell in the 1s orbital four in the second shell, two in the 2s orbital and two in the 2p orbitals which can hold six electrons so one p orbital is empty (sp_x , sp_y , and sp_z), shown in Figure 3.

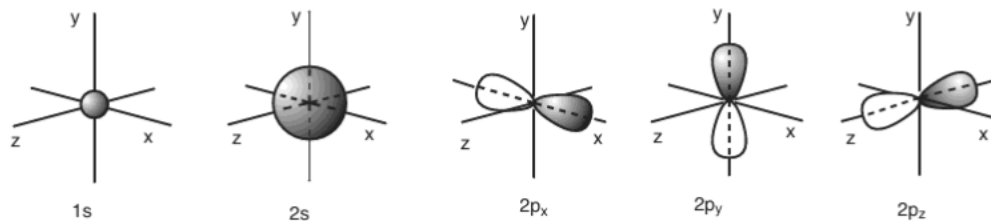


Figure 3. Atomic orbitals of carbon. Source: [28].

Carbon can hybridize its electron shells which allows it to bond with a multitude of materials in different orientations. Carbon can mix or hybridize its 2s orbital with all three 2p orbitals, two 2p orbitals or one 2p orbital called sp^3 , sp^2 and sp hybridization respectively [28]. CNTs are made up of aromatic rings, making honeycomb network of sp^2 hybridized carbon atoms [29]. Aromatic rings are comprised of six sp^2 hybridized carbon

atoms, each forming three sigma bonds, and a pi bond. A sigma bond is where orbitals overlap, and a pi bond is where orbitals overlap above and below the nucleus, shown in Figure 4. The sigma bond is stronger than the pi bond, this leads to high strength in plane with the rings of carbon [29].

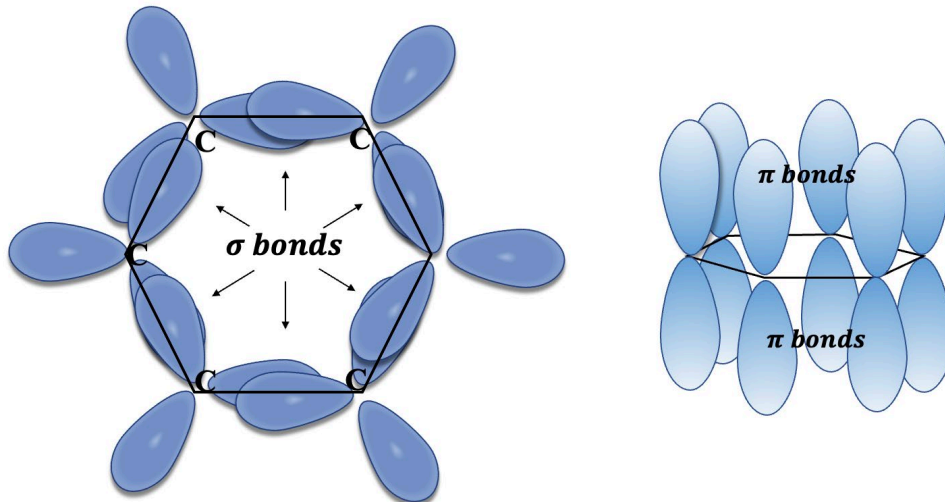


Figure 4. Hybridized orbitals sp^2 , sigma bonded and $2p_y$ orbitals bonded with pi bond

CNTs are essentially rolled tubes of graphene. Graphene is a sheet of carbon atoms arranged in honeycomb lattices [29]. Graphite is composed of sheets of graphene, graphite has weak interplanar pi bonding and strong sigma bonding in plane [29]. As seen in Figure 5 the molecular structure of a sheet of graphene is identical to a CNT, the CNT is just rolled into a cylinder. Like graphene, CNTs have weak surface bonding to other CNTs. However, they have a much greater surface area compared to graphene as well as the ability to be wrapped around and tied like hair, which is what causes them to agglomerate so easily [7]. In addition, CNTs are hydrophobic making water a poor solution for them [7].

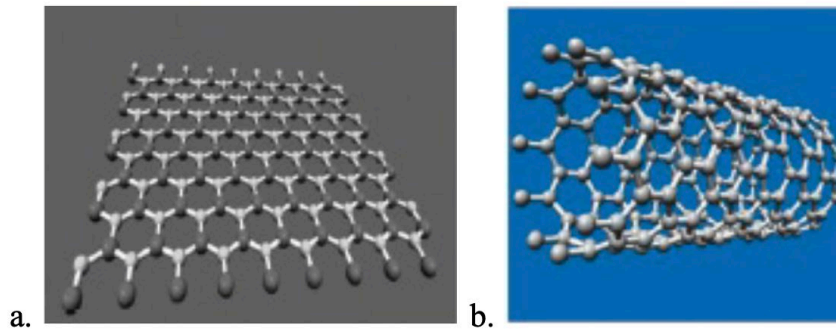


Figure 5. a. Graphene, b. Carbon nanotube. Source: [29].

C. HOMOGENOUS DISPERSION OF CARBON NANOTUBES

Dispersion is a crucial factor in composites because clusters of CNTs are not effective reinforcers. CNTs do not disperse well because of van der Waals forces and high aspect ratio [19], [30]. In general, a composite is a material comprised of a continuous matrix and a reinforcement material [27]. Material combinations are made to realize improved material properties. Usually, the goal of a composite is to combine the ductility of the matrix material with the strength of the reinforcement material. It is crucial to have adequate interfacial bonding between the reinforcement and the matrix for load transfer to occur [27]. If a reinforcer is not properly dispersed and adhered to the matrix, the load cannot be transferred from the weak ductile matrix to the strong reinforcement. Therefore, large clusters or agglomerations lead to a poor composite material, so it is critical that the CNTs are properly dispersed in the MMC [7].

1. Mechanical Mixing

High energy ball milling (HEBM) is a simple and effective method of mixing powders. Samples are mixed by placing them in a milling container with milling media and then rapidly shaking the container. The container and milling media are generally made from the same hard unreactive material, for example stainless steel (SS) or yttria (Y_2O_3) stabilized zirconia (ZrO_2). The inertia of the container transfers energy to the sample and milling media. This transfer and impact against the container walls can help to break up CNT agglomerations and disperse it within the metal powder [7]. The most important

parameter is the ball-to-powder ratio (BPR). A higher BPR means more energy is transferred, if the BPR is too high it can result in an increase in particle size and creation of small high aspect ratio flakes [31]. This can lead to the particles becoming too large for CS. Milling and rest duration also influences powder quality. More rest time between milling cycles allows heat to dissipate.

A similar technique to HEBM is cryogenic mechanical milling also known as “cryomilling” and is mechanical milling at cryogenic or sub-zero temperatures [7], [32]. Cryogenic temperatures are achieved by milling in a liquid nitrogen bath. The advantages of cryomilling over room temperature milling is that the lower temperature limits agglomeration, welding and oxidation of metal powders [32]. In addition, cryomilling can fabricate nanocrystalline Al which by the Hall-Petch relationship leads to a significant strength increase [32], [33]. Maiti et al. [32]. observed less CNT agglomeration in cryomilled Al-CNT compared to low energy ball milled Al-CNT, however there was more structural damage to the cryomilled Al-CNT composite.

2. Wet Chemistry

CNTs have been successfully dispersed in aqueous suspensions by ultrasonication with different surfactants and solvents [34]–[37]. Ultrasonication works by generating sound waves in a liquid that causes acoustic cavitation, or the rapid growth and collapse of bubbles, from the pressure differentials [35]. The shear forces from the cavitation phenomena break up CNT agglomerations [35]. There are several types of ultrasonication: probe and bath. Probe sonication uses a resonator connected to a transducer and finally a rod or tip directly in the liquid. In a bath set up the ultrasonic waves are transferred to the liquid through the tank walls. The probe method allows for a much higher power density but can cause damage to the CNTs [35].

CNTs have been sonicated in solutions with different surfactants to create more dispersed suspensions. Surfactants are amphiphilic molecules meaning they have a hydrophobic and a hydrophilic part [28]. Surfactants usually align themselves at air water interfaces with the hydrophobic tail in the air and the hydrophilic head in the water. These

work well for CNTs because the hydrophobic tail can attach to hydrophobic CNTs, instead of air and the head attaches to water molecules, therefore deagglomerating the CNTs.

Jiang et al. [34]. used a surfactant called sodium dodecyl benzene sulfate (SDBS) to disperse the CNTs. The Al surface was modified with polyvinyl alcohol (PVA) as shown in Figure 6 to increase the absorption of CNTs onto the Al [34]. The CNTs are dispersed with the agitation from the ultrasonic bath and with the aid of SDBS. It is difficult to disperse CNTs in just water because they are hydrophobic, in water they just agglomerate more. The surfactant gives them another hydrophilic item to latch onto instead of just other CNTs. Jiang et al. [34]. were able to disperse up to 20 vol% CNTs in an Al matrix. They were able to accomplish this by using functionalized CNTs which have more bonds that can attach to PVA and by using Al flakes. The flakes had a larger surface area and the flat morphology aided in the ability to uniformly disperse such a high-volume percentage of CNTs. This is not applicable for CS because the Al flakes would clog the line and nozzle.

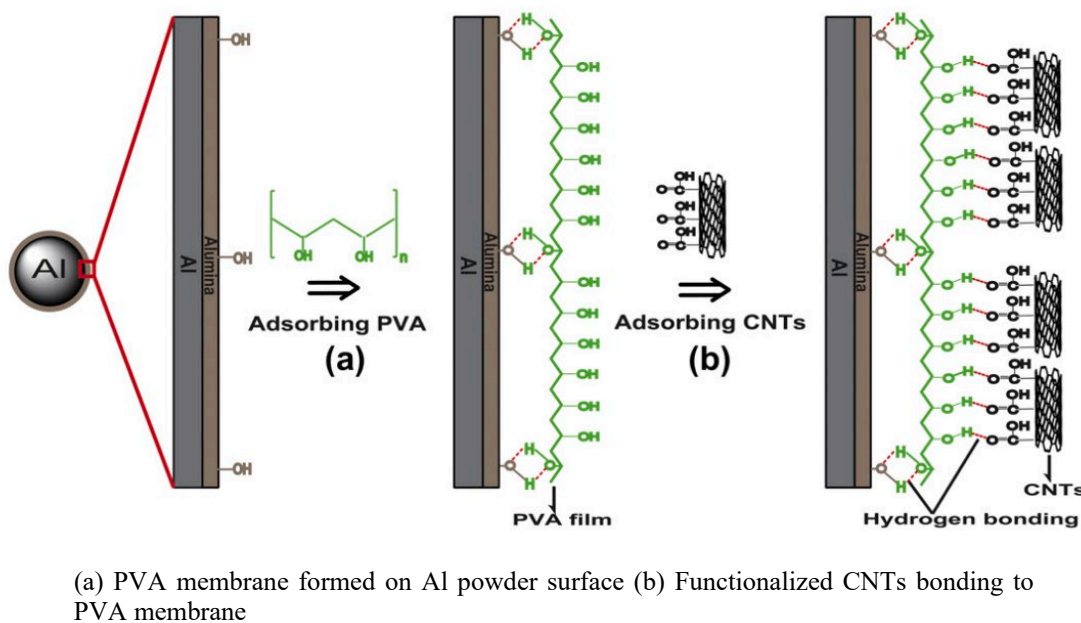


Figure 6. PVA Al CNT attraction. Source: [34].

Functionalized CNTs have functional groups added to their surface to aid in dispersibility [38]. Covalent functionalization involves the direct addition of functional

groups to the sidewalls or ends of the CNTs [38], [39]. The CNTs are treated with a strong acid to shorten and remove end caps of the CNTs and add oxide groups to the defect sites and ends as shown in Figure 7 [9]. Functionalizing CNTs is done to improve the interfacial bonding between the CNTs and the composite matrix. Noncovalent functionalization refers to using surfactants to coat the surface of the CNTs but bonding only noncovalently [9]. Chen et al. [38]. used thermal functionalization, raising the CNTs to high temperature, as an alternative to acid treatments with positive dispersion results.

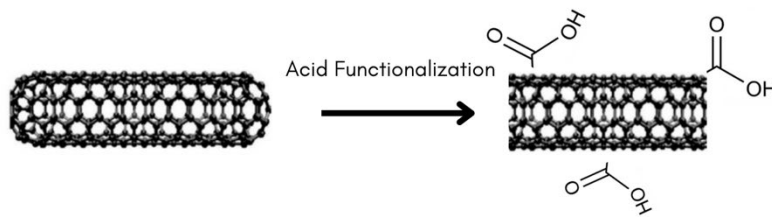


Figure 7. CNT acid functionalization. Adapted from [9].

III. EXPERIMENTAL PROCEDURE

A. MATERIALS

The base powder for all Al-CNT trials used was pure aluminum described Table 1. The as received powder is varying in shape and size as shown in Figure 8.

Table 1. Aluminum powder specifications

Composition	Size [μm]	Composition	Density [g/cm ³]	Vendor	Identification
Al	5–45	Al	2.66	Centerline	SST-A5001

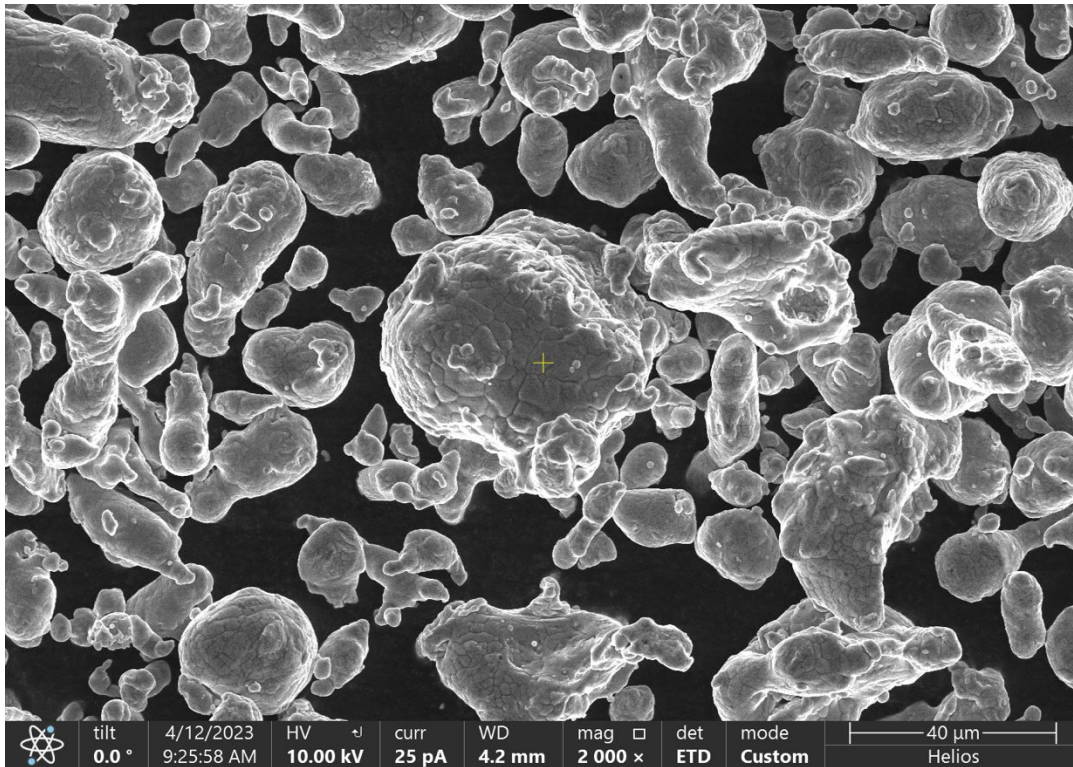


Figure 8. SEM image of as received Al powder

The reinforcement used were CNTs as described in Table 2. The as received CNTs are in Figure 9, the left-hand image shows the extreme agglomerations prior to any processing.

Table 2. CNT specifications

Composition	Diameter [nm]	Length [μm]	Density [g/cm^3]	Vendor	Identification
C	10–20	10–30	2.1	Cheap Tubes Inc.	CAS: 308068-56-6

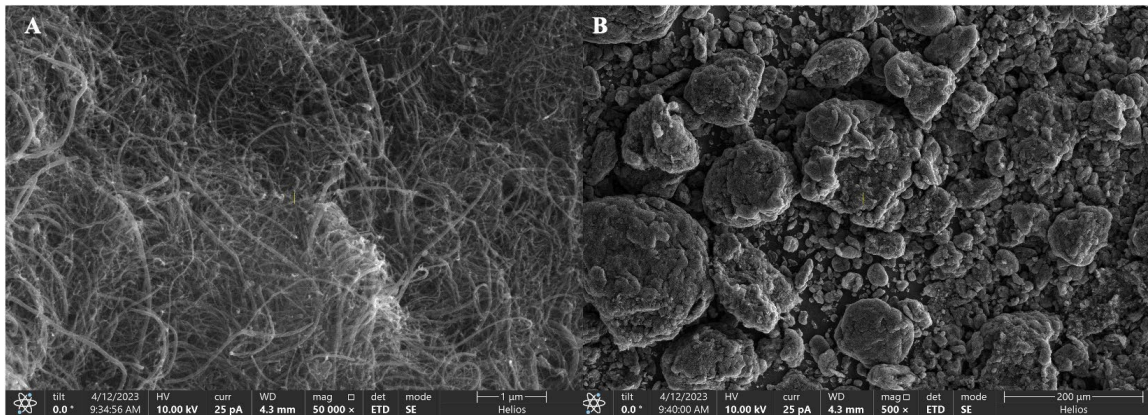


Figure 9. SEM image of as received CNT agglomerations a) higher magnification b) lower magnification

The dispersing agents tested were DI water, SDBS, PVA and acetone. All dispersing agents were tested on CNTs alone to create aqueous suspensions. SDBS and PVA were tested together following a procedure done by Jiang et. al [34]. SDBS is an anionic surfactant, its molecular structure is shown in Figure 10. SDBS noncovalently functionalizes the CNTs allowing them to be put in an aqueous suspension.

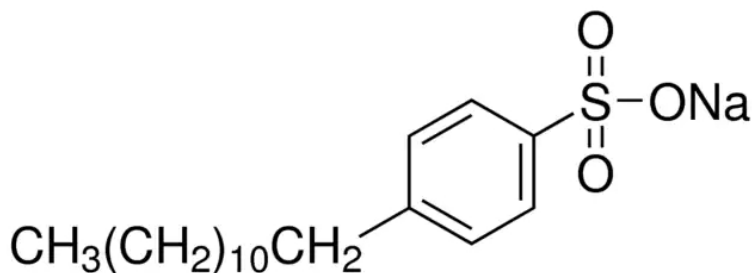


Figure 10. SDBS molecular structure, anionic surfactant. Source: [40].

PVA is a hydrophilic polymer used to modify the Al surface so more CNTs can be absorbed [34]. PVA has a simple molecular structure as shown in Figure 11. PVA also has excellent film forming properties [34]. Which is why it was also used to create an aqueous suspension of CNTs attempting to noncovalently functionalize the CNTS. Ultimately, PVA was not used in the final powder synthesis due to the difficulty of removal.

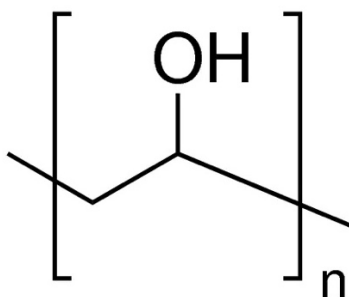


Figure 11. PVA structure. Source: [41].

Acetone was also used to disperse CNTs in an aqueous solution. Kwon et. al. tested ethylene glycol and acetone to disperse CNTs on a polymer joint [17]. In their study the ethylene glycol was the slightly better dispersing agent; however, it leaves a residue after evaporation which led them to choose acetone as their dispersing agent [17]. In this study, acetone was also chosen as the ultimate dispersing agent due to its dispersing performance and ease of removal with no residue.

B. CNT DISPERSION AND POWDER SYNTHESIS

1. Cryogenic Milling

Four powders were synthesized in the Spex 6870 Freezer/Mill shown in Figure 12. All the same composition of 1 vol% CNTs with varying numbers of cycles as shown in Table 3.

Table 3. Cryogenic milling parameters

Mass of powder	Composition	Milling Media	Bath	Run Rest time	Number of Cycles
25 g	1 vol% CNT 99 vol% Al	SS Impactor	Liquid Nitrogen bath	2 min on 2 min off	1,2,3,5



Figure 12. Spex 6870 Freezer/Mill. Source: [42].

2. High Energy Ball Milling

Three powders were synthesized using HEBM parameters listed in Table 4 at 1 vol%, 2 vol%, and 3 vol% CNT-Al composite powder. 1 to 5 BPR and 1 to 3 BPR were tested but 1 to 2 gave the best dispersion.

Table 4. HEBM parameters

Mass of powder	Milling Media	Containment	BPR	Run Rest time	Number of Cycles
50 g	3 mm 504 SS balls	SS Jar	1:2	5 min on 5 min off	10



Figure 13. Spex 8000D Dual Mixer/Mill. Source: [43].

3. Ultrasonication

All wet chemistry techniques utilized bath ultrasonication. Ultrasonication was conducted in a Fisherbrand 11209 series Advanced Ultrasonic Bath. Initial CNT dispersion tests using DI water, SDBS, PVA and acetone were conducted and compared. Success was dependent upon getting an inky black solution after ultrasonication. Acetone trials were

done to determine the highest concentration of CNTs that still resulted in a successful suspension to use the smallest amount of acetone.

a. PVA Dispersion Method

Jiang et al. [34]. demonstrated a slurry-based dispersion method, which was used to create Al-CNT powder that was later analyzed in XRD. The process involved initially dispersing the CNTs by sonicating them in a 1.5 wt.% SDBS aqueous solution for 2 hours. Al powder was stirred in a 3 wt.% PVA aqueous solution for 1 hour then filtered and rinsed with DI water. This step is to obtain Al powder with a PVA membrane as shown in Figure 6. The CNT SDBS solution was then added to the Al-PVA slurry. The slurry was then mixed for 2 hours. The goal was for the solution to change from black to transparent indicating that the CNTs attached to the Al, but this color change did not occur. This was due to the difference in CNTs. Jiang et. al. used functionalized CNTs which have been modified to be more reactive, so they attach to the Al-PVA membrane. The Al-PVA-CNT slurry was slowly dried in a furnace at 70 °C. The PVA was then removed via pyrolysis. The dried Al-PVA-CNT powder was heated to 500 °C for 2 hours under flowing argon. The post-pyrolysis powder was a deep brown color compared to the original light gray powder. This powder was not used to create any coatings.

b. Acetone Method

The alternative method was sonicating CNTs in acetone. Acetone is not the best dispersing medium for CNTs, but it is the simplest to remove with no residue. The CNTs were sonicated in acetone for 30 minutes at a concentration of 9.8 mg/ml. Then the Al was added and stirred while sonicating continued for an additional 30 minutes. This slurry evaporated under a fume hood until dry, which takes approximately 24 hours. Three powders were synthesized using this method 1 vol%, 2 vol%, and 3 vol% CNT-Al composite powder.

C. COLD SPRAY

CS coatings for the control, and all HEBM samples and the 1 vol% CNT ultrasonicated (US) were created using the parameters listed in Table 5.

Table 5. CS parameters control and HEBM samples

Pressure	Temperature	Feed Rate	Traverse Speed	Passes	Gas	Stand-off Distance
1.65 MPa (240 psi)	425°C	5 % (4.28 g/min)	40 mm/s	2	Nitrogen	12.7 mm

The 2 and 3 vol% CNT U.S. powders had issues with clogging and reduced deposition efficiency. The parameters were optimized to attempt to create coatings with similar thicknesses to the control and the HEBM samples. The traverse speed was reduced significantly to increase deposition efficiency and coating thickness as shown in Table 6.

Table 6. CS parameters U.S. samples

Pressure	Temperature	Feed Rate	Traverse Speed	Passes	Gas	Stand-off Distance
1.65 MPa (240 psi)	425°C	5% (4.28 g/min)	10 mm/s	2	Nitrogen	12.7 mm

D. MECHANICAL TESTING

1. Wear Track

Dry sliding ball-on-disk wear testing was conducted three times on each coating. Each coating had a series of three wear tests conducted. All wear tests were conducted on a standard modular tribometer, specifically the Nanovea T50. The tests were conducted with the parameters outlined in Table 7. Each test's mass loss, the coefficient of friction and the decoder depth were recorded. Wear tracks were also examined using optical profilometry to obtain more accurate depth readings to calculate the specific wear rate.

Table 7. Wear test parameters

Test type	Counter Surface	Load	RPM	Duration	Wear track Diameter
Ball-on-disk	3 mm SS 304 ball	1 N	100	1 hour	3 mm

2. Corrosion

A 2000 hr corrosion test was conducted using the MX-9204 salt fog chamber (SFC) with a 3.5 wt.% NaCl aqueous solution, which is the average salinity of seawater, to simulate a marine environment. Corrosion tests were conducted in accordance with ASTM B117 [44]. Custom 3D printed polylactic acid (PLA) trays were used to hold the samples in the chamber. The PLA trays have a drainage cavity to prevent immersion and hold the samples at a 20-degree angle from the vertical. Mass measurements were collected on a weekly basis.

E. CHARACTERIZATION

1. X-Ray Diffraction

For x-ray diffraction (XRD) analysis, the powdered sample was sprinkled onto double-sided carbon tape until completely covered. A fine powder is desirable because the substantial number of random orientations ensures that at least some of the sample will have the correct orientation to produce constructive interference. It was then loaded into a Rigaku MiniFlex 600 XRD with an ASC-6 attachment. The samples were then subjected to a continuous scan of Cu K α X-rays (40 kV and 15 mA), ranging from 10–100 degrees with a speed of 5 degrees/min. The peak intensities for the angles measured were then processed, and the qualitative analysis provided the likely elements present based on the crystal structures determined by relating the peak locations with a database of existing information.

2. Sample Preparation

Each sample was cross sectioned, cutting perpendicular to the coating and cold mounted in epoxy. The epoxy used was Stuers ClaroCit clear acrylic with silicon molds.

Once mounted the samples were ground and polished to a mirror finish to expose microstructural details under the optical microscope. Samples were ground and polished according to the parameters in Table 8.

Table 8. Grinding and polishing steps

Step	Grit/Solution	Time [min]	RPM
1	320	5-10	250
2	600	10-15	250
3	800	10-15	250
4	1200	15-20	250
5	3 μ m Diamond	5-10	250
6	1 μ m Diamond	5-10	250

After grinding and polishing the samples were etched using Keller's reagent (2.5 vol% nitric acid, 1.5 vol% hydrochloric acid, and 1 vol% hydrofluoric acid in water). The reagent was applied with a cotton swab and left on for 30 seconds then rinsed with DI water. This was done to corrode the splat boundaries so they would be visible in the OM and SEM [45].

3. Microscopy

All the powders and coatings were imaged using a scanning electron microscope (SEM). The SEMs used were the Zeiss Neon 40 SEM and the Helios 5-UX Thermo-Fisher Scientific. Powder samples were applied to double-sided carbon tape and mounted on stubs. The epoxy mounted coating samples were sputter coated to improve resolution. Sputter coating was done with the Cressington Sputter Coater 208HR under an argon vacuum. The images were taken with a working distance (WD) of about 4 mm, electron potential (or high voltage) = 5 kV, and an aperture of 30 μ m. Optical microscopy (OM) was also conducted on epoxy mounted CS coating samples and corrosion samples.

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IV. RESULTS AND DISCUSSION

A. CNT DISPERSION

Initial sonication tests were conducted with DI water, PVA, and SDBS with different amounts of CNTs. The goal was to create a long-lasting ‘inky black’ aqueous suspension of CNTs. The blacker the solution the better dispersed the CNTs. DI water could disperse small amounts of CNTs if sonicated for 90 minutes, but they would fall out of suspension in under 30 minutes. Figure 14 compares the DI water suspension of 0.01 g of CNT to an equivalent amount in a 1.5 wt. % PVA solution, 30 minutes after sonication. The CNTs in the DI water quickly agglomerate and sink. Since DI water could not maintain a suspension of CNTs, it was eliminated as a dispersion solvent.



Figure 14. Left DI water CNT suspension, right PVA 1.5 wt.% CNT suspension

Acetone, PVA and SDBS proved to be effective in producing stable and long-lasting solution CNT suspensions. It should be noted that following the process proposed by Jiang et. al., only involved treating the Al with PVA. In this study; however, PVA was tested as dispersion method in combination with an Al surface treatment [34]. After

sonication the Al powder was added and stirred and then evaporated to get a composite Al-CNT powder. The PVA-SDBS solutions resulted in a product found to be unusable for CS as it failed to retain its powder form. The PVA would polymerize during evaporation and made it difficult to remove the mixture from the jars as shown in Figure 15. In addition, it required a heat treatment under flowing argon to remove it.



Figure 15. Polymerized PVA

Dispersion in acetone compared to DI water is shown in Figure 16. Thirty minutes after sonication, the CNTs stayed in suspension in the acetone where in the DI water they quickly fell out of suspension.



Figure 16. DI water and CNTs on left, acetone and CNTs on right

Upon reflection, it became clear that a simpler approach using acetone to disperse the CNTs from the remaining mixture would be more effective for producing the desired powder form for use in CS. However, it should be noted that the use of PVA or SDBS could still be desirable in other processes such as sintering or filament creation for additive manufacturing.

B. POWDER ANALYSIS

CNT agglomerations for each dispersion technique were measured using ImageJ. The three largest agglomerations were found in the SEM and then the longest vertical and horizontal projection were measured and averaged. This was to obtain a rough estimate on agglomeration size to narrow down which dispersion techniques would be used to create CS coatings. The results of these measurements are listed in Table 9. The methods with the smallest agglomeration sizes were the HEBM with a BPR of 1 to 2 and the acetone sonication.

Table 9. CNT agglomeration measurements

Dispersion Technique	Average Agglomeration Size (μm)
HEBM BPR 1 to 2	56.89
HEBM BPR 1 to 3	76.08
HEBM BPR 1 to 5	159.55
Cryogenic Milling	174.94
Acetone Sonication	12.39

1. Cryogenic Milling

Cryogenic milling was tested at 1, 2, 3 and 5 cycles. At 5 cycles large Al flakes around 600 μm formed as shown in Figure 17. The CNT agglomerations found were also the largest of all methods. The largest agglomeration seen in Figure 18 was over 300 μm in the three-cycle sample. The large flakes and large agglomerations eliminated it as a viable dispersion method for CS coatings.

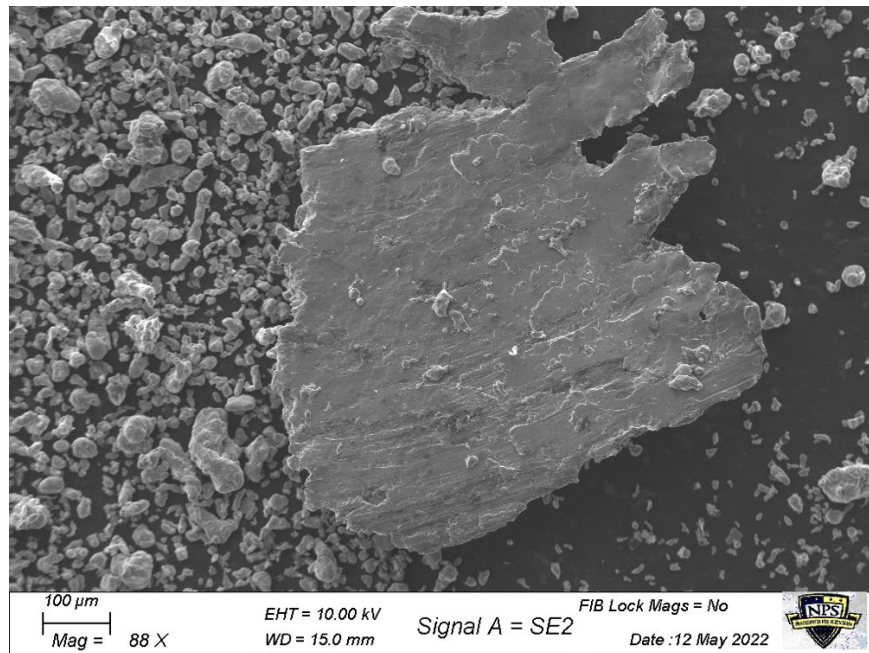


Figure 17. Al flake, 5 cycles cryomilled

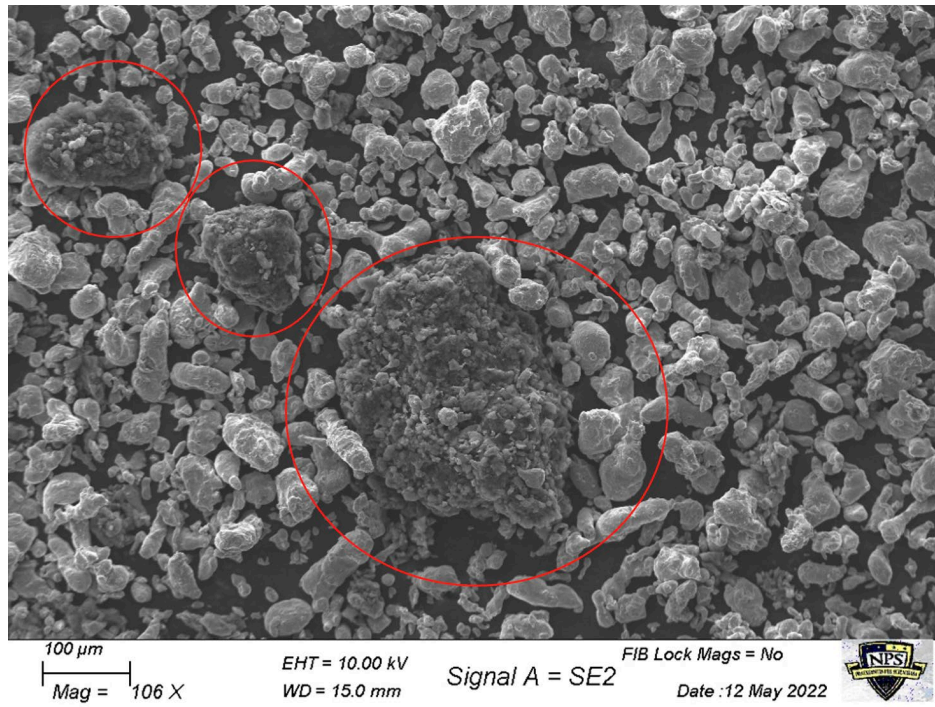


Figure 18. CNT agglomerations, 3 cycles in cryomilled

2. HEBM

The lowest intensity BPR tested was 1 to 5 and it resulted in large CNT agglomerations. The goal was to find a BPR that could disperse the CNTs but not cause particle growth by cold welding of the Al or severe deformation of the Al particles. Figure 19 shows an agglomeration over 200 μm in horizontal and vertical projection the largest agglomeration across BPRs. In Figures 19–22 the high magnification in all of the HEBM samples show the tightly bonded and entangled CNT agglomerations very similar to the AR CNT agglomerations. This is pointing to the fact that mechanical mixing is limited in its ability to break the van der Waals forces holding the CNTs together.

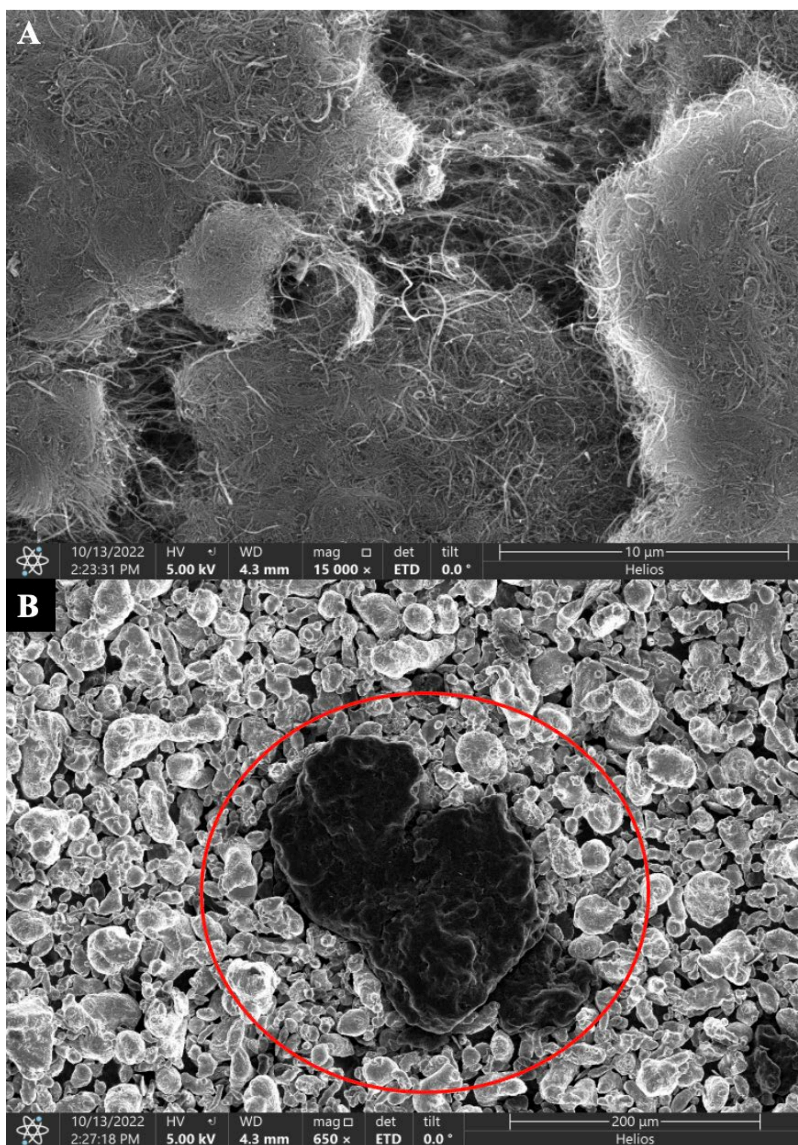


Figure 19. BPR 1 to 5 CNT agglomeration a) high magnification of agglomeration b) low magnification of agglomeration

The next BPR tested was 1 to 3 to put more energy into the system to break up the CNT clusters. As seen in Figure 20, one of the larger agglomerations was approximately half of the size of the 1 to 5 agglomerations at around 100 μm . Another promising aspect was CNTs were found attached to the Al particles as shown in Figure 21.

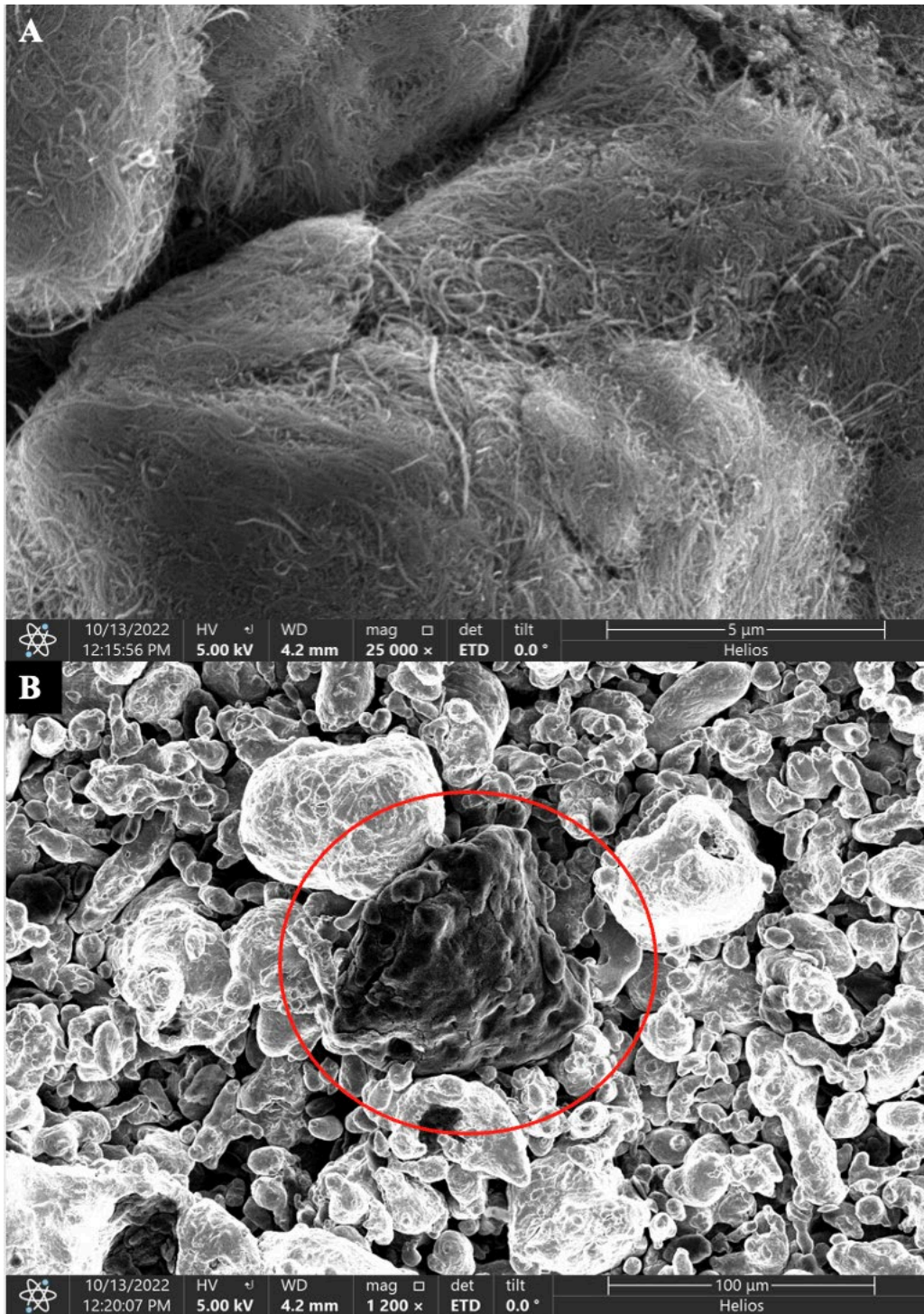


Figure 20. BPR 1 to 3 CNT agglomeration a) high magnification of agglomeration b) low magnification of agglomeration

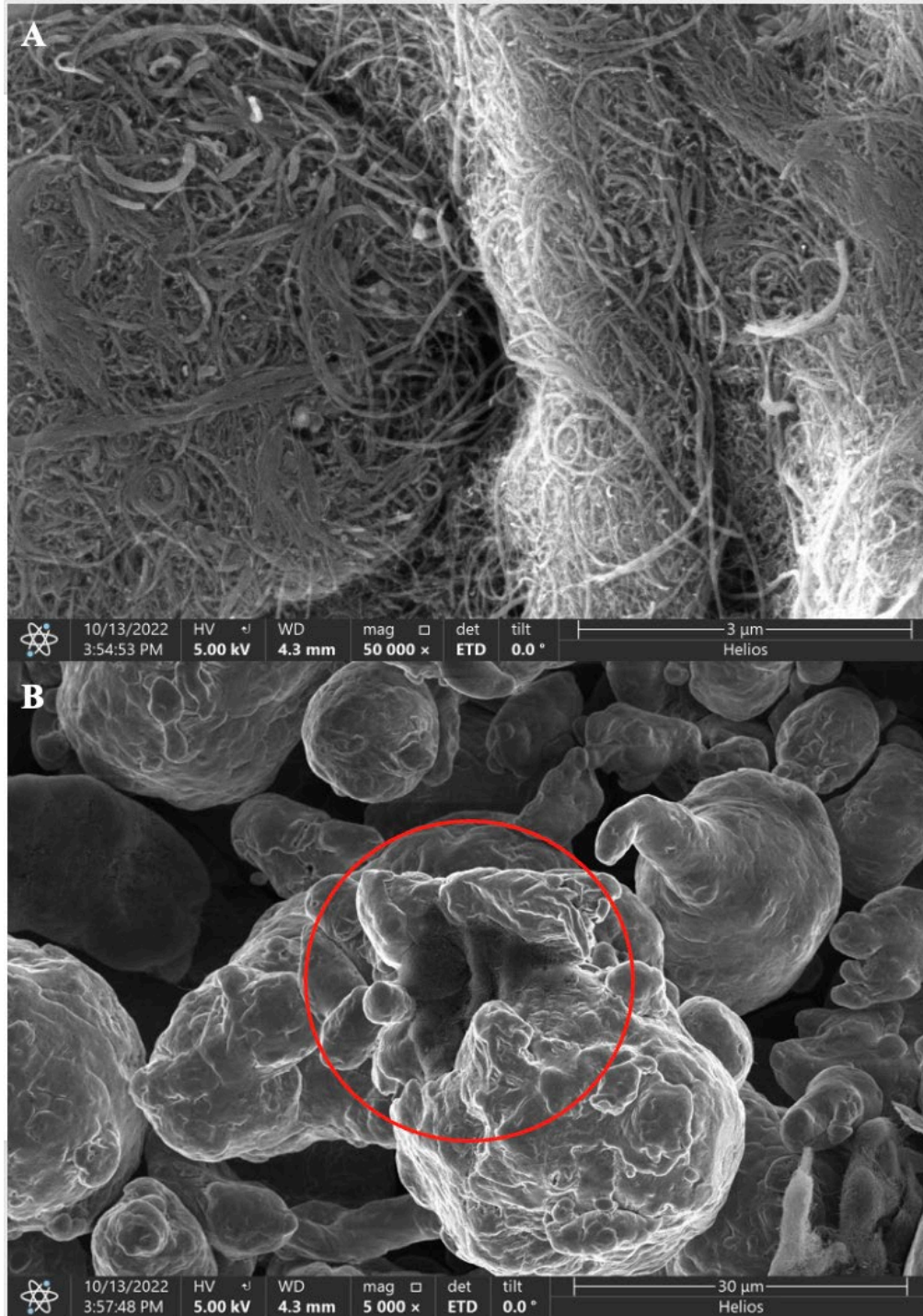


Figure 21. BPR 1 to 3 CNT cluster attached to Al particle a) high magnification of cluster b) low magnification of cluster.

The Al particles weren't cold welding at 1 to 3 BPR, so to disperse the CNTs more effectively, a BPR of 1 to 2 was tested. Once again, the CNT agglomeration size was reduced. As seen in Figure 22, one of the largest CNT agglomerations was around 60 μm . The 1 to 2 BPR was the best dispersion between HEBM samples due to the smaller CNT agglomerations.

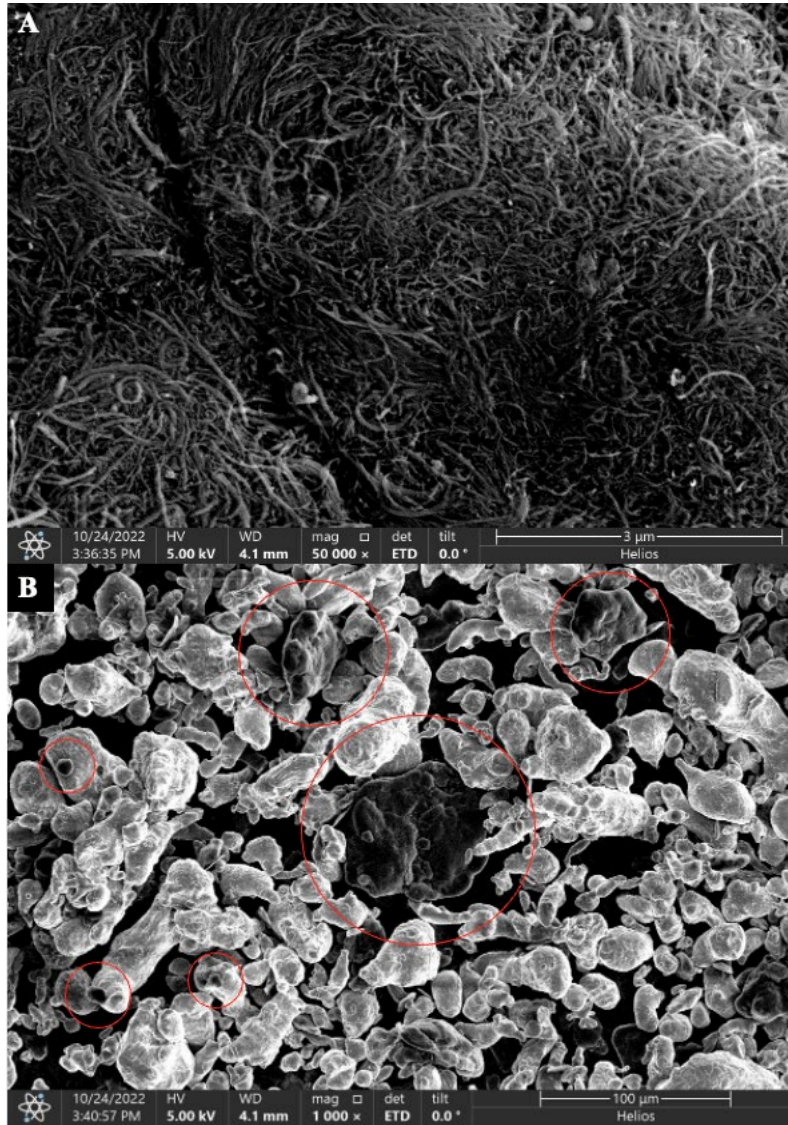


Figure 22. BPR 1 to 2 CNT agglomerations a) high magnification of agglomeration b) low magnification of agglomeration

3. Acetone Ultrasonication

The acetone ultrasonication method demonstrated superior performance in reducing CNT agglomeration size compared to both HEBM and cryogenic milling. Additionally, the acetone method resulted in the loosening of CNT agglomerations. Figure 23 and Figure 24 display single CNTs attached to the Al surface. The CNTs are significantly different from the AR CNT agglomerations with some of the CNTs completely separated from clusters and attached the Al surface.

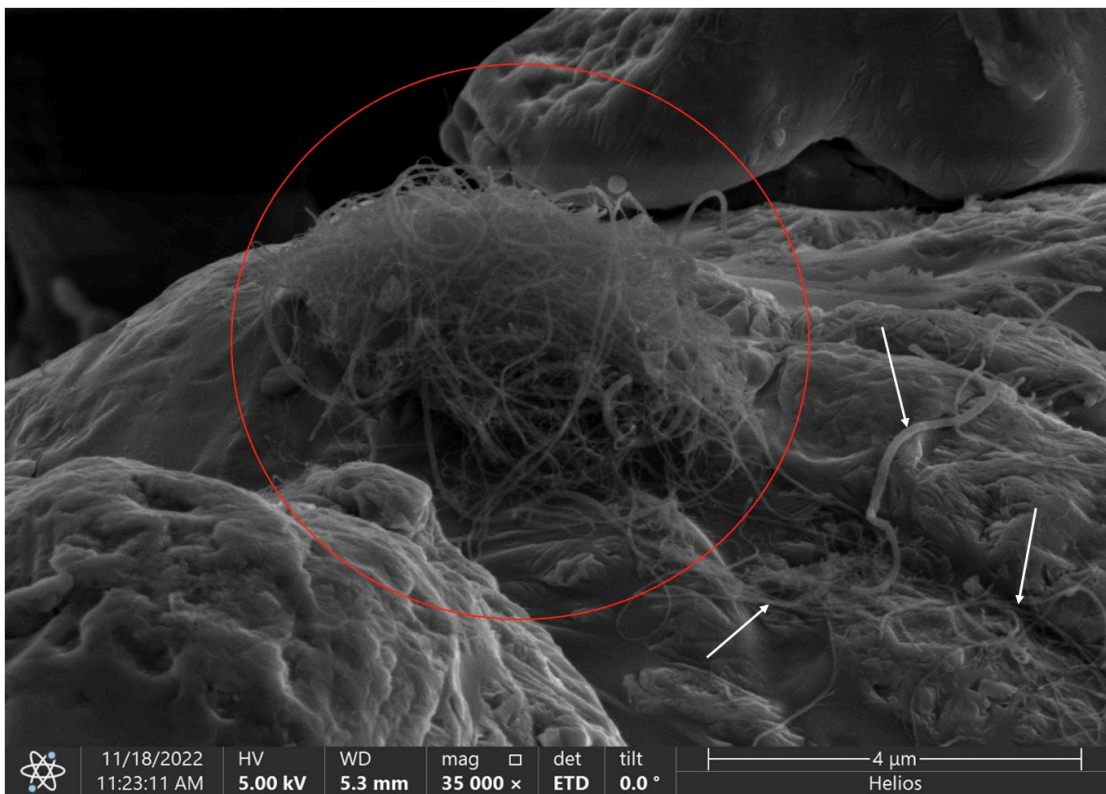


Figure 23. Acetone CNT Al powder, CNT cluster circled some CNTs on Al surface indicated with arrows

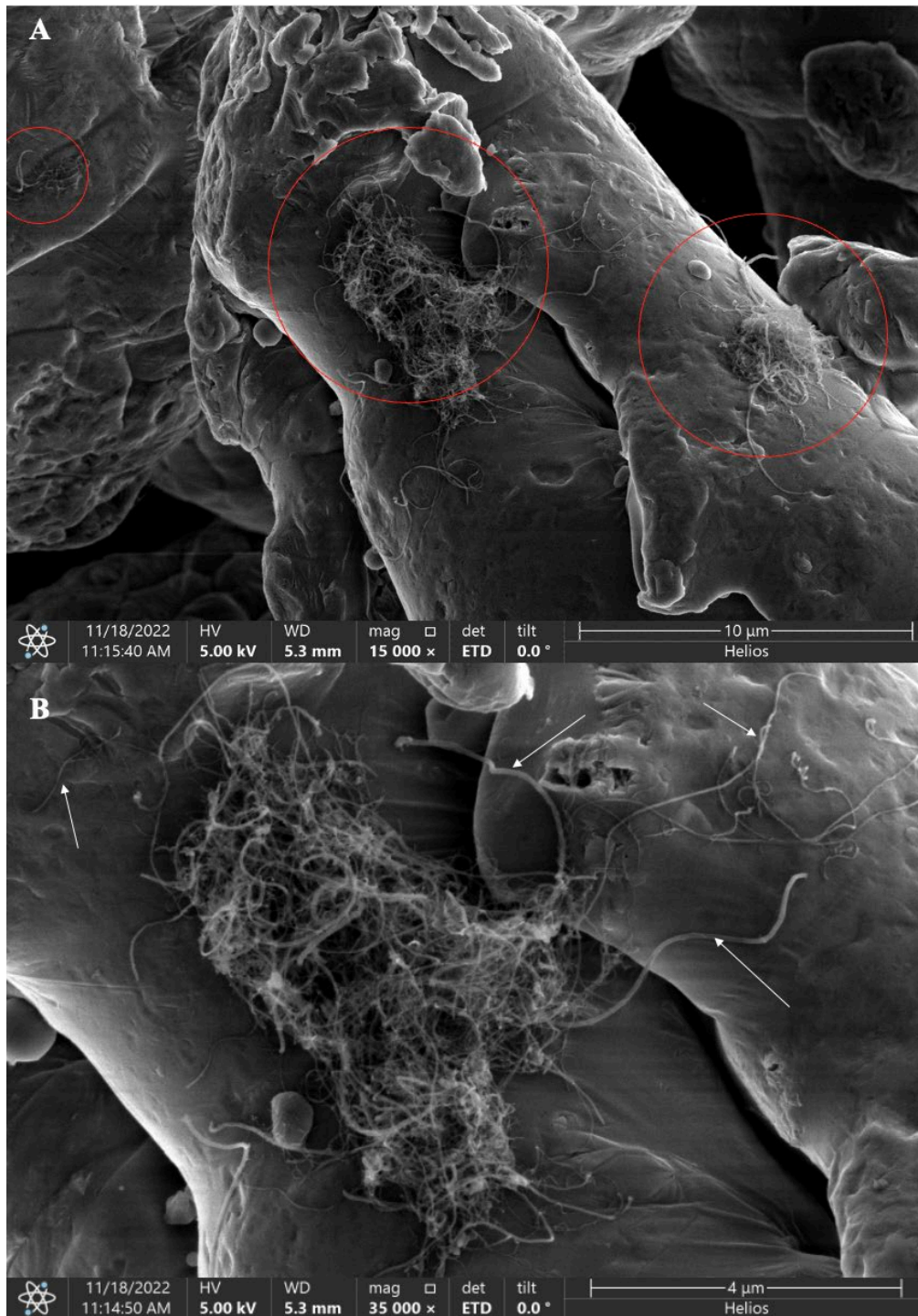


Figure 24. Acetone CNT Al powder a) low magnification clusters circled b) high magnification CNTs indicated with arrows

4. PVA SDBS Al-CNT

A powder was created following Jiang et. Al.'s process of sonicating CNTs in SDBS and then mixing with PVA treated Al [34]. Jiang et. Al. used functionalized CNTs which are more effective to attach to the PVA treated Al. The CNTs used in this study were not functionalized and did not attach to the Al the same way. After mixing the CNT solution and the PVA treated Al slurry, the CNTs should have attached to the Al. This would have been indicated by the black solution turning transparent but the CNTs stayed in suspension. This is attributed to using non-functionalized CNTs because of their lack of added functional groups they weren't attracted to the PVA treated Al. The solution was then evaporated in a furnace. The PVA polymerized and was removed from the jar, it was then ground up using a mortar and pestle. This powder underwent the heat treatment under flowing argon to remove the PVA.

The post heat treatment powder was analyzed using XRD for trace amounts of PVA left over after the heat treatment. Most of the material was aluminum with trace amounts of carbon in the form of graphite-2H, with peaks 1 and 3 corresponding to graphite-2H and peaks 2, 3, 5, 7, and 8 corresponding to Al. In addition, three unidentified peaks were recorded with low intensities at peaks 4, 6, and 9, with diffraction angles of 45.94, 67.13, and 99.117, respectively. It is possible the unknown peaks are products from the chemical breakdown of the PVA. The peak information is listed in Table 10. Figure 25 shows the plotted data along with peaks corresponding with the Al crystal structure or carbon. It is assumed that the graphite peaks are identifying CNTs. This powder was found unusable due to the extra steps of the PVA removal and the non-functionalized CNTs not attaching to the Al. This process has no way to scale up to create large amounts of powder for CS.

Table 10. XRD peaks

Number	2 θ (deg)	Height (cps)	Phase Name
1	26.823 (17)	891(86)	Graphite-2H (0,0,2)
2	38.6025 (9)	136121(1065)	Aluminum, syn (1,1,1)
3	44.838 (10)	63581 (728)	Aluminum, syn (2,0,0), Graphite-2H (1,0,1),
4	45.94 (5)	855 (84)	Unknown
5	65.1859 (9)	45241 (614)	Aluminum, syn (2,2,0)
6	67.13 (6)	616 (72)	Unknown
7	78.2908 (10)	50413 (648)	Aluminum, syn (3,1,1)
8	82.5000 (15)	15213 (356)	Aluminum, syn (2,2,2)
9	99.117 (3)	5904 (222)	Unknown

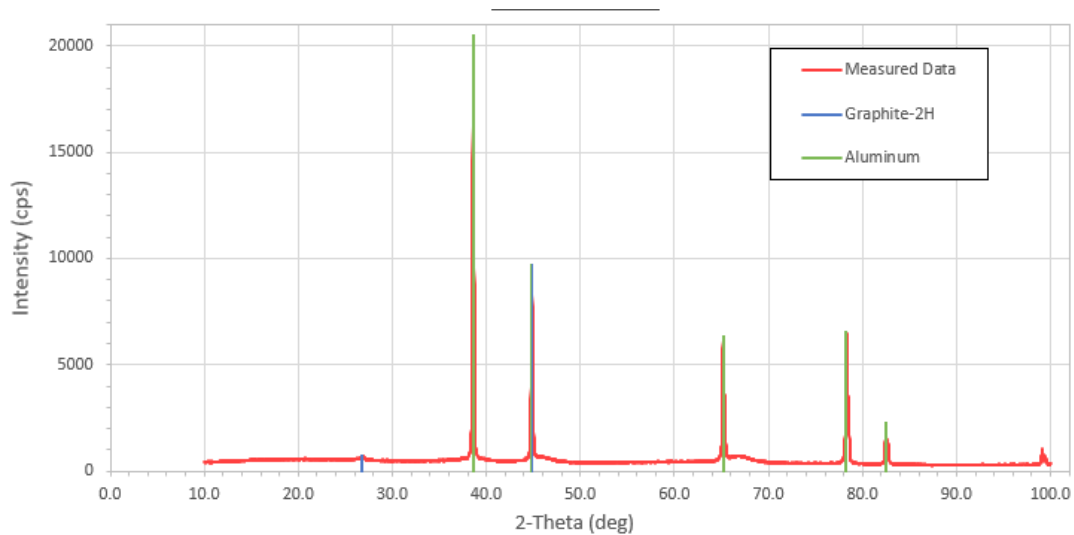


Figure 25. Plotted XRD data for Al-CNT-PVA powder

C. COLD SPRAY MICROSTRUCTURAL ANALYSIS

The thickness of each coating was measured on OM images using ImageJ. Each coating had at least ten thickness measurements across three different frames. The average thickness for each coating is listed in Table 11.

Table 11. Average coating thickness

Sample	Average Thickness [μm]	Range [μm]	Standard Deviation [μm]
Al Control	210.35	28.9–339.2	112.03
HEBM 1 vol% CNT	172.92	131.17–212.93	17.38
HEBM 2 vol% CNT	59.15	28.44–99.59	15.83
HEBM 3 vol% CNT	94.13	57.77–125.49	18.76
US 1 vol% CNT	47.052	18.97–76.29	13.62
US 2 vol% CNT	21.10	8.19–44.39	9.05
US 3 vol% CNT	22.63	7.12–40.63	8.42

The ultrasonicated powders resulted in the formation of the thinnest coatings, which aligns with the reduced deposition efficiencies (DE) observed for these powders. DE values were determined by dividing the coating mass by the mass of the powder sprayed. It should be noted that although the powder was collected, there were inherent losses such as overspray and powder remaining in the line, which were estimated at 15% for each run and was subtracted from the measured powder sprayed. The coating mass was calculated by measuring the weight of the substrate before and after spraying. The coating mass was then divided by the mass of powder sprayed to determine the deposition efficiency. The deposition efficiencies are presented in Table 12.

Table 12. Cold spray deposition efficiency

Sample	Deposition Efficiency (DE)
Al Control	13.6 %
HEBM 1 vol% CNT	13.0 %
HEBM 2 vol% CNT	7.6 %
HEBM 3 vol% CNT	9.0 %
US 1 vol% CNT	2.9 %
US 2 vol% CNT	1.9%–5.6%
US 3 vol% CNT	0.8 %

To improve the deposition efficiency, the traverse speed was lowered for the ultrasonicated samples containing 2 vol% and 3 vol% of CNTs. The initial deposition efficiency for the ultrasonicated 2 vol% CNT sample was 1.9% but increased to 5.6% after reducing the traverse speed. However, the ultrasonicated 3 vol% CNT sample still exhibited a very low deposition efficiency, even after using the updated parameters. This is presumed to be a result of the well-dispersed CNTs clogging the powder line, leading to inefficient powder transfer and deposition.

The variations in deposition efficiency among different powder types and processing parameters highlight the importance of optimizing the coating process for achieving desired coating thicknesses and deposition efficiencies. Further investigations are warranted to understand the specific factors influencing the deposition efficiencies and to develop strategies for effectively mitigating issues such as powder clogging.

The U.S. powders had very low deposition efficiencies including the control, which had a low deposition efficiency as compared to those found for D. Tauber and S. Rice [46], [47]. These values for deposition efficiencies indicate that the particles are not reaching the critical velocity required to adhere to the substrate. Figure 27 illustrates the difference in particle behavior based on whether it reached critical velocity. If the particles hit the substrate below a critical velocity, they will not have a splat morphology instead they

remain like their initial shape as seen in the circled areas on Figure 26. This leads to weak bonding between the particles and the substrate as well as the subsequent layers and a poor coating. Particles with speeds lower than the critical velocity will may also bounce off the surface, not adhering to the substrate. This is likely the biggest contributor to the low deposition efficiency.

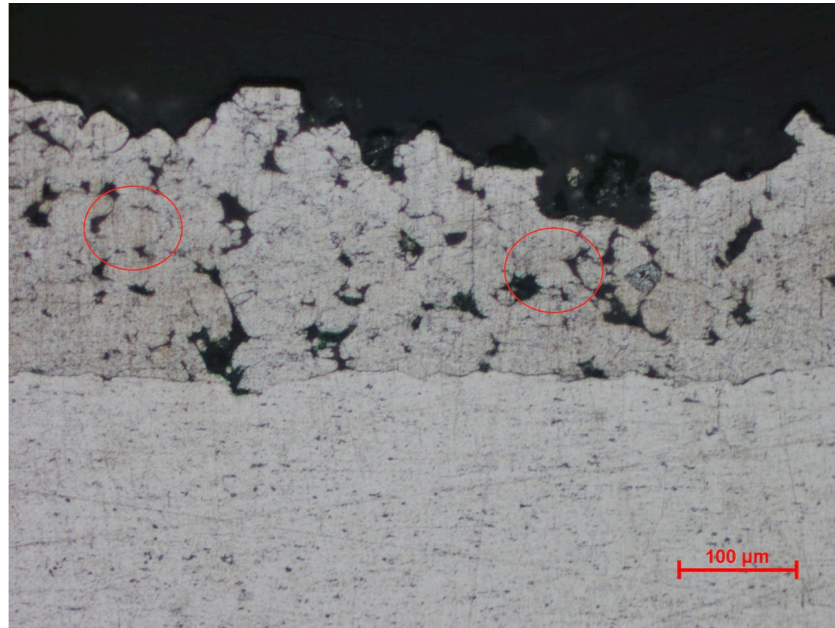


Figure 26. Pure Al CS coating morphology

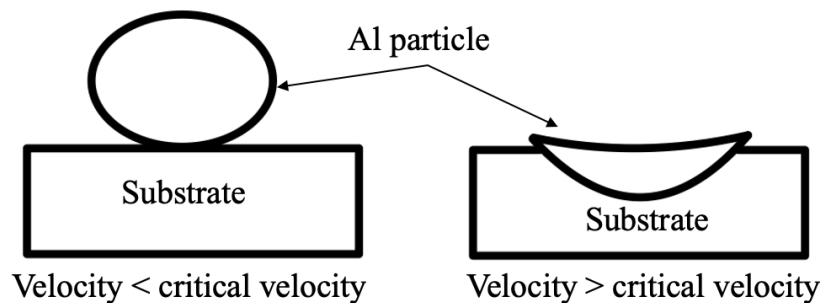


Figure 27. Particle behavior based on velocity

Alongside the undeformed particles, there were particles in the control coating exhibiting a dendritic microstructure as seen in Figure 28. This occurrence was surprising given the predetermined spray temperature and pressure parameters. It is possible that these dendritic structures arose due to a lower gas temperature than what the machine indicated. Low gas temperature can lead to insufficient softening and plastic deformation of the particles upon impact with the substrate. This reduced plastic deformation limits the ability of the particles to flatten and spread, resulting in a more dendritic-like structure [12].

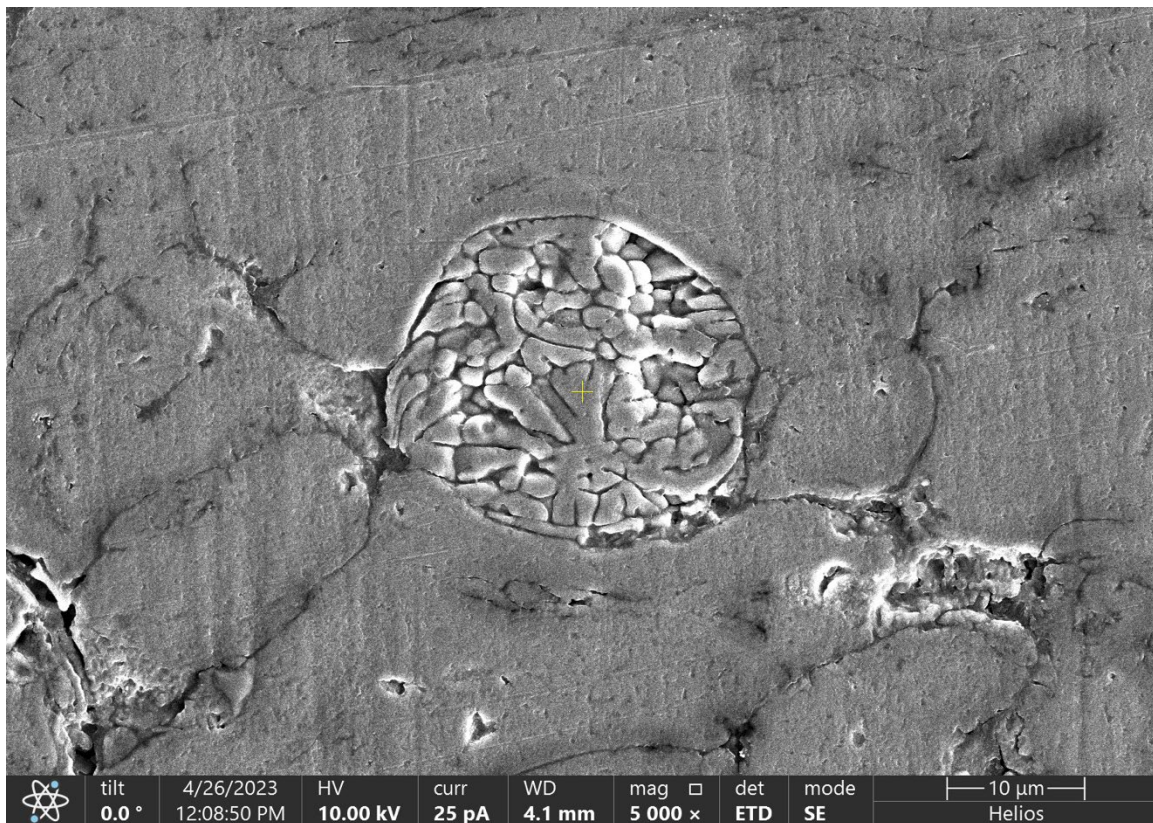


Figure 28. Dendritic Al particle in control CS coating

Figure 29 shows a splat in the control coating and a higher magnification of that splat boundary with no reinforcements for later comparison with the CNT reinforced coatings. The particle above this splat boundary is deformed and closer to what an ideal CS microstructure would be however, there are also large voids just above this particle and to the left which is not ideal.



Figure 29. Pure Al coating series of splat boundaries with no reinforcements
a) splat boundary circled b) high magnification splat boundary

Figure 30 shows a pocket of CNTs located in a splat boundary of the HEBM 3 vol% CNT coating. The CNTs in this case is shaped more like another particle compared to

sandwiched at a thin splat boundary. This is indicative of the poor dispersion of the CNTs in the Al powder prior to CS.



Figure 30. HEBM CS coating 3 vol% CNT a) CNTs in splat boundary circled
b) high magnification of CNTs in splat boundary

In Figure 31, there is a CNT agglomeration next to a void in the HEBM 3 vol% CNT CS coating. The presence of voids in the coating is likely attributed to insufficient particle deformation. Having the CNT reinforcement located directly next to a void is undesirable since the absence of attachment between the CNTs and the Al substrate hinders load transfer from the soft Al to the CNT reinforcement, thereby defeating the fundamental purpose of the composite structure.

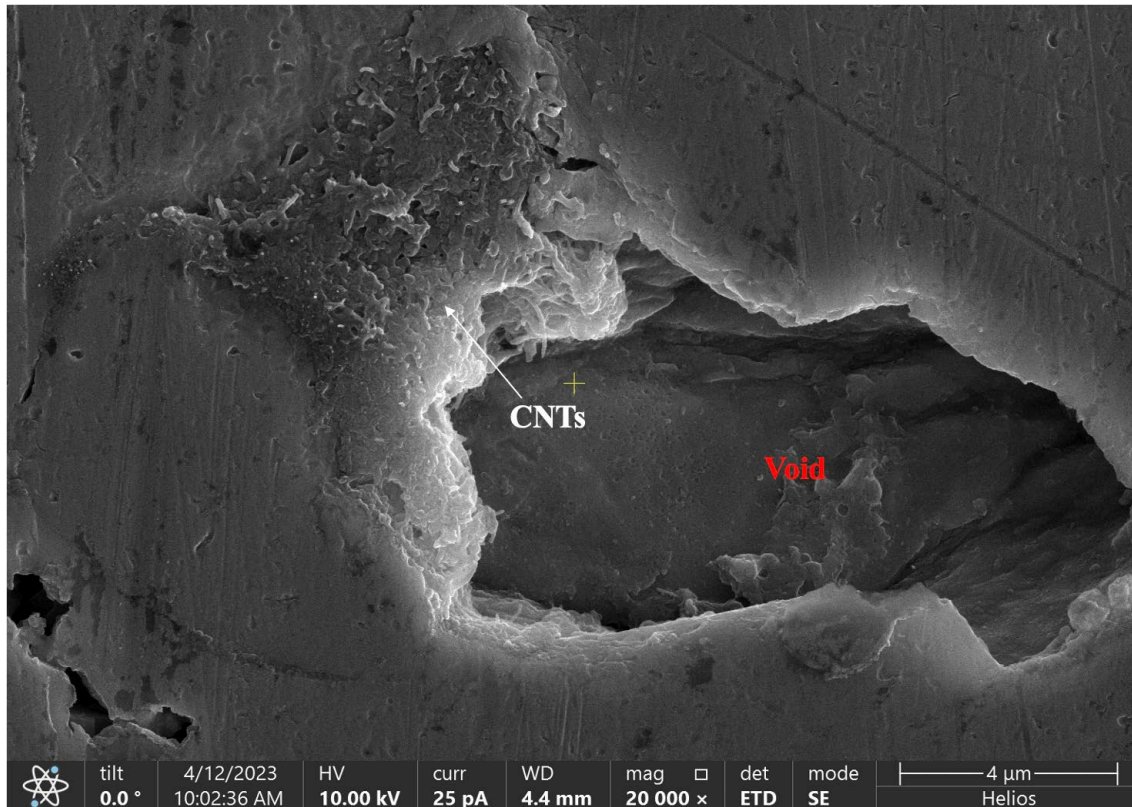


Figure 31. CNT agglomeration and void in HEBM CS coating 3 vol% CNT

Figure 32 shows a smaller more dispersed group of CNTs in a splat boundary in the U.S. 3 vol% CNT coating. The CNTs are thin line sandwiched between the Al in the U.S. coating compared to more of a ball of CNTs in a void present in the HEBM sample. This indicates better initial dispersion in the U.S. coating compared to the HEBM coating.

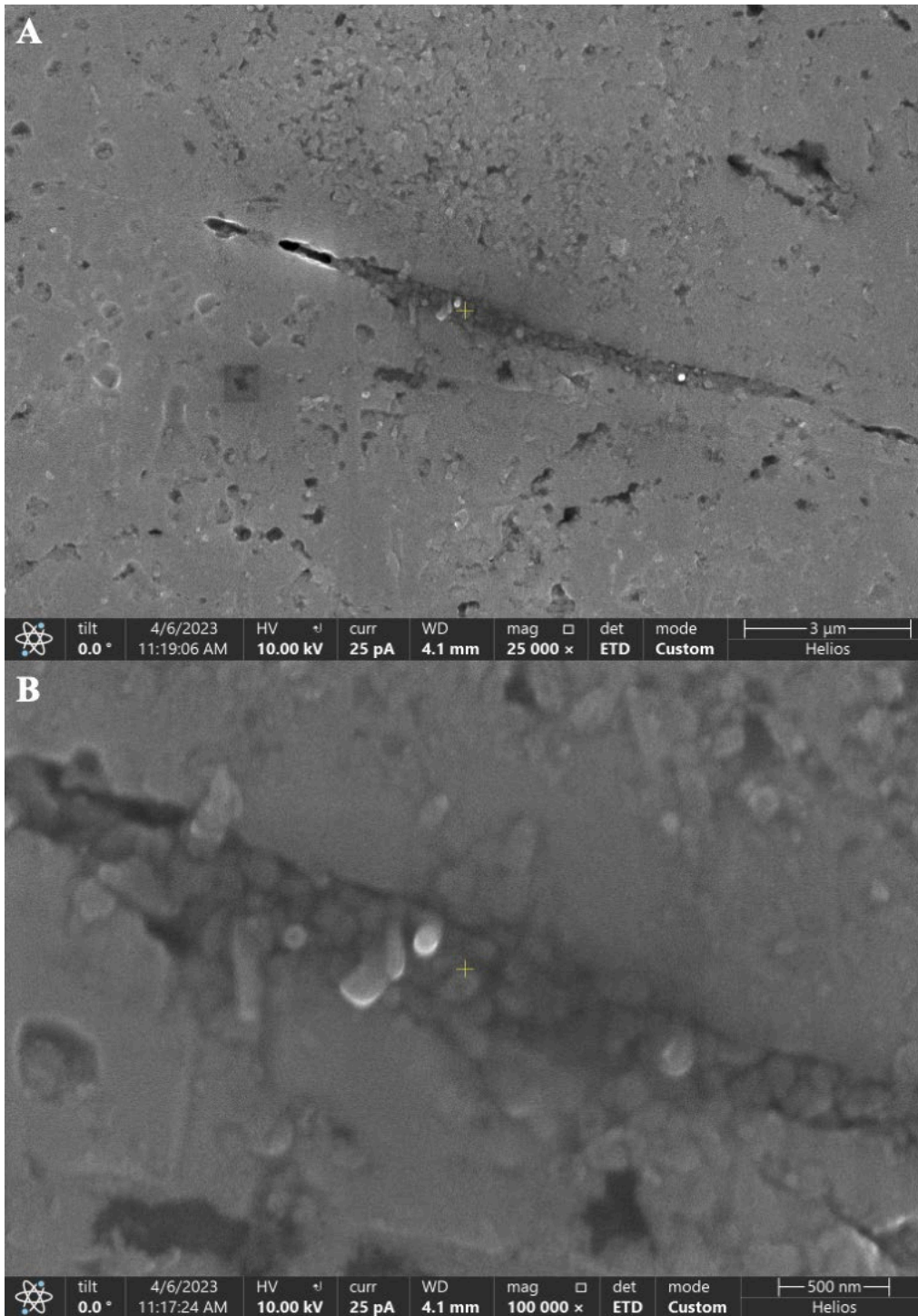


Figure 32. U.S. CS coating 3 vol% CNT

D. MECHANICAL TESTING

All the coatings are too thin to draw conclusive evidence from the following wear and corrosion results.

1. Wear Test Results

The wear test results have been compiled in Table 13. The average coefficient of friction (COF) was calculated by taking the average of the recorded COFs after the first ten minutes of the test. The mass loss was averaged across the three tests for each coating. Three of the deepest points were measured with optical profilometry on one test of each coating and then averaged. Based on the depth from optical profilometry the decoder went through the coatings on all the U.S. samples. The specific wear rate for the control and HEBM samples were calculated by estimating the wear volume from the optical profilometry data and dividing that by the sliding distance multiplied by the force applied. The specific wear rates were not calculated for the U.S. samples because it is unclear where exactly the decoder went through the coating and would be inaccurate.

Table 13. Wear test results

Sample	Average CoF	Average Mass loss (mg)	Average Depth (μm)	Specific Wear Rate ($10^{-4} \text{ mm}^3/\text{mN}$)
Al Control	0.43	0.53	59.05	0.91
HEBM 1 vol% CNT	0.49	0.73	66.09	1.14
HEBM 2 vol% CNT	0.47	0.67	52.60	0.72
HEBM 3 vol% CNT	0.41	0.70	82.17	1.77
US 1 vol% CNT	0.36	0.40	58.39	N/A
US 2 vol% CNT	0.41	0.57	46.76	N/A
US 3 vol% CNT	0.32	0.93	49.12	N/A

The low COFs of the U.S. CNT coatings are most likely from wearing through the rough CS coating and taking measurements from the smooth substrate surface. The HEBM 2 vol% CNT performed slightly better than the control based on specific wear rate, however, the control lost the least amount of mass. This is most likely due to the poor deposition of the coatings with CNTs.

2. Corrosion Results

The average weekly mass change is presented in Figure 33. All the samples gained mass over the first week, which was presumably a protective passivation layer. The second week, most samples had a mass loss followed by a small mass gain the next week. The subsequent weeks had mass changes mostly under 0.02 g. This seems promising for the corrosion resistance of the CS coatings. However, this data is not that helpful in deciphering what happened to the coatings because they were so thin.

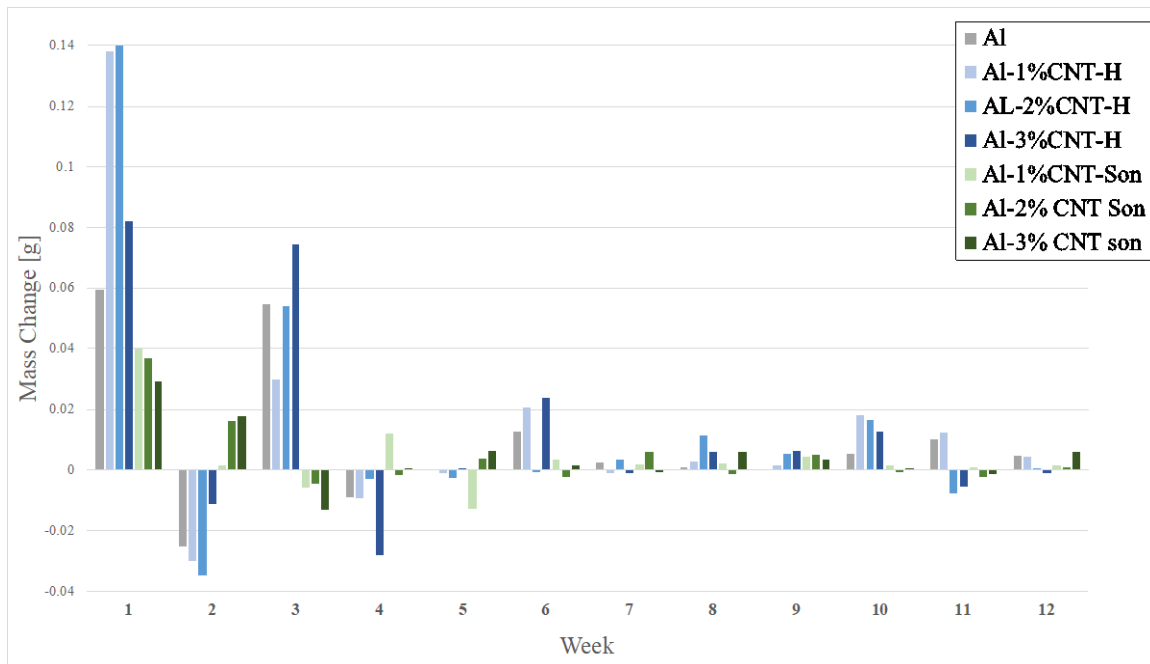


Figure 33. Weekly average mass differences of corrosion samples

After cleaning it was evident that the higher percentage CNT coatings had entire sections of the coating corrode away. Figure 34 is a top-down view of one sample of each

coating. The HEBM 3 vol% CNT coating showing a large section of coating completely missing and exposing the Al substrate below. One previous study found that CNTs can form a galvanic couple with Al leading to accelerated corrosion [48]. CS also induces a large amount of stress on the particles which could lead to stress corrosion. Coatings would probably perform better if heat-treated to reduce these stresses.

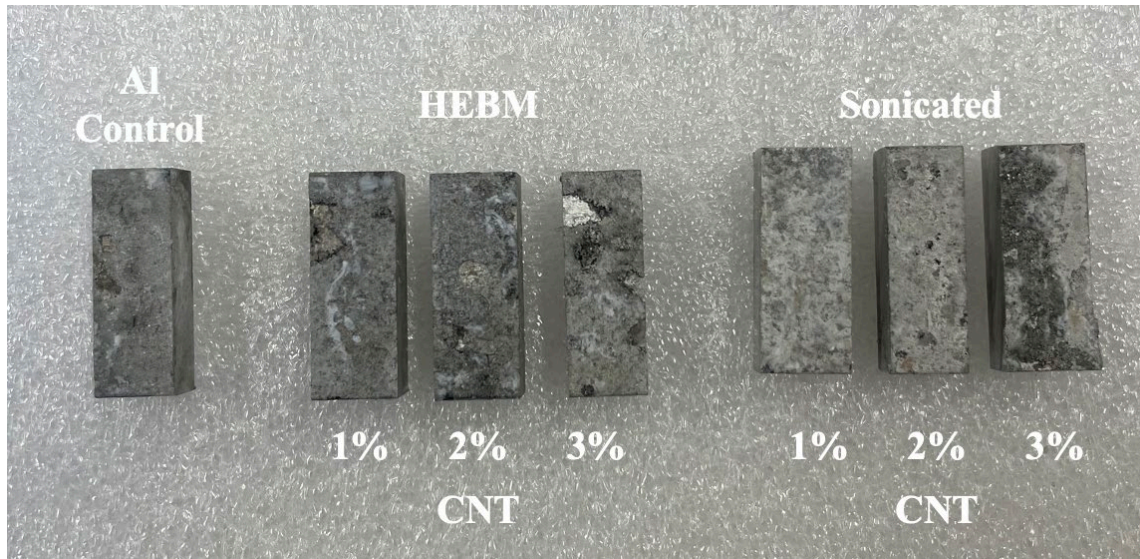


Figure 34. Top-down view of corrosion samples

Corrosion along the splat boundaries in the Al control coating is evident in Figure 35. This occurrence is most likely attributed to inadequate bonding between neighboring splats, which creates pathways for corrosive substances to infiltrate the coating. Insufficient bond strength between splats can result in localized attack and eventual delamination as corrosion initiates at the splat boundaries. In Figure 36, the exposed substrate is visible where the coating has corroded away. Comparatively, the HEBM samples exhibit larger areas of exposed substrate in contrast to the control and U.S. samples. However, it should be noted that the U.S. coatings were exceptionally thin, making it an unfair comparison as their reduced thickness could have contributed to less apparent corrosion. Nevertheless, it is conceivable that the larger agglomerations in the HEBM samples accelerated corrosion in certain sections of the coating.

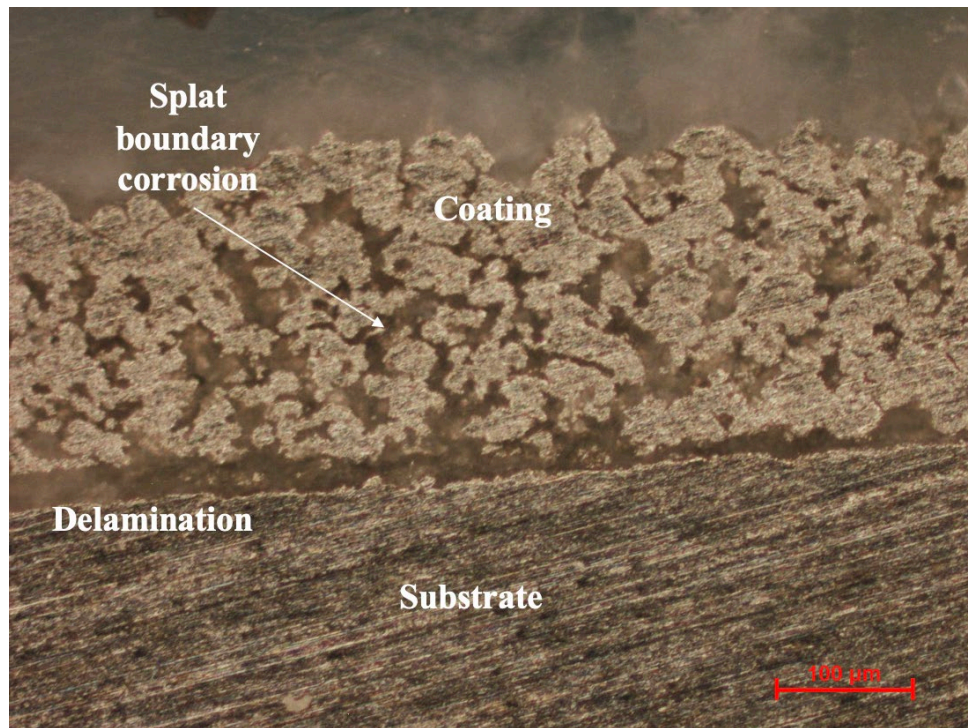


Figure 35. Al control corrosion

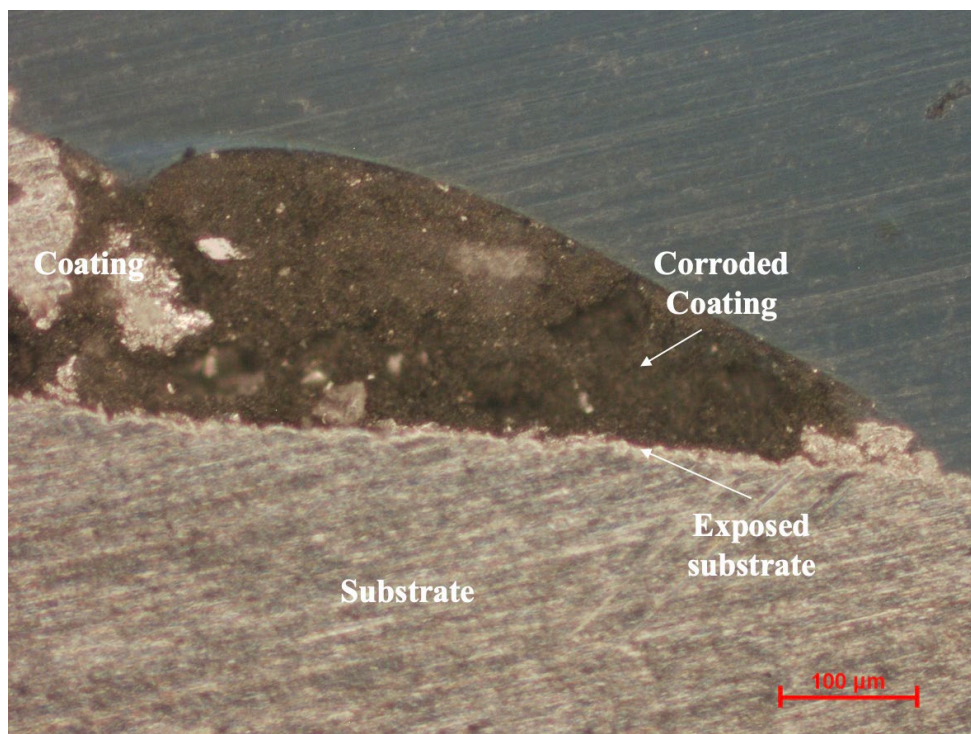


Figure 36. Exposed substrate on Al control coating

Figure 37 shows the HEBM 3 vol% CNT coating where the coating has delaminated from the substrate. This delamination is likely due to insufficient preparation of the substrate, resulting in a weak bond between the coating and substrate. Consequently, the coating becomes susceptible to detachment from the substrate. Figure 38 shows an area where the coating has corroded away, exposing the underlying substrate.

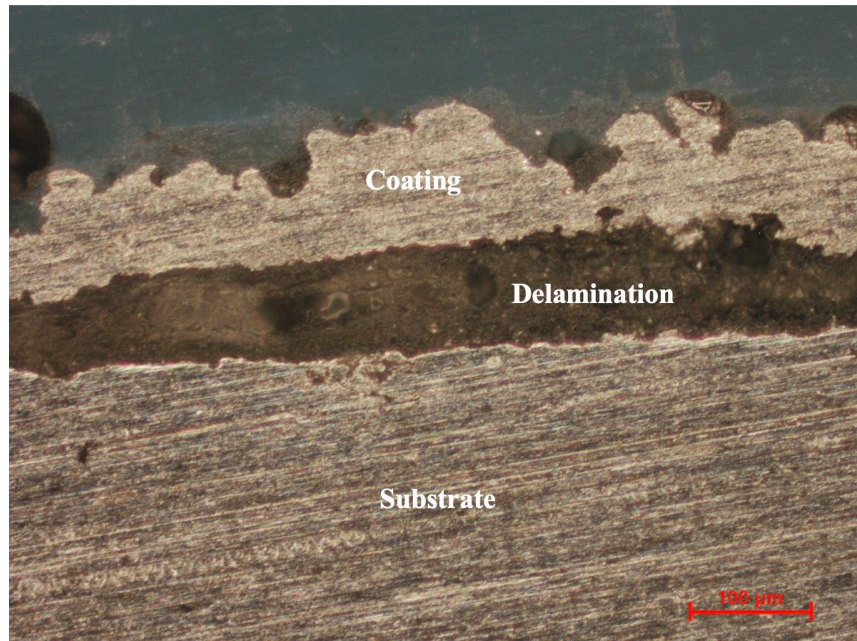


Figure 37. HEBM 3 vol% CNT coating delamination after corrosion

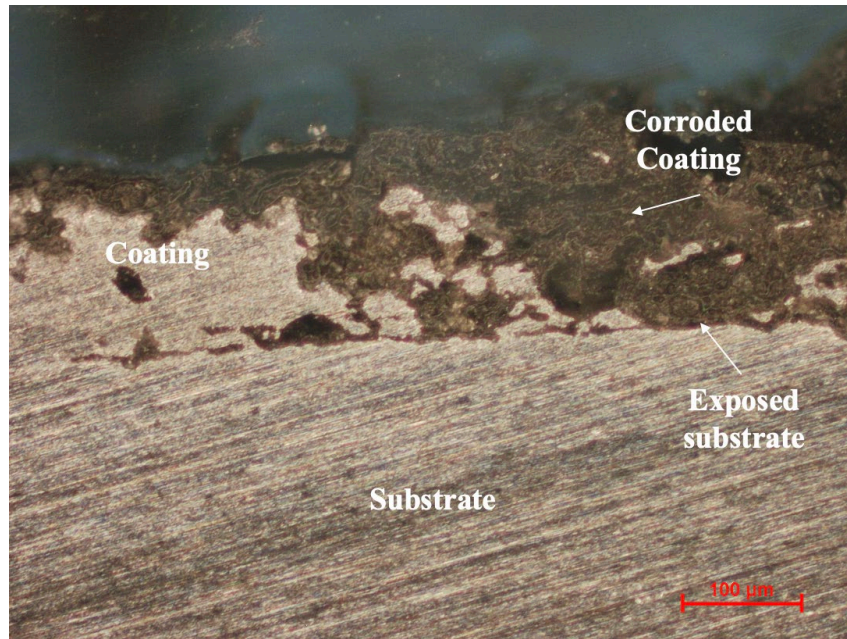


Figure 38. HEBM 3 vol% CNT exposed substrate

Similar behavior can be observed in the 3 vol% CNT U.S. coating. Figure 39 highlights an area where the coating has corroded and worn away, revealing the underlying substrate.

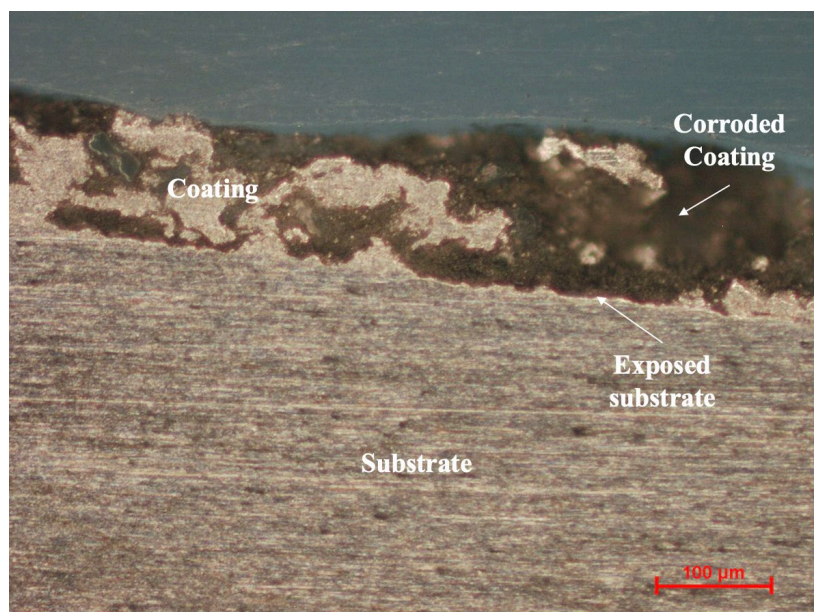


Figure 39. U.S. 3 vol% CNT corrosion sample

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V. CONCLUSION

A. SUMMARY

Based on the comparison of dispersion techniques for CNTs within Al powder, namely HEBM, cryomilling, and wet chemistry ultrasonication, it was determined that ultrasonication in acetone yielded the most favorable results. This technique resulted in the smallest CNT agglomerations and even showcased individual dispersed CNTs. In comparison, HEBM demonstrated smaller agglomerations compared to cryomilling, but these agglomerations appeared densely packed. The ultrasonication of CNTs in acetone proved to be highly effective in dispersing the CNTs uniformly within the Al powder. Furthermore, acetone possessed the advantage of being easily evaporated without leaving any residue. This quality eliminated the need for additional processing steps that were encountered when employing PVA and SDBS as dispersion agents. These findings highlight the advantages of utilizing acetone-based ultrasonication for CNT dispersion in future research and practical applications.

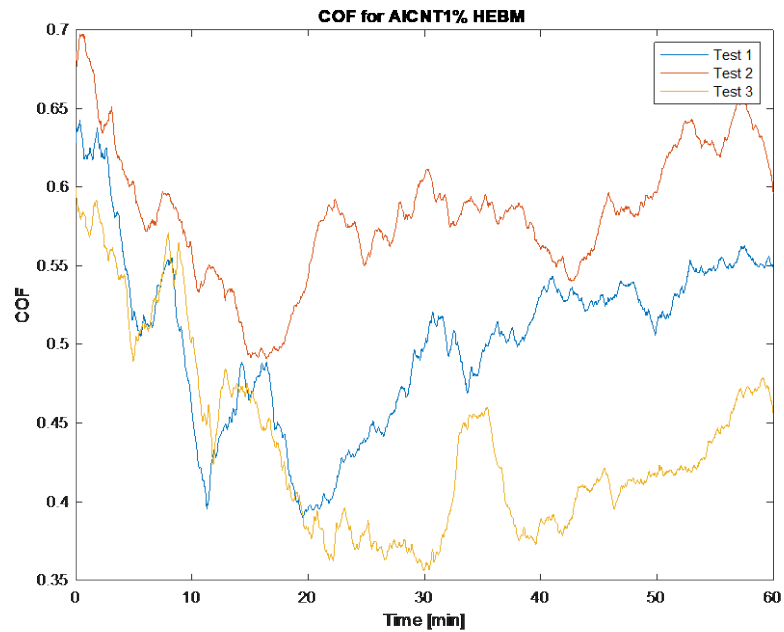
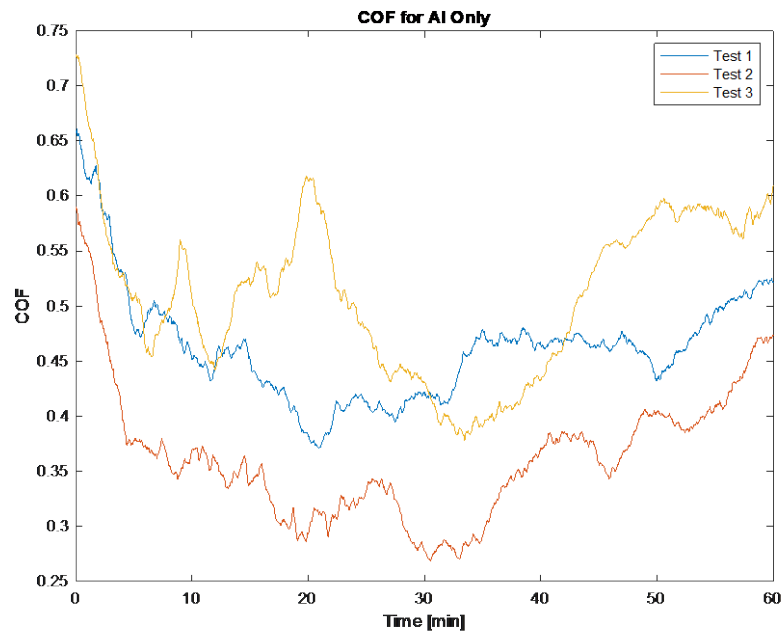
The HEBM and acetone dispersion powders were used to create CS coatings. The acetone dispersion method proved to be highly effective in dispersing the CNTs; however, it caused issues with the cold spray process as the CNTs clogged the powder line, resulting in poor deposition efficiency. In addition, the coatings created using both the control and HEBM methods exhibited undesirable characteristics such as the presence of undeformed particles, and dendritic structures. These issues affected the accuracy and reliability of the wear testing results, particularly in the case of the acetone ultrasonicated coatings, where the coatings were too thin, and the decoder penetrated through them. Although the results from the sliding ball wear testing and the 2000-hour SFC corrosion test are presented, it should be noted that the deposition efficiency of the acetone sonicated coatings was extremely poor, making it difficult to draw substantial conclusions from the obtained data.

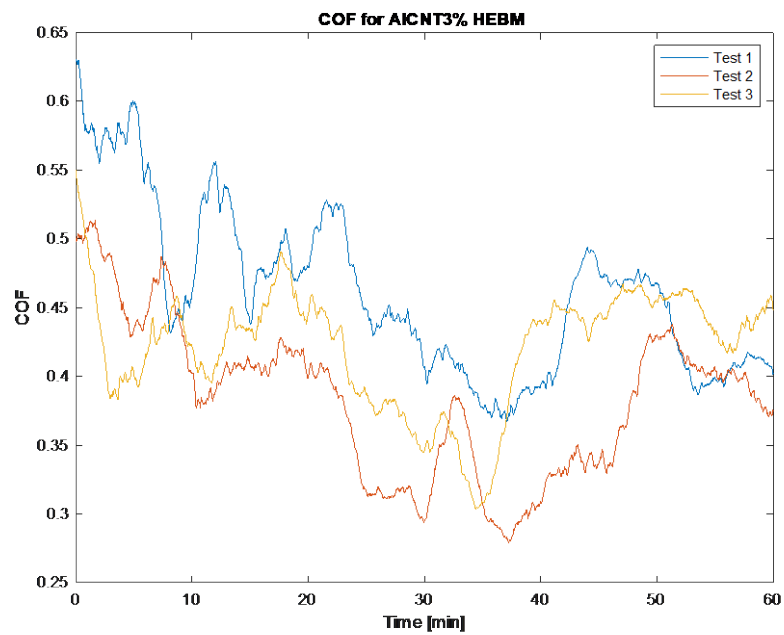
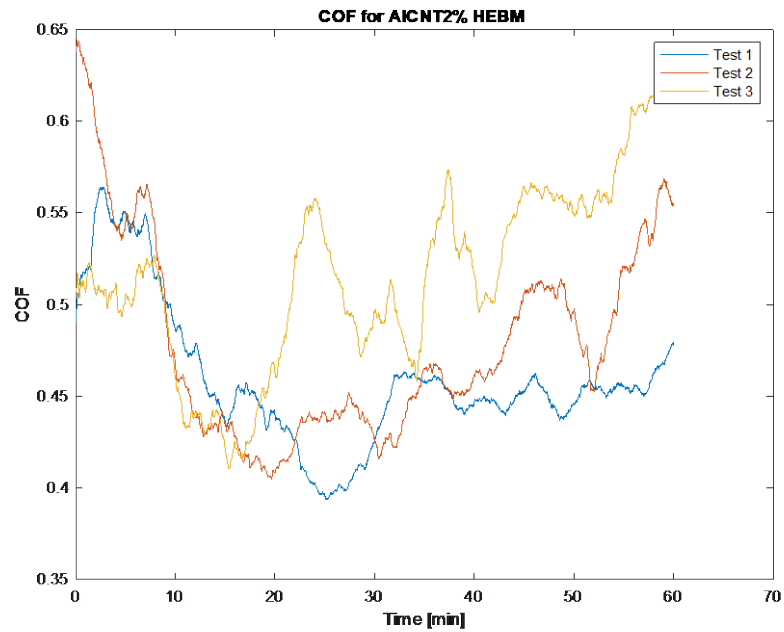
B. FUTURE WORK

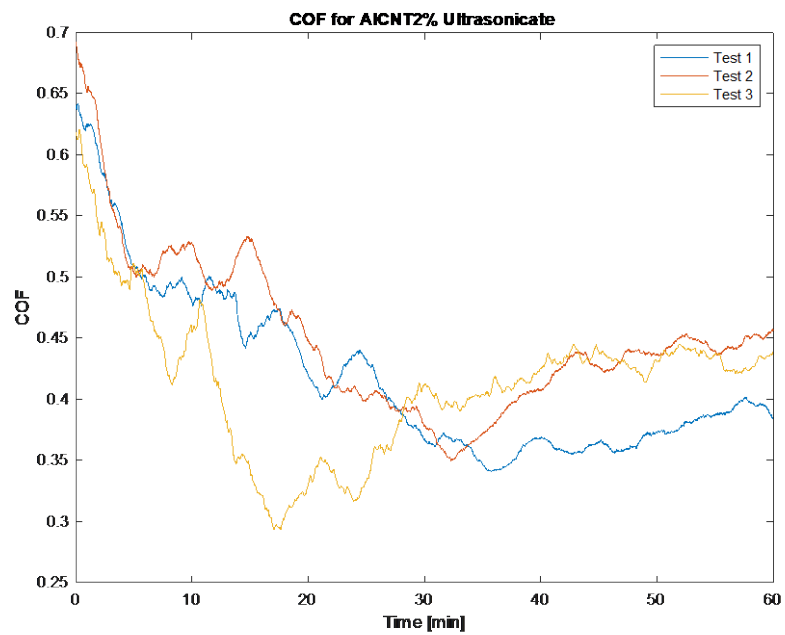
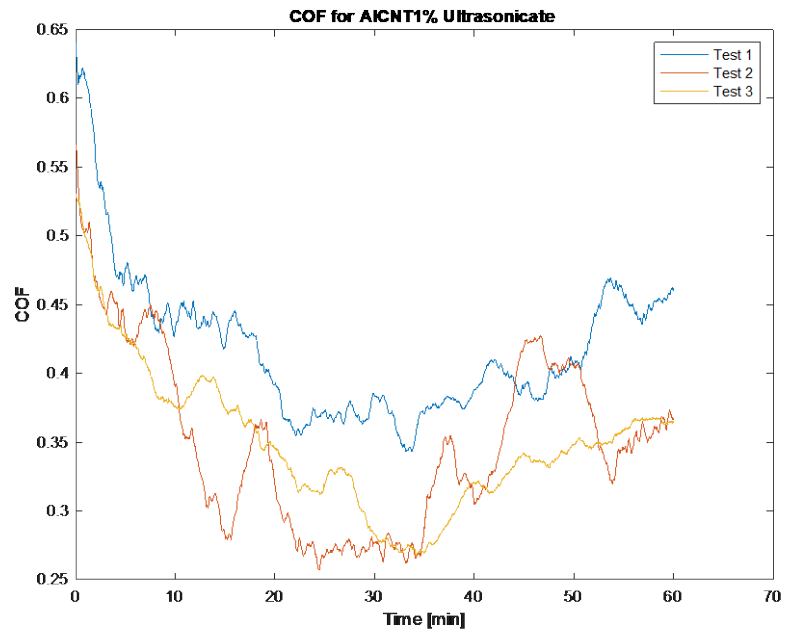
Further testing is needed to optimize the CS parameters using the ultrasonication method with acetone. To obtain a thick coating and assess the suitability of CNTs as a

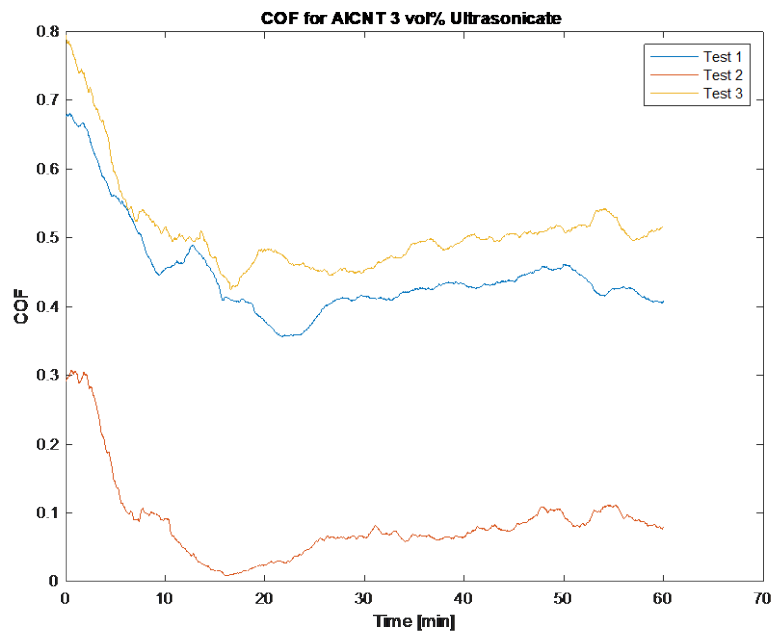
reinforcement for Al MMC. Some ideas for CS parameter optimization are surface preparation, preheating the substrate, using helium instead of nitrogen as a working gas. If it is possible to create a thicker coating subsequent performance parameters like wear testing and corrosion. By conducting these tests and analyses, it will be possible to determine if CNTs are a suitable choice as a reinforcement material for Al MMC and to gauge the potential improvements in mechanical properties that can be achieved through their incorporation.

APPENDIX. COF GRAPHS









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