

EXPERIMENTAL STUDIES AND ANALYSIS OF ELECTROPLATING OF COPPER ON TUNGSTEN POWDER

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Abstract— Strengthening, resistant and shielding properties, to name a few, can be achieved by implementing a surface material coating onto an engineering component. Various elements of these compounded parts can augment the functionality of the part, such as, increased life time and more interactive surfaces. Tungsten has proven to be a challenge to plate with other metals, but if done correctly, the results can allow for the cold spray of tungsten. Cold spraying tungsten particles alone provides a challenge because the powder is too hard and instead of adhering, it erodes the surface it is attempting to plate. Coating tungsten in a softer metal, like copper, will allow for the particles to adhere to the surface and create a strengthened and radiation shielded component. It also yields a better surface to electroplate onto in the future, as tungsten itself is hard to plate onto, so the copper layer provides the ability to easily plate other metals.

The purpose of this thesis project is to encapsulate tungsten powder within copper, then scale up the process to produce bulk amounts of the material in a batch process. The particles will be encased using an electroplating method, that has been turned into a semi-autonomous process for the ease of producing bulk powder. While electroless deposition has previously shown positive results for attaining a uniform coating, making it a semi-batch process for bulk material would have an extreme cost in comparison to electrolytic deposition. The tungsten particles have been successfully enclosed in copper by electrolytic deposition in this set of experimentation using an HF electro-etch pretreatment and ultrasonic agitation during electroplating. Further experimentation will include improved methods of stirring and transferring powder, as the transfer takes too long between the etch and the onset of plating and the stirring method is bulky and reduces the area that can be efficiently plated on.

Index Terms— Electroplating, Tungsten Powder, Copper, Softer Metal.

I. INTRODUCTION

A. Purpose

Desirable material properties can be gained as the result of coating a component with a surface material. In some cases, these surface coatings can provide different abilities, such as added strength, solderability, and wear resistance. The purpose

of this thesis is to explore various methods for plating tungsten (W from Buffalo Tungsten), with copper, for a proprietary application. The grains of powder are being encased using an electroplating method, invented by Pay Yih (patent # 5,911,865) in 1997 [1]. A copper coating on the tungsten powder will give it a better chance to bond to a metal surface in a cold spray process. Copper is a softer metal that makes the deformation of particles more favorable, which is a key to the success for bonding in the cold spray coating process.

Metals have been applied to the surface of materials for various reasons, like adjusting the friction coefficient of the surface and to provide a new layer of wear resistant material[2].

B. Thesis Outline

The background information regarding this thesis is found in the form of a literature review in Chapter 2; the chapter covers: cold spray, tungsten, mechanics, electroplating of copper, and calculations used to initialize and evaluate the experiments. Chapter 3 describes the results from completed experiments, including all the macroscopic and microscopic substrate tests with all the pretreatments. It includes details regarding the experimental setup and an overview of result analysis. Chapter 4 provides a summary of the results and the experiments conducted throughout the study. Chapter 5 describes the conclusions that were able to be drawn from the experiments, while Chapter 6 describes further testing that should be conducted to attempt to find a more efficient solution.

II. BACKGROUND

A. Introduction

Metal plating has been used in many different applications over many years, like wear resistance, corrosion resistance, and enhanced engineering properties. Tungsten coating has also begun to emerge in the fire-proofing and anti-radiation industries, as it has a higher density than other popular anti-radiations materials, such as lead. However, its cost is much higher, leading to the use of tungsten only when the space for

the radiation protection is less favorable for lead [3]. As for fire-proofing, tungsten has the highest melting point among all metals, not just the transition metals, and it can retain its strength at those high temperatures. Overall, tungsten's hardness and high density give it many functions, for general and military purposes, as a coating layer on a component.

Cold spray is a solid-state deposition process in which metal powder is propelled at high velocities and temperature well below the melting point of the material, causing particle deformation on impact that results in a strong metallurgical bond. The significant plastic deformation experienced by the particles forms an adiabatic shear instability upon contact, breaking down surface oxides. Due to this break, shear is developed at the contact interface and material is expelled from the contact. This shear between particles and at the spray

contact interface causes the solid-state metallurgical bonding[4].

There are many modern metal spray techniques used throughout industry, Figure 1 demonstrates the operational threshold for each of the techniques. The cold spray process operates at the lowest temperature of all the conventional spray techniques and the highest velocity. The high temperatures of plasma, detonation and High Velocity Oxygen Fuel (HVOF) create melted particles that shrink upon cooling. This leaves high tensile residual stresses. Due to the low temperatures of cold spray, the particles are not melted, resulting in a much smaller, and compressive, residual stress, in comparison to the other methods. The crystalline structure also remains mainly unchanged during deposition in cold spray, unlike the particles of the higher temperature depositions, which tend to change their crystalline structure upon resolidification[5].

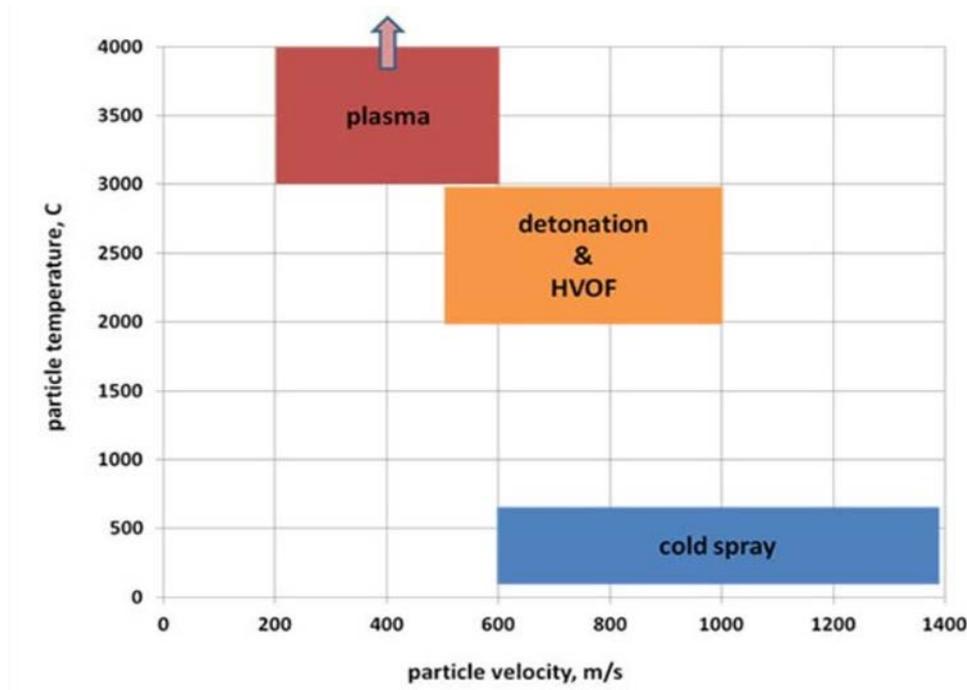


Figure 1: A view at the operating ranges for metal deposition coatings. Plasma, detonation and HVOF all operate at higher temperatures than cold spray, but detonation and HVOF have some velocity overlap with cold spray, whereas plasma is strictly low velocity application

B. Applications and Requirements

1) Tungsten (W)

W is a unique transition metal that is unparalleled by all materials in many categories, including the highest melting temperature and tensile strength. The powder used throughout these experiments was made by Buffalo Tungsten Inc. The particles had diameters in the range of 5-10 μm with an apparent density of 3.0-5.5 g/cc. W itself has many useful applications, including light bulb filaments, electrical contacts, heating elements, plastic densification, aiding in the

production of tungsten carbide, and additive strengthening of steel. Among metals, tungsten has the highest melting point, the lowest coefficient of thermal expansion, and the lowest vapor pressure. It also has unusually high strength at extreme temperatures. These properties make it a desirable material to coat with, as its strength and durability at high temperatures make it unique for many military applications, as many bullets, missiles, and rocket parts are coated with forms of tungsten. Not only does it have these extraordinary properties, but they are coupled with other compelling characteristics,

such as high resistance to corrosion, high modulus of elasticity, and high resistance to thermal creep [6]. The W particles, from Buffalo Tungsten, were blocky in shape, with a scatter of fused clusters. The surfaces are not

particularly smooth, and the particles appear to have agglomerates on them. A closer look at the particles can be observed below in Figure 2.

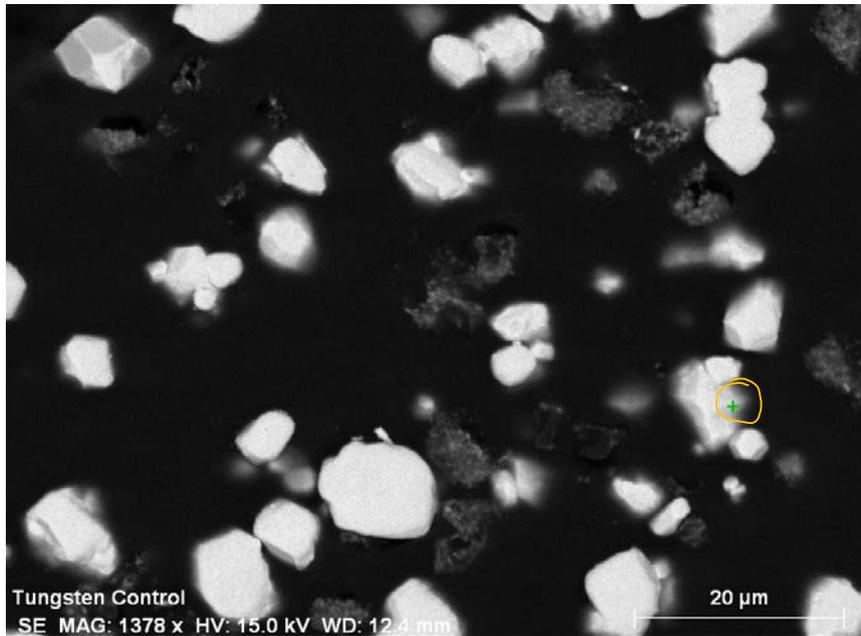


Figure 2: Image of W powder particle from a backscattered electron view. The powder particle was mounted in an epoxy puck, ground and polished, so that cross- sections of the particulate could be seen. The cloudy edges of the particles give it the appearance of being coated, so the particle was analyzed with EDS imaging to realize the makeup. The particular portion that was analyzed in this case is the plus sign in the yellow circle.

2)W composition

In an initial, control test, W particles were mounted into an epoxy resin and then ground and polished. Below, in Figure 5, W particles can be seen and the cloudy outline around the particle that can be easily mistaken for a coating in a backscatter image, is denoted with a plus sign. This spot

marked by the sign was analyzed with energy dispersive x-ray spectroscopy (EDS), to reveal the elemental composition of the spot.

The resultant plot of the elemental composition is shown in Figure 3. The cloudy regions were shown to have only W and little to no traces of copper.

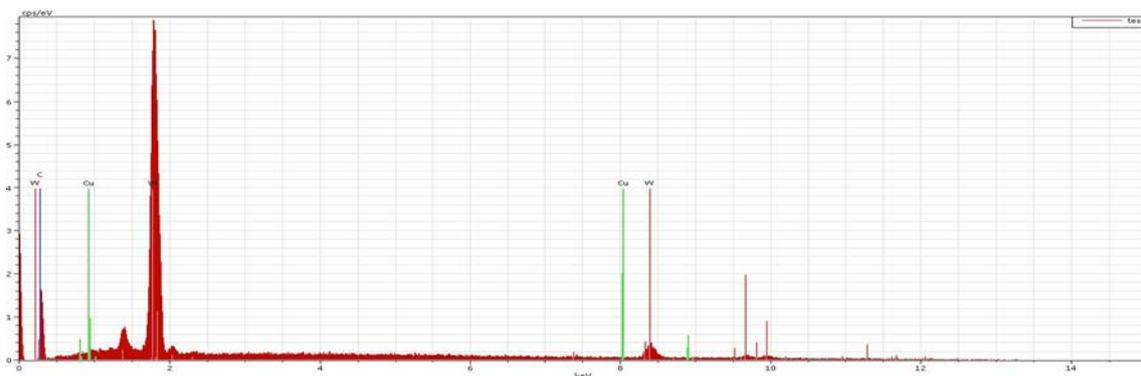


Figure 3: EDS spectra graph of W region that appeared to be coated in Figure 5. This figure shows that most of the W x-ray energy matches with the $M\alpha$ x-rays and a smaller, insignificant amount with the $L\alpha$ and $L\beta$ x-rays, as the leftmost peak is the carbon from mounting, labeled with a C

The figure above displays a high concentration of W on the left side of the figure, $M\alpha$ x-rays and a smaller amount of W after at a smaller peak on the right, the $L\alpha$ and $L\beta$ x-rays. The even height, vertical lines throughout the image, denote the areas in which energies are expected for the specific elements. The lines are labeled with the element that correspond to that energy peak. These results are consistent with the concentration of W given by Buffalo Tungsten Inc. of 99.9% W in powder [7]

III. ELECTROLYTIC DEPOSITION

A. Purpose

The goal was to create a successful and efficient method for copper plating W powder. Electroplating was selected due to its low cost and efficiency in adhering to conductive materials. Preliminary experiments were performed, isolating different experimental variables, using a macroscopic substrate, to ensure the validity of the solution, the setup, and the procedure. Then, the experiments containing the microscopic W powder were performed to demonstrate the influence that substrate size had on the experiment.

B. Experimental Procedures

1) Electrolyte Solution

All the ingredients used to create the electrolyte solution were weighed using a Fisher Scientific Education scale or dispensed from a graduated cylinder. The components and their quantities are shown below in Table 1.

Table 1: This table shows the solution composition for a 225mL electrolyte solution for electroplating copper that was used for a single test.

Ingredient	Amount (mL)
Copper Sulfate (CuSO ₄)	200 mL of 0.1 M (5.02 grams of powder with DI water to reach 200 mL)
Sulfuric Acid (H ₂ SO ₄)	25 mL of 0.5 M
pH	Between 2 and 5

All the ingredients in Table 1 were placed into a beaker and mixed with the magnetic stirring bar. The 2" nylon

stirring bar was placed into the beaker and stirred the solution for 30 minutes, when all of the copper sulfate powder residue was dissolved.

Once the solution was homogenous, it was stored and sealed in an Erlenmeyer flask, labeled in accordance with Environmental, Health, and Safety (EHS) policies.

2) Electroplating Experimental Procedure

The first step was stirring. The method of stirring switched between two techniques, depending on the availability of the magnetic stirring drive. The first method, with no ultrasonic bath, used a magnetic stirring rod. The powder particles were vigorously stirred using the magnetic stirring bar at 1100 rpm. The second method, with the bath, used a corded power drill and a polypropylene paddle stirrer. The drill was suspended over the bath and a hole was drilled through the copper anode to facilitate the stirring of the solution. These methods allowed the particles to be uniformly suspended in the solution and fall randomly back to the cathode so that new particles may be plated.

They were intended to break up any copper bridges that may have formed in the previous plating cycle. This method also reduces the concentration gradient of copper ions in the electrolyte bath that were formed by high-current electroplating.

The final step of the cycle is electroplating. Once the particles have settled onto the cathode, a direct electric current is passed between the anode and cathode, reducing copper from ions in solution onto the powder for 60 seconds. After that time, the current is stopped, and the cycle begins again.

3) Analysis Procedure

To view the effectiveness of the electroplating experiments, energy dispersive x-ray spectroscopy (EDS) and back-scattered electron (BSE) techniques were utilized.

The SEM allowed for the determination of the average W particle size range. In the preliminary test for control analysis, the W powder was placed into the SEM without any solution interaction or plating. The samples were analyzed using a Zeiss Evo 50 scanning electron microscope (SEM), with back-scattered electron imaging. An image of this is shown below in Figure 4.

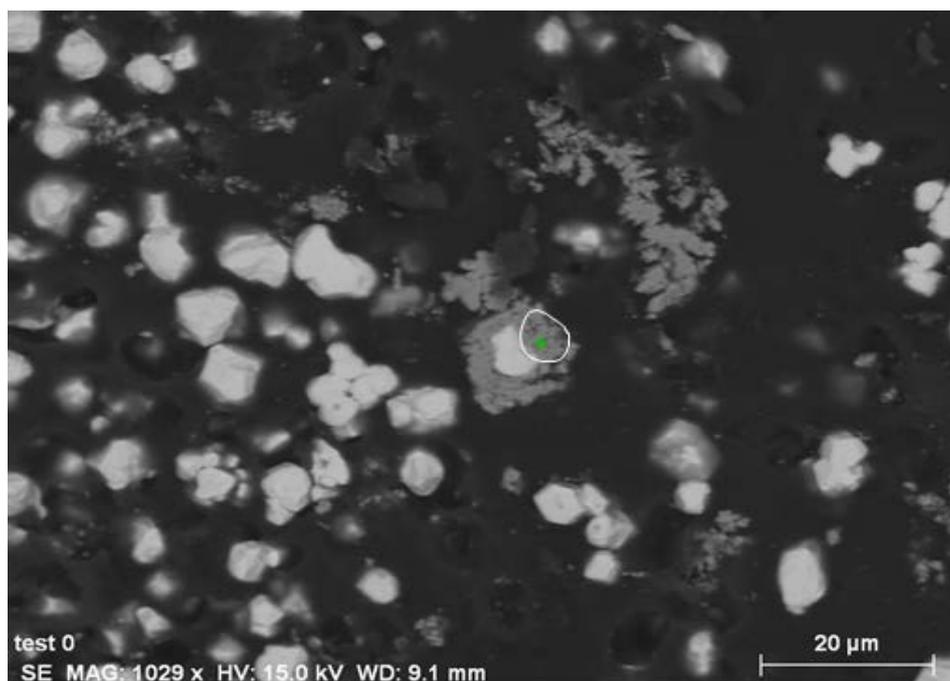


Figure 4: W particles (white) with copper (gray) in the powder. Taken using an SEM, with 20 μm scale bar for reference to particle size. The plus sign discussed in the text is circled in the figure.

In the SEM, the sample was magnified, the BSE images were used to determine the plating thicknesses and an image was captured so EDS analysis could be done on the particulates, to determine the elemental composition of the powder. A sample EDS plot was shown in Section ii-B-2, and another is pictured below in Figure 9 showing peaks of Cu and W. The y-axis of the EDS plot shows the number of counts taken per second over a one-minute period and the x-axis represents the energy level for those counts. Various peaks present on the graph labeled W and Cu represent the different x-ray phases, they are labeled with colored lines of uniform height to show the

expected wavelengths of the peaks for Cu and W. W is a heavier element, which means that it has more electron orbitals, providing more opportunities to excite different transitions, in turn, leading to W being defined by higher order x-rays. The largest peak of the W represents the M- α series x-rays, the leading W peak represents the M- ζ x-rays and as the energy levels get larger, the L-series x-rays are represented by smaller peaks, and the L-series x-rays are used to define the composition of the elements present in solution, that are referred to in Section (ii-B-2).

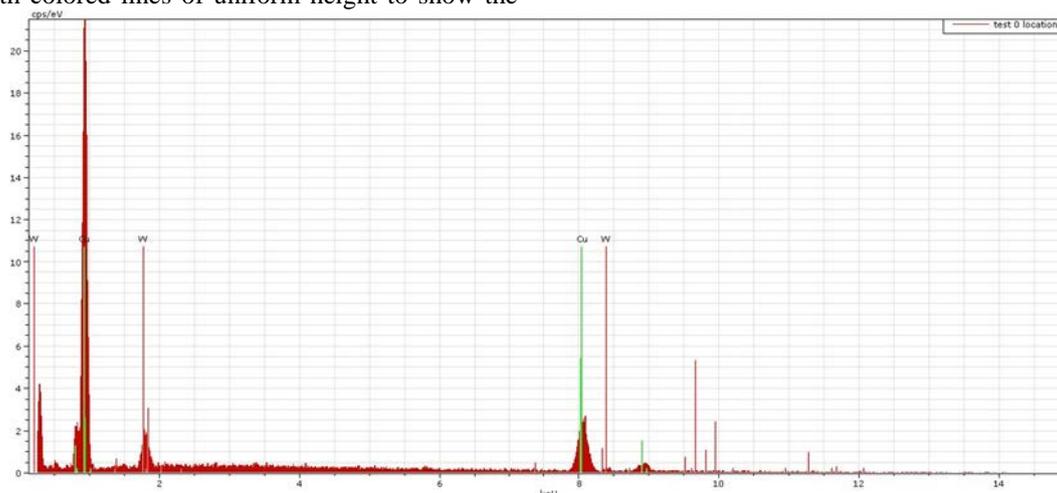


Figure 5: EDS plot: The data was retrieved where the plus sign is in mostly darker material, indicating a lower atomic mass, so it is expected that copper would be prominent, it was expected to see trace amounts of W in an area like this. These expectations are confirmed in the graph, with a small peak at W M α x-rays

C. Results and Discussion

Figure 12 displays a backscattered electron image of one of the coins that was electroplated for approximately two hours in the HCl electrolyte bath. Using the maximum plating thickness

displayed in Figure 6, 15.12 μm , Table 4 was constructed to display the theoretical calculation and the observed values of plating thickness.

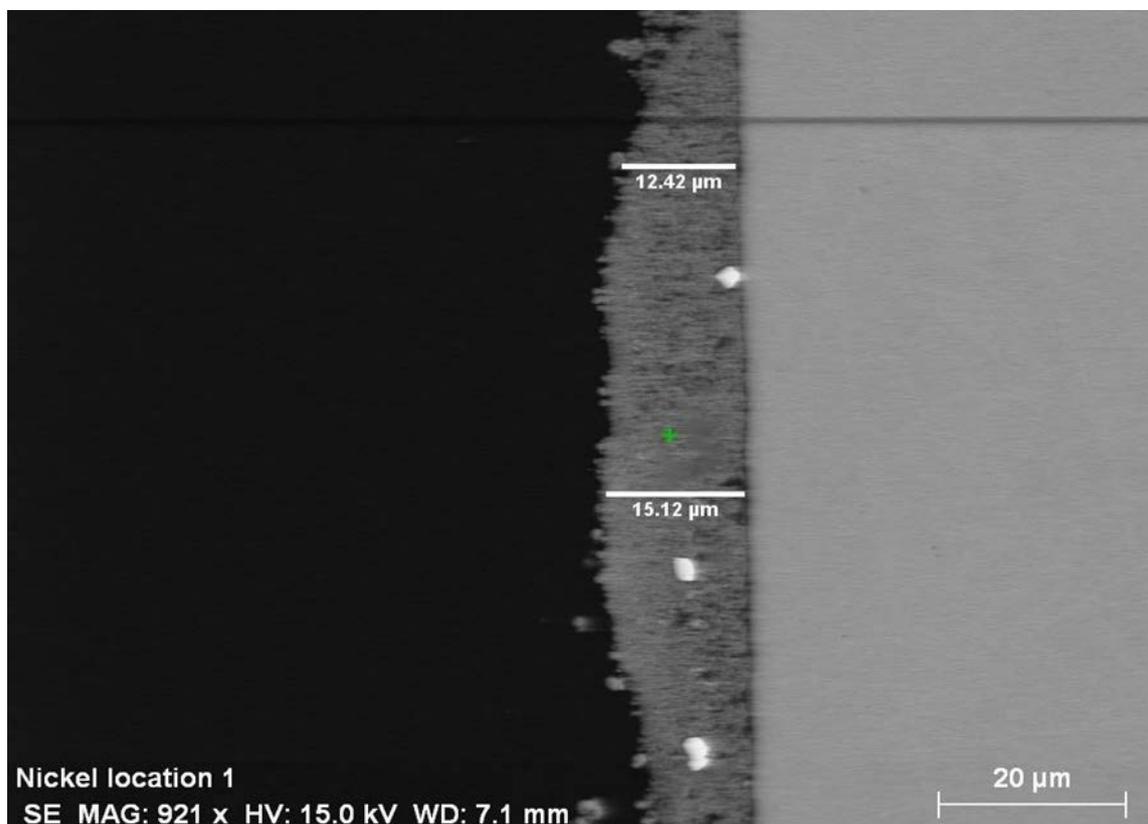


Figure 6: This figure depicts the variable thicknesses of copper plated on a nickel coin for approximately 2 hours

Table 2: This table illustrates the calculated and observed thicknesses for the nickel coin plated in copper that is shown in Figure 9.

Nickel Plating Thickness	Calculated	Observed	Efficiency
Thickness ($\mu\text{m}/\text{min}$)	0.20	N/A	N/A
Thickness ($\mu\text{m}/2 \text{ hr}$)	23.40	15.12	65%

In Figure 6, the contrast between the copper and nickel coin is very distinct, the coin is the smooth surface, while the copper is the darker, more variable surface. This contrast allowed for the simple measurement of plating thickness, shown on the figure to be 15.12 μm . The thickness is visibly not constant along the nickel surface, with a second thickness value being displayed on the figure. The thickness along the boundary is slightly variable, but there are no areas where the coin was drastically different from the others.

Table 2 depicts the calculated thickness values that were expected on a nickel coin after 2 hours. Note that the actual value is slightly lower than the expected due to copper losses to the cathode during plating, so the efficiency was only 65%. The rate of deposition during the experiment was not constant, which can be credited to the extra plating onto the cathode. Figure 7 illustrates the deposition of copper onto the cathode with small dendrites forming on the top during the electrolytic deposition during a macroscopic substrate test, in this case foil, but the nickel coins had the same results.

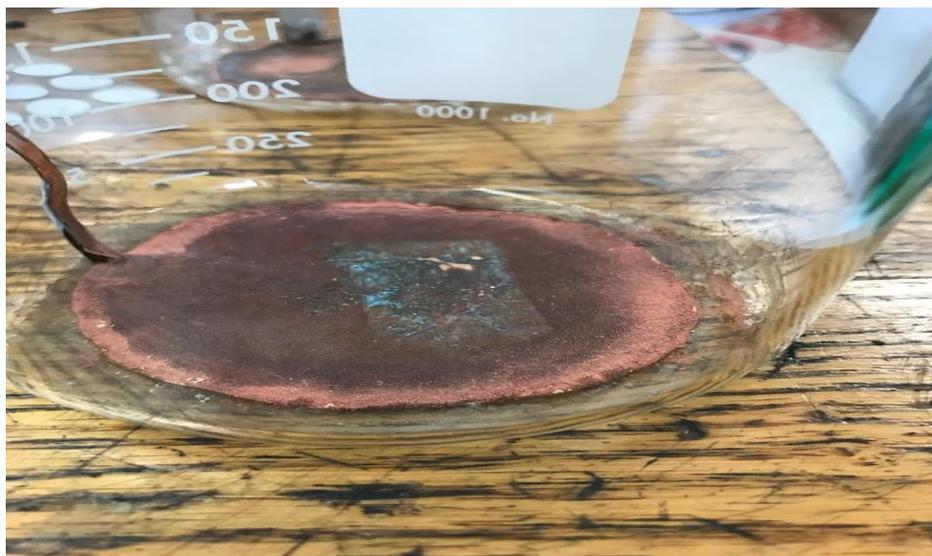


Figure 7: This figure depicts copper deposition and dendritic growth on the cathode, while showing the shadow of where the HF pretreated foil was during the deposition.

The shadow towards the center of the cathode is the place where the HF pretreated foil rested, other tests had similar imprints for W foil and nickel pieces. The main takeaway is the copper deposition onto the cathode. Dendrite growth can be seen on the cathode away from the foil spot, showing that

some of the copper was consumed by the dendrites instead of the nickel or W foil, leading to the lower efficiency value. Figure 14 provides a second example of a post experiment beaker that highlights the foil imprints for a test of the other foil types.

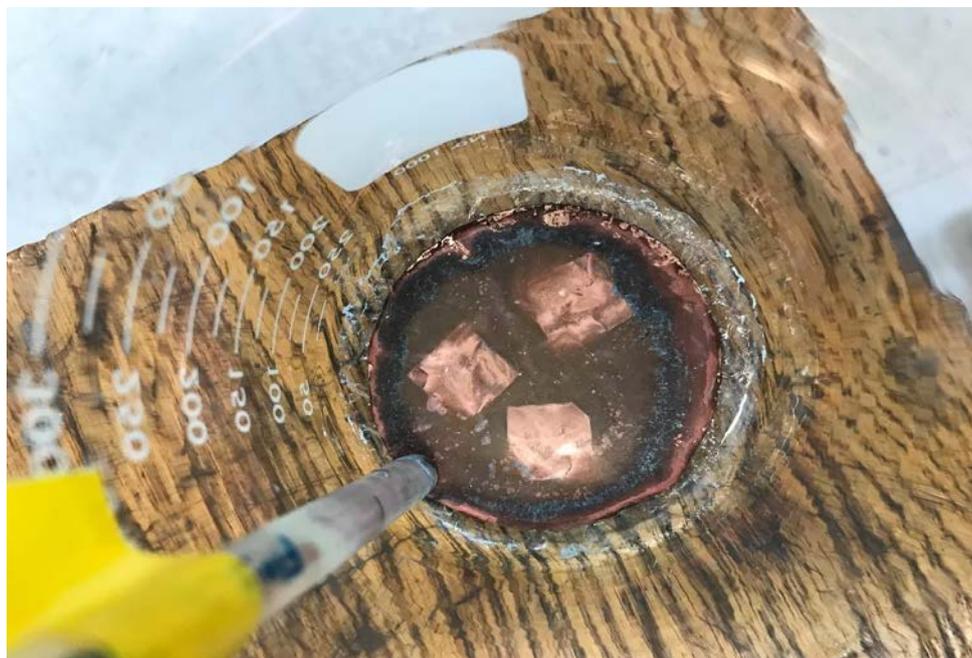


Figure 8: Experimental beaker after a foil test with a nitric acid, abrasion, and no pretreatment foil test. Note the prominent shadows left on the cathode where the foil was.

Figure 8 displays the discussed shadows from the macroscopic substrates more clearly. In this experiment, 3

types of pretreatment for the W foil were tested, a nitric acid pretreatment, an abrasion pretreatment, and no pretreatment.

D. W Powder with Nitric Acid Pretreatment

1) Overview

These powder experiments were conducted to assess the effectiveness of a nitric acid pretreatment on the W powder to remove the surface oxide. The experiments allowed for the analysis of the effects of current density, electrolyte solution and the bonding tendencies at the W and Cu boundary for this pretreatment.

2) Procedure

Refer to Section (iii-E-2), as the procedure used for these two experiment types were the same. However, this experiment did have a pretreatment process that is outlined in Appendix B.

This process is like that presented in [8], which has obtained successful results in encasing W particles in copper.

3) Results and Discussion

The nitric acid pretreatment tests yielded similar results to those of the no pretreatment, however, there were cases of bonding between the W particles and the copper. Largely, the nitric acid wash produced the same cluster of particles at higher current densities and showed some plating, although fewer dendrites, than the powder that was not pretreated. Figure 21 shows a nitric acid pretreatment that was run at the upper bound of the current density in the HCl electrolyte solution.

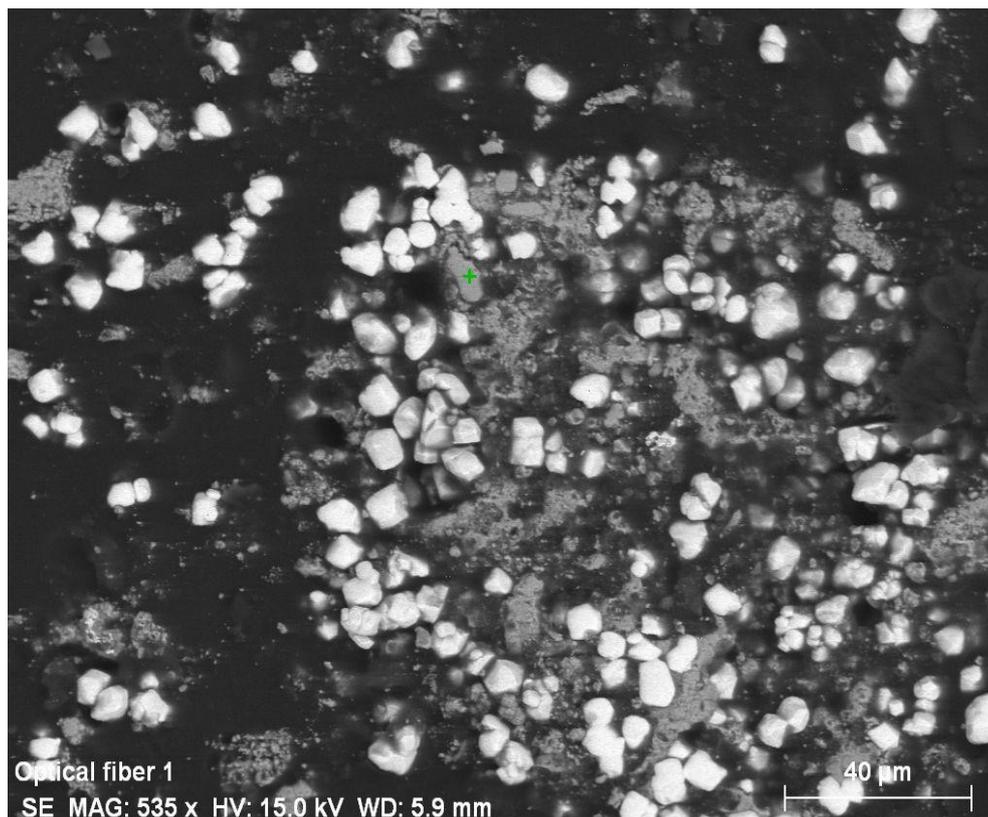


Figure 9: This figure depicts a high current, 3A, being passed between the anode and cathode, after a nitric acid pretreatment

Figure 9 exhibits clustering, like that of the non-pretreated powder, however, clusters are not as drastic. From these results, it was possible that the high current density was causing extremely high local current densities in places that had limited surface oxides and that the nitric acid wash did not remove the surface oxide layer as anticipated, accounting for the massive amount of agglomeration and limited plating. There are traces of bonding between the copper and W powder, however, these connections could be due to gaps in the oxide

layer, rather than actual surface cleaning, as was seen in the non-pretreated powder. While it is a step closer to the goal of encapsulating the W particles, the nitric acid wash was not effective at this current density. The absence of dendrites was consistent with the results from the non-pretreated powder at the high current density. However, unlike the non-pretreated powder, a deeper analysis of the powder sample revealed some particles containing sufficient bonding between the W and Cu, shown in Figure 10.

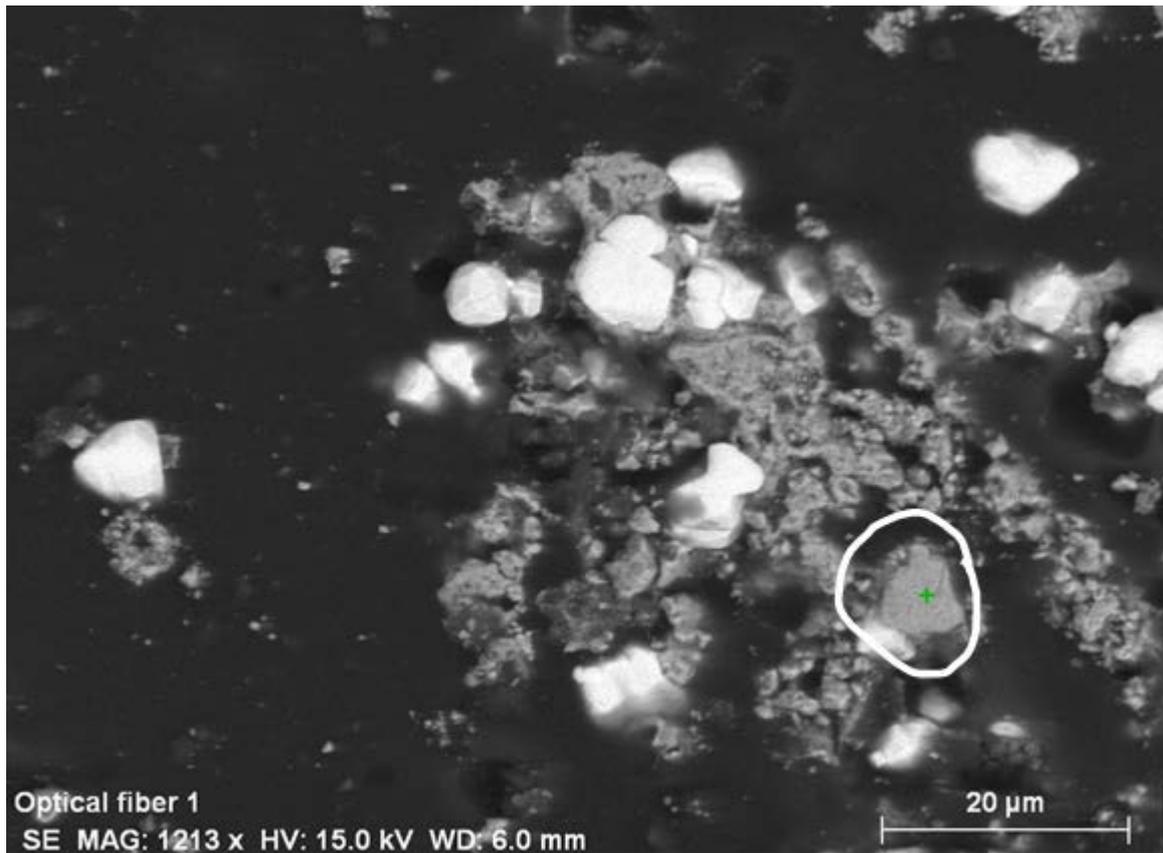


Figure 10: Nitric acid pretreatment at high current showing copper adhering to W surface. Particle shaped agglomeration is circled in bottom right

Figure 10 depicts that the high current density allowed for plating into the obscure geometries of the particles, but the coating itself was not uniform and contained a very uneven surface, if the plating was successful. Once again, it looked to be a result of plating in an oxide layer gap, then having copper ions being attracted there due to its high local current density. This is supported by excess of copper surrounding the W particles and only adhering to the particle in a few areas.

IV. SUMMARY

Electroplating copper on W was a success on both the macroscopic and microscopic scales. On the macroscopic scale, the copper sulfate and H₂SO₄ electrolyte solution was successful for both the W foil and the nickel coins. The solution was tested on its ability to plate 23.4 μm onto the substrate, this amount of plating was accomplished over a 2-hour period at a constant current of 0.25A. The nickel was successfully plated with a 15.12 μm coating on the coin and a 20.97 μm coating on the W foil. The 23.4 μm coat was assuming a plating efficiency of 100%, but some copper was lost due to deposition onto the cathode and the formation of dendrites on the cathode that acted as high current density areas and attracted copper. The plating efficiencies seen in the foil test ranged from 83% to 91%.

V. CONCLUSION

Preliminary experiments showed successful electrode position of Cu on W on a macroscopic and microscopic scale.

Some conditions reported in the literature as providing for success did not work for either W foil or powder, but one set worked. HF pretreatment showed the best results when combined with the copper sulfate and sulfuric acid bath solution for both macro and microscopic substrates. Nitric acid wash and non-pretreated powders were ruled out, as they did not produce successful coatings. This was attributed to an oxide layer remaining on the particles, where for the HF experiments, it was successfully removed.

Literature reports that an ultrasonic bath is necessary to keep particles agitated throughout the experiment to limit agglomeration. Tests confirmed that HF-pretreated powder plated in the presence of ultrasonic agitation had greatly reduced agglomeration, consistent with the literature. Tests were not performed to isolate the effects of these two changes.

The HF pretreated powder allowed good plating and showed promise for replicating the industrial powder that is no longer available. Additionally, the method of electrolytic deposition is a low-cost plating procedure that provides promise for use to obtain industry standard particles.

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