

Electroplating of Copper on Tungsten Powder

Rajesh Kumar Verma¹, Pramod Kumar²

¹Research Scholar, Department of Mechanical Engineering, Rattan Institute of Technology and Management, Haryana, India

²Assistant Professor, Department of Mechanical Engineering, Rattan Institute of Technology and Management, Haryana, India

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.

INTRODUCTION

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].

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 solidification.

ELECTROLYTIC DEPOSITION

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.

EXPERIMENTAL PROCEDURES

Electrolyte Solution

The experiment used one of the electrolyte baths described in Section 2.3.1.2. A large batch was made to maintain a constant solution throughout the experiments. 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

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_2SO_4)	25 mL of 0.5 M
pH	Between 2 and 5

All the ingredients in Table 3 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.

Electroplating Experimental Procedure

Metal powder plating experiments were carried out using the methods described in Section 2.3.1. It was estimated that over 367 cycles were needed to encase all the particles of a 100-gram sample, so that they contained 25 % wt. copper. As mentioned, each cycle included three steps. 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 second step is sedimentation. The stirring is stopped, and the particles can settle back on the cathode. Sedimentation time for this experiment is calculated using Equation 2-8, in Section 2.4.4. After sedimentation, the newly exposed particles can be plated. A secondary effect of this step is that the loosely settled particles create channels that allow the electrolyte solution to spread to particles below the top surface of the powder. This allows for a small amount of copper to deposit on particles that are below the surface layer, slightly increasing the deposition area. 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.

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 31 electron microscope (SEM), with back-scattered electron imaging

MACROSCOPIC SUBSTRATE

Overview

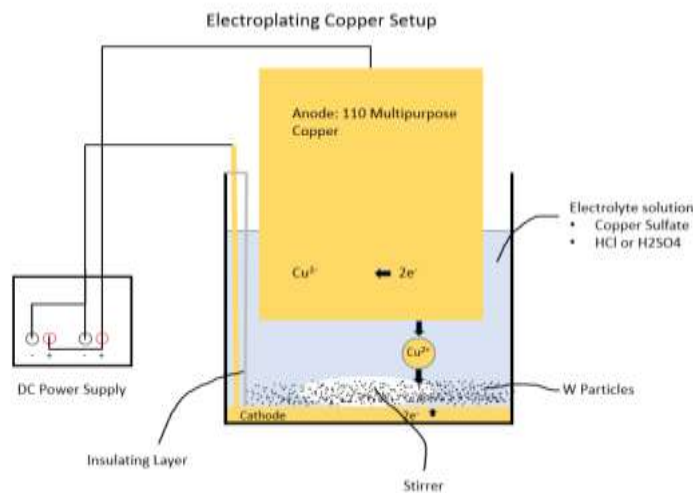
For the nickel coin and tungsten foil substrates, no stirring was used, and the electroplating setup contained no ultrasonic bath. These tests were designed to provide clear tests about electroplating with the apparatus onto a familiar substrate, and then onto tungsten. They were used to provide essential results regarding the current density, sample thickness, the effect of varying pretreatments, and verification of the appropriateness of the electrolyte bath.

Equipment

For the macroscopic substrate tests, the cathode was made of copper foil that covered the bottom of the beaker with a thin tail that was fed up the side of the beaker, to allow contact with the negative power supply lead. The anode used for these experiments was a 2" diameter copper rod, connected to the positive power supply lead. No magnetic stirring was used in the macroscopic experiments.

Setup

To visualize the electroplating apparatus used in this experiment, Figure 11 below, gives a breakdown of the setup and the general concept behind the electroplating mechanism used. For the macroscopic substrate, no stirring bar was used, but the remainder of the setup is consistent. Current is applied by a DC power supply connected in parallel, producing a current of approximately 0.25 A through the solution. The copper rod anode was mounted to a ring stand with a clamp attachment to hold the rod in place. For the macroscopic substrate and initial powder testing, the beaker was placed on top of the magnetic stirring pedestal, but magnetic stirring was only used in the microscopic 36 testing. Note that in Figure 11, the copper foil tape cathode has a contact strip that extends out of the beaker, this contact was insulated from reacting with the anode before the cathode using a polypropylene tube [11]. This contract strip method was developed by Rigali in order to plate powders in a beaker and it played an integral role in achieving a working apparatus.

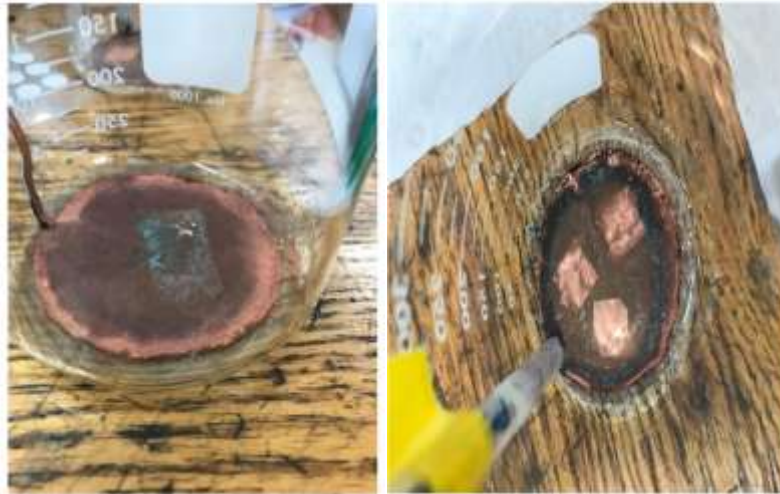


Procedure

Both macroscopic substrates, the coin and the W foil had the same electroplating procedure, although the W foil had extra pretreatments, including a nitric acid wash or a hydrofluoric acid etch, outlined in Appendix B. The substrates were placed on top of the cathode and the anode was lowered over them to create a 30 mm separation. A direct current of approximately 0.25 A was then constantly applied for two hours to each of the substrates. This current corresponded to an ideal current density for the acid copper baths [2]. It was found that 0.25 A was a sufficient current that created enough overpotential to achieve a current density in the ideal range for an acid copper bath, but did not provide an excessive amount, which would have led to the creation of hydrogen bubbles in the solution if the copper ions became exhausted from the boundary layer at the cathode. Accordingly, a current of 0.25 A was used throughout the macroscopic and later microscopic experiments.

RESULTS AND DISCUSSION

Using the thickness calculation presented in Section 2.4.2, the thickness coating on a coin and W foil was able to be approximated under the assumption that the deposition was 100% efficient. 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 12, 15.12 μm , Table 4 was constructed to display the theoretical calculation and the observed values of plating thickness.



CONCLUSIONS

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.

FUTURE WORK

Encasing W particles in copper for cold spray is possible and should have further research put in to accomplishing this task. Electrolytic deposition of copper onto HF electro-etched W powder is currently the most promising method for coating powders for cold spray and further research should be conducted to make the process more efficient to achieve an even better result. The first thing to be done moving forward is to test the experiment over its full duration and analyze the results to ensure most of the particles are getting uniformly plated with the desired thickness of copper. Once this has been determined, the apparatus should be improved to produce a more efficient plating result. Currently, the stirring paddle is blocking a big portion of the cathode from a clear path for ions to move through the solution. Where the stirring mechanism is working, it is rigged together and a more permanent, sleek, design can take its place and increase the clear cathode surface area. The new method must still take place in an ultrasonic bath, as the constant agitation has been shown to increase plating efficiency. A modified set up with a lower profile stirrer or a magnetic stirring drive in an ultrasonic bath may prove more effective for electroplating. Another improvement that should be made is the procedure for transferring the HF pretreated powder into the electrolyte bath. Polarization should be maintained for as long as possible and when taken away, be brought back as quickly as possible. The 71 current method of switching solutions in the beaker takes too long and causes some particles to react with the aqueous solutions to reform the oxide layer. So, a faster or more efficient method of transferring

from the electro-etch to the electroplating would likely increase plating efficiency, as there would be less time for the W particles to reform an oxide layer. Lastly, HF is a dangerous acid and needs to be handled with caution. It is worth searching for a way to remove the oxide without the use of HF to reduce the amount of safety equipment and training necessary to perform the test.

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