



(RESEARCH ARTICLE)



An analytical investigation pertaining to autocatalytic plating of chromium nickel carbide powder on copper alloys using electroless deposition method

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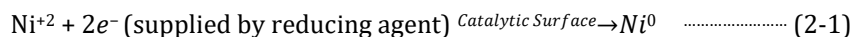
Abstract

Engineered components can gain desirable properties when coated with surface materials. Hard chromium has been given priority in material selection list while making choice for certain wear and corrosion- resistant coatings because of its desirable combination of chemical resistance, adhesion, and mechanical properties. Owing to the existing environmental safety concerns, there is restrictions on the employability of hexavalent chromium ions as plating material. This substantiates a need to develop an environmentally friendly process for alternative coatings. Today, Chromium Nickel Carbide (Cr-Ni-C) is emerging as good quality plating substrate with no the toxic compounds as compared to existing chromium complex. The purpose of this research paper is to investigate electroless processes for plating metal powder, chromium nickel carbide with nickel. These particles were successfully encapsulated with Ni by electroless deposition method using different solutions.

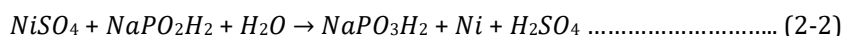
Keywords: Electroless deposition method; Nickel sulphate; Plating; Chromium nickel carbide powder; Copper penny; Encapsulation

1. Introduction

Electroless nickel deposition also known as autocatalytic deposition, is basically a chemical reduction process makes metallic ions achieve a balanced metal state and deposits on the surface of the cathode. Now electroless deposition has yielded deposits of Ni, Co, Pd, Cu, Au, and Ag on various substrates.[3] In electroless deposition of nickel, a reducing agent supplies electrons to metal ions converting them into their metal form, shown in equation (2-1).



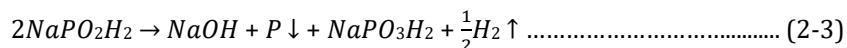
The overall reaction is described by equation (2-2). Nickel sulphate, sodium hypophosphite, and water react to produce nickel, sodium dihydrogen phosphite and sulfuric acid.



Catalytic surfaces are the only place where equation (2-2) reaction takes place. As Ni is deposited, sulfuric is being produced, reducing the pH of the solution. Therefore, ammonia will need to be added to counter the sulfuric acid produced during deposition. Depending on the chemical composition of the bath, there are a wide range of pH values that are acceptable for electroless nickel plating. Acidic baths result in increased phosphorus content, up to 25% at pH value of 4 [3]. Alkaline (basic) solutions can produce less than 1% phosphorus [3] in the nickel coating. With a higher

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concentration of phosphorus, a nickel coating will have a higher corrosion resistance, but the hardness and wear resistance decreases [11]. Equation (2-3) shows the chemical reaction that occurs for phosphorus deposition.



In the equation above sodium hypophosphite disproportionates and produces sodium hydroxide, phosphorus (solid state), sodium dihydrogen phosphite and hydrogen gas. This reaction occurs in parallel with the reduction of Ni, consuming the reducing agent and co-depositing P. As the Ni reaction (2-2) produces acid and the P reaction (2-3) produces alkali, the pH of the solution controls the relative rates of these two reactions.

2. Literature Review

Metal plating has been used for many years to improve the wear and corrosion resistance of materials. Hard chromium has been the plating material of choice for certain wear and corrosion-resistant coatings because of its desirable combination of chemical resistance, adhesion, and mechanical properties. Conventional methods of electroplating will not work on powders. In conventional electroplating the cathode is a large, approximately flat substrate. Powders have to make contact with a cathode and then plate for a short period of time or they will be bonded to the cathode by the plating. The process does not allow for deposition between particles and between the particles and the cathode. Due to the small size of the particles, a new approach was needed. Metal coatings on the particles can be obtained by other technologies, such as chemical vapor deposition (CVD) and physical vapor deposition (PVD) processes. However, the drawbacks of these processes include limited kinds of metal which can be coated on the particles, relatively low metal deposition rate, and high cost [1]. To get Cr-Ni-C powder ready for cold spray, the particles need to be coated with nickel to be able to plastically deform and bond on the surface of another metal. This has been done previously with other materials, such as hexagonal boron nitride, at Pennsylvania State University, using an electroless nickel encapsulation process [2]. Electroless nickel deposition was discovered accidentally by Brenner and Riddle in 1946 [7]. They observed that the additive of sodium hypophosphite caused the cathode efficiency in electroplating to be above 100%. This led to the conclusion that in the solution, a chemical reduction process makes metallic ions achieve a balanced metal state and deposits on the surface of the cathode. Now electroless deposition has yielded deposits of Ni, Co, Pd, Cu, Au, and Ag [3] on various substrates. Plating metal powders is a difficult process to obtain on a micrometer particle scale. Pennsylvania State University has had success encapsulating hexagonal boron nitride with nickel using electroless deposition [2]. Using a similar recipe for electroless encapsulation, Cr-Ni-C powder was also coated in the present work. In this experiment, sodium hypophosphite is the reducing agent. Nickel sulfate is the metal salt (source of ions) that is being reduced. Nucleation sites and the size of the sites are time-dependent functions during the immersion period in the metallizing bath [3]. Cleaning the surface to optimized catalyst sites, as seen in Pennsylvania State University experiment [2], the powders were prepared with a nitric acid solution experiment. The nitric acid should clean the surface of the particles from any contamination, make the surface hydrophilic, and assist with nucleation sites. In other studies, the metal powders were not sufficiently catalytic to initiate the plating reaction and required pretreatment before plating. This was done using sensitizers and catalyst baths, usually tin (Sn) and palladium (Pd) respectively [2] [3] [8]. Depending on the chemical composition of the bath, there are a wide range of pH values that are acceptable for electroless nickel plating. Acidic baths result in increased phosphorus content, up to 25% at pH value of 4. [3] Alkaline (basic) solutions can produce less than 1% phosphorus [3] in the nickel coating. Praxair has reported that Cr-Ni-C particles have a better corrosion resistance than current chromium carbide and nickel chromium powders. The cold spray process operates below the melting point of metals, requires no combustible fuel or gases, and results in a recrystallized structure with compressive residual stresses. In cold spray, solid-state bonding uses the mechanical mixing of particles and the substrate to achieve a strong metallurgical bond. The plastic deformation of particles disrupts oxide films and provides increased strength. High-density deposits. Form thick coatings at high deposition rates, provide low oxide and porosity content. [5] Cr-Ni-C is a fine carbide dispersion in a metallic matrix (fully alloyed), made by Praxair surface technologies. The particle size is 11 μm with an apparent density of 3.715 g/cc. Cr-Ni-C presents a better corrosion resistance compared to other nickel chromium and chromium carbide powders available today. It also shows a higher hardness than chrome plate and currently has the best wear properties of all Carbide – Advanced Powder Technology (C-APT). [6] To deposit nickel onto a substrate using an electroless process, a solution is used to reduce the metal ion to be deposited. The solution may use sodium hypophosphite as the reducing agent. Some advantages of electroless deposition include uniform coating, formation of coatings with unique properties, coatings of non-conductive substrates, and the lack of sophisticated equipment [8]. The only equipment required is a deposition tank, agitation device, heaters, filters and the required chemicals. The main disadvantage is the high cost of chemicals, specifically the reducing agent. The benefits of electroless deposition are a uniform deposition yielding superior corrosion resistance and no edge build up, natural flexibility, and freedom from porosity [9]. To make this process successful, many parameters must be controlled. The following parameters determine the success of deposition:

pretreatments, concentration of nickel in solution, concentration of reducing agent, pH, and temperature, compatibility of depositing metal with substrate, particle size, and particle distribution [9]. With a higher concentration of phosphorus, a nickel coating will have a higher corrosion resistance, but the hardness and wear resistance decreases [11]. Another way to increase deposition rate and lower phosphorus content in a deposition is by using ultrasonic waves in the solution. A study reported that the plating rate of an alkaline hypophosphite electroless nickel plating bath increased 15 times, from 5 μm in 45 minutes to 25 μm in 15 minutes, by the addition of ultrasonic excitation of 20 kHz [13]. In 1978, a similar study to investigate the effects of ultrasonic excitation on electroless nickel plating was published [14]. In this study, the bath constants were: nickel salt, sodium hypophosphite, thiourea. It is shown that in this experiment that the pH was constant at 4.8 and the chemicals being varied were the complexing agents. These should help maintain pH levels, reduce the concentration of free nickel ions, and prevent precipitation of nickel salts such as phosphides [3]. The enhanced performance has attributed to a phenomenon known as cavitation [13]. Bubbles on the substrate's surface develop due to evaporation of the liquid in low pressure regions caused by the ultrasonic wave. The standing waves cause alternating compression and tension/rarefaction. The latter cause's evaporation. The collapsing of the bubbles releases localized energy that is sufficient to break chemical bonds [14]. Agitation also increases the rate of deposition because, due to the production of hydrogen ions at the surface of the substrate, the pH at the surface must be lower than in the body of the solution. The additional mixing due to the ultrasonic waves reduces the thickness of the diffusion layer on the surface and brings the surface interface pH closer to that of the bulk solution. [15]. another class of additives used in electroless baths is called stabilizers. Some bath solutions can be used for a long time without using a stabilizer, while other solutions can decompose very quickly. This decomposition of the bulk solution is usually signified by an increase in bubble formation, hydrogen gas, followed by the precipitation of fine black particles before the solution exhausts itself completely.

2.1. Need of Research

During research process various constraining were encountered amid the process of deposition. The problem to be countered was deposition velocity of cold spray particles which prevents the bonding of Cr-Ni-C to metal surfaces. If the cold spray particles are moving too slowly; they bounce off the substrate. If the particles are moving too fast; they erode the surface of the substrate similar to sand blasting. Cr-Ni-C is a very hard particle that tends to erode the substrate before it can bond to the surface. Hence to accomplish the coating process need to be performed the particles of softer metal that will allow maximum deposition with minimum erosion of the substrate. To get the powder to adhere to another metal using a cold spray process the substrate needs to be coated with nickel. This will allow for the powder to deform at high speeds and bond with a surface substrate.

3. Methodology and experimental set up

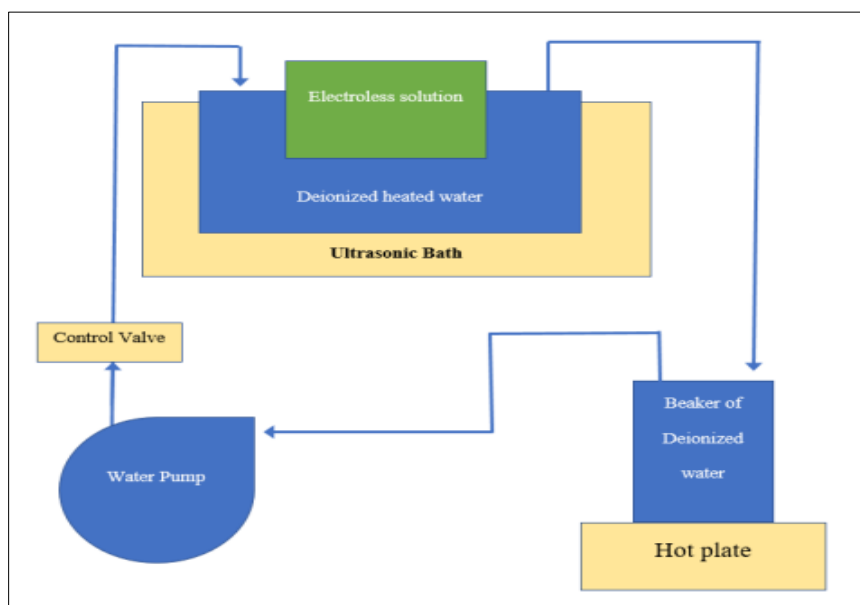


Figure 1 Block diagram of electroless deposition apparatus setup

A new apparatus was utilized for the Cr-Ni-C experiments to achieve a more gradual temperature gradient throughout the solution and use ultrasonic waves to suspend particles one the electrolyte solution.

A copper substrate at 1.9 cm diameter & 0.152 cm thick (a penny of copper was used). In the experiment the water was heated and pumped into the ultrasonic bath. Then water was gravity fed back to the beaker on the hotplate to be heated again. The pump was controlled by regulating the voltage and operating a control valve to maintain a flow rate equal to that in the gravity fed return line flow rate.

3.1. Experimental equipment setup

- Copper penny
- Hotplate
- Thermometer
- Weigh scale
- 20 ml Glass beaker



Figure 2 Electroless nickel plating setup with ultrasonic bath and water pump

3.2. Procedure

For accomplishing the coating process, chromium nickel carbide particles in powdered form was taken as source of bombardment to nickel substrate. The task of coating was performed through these steps:

- A nitric acid solution was used to clean contaminants from the surface of the Cr-Ni-C particles and to create a hydrophilic surface, favorable for deposition. It is called pretreatment process.
- First of all, Cr-Ni-C particles were mounted into epoxy resin pucks and then ground and polished. The particles that were observed ranged from less than 10 μm to approximately 50 μm . Most of the particles were spherical. However, some particles merged together and created different structures. It can also be observed that the particle surfaces are not uniformly smooth and look to have agglomerates on the surface.
- Preliminary experiments were conducted isolating experimental variables and observing a well characterized macroscopic substrate, allowing for the solution, apparatus, and procedures to be evaluated. The microscopic Cr-Ni-C particle experiments were then conducted to evaluate the impact of changing size and material has on performance shown in previous experiment.
- Then Nickel sulfate solution is prepared which was therefore used in experiments on electroless deposition. The ultrasonic bath apparatus allowed for the electroless solution to plate Ni at a temperature of 60 °C compared to the hotplate process that started plating around 85 °C. The initial addition 33 % of ammonia extended the plating process and made it easier to maintain a consistent alkaline pH level throughout the process and lowered the reaction temperature to 44 °C.
- The penny was placed in the solution and the initial pH was measured using pH strips. The hotplate was then set to 150 °C resulting in heating the solution at an initial rate of $\sim 6^\circ\text{C}/\text{min}$. When the solution temperature reached 87°C, the hotplate was turned down. The pH was checked every change in temperature change of +/-

5°C. If the pH dropped by 1, 1 ml of ammonium hydroxide was added to the solution. This was done in an effort to counter the production of sulfuric acid by the plating reaction and maintaining a pH of 10.

- In Figure 2, the solution is being heated to an activation temperature. The electroless plating process lasted 24 minutes from start to finish. The solution was made to add 25% nickel by weight to each Cr-Ni-C particle. For 20 g of pretreated Cr-Ni-C powder, 1/3 of that mass is the required mass needed of nickel, assuming that 100% of the nickel was to be plated on Cr-Ni-C surfaces.
- After about 5 minutes of heating the solution with the hotplate the temperature reached 85 °C. Hydrogen bubbles began to form on the surface slowly and then the production of hydrogen bubbles increased rapidly.
- From the calculations nickel sulphate measured out and placed into a glass beaker. Deionized water was added until solution volume reached the required level. Then the solution was stirred using a magnetic stirrer bar at 700 RPM. Once the powder had dissolved completely, ammonium hydroxide was added to bring solution to a pH of 10.
- The electroless nickel deposition produced sulphuric acid (hydrogen ions) at a faster rate than the ammonia was being added. Therefore, the pH of the solution fell, eventually reaching a pH of 6. Eventually the solution concentration of Ni falls.
- The reaction favors the disproportion of hypophosphite to nickel sulphate. The hypophosphite begins to decompose and phosphorus react with nickel producing Ni-P alloy precipitates in bulk solution. Figure 2, shows the visual change in the solution as plating is occurred.

4. calculation

All measurements were performed inside fume hood with plastic weigh boats. The current and time needed to deposit a given thickness may be calculated as described below. First, amount Ni that can be deposited can be calculated using equation

$$W = \frac{ItA}{nF} \dots\dots\dots(2-7)$$

- W = mass of deposited metal in grams
- I = Ampere
- t = Time in seconds
- A = Atomic mass of metal in grams per mole
- n = Number of valence electrons (Nickel n = 2)
- F = Faraday number (96,485.309 coulombs/mol)

Now the thickness of nickel to be plated (t) can be with a known weight and surface area can be calculated using equation.

$$T = \frac{W}{\rho As} \dots\dots\dots (2-8)$$

On putting the values of current I= 3A and cathode area (A_s) =28.27 cm², rate of plating of nickel on copper penny comes out as 2.23 μm/min.

Observation

- Initially it was observed that hydrogen was only being produced on the surface of the penny.
- With the onset of process, the hydrogen bubbles were also being produced on the bottom surface of the beaker. This was due to the temperature at the bottom of the beaker was substantially greater than that of the bulk solution.
- It was also observed that once the process began, the solution began to cool down even though the solution was being heated by the hotplate. Initially the hotplate was set to 150 °C until the solution reached a temperature of 87 °C. Then the hotplate was lowered to 100°C until the solution reached 80 °C, at which point the hotplate was increased back to 150 °C.
- The electroless macroscopic experiment shows that the process lasted about 22 mins and the pH dropped at a steady rate until ammonia was added where the pH remained constant

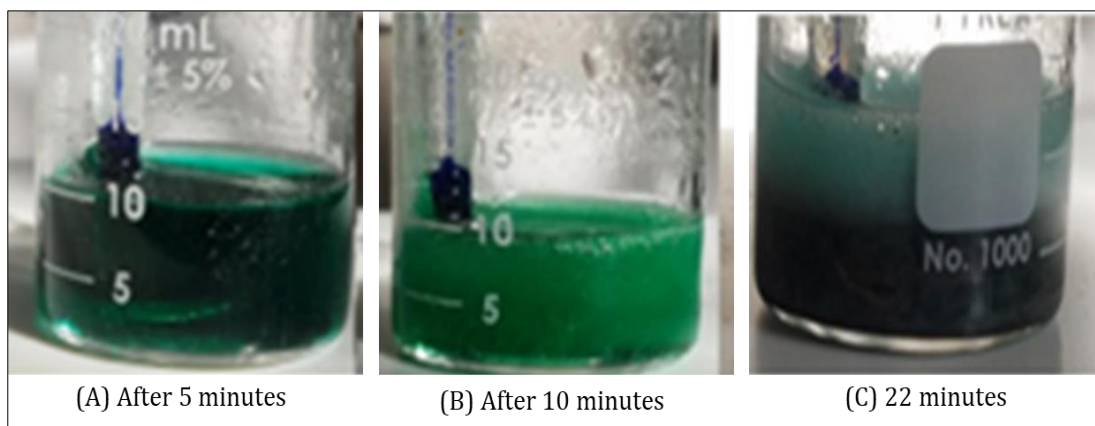


Figure 3 In process images of electroless nickel powder plating on copper penny

- It was observed shows the solution temperature decreased even when the hot plate temperature increase. This decrease in temperature can be attributed to the boiling of the ammonia, absorbing its heat of vaporization.

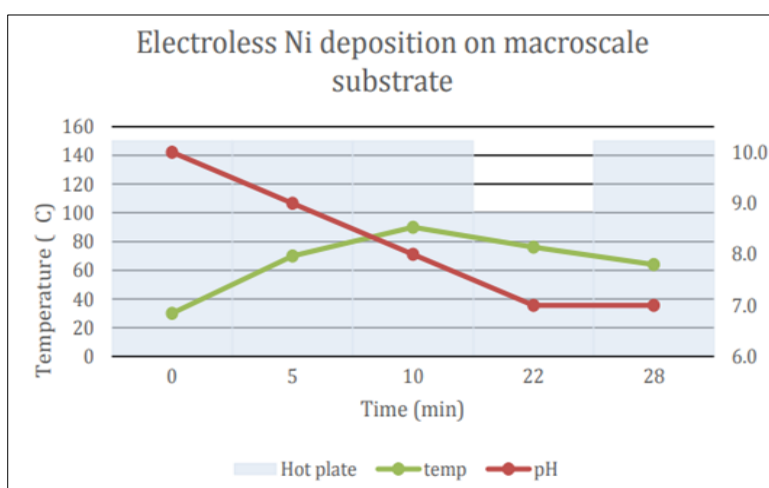


Figure 4 Electroless Ni deposition on macroscale substrate (penny)

- Electroless experiment with no initial ammonia surplus shows a constant rise in temperature and a sharp drop in pH at 19 minutes leveling off after 22 minutes with a pH of 6.

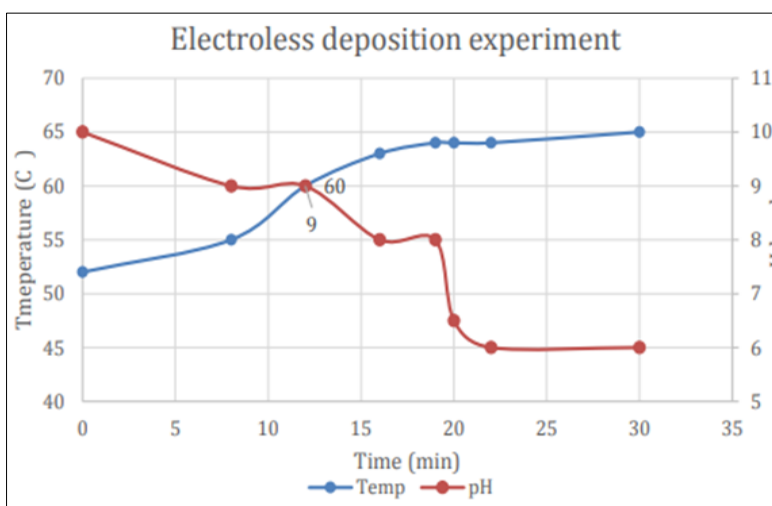


Figure 5 Variation of rise in temperature and pH level during electroless deposition level

5. Results

- The apparatus worked as intended and allowed for a lower temperature gradient throughout the solution compared to the hotplate.
- No particulates were deposited on the beaker except for a thin layer of black precipitates above the surface of the solution deposited by droplets of solution splattered by the bubbles and ultrasound.
- The reaction began at a temperature of about 60 °C and the duration of deposition was 22 minutes. Before a reduction in the rate production of hydrogen bubbles was observed, a small sample was removed from solution, about 15 minutes after the production began. After the hydrogen bubble production reduced to small isolated areas and not throughout the bulk solution, the entire solution then was removed from the ultrasonic bath.
- The penny was fully coated by nickel as shown in Figure 6. The black rough surface was due to nickel phosphorus alloy that precipitated at the end of the experiment as the remaining solution decomposed.



Figure 6 Electroless Nickel coated Penny

- This can be attributed to two reasons:
 - Decrease in pH levels allows for a greater percentage of phosphorus deposition and
 - Reduction of nickel concentration in the bulk solution allows for the phosphorus to co-deposit with the remaining nickel.
- Backscattered electron image of Ni coating using electroless deposition. The image shows a total coating thickness of approximately 15.41 μm with approximately 13.33 μm of almost pure Ni.

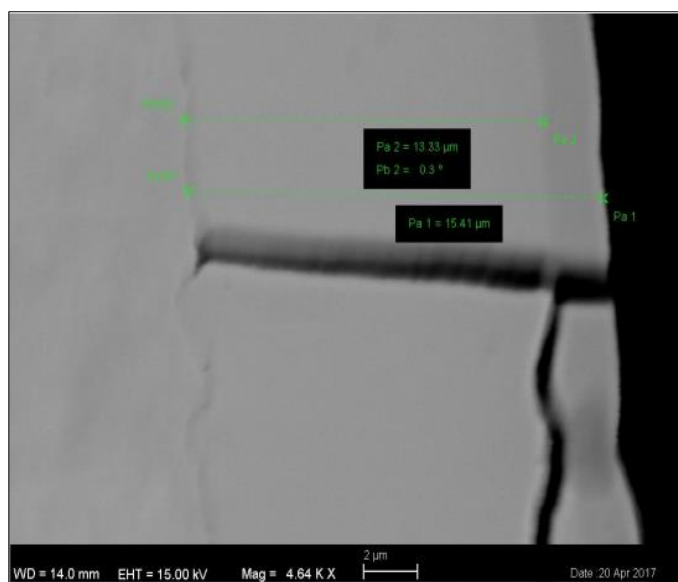


Figure 7 Backscattered electron image of Ni coating using electroless deposition

- Through energy dispersive spectroscopy (EDS), the composition of the materials being imaged can be identified. Figure 8 is an EDS image of the electroless nickel encapsulated copper penny that was cut with a diamond blade and then ground and polished. Through energy dispersive spectroscopy (EDS), the composition of the materials being imaged can be identified.

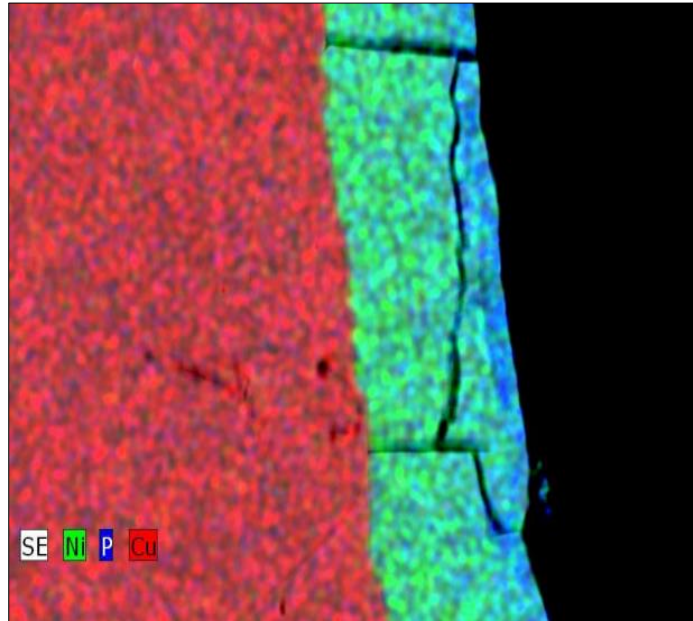


Figure 8 The EDS image of an electroless deposition on a penny

The above figure uses EDS to highlight different atomic species present in the sample. Green is Ni, blue is P, and red is Cu. A point capture in EDS shows that the green section is almost pure Ni. It shows that a large amount of Ni was being deposited until the end of the process.

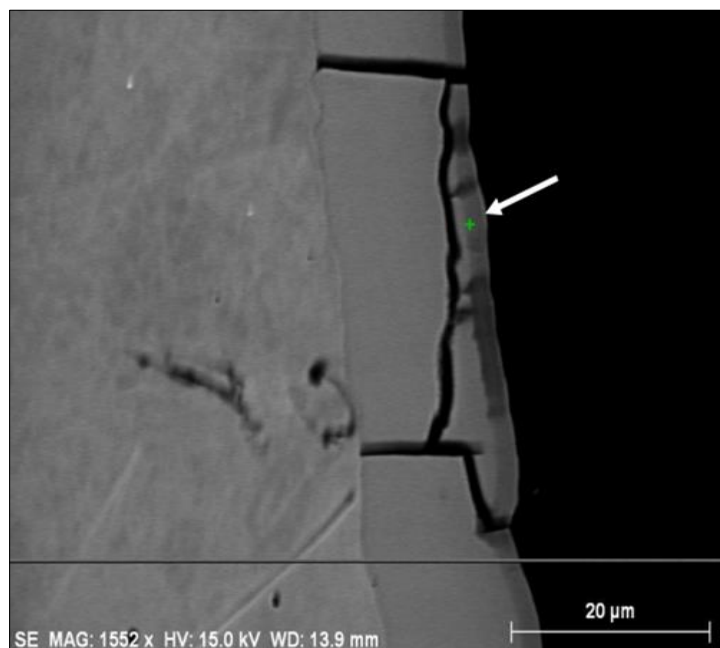


Figure 9 Backscattered electron image of the same region of coating, with the location of a point analyzed by EDS superimposed

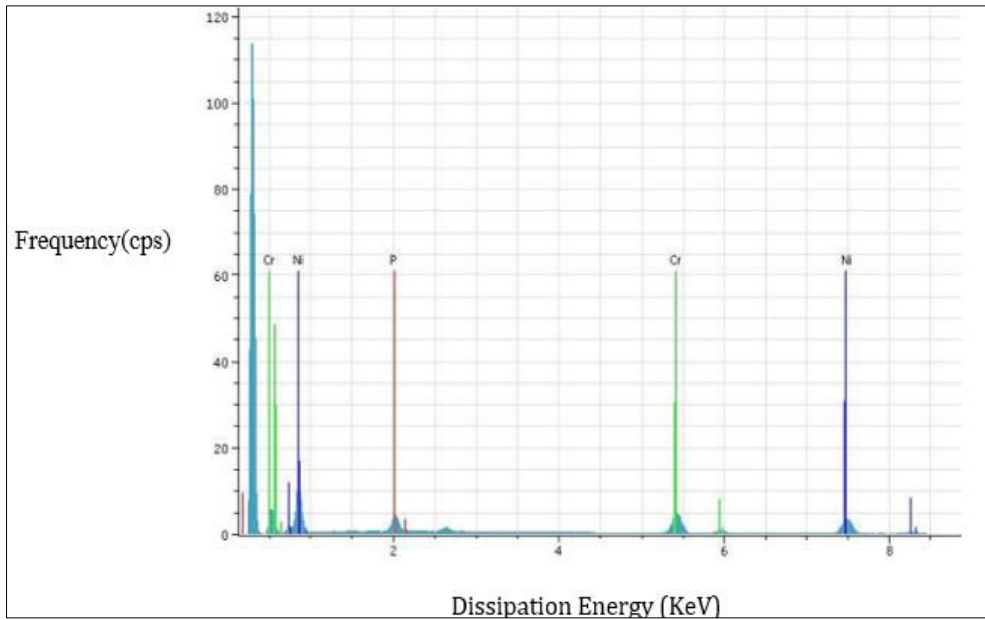


Figure 10 The EDS Spectrum of the point indicated point on backscattered electron image

- EDS Spectrum shows that this outer layer of the deposit is Ni. The large spike on the left is comprised of low-energy Ni and Cr x-rays superimposed with carbon, therefore are disregarded in the quantification. The carbon x-rays are from the carbon coating covering the epoxy.

Table 1 EDS Concentration data from EN Penny point capture in high phosphorus area

| Element | Norm. wt.% | Norm. atomic % |
|------------|------------|----------------|
| Phosphorus | 12.99478 | 22.08972 |
| Nickel | 84.9702 | 76.22414 |
| Copper | 2.035016 | 1.686144 |
| Total | 100 | 100 |

Table 2 ED's composition of electroless sample

| Element | Norm. wt.% | Norm. atomic % |
|------------|------------|----------------|
| Phosphorus | 7.09 | 12.22 |
| Chromium | 28.51 | 29.25 |
| Nickel | 64.38 | 58.51 |
| Total | 100 | 100 |

Table 3 Efficiency of plating process on copper pennies achieved in the experiment

| | |
|---|--------|
| Theoretical thickness of Ni calculated from equations (μm) | 2.2374 |
| Actual thickness of Ni achieved during experiment(μm) | 1.929 |
| Plating efficiency achieved during the experiment | 86% |

Inference

- Electroless nickel plating was a success at the microscale and on microscopic Cr-Ni-C powders with the nickel sulfate solution. The nickel chloride solution failed to deposit any nickel during the macroscopic experiment therefore was not tested on the powder.
- The nickel sulfate solution was tested in on a hot plate with a copper penny with enough nickel to provide a 20 μm thick coating and was successful in producing a 15 μm thick coating. Some of the nickel was lost due to deposition on the bottom of the glass beaker and formation of Ni-P alloys.
- For the electroless experiments, the temperature of which the reaction began varied depending on the apparatus used. The penny experiments conducted on a hot plate activated at 85°C where as in the ultrasonic bath the Cr-Ni-C experiments began at 60°C with no surplus of ammonia and 44°C when an initial surplus of ammonia was used.

6. Conclusion

The research mainly focused on deposition of Cr-Ni-C on copper alloy (penny) by electroless plating method. The electroless method shows much more uniform coatings and much less agglomeration than electrolytic method. Electroless deposition is currently the most promising method for testing of coated powders for cold spray, but with further electrolytic research, and electrolytic apparatus could be designed to outperform the electroless method. Within the electroless deposition experiment, the best results were achieved with initial excess of ammonia, which improved both the controllability of the plating process.

Future work

Encapsulating Cr-Ni-C particles for cold spray application is possible and should have further research conducted to accomplish this task. The electrolytic apparatus can be improved with designing an anode that matched the surface of the cathode and allow a mixing device to be utilized. The anode could be shaped into a doughnut design that would allow a nonmagnetic stirring device to be mounted in the center. The electrolytic apparatus could also be conducted in an ultrasonic bath. Further experiments, should be conducted in an ultrasonic bath without using a mixing device and only using the agitation.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

Author declares that there are no conflicts of interest in any form. It is declared that there is no relevant or material financial interests of both authors pertaining to the research work. The data used in this research is proprietary in nature.

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