SYNTHESIS AND CHARATERIZATION OF Ni-P-W COATING ON COPPER SUBSTRATE

By

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Abstract

Nickel phosphorus coating is widely used in various industrial applications, due to its excellent corrosion and wear resistance properties. The coating can be further improved by the addition of various elements to form composite coatings. The primary objective of this work was to incorporate tungsten into nickel phosphorus coating by using electroless and electrolytic processes. Surface characterization of the coatings were done examined using scanning electron microscope and energy-dispersive X-ray spectroscopy. Corrosion behaviour of the coatings were evaluated using cyclic polarization and electrochemical impedance spectroscopy. Cyclic polarization was used to determine the passivation range along with re-passivation potential. Electrochemical impedance spectroscopy was used to evaluate the impedance of the coatings. The details of the results are discussed in thesis.

List of Abbreviations and Symbols

SEM	Scanning Electron Microscope
EDS	Energy Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
CP	Cyclic Polarization
SCE	Saturated calomel electrode

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Chapter 1 Introduction

1.1 Background and objectives

Nickel phosphorus coatings are commonly used in the various industry. They feature good hardness and corrosion resistance with good economics. These properties help extend the life time of mechanical parts such as gears and equipment such as pipelines [1]. If sulfur oxidation bacteria or sulfur reduction bacteria exist, the steel pipeline will be more seriously corroded. The corrosion resistance of the Ni-P coatings is a result of a passive film that forms on its surface which has the ability to significantly reduce mass transfer of oxygen thus reducing corrosion [2]. Excellent wear resistance is also an advantage of Ni-P coatings, as these coatings are hard and self-lubricating. They provide a tougher surface compared to steel, reducing material loss due to erosion thus protecting steel structures [1].

In this research, copper is used as the substrate material. It has excellent stability in dry condition, which allows it to be stored for extend period without re-finishing the surface. However, copper will be oxidized quickly in wet and oxidation agent rich environment. Pure copper will also be oxidized when high temperature condition is applied [3]. It forms a passive film which protects the metal underneath, preventing further corrosion from happening. However, when in contact with acidic species, the passive film will dissolve, exposing base metal and generating toxic copper cations in aqueous solution. It might be harmful to human health, especially when used as cooking equipment, food container and water pipelines [3]. Applying nickel based coatings is a solution to this problem. Copper will not get involved in plating processes since it is more noble than nickel. This could eliminate side reactions like sodium tungstate reacting with copper to deposit tungsten. Copper is a very good conductor but not a magnetic material. It would provide good grounding when performing SEM-EDS without generating its own magnetic field which might interfere with the coating.

The objective of this study was the production of Ni-P-W coatings by electroless and electrolytic processes. Their physical and electrochemical properties will also be evaluated as the secondary objective, if the plating process is successful. This research provides a comparison of Ni-P and Ni-P-W coatings produced by different coating method. The specific objectives of each research stage are summarized as follows:

1. Formation of Ni-P-W composite coating by electroless and electrolytic processes.
2. Surface characterization by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)
3. Electrochemical evaluation of different coatings by using cyclic polarization (CP) and electrochemical impedance spectroscopy (EIS)

4. Wear resistance and toughness measure and comparison using scratch test and micro indentation.

1.2 Electroless nickel-based coatings

Electroless coating process is commonly used to achieve nickel-based coatings. It is an autocatalytic process which does not require external electrical energy input. Thermal energy is the only energy required for the coating process thus making the process simple. It provides a uniform coating regardless of the shape or geometry [1].

Ni-P coating can be further improved by the addition of various elements into the lattice. They are known as nickel phosphorus composite coatings. Examples of additives are titanium, graphene, manganese, cobalt or tungsten. It is known that a co-deposition with some transition metal, transition metal oxides or none-metallic elements may result in better erosion and corrosion performance [4]. With the addition, the cost of the solution may increase. The reaction mechanism of composite coating is more complex thus hard to be determined. For some elements or materials, the common coating procedures might not work resulting in no or reduced deposition. In this thesis, tungsten was the element to form a composite coating.

1.2.1 Plating solution

Electroless coating solution contains a metal source and a reducing agent. The metal source is usually a nickel salt such as nickel sulfate [5]. Reducing agents are varying. Sodium borohydride is used for high pH application. The plating solution has a pH of 12-

14. The use of borohydride yields a high nickel concentration up to 99.9% nickel as nickel is in favor to be reduced in alkaline condition. The issue with using boron compounds is the waste treatment. It is no longer used for electroless nickel plating due to its environmental concerns. Sodium hypophosphite, which has an operating range of pH from 4-6 or 7-10, is more widely adopted in present day electroless nickel plating as a reducing agent [5]. However, acidic and basic plating solutions have different additives thus directly adjust pH of from acidic to basic condition and vice versa is not recommended, which might cause solution dissociation.

Other constituents necessary for electroless nickel plating, are complexing agents and stabilizers. Complexing agents are organic acids or their salts such as acetate and citrate, with two exceptions of inorganic pyrophosphate anions, which are used exclusively in alkaline solutions, and ammonium ions, which is usually added into the plating bath for pH control. Complexing agents have three principal functions. They perform a buffering action that prevents the rapid decrease of pH during the coating process. They also prevent the precipitation of nickel salts as well as reduce the concentration of free nickel ions [5], making the solution a more stable environment through the entire plating process.

Stabilizers are used to prevent subsequent random decomposition of the entire plating solution. A decomposed solution contains finely-divided black precipitate through the bulk of the solution. However, electroless nickel plating solutions can be operated under normal conditions for an extended period of time without adding stabilizers. If the plating solution can be made right before the coating process, the chance of random decomposing will be minimized [5].

The reaction mechanism of electroless nickel phosphorus has been thoroughly studied in previously research [5]. The core reactions are hydrogen-surface catalyzed reactions. First, hypophosphite reacts with water to form atomic hydrogen on the surface of the substrate or existing Ni-P coating. The reaction is shown in $R-(1)$. The second stage consists of two reactions occuring simultaneously. The first one, shown in $R-(2)$, is hypophosphite reacting with atomic hydrogen to form hydroxide anion and elemental phosphorus. In the second reaction, $R-(3)$, nickel cations are reduced by atomic hydrogen on the surface into nickel metal. Elemental phosphorus co-deposits with nickel to form Ni-P coating. Atomic hydrogen is oxidized into hydrogen cations and returns to the solution. For each nickel ion reduced into metal, the reaction produces a hydrogen cation [6]. For a batch process, hydrogen cations accumulate in the bath, causing a decrease in the pH. If the pH is too low, electroless nickel coating will slow down and eventually stop [5].

$$H_2PO_2^- + H_2O \rightarrow H^+ + H_2PO_3^{2-} + 2H_{(atomic)} \qquad R-(1)$$

$$H_2PO_3^- + H_{(atomic)} \rightarrow H_2O + OH^- + P \qquad R-(2)$$

$$Ni^{2+} + 2H_{(atomic)} \rightarrow Ni + 2H^{+} \qquad R-(3)$$

Hydrogen generation is a side reaction in electroless coating. In this process, hydrogen cations are reduced to form hydrogen gas. This process will decrease the number of cations in the solution, slowing down pH reduction. Ni-P coating is a catalyst of this process [7].

For Ni-P-W coating, the solution is mostly the same as the electroless nickel solution. The only difference is that sodium tungstate is added as a metal source for tungsten.

A possible reaction mechanism is proposed based on the chemical properties of tungsten and the solution environment. Tungsten itself does not have a stable ion in the solution like nickel. Tungsten oxide anions are more common to exist in plating solution environment. Tungsten is usually presenting as tungstate, WO_4^{2-}, in the solution as it is the most stable state [8]. During the electroless coating process, tungstate would be reduced by the hypophosphite into tungsten oxide or tungsten metal [9]. The chemical reactions are:

$$WO_4^{2-} + 4H^{+} + 2e^{-} \rightarrow WO_2 + 2H_2O \qquad R-(4)$$

$$WO_4^{2-} + 8H^{+} + 6e^{-} \rightarrow W + 4H_2O \qquad R-(5)$$

The standard chemical potential of WO_4^{2-} reduced to WO_2 is 0.386 V. The chemical potential of WO_4^{2-} reduced to tungsten metal is 0.049 V. The standard chemical potential of nickel is 0.25 V [10]. Reaction of WO_4^{2-} to WO_2 is higher than standard chemical potential of nickel. That means, thermodynamically, tungsten is more possible to spontaneously be reduced than nickel cations. Tungstate has a slightly lower reduction potential than hydrogen cations. Tungstate should be reduced prior to hydrogen generation [11].

1.2.2 Factors affecting the properties of the coatings

During the electroless coating process, the composition of the coating is affected by both the substrate material and solution condition. The influence of the substrate material includes its composition, surface finish due to polishing and possible contaminations like oxidation layer and oil [12].

Although the substrate is important in electroless coating, the coating quality depends mainly on the coating solution. Concentration of various ions, pH level, temperature, pressure and stir rate of the solution are some of the variables. The lower the pH of the coating solution, the higher the phosphorus content. It is because in low pH solutions, the reduction of nickel slows down resulting in a lower deposition rate [13]. Temperature plays an important role too, since it is the only energy input, and if the temperature is too low, the reaction may slow down to a complete halt [14]. The coating will be thinner compared with a higher temperature process. Agitation helps distribute the ions more uniformly. It prevents local depletion of the ions near the substrate. It also helps to increase the kinetics thus produces a thicker coating [15].

1.2.3 Surface morphology and composition

Electroless Ni-P and Ni-P-W coatings both have cauliflower structures consists of randomly distributed nodules. Ni-P-W coating has slightly reduced surface roughness as shown in the figure 1. However, the scanning is focused on a small section, a larger are should not show such a significant difference [16].

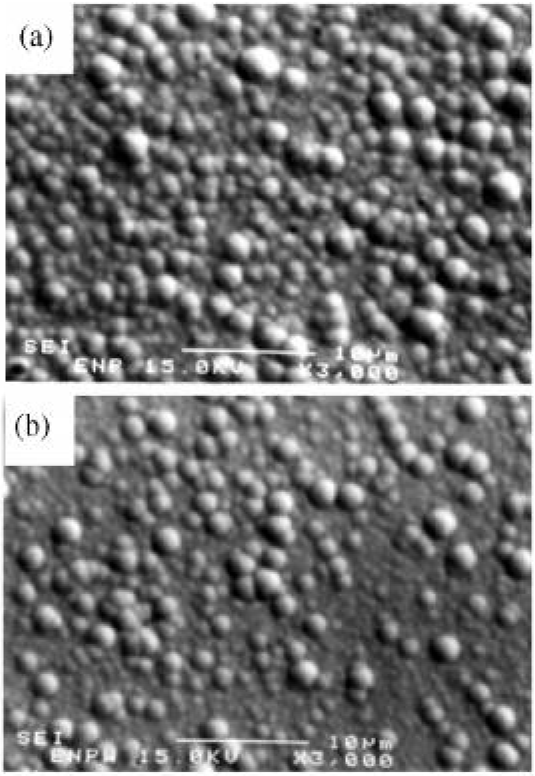


Figure 1: SEM images of (a) electroless Ni-P and (b) electroless Ni-P-W coatings [16]

The composition of Ni-P coating varies. Low phosphorus coatings (1 – 4 %) are microcrystalline structures and possess high hardness. High phosphorus (> 10 %)

coatings have better salty and acidic resistance [17]. Ni-P-W composite coatings have lower phosphorus content. The nickel content mostly remains unchanged [18].

1.2.4 Mechanical and electrochemical properties

Ni-P coating is already a hard-coating material used to increase wear resistant of the substrate it is deposited on. Low phosphorus content coating has wide real-world application such as pipeline steels [19]. Tungsten may improve this even further as it is a hard element by nature. Tungsten carbide is an extremely hard material used for the construction of the first nuclear bomb “Little Boy” [20]. It makes tungsten a potential composite coating to provide good erosion resistance. Literature shows that by reducing grain size to 20 nm, the hardness can be significantly improved [9].

Like nickel, tungsten is thermodynamically easy to be oxidized. However, tungsten’s most favored state of charge is +6. It will form tungsten trioxide which is an oxidation film that reduces the mass transfer of oxygen [9], making it possible to be a corrosion resistance coating. A former study shows incorporating a low tungsten content of 1 – 5 % in Ni-P-W coatings, the corrosion resistance increases [21]. However, the corrosion resistance drops slightly between 5 -15 % due to galvanic corrosion in solid solution of tungsten in nickel [21].

1.3 Electrolytic nickel-based coatings

Electrolytic coating requires electrical energy input. During the plating process the substrate to be plated is connected to the negative terminal of a DC power source and made the cathode. The positive end of the power supply is connected to an anode made of materials necessary to replenish the depleted ions. Nickel is normally used as anode. It replenishes the used nickel during plating. Since this is nickel and tungsten composite coating, a nickel tungsten alloy should be used. However, the melting point of nickel is 1522 °C while tungsten is at 3442 °C [22] [23]. Using nickel tungsten alloy manufactured by conventional pyrometallurgy is impractical. From former study, a solution consists of different metal cations is used with a non-reactive anode [24]. Thus, the plating solution in the electrolytic plating process is very similar to the one used for the electroless one.

1.3.1 Plating solution

The solution of electrolytic nickel-based coating is similar to electroless coating solution. Electrolytic coating requires solution with high conductivity. Since electrical energy is needed, a reduced solution resistance can reduce the voltage requirement. This could increase the plating efficiency. However, commercial electroless plating solutions usually have proprietary additives, which some of these additives will inhibit certain reactions if electrolytic plating process is used. Some of the ingredients will only react at higher temperature, which will not get involved in electrolytic plating at room temperature.

1.3.2 Factors affecting the properties of the coatings

Most of the factors affecting the properties of the coating are the same as electroless process with the exception, that an electrical current is applied. The higher the current flows, the faster the coating will be produced. However, in electrolytic coating, current density and current distribution will affect the properties of the coating. If the current density is too high, the plating processes will happen too fast thus a smooth consistent coating may not be developed. Current distribution will affect the uniformity of the coating. A perfect parallel current distribution between cathode and anode would yield a coating of similar thickness. In real world scenarios, current distribution is not perfectly uniform, which will result in a thicker coating in the center of the substrate and a thinner coating at the edges.

1.3.3 Surface morphology and composition

The surface morphology and composition of electrolytic coatings should be similar to coatings produced by electroless process. However, the thickness of the coating might be different due to different reaction mechanisms. Meanwhile, electrolytic coating is more sensitive to substrate surface structures since it will affect current distribution. The surface of electrolytic coating might be rougher than electroless coating as nickel and tungsten would deposit on sharp edges generated by polishing processes rather than uniformly coating the entire surface.

1.3.4 Mechanical and electrochemical properties

The mechanical and electrochemical properties are expected to be similar to the electroless coatings. If the coating composition is different, the properties will change to reflect that.

Chapter 2 **Experimental**

2.1 Sample preparation

Sample preparation was done for both electroless and electrolytic plating processes. In both cases a 99.99% pure copper bar with a 2.5 cm diameter was cut into 10 mm thick disk-shaped samples using a band saw.

All samples were ground using 80 grit aluminum oxide grinding paper and 240, 320 and 400 grit SiC polishing discs. Halfway through the experiment, further polishing using 9, 3 and 1 µm diamond paste were performed due to the potential requirement of performing wear test and nanoindentation. As an applied electrical current is needed for the electrolytic plating process, an electrical wire was soldered to the back of each sample. The wire and sample assembly were then coated with Plastidip to isolate them from the plating solution. Three layers of paint are applied with 30 minutes of drying time in between. The fully painted sample will be placed in the fume hood for 24 hours to reach completely dry. It is then tested using a digital multimeter. Samples with a perfect electrical insulation between the side and the wire will be accepted to perform electrolytic coating.

Due to instrument limitation, the diameters of the electrolytic plating samples were reduced to 1.5 cm in order to be able to fit into the surface profiler and scratch tester.

During painting process, it shows that paint will concentrate into small droplets, where sharp edges and corners of the sample could not be covered by paint. To solve this problem, poly-ethylene resin is used to seal the edges. The resin is applied using a paint brush. 24 hours later, the same electrical conduction test will be performed to make sure only hardened and well insulated samples will go through the coating process.

Following polishing and soldering, all samples were rinsed using tap water and then dried using filtered compressed air. They were first stored in small sample Ziplock, which were then transferred into a plastic sample storage box for coating processes.

2.2 Solution preparation

Three solutions were prepared:

1. Atotech electroless and electrolytic nickel phosphorus coating solution
2. Atotech electroless and electrolytic nickel phosphorus tungsten coating solution
3. Inhouse electrolytic nickel phosphorus tungsten coating solution

Atotech electroless and electrolytic nickel phosphorus coating solution was made based on ATOTECH® NICHEM 2500 concentrated coating solution shown in figure 2. Nickel phosphorus solution was made first by adding 80 ml of solution A and 150 ml of solution B are used. The exact composition of the solution is kept confidential by the manufacture. From the safety data sheet, solution A contains 30 grams of nickel sulfate per liter. Solution B contains 5 to 30 grams of hypophosphite per liter. The mixture of solution A and B was then topped to 1 liter using 770 ml of distilled water. Since all contents are in aqueous form, stirring is not needed. There is no tungsten in this solution. It is used for test and comparison purpose.

Figure 2: Atotech concentrated electroless nickel solution

Sodium tungstate was added when Ni-P-W coating was needed. EMSURE® sodium tungstate dihydrate powder was used for this experiment. After making 1 L of Ni-P plating solution using Atotech concentrates, 5g, 15g or 25g of sodium tungstate was added into the solution. The amount of tungstate was based on previous literature and experimental requirements. At the beginning of this project, solution containing sodium tungstate was placed into an ultrasonic mixer to dissolve the powder. Later in the experiment, the solution was placed on to a heating stirrer, heated to 60 °C while stirring at 100 rpm. Using heat and magnetic stirrer can dissolve the powder faster. It takes around 5 minutes to dissolve all sodium tungstate compared with 10 to 15 minutes using ultrasonic.

The solution can be used for about 20 operating hours. This was because the samples are small, the reduced amount of nickel and tungstate depleted from the solution was insignificant to cause a compositional change for the coating. The color change of the solution was an indication when the solution should be replaced.

In-house solutions were made for testing without using Atotech solution from industrial supplier. They were made using all powder chemicals. The brands and catalogue numbers of these chemicals are included in the Appendix A. Strictly following the notes provided by former study [25], the composition was as follows: 20 g/L of citric acid, 30 g/L of nickel sulfate, 50 g/L of sodium tungstate, 1 g/L of sodium hypophosphite, 2 g/L of sodium allyl sulfonate and 1 g/L of saccharin. Since most of the chemicals are delivered as hydrates, the weight was recalculated before proceeding. A wetting agent was proposed in the plating formula found. However, it was not used since copper samples were chosen as substrate which does not require wetting agent to maintain the surface hydrophilic. Nickel sulfate hexahydrate has a unique bright blue color. When dissolved, the solution color was green, which was the same as the industrial coating solution from Atotech.

It was recommended to adjust the pH to 8 using ammonia hydroxide at 60 °C. However, during the experimental phase, it was found that white precipitation forms at pH=6.5. The solution becomes heterogenous at pH=8 in figure 3. It was well enough to say a solution dissociation happens at a pH higher than 6. To be safe for coating, the pH of the solution was adjusted to pH=4.5.

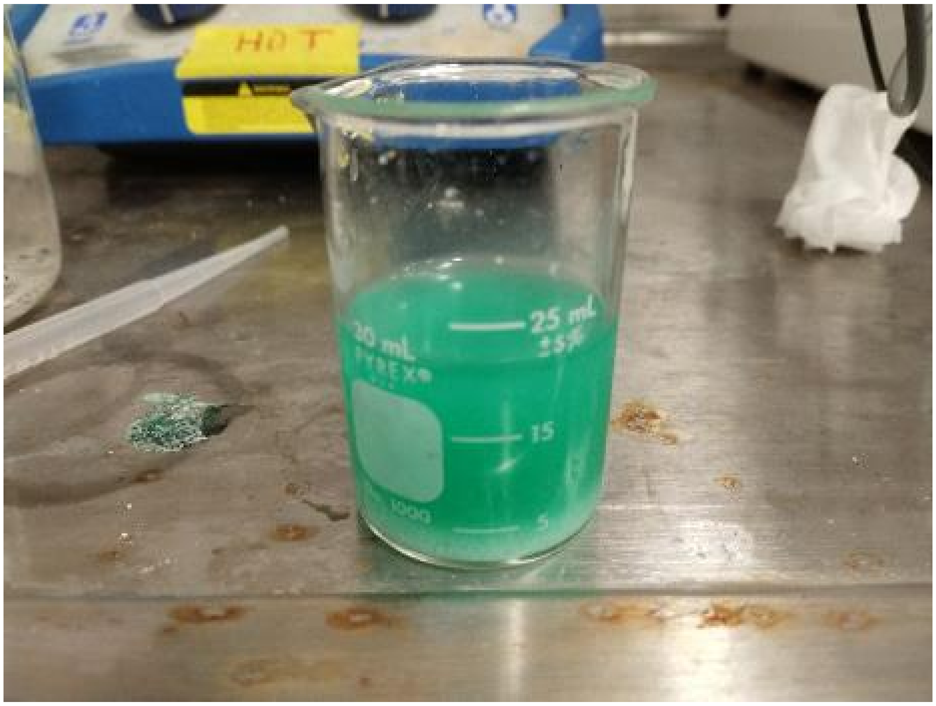


Figure 3: Solution dissociation to be heterogenous at pH=8

2.3 Equipment

There are two categories of equipment: glassware and instruments. Three types of glassware are used. A round bottom flask is used for electroless coating. Figure 4 shows the equipment setup of electroless coating process. Flat bottom flask is used for electrolytic coating. The anode of the electrolytic process can only be placed on the flat bottom. Finally, a flat cell is used for all electrochemical evaluations.

An electrothermal heat mantle is used in electroless coating to heat up and stir the solution. A Hitachi S-4700 scanning electron microscope in Figure 5 coupled with OXFORD X-Max 80 mm^2 EDS detector, Figure 6, are used in SEM-EDS test. They were used to characterize the surface. For electrolytic coatings and electrochemical evaluations, PAR 273 Potentiostat and Solartron 1253 Frequency Response Analyzer, Figure 7, are used. For mechanical tests, two different equipment are used. Scratch tests are performed on CETR scratch tester shown in Figure 8, while micro indentation tests are performed on PASCO indentation tester shown in Figure 9.

Figure 4: Electroless coating set up with Electrothermal heat mantle

Figure 5: Hitachi S-4700 scanning electron microscope with vacuum pump below

Figure 6: OXFORD X-Max 80 mm^2 EDS detector

Figure 7: PAR 273 Potentiostat and Solartron 1253 Frequency Response Analyzer

Figure 8: CETR scratch tester

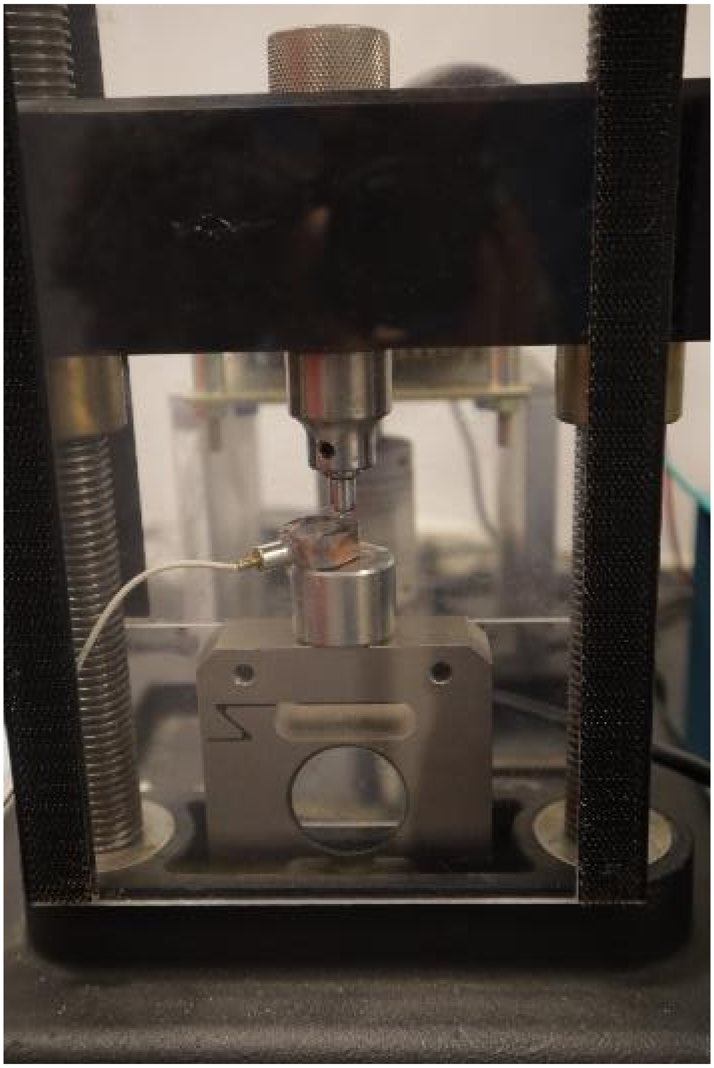


Figure 9: PASCO micro indentation tester

2.4 Coating procedure

2.4.1 Electroless process

Early in the experiment, a degreasing process was used. The copper substrates were submerged in two cleaning solutions in a sequence. The basic solution was made of 15 g/L sodium hydroxide, 10 g/L of sodium phosphite and 10 g/L of sodium carbonate. It was first heated to 60 °C using a hot plate. The copper sample was then submerged into the hot solution for 3 minutes. The acidic solution consisted of 10 % sulfuric acid solution. The sample coming out from the basic solution was dipped into the acidic solution for 10 seconds. It was then fully washed by distilled water before placing into the coating solution.

The degreasing process proved as an unnecessary process. The detail is mentioned in the discussion. Later in the project, the copper samples were only rinsed by distilled water before submerging. For Ni-P electroless coating, polished sample were hung vertically in the plating solution using a plastic wire. A heating mantle was used to maintain the temperature of the solution at 90 °C while provides stirring at 100 rpm. Rubber stoppers were used to cap the cell open ports in order to minimize solution evaporation. The samples were coated for 1, 2 and 3 hours. After several unsuccessful runs at 90 °C, the temperature was then set to 95 °C.

For Ni-P-W coatings the same procedure as Ni-P electroless coating was used. Only 95 °C is used. It was to maintain consistency of the plating environment for future comparison. Figure 10 shows the sample holder.

Figure 10: Electroless coating sample holder

After coating, samples were removed from the sample holder, rinsed with distilled water, dried using compressed air or hair dryer and then stored in a desiccator or clear plastic sample box.

2.4.2 Electrolytic process

For the electrolytic coating process, a flat bottom cell was used instead of a round bottom cell. That was done in order to allow the counter electrode to lay parallel to the working electrode as can be seen in figure 11. This also makes the distance between it and the working electrode easy to control and measured.

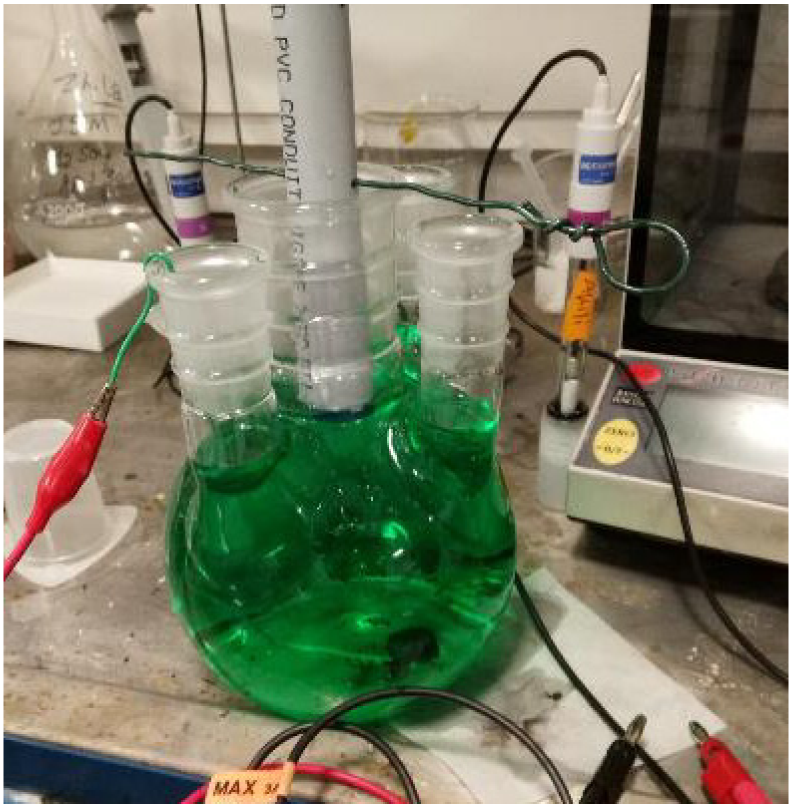


Figure 11: Electrolytic coating whole cell setup

In the electrolytic coating process, the counter electrode is usually made of the metal to be coated, in order to replenish the ions depleted from the coating solution. Since there is no nickel tungsten alloy, an unreactive conductive material was used. In the present work the counter electrode consisted of a graphite disk and the plating solution contained both nickel and tungsten. For the first graphite disk anode, the wire is attached using poly-enerethyl resin with conductive graphite mixed in. This proves to be not ideal. The conductive resin generates huge impedance, which requires a higher voltage to overcome. This might generate localized arcing in the solution. The revised graphite anode was made of a significantly larger graphite piece which increases the frontal surface area. A hole was drilled from the side so the wire had a direct connection with the graphite. The hole was then sealed using paint so it did not contact with the solution, which might cause unwanted side reactions.

In order to securely connect the counter electrode to the power supply, a conductive wire was soldered to the back of it using regular unleaded solder as shown in figure 12. The sample was then sealed with a coat of insulating paint, leaving only the face exposed. The whole assembly was then inserted in a 1-inch diameter tube. The tube was lowered from the top center port of the plating cell as shown in figure 13. The distance between the sample (cathode) and the graphite anode was fixed at 10 centimeters using a horizontal holding wire. During the trial phase 10, 5 and 3 cm were used to observe whether the distance between the electrodes will cause a difference in the coating composition. A shorter distance can reduce solution resistance thus increase current efficiency. Bringing two electrodes closer can also reduce the ion concentration gradient, providing a more homogenous environment between cathode and anode.

An initial current density of 4 mA/cm^2 was used for all electrolytic coating samples. The current used was based on previous literature [25]. If tungsten can be successfully coated, varying the current density would provide more information. By using this value, the current for plating samples with a diameter of 2.5 cm was 0.02 A. To plate samples with a diameter of 1.5 cm, the current is 0.00742 A. The samples were plated for 1 hour, 2 hours or 3 hours.

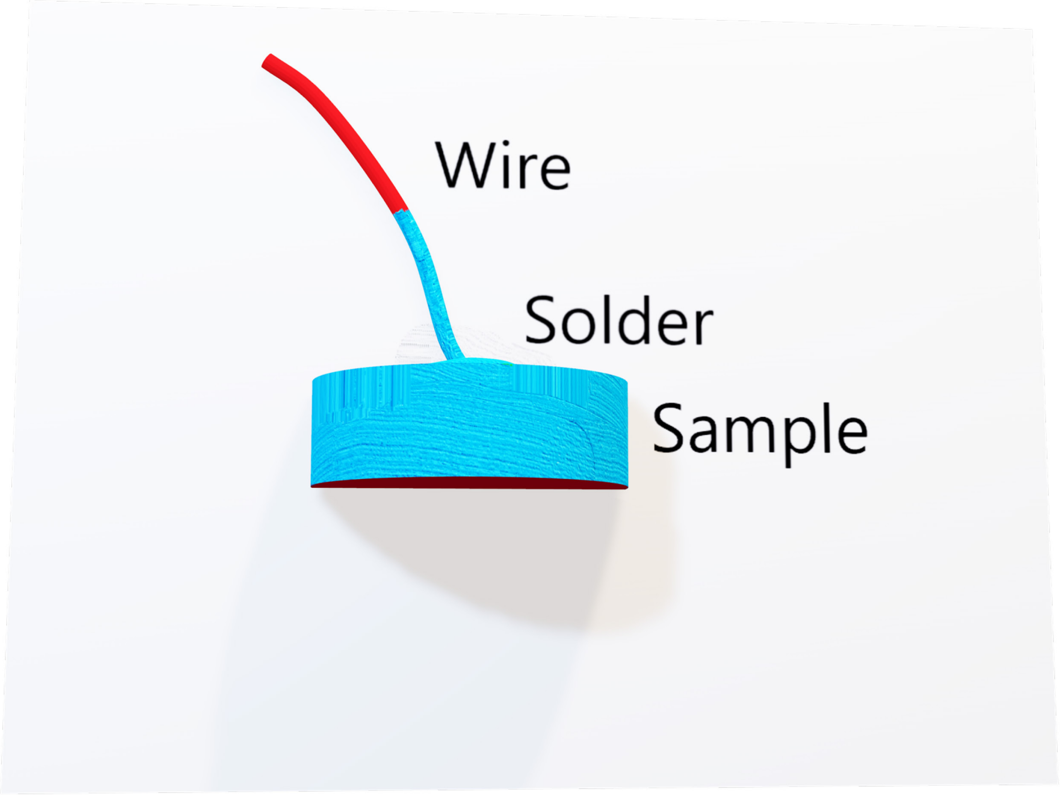


Figure 12: Schematic of electrolytic coating sample design

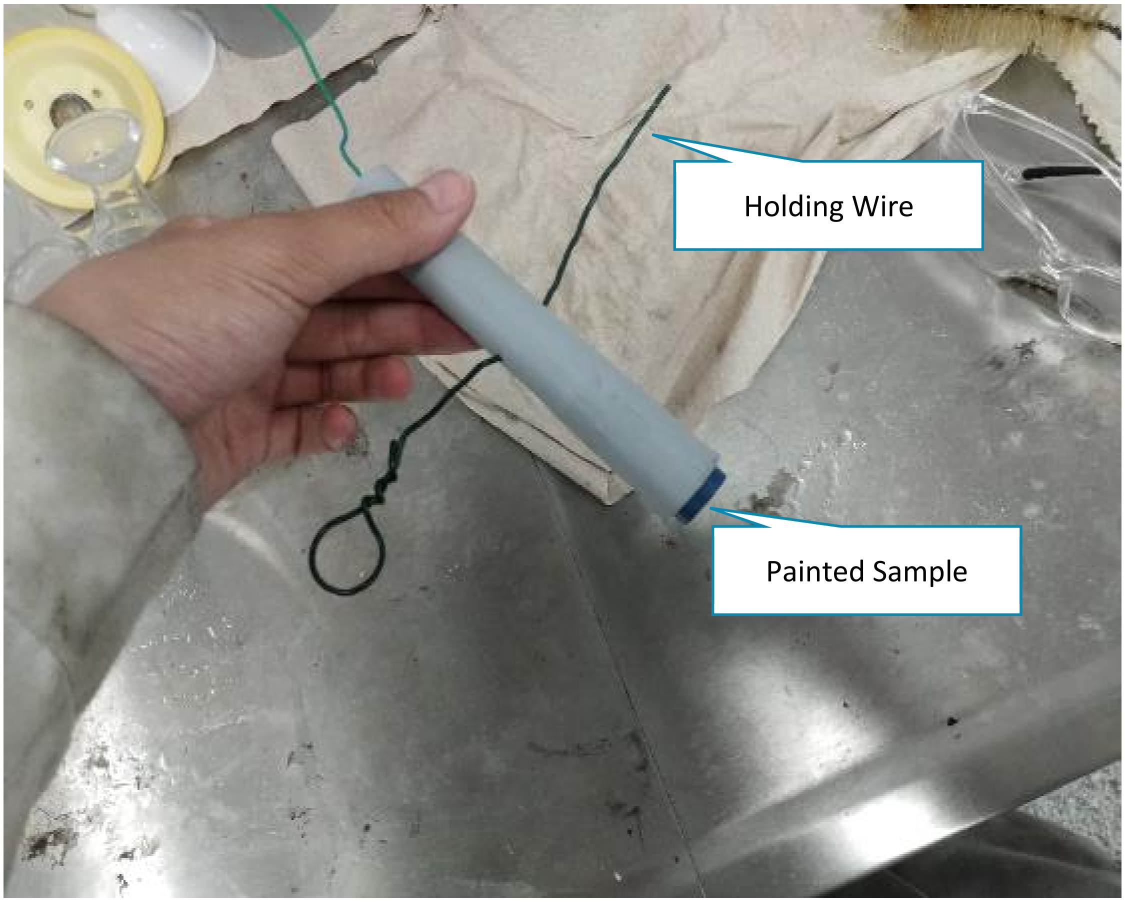


Figure 13: Cathode setup with painted sample and assembly holder

Electrolytic coating in the in-house prepared solution was carried out at two temperatures. One at 60 °C and the other at room temperature. This was done in order to investigate the extent of the effect the temperature has on the deposition rate of tungsten.

After plating, the paint was stripped from the sample and the wire was removed from the back. For samples painted with resin, only the wire was removed, the resin was kept on the side of the sample.

2.5 Coating characterization

2.5.1 SEM-EDS

Scanning electron microscopy was used to examine the surface structure. For all tests, the accelerating voltage and the emission current were set at 15 kV and 15 mA, respectively. The working distance was set to 11.7 mm. For SEM, pictures are taken with both low and high magnification. On the surface of each sample, 2 to 3 sites were selected to take pictures. EDS was used to determine the surface chemical composition. Nickel, phosphorus and tungsten are the focusing elements. Two 200 μm by 200 μm sites were selected each sample for EDS scan. Three Ni-P electroless coating samples and the successfully plated Ni-P-W coating samples were grinded and polished on the sides so they can go through an SEM-EDS test for thickness and composition.

2.5.2 Electrochemical Impedance Spectroscopy (EIS)

Corrosion resistance of the coatings was evaluated using electrochemical impedance spectroscopy (EIS) and cyclic polarization (CP). Saturated calomel electrode (SCE) is the reference electrode used. As EIS is a non-destructive testing method, it was performed before any other chemical or mechanical testing. EIS experiments were conducted using a flat electrochemical cell containing 3.5 wt% sodium chloride solution. The flat cell is designed to expose 1 cm^2 of the sample to the electrolyte. A Solartron 1255 FRA and a PAR 273 potentiostat controlled by Scribner Associates Electrochemical Impedance software, CorrWare and ZPlot, were used to conduct all the EIS experiments. The instrument and cell set up are shown in figure 12. The cell was placed in a grounded faraday cage to minimize electrical noise. Detailed software setup is included in the Appendix B.

Figure 14: Corrosion testing cell setup inside Faraday Cage

Before each EIS experiment, the samples were kept at open circuit for 1 hour in order to achieve a steady state. Electrochemical impedance spectroscopy measurements were performed at open circuit potential. During a typical experiment, a small AC amplitude signal, a potential of 10 mV is applied to the sample over a range of frequencies from 1 mHz to 1 kHz. The FRA collected and recorded the real and imaginary components of the impedance response of the system. The collected data were then used to model the behaviour of the coatings.

2.5.3 Cyclic Polarization (CP)

CP tests are conducted to investigate the pitting corrosion resistance of the coatings. The experiments were conducted using a PAR 273A potentiostat controlled by a Scribner software, CorrWare. All experiments were conducted using the same flat cell as the EIS experiments. During a typical CP experiment the potential is increased from -0.5 V to 1 V and then back to -0.5 V versus open circuit potential. Current values are collected and plotted versus potential. All CP experiments were conducted after the EIS experiments, with a 10-minute open circuit between the two experiments to ensure the cell was stable. The setup screen is also included in the Appendix C.

2.5.4 Scratch test

Scratch tests are performed to examine the wear resistance of the coatings. They were performed on a scratch tester. Each sample was scratched using a 0.4mm diamond indenter to achieve a scar length of 5, 15,30,60 mm. The scar width was then measured under optical microscopy. By calculating the volume of materials removed using the equation below, a graph could be plotted thus estimating the wear resistance.

$$Scar\ Volume = \frac{D^2 t}{8}[2\sin^{-1}\frac{b}{D} - \sin(2\sin^{-1}\frac{b}{D})]$$

In the formula, D is diameter of diamond indenter, t is scar length and b is average scar width measured using optical microscopy.

2.5.5 Micro indentation test

Micro indentation tests were performed on the micro indenter. During the test, a slowly increasing force is applied to a threshold, in this experiment, 1200 N. An ultrasonic sensor is used to measure the amplitude of the noise from cracking. By plotting both force and noise change on the same graph, the exact force where the coating get cracked could be determined. The toughness of the coating could then calculate based on force and deformation of the coating.

Chapter 3 Results and Discussion

3.1 Substrate Preparation Process

Polishing copper samples shows a problem of corrosion. Copper would not corrode in dry and clean condition. It will corrode very fast when directly contacts with moisture. This phenomenon was observed when freshly polished samples still have water on the surface. The color of the copper will change from shiny red to dark brown. Oxygen dissolved in the water reacts with copper on the substrate, forming copper oxides, causing a color change [3]. Samples with oxidation needs to be repolished to remove the oxidations on the surface.

This problem was solved by immediately drying the sample using compressed air. It eliminates the problem of surface oxidation. To further protect the sample, they are kept in the sealed sample box, with some silica to absorb moisture.

3.2 Coating Processes

In this work, as mentioned previously, copper samples were plated, both electrolessly and electrolytically. In addition, electroless and electrolytic plating were conducted in both commercial and in-house prepared solutions. During plating processes, there were different kinds of phenomena. These anomalies were all discussed in this section.

3.2.1 Electroless coating

Initially, a degreasing process is used. All the samples could not be plated after this process. The sample will become purple with solution streaks, as can be seen in figure 13. These samples will no longer be able to plate even after polishing.

Figure 15: Samples failed to electroless plating with purple streaks

After trial, it was found that by degreasing copper in high temperature alkaline solution, copper will be corroded. Copper green formed on the surface of the samples. A 10 second acidic solution dip could not remove the oxidation layer and expose fresh copper. The oxidation layer would prevent electroless plating from initiating, resulting in unsuccessful electroless coating. This problem was solved by not degreasing the copper sample at all.

To increase productivity, 3 to 4 samples were hung together in one solution during plating process. One of the problems found is that only 1 or 2 samples will be successfully plated per batch. Meanwhile, those samples failed to plate were seriously oxidized, leaving the same surface characteristics as those samples degreased before. One possible explanation is the difference in surface energy. Although carefully polished, some samples would have a higher surface energy than others. Ions in the solution all got reacted on the sample with high surface energy, leaving the sample with low surface energy behind. The technique used to solve this problem is placing at most two samples at the sample time in the same bath. In addition, these two samples need to separate apart with a minimum distance of 8 cm. By doing this, the difference in surface energy will not cause unsuccessful coating. The disadvantage is that the throughput of the samples will be reduced, causing delays for experiments following up.

After removing the degreasing step and reducing the samples plating in the same time, all samples can be successfully plated with a nickel. This can be identified as an obvious color change on the surface from copper red to nickel silver. The problem of failing to plate comes again when some colleagues etched the glassware using nitric acid. None of the copper samples were plated in this cell.

For troubleshooting this problem, the first thought was nitric acid residue causes contaminations in the plating process. Nitric acid will react with copper. Even at low concentration, copper will be oxidized thus inhibit electroless coating from happen. A small amount of nitric acid might generate nitrogen containing organic compounds at higher temperature in the electroless plating solution [3]. These unknown side reactions may have a negative effect on the plating process. Different methods had been used to address this problem. First, the vessel was washed with distilled water at high temperature for three time, trying to remove any nitric acid related residues which might embedded in the glass. This process showed ineffective. It did not solve the problem. Second, the vessel was submerged in ultrasonic cleaner for more than 30 minutes. Again, this trial is another failure to solve this problem. Finally, requested by supervisor as the last method, the vessel was sent to mineral engineering center to perform a hydrofluoric acid rinsing. By removing a surface layer of glass, the contamination problem should be solved. After this process, it was found that copper still cannot be plated.

The trials of cleaning the vessel shows that contamination of glassware might not be the cause of plating failure. A further literature review show that copper is different compared with steel or aluminum as electroless plating substrate. Copper cannot initiate the autocatalytic process of nickel phosphorus deposition [5]. This is due to copper being more noble than nickel thus unable to exchange some nickel cations out of the solution as catalyst. In order to trigger the plating process, using the commercial solution, submerged copper samples were brought in contact with nickel samples, setting up a galvanic couple and depositing a small amount of nickel on the surface of the copper samples. In this experiment, a previously successfully plated sample was submerged into the bath first. Once electroless plating happens on the surface of the old sample (hydrogen gas bubbling), it can be used to activate fresh new sample. The seeding process activates the copper surface. Hydrogen gas bubbles presented on the surface during coating process. This matches the reaction mechanisms mentioned in literature review.

For electroless plating done using the in-house prepared solution, coating could not be initiate. Trials of using old nickel-plated samples were performed to see the possibility of electroless coating. However, these samples could not start a plating process. There is no indication of any hydrogen generation.

Failure of performing electroless plating is most likely due to the presence of proprietary additives in the industrial solution, although this solution was made from an electroless nickel phosphorus coating provided by supervisors. However, it was found that the solution did not dissociate at a temperature as high as 95 °C. This indicates that the solution is at least stable under high temperature conditions.

3.2.2 Electrolytic coating

Electrolytic coating was performed in both Atotech solution and in house made solution. Similar phenomenon was expected to be observed during electrolytic coating process using both solutions, like hydrogen gas generation from the cathode. Different from electroless plating where hypophosphite is oxidized on the surface of the substrate using nickel as a catalyst, it is expected to be oxidized on the anode.

Observation showed slightly different results between these two solutions. Gas bubbles were generated on the anode surface when using Atotech solution. Based on electrochemical reaction, it is likely that water was electrolyzed, forming oxygen gas and hydrogen cations. Oxygen gas bubbles leaving the anode surface buoyance through the solution. This might be caused by proprietary additives which are designed to activate hypophosphorus to react with water. With electrical energy, water is directly electrolyzed at the anode to form oxygen gas. If further analysis is needed, testing the concentration change of hypophosphite and phosphite is needed.

There was no bubbling from the anode when in-house made solution is used for electrolytic coating at first. In this solution, hypophosphite might be easier to be oxidized in the solution environment due to lack of stabilizers. Coatings performed at 60 °C do not perform very well. The coating barely sticks to the surface of the substrate. It was so fragile that they flake, which can be seen in figure 16. Gas bubble generation was observed later in additional plating processes. One reason might be the change of surface structure on the graphite anode surface. During plating process, fouling would happen. It destroyed the smooth characteristic of surface which might cause localized high voltage spikes.

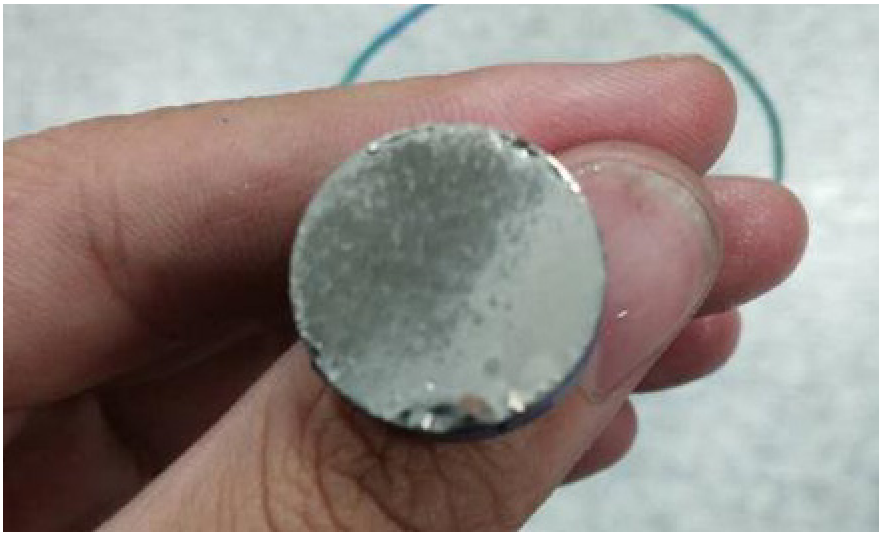


Figure 16: Fragile coating with layer separation at 60 °C

Additional tests resulted in a strange surface characteristic. There are black spots everywhere on the surface of the coating, which can be seen in figure 17, although all the procedures were the same. Samples had a plating time of 2 hours and the other two had a plating time of 3 hours. The problem found was that fouling on the anode might disrupt current distribution through the solution, causing "burn out" on the surface of the coating. By replacing the anode with a clean significantly larger graphite piece, the problem was partially solved.

The anode needed to be polished and cleaned every time after plating to maintain consistency and reduce the possibility of uneven current distribution. Even though, some samples still showed signs of black spots. Moreover, frequently pulling out and placing the anode back causes metal fatigue at the connection point between the wire and the graphite anode. It was broken after 4 times of plating. The photo of the broken anode assembly was shown in figure 18.

Figure 17: Electrolytic plated samples with black spots on the surface

Figure 18: Broken wire from anode at connection point

The potential curve of the electrolytic coating was also observed. The voltage was low when coating starts. It increases with time then stays stable for the most time. It is because the resistance is low at the beginning. When nickel was coated, the impedance of the cathode increases significantly. The applied voltage needs to be increased to maintain a constant current. An increasing amount of stagnant gas between two electrodes will increase the solution resistance, but in this project, the electrode distance was too far to cause this problem.

3.3 Electrolytic Coating Applied Voltage Comparison

Electrolytic coating consumes electrical energy as current is held constant throughout the coating process. Voltage tends to change over time. The higher the average voltage, the higher is the energy consumption. If the voltage changes frequently, the voltage vs. time curve will be rough, which indicates a high noise thus unstable environment.

Figure 19 shows the voltage change over 10 minutes of Ni-P coating and Ni-P-W coating in the Atotech solution. Ni-P-W coating has a higher potential requirement than Ni-P coating. The reason might be higher ion concentration close to the surface of the electrodes due to the addition of sodium cations and tungstate anions. It generates a potential barrier which requires a higher over voltage.

Figure 20 shows the voltage change over 1 hour of Ni-P-W coating using Atotech solution at different distances between the cathode and the anode. The original purpose is trying to reduce tungstate on to the substrate surface forming Ni-P-W coating. Tungstate is negatively charged so under an electrical field, it tends to migrate to the anode where tungsten at a state of +6 could not gain electrons at the anode. By placing the two electrodes closer, the solution will be more homogenous thus tungstate will have a higher possibility to be reduced on the cathode. Although it turned out to be a failure after EDS test, the voltage shown in the process could still provide some valuable information.

The potential change due to various electrode distance was expected. This is because a shorter distance between cathode and anode yields a lower solution resistance. To maintain the same coating current, the potential requirement is lower. Translating to energy consumption, the higher the voltage, the higher the energy requirement is. Another detail on the curve is that with the decreasing distance, the variation in the line also decreases. It showed that with the reduction in distance, electrolytic coating reactions are more stable.

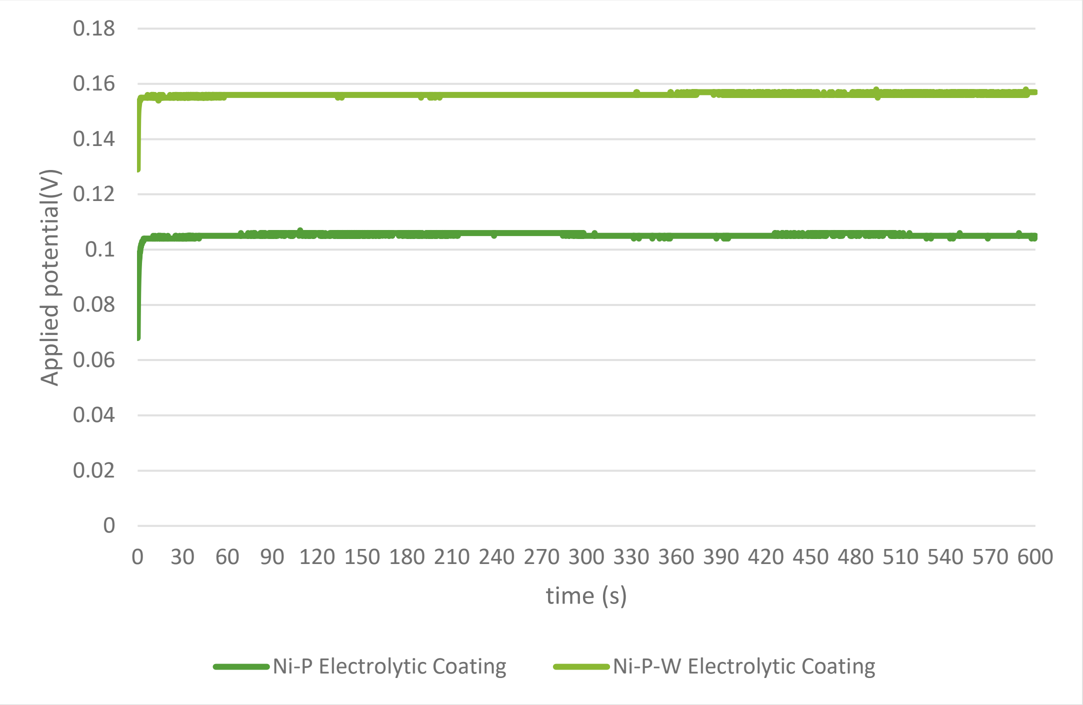


Figure 19: Applied potential for 10 min Ni-P and Ni-P-W electrolytic coating

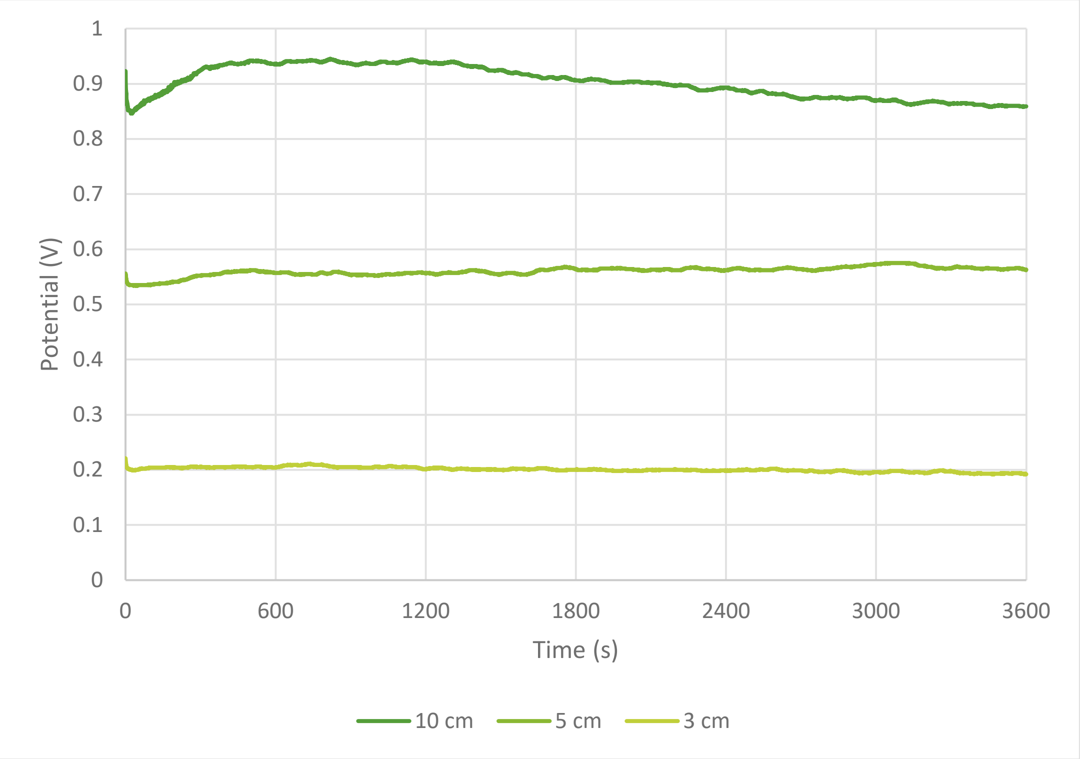


Figure 20: Applied potential for 1-hour Ni-P-W electrolytic coating at different distance

Figure 21 shows the samples which generates unstable voltage noise curves. Only 2 hours and 3 hours sample were shown in this figure since the 1-hour coating was not performed to save samples as requested by supervisor. The 2 hours coating was noisy across the entire coating period. The 3-hour coating was noisy for the first hour, after that, the noisy slowly decayed to return smooth. There are two possible reasons, the first one is samples themselves have different characteristics. It does not only include the coating surface, which is copper in this project. The paint finish, soldering and the placing orientation of the samples are all uncertain factors in this case. The second one is the anode surface. A rough anode surface would cause this problem. However, it could not explain why the voltage returned to smooth for the sample with 3 hours of plating time.

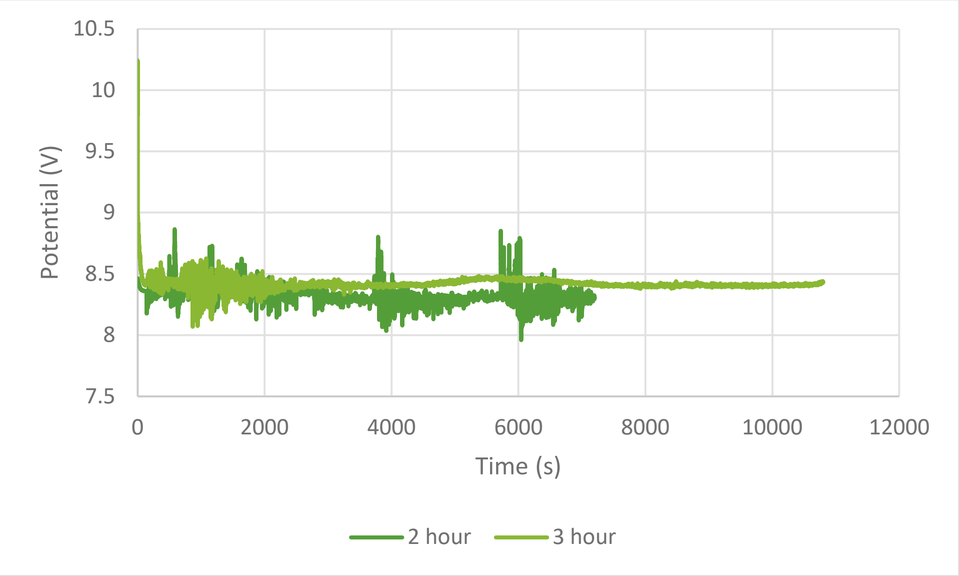


Figure 21: Unstable potential of samples in electrolytic coating

Figure 22 shows the voltage difference of electrolytic coating in in-house made solution for different length of time. The distance between the cathode and anode were all kept at 10 cm. The two hours coating misses the data for the second hour. It was due to an unknown reason where the computer did not log and store the data. 1 hour and 2 hours coating had similar voltage with the 2 hours coating slightly higher. The 3 hours sample had a significantly higher voltage. This might be caused by surface variation. A common trend is that all of them has a decreasing voltage over the time of plating. Comparing the in-house made solution samples with the Atotech solution samples, the voltage of in-house made solution samples were all higher than Atotech solution samples. The reason is commercial solution has unknown additives which would increase the conductivity of the solution, yielding a lower voltage at plating.

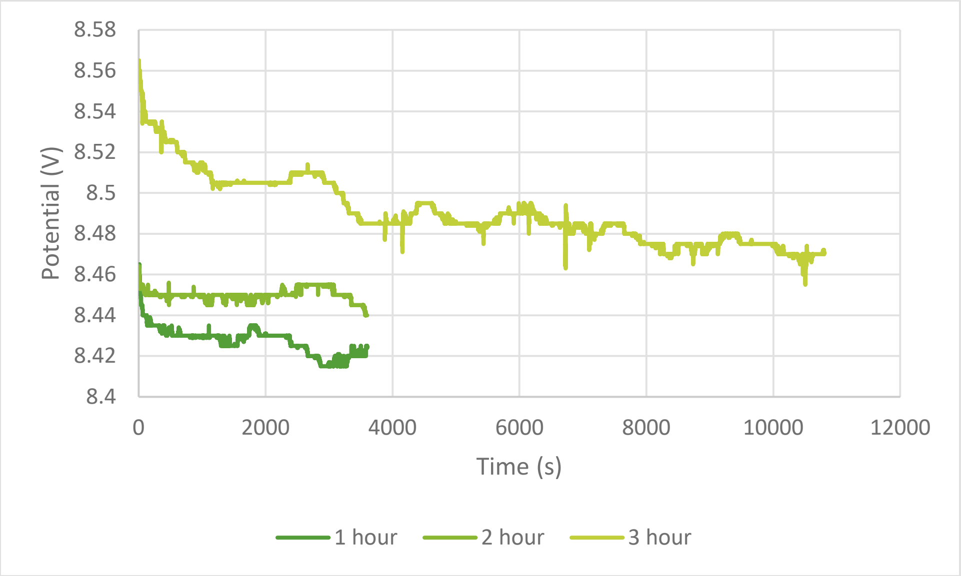


Figure 22: Applied potential of electrolytic coating with in house made solution

3.4 Coating Characterization

3.4.1 Surface morphology

Scanning Electron Microscopy was performed to examine the surface structure of the coatings. For most of the samples, the surface is scanned. Specifically picked some samples, the cross-sectional areas were scanned. The coating thickness will be estimated based on the scale on the micrographs.

A few 400 grit polished samples were plated before switching to diamond polishing. Both 400 grit and diamond polished samples were examined as long as coatings presents on the surface. The magnified view of 400 grit polished Ni-P coating can be seen in Figure 24, the surface has ridges with some cauliflower structures. In figure 23, the plating is uniform over the surface with minor dents or cracks. These might be caused by hydrogen gas bubbles that form when hydrogen cations are reduced on the surface of the sample. The cations form hydrogen gas bubbles that might stay on the surface and or get trapped under the coating. Surface bubble will cause the groove, while the trapped bubbles cause the cracks when they pop and escape. Another possible cause is the surface structure. Since they were only polished using 400 grit sand paper, localized stress on the surface would cause bents and cracks during coating. Finally, temperature change would also cause this problem. Copper substrate and nickel phosphorus coating have different thermal properties. The plating process happens at a temperature of 95 °C. Once finished, the sample will be immediately rinsed by huge amount of cold distilled water. They were then also dried by using a hot air hair dryer. These thermal changes will cause difference of expansion and contraction between the coating and the substrate. It will generate these unexpected surface structures.

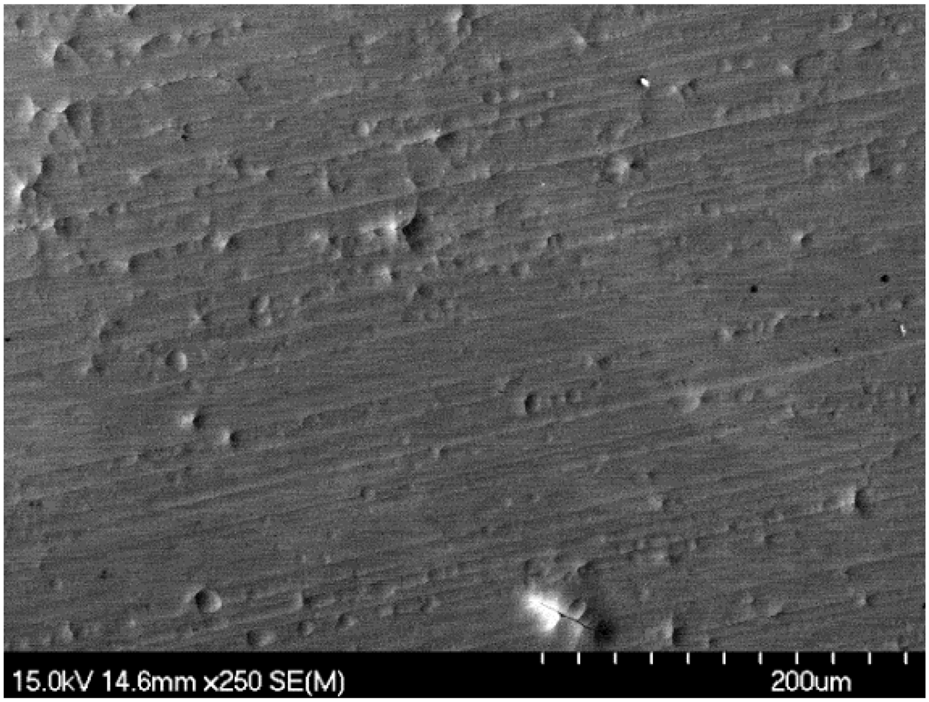


Figure 23: SEM of Electroless coating (Atotech solution, Ni-P, 95 °C, 400 grit polished, 1 h) (low magnification)

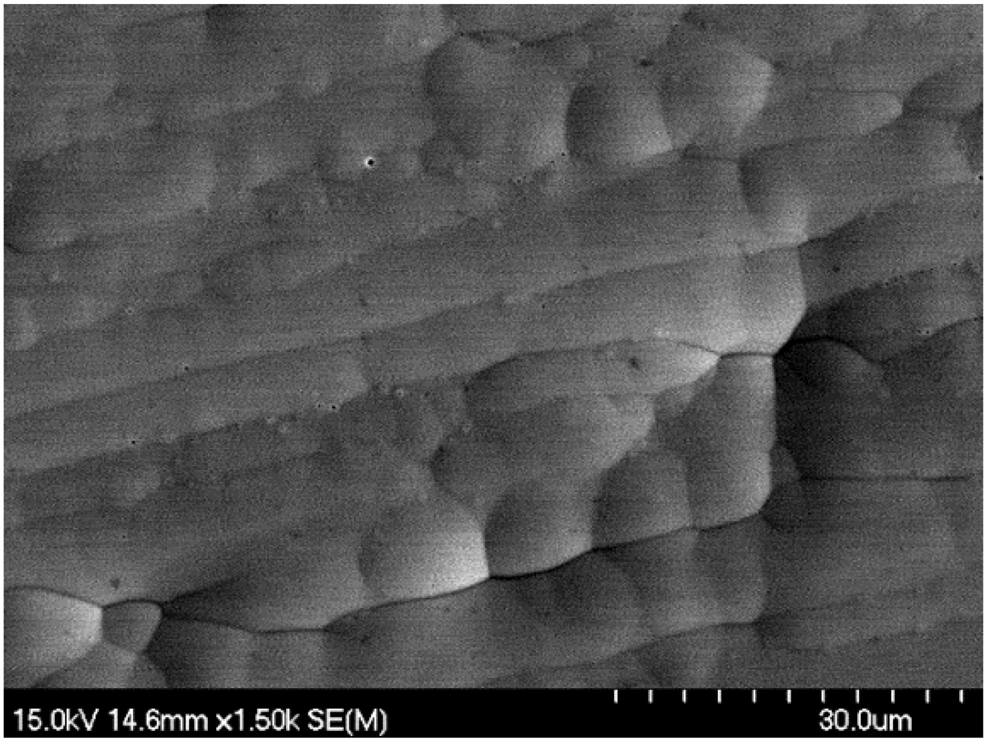


Figure 24: SEM of Electroless coating (Atotech solution, Ni-P, 95 °C, 400 grit polished, 1 h) (high magnification)

For the same polishing grade of 400 grit, the results from electroless Ni-P-W samples have slightly different results. Figure 25 and 26 show more cauliflower structures on the surface with clearer ridges to be seen. The horizontal bands on the surface are scanning result. It is because the detector is a line by line scanning device where the upper portion of the picture is slightly older than the lower portion. The 10k magnification picture shows a vivid picture of the cauliflowers. The structures were more obvious and continuous compared with Ni-P coated samples. This could be attributed to the presence of sodium tungstate in solution. With large ions of tungstate, it slows down the deposition rate of nickel, contributing to a finer growth of micro structure.

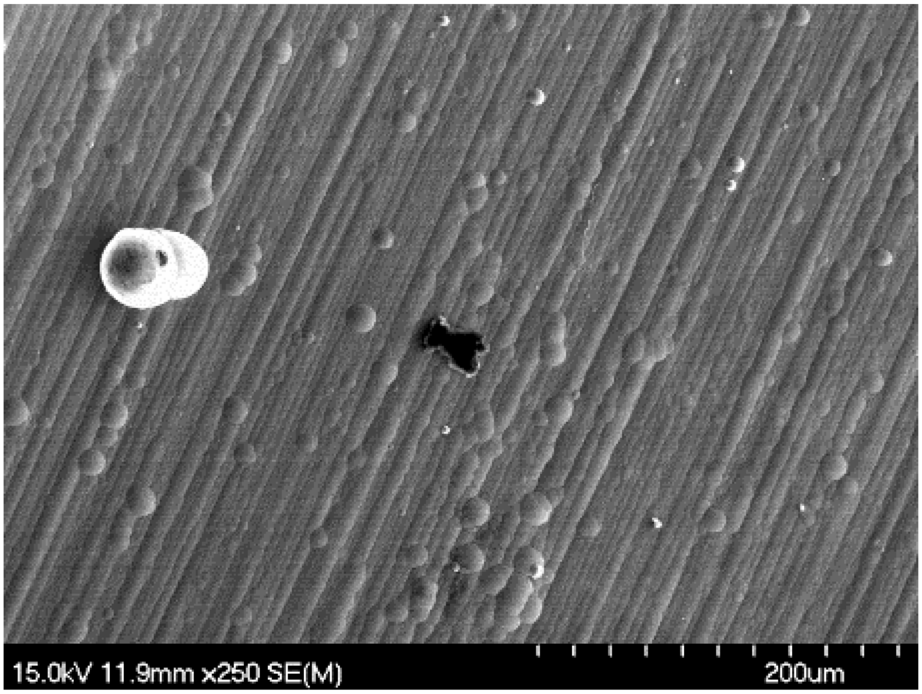


Figure 25: SEM of Electroless coating (Atotech solution with tungstate, Ni-P-W, 95 °C, 400 grit polished, 1 h) (low magnification)

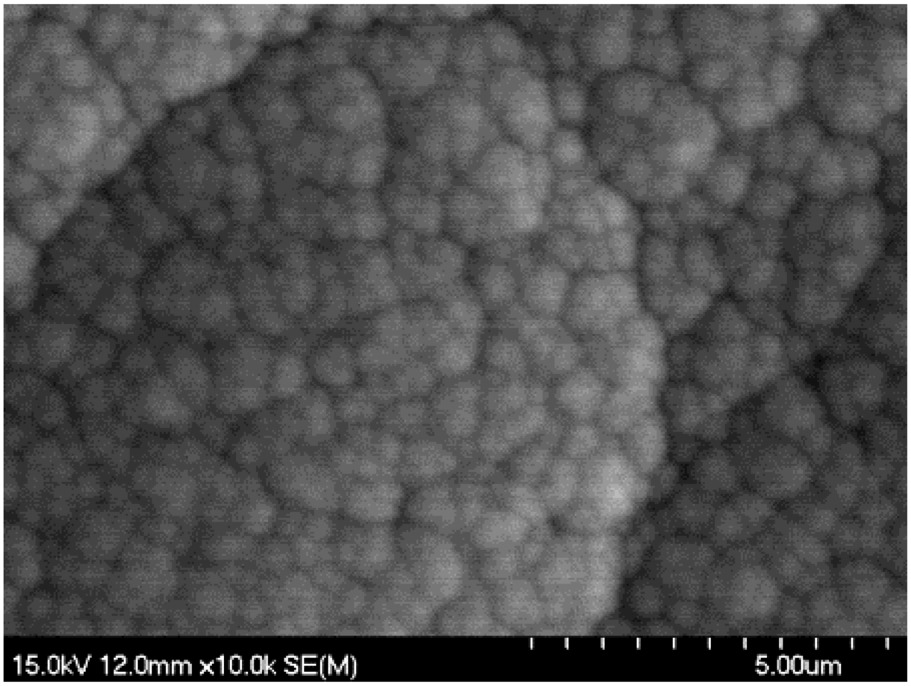


Figure 26: SEM of Electroless coating (Atotech solution with tungstate, Ni-P-W, 95 °C, 400 grit polished, 1 h) (high magnification)

The rest of the samples were all polished until diamond finish as decided by team. It is meant to improve surface consistency, reducing unknown micro-variations and preparing for future experiments if needed.

For Ni-P samples with a diamond polishing finish, shown in Figure 27 and 28, the surface is significantly smoother. Polishing method does have a significant impact on the finish of the coating. It is hard to see cauliflower structures even at high magnification. By examining multiple sites of different samples, the plating is consistent of a smooth finish with no distinct cauliflower structures. That is why these samples were all shiny when viewed by naked eye. Nature of the substrate as well as its smoothness would attribute to this phenomenon. Copper is much more noble than nickel and hence the latter needs area of high surface energy to deposit. This is explained with the findings on the 400 grit polished samples, where the cauliflower structure characteristics was observed along ridges left from polishing processes.

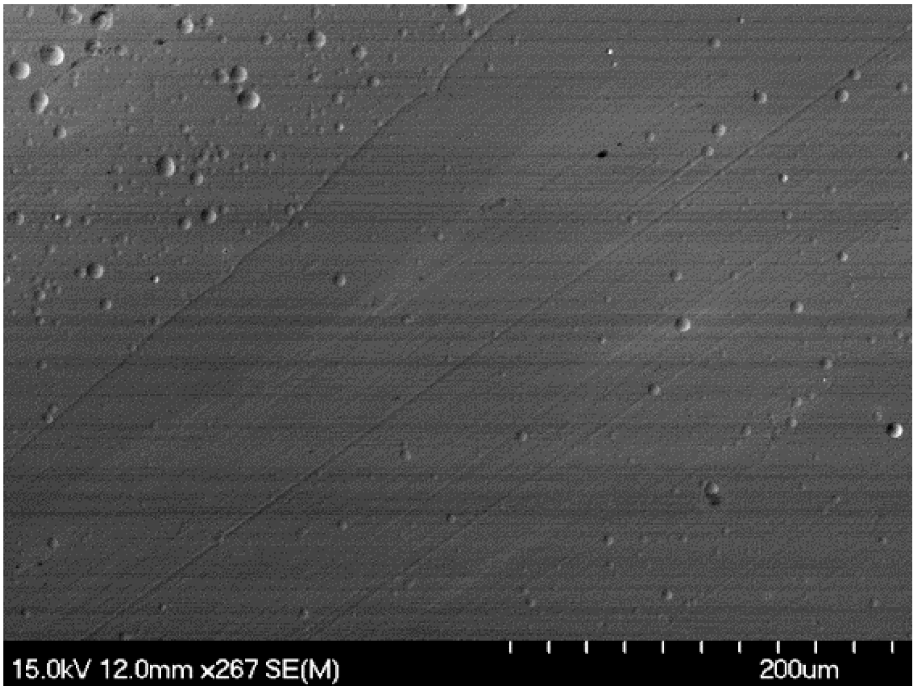


Figure 27: SEM of Electroless coating (Atotech solution, Ni-P, 95 °C, diamond polished, 1 h) (low magnification)

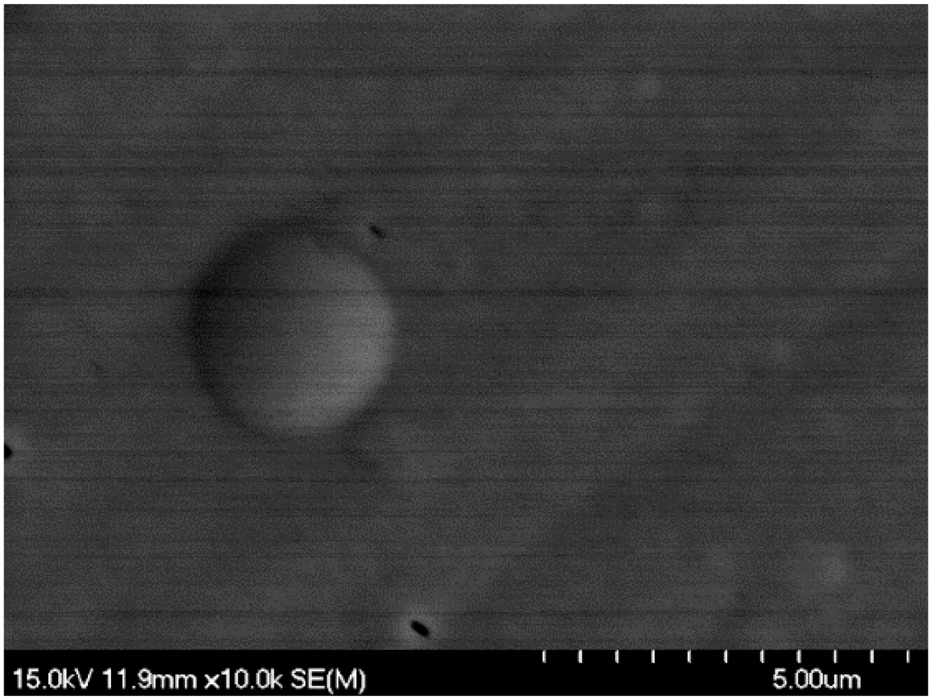


Figure 28: SEM of Electroless coating (Atotech solution, Ni-P, 95 °C, diamond polished, 1 h) (high magnification)

Electroless coating using the Atotech solution with the addition of tungsten shows inconsistent results. In Figure 29, the sample had a more uneven surface. These might be a sign of cauliflower structures. They did not have a pattern compared with 400 grit polished samples, where is cauliflowers follows the ridges of the polish. Figure 30 shows the surface of a sample went through the same coating process. It was a lot smoother. This inconsistency could not be explained based on the current information on hand. The uneven surface could also be bubbles on the surface. One reason to identify them as bubbles is that some of them have circles of different illumination around them. This might be due to hydrogen staying on the surface more frequently compared to nickel phosphorus coating. It will contribute to the dents on the surface of the coated sample. Another reason might be tungstate anions. The anions stay on or close to the surface of the substrate or the coating, causing localized damage, preventing hypophosphite from reacting on the surface. SEM shows that the surface has more bubbles, this was different than Ni-P coating.

Diamond polished samples exhibited fairy inconsistent plating surfaces when sodium tungstate was added into the solution. As can be seen from figure 29 and 30. The coatings had several smooth areas as well as patches of rough surface with cauliflower structures. The reason of inconsistency in coating finish might be surface energy, the existence of high energy areas would be more active.

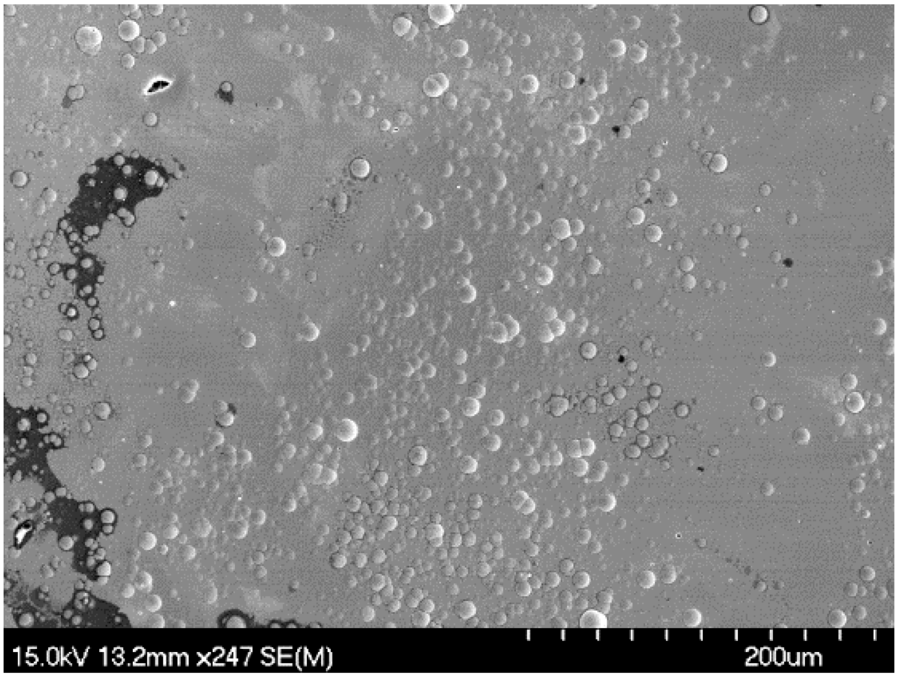


Figure 29: SEM of Electroless coating (Atotech solution, Ni-P, 95 °C, diamond polished, 2 h) (low magnification) (unsmooth surface)

Figure 30: SEM of Electroless coating (Atotech solution, Ni-P, 95 °C, diamond polished, 2 h) (low magnification) (smooth surface)

Electrolytic coatings produced after 10 minutes of plating shows similar but slightly different results in figure 31. The 400-grit polished electrolytic Ni-P coating sample had more obvious lines on the surface compared with electroless coating. The explanation is that electrolytic coating requires electrical current to do the work. At the peaks of polishing surface, charges are easier to accumulate thus the reaction rate is higher at these localized regions. They would provide more obvious peak and valley differences compared with electroless coating where the whole surface is plated uniformly.

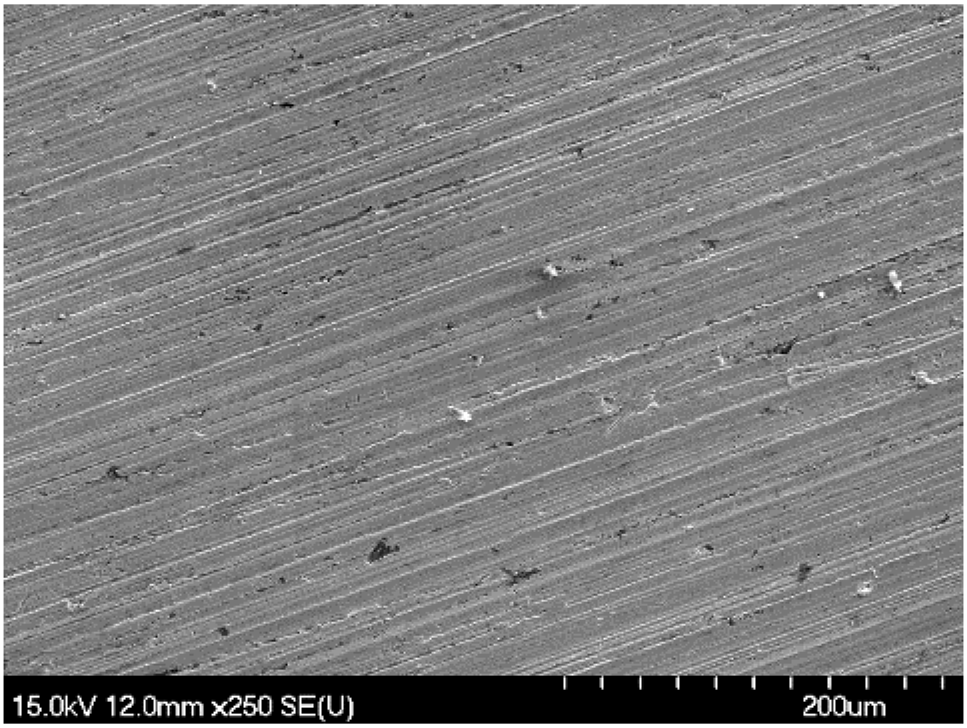


Figure 31: SEM of Electrolytic coating (Atotech solution, Ni-P, room temperature, 400 grit polished, 10 min) (low magnification)

The diamond polished samples, in figure 32 to 34, regardless of Ni-P or Ni-P-W coating, had fewer observable grooves as compared with 400 grit polished samples, although the polishing lines were still visible in the SEM result. One common feature on these samples were the random black spots on the micrographs. There are two explanations for this phenomenon. The first one is due to polishing imperfections. The surface might not be well polished, leaving some places where electrolytic plating could not well perform. The second one is plating time. 10 minutes of plating time is too short, some of the substrate surface could not be covered completely. Based on this result from SEM along with the test results from EDS of these samples, a plating time of 1 hour or longer was used.

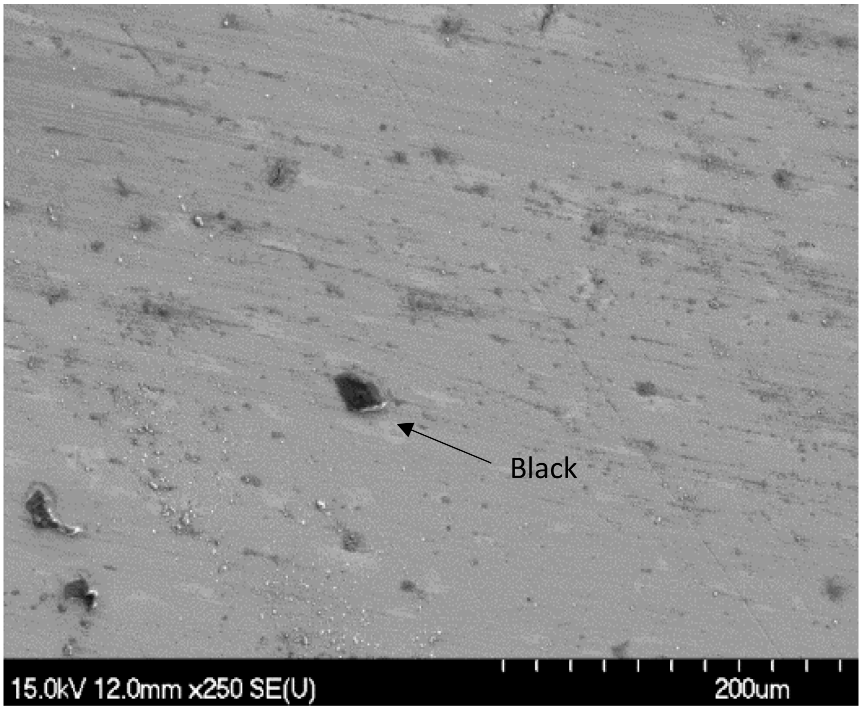


Figure 32: SEM of Electrolytic coating (Atotech solution, Ni-P, room temperature ,diamond polished, 10 min) (low magnification)

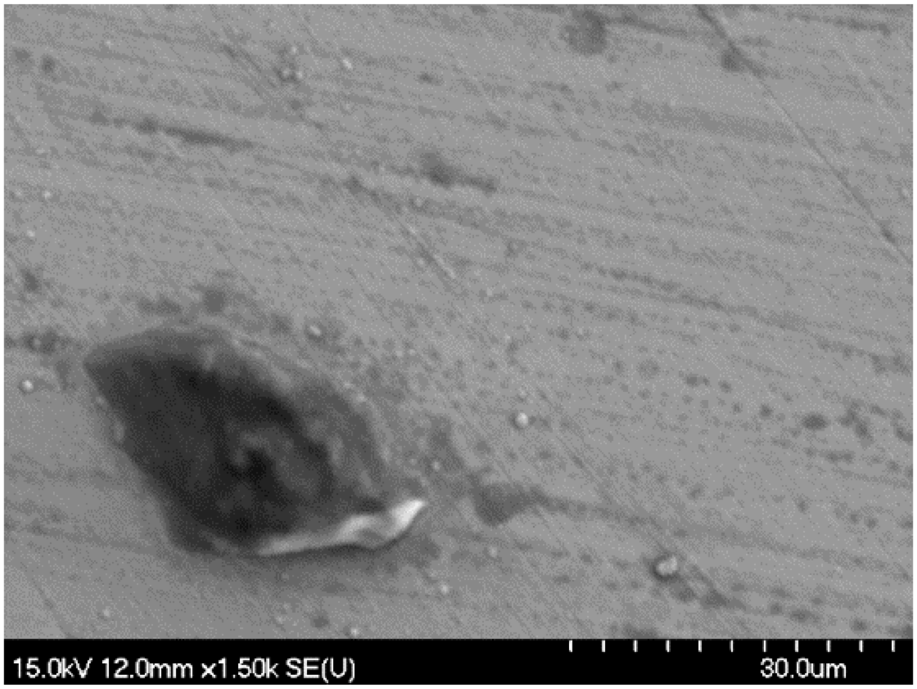


Figure 33: SEM of Electrolytic coating (Atotech solution, Ni-P, room temperature, diamond polished, 10 min) (high magnification)

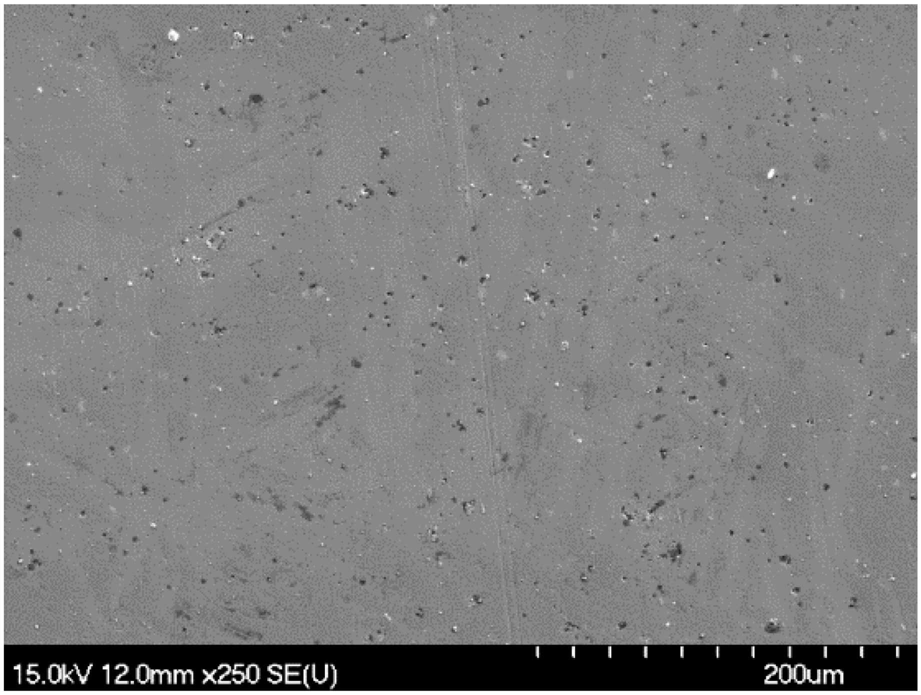


Figure 34: SEM of Electrolytic coating (Atotech solution with tungstate, Ni-P-W, room temperature, diamond polished, 10 min) (low magnification)

Electrolytically coated samples using the in-house solution at 60 °C had visible white streaks and points on the surface, shown in figure 35 and 37. At higher magnification, the white spots can be observed. They are like small crystalline spots. For sample coated at room temperature, in figure 37 and 38, the surface shows different sectional crack lines. It might have a higher erosion resistance but more fragile. However, the crack lines on the surface of the room temperature sample were not the same as the white streaks on the 60 °C plated samples.

Figure 35: SEM of Electrolytic coating (In-house made solution, Ni-P-W, 60 °C, diamond polished, 1 h) (low magnification)

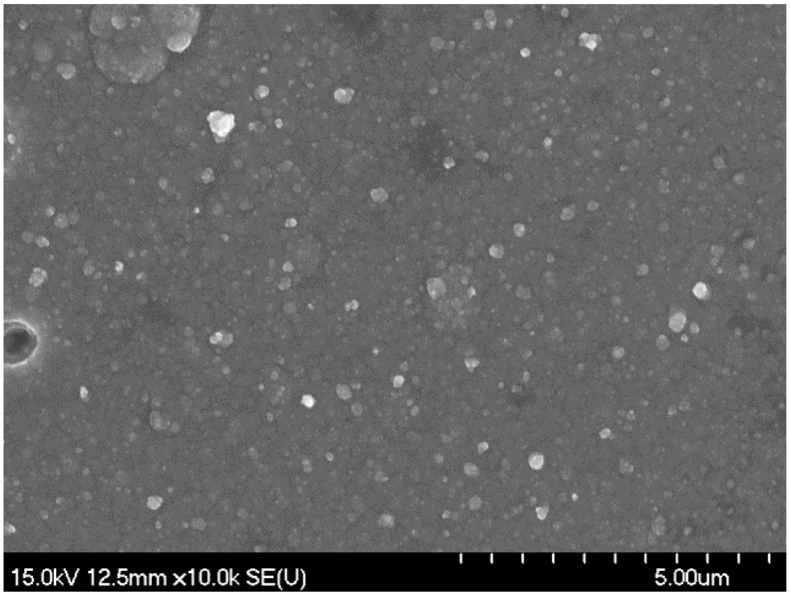


Figure 36: SEM of Electrolytic coating (In-house made solution, Ni-P-W, 60 °C, diamond polished, 1 h) (high magnification)

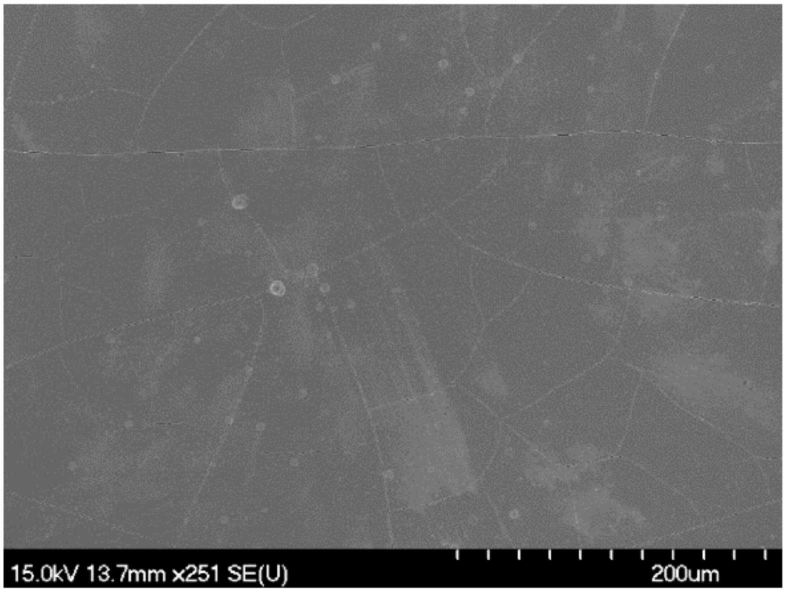


Figure 37: SEM of Electrolytic coating (In-house made solution, Ni-P-W, room temperature, diamond polished, 1 h) (low mag)

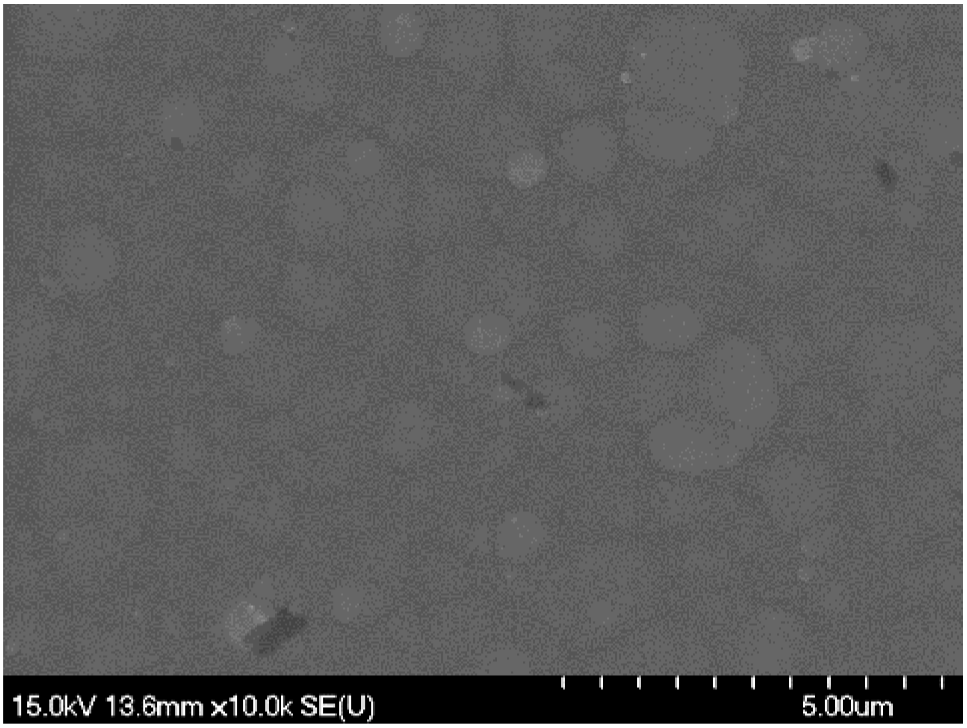


Figure 38: SEM of Electrolytic coating (In-house made solution, Ni-P-W, room temperature, diamond polished, 1 h) (high mag)

The electrolytic plating using in house made solution showed huge inconsistency when more experiments were performed. Figure 39 shows the surface of another 1-hour Ni-P-W plated sample following the exact same process. There was not a lot of sectional cracks compared with previous sample in figure 37. Looking at the magnified view in figure 40, globose geography can be observed. Initial thinking was these globes are cauliflower structures. The technician on site suggested that these are contamination. They so called the surface of the sample is not “clean” due to unclean polish or sample storage.

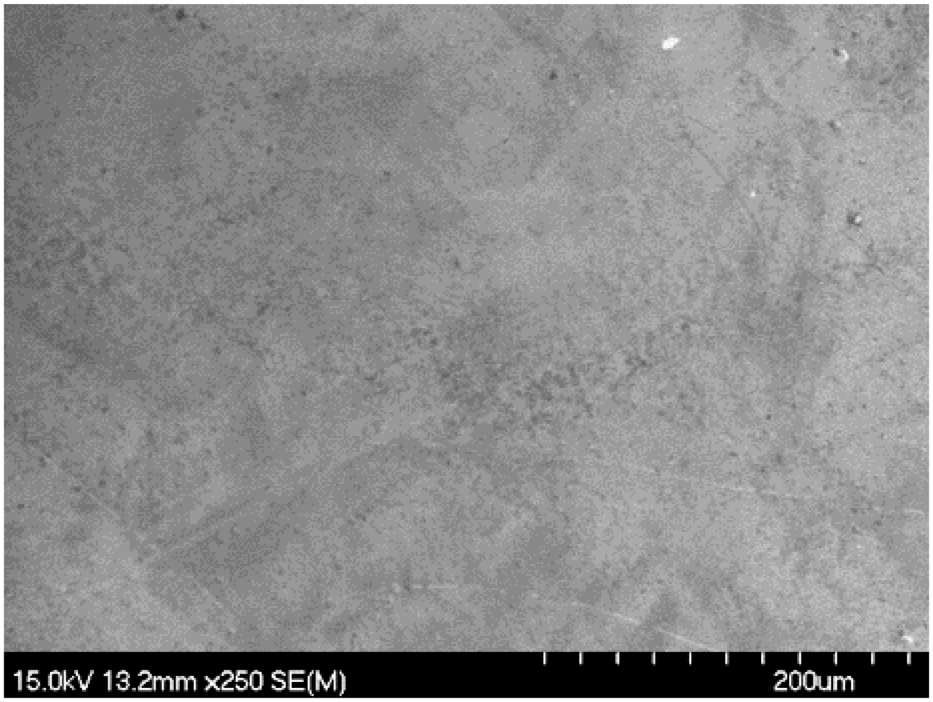


Figure 39: SEM of Electrolytic coating (In-house made solution, Ni-P-W, room temperature, diamond polished, 1 h, resin sealed) (low mag)

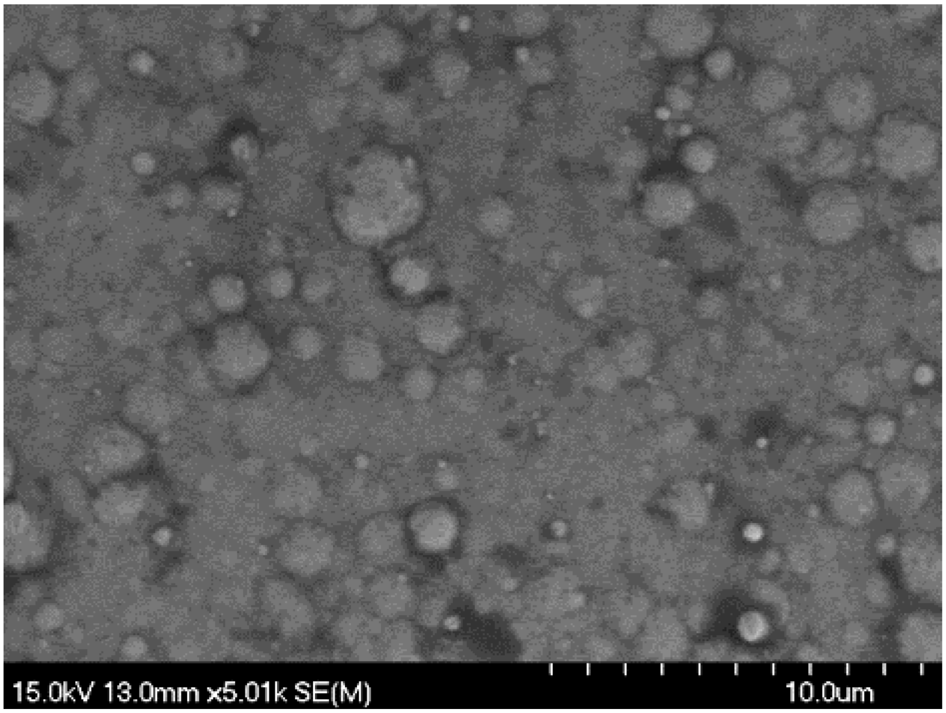


Figure 40: SEM of Electrolytic coating (In-house made solution, Ni-P-W, room temperature, diamond polished, 1 h, resin sealed) (high mag)

2 hours of electrolytic plating shows a return of sectional cracks, as shown in figure 42. Meanwhile, the surface has similar characteristic at high magnification as 1 hour plated sample in figure 39, which is in figure 41. The surface is also rougher at lower magnification, which cannot be observed in figure 39. Samples plated for 3 hours shows similar surface characteristic as 2-hours samples when viewed under SEM.

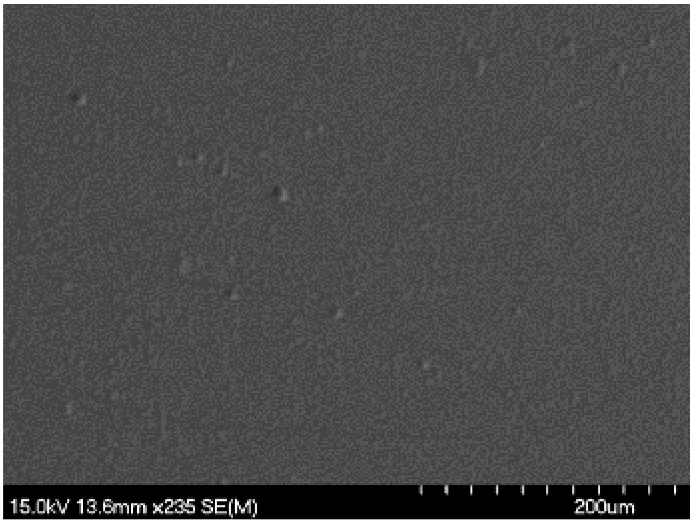


Figure 41: SEM of Electrolytic coating (In-house made solution, Ni-P-W, room temperature, diamond polished, 2 h, resin sealed) (low mag)

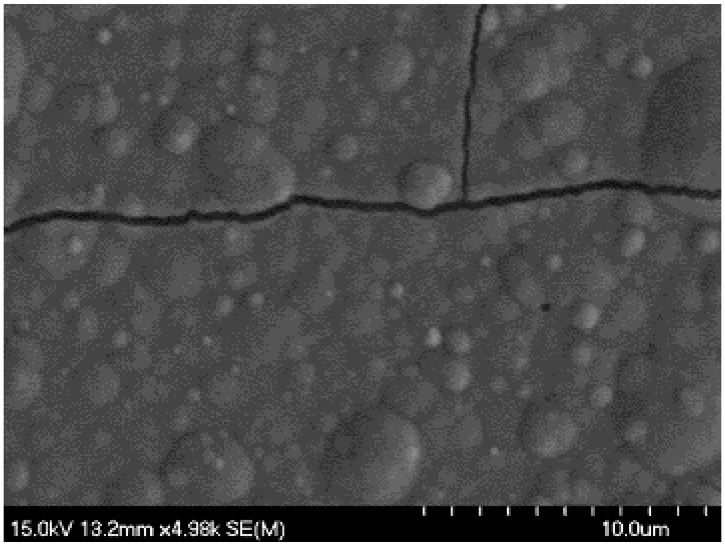


Figure 42: SEM of Electrolytic coating (In-house made solution, Ni-P-W, room temperature, diamond polished, 2 h, resin sealed) (high mag)

Cross section scan was proposed by the committee members, it was meant to measure the plating thickness. EDS measurements were also performed on the cross sections to find out the elemental composition.

Electroless plating of nickel phosphorus does not have a consistent pattern on the coating thickness. Figure 43 to 45 shows the coating thickness of electroless Ni-P samples from 1 hour to 3 hours of plating time. The 1-hour sample has a thickness of around 40 µm. By convention, 2 hours and 3 hours of plating should have a linear increase in thickness. However, the 2 hours plated sample in figure 38 shows a visible thickness of only 10 µm. The random shapes on the right of the coating might be coating products. They might also be residues comes from the polishing processes. The 3 hours plated sample had the same thickness as the 2 hours plated sample, which is 10 µm. However, it has the shiniest thus easy to be observed coating.

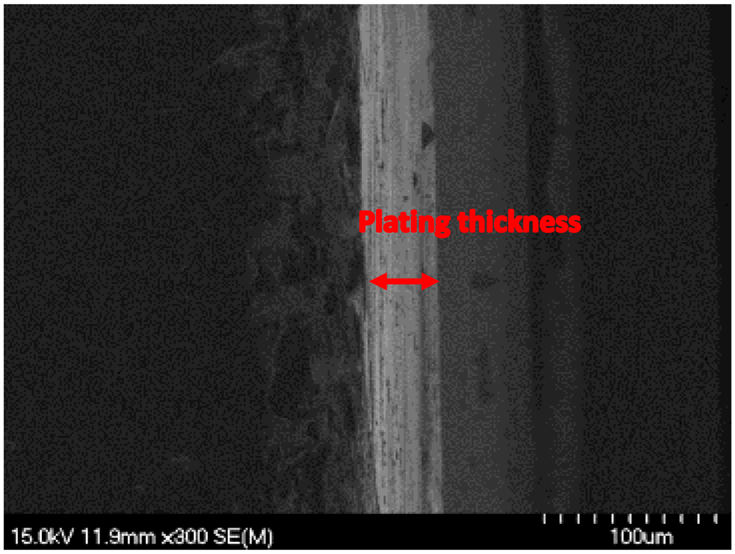


Figure 43: SEM of Electroless coating cross section (Atotech solution, Ni-P, 95 °C, diamond polished, 1 h)

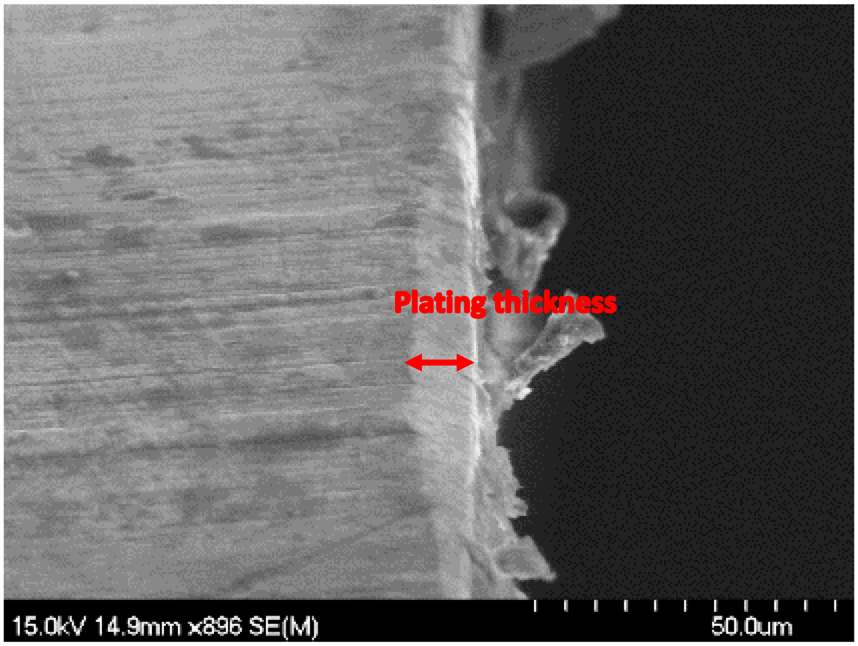


Figure 44: SEM of Electroless coating cross section (Atotech solution, Ni-P, 95 °C, diamond polished, 2 h)

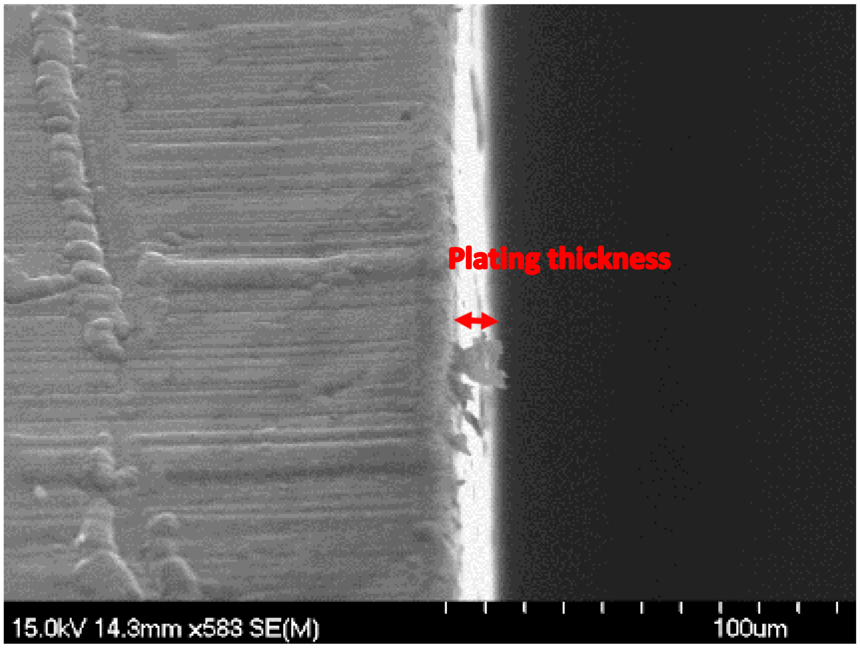


Figure 45: SEM of Electroless coating cross section (Atotech solution, Ni-P, 95 °C, diamond polished, 3 h)

The coating thickness of the electrolytic coating sample in the in house made solution is significantly larger. Figure 46 shows a coating thickness of nearly 250 µm. The contrast is similar to 1-hour electroless Ni-P coating. Electrolytic coating has a variation in its thickness. It is thicker in the middle while thinner at the edges, by comparing the thickness between figure 46 and figure 47. This is due to current distribution during the coating process. If the surface area of the cathode and the anode are the same and being perfectly aligned, the thickness might be more uniformly distributed.

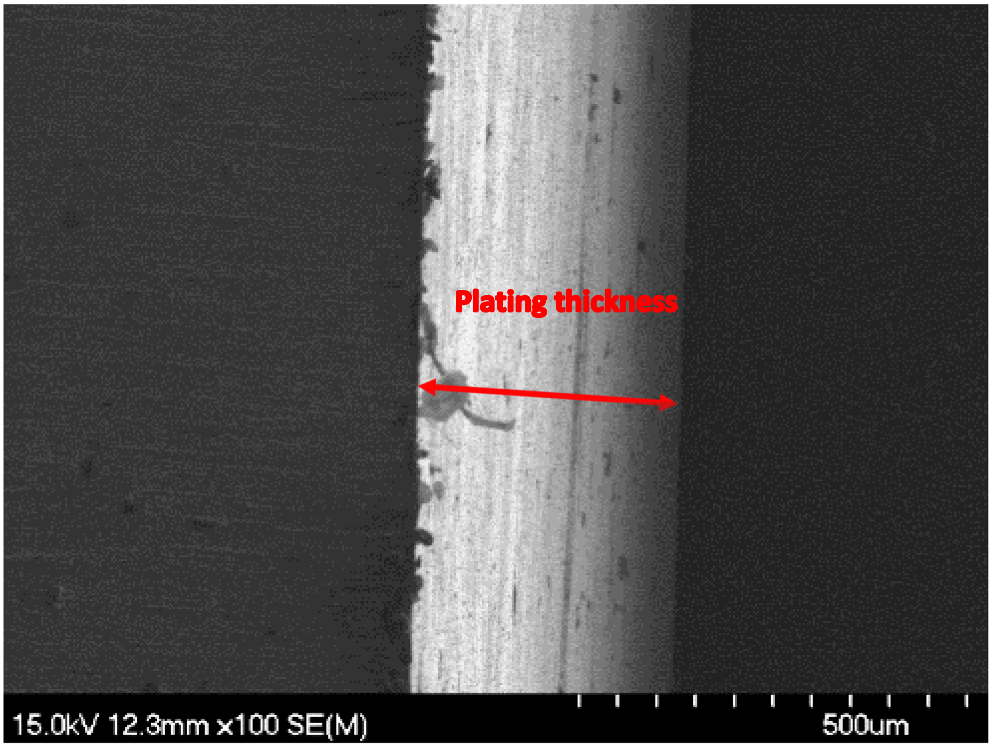


Figure 46: SEM of Electrolytic coating cross section (In-house solution, Ni-P-W, room temperature, diamond polished, 1 h) (middle section)

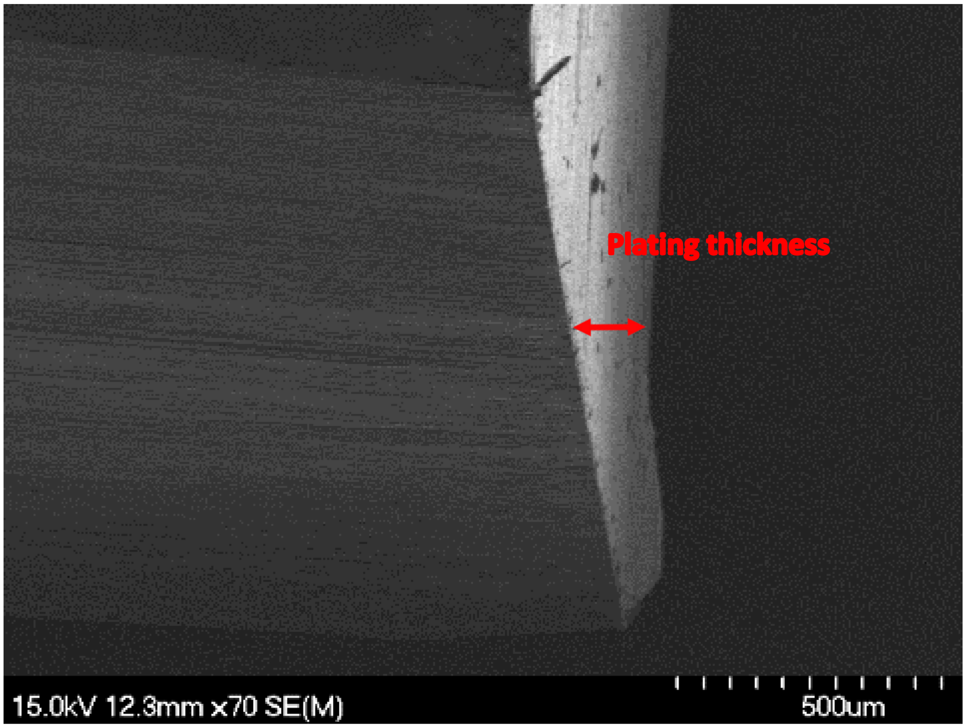


Figure 47: SEM of Electrolytic coating cross section (In-house solution, Ni-P-W, room temperature, diamond polished, 1 h) (edge section)

The 2 hours and 3 hours electrolytically plated Ni-P-W samples could not perform a cross section scan. This is because poly-enerenthyl resin is applied to seal the small samples. Polishing these samples were too difficult and would introduce additional contaminations onto the cross section.

3.4.2 Coating chemical composition

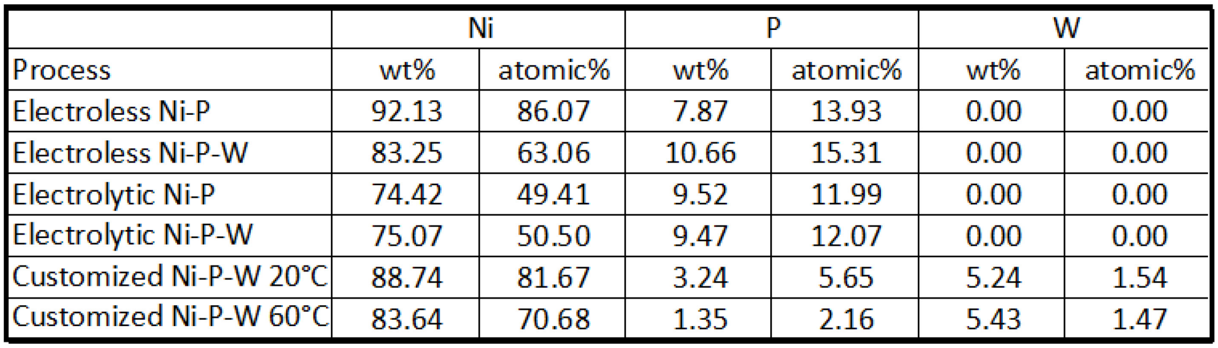
EDS was used to examine the chemical composition of the coating. Three 500 µm by 400 µm area on each sample were used to make EDS measurements. The precision of these measurements is around 0.5%. If the reading is below 0.5%, the sample could be considered as no targeted element in the coating.

Early in the experiment, all samples were pre-coated for 30 minutes in Atotech electroless nickel phosphorus coating solution. The results showed none of the samples would have tungsten after pre-coating. The pre-coating process was later on removed once found that even without pre-coating, the samples could still develop a coating layer in the electroless coating solution with the addition of sodium tungstate.

The results tabulated in Table 2 shows the composition of different samples. No tungsten presence in any coatings produced using the solution made from the Atotech stock solution, regardless of electroless or electrolytic process. Coatings electrolytically produced using the in-house solution contained 5.3 wt% tungsten Solution temperature did not affect the coating composition. Only nickel, phosphorus and tungsten were listed in the table. All other elements were not listed. The most common two additional elements were carbon and oxygen. There are many sources for carbon, like oil contamination from hand holding the samples. When stored in the plastic storage container, the container might generate gasous compounds which deposited on to the sample. Oxygen has more sources. The organic compounds which brought in carbon would also bring oxygen into the EDS result. Meanwhile, the sample might be oxidized during the storage time. This leads to the phenomena when the cross-sectional scans were made.

Another important observation was the content of phosphorus in the coatings. For Ni-P-W coating, the amount of phosphorus in the coating was significantly lower than that in the Ni-P coating. This might be attributed to the presence of tungsten in the coating which reduces the amount of phosphorus in the coating [26]. The solution difference might also be a reason as different solution chemistry will yield different chemical reactions during coating process. Literature shows when the weight % of phosphorus was at 5.2% or lower, the coating has a partially crystalline deposition after heat treatment [27]. At a phosphorus amount at low at 1.35 %. It was highly likely that a crystalline structure can be obtained with proper heat treatment at this composition.

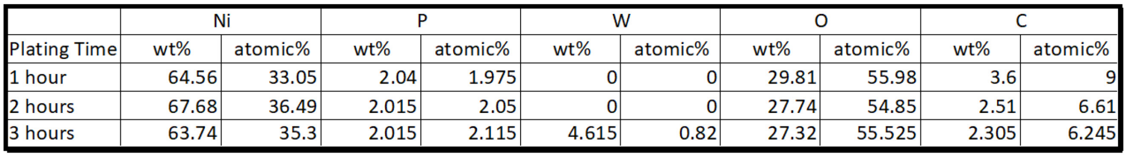
Table 1: Coating composition of all important samples



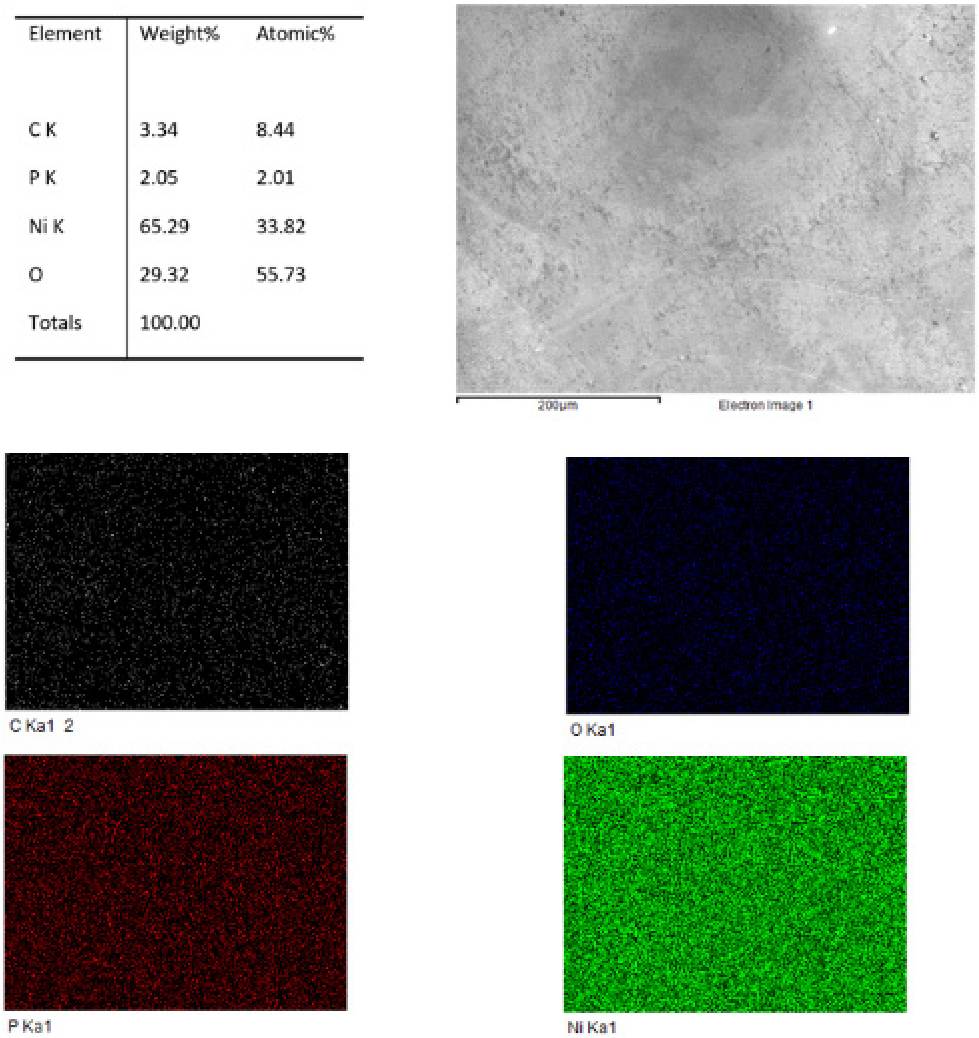
	Ni		P		W	
Process	wt%	atomic%	wt%	atomic%	wt%	atomic%
Electroless Ni-P	92.13	86.07	7.87	13.93	0.00	0.00
Electroless Ni-P-W	83.25	63.06	10.66	15.31	0.00	0.00
Electrolytic Ni-P	74.42	49.41	9.52	11.99	0.00	0.00
Electrolytic Ni-P-W	75.07	50.50	9.47	12.07	0.00	0.00
Customized Ni-P-W 20°C	88.74	81.67	3.24	5.65	5.24	1.54
Customized Ni-P-W 60°C	83.64	70.68	1.35	2.16	5.43	1.47

Since the Ni-P-W coating using in-house made solution showed positive result on tungsten, this procedure was repeated, trying to verify the repeatability of the coating process. However, the result shows the 1 hour plated Ni-P-W sample did not have tungsten in the coating. EDS Mapping shown in figure 48 indicates a featureless geography without tungsten at all. The 2 hours plated sample also had no indication of tungsten. The 3 hours plated sample had tungsten in its coating though. However, the concentration of tungsten in its coating is only 0.82 atomic%, which is even lower than the 1-hour sample coated for the first time. This means the coating result is very inconsistent. The conclusion of a successful Ni-P-W coating could not be achieved at this stage. From table 2, the oxygen amount increased significantly compared with the samples in table 1. Accompanying with the increasing amount of oxygen, the % of nickel and phosphorus decreased. One reason might be samples have been oxidized through the processes.

Table 2: Electrolytic coating in in-house made solution for different plating time



	Ni		P		W		O		C	
Plating Time	wt%	atomic%	wt%	atomic%	wt%	atomic%	wt%	atomic%	wt%	atomic%
1 hour	64.56	33.05	2.04	1.975	0	0	29.81	55.98	3.6	9
2 hours	67.68	36.49	2.015	2.05	0	0	27.74	54.85	2.51	6.61
3 hours	63.74	35.3	2.015	2.115	4.615	0.82	27.32	55.525	2.305	6.245



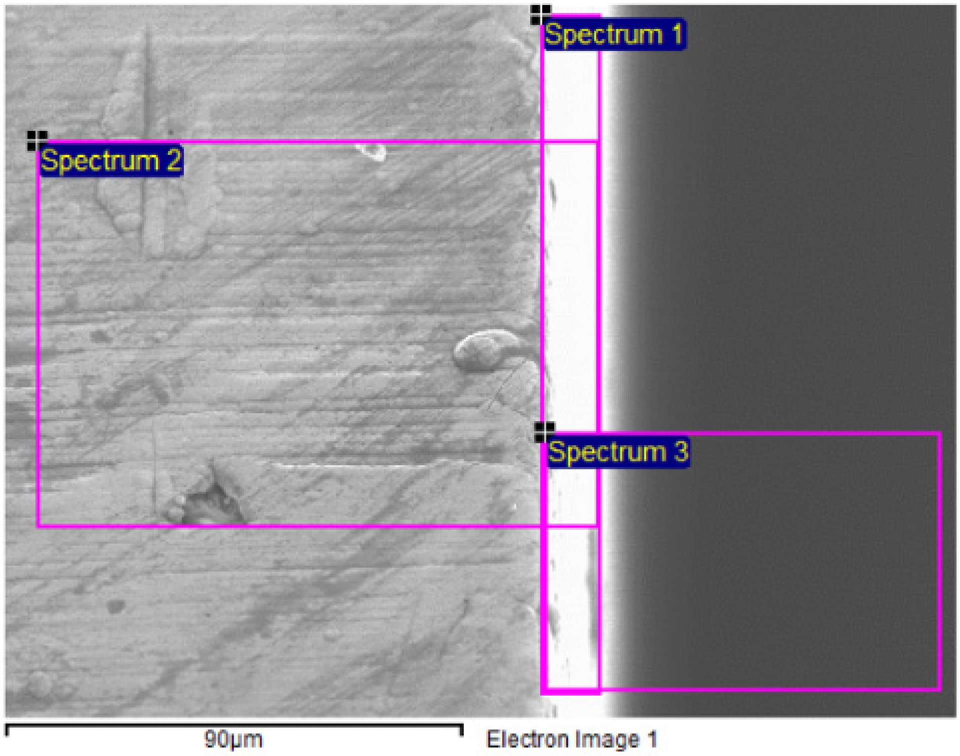
Element	Weight%	Atomic%
C K	3.34	8.44
P K	2.05	2.01
Ni K	65.29	33.82
O	29.32	55.73
Totals	100.00	

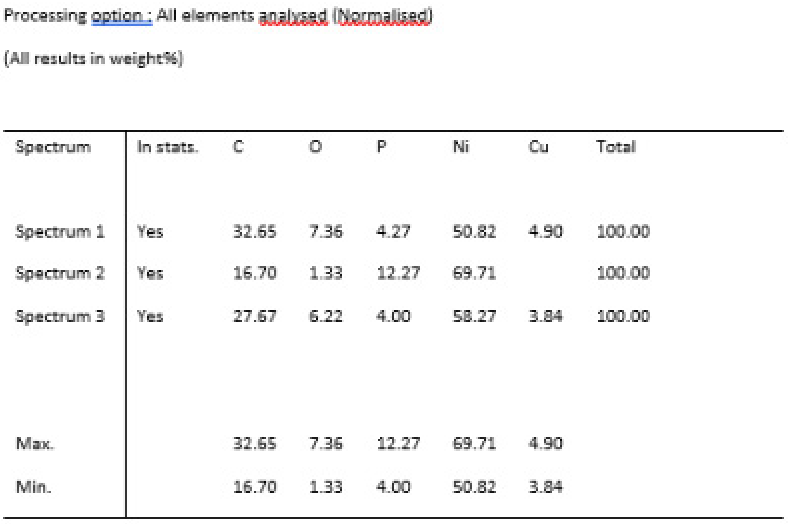
Figure 48: EDS Mapping of 1-hour electrolytic plating in in-house solution with new samples

The samples which have gone through a cross sectional SEM were also performed an EDS measurement. Three sections were scanned on each sample for comparison and estimation. Spectrum 1 is the coating itself without any influence from substrates or sample holders. Spectrum 2 includes part of the substrate; all EDS scans should show a significant amount of copper. Spectrum 3 includes part of the sample holder, which is made of aluminum.

Figure 49 shows the spectrums of a 3 hours electroless Ni-P sample in Atotech solution. The scanning result is different than projection. The rough area on the left is the substrate. However, on the EDS result, spectrum 2 has no indication of copper. Instead, spectrum 1 and 3 shows the existence of copper. Even more strange is that spectrum 1 shows more copper than spectrum 3, while spectrum 1 exactly measures the cross section of the coating and spectrum 3 includes a huge amount of sample holder which is made of aluminum.

The first two EDS scans of the cross-sectional areas of an electrolytically plated Ni-P-W sample showed copper could be detected when scanning onto the substrate. Oxygen content is lower when comparing spectrum 2 with spectrum 1, which is included in the table of figure 50. This implies that the copper is protected thus it is harder to be oxidized. Tungsten could not be detected at all in these scans. In case tungsten only presented on the top surface layer, an area of spectrum 3, shown in figure 51, was also scanned to examine the composition above and below the coating layer. However, this time, not only tungsten was not detected, copper was not detected at all in the location of spectrum 2.



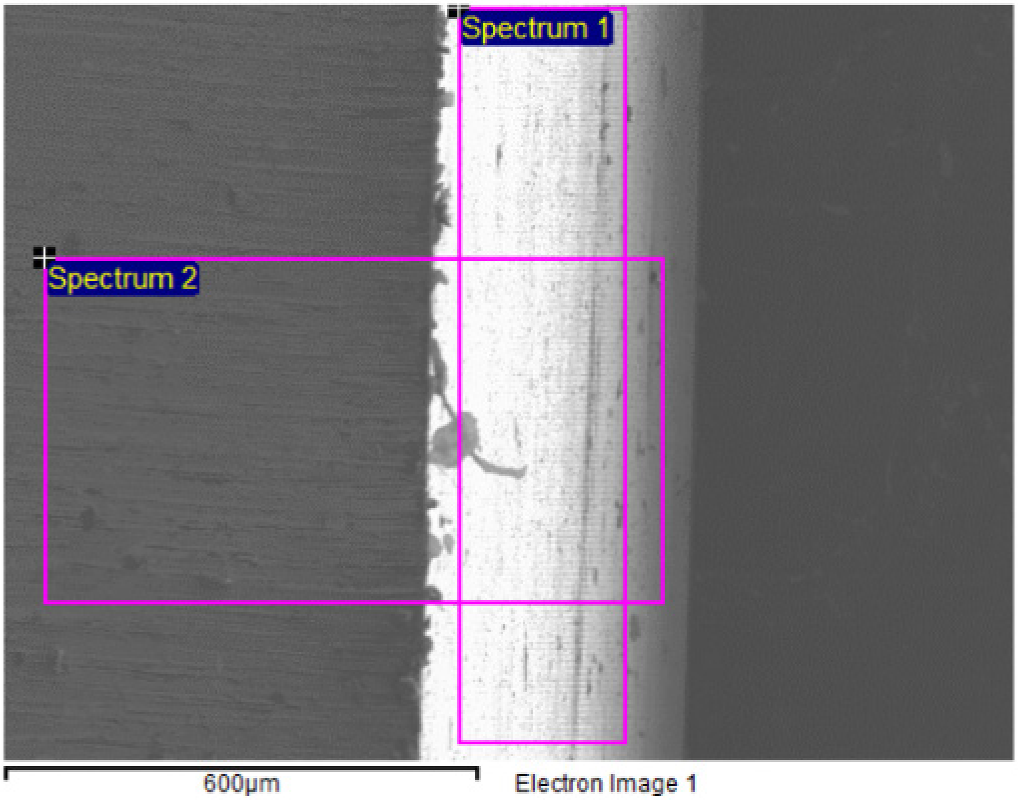


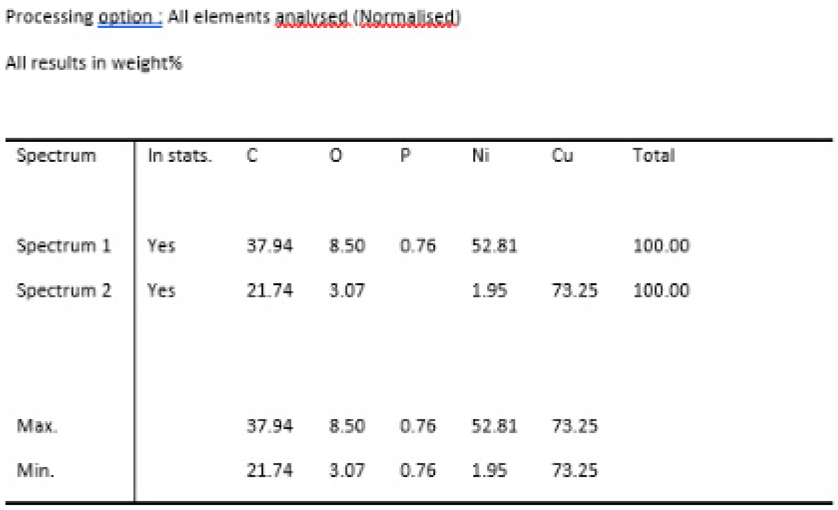
Processing option : All elements analysed (Normalised)

(All results in weight%)

Spectrum	In stats.	C	O	P	Ni	Cu	Total
Spectrum 1	Yes	32.65	7.36	4.27	50.82	4.90	100.00
Spectrum 2	Yes	16.70	1.33	12.27	69.71		100.00
Spectrum 3	Yes	27.67	6.22	4.00	58.27	3.84	100.00
Max.		32.65	7.36	12.27	69.71	4.90	
Min.		16.70	1.33	4.00	50.82	3.84	

Figure 49: Cross section EDS of 3 hours electroless Ni-P coating sample



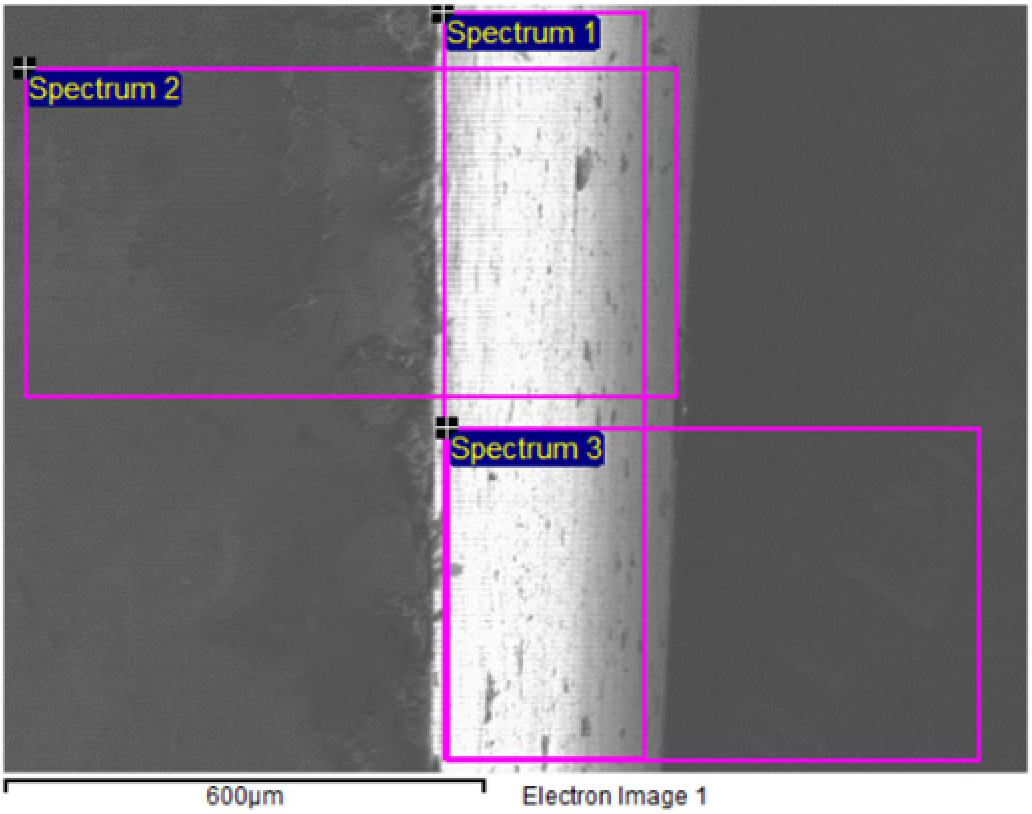


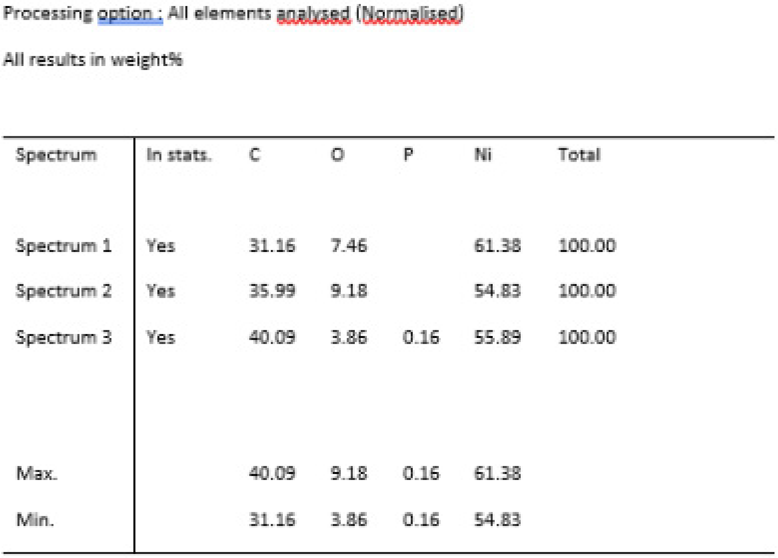
Processing option : All elements analysed (Normalised)

All results in weight%

Spectrum	In stats.	C	O	P	Ni	Cu	Total
Spectrum 1	Yes	37.94	8.50	0.76	52.81		100.00
Spectrum 2	Yes	21.74	3.07		1.95	73.25	100.00
Max.		37.94	8.50	0.76	52.81	73.25	
Min.		21.74	3.07	0.76	1.95	73.25	

Figure 50: Cross-sectional EDS of 1- hour electrolytically plated Ni-P-W coating in in-house made solution





Processing option : All elements analysed (Normalised)

All results in weight%

Spectrum	In stats.	C	O	P	Ni	Total
Spectrum 1	Yes	31.16	7.46		61.38	100.00
Spectrum 2	Yes	35.99	9.18		54.83	100.00
Spectrum 3	Yes	40.09	3.86	0.16	55.89	100.00
Max.		40.09	9.18	0.16	61.38	
Min.		31.16	3.86	0.16	54.83	

Figure 51: Cross-sectional EDS of 1-hour electrolytically plated Ni-P-W coating in in-house made solution

There are many reasons for these inconsistent results. The first one is scanning error. The scanning area is smaller compared with frontal aerial scan. As discussed with colleague, the surface might be miss measured. This will lead to inconsistent measurements. The second reason is of polishing issue. The polishing processes followed was suggested by the colleague to minimize contaminations. However, the silicon carbide sand paper and diamond suspension will introduce carbon contaminations onto the sample. Completely removing the amount of carbon through washing by distilled water is impossible. While polishing, it is hard to hold the sample perfectly straight. Polishing at an angle might destroy the thin coating, yielding faulty SEM-EDS results. The third reason is the plating process itself. Although tungsten plating seems successful when surface scan was performed, it might only be a surface ion layer which is the original tungstate anions precipitated onto the surface. The ions are attracted through electrical charge which could not be fully washed out during the cleaning phase. When scanning the cross section, the ion layer is too thin to be registered on the screen. The concentration of tungsten in this scan will then be low to a level where it is negligible to the EDS detector. It would be an indication that tungsten coating was not succeeded in its performing. The plating solution uses huge number of organic additives like critic acid and sodium saccharin. They could easily introduce carbon into the plating. Finally, the anode is made of graphite. Although it is placed at the bottom of the cell, tiny particles of carbon breaking down would be carried up by gas bubbles generated on the electrode or convection of the solution. They will be transferred on to the surface of the cathode, which might be deposited to cause carbon containmination.

In short summary, the chemical composition of the coating is not consistent. Many scanning results did not match the original estimation, while some of the EDS data even showed contradiction with each other. Showing no indication of tungsten element provided a negative confirmation of successful nickel phosphorus tungsten plating in the cross-sectional scans. Again, the cross section of the newly plated samples, which went through in-house electrolytic plating for 2 hours and 3 hours could not perform a cross-sectional chemical composition analysis. The resin on the side will not only be hard to remove but will also introduce lots of unknown organic contaminations.

3.4.3 Coating electrochemcial impedance

Increasing corrosion resistance was the primary objective of implementing tungsten into the composite coating. The higher the impedance, the better the corrosion resistance. Three factors will affect the impedance. The first one was coating time. The longer the coating time, the thicker the coating will be. A thicker coating should have a higher impedance compared with a thinner coating. The second parameter was surface smoothness. If a surface was smoother, the impedance was higher due to a smaller microscopic surface area [28]. It means, for this project, diamond polished samples should have a higher impedance than 400 grit polished samples. Tungsten was the last factor. By forming tungsten composite, the impedance increases significantly [26]. Since three continuous runs of EIS were performed on each sample, the precision calculated from the data is 5%.

The data from the EIS experiments were fitted using equivalent circuits. The circuit diagram is shown in figure 52. The most important parameter was the capacitance. R_s was the solution resistance. The table shows this value was very consistent through the board. It means the experimental setup was good thus data can be trusted. In this RC circuit, a capacitor with higher capacitance increases the passing frequency of the signal [29]. Compared with previous research, the impedance of this coating is higher than Ni-P-W coating on magnesium substrate [30]. In corrosion, it translates to high impedance, which low frequency corrosion current has a harder time to pass through the coating. If corrosion current is harder to pass, the sample will have a higher corrosion resistance.

Table 3 to 5 show the equivalent circuit simulation results. Table 3 shows the results of electroless plated samples in Atotech solution. None of them containes tungsten in their coating based on EDS analysis. Samples in table 4 were electrolytically plated in two different solutions. The first row is for the samples plated in Atotech solution, it does not contain tungsten in the coating. The second line is the sample plated in homemade solution, it does contain tungsten on the coating surface, but could not be observed when scanning the cross-sectional area. Table 5 contains EIS results from samples plated in homemade solution for different period of time, only the 3 hours coatings had tungsten on the surface during EDS. The capacitance of all electrolytically plated samples are higher than electroless plated samples. This is because electrolytic coating yields looser layering of the coating, increasing the capacitance of the plating. The coating might also not be adhered to the substrate as good as electroless coating, which increases the capacitance. However, the coating resistance is mostly lower than that of the electroless plated samples. Electrolytically coated Ni-P-W samples in homemade solution with tungsten on the surface have a similar film resistance compared to electroless Ni-P coating polished to diamond grade, while the electrolytic coated Ni-P-W sample in homemade solution without tungsten on the surface has a slightly higher resistance compared with electroless coating samples for the same amount of time. The analysis also shows that for all diamond polished samples trying to achieve Ni-P-W coating, the coating resistance decreases with the increase of plating time.

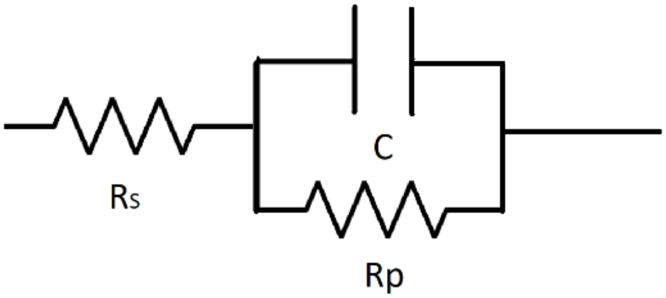


Figure 52: EIS RC Equivalent Circuit

Table 3: EIS equivalent circuit simulation of electroless samples

		1			2			3		
		Rs	C	Rp	Rs	C	Rp	Rs	C	Rp
Electroless 400 Grit	Ni-P	22.45	2.66E-05	6821	18.99	1.80E-05	9645	17.16	2.31E-05	16420
	Ni-P-W	19.69	1.31E-05	13622	17.13	2.44E-05	27149	17.16	2.30E-05	28617
Electroless Diamond	Ni-P	16.92	1.80E-05	7325	20.17	1.11E-05	62036	18.03	2.99E-05	42033
	Ni-P-W	17.85	1.66E-05	33925	17.2	2.17E-05	27959	19.6	1.73E-05	22342

Table 4: EIS equivalent circuit simulation of electrolytic samples using different solution

		1		
		Rs	C	Rp
Eletrolytic Coating	Ni-P-W	19.76	4.41E-05	7795
	Homemade	20.73	5.51E-05	7373

Table 5: EIS equivalent circuit simulation of electrolytic samples with different plating time

		1			2			3		
		Rs	C	Rp	Rs	C	Rp	Rs	C	Rp
Electrolytic Diamond	Homemade Ni-P-W	23.97	3.16E-05	9880	20.41	7.04E-05	3639	35.5	7.27E-05	2951

3.4.4 Coating critical pitting potential

Pitting corrosion was one of the corrosion types. During pitting corrosion, the passive film on the surface of the protected body is attacked by halide anions. An autocatalytic reaction occurs and propagates to attack the whole protective film thus corrosion happens [2].

Cyclic polarization was used to evaluate the coating resistance to pitting corrosion under salt water condition. Chloride anions will attack the coating. Cyclic polarization data were plotted on potential vs. current density graphs, shown in figure 53 to 57 to better visualize the whole passivation, pitting and re-passivation process. The arrows on the diagram indicate the direction of the potential sweep. From data analysis, the precision of these measurements yields an error of approximately 10%. Considering about variations between samples, this precision is acceptable.

Figure 53 and Figure 54 shows the cyclic polarization result of electroless coating samples polished to 400 grit. For Ni-P samples, the longer the coating time, the smaller their corrosion current was. This might be a result of thicker and denser coating. However, the Ni-P-W samples shows a longer coating time will make the coating less resistant to corrosion. Even though these tungsten coating samples did not have any tungsten present in their coatings, the negatively charged tungstate anions might have reduce the coating thickness and also coating density, resulting in less corrosion resistance.

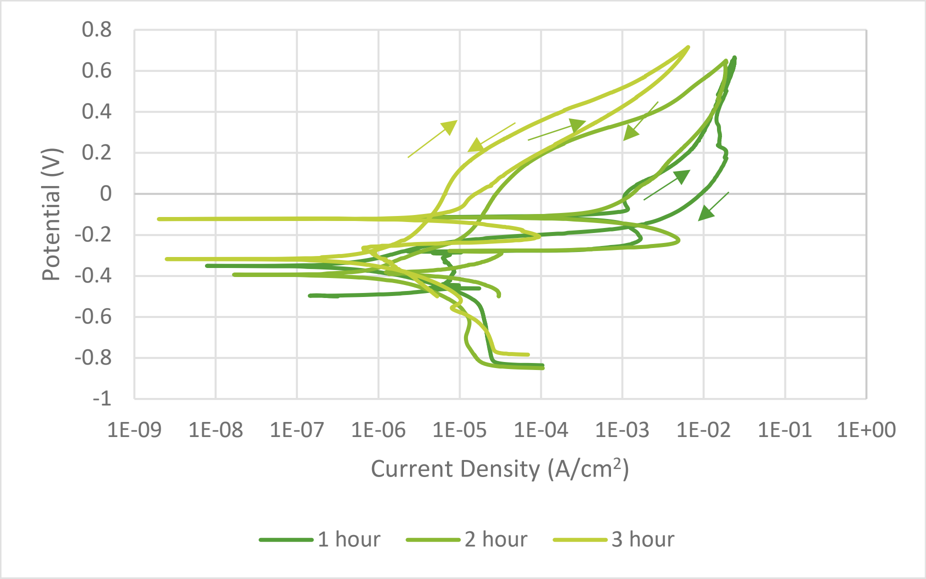


Figure 53: CP of 400 Grit Electroless Ni-P Coating

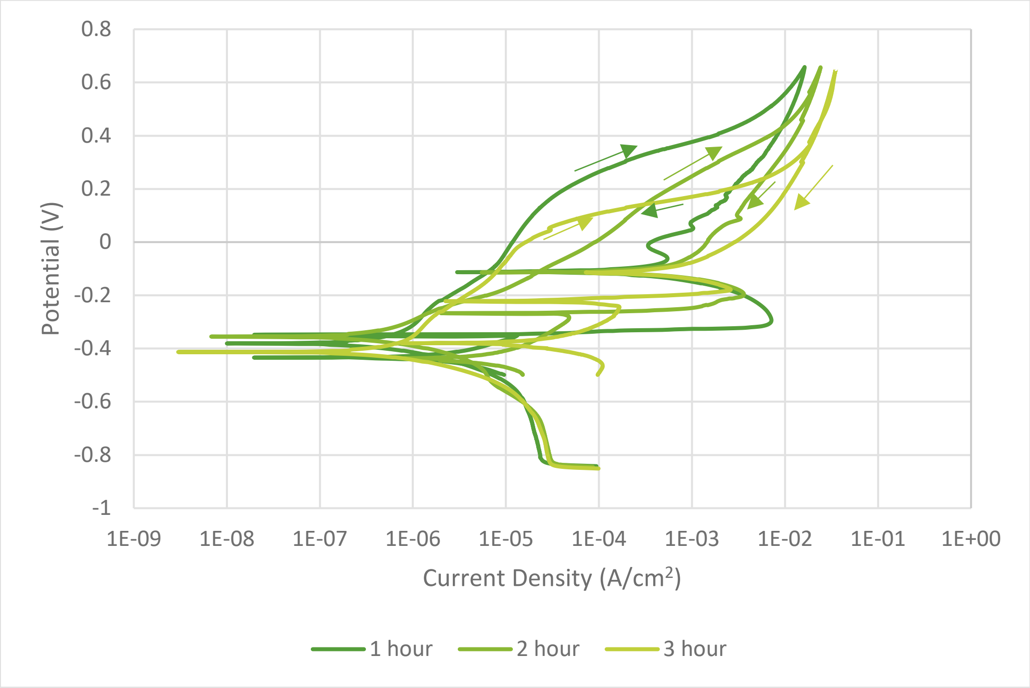


Figure 54: CP of 400 Grit Electroless Ni-P-W Coating

Figure 55 and figure 56 show the cyclic polarization result of Ni-P and Ni-P-W electroless coating samples polished using diamond suspension. The results are quite similar to 400 grit polished samples.

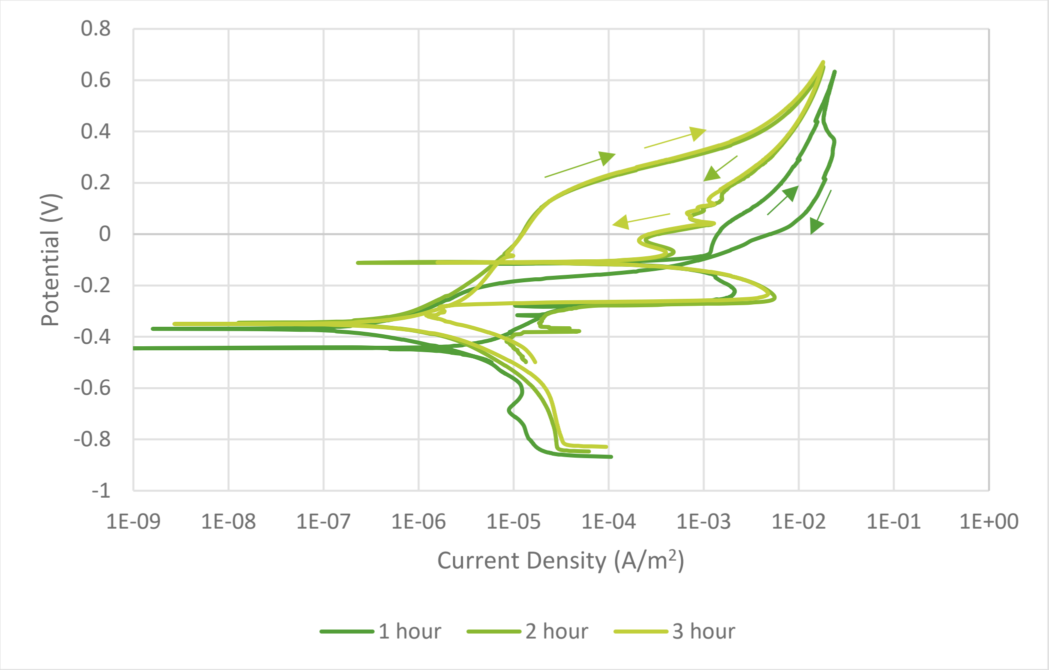


Figure 55: CP of Diamond Polished Electroless Ni-P Coating

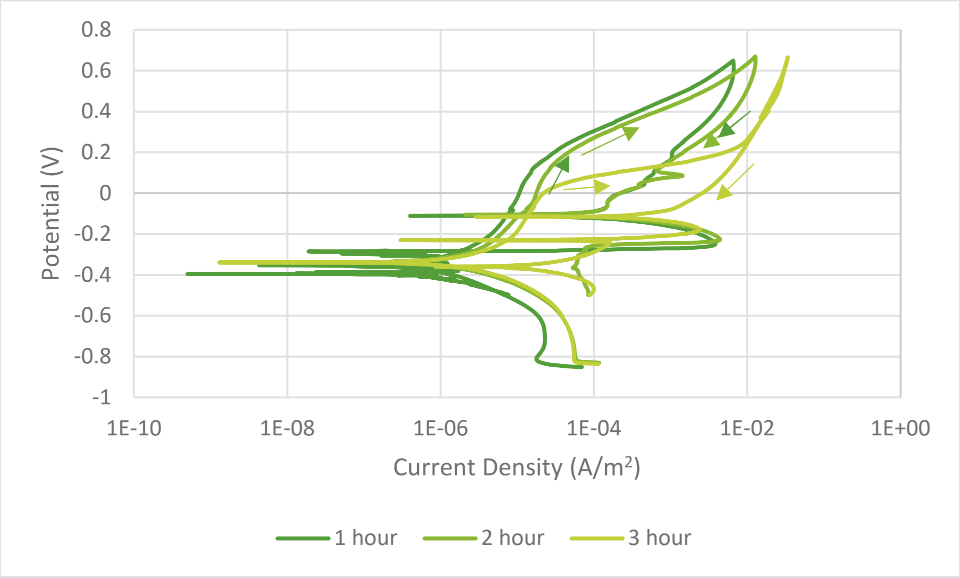
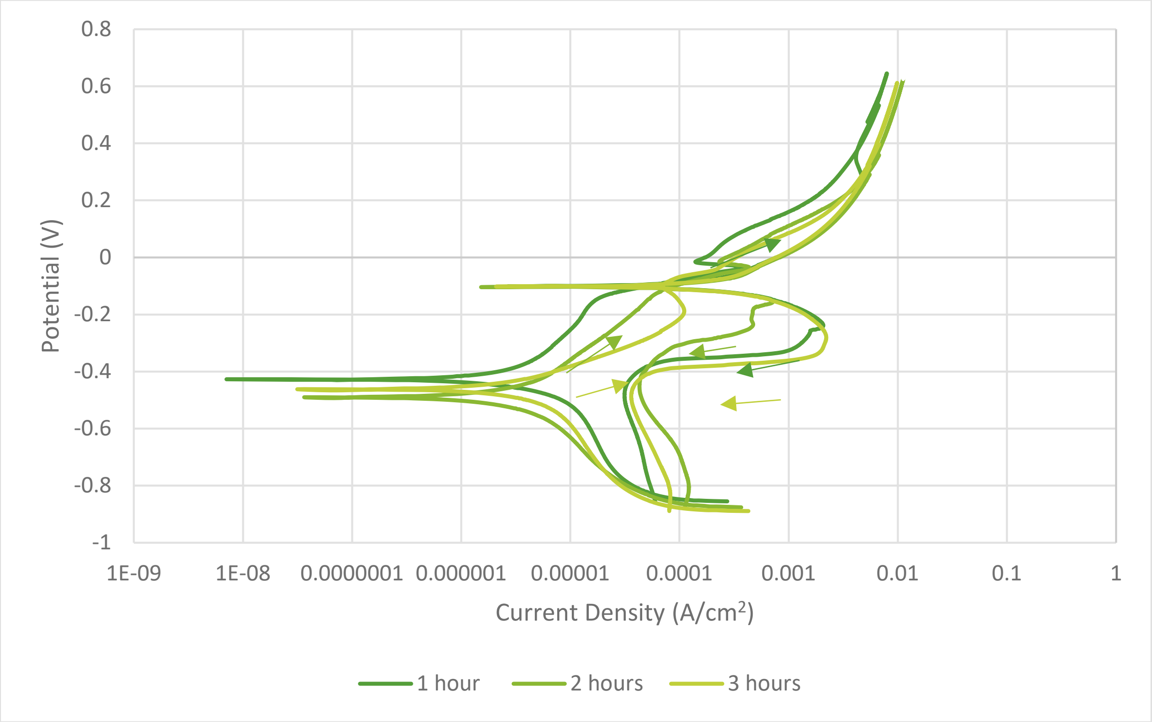


Figure 56: CP of Diamond Polished Electroless Ni-P-W Coating

Electrolytic plating of Ni-P-W may have different corrosion resistance compared with electroless plating. Figure 57 shows the cyclic polarization scans of all electrolytic Ni-P-W plating samples prepared using homemade solution. The result is very similar to Electroless Ni-P-W coatings although the solution environment and the plating technique are totally different. The 3 hour sample has tungsten on the surface while the 1 hour and 2 hour sample have none.

Figure 57: CP of electrolytic Ni-P-W coating produced in homemade solution



Three potentials on each cyclic polarization diagram are analyzed. The passive, the transpassive and the repassivation potential. The passivation potential is the potential value at which a passive layer starts to form. The transpassive potential is the potential where chloride ions attack the coating, causing it to break down thus lose protection performance. The re-passivation potential is the potential at which the surface re-passivates [2]. A lower passivation potential is always preferred as this makes it easier for the coating to passivate at lower potential. A higher transpassive potential is favored, as this translates to having a coating more resistant to pitting. Combined with a low passivation potential, it will provide a wide passive region thus very resisting to pitting corrosion. A higher repassivation potential is also desirable because if pitting has already occurred, a small drop on the potential is enough to passivate the surface, protecting the substrate [31]. The trans passive potential and re-passivation potentials are tabulated in Table 6. It shows that the passivation potential of the successful Ni-P-W coating has all three parameters higher than the 1 hour coated Ni-P coating samples. A high passivation potential is not desirable, as that meant the sample is easier to be corroded before passivation. However, the passivation range was slightly larger when compared with that of electroless Ni-P samples produced by using commercial solutions. This is a good sign as the larger the passive region, the more resistant a coating is to pitting corrosion. The repeated electrolytic coatings show a different result. The passivation potential of these samples are 0.1 to 0.2 volts lower compared with electroless platings, which is good for passivation to happen on the surface. The lower transpassive potential is not a good sign. In fact, all electrolytic plating samples have a lower transpassive potential, which indicates the coating film is easier to break down. Comparison between the electrolytic plated samples shows that with an increase in the plating time, the transpassive potential would decrease, resulting in easier passive film breakdown in corrosion environment. The measurement matches the cyclic polarization scan figure where the three-hour plated sample has the highest corrosion current density while the one hour sample has the lowest.

Table 6: Three potential parameters of samples using Cyclic Polarization Analysis

	400 Grit Ni-P			400 Grit Ni-P-W		
	1 hour	2 hours	3 hours	1 hour	2 hours	3 hours
Passivation Potential	-0.31	-0.24	-0.2	-0.2	-0.15	-0.2
Trans Passive Potential	-0.22	0.15	0.25	0.22	0.2	0.06
Re-Passivation Potential	-0.26	-0.11	-0.1	-0.1	-0.1	-0.1
	Diamond Ni-P			Diamond Ni-P-W		
	1 hour	2 hours	3 hours	1 hour	2 hours	3 hours
Passivation Potential	-0.32	-0.22	-0.27	-0.2	-0.25	-0.25
Trans Passive Potential	-0.2	0.15	0.18	0.2	0.18	0.02
Re-Passivation Potential	-0.25	-0.1	-0.1	-0.1	-0.1	-0.1

	Customized Ni-P-W 1 hour
Passivation Potential	-0.22
Trans Passive Potential	-0.09
Re-Passivation Potential	-0.13

	Homemade solution Ni-P-W		
	1 hour	2 hours	3 hours
Passivation Potential	-0.36	-0.41	-0.41
Trans Passive Potential	0.05	0.01	-0.08
Re-Passivation Potential	-0.1	-0.1	-0.1

3.4.5 Coating scratch resistance

Wear resistance is to measure how good the coatings resist to wear. The idea of incorporate tungsten into the coating is to increase the coating hardness. Since tungsten is hard, it is predicted that the composite coating with tungsten should be harder than Ni-P coatings.

Scar Volume vs. Scratch Length of all available samples were plotted in Figure 58. The slope of each line is the wear rate of each sample. By taking the reverse of the slope, the wear resistance tabulated in Table 7 can be obtained. The Ni-P coatings are all produced from electroless processes while Ni-P-W samples are all from electrolytic. Only 1 hour and 3 hours Ni-P-W samples have tungsten on the surface, 2 hours sample does not.

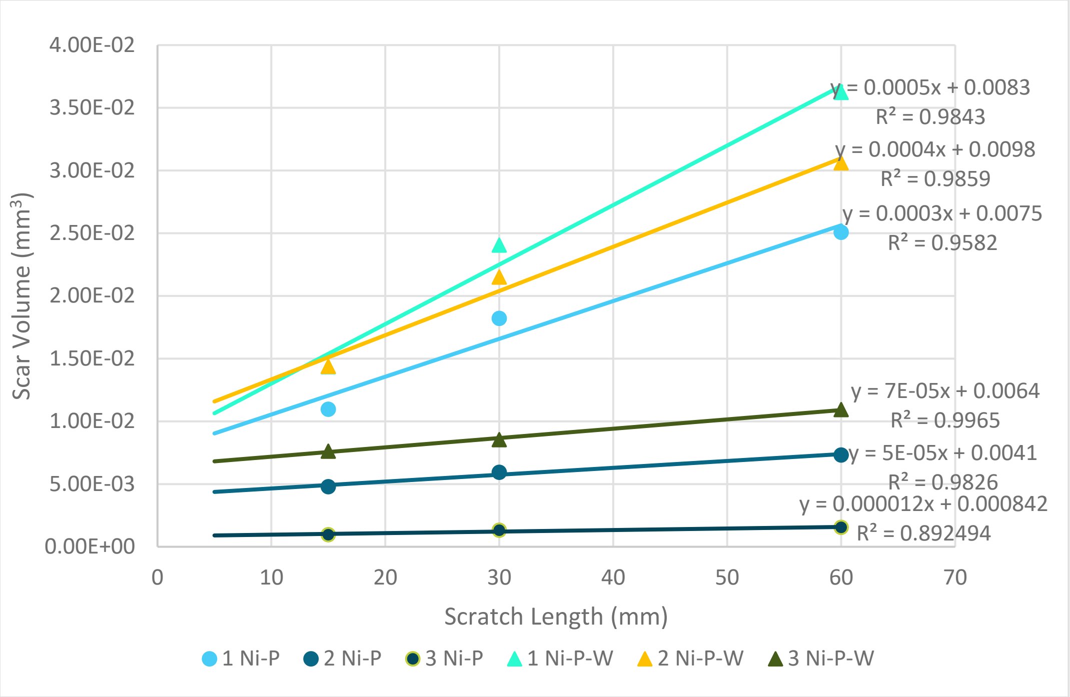


Figure 58: Scar Volume vs. Scratch Length of Electroless Ni-P and Electrolytic Ni-P-W coatings

Table 7: Wear resistance of electroless and electrolytic plated samples (mm/mm^3)

	1 hour	2 hour	3 hour
Electroless Ni-P	3314.65	18240.90	81354.03
Electrolytic Ni-P-W	2107.68	2836.72	13450.22

It is clear to see that all electrolytic Ni-P-W samples have lower wear resistance than electroless Ni-P coatings. There are multiple reasons for this. The first one is the coating processes. Electroless coating tends to have stronger bonds thus the whole structure is more rigid and uniform. On the other hand, electrolytic coating is difficult to achieve very densely packed coatings. The other reason is the solution. Commercial solution is used for electroless plating, which has already been optimized by commercial companies. The electrolytic plating solution is homemade, which is not designed to provide excellent coating products. Finally, the existence of tungsten in the solution might have effect on the reaction mechanism, it will result in a different surface characteristic compared with Ni-P.

From the data of electrolytic Ni-P-W samples, the wear resistance might have an increase with the presence of tungsten in electrolytic platings. The 1 hour plated Ni-P-W sample has a lower wear resistance than 2 hour Ni-P-W plating, but the difference between them is not as significant as the samples went through electroless processes.

In summary, electrolytic Ni-P-W coating is not as wear resistance as electroless Ni-P coating on copper substrate. It is not recommended to replace Ni-P coating for wear resistance application.

3.4.6 Coating toughness

Micro indentation test is used to examine the toughness of the coating. With an increase in the toughness of the coating, the coating could withstand a higher impact energy before breaking. Deformations will happen on the surface if a force is applied. However, the deformations should be elastic deformation. Once the force no longer applies, the coating should return to its original state.

From the observations of the coatings, samples from electrolytic plating breaks down on the edges of the coating. It is estimated that electrolytic Ni-P-W platings would be extremely brittle. They could not take as much load as electroless nickel samples, thus they will have a reduced hardness. However, the toughness should increase with the increase of plating time since the plating time would be longer.

The toughness of Ni-P coatings follows the pattern predicted. Figure 59 to 61 shows the micro indentation results for all Ni-P samples. It is clear in the graph that the longer the plating time, the larger indenting force the coating could withstand. The coatings are thus tougher. Table 8 is made to show the toughness of all Ni-P platings.

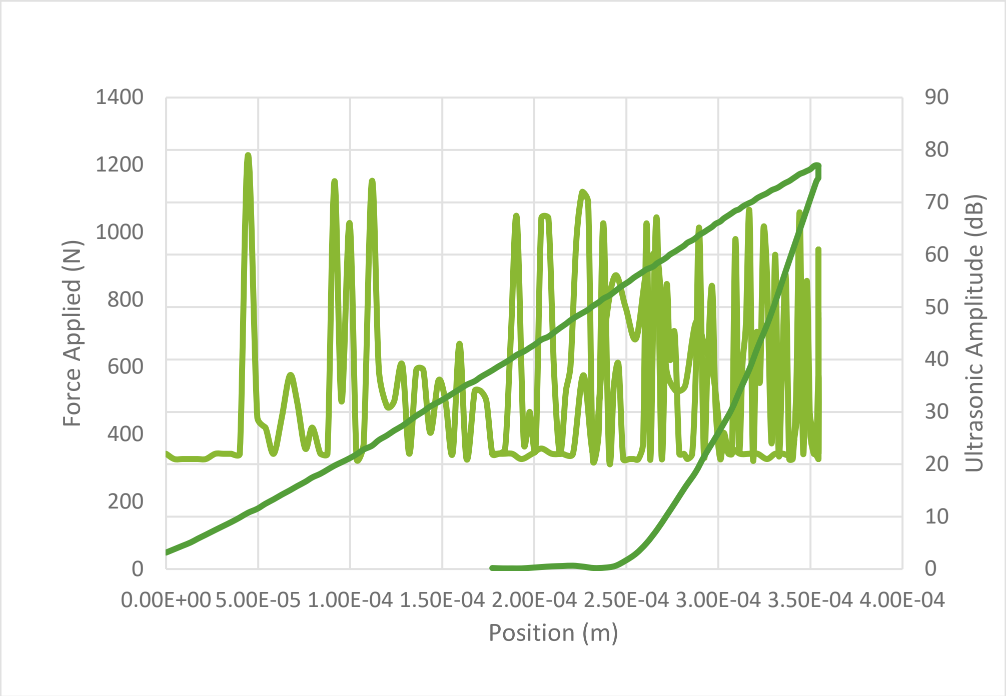


Figure 59: 1Ni-P micro indentation result

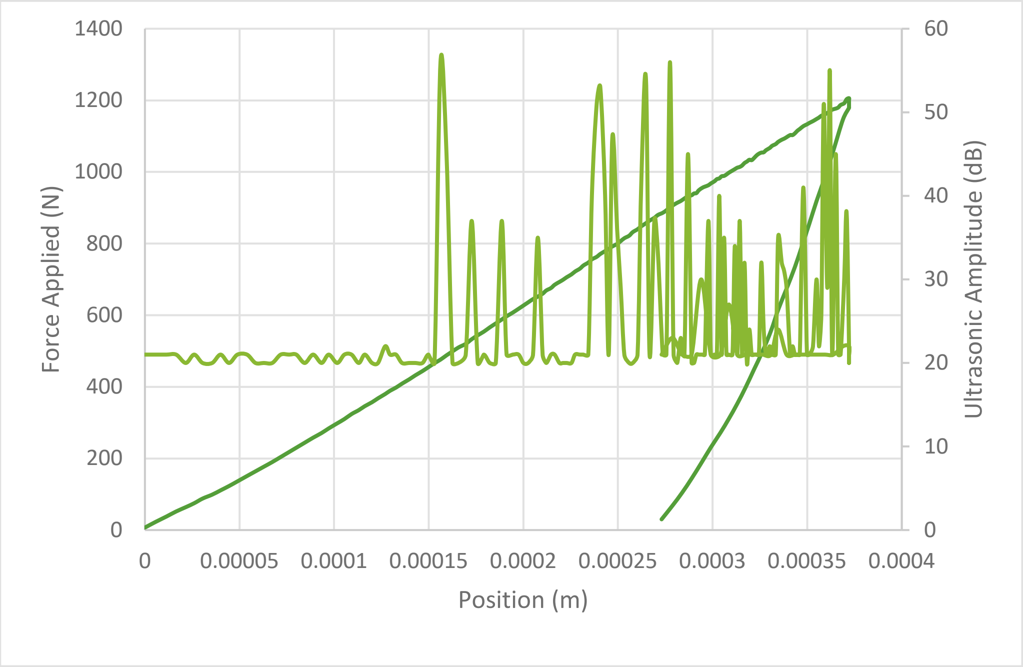


Figure 60: 2Ni-P micro indentation result

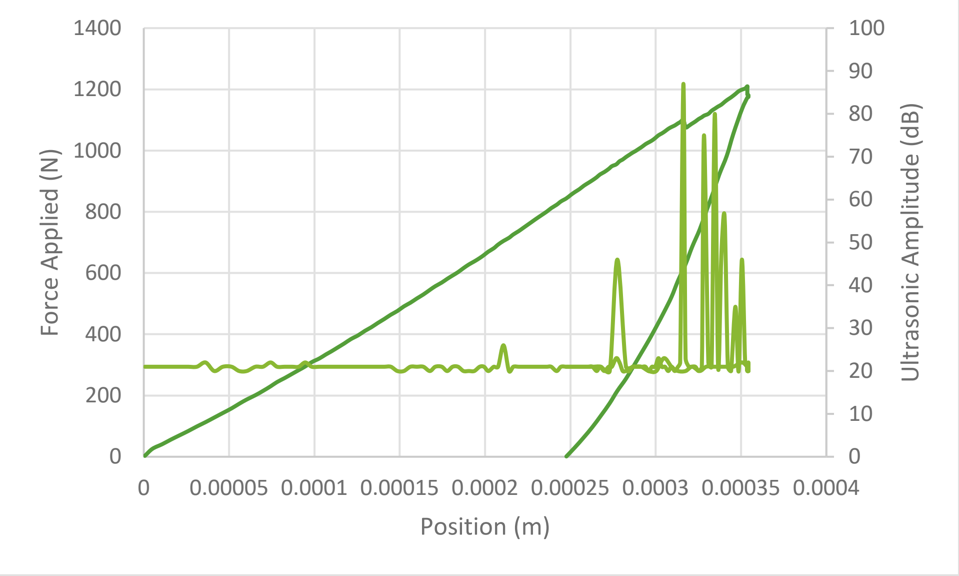


Figure 61: 3Ni-P micro indentation result

Table 8: Toughness of electroless Ni-P samples

	1 hour	2 hour	3 hour
Toughness (mJ)	6.1	71.3	255.7

When examining the samples under optical microscope, the micrographs prove the analysis is correct. With a longer plating time, coating of 3 hour Ni-P in figure 64 has fewer cracks than 1 hour and 2 hour samples shown in figure 62 and 63. Cracks on all these samples are radially out from the center of the indentation. There are no fragments observed near the coating, which means the coating is adhered quite well with the substrate. The results from electrolytic Ni-P-W is totally different from Ni-P, which is discussed in the next paragraph.

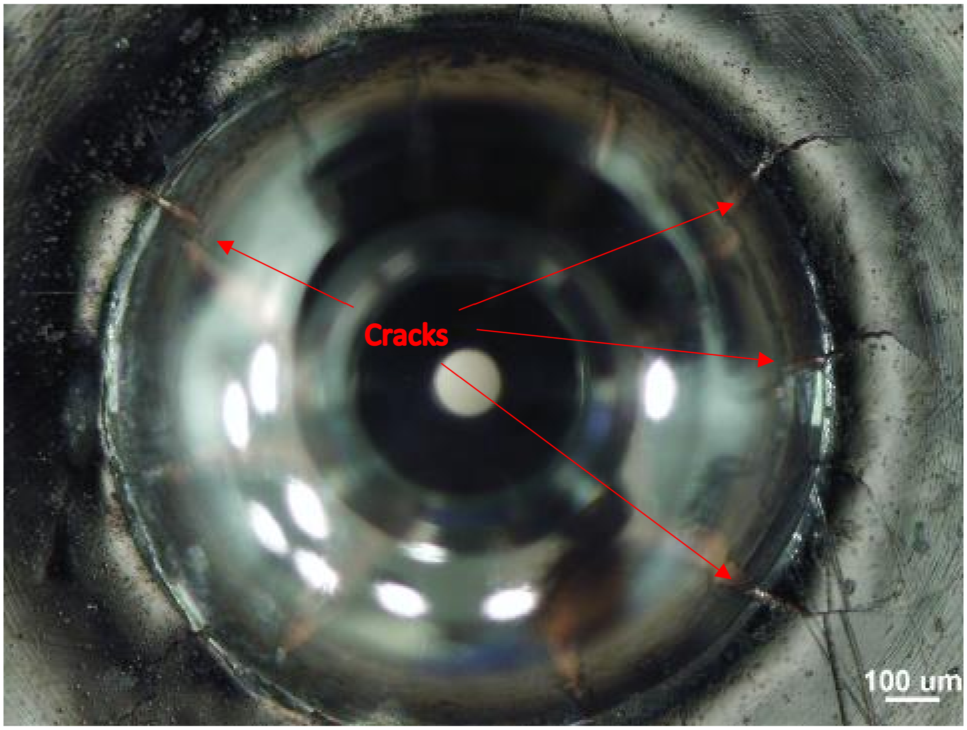


Figure 62: Micrograph of 1 hour Ni-P plating indentation result

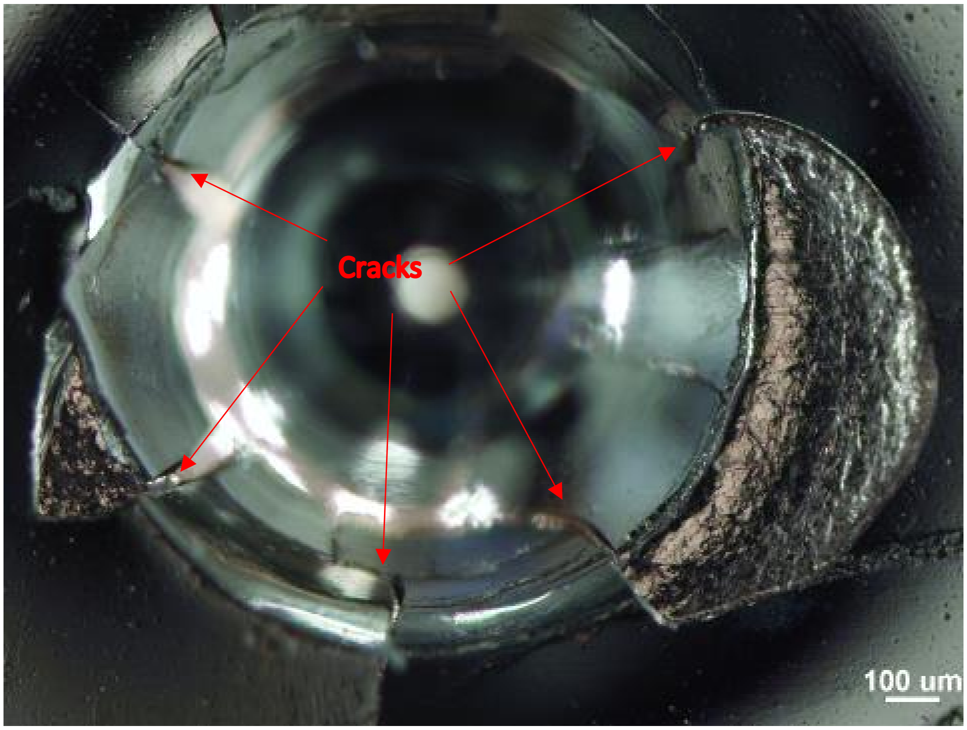


Figure 63: Micrograph of 2 hour Ni-P plating indentation result

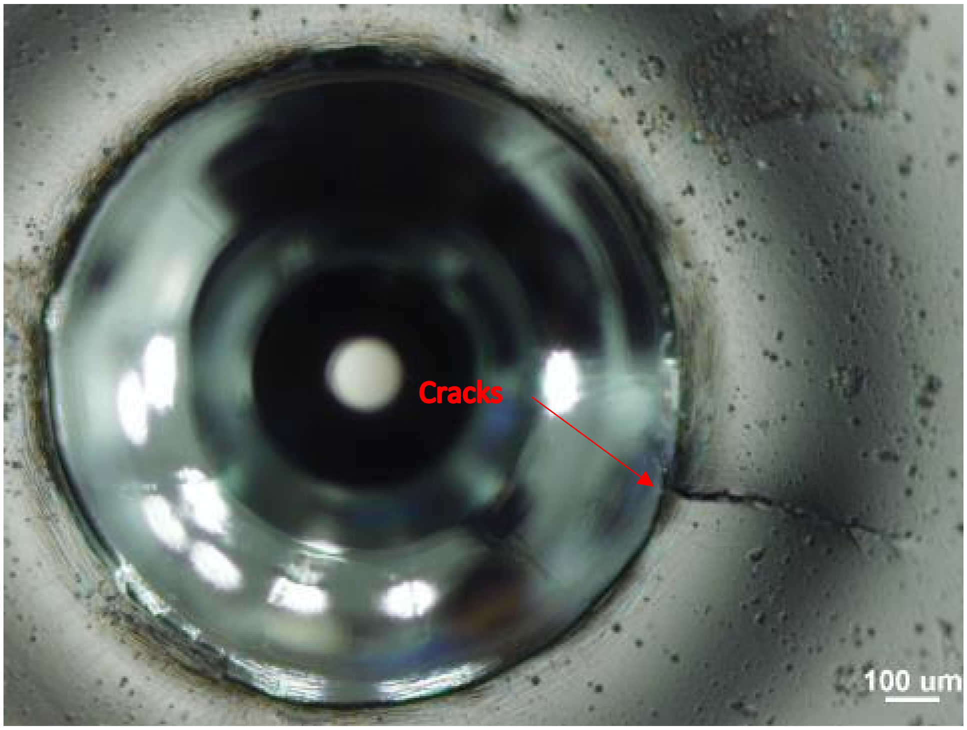


Figure 64: Micrograph of 3 hour Ni-P plating indentation result

Electrolytic platings have a different result. From the measurements plotted in figure 65 to 67, the coating fractured when contacted with the indenter. It was indicated by the high amplitude ultrasonic signal logged by the instrument. Based on the graphs, the toughness could not be calculated as the ultrasonic response was already higher than the 20 dB base noise once the force is applied. The results from microscopy proves this measurement.

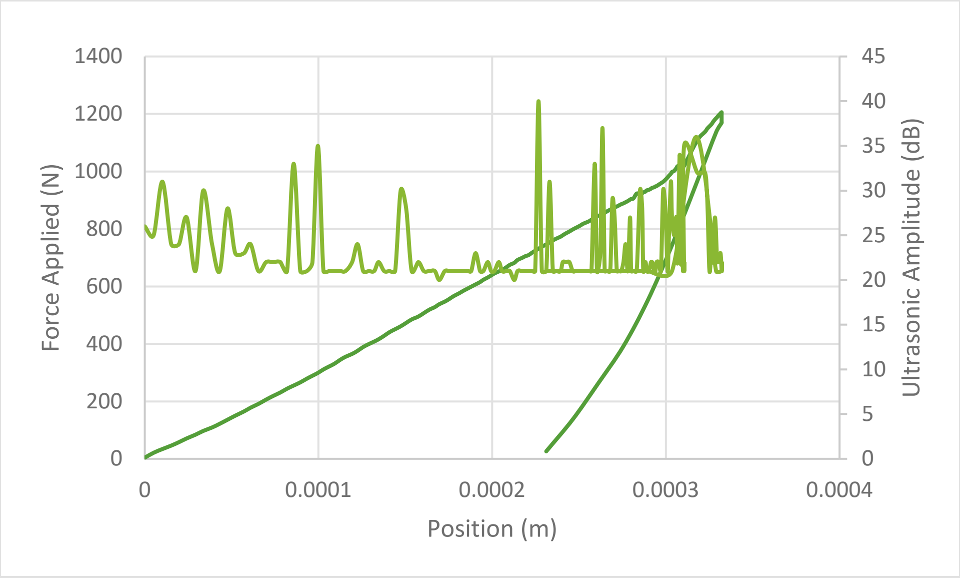


Figure 65: 1 hr Ni-P-W micro indentation result

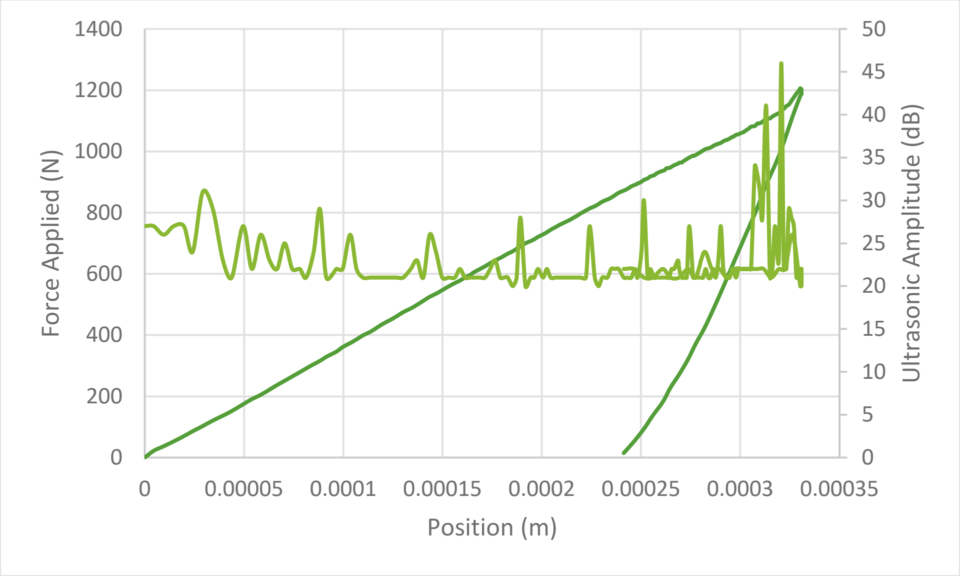


Figure 66: 2 hr Ni-P-W micro indentation result

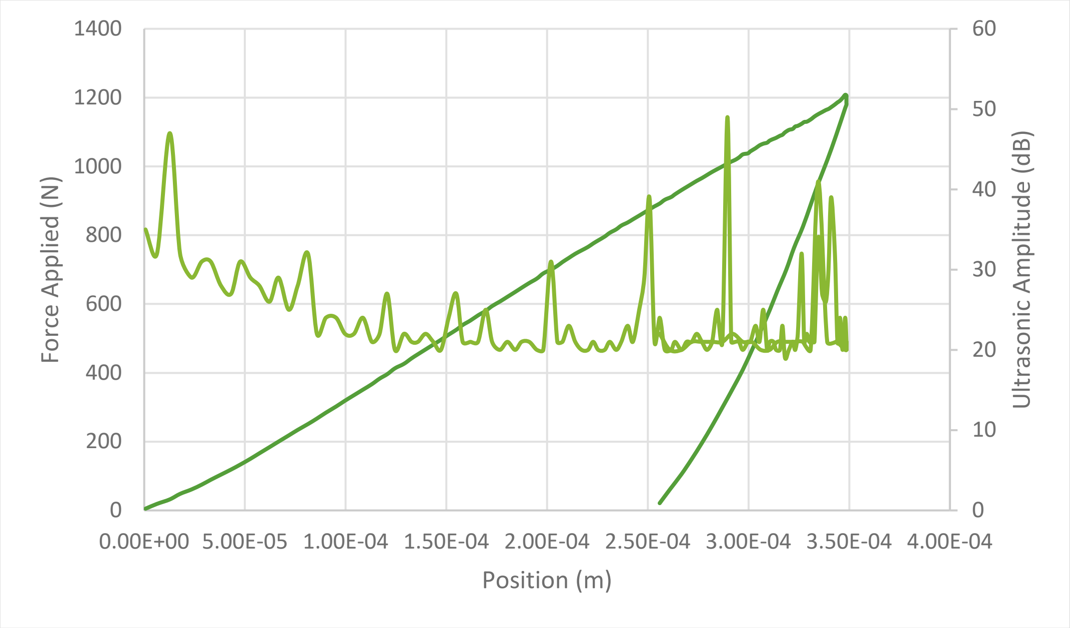


Figure 67: 3hr Ni-P-W micro indentation result

The pictures of samples under microscopy are shown in figure 68 to 70. All of them shows fractals of coating. The fractals are separated from the substrate, revealing the copper substrate in the color of brown to red. It shows the poor adhesion between the Ni-P-W coating and the copper substrate for electrolytic processes. The cracks are not as large as those observed in electroless Ni-P coatings. However, there are significantly more fine cracks on the electrolytic plated samples. The cracks are still in a radial pattern.

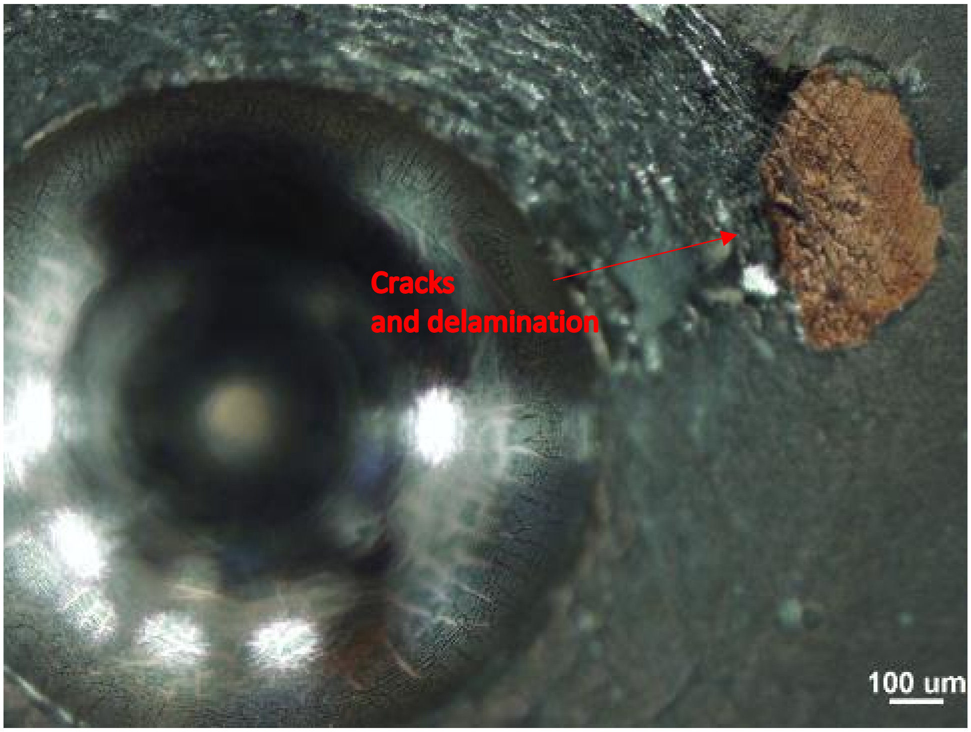


Figure 68: Micrograph of 1 hour Ni-P-W plating indentation result

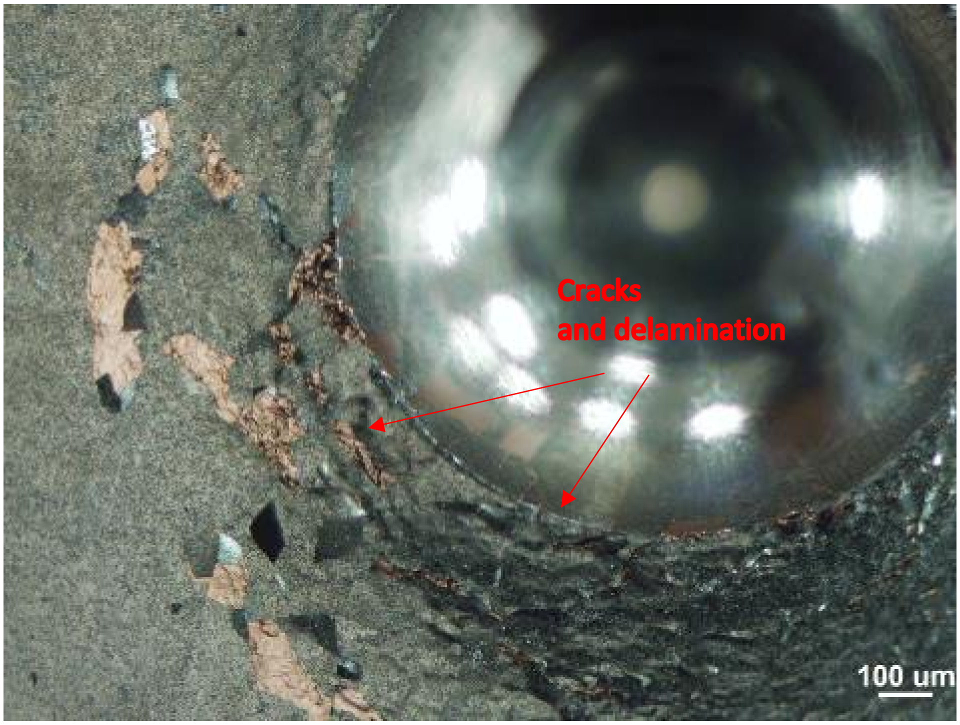


Figure 69: Micrograph of 2 hour Ni-P-W plating indentation result

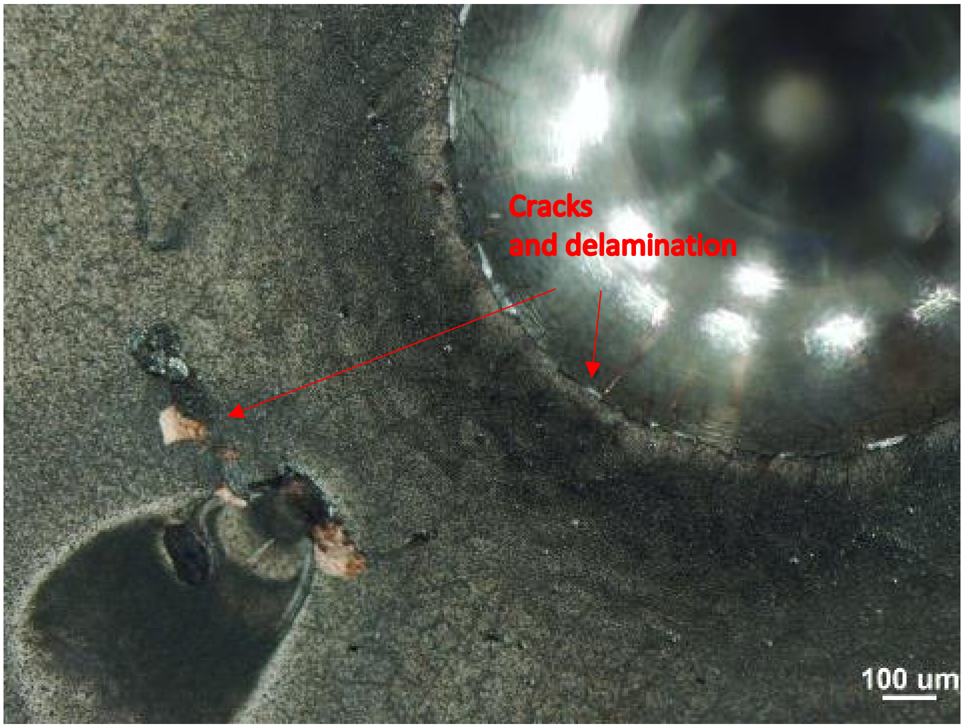


Figure 70: Micrograph of 3 hour Ni-P-W plating indentation result

Chapter 4 Conclusions

The primary objective of this research was to achieve Ni-P-W composite coatings. The electroless coating process did not achieve the desired results. Electrolytic coating using Atotech industrial solution was still a failure as tungsten is not presented in the coating at all. Electrolytic coating initially succeeded to produce a composite layer with 5 weight % of tungsten when the in-house prepared solution was used. However, further tests showed inconsistent result where electrolytic coating using in-house made solution did not produce any tungsten on the surface for 1 hour and 2 hours, but 3 hours of coating time. The oxygen level in these samples were also significantly increases, which is an indication of oxidation on the surface. It was noticed that with the presence of tungsten or oxygen, the amount of phosphorus in the coating decreases.

Cross-sectional scan of the samples also showed an inconsistent coating thickness. It might be a measurement error but also likely to be polishing imperfection or coating process problems. The EDS results not only shows no tungsten on the coating, but also shows an increasing in carbon content. At locations where copper should be observed, there was no consistent scanning result of copper.

Although coating of Ni-P-W samples did not achieve consistent success, electrochemical evaluations and mechanical tests were still carried out. It shows that the capacitance of electrolytically coated Ni-P-W samples are all higher than electroless samples. The resistances of the passive films are lower for electrolytic coatings. Electrochemical impedance spectroscopy and cyclic polarization shows that the longer the plating time is, the less corrosion resistance Ni-P-W coatings are, regardless of electroless or electrolytic process. Scratch and micro indentation shows that the wear resistance and toughness of electrolytic Ni-P-W coatings are both lower compared with electroless Ni-P coatings.

In conclusion, the synthesis of Ni-P-W coating on copper substrate shows negative on achieving tungsten using electroless processes. Using electrolytic processes achieves some success, but the result is not consistent. There is no repeatability in coating compositions and coating surface structures. The quality of the coating could not match the mature processes of Ni-P coating. It is not suitable for real world applications.

4.1 Recommendations

During the project period, there are some limitations due to instruments and operation process. Some recommendations are carried out here, so improvements can be made in the future.

1. Instruments should adapt different sample sizes and variants. During the research period, some experiments cannot be carried out due to the sample cannot be fit for experimental process at all.
2. A distilled water system needs to be used in the lab. Carrying distilled water from mineral engineering center back to the laboratory was cumbersome and dangerous. For people who work after hour, running out of distilled water was a potential risk.
3. A better coordination between research groups was proposed. There are at least 4 research groups sharing the lab environment. It creates time delay in information transfer and communication difficulties.

4.2 Future Work

Based on this research project, some future works are proposed here. If continuing research was going to be performed, here are some directions.

1. Change the cell structure of electrolytic plating. Using flat plates with equal spacing distance and same electrode surface area is recommended. Furthermore, changing the anode material to tungsten in order to introduce tungsten cations might help to develop a coating with tungsten elements.
2. Use customized solution to coat Ni-P samples without the addition of sodium tungstate. This analysis can provide straight forward comparison between Ni-P and Ni-P-W coating which are all produced in a controlled and consistent environment.
3. Heat treatment was the third proposed item. With heat treatment, it was highly likely the surface molecular structure will change. A change in the molecular structure may change characteristic of the coating.
4. Use copper substrate in different shape may result in different coating. The two recommended substrates are copper wire and copper plates. Copper wires are mostly used for electrical connections. The Ni-P-W coated wires can be used to do conductivity test and thermal test. The Ni-P-W plated plates can be used to perform XRD test. If possible, an independent coating can be achieved.

5. Coating with different substrate material such as iron or aluminum was an alternative. Since it was electrolytic coating, the coating process will be the same.

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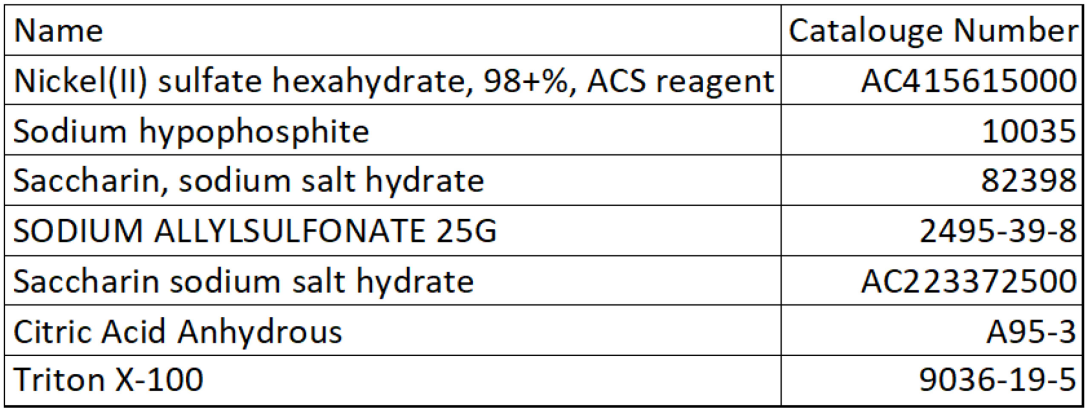
Appendix A: Chemicals used for customized solution



Name	Catalouge Number
Nickel(II) sulfate hexahydrate, 98+%, ACS reagent	AC415615000
Sodium hypophosphite	10035
Saccharin, sodium salt hydrate	82398
SODIUM ALLYLSULFONATE 25G	2495-39-8
Saccharin sodium salt hydrate	AC223372500
Citric Acid Anhydrous	A95-3
Triton X-100	9036-19-5

Appendix B: EIS Test Parameter Setup

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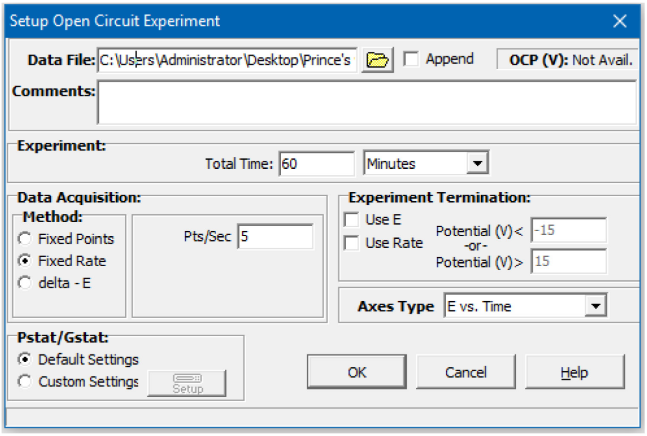
1. In CorrWare, setup an open circuit for 1 hour to reach steady state. The parameters should be like below.



Setup Open Circuit Experiment

Data File: C:\Users\Administrator\Desktop\Prince's ☐ Append **OCP (V):** Not Avail.

Comments:

Experiment:

Total Time: 60 Minutes

Data Acquisition:

Method:
- ○ Fixed Points
- ● Fixed Rate
- ○ delta - E

Pts/Sec 5

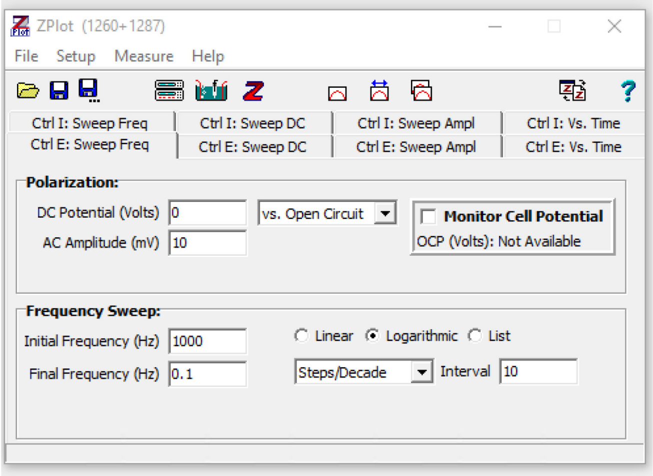
Experiment Termination:
- ☐ Use E
- ☐ Use Rate

Potential (V)< -15
-or-
Potential (V)> 15

Axes Type E vs. Time

Pstat/Gstat:
- ● Default Settings
- ○ Custom Settings

2. In ZPlot, setup the frequency response analyzer's parameter. Remember to give this file a name, it will later be linked from CorrWare.



ZPlot (1260+1287)

Polarization:

DC Potential (Volts) 0 vs. Open Circuit

AC Amplitude (mV) 10

☐ **Monitor Cell Potential**
OCP (Volts): Not Available

Frequency Sweep:

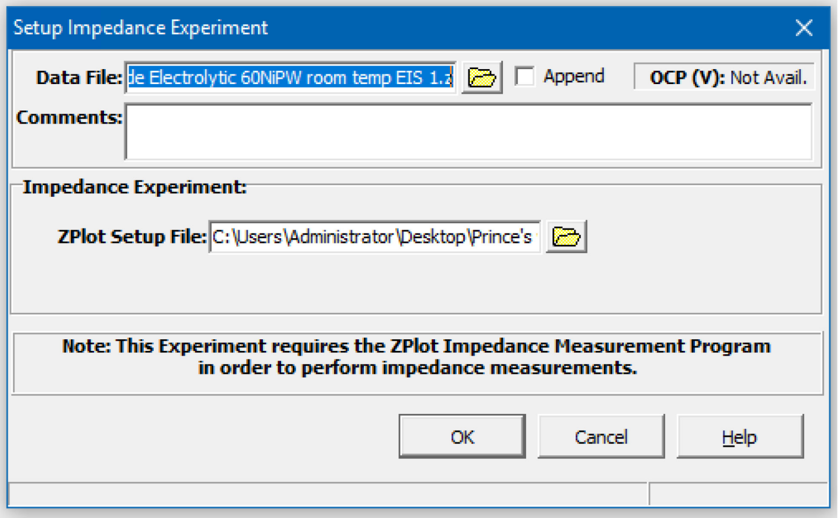
Initial Frequency (Hz) 1000

Final Frequency (Hz) 0.1

○ Linear ● Logarithmic ○ List

Steps/Decade Interval 10

3. Return back to CorrWare, insert “Impedance” procedure. Link the ZPlot Setup File into Impedance Experiment.



Data File: de Electrolytic 60NiPW room temp EIS 1.z

☐ Append

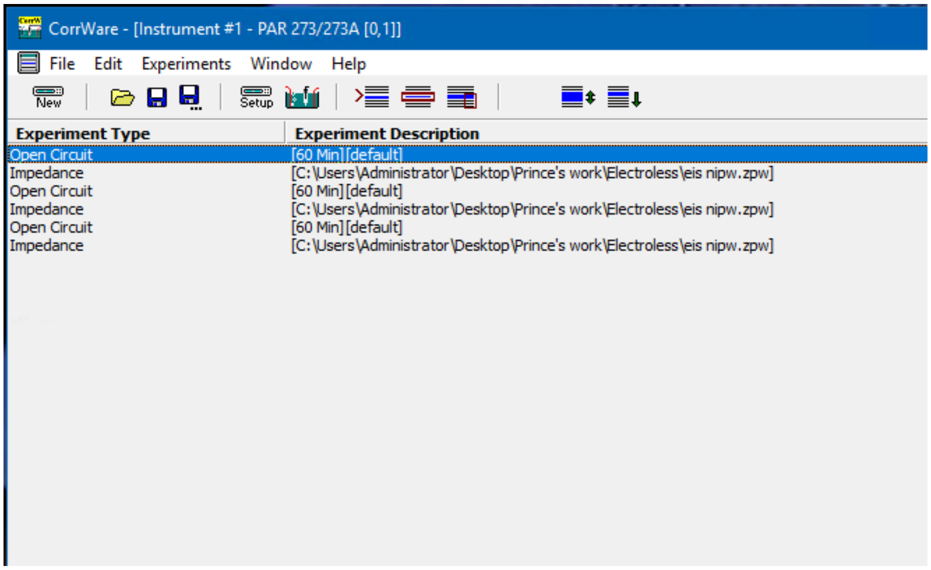
OCP (V): Not Avail.

Comments:

ZPlot Setup File: C:\Users\Administrator\Desktop\Prince's

Note: This Experiment requires the ZPlot Impedance Measurement Program in order to perform impedance measurements.

4. Copy the open circuit and Impedance test and paste it twice to make three runs. These three runs will be executed in sequences. All data will be logged for analysis.



Experiment Type	Experiment Description
Open Circuit	[60 Min][default]
Impedance	[C:\Users\Administrator\Desktop\Prince's work\Electroless\eis nipw.zpw]
Open Circuit	[60 Min][default]
Impedance	[C:\Users\Administrator\Desktop\Prince's work\Electroless\eis nipw.zpw]
Open Circuit	[60 Min][default]
Impedance	[C:\Users\Administrator\Desktop\Prince's work\Electroless\eis nipw.zpw]

Appendix C: Cyclic Polarization Parameter Setup

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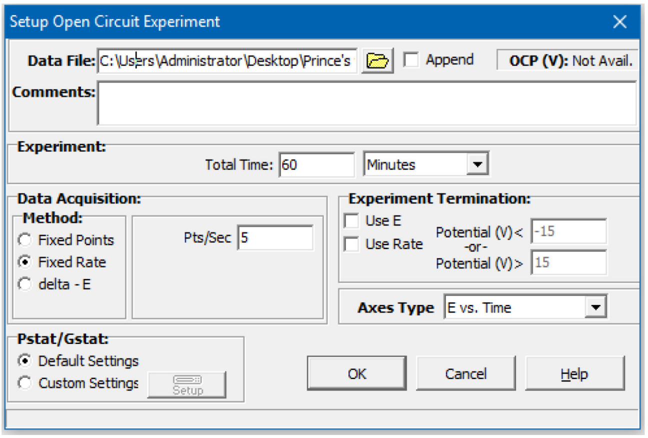
1. Open circuit was necessary for cyclic polarization. Insert a new step as open circuit.



Setup Open Circuit Experiment

Data File: C:\Users\Administrator\Desktop\Prince's

☐ Append

OCP (V): Not Avail.

Comments:

Experiment:

Total Time: 60 Minutes

Data Acquisition:

Method:

○ Fixed Points
● Fixed Rate
○ delta - E

Pts/Sec 5

Experiment Termination:

☐ Use E
☐ Use Rate

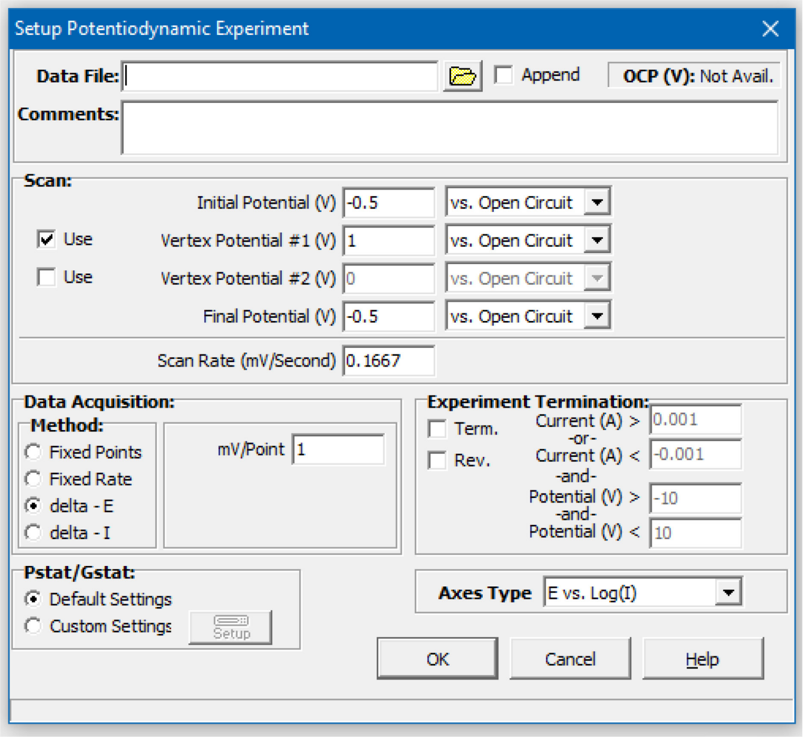
Potential (V)< -15
-or-
Potential (V)> 15

Axes Type E vs. Time

Pstat/Gstat:

● Default Settings
○ Custom Settings

2. Insert a potentiodynamic experiment. The parameters are as followed. Vertex 1 was the upper point, which was set to 1 V above open circuit. Vertex 2 was not used in this experiment.
3. Since cyclic polarization was destructive test method, the test process will not be repeated.



Data File:
☐ Append
OCP (V): Not Avail.
Comments:

Scan:
Initial Potential (V) -0.5 vs. Open Circuit
☑ Use Vertex Potential #1 (V) 1 vs. Open Circuit
☐ Use Vertex Potential #2 (V) 0 vs. Open Circuit
Final Potential (V) -0.5 vs. Open Circuit
Scan Rate (mV/Second) 0.1667

Data Acquisition:
Method:
○ Fixed Points
○ Fixed Rate
● delta - E
○ delta - I
mV/Point 1

Experiment Termination:
☐ Term. Current (A) > 0.001
-or-
☐ Rev. Current (A) < -0.001
-and-
Potential (V) > -10
-and-
Potential (V) < 10

Pstat/Gstat:
● Default Settings
○ Custom Settings

Axes Type E vs. Log(I)

Appendix D: Composition of all samples from EDS

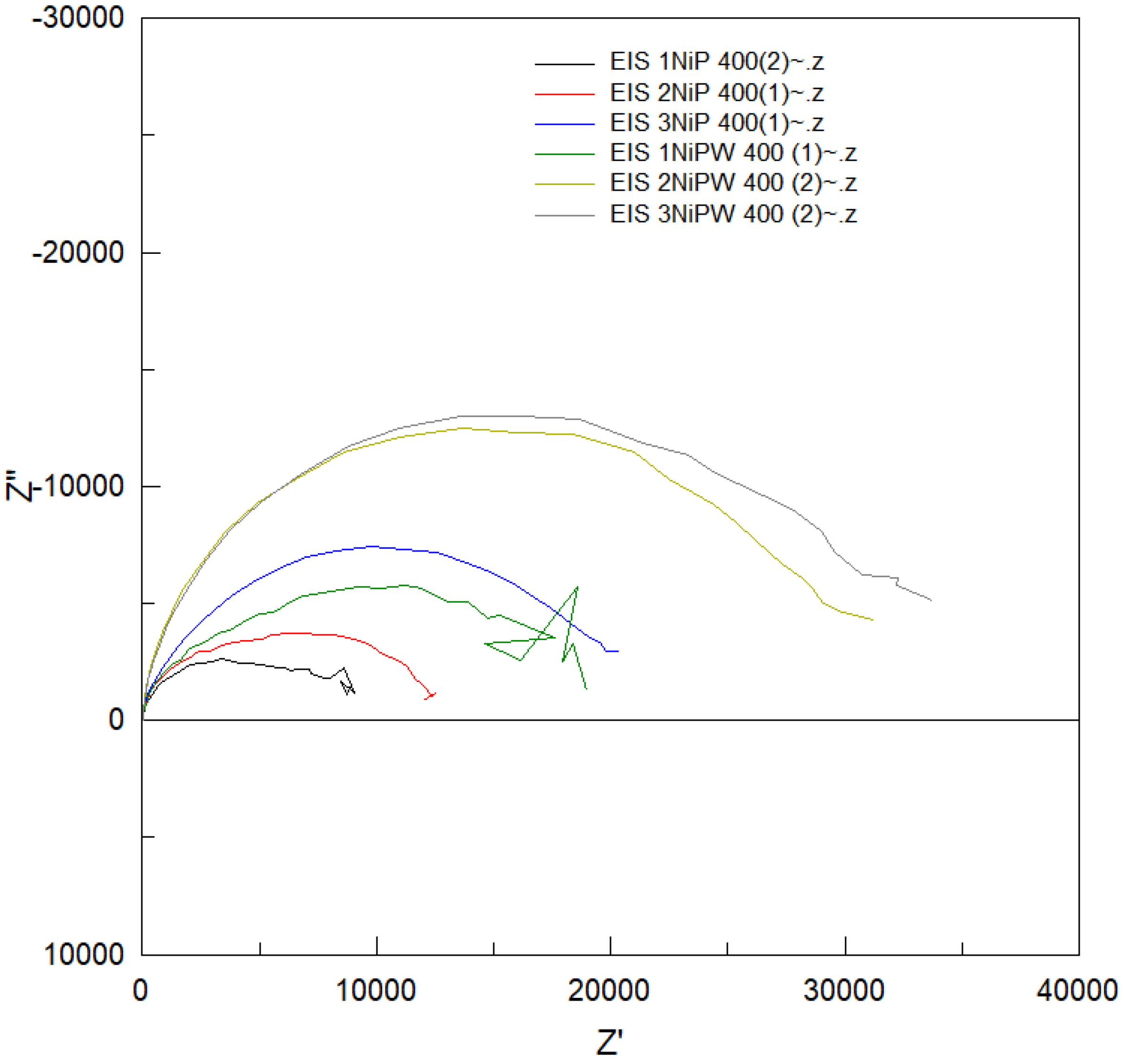
	Solution condition	Polishing	Time (hr)	Ni		P		W	
				wt%	atomic%	wt%	atomic%	wt%	atomic%
Electroless Coating	Ni-P	400 grit	1	92.13	86.07	7.87	13.93	0.00	0.00
			2	87.69	74.40	10.03	16.13	0.00	0.00
			3	89.04	81.09	10.96	18.91	0.00	0.00
	Ni-P-W 25g/L	400 grit	1	83.25	63.06	10.66	15.31	0.00	0.00
			2	86.20	71.48	10.93	17.18	0.00	0.00
			3	68.03	39.81	9.77	10.82	0.96	0.18
	Ni-P-W 15g/L	diamond	1	93.07	87.63	6.93	12.37	0.00	0.00
			2	90.71	83.74	9.29	16.26	0.00	0.00
			3	86.11	72.95	11.98	19.23	0.00	0.00

	Solution condition	Electrode Distance	Polishing	Time (min)	Ni		P		W	
					wt%	atomic%	wt%	atomic%	wt%	atomic%
Electrolytic Coating	Ni-P	10 cm	400 grit	10	74.42	49.41	9.52	11.99	0.00	0.00
			Diamond	10	81.08	57.58	10.70	14.40	0.00	0.00
	Ni-P-W 5g/L	10 cm	400 grit	10.00	75.07	50.50	9.47	12.07	0.00	0.00
			Diamond	10.00	82.32	60.62	10.66	14.88	0.00	0.00
			Diamond	60.00	78.39	57.99	11.05	15.50	0.00	0.00
	Ni-P-W 5g/L	5 cm	Diamond	60.00	78.50	57.76	10.93	15.24	0.00	0.00
	Ni-P-W 5g/L	3 cm	Diamond	60.00	78.81	58.09	11.55	16.42	0.00	0.00
	Ni-P-W 5g/L 60 °C	5 cm	Diamond	60.00	77.54	49.62	9.13	11.08	0.00	0.00

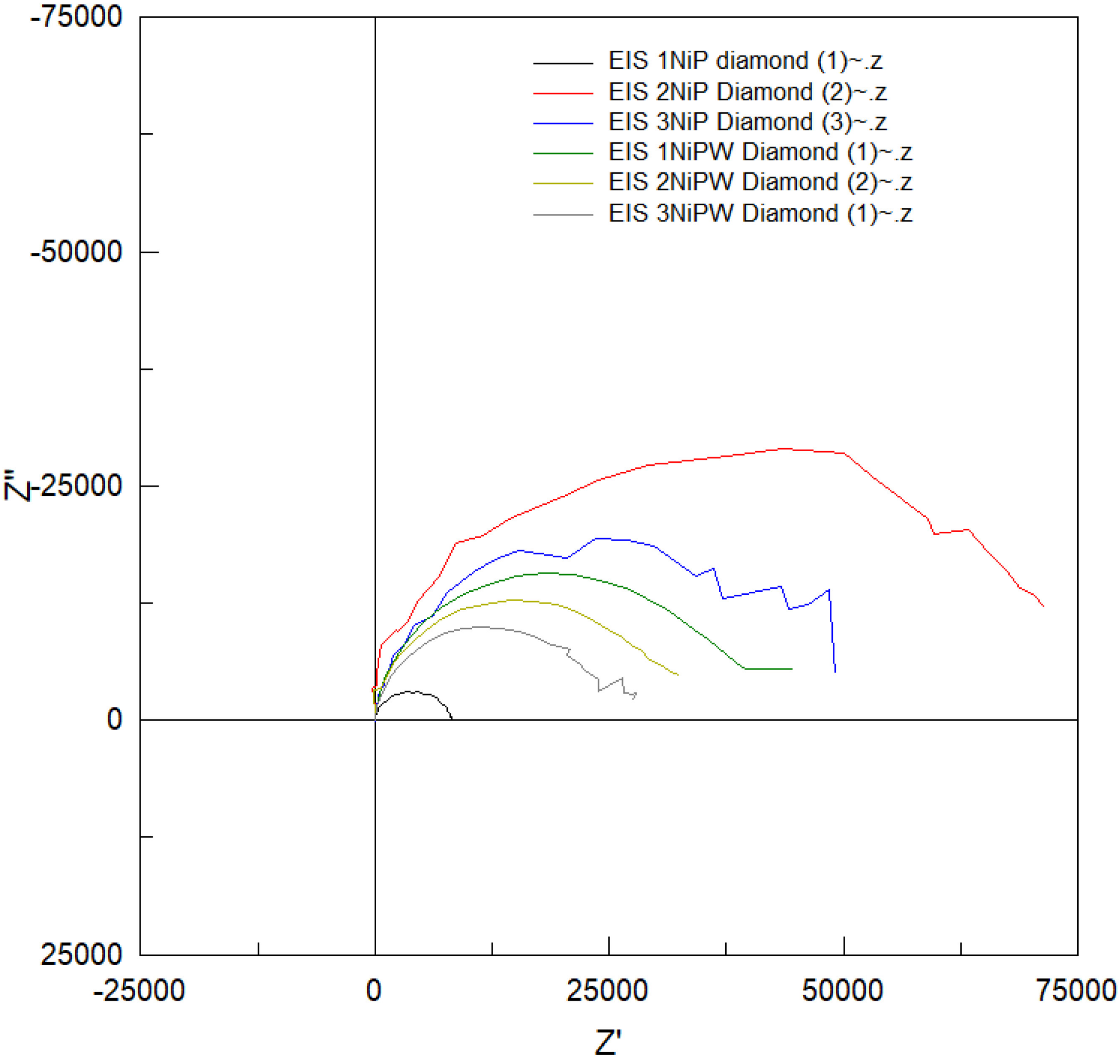
	Solution condition (Powder made)	Electrode Distance	Polishing	Time (min)	Ni		P		W	
					wt%	atomic%	wt%	atomic%	wt%	atomic%
Electrolytic Coating	Ni-P-W 50g/L	10 cm	Diamond	60.00	88.74	81.67	3.24	5.65	5.24	1.54
	Ni-P-W 50g/L 60 °C	10 cm	Diamond	60.00	83.64	70.68	1.35	2.16	5.43	1.47

Appendix E: Nyquist Plot of EIS result

EIS of 400 grit electroless coating samples



EIS of diamond grade electroless coating samples



EIS of electrolytic coating samples