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Electroplating Zn on Mg as a biodegradable material

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Abstract

Magnesium has long been deemed as a revolutionary bio-material for its great biocompatibilities and mechanical properties. The biodegradability of magnesium makes it an ideal choice for implant material. However, the bio-corrosion of magnesium is too rapid, the implant would degrade before the tissue fully recovers^[1]. Zinc, as another biodegradable material, has a degradation rate which is below the benchmark to be ideal. This project studies on the feasibility of electroplating zinc on magnesium to meet the standard requirement as a biodegradable material. Several electroplating processes were adjusted and tested to avoid the involvement of toxic elements like heavy metals and aluminum which were used in some conventional electroplating methods. By analyzing the surface performance and corrosion behavior of the electroplated magnesium sample, the best electroplating method was given. The feasibility of electroplating zinc on magnesium to improve corrosion resistance of the material is confirmed.

1. Introduction

With the rapidly developing of the modern medicine, the operating treatment technologies and skills have attained a new high level. As an effective and fully developed treatment, stents have been widely used in treating cardiovascular disease and bone revision. Conventionally, the stents used were permanent metals, which came along with several disadvantages. The stents have to be removed after the body tissue fully recovered, a removal surgery would be undergone. The patient had to suffer from the pain and the risk for secondary injury or infection. Also the existence of the permanent implants would have impacts on the mechanism how the tissue recovers, when removing them, negative effects like stress shielding effect would occur. ^[2] One ideal solution was given from the material science area: stents in degradable materials. The issues mentioned above would be automatically disappear when the stents could dissolve at the same rate as the tissue recovers. However, the degradation of magnesium always could not meet the requirement, it degrade too rapidly. When the degradation

kinetics couldn't match the expected healing period, the loss of mechanical properties would waste all the previous effort.

To effectively increase the corrosion resistance of magnesium thus extend the degradation period, many different solutions were used. One obvious solution is to alloy magnesium with other metal materials. However, the degradation process of the alloys are much more complicated, the degradation speed is harder to study and control. Even more, not many frequently used alloy materials themselves and their corrosion reaction products are biocompatible. [3] The other solution is surface treatment, which mainly refers to coatings on magnesium. The hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HA] was widely considered as the ideal coating materials, since HA ceramics have already been used as implant materials. Zinc is also a great option as the coating material.

Zinc is biocompatible and biodegradable, the degradation rate of zinc is much lower than magnesium. To coat zinc onto magnesium, possible methods include immersion, electroless deposition and electroplating. In this case, a uniformly covered zinc layer is expected. Because the thickness of the zinc layer would be easier to measure, the different surface morphology could bring more difficulty. Electroplating is obviously the best and most effective way to get a uniform surface. To control the formula of electroplating bath and parameters like electroplating time, current density and temperature, the zinc coated magnesium with highest corrosion resistance could be obtained.

However, both electroless plating and electroplating techniques on magnesium is still at developing stage, far from mature. [4] Especially when searching for journals and research about electroplating zinc on magnesium, virtually few articles on this particular area. Electroplating on magnesium is perceptibly difficult, since magnesium is known as a "difficult to plate metal", since film of oxide and hydroxide is easy to develop on the surface and could prevent the adhesion of the coating metal. [5] Even so, ideas and details of some methods like electroplating nickel on magnesium could be learned from.

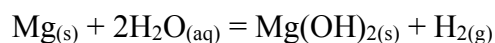
2. Literature review

2.1 Mg as a new degradable biomaterial

Magnesium and magnesium alloys have been in the center of people's attention as the new degradable biomaterials. The biocompatibilities, excellent mechanical properties of magnesium and magnesium alloys have the vital effect. To be more specific, firstly, the density $1.74 - 2.0 \text{ g/cm}^3$ is closer to the bone of human body, which is $1.8 - 2.1 \text{ g/cm}^3$, much lighter than another biomaterial titanium and titanium alloys ($4.4 - 4.5 \text{ g/cm}^3$).^[6] Secondly, Magnesium is an important element for human body, not only participates in forming bone structure, but also keeps the structure of generic materials stable^[7], which guarantees that the degraded magnesium would not be redundant. Thirdly, magnesium and its alloy have the ideal mechanical properties, a similar elastic modulus to human bones, and even greater fracture toughness than ceramic biomaterials^[8]. Furthermore, the standard electrode potential -2.37V determines that magnesium is much easier to degrade in the physiologic environment of human body than other traditional biomaterials. As a result of all these great properties, magnesium and magnesium alloys are considered and developed as the new biocompatible and biodegradable metal material for human body.

Many researchers have noticed the potential of magnesium in this area, most of them concentrate on improving the biocompatibility of magnesium alloys. The most commonly used magnesium alloys, like AZ31 and AZ91, contain aluminum and some other metal elements which are neurotoxic and hepatotoxic^[9, 10]. Thus, a new magnesium alloy system without these toxic rare earth elements is also the point of focus. Yet, how to assess the biocompatibility of a new alloy system is still a question.

However, using magnesium as a new biodegradable material still faces a challenge: the corrosion rate, or in this situation, degradation rate, is too fast. The degradation mechanism of magnesium based materials is clear. They basically corroded in aqueous environments through the reaction given below:



Cl^- ions in physiological environment can cause pitting corrosions on magnesium alloys, even more, when the concentration attains 30 mmol/L , the magnesium

hydroxide formed in the reaction will react with magnesium to form a highly soluble magnesium chloride and increases the degradation rate.^[11] SO_4^{2-} ions were also reported to accelerate the corrosion of magnesium^[12]. However, the HPO_4^{2-} ions in the physiological environment could form the precipitation of magnesium phosphate, which will slow down the corrosion, particularly, the pitting corrosion. So will some of the proteins like albumin, which have been proved could form a corrosion blocking layer on the magnesium alloys^[13].

Additionally, stress corrosion cracking is easier to happen on magnesium alloys in an environment containing chloride. The stents, plates and screws are under the loading of blood vessel, blood flow, body movement and body weight. The dissolution of magnesium is promoted.

In this situation, several coating techniques are considered to slow down the biodegradation and increase the biocompatibility. Coatings on magnesium has been investigated for industrial purposes. However, the industrial coatings are often using the non-biocompatible materials and not appropriate for clinical use.

Calcium phosphates (CaP), which have been successfully used as coatings on titanium orthopedic materials, is one possible choice in this area. Since the biologically relevant CaP is included in the orthophosphate group, some of them naturally occur in biological structures, like bones and tooth. CaP is the inorganic component of bones (organic component basically consists of water and collagen). And the synthetic hydroxyapatite (HA) has been found to share similar properties with the CaP in the bones^[14]. This is the reason why, in recent years, utilization of calcium phosphates as biocompatible coatings on magnesium has been more widely explored. The calcium phosphates phases include Calcium phosphate dehydrate – brushite (DCP), Anhydrous calcium phosphate – monetite (ADCP), Octacalcium phosphate (OCP), Tricalcium phosphate – whitlockite (TCP) and Hydroxyapatite (HA). Current coating techniques include biomimetic, sol-gel and electrodeposition (ED). Biomimetic basically happens in simulated body fluids, calcium phosphate precipitates and grows on the surface of

substrate^[15]. The sol-gel technique is named for immersing the substrate into a concentrated solution like gel.

2.2 Zn as biodegradable materials

Due to the fact that traditional materials for coronary stents are corrosion-resistant metals such as titanium and stainless steel, zinc and its alloys have emerged to become the new biodegradable candidate material.

The tensile strength of pure zinc is 80-120 MPa, nearly just one third that of pure iron, but similar to that of magnesium, which is 86 MPa^[16]. The elongation to failure is the advantage of zinc, 60-80% is much better than that of iron (18%) and magnesium (13%). This could guarantee zinc to attain the strength to the level of iron. The studies on zinc as biomaterial, especially as stent material, showed that zinc has a good biocompatibility and a degradation rate of 0.01-0.02 mm/yr, which is just a little below the benchmark rate for ideal biodegradable materials^[17]. Studies showed that the implants made of zinc could remain intact inside the arterial wall of murine after even 180 days of residence, and the first 90-180 days after the implantation was considered a critical period for coronary stent scaffolding^[16]. Meanwhile, zinc is one of the micronutrients for human body, and relatively nontoxic. Although acute zinc toxicity possibly causes the symptoms of lethargy, headache, diarrhoea, abdominal pain and nausea. Excessive zinc is associated with copper deficiency, which leads to anemia, neutropenia and leukopenia^[18]. However, the estimated daily intake for the degradation of pure zinc stent is only 150 $\mu\text{g/day}$, far from the rates for moderate symptoms to happen, which is 100-300 mg/day, say nothing of the 225-450 mg/day for acute toxicity^[19].

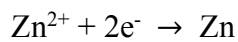
Since using zinc as a stent biomaterial is still novel comparing to the others, no metallographic studies have been done on zinc implants' long term corrosion, like over 20 months. At the very beginning, the most important part of exploring a new biodegradable stent is to study on the short-term corrosion behavior to make sure the possibility, and later, long-term corrosion experiment should be conducted to investigate the detailed corrosion behavior like tissue clearance. As for zinc, the earlier

studies have confirmed the feasibility. Yet, the influence of activities like the formation of passivating corrosion products and wire fibrous encapsulation, which could possibly retard the zinc corrosion rate, haven't been revealed.

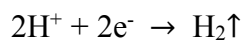
2.3 Zn coating on Mg

Zinc coating techniques are relatively mature these days. The current process to apply zinc coatings on metal materials include electroplating, hot dipping, sputter coating and hot spray.

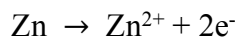
Electroplated zinc coatings are applied by cathodic polarization of the reaction give below:



And the side reaction of H^{+} :



The reaction on the zinc anodic is:



And the side reaction:



When using magnesium as a substrate to apply coatings, the most common way is to pretreat the surface of magnesium through cyanide copper process or electroless nickel process. As for the cyanide copper process, it includes soak clean, rinse, acid activation, zincate, cyanide strike, cyanide plate and remainder of nickel/chrome process. Not only the process is complicated, but also the cyanide highly toxic. As for the electroless nickel process, it includes soak clean, rinse, acid activation, zincate, electroless nickel treatment, acid copper/nickel/chrome process. In this process, the nickel plating solution is not as stable, and the cost of nickel is high^[20]. The standard non-cyanide copper process does not work on the magnesium process, a reformulation in process that improves adhesion and the salt spray hours was also used, which is called

the alkaline non-cyanide copper process. It includes soak clean, rinse, acid activation, zincate, alkaline non-cyanide copper, acid copper, buff acid copper and plating.

One relatively well-improved zinc-plating process was using NaOH, ZnO, FeCl₃, NaKC₄H₄O₆·4H₂O, to zincate 5-8 min at room temperature and later apply alkaline zinc plating.

2.4 In vitro tests for magnesium

In vitro tests for magnesium can be divided into two big categories: testing on biodegradation behavior or on biocompatibility/toxicity. Clearly, the toxicity or biocompatibility is related to the degradation behavior, because a high degradation rate can lead to the toxicity and some negative reactions. The toxicity tests are often conducted in the presence of living cells, which is not necessary in the biodegradation tests. However, to characterize the bio-corrosion behavior of magnesium is complex, it needs to combine several various methods to characterize completely^[21].

The different test techniques to measure the bio-corrosion can be classified into two categories: unpolarized tests, not in the presence of electrochemical polarization as driving force, and polarized tests, in the presence of electrochemical polarization. The following Table 2-1 shows the various testing methods for bio-corrosion of magnesium, and their advantages and limitations are also provided.

It should be mentioned that the correlations between in vivo and in vitro corrosion testing result have not yet to be established now. According to some of the studies, when applies in vitro tests to in vivo, researchers could suffer from uncontrolled unphysiological pH^[22-24], uncontrolled amount of solution on surface area^[25], or not enough results^[26-28].

Table 2-1 Advantages and limitations of in vitro test

Testing Method	Advantages	Limitations
Mass loss	<p>Low cost</p> <p>The data is accurate and clear</p> <p>Can be set up along polarized experiments</p> <p>Simple to conduct</p>	<p>Several samples are needed for one test</p> <p>Can't show the corrosion behavior depending on time</p> <p>The solution has to be changed for several times</p>
Hydrogen evolution measurement	<p>Low cost</p> <p>The measurement is real-time</p> <p>The corrosion product won't affect the result of measurement</p> <p>H₂ should be critically considered before in vivo tests</p>	<p>Several samples are needed for one test</p> <p>Experiments with flow are harder to measure</p> <p>Can't be set up along polarized experiments</p> <p>The setup is complex which could impact the accuracy</p>
pH monitoring	<p>Low cost</p> <p>Very simple to set up</p>	<p>Changing pH is usually avoided for in vitro test</p> <p>The changing pH could affect the corrosion behavior and create unrealistic testing environment</p>
Potentiodynamic polarisation	<p>Able to test on instantaneous reactions and get the corrosion rate</p> <p>One sample can be used multiple times</p> <p>Able to determine the cathodic/anodic control</p> <p>Elucidates thermodynamic differences</p>	<p>Several specialized equipment needed</p> <p>The test will destruct the surface of samples, re-polishes are required</p> <p>Little information about contribution of different coating layers</p> <p>Investigator error can cause large differences</p>
Electrochemical impedance spectroscopy	<p>Relatively simple to setup</p> <p>The measurement is real-time and continuous</p> <p>One sample can be used multiple times</p> <p>Can get the information of every surface layer</p>	<p>The frequency of measurement is low but some samples may corrode rapidly</p> <p>No information on revealing cathodic/anodic contributions</p> <p>Susceptible to corrossions occur over time</p>

3. Experiment instruments and reagents

3.1 The substrate

Pure magnesium was used as the substrate in this experiment.

3.2 Main chemical reagents

Table 3-1 shows the main chemical reagents used in the experiment:

Zn	Pure Zinc used as anode, polished and punched
ZnSO ₄	UNILAB; 99.0%
ZnO	UNIVAR; 99.0%
NaOH	UNIVAR; 97.0%
K ₄ P ₂ O ₇	SIGMA – ALDRICH; 97.0%
Na ₂ CO ₃	Scharlau; 99.9%
Na ₂ SO ₄	VETEC; 99.0%
H ₃ PO ₄	SIGMA – ALDRICH; 85 wt. %
NH ₄ HF ₂	SIGMA – ALDRICH; 98.0%
NaF	CHEM – SUPPLY; 97.0%
Na ₂ C ₆ H ₅ O ₇	CHEM – SUPPLY; 99.5%

Table 3-1 Main chemical reagents

3.3 Experiment instruments

Table 3-2 shows the main experiment instruments used in the experiment:

Instrument name	Model	Manufacturer name
Cutting machine	Accutom-50	Struers
Power supply	S-305DII	STANDIG
Heating plate	MR5K01	Lab.Co
Electrochemical system	2263	PARSTAT
Thermostatic bath	GR150	GRANT
Electronic balance	AB204-S	METTLER TOLEDO
SEM	Tm3030	Hitachi

Table 3-2 Experiment instruments

4. Methodology

4.1 Preparation

Pure magnesium was cut into 6mm*15mm*15mm sample pieces using cutting machine. Punched a hole of 1 mm diameter on the smaller area which is used to fix the sample on one side of the thick copper wire. Polished using water proof abrasive papers with 1600 degree and 4000 degree under water rinse. Rinse using ethanol and dried.

All polished samples are fixed on one side of the thick copper wire and labeled. Each sample will be measured the original size and weight.

4.2 Electroplating

The schematic diagram of the electroplating process is shown in figure 4-1(left):

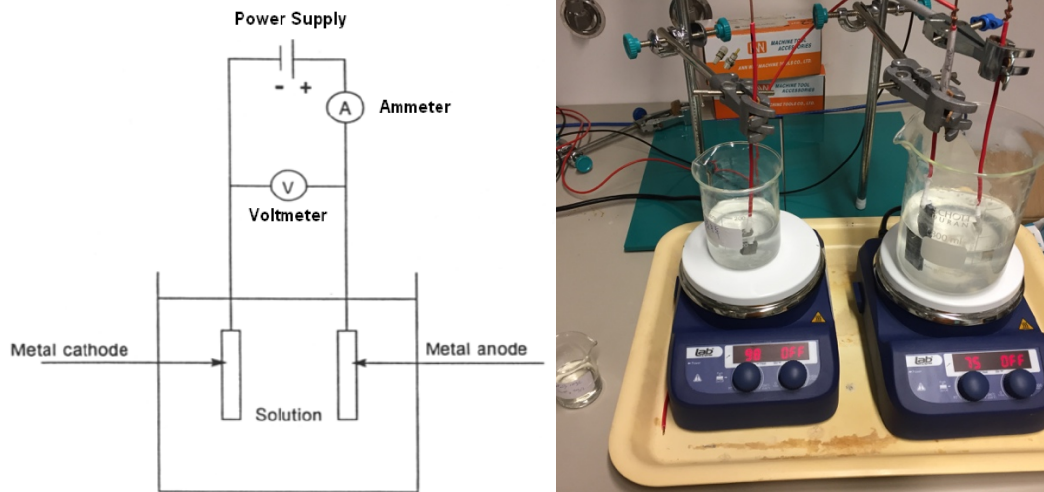


Figure 4-1 The schematic diagram and photo of electroplating process

Zinc was used as the metal anode, and magnesium samples are used as the cathode after pre-treatment. Figure 4-1(right) is the photo of the electroplating process, in which the beaker on the right side is the electroplating bath, the left beaker is the pre-treatment process(in this photo, zinc immersion). The heating plates were used to control the temperature of the solution. The setting temperature should be a little higher than the desired temperature.

4.3 Hull cell test

Hull cell test was used to preliminary estimate the current density range for the best electroplating result. The shape and dimensions of the hull cell used is shown in the figure 4-2 and table 4-1 And figure 4-3 is a photo of the hull cell used in this experiment.

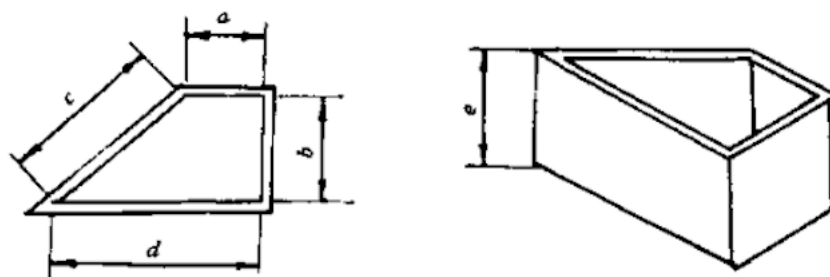


Figure 4-2 The schematic diagram of hull cell

Volume of the cell	a	b	c	d	e
250	48	64	102	127	65

Table 4-1 The dimensions of the hull cell

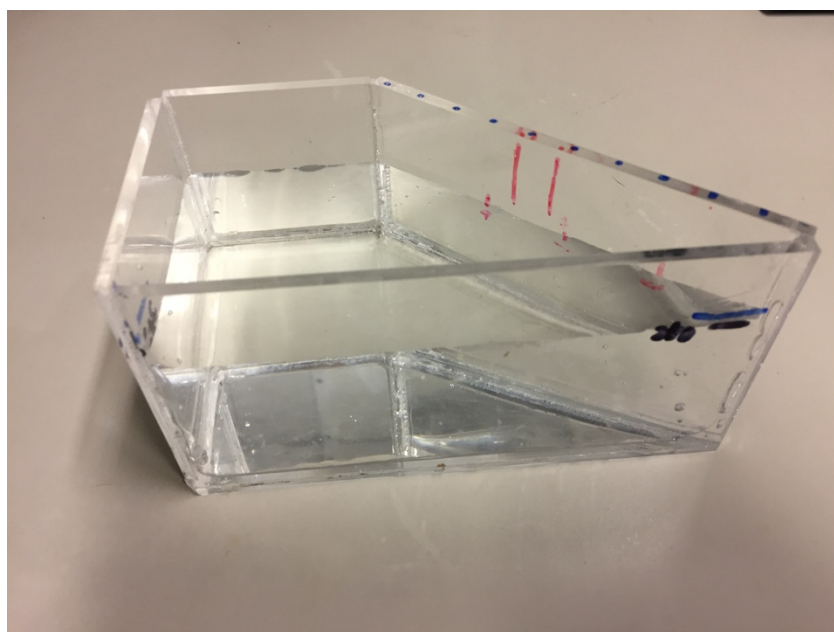


Figure 4-3 The hull cell used in this experiment

How the hull cell works is shown in the figure 4.4. The cathode sample was placed on the hypotenuse side of the trapezoid shaped cell. The certain volume(250ml) of electroplating solution is prepared and added to the hull cell. The electroplating time and temperature are controlled. The best current density range could be chosen based on the coating performance on the cathode panel. The current density of a certain point on the panel could be figured out by:

$$J_c = I (C_1 - C_2 \log L)$$

L: The distance on the hypotenuse from the point to the near anode side (cm)

I: The current used (A)

J_c : The current density of that point (A/dm^2)

C_1, C_2 : Solution-dependent constant, here $C_1=5.10, C_2=5.24$

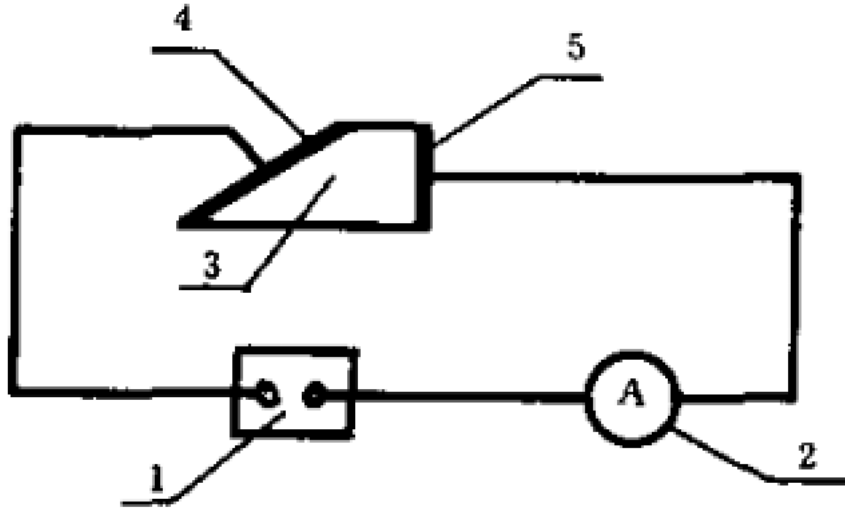


Figure 4-4 The circuit diagram of hull cell test. 1. Power supply, 2. Ammeter, 3. Electroplating bath in the hull cell, 4. The cathode, 5. The anode

4.4 Electroplating Zinc on Magnesium

4.4.1 Zincate solution electroplating

When it comes to zinc electroplating, zincate solution is always a good choice, furthermore, the alkaline electroplating is more suitable for electroplating on magnesium, so the zincate solution electroplating was firstly used in this experiment.

(1) Electroplating process

The process is as follows:

Polishing → Acid cleaning → Rinse → Activation → Electroplating → Rinse → Drying

In this electroplating process, zinc comes from the ZnO. The content of ZnO has a major impact on the performance of the electroplating bath and the quality of the zinc coating layer. When the content of Zn in the solution is high, the efficiency of the current is higher, yet the dispersal capability is weak, the deposition rate is high, so is the layer roughness. However, when the content of Zn in the solution is low, the

efficiency of the current is lower, the dispersal capability is better, lower surface toughness will be obtained but the deposition rate is low. Normally, the content of ZnO is 8.0 – 10.0 g/dm³, in this experiment, 10.0 g/dm³ ZnO was used. The NaOH has effect on both the complexation process and electric conductivity. Excess NaOH is needed to stabilize the solution, to guarantee that zinc in the solution exists as Zn(OH)₄²⁻. When pH of the solution is lower than 10.5, Zn(OH)₄²⁻ will transfer into Zn (OH)₂ deposit. That's why the ratio of NaOH/Zn should be controlled in this experiment, normally at around 11.0 ~ 13.0. When there's too much NaOH, the chemical dissolution of anode is too rapid, excess Zn ion will be in the solution. To sum up, the content of NaOH should be at around 100.0 ~ 120.0 g/dm³.

In this electroplating process, hull cell test was used first.

The details of acid cleaning, activation, electroplating procedures are listed in the table 4-2:

Procedure	Solution	Condition
Acid cleaning	CrO ₃ 200g/L; AgNO ₃ 2g/L	Room Temperature; 10s
Activation	Phosphoric acid(85%) 200ml/L; NH ₄ HF ₂ 90g/L	Room Temperature; 3min
Electroplating bath	NaOH 100g/L; ZnO 10g/L	2.0-2.5 A/dm ² ; Room temperature; 45min

Table 4-2 The zincate electroplating procedures

4.4.2 Zinc sulfate solution electroplating

The zinc sulfate solution electroplating uses zinc sulfate as the source of zinc.

The process is as follows:

Polishing → Acid cleaning → Rinse → Activation → Electroplating → Rinse →
Zinc immersion → Drying

In this process, since the substrate magnesium is prone to be corroded by the SO_4^{2-} in the electroplating bath, zinc immersion pretreatment was used. The zinc immersion process is to deposit a thin layer of zinc on the surface of magnesium before electroplating. The zinc layer can not only protect the surface from corrosion by the electroplating solution, but also give the electroplating procedure a substrate surface easier to deposit on than the surface of magnesium substrate.

The Na_2SO_4 in the electroplating bath increase the conductivity of the electroplating solution. NH_4HF_2 was added to the solution to prevent the electroplating solution form being too corrosive for magnesium substrate.

Thus, the details and electroplating bath formula of the zinc sulfate solution electroplating is listed in the table 4-3:

Procedure	Solution	Condition
Acid cleaning	CrO_3 200g/L; AgNO_3 2g/L	Room Temperature; 10s
Activation	Phosphoric acid(85%) 200ml/L; NH_4HF_2 90g/L	Room Temperature; 3min
Zinc Immersion	ZnSO_4 30g/L; $\text{K}_4\text{P}_2\text{O}_7$ 150g/L	Room Temperature; 5min
Electroplating bath	ZnSO_4 480g/L; Na_2SO_4 50g/L; NH_4HF_2 8g/L	2.0-3.0 A/dm ² ; 40°C; 20min

Table 4-3 The zinc sulfate electroplating procedures

4.4.3 Zinc sulfate, potassium pyrophosphate solution electroplating

The zinc sulfate, potassium pyrophosphate solution electroplating was actually improved from the zinc sulfate electroplating solution formula, since the zinc sulfate solution did not work well, which will be mentioned later in the experiment result.

Comparing to the zinc sulfate electroplating process, several changes were made. The solution used in the activation procedure changed from acidic solution featuring

phosphoric acid to alkaline solution to keep the surface of the substrate more uniform. And using $K_4P_2O_7$ in all procedures except the acid cleaning to make the solutions consistent. In zinc immersion procedure, Na_2CO_3 was added to control the pH of the solution. Since zinc deposition was slow in the zinc immersion process, NaF was added to increase the dispersity of the solution. To be more effective, high temperature was used, 75-80°C was the appropriate temperature which is high and easy to control, comparing to the temperature close to the boiling point of water. The detailed procedure is listed in the table 4-4.

Procedure	Solution	Condition
Acid cleaning	CrO_3 200g/L; $AgNO_3$ 2g/L	Room Temperature; 10s
Activation	$K_4P_2O_7$ 150g/L; Na_2CO_3 40g/L	65°C; 2min
Zinc Immersion	$ZnSO_4$ 30g/L; $K_4P_2O_7$ 150g/L; NaF 7g/L; Na_2CO_3 5g/L	75-80°C ; 10min
Electroplating bath	$ZnSO_4$ 30g/L; $K_4P_2O_7$ 130g/L; NaF 8g/L; Na_2CO_3 5g/L; $Na_2C_6H_5O_7$ 20g/L	1.5-2.0 A/dm ² ; 40-55°C; 15-20min

Table 4-4 The zinc sulfate and potassium pyrophosphate electroplating procedures

In the electroplating bath, $ZnSO_4$ was used to supply zinc ions in the solution, $K_4P_2O_7$ work as the complexing agent, it could form $[Zn(P_2O_7)_2]^{6-}$ together with the zinc ions in the solution. To make sure the complex is stable in the solution, there should be free $K_4P_2O_7$ in the solution. $K_4P_2O_7$ could also avoid the deposition and increase the dispersity of the solution to improve the quality of the plating zinc layer.

NaF was added as the conducting salt, to increase the electric conductivity of the solution, fluoride is always the good choice. When the content of NaF is high, the conductivity rises significantly, however, the deposition rate is too high, the dispersity could catch up, a high roughness zinc layer will be obtained. So, in this experiment, the content of NaF was 8g/L.

Na₂CO₃ was used to control the pH of the electroplating solution, and it also works as the corrosion inhibitor. Na₂C₆H₅O₇ is the assist complexing agent in the solution.

4.5 Testing and evaluation

4.5.1 Zinc Layer Thickness Evaluation

After the zinc electroplating process, the samples using would be tested to get the best condition used for electroplating. The average thickness and performance of the zinc layer would be evaluated. To estimate the average thickness of the samples, the thickness could be figured out by:

$$T = (G_1 - G_0) / 2\rho S_0$$

T: Average thickness

G₀: Original weight of the sample before electroplating

G₁: Weight of the sample after electroplating

ρ : Density of Zinc

S₀: Surface area of the sample before electroplating

The average of zinc layer average thickness of samples from the same electroplating condition is taken, data from different conditions are compared in a control variable method.

4.5.2 Potentiodynamic curve

Potentiodynamic curve was drawn and evaluated for certain electroplating bath, to show the most effective current density range for electroplating zinc on magnesium in that condition.

4.5.3 Morphology evaluation

To better know the microstructure of the zinc coating layer, especially in different conditions, SEM (Scanning Electron Microscope) was used to photograph the surface.

Samples from different electroplating conditions were scanned using different magnification.

To further evaluate the composition of the layer, SEM mapping was also used.

4.5.4 Tafel curve testing

To analyze the corrosion resistance behavior of the new material, the Tafel curve test for samples in the Hanks solution was used. The test was conducted by software PowerSuite. The Tafel template performs a scan starting at -250mV vs. oc, and scans to +250mV vs. oc at a scan rate of 0.166mV/s. The Ag, AgCl/KCl(sat'd) electrode was used as the reference electrode. The total surface area of the samples was entered to the system.

After obtaining the Tafel curve for the sample, the Tafel fit was applied to the curve, the I_{corr} of the sample would be given, thus the corrosion rate could be figured out.

5. Electroplating

5.1 Zincate solution electroplating

Zinc electroplating using zincate solution was first explore in the project. Since the zincate solution is widely used in industrial manufacturing process.

When adjusting the current density to a relatively effect range, significant depositing process can be seen on the surface of magnesium.

After electroplating, the sample was as shown in the figure 5-1 a&b, the magnesium was covered by a dark porous layer of zinc. The zinc layer could be removed easily by hand. The sample after the zinc layer being removed is shown in the figure 5-1 c&d, the metallic luster of magnesium substrate can be seen. After removing all the macroscopic left zinc layer on them, samples were weighed, the weight of the samples were nearly the same as their original weight. This means almost all the electroplated zinc has been removed. And this further illustrate that the binding force of the coating was terrible.

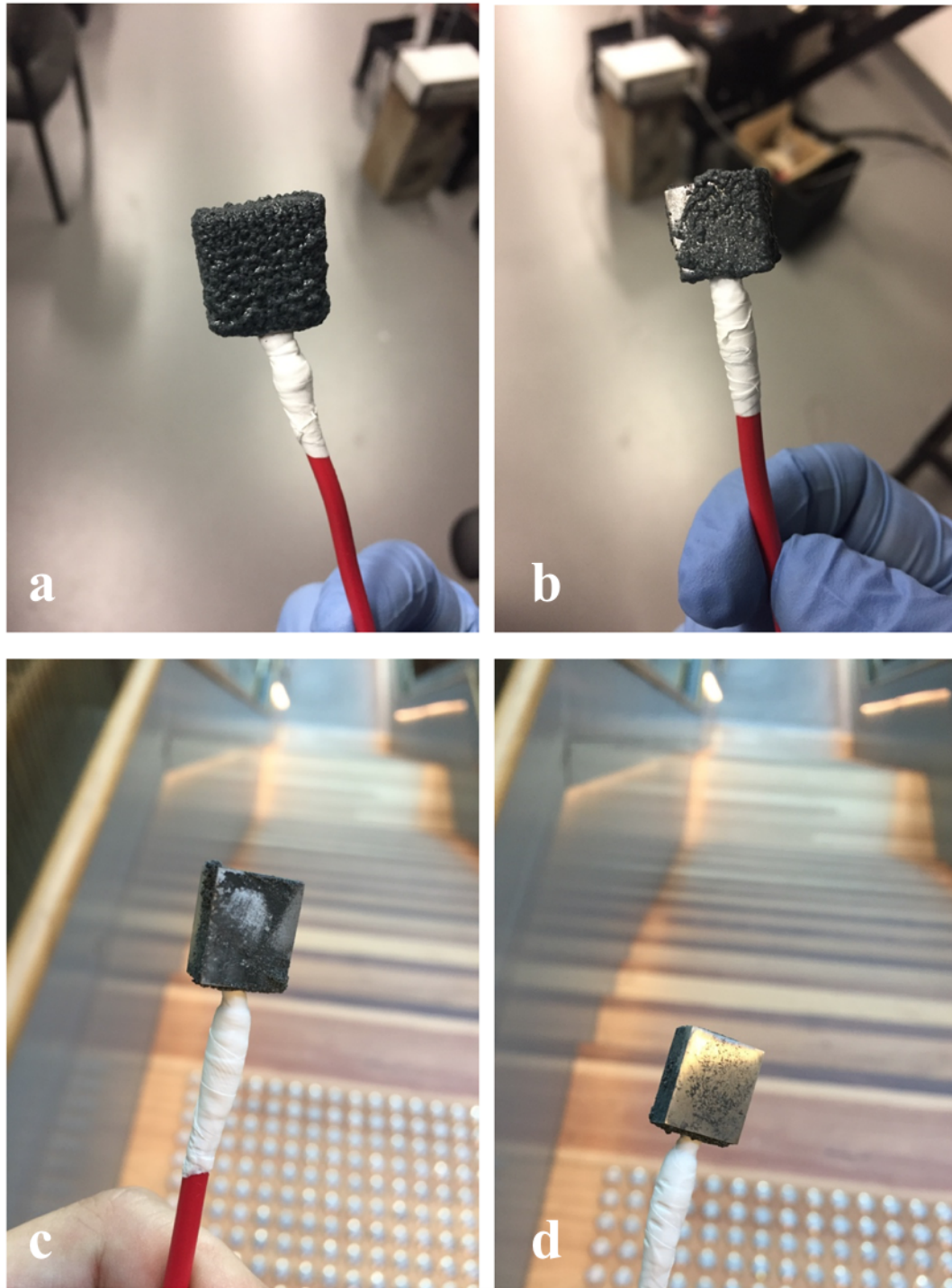


Figure 5-1 a, b Electroplated sample; c, d Electroplated sample after removing the coating.

To improve the adhesion of the zinc layer, different electroplating time was first used. The samples electroplated from 5 minutes to 65 minutes were obtained. The result is shown in the table 5-1.

Electroplating time	Performance
5min – 15min	Zinc coating layer gradually covers the surface of magnesium substrate as time increases.
20min – 50min	The thickness of dark zinc layer increases slowly.
55 min – 65min	The thickness of dark zinc layer increases rapidly and more non-uniform.

Table 5-1 The electroplating process as time increases

When the electroplating time 5 minutes, the bottom layer of coating zinc starts to form, and gradually covers the whole surface. After 15 minutes, the coating zinc has already fully covered the magnesium substrate and starts to “grow” outward. From 20 to 50 minute, the growth of the zinc layer is slow, the thickness of zinc layer does not increase slowly, some of the pores are being filled up during this period. When the electroplating time gets longer, form 55 minutes to 60 minutes, the growth of zinc layer starts to be faster. Some dendritic zinc can be seen on the edges of the samples. This is possibly because of that the solution is not evenly distributed after long time. However, even in the time period that thickness of zinc layer increases slowly, the strength and adhesion of the layer didn’t improve much. The layer is always dark and porous, which means electroplating time is not the parameter that cause the problem.

Later different temperatures were used in the electroplating, the result is largely similar to that of the different electroplating time. So was the current density.

No matter under what condition, the coating zinc layer is always dark, porous, loose and rough.

To figure out what’s the problem with this electroplating method, more literature was reviewed. According to some articles^{[29] [30]}, the lack of some organic additives could be the reason. Those organic additives includes DE-95 and ZB-95, both of which could significantly improve the performance of the zinc coating layer. DE-95 has a great absorbability, it was used to get crystallization meticulous coatings. ZB-95 works as a brightener, it has impact on the throwing power and coating power, which could influence the grain size of coating zinc layer. The using of both organic additives could

obtain a bright, smooth and uniform appearance coating. However, both of the organic additives are widely used in industrial manufacturing and easy to obtain in many big industrial countries, not in Australia.

The electroplating using zincate solutions end up with the lack of the organic additives.

5.2 Zinc sulfate solution electroplating

After the failure of zincate solution electroplating, zinc sulfate solution electroplating was used. Using the process mentioned in the methodology part, the result of initial attempts are shown in the figure 5-2 (before and after rinsing):

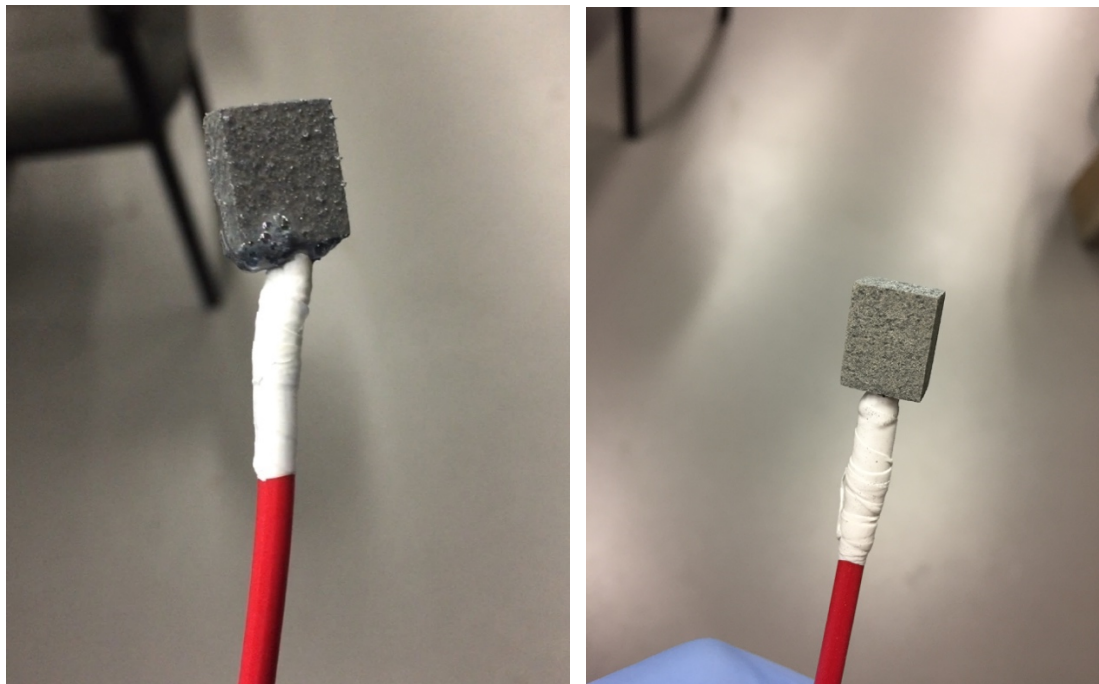


Figure 5-2 Electroplated samples (before and after rinse)

From visual inspection, it seems the magnesium substrate was covered by a new formed layer. However, after rinsing and drying, as shown in figure, the surface looks rough without metallic luster. To further confirm the structure and composition of the surface layer, SEM was used. The photos of the electroplated surface taken by SEM are shown in the figure 5-3:

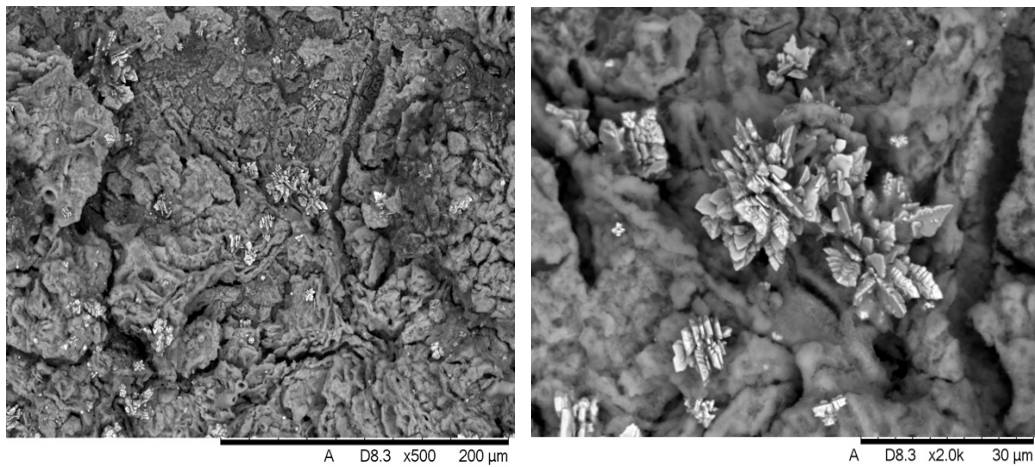


Figure 5-3 SEM photo of sample surface (500, 2000)

In the left photo of figure 5-3, with a magnification of 500, a nonuniform surface is shown. To know the composition of the surface, SEM mapping was used. The most area seen in the figure was actually covered by corrosion product of magnesium and formed a rough surface. Very little zinc was left on the surface. Like in the center area, when using a magnification of 2000, like shown in figure 5-3 (right), the brighter parts are the only zinc crystallization organizations lying on the surface in this area. This means although there could be a zinc layer on the surface, it has already been rinsed off. The weight of the sample had little increase which also confirm this situation. The adhesion of the zinc coating layer is still a problem.

Different electroplating conditions are also tried in this solution. Firstly, different temperatures was used. It turns out that the corrosion has been partly prevented, yet the adhesion issue hasn't been solve.

When controlling the electroplating time, the results are almost the same as before. When electroplating time gets longer, the electroplated samples are like the one shown in figure 5-4:



Figure 5-4 Overplated sample

Dendritic zinc crystallization organizations appear on the corners and edges of the sample. The other areas weren't even well covered as those. And same as before, the adhesion of the zinc on the surface was far from satisfying, barely nothing left after rinse. Under SEM, the rinsed surface could be seen as shown in figure 5-5. The adhesion and corrosion protection hadn't been improved.

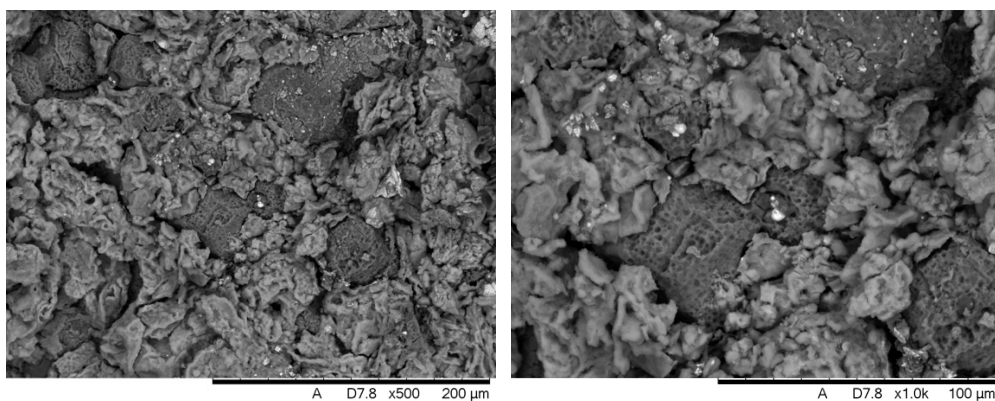


Figure 5-5 SEM for electroplated sample

The terrible adhesion and bad protection from corrosion are like a vicious cycle, when the coating isn't adhesive, it couldn't coat the magnesium substrate from being corroded by the solution. When the corrosion appears, the corrosion product would only weaken the binding force between the zinc coating layer and the magnesium substrate. It seems the electroplating solution formula should be adjusted and improved to avoid

all these from happening, or maybe just as the zincate solution formula, some additives are necessary.

5.3 Zinc sulfate, potassium pyrophosphate solution electroplating

The zinc sulfate and potassium pyrophosphate solution electroplating was the improved version of the zinc sulfate solution electroplating.

The initial attempts showed that $K_4P_2O_7$ used in the electroplating bath was important, and zinc layers had formed on the samples, as shown in the figure 5-6.



Figure 5-6 Electroplated sample using zinc sulfate, potassium pyrophosphate solution

According to the increase of weight, the average thickness of zinc layer on samples is around $9\mu\text{m}$. To confirm the coating layer is pure zinc, and inspect the microstructure of the layer, SEM was used. The photos of the coating layer on the surface is shown in figure 5-7:

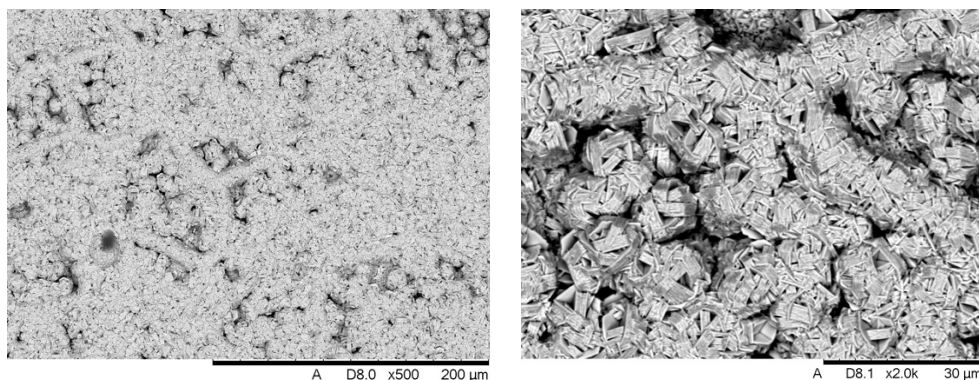


Figure 5-7 SEM of the zinc coating layer (500, 2000)

We can see the surface of magnesium substrate has already been fully covered by

the depositions. In a zoomed in view, the structure of the coating could be seen more clearly, the coating was formed in several layers, through the gaps on the surface layer, the underlayers could be seen.

To confirm the coating layer was pure zinc, SEM mapping was used. The result is shown in the figure 5-8:

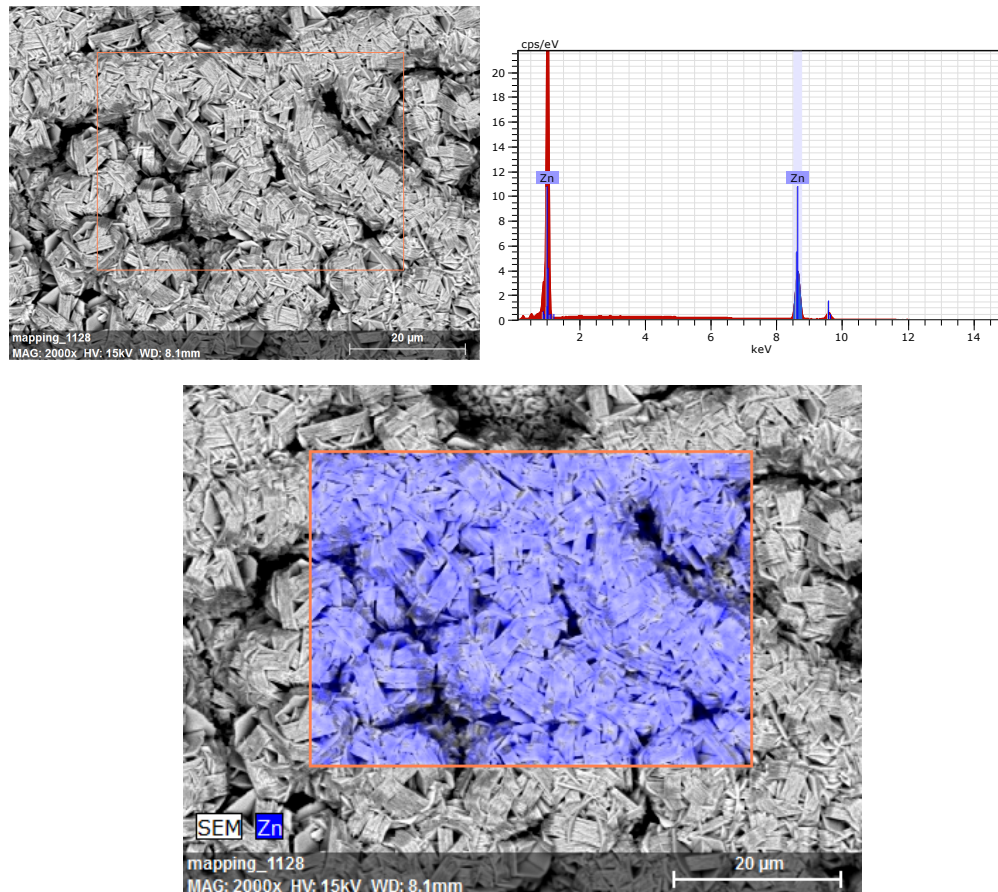


Figure 5-8 SEM mapping for coating layer

From the SEM mapping, the zinc sulfate and potassium pyrophosphate electroplating solution was satisfying that the magnesium substrate had been covered with zinc layer. Thus more samples were electroplated using the same solution under different conditions to figure out the best parameter ranges.

(1) Current density

To get the best current density range, the potentiodynamic curve of magnesium in the zinc sulfate and potassium pyrophosphate electroplating solution was drawn. From the curve (figure 5-9), an effective current density range was known, 0.5A/dm² to

3A/dm².

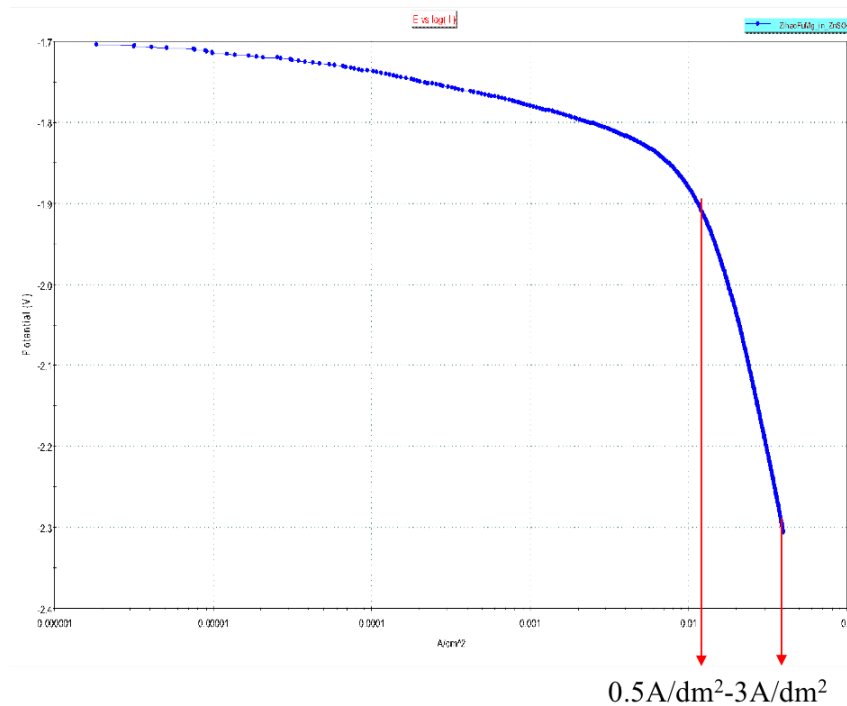


Figure 5-9 Potentiodynamic curve of Mg in electroplating solution

Samples was electroplated using different current densities between 0.5A/dm² to 3A/dm². The average coating thickness which was calculated from the increased weight and surface area was the main parameter used in judging the current density. From the figure 5-10, we can see that when current density is between 2 A/dm² and 2.5 A/dm², the average coating thickness is relatively stable.

The current density used is related to the efficiency of the current, when the current density is too low, the efficiency is low as well, thus the coating thickness is low after the same time. Meanwhile, the low current density makes the current couldn't provide enough protection to the cathode, the coating layer wasn't dense. Although the actual thickness of the zinc coating layer is higher than the estimated average thickness by mass difference. Those are why when current density is lower, the average coating thickness would be lower.

When the current density is high, the deposit rate is high, however the zinc grain is coarse and the accumulation of zinc occurs. A rough surface with large sized zinc grain is the least we need. Although the average coating thickness is high, the high quality of coating layer could not be guaranteed.

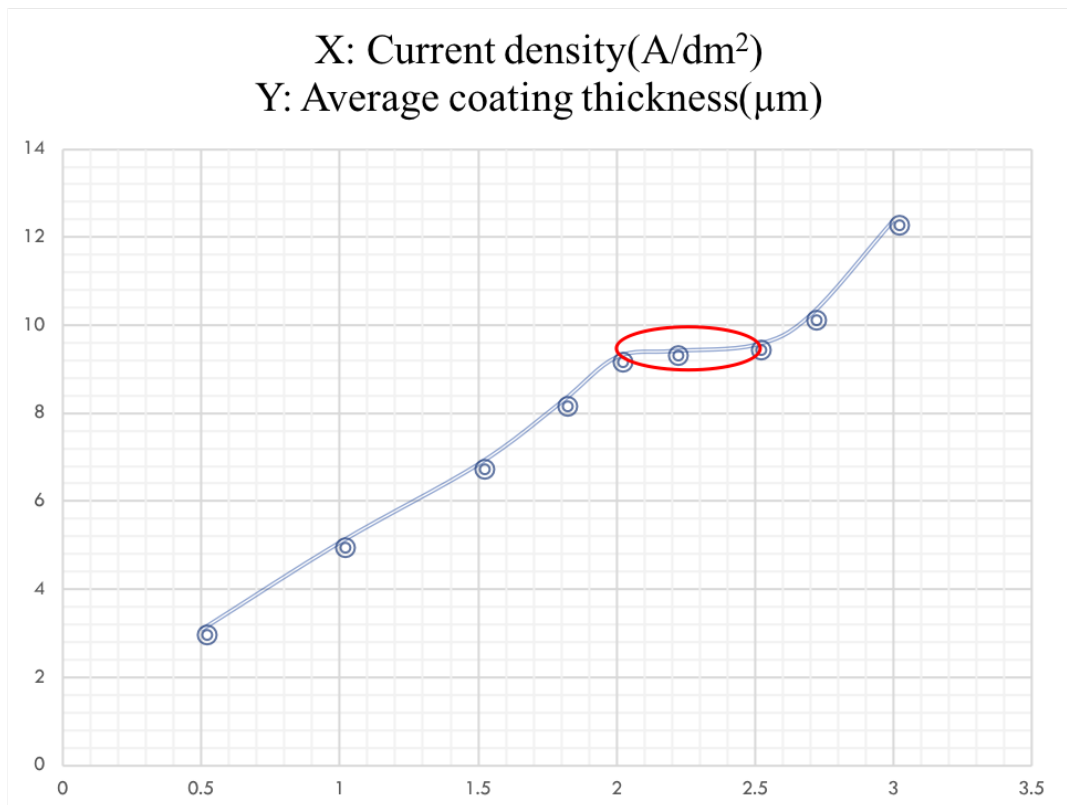


Figure 5-10 Average coating thickness in different current densities

When the current density is even higher, higher than 4 A/dm², which is not shown in the figure, the passivation of anode occurs. The average coating thickness grows slower, which means the efficiency of current drops back. The coating layer is not dense as well.

The most suitable current density range here is 2 A/dm² to 2.5 A/dm².

(2) Electroplating temperature

The electroplating temperature is another important parameter to consider about.

Samples was electroplated using different electroplating temperatures between room temperature 25°C to 65°C. The average coating thickness which was calculated from the increased weight and surface area was the main parameter used in judging the current density. The figure 5-11 shows the diagram of average coating thickness on magnesium samples in different electroplating temperatures.

In general, the average coating thickness increases as the temperature gets higher, at first the average coating thickness increases significantly. After 40°C, the average coating thickness grows slowly.

When the temperature is low, the depositing speed is slow, the electric conductivity of the solution is poor.

Higher temperature causes the molecules to move faster, the electroplating solution's degree of dispersion would be higher. At a lower temperature stage, this would directly increase the depositing speed. When it comes to 40°C, the dispersion of the solution and the depositing speed both attain a high level.

When the temperature continues to be higher, the performance of the zinc coating layer begins to get worse. When the temperature is higher than 60°C, the potassium pyrophosphate in the solution is prone to hydrolysis, which could make the electroplating solution more unstable.

The most suitable temperature range for zinc electroplating is 40°C to 55°C.

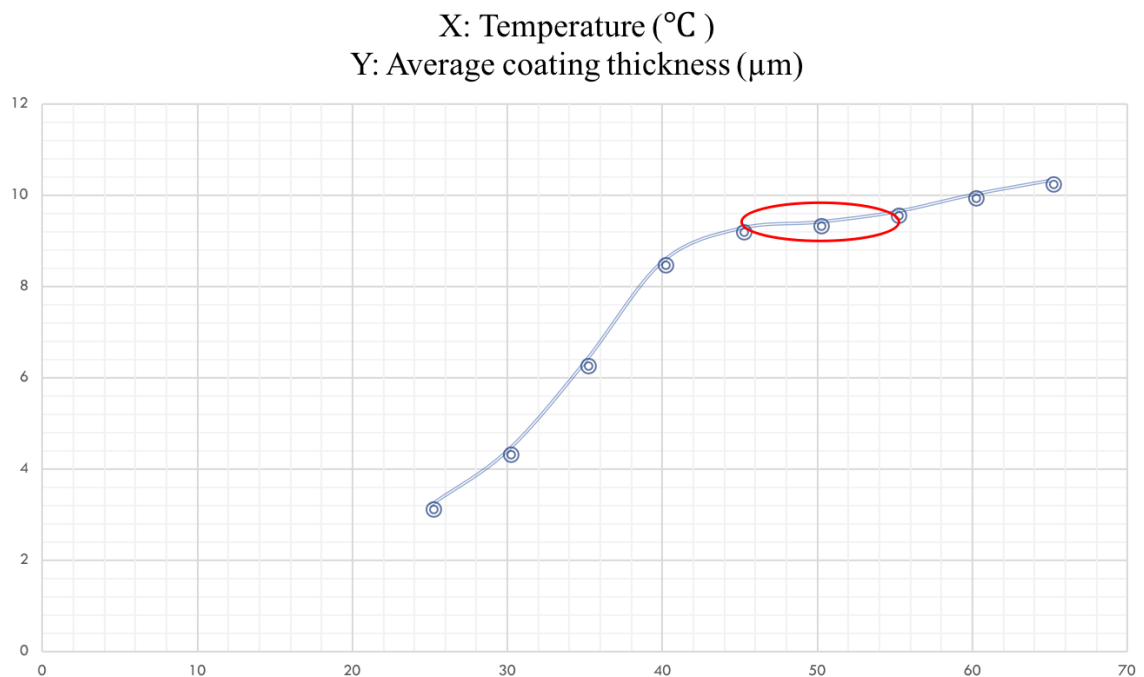


Figure 5-11 Average coating thickness in different electroplating temperature

(3) Electroplating time

Electroplating time is undoubtedly another important parameter to control the average thickness and quality of zinc coating layer. At the same time, a good choice of electroplating time can help guarantee that the efficiency of current is always at a high level.

Samples was electroplated using different electroplating times between room temperature 5 minutes to 30 minutes. The average coating thickness which was calculated from the increased weight and surface area was the main parameter used in judging the current density. The figure 5-12 shows the diagram of average coating thickness on magnesium samples in different electroplating times.

As expected, the figure 5-12 suggests that average coating thickness generally grows as the time extends, the growth is at a relatively constant speed. This means that the depositing speed is steady.

To better understand the influence electroplating time has on the zinc coating quality on magnesium, samples using similar electroplating methods, same temperature and same current density, different electroplating times were scanned using SEM. The SEM photos are shown in the figure 5-13.

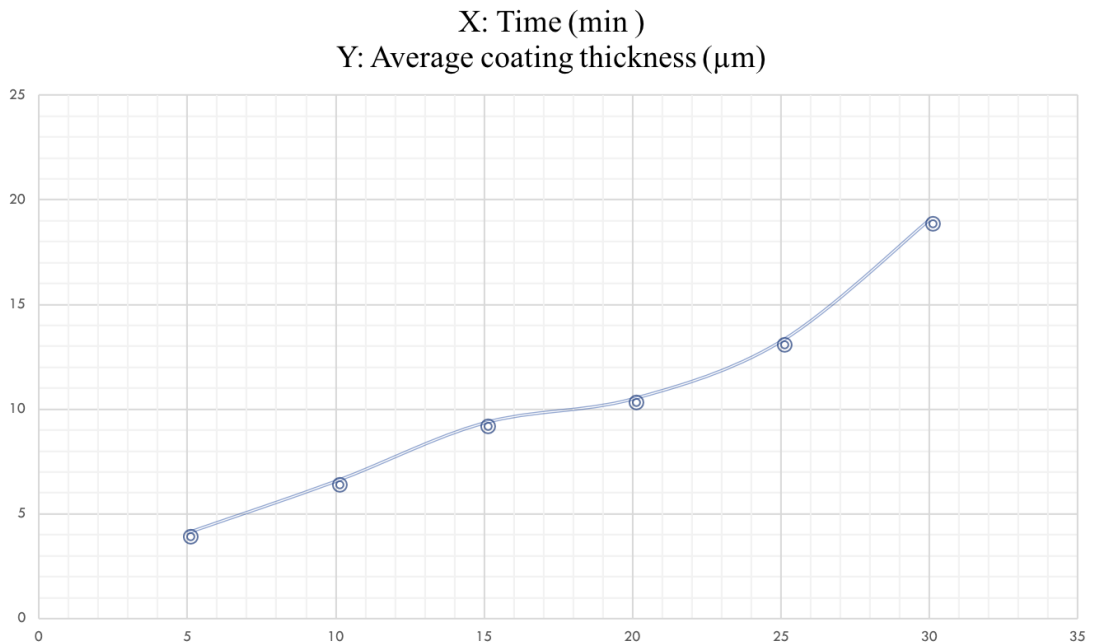


Figure 5-12 Average coating thickness in different electroplating time

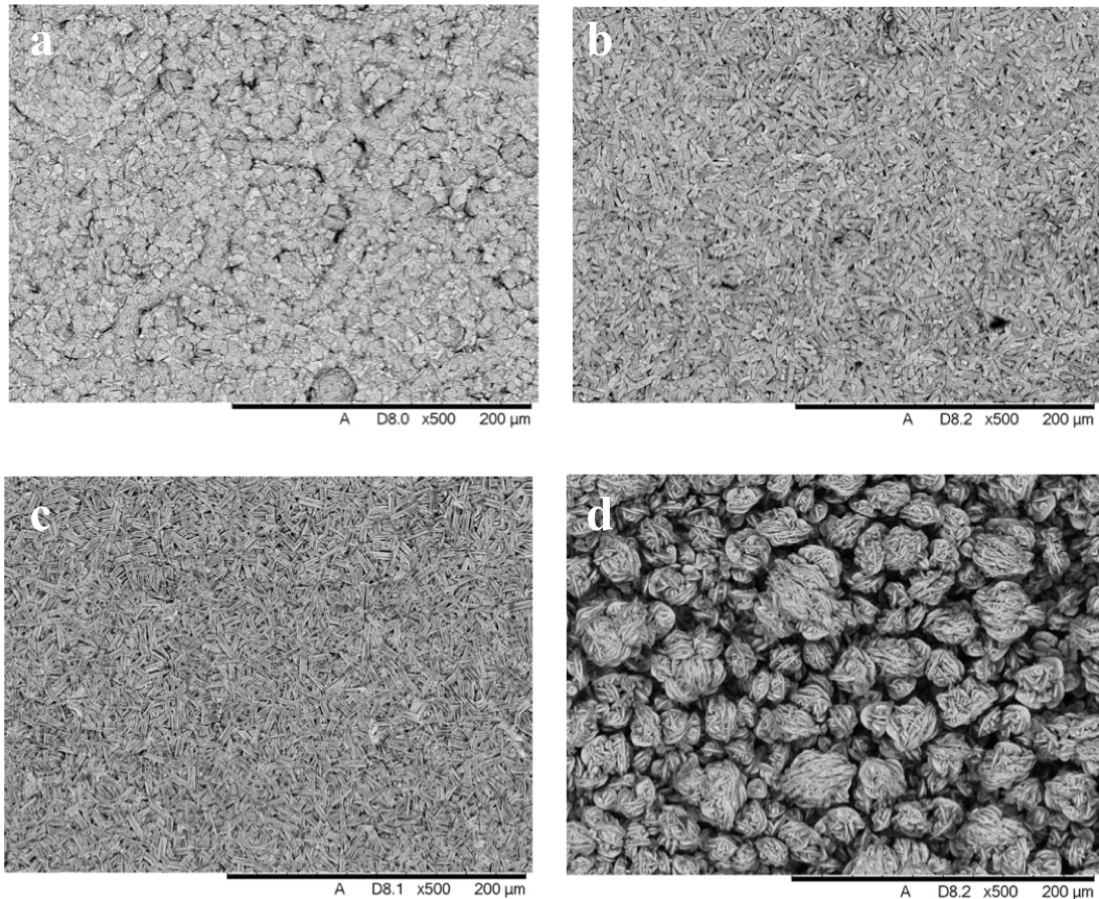


Figure 5-13 SEM(500) photos for sample surface of different electroplating time (a.10min, b.15min, c.20min, d.30min)

The figure shows the surface morphology of zinc electroplated samples using 10, 15, 20, 30 minutes, while the other electroplating conditions were the same. The magnification of all four photos are 500.

We can see that after 10 minutes, the surface of magnesium substrate has already been covered with zinc, yet the degree of plainness is low. We can see that there are some higher areas and lower areas, with small gaps and defects among them.

When electroplating time extends to 15 minutes, the surface could be described as more uniform. Barely any obvious defect can be seen.

After 20 minutes, the surface area shown in the photo has even less defects than 15 minutes. The shape of zinc crystals defers as well.

As for 30 minutes, the surface is nonuniform again, with zinc crystal clusters covers the surface.

The surface was later further magnified(4000) to see the crystal growth of zinc, the samples under 10, 15, 20, 30 minutes electroplating is shown in the figure 5-14. We can

see that the shapes of zinc crystals are similar in 10 minutes and 15 minutes, both are like block-shaped. The zinc crystals after 15 minutes, however, cover the surface better than those in 10 minutes. The crystals bonded with each other more tightly, less gaps were left. After 20 minutes of electroplating, the zinc layer area shown is covered by longer thinner zinc crystal pieces. Hard to say which crystal shape comparing to those of 15 minutes is more desirable, the evenness is still high.

The 30 minute sample was covered by sphere shaped zinc crystals like shown in figure. The sphere shape results in the large gaps and interspace appear between them and the sacrifice of the uniformity of the surface. Since the time gap between the 30 minute sample and the others are long, it is very possible that the cluster layer seen has actually grown on top of one of some former layers instead of transferring from them. Although the thickness of the total zinc layer did get higher this time, the electroplating efficiency was much lower.

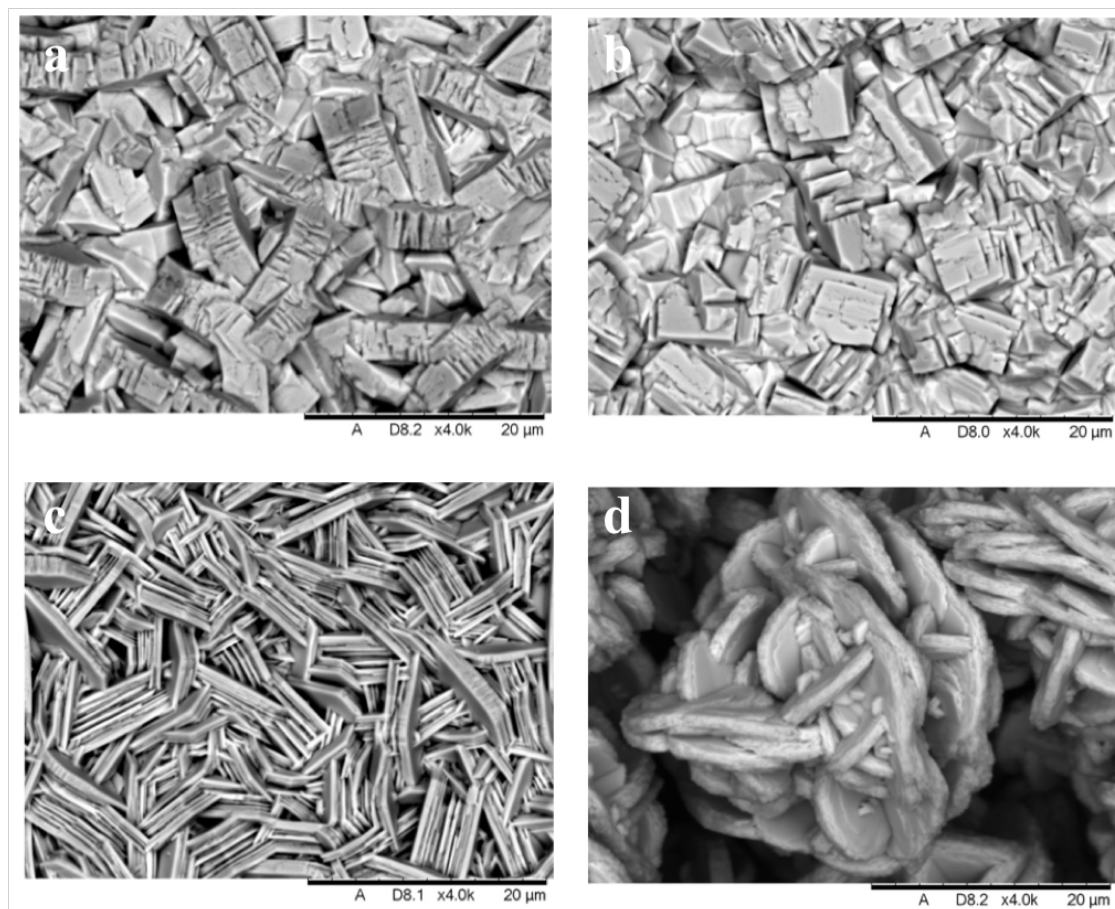


Figure 5-14 SEM(4000) photos for sample surface of different electroplating time (a.10min, b.15min, c.20min, d.30min)

From the analysis above, we can see that 15 minutes to 20 minutes could be the possibly best electroplating time. When the time is shorter, the zinc crystals haven't cover the surface well. When the time is longer, the efficiency drops. That's why we choose 15 – 20 minutes as the suitable electroplating time range.

(4) Summary

As above, the relatively suitable and effective range of all three electroplating parameters was given using a control variable method. The most suitable current density range for zinc electroplating is 2 A/dm^2 to 2.5 A/dm^2 , the most suitable temperature range is 40°C to 55°C and 15 – 20 minutes is the best electroplating time. Using the parameter range we get, more magnesium samples were electroplated. The figure 5-15 is a photo of the electroplated sample, and figure 5-16 shows an SEM photo of the surface of the electroplated sample.



Figure 5-15 Zin electroplated sample

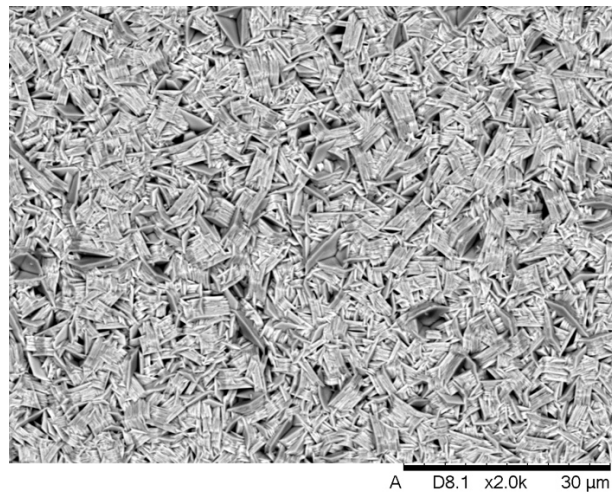


Figure 5-16 SEM for sample surface

6. Corrosion resistance analysis

Electrochemical tests were conducted to analyze the property of the zinc electroplated magnesium samples, and find out the very best electroplating condition in the range.

Because under the existing conditions, the electroplating temperature is hard to be controlled at a certain point. The exact temperature will not be studied at this point. So

the current density and electroplating time are what will be focused on. Samples electroplated under 40 – 50°C in 15 minutes using various electroplating current densities: 1.5, 2, 2.5 A/dm² and samples electroplated under 40 – 50°C using a electroplating current density of 2 A/dm² in 15, 20, 25 minutes were used to obtain the Tafel curve of each condition. Using the Tafel curve, the corrosion rate of each sample were figured out and compared, the best electroplating conditions could be known. Under each conditions, two samples were used to minimize the error. And for each sample, the open circuit potential test was first conduct to stabilize the surface potential before obtaining the Tafel curve.

Figure 6-1 is the Tafel curve for one sample, and figure 6-2 is the Tafel fit to that sample.

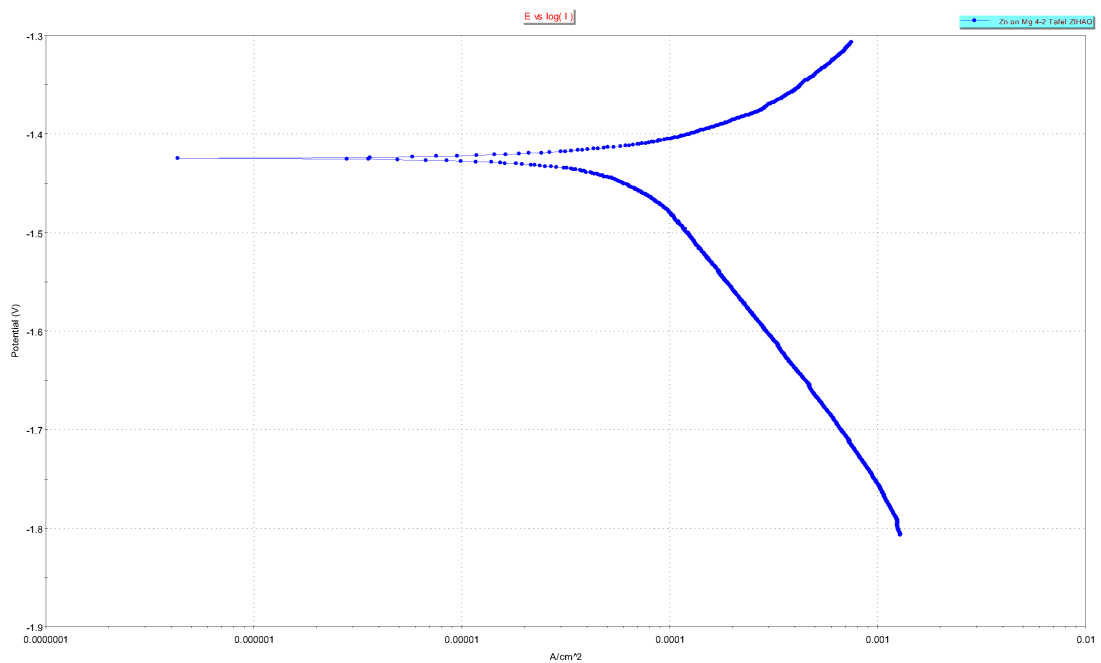


Figure 6-1 One of the Tafel curves for electroplated samples

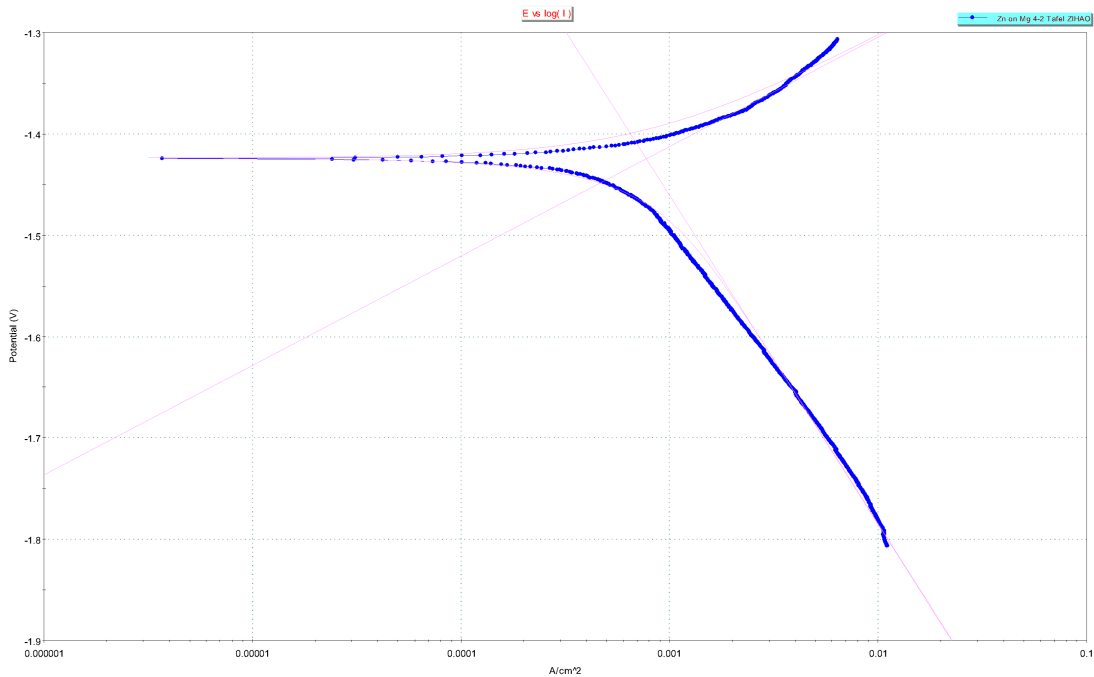


Figure 6-2 Tafel fit

After obtained the Tafel curve for all the samples, the average I_{corr} was calculated and shown in the Table 6-1 and Table 6-2.

Current density (A/dm ²)	I_{corr} ($\mu\text{A}/\text{cm}^2$)
1.5	659.15
2	573.2
2.5	2118

Table 6-1 I_{corr} in different current density

Electroplating time (min)	I_{corr} ($\mu\text{A}/\text{cm}^2$)
15	583.1
20	807.2
25	347.3

Table 6-2 I_{corr} in different electroplating time

We know that a lower I_{corr} stands for a better corrosion resistance. From Table 1, we can see that when current density was at 1.5 to 2 A/dm², the I_{corr} are almost the same(considering about the possible error), around 600 $\mu\text{A}/\text{cm}^2$, but when the current density increases to 2.5 A/dm², the I_{corr} comes to an astonishing 2118 $\mu\text{A}/\text{cm}^2$. This possibly is because that the zinc coating layer formed in this high current density wasn't as dense.

As for electroplating time, we found that the I_{corr} was low at 15 minutes, later attain a high point in 20 minutes, and decrease to the best performance when it's 25 minutes.

It could be understood by assuming that after 15 minutes, a dense, uniform zinc layer had formed. After 20 minutes, the dispersity of the solution continued to decrease, the grown zinc layer wasn't as dense and uniform as 15 minutes. But later, the deposition of zinc began to fill up the gaps and defects of the surface. Or because the new shape of zinc crystals appeared on the surface, which also explains why the shape of zinc crystal was so different when the time extends to 30 minutes. However, all the I for different time was in the appropriate range comparing to other obtained data and the although the 25 minute samples showed a better performance, the efficiency of electroplating may not be high considering the time spent. So the very best electroplating time need to be determined by some further research. Here, 15 min to 25 min is used as the suitable time range for electroplating.

Using the best I_{corr} obtained was $240.3 \mu\text{A}/\text{cm}^2$, the corrosion rate (penetration rate P) for this material in the Hanks solution could be figured out using:

$$P = 3.28 I_{\text{corr}} M / nd$$

Where: M = atomic mass (65.39 for Zinc)

n = number of electrons freed by the corrosion reaction (here n=2)

d = density ($7.14\text{g}/\text{cm}^3$ for Zinc)

Thus, the penetration rate here is 3.6 mm/year. It isn't a very ideal result, since it's still a little too high. But it's already at the same order of magnitude with same magnesium alloys' penetration rate in hanks^[31]. This means the idea of electroplating zinc on magnesium is feasible and some more research should be carried out.

7. Conclusion

1. Additives are necessary for zincate electroplating on magnesium to get a uniform and dense zinc layer.
2. Zinc sulfate and potassium pyrophosphate solution zinc electroplating is a feasible method to electroplate zinc on magnesium substrate. Average thickness of $9\ \mu\text{m}$ zinc coating layer could be obtained. The appropriate electroplating condition should be : $1.5 - 2\ \text{A}/\text{dm}^2$, $15 - 20\ \text{min}$, 40°C to 55°C .
3. The corrosion resistance of the zinc coating layer wasn't very satisfying in this experiment, however, it demonstrates the feasibility of this method for creating a new biodegradable material.
4. More research should be carried out to find the exact relationship between the electroplating parameters and deposition process of zinc, as well as the morphology of zinc crystallization organizations.
5. Future research should be focused on the improvement of the electroplating method to obtain zinc coating layer with better properties and use the zinc layer as substrate surface to electroplating other metal materials to further increase the corrosion resistance since electroplating on zinc could be easier than on magnesium.

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Appendix

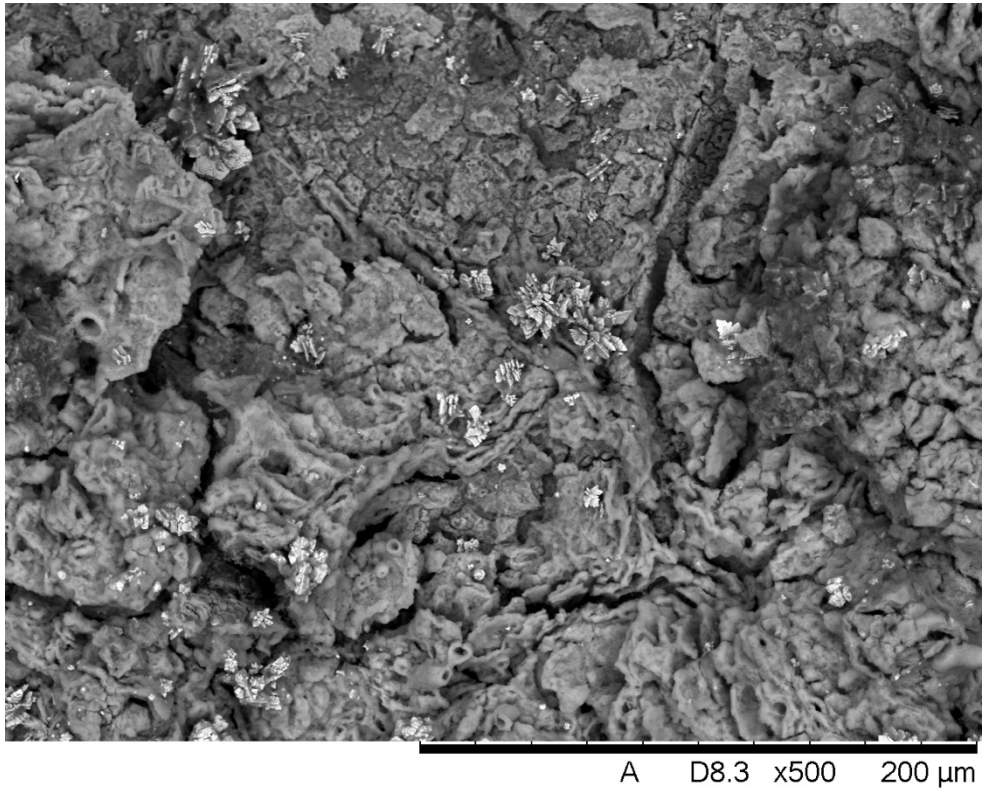


Figure 5-3 SEM photo of sample surface(500)

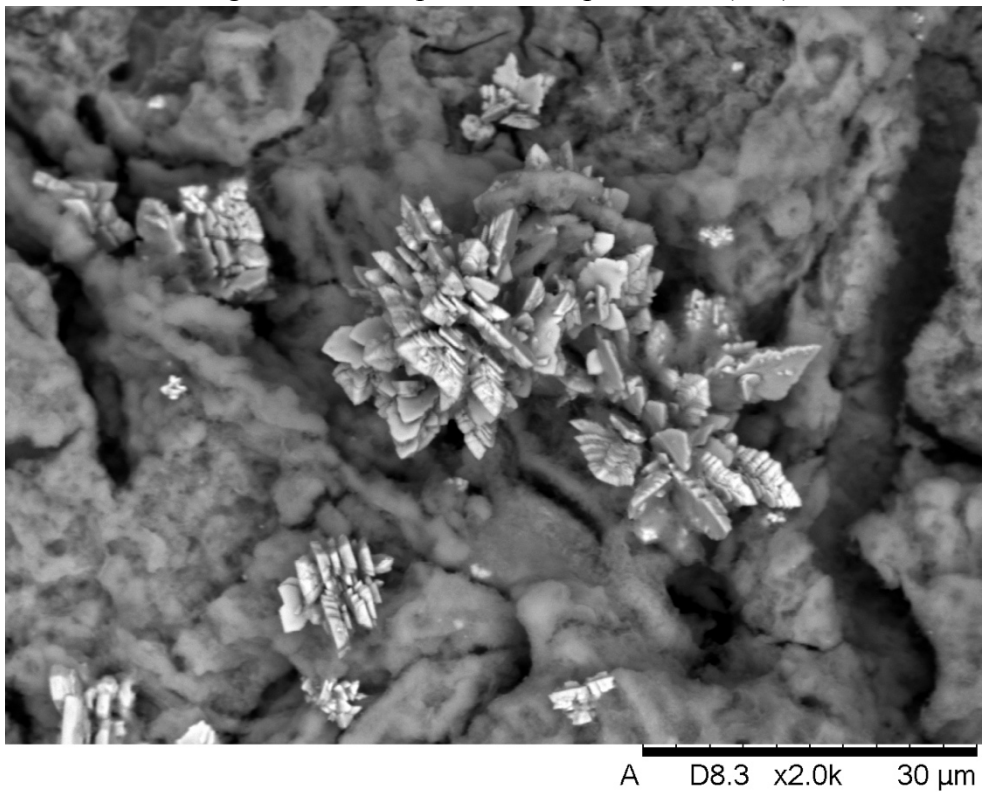


Figure 5-3 SEM photo of sample surface(2000)

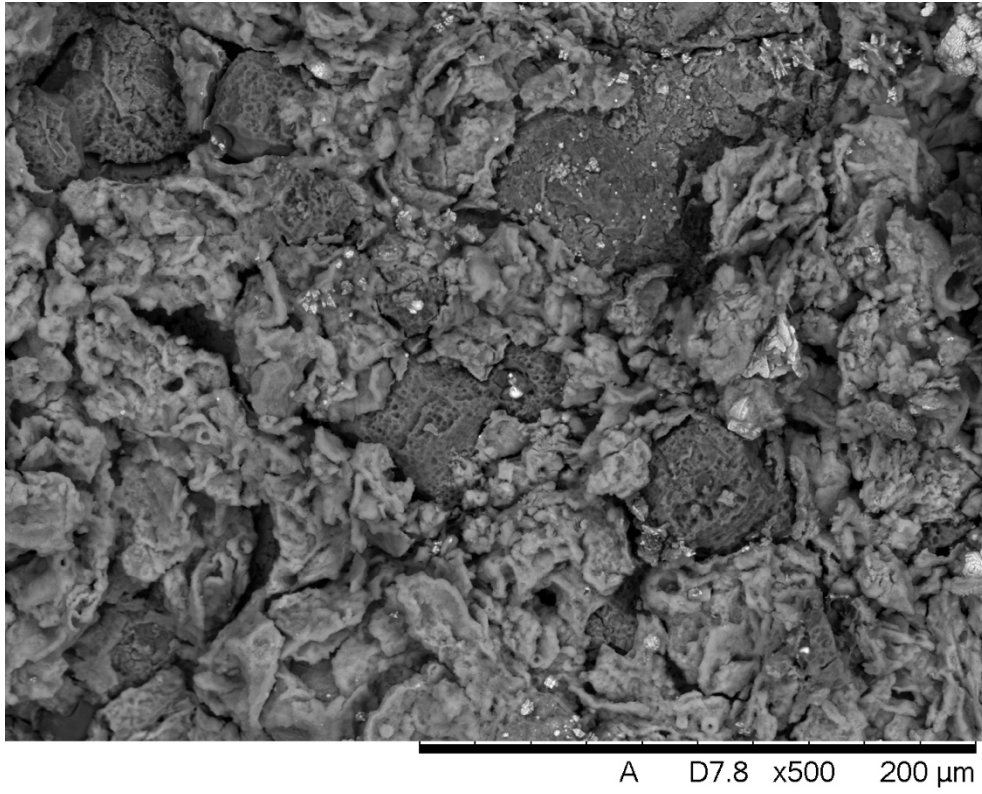


Figure 5-5 SEM photo of sample surface(500)

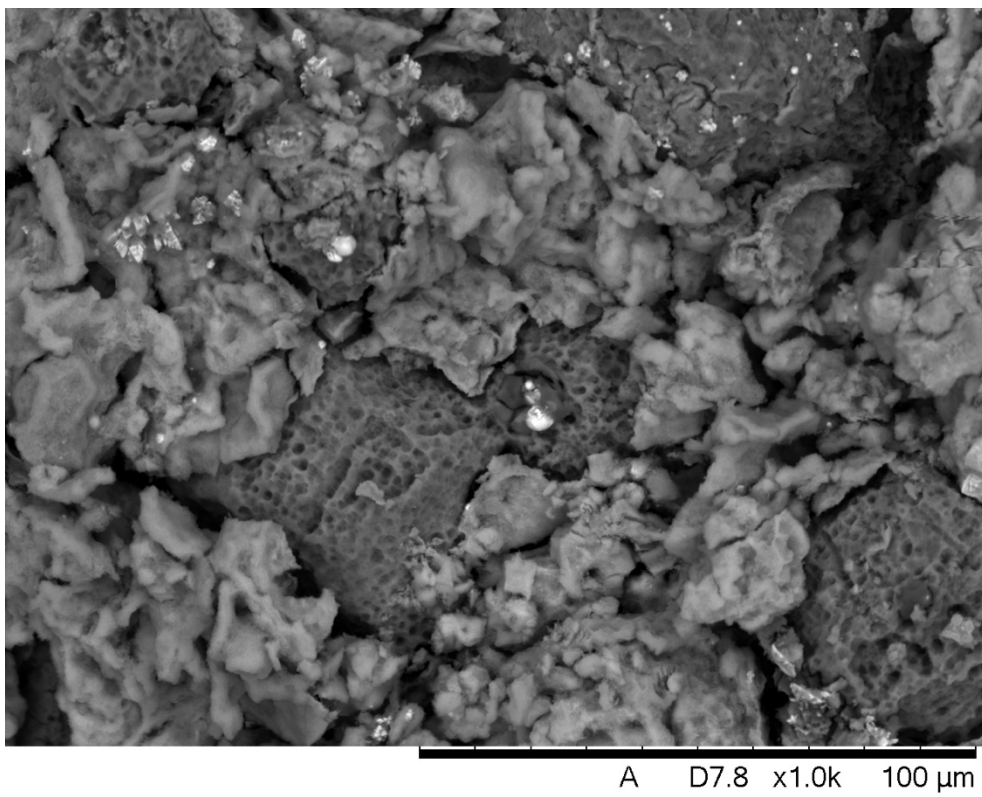


Figure 5-5 SEM photo of sample surface(1000)

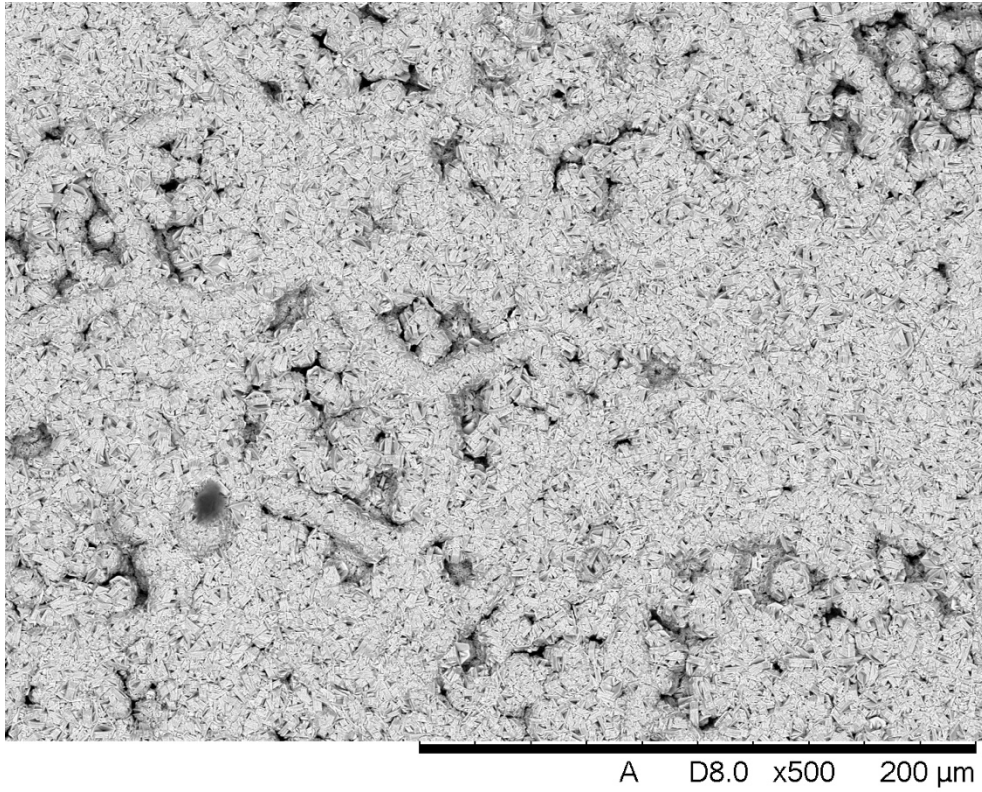


Figure 5-7 SEM photo of sample surface(500)

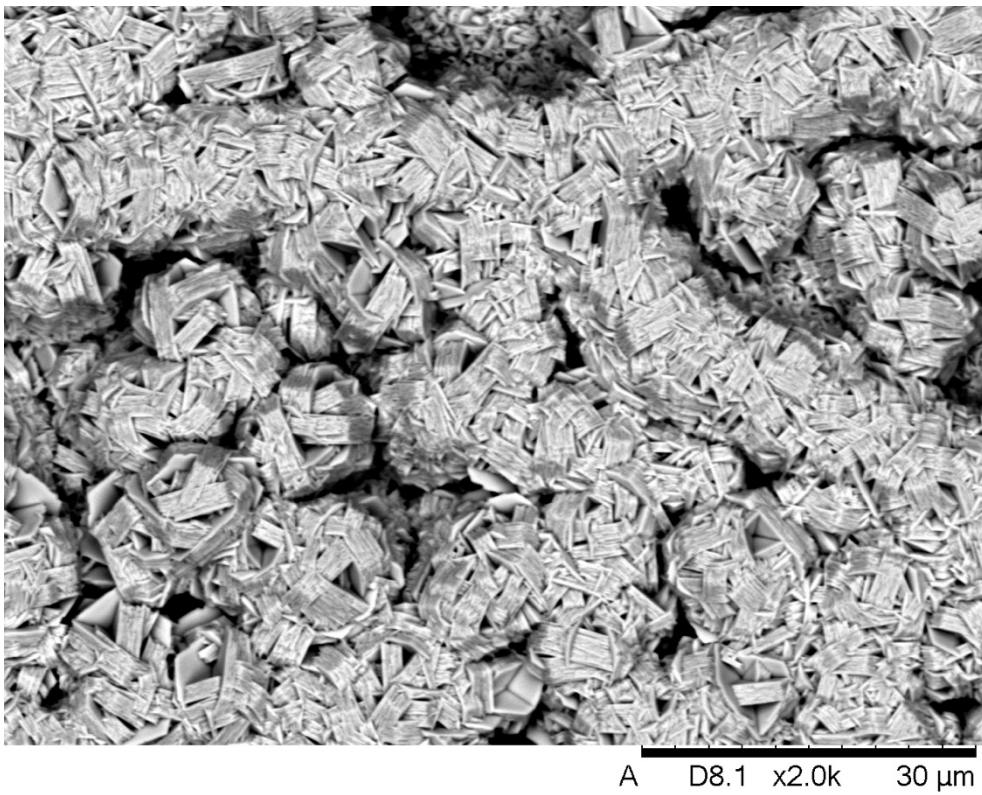
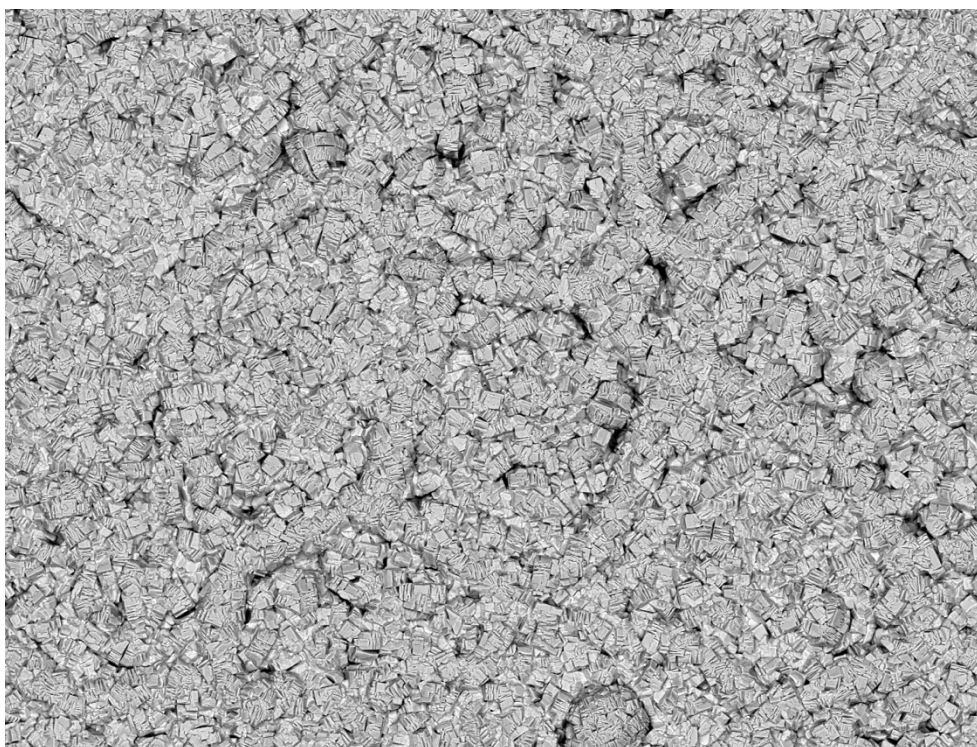
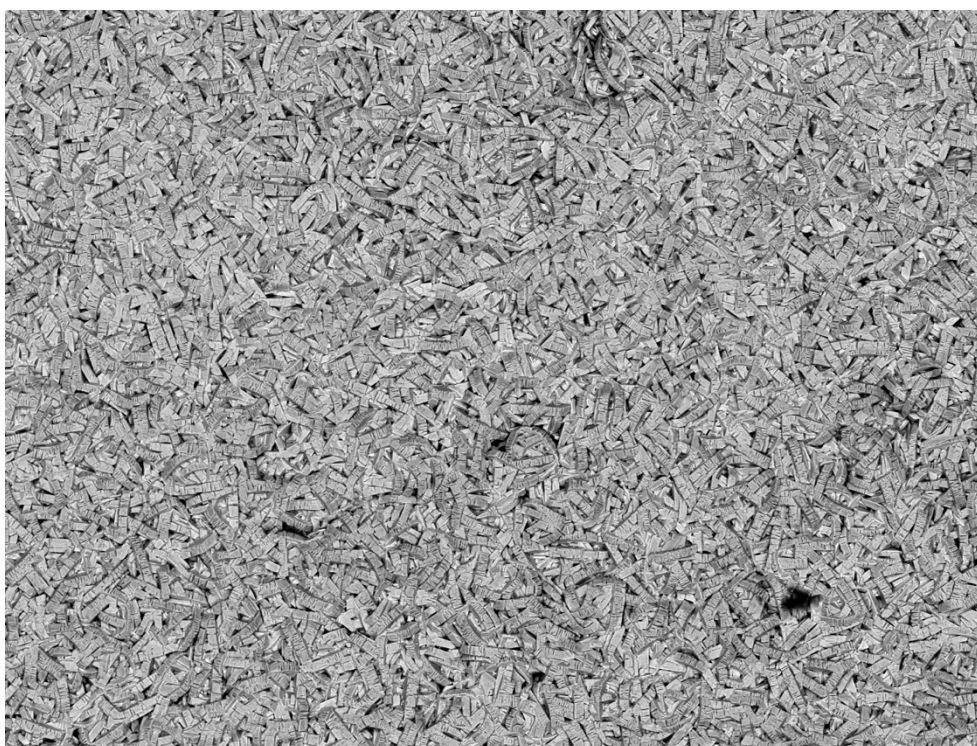


Figure 5-7 SEM photo of sample surface(2000)



A D8.0 x500 200 μ m

Figure 5-13a SEM photo of 10 min electroplating sample surface(500)



A D8.2 x500 200 μ m

Figure 5-13b SEM photo of 15 min electroplating sample surface(500)

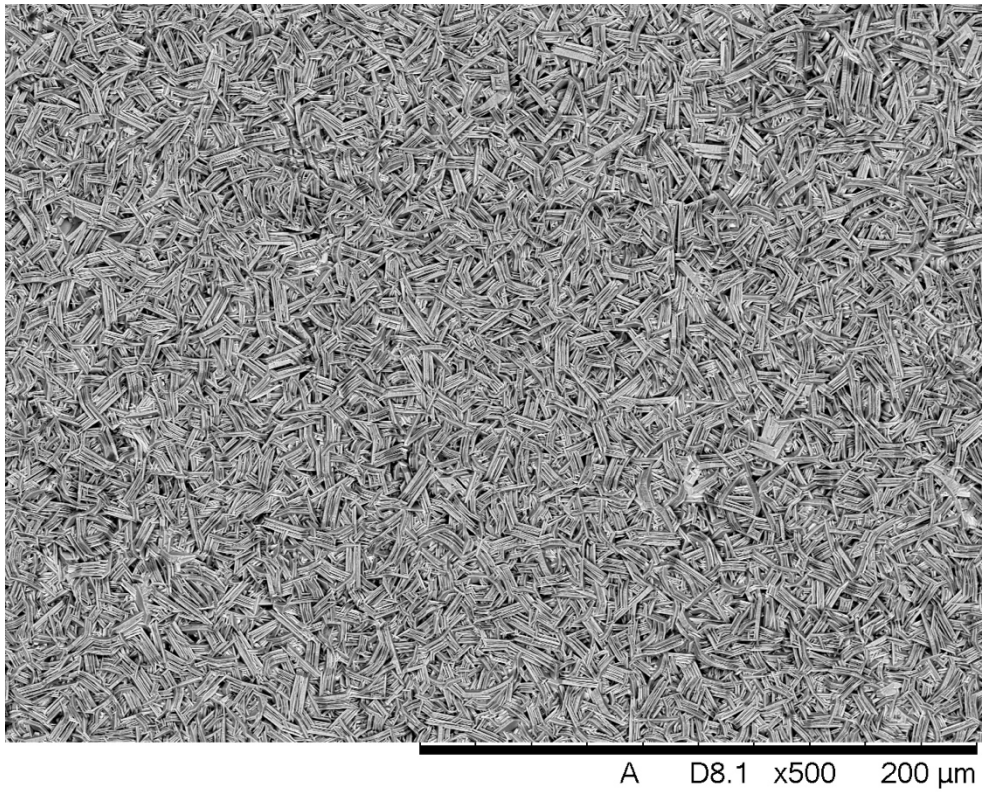


Figure 5-13c SEM photo of 20 min electroplating sample surface(500)

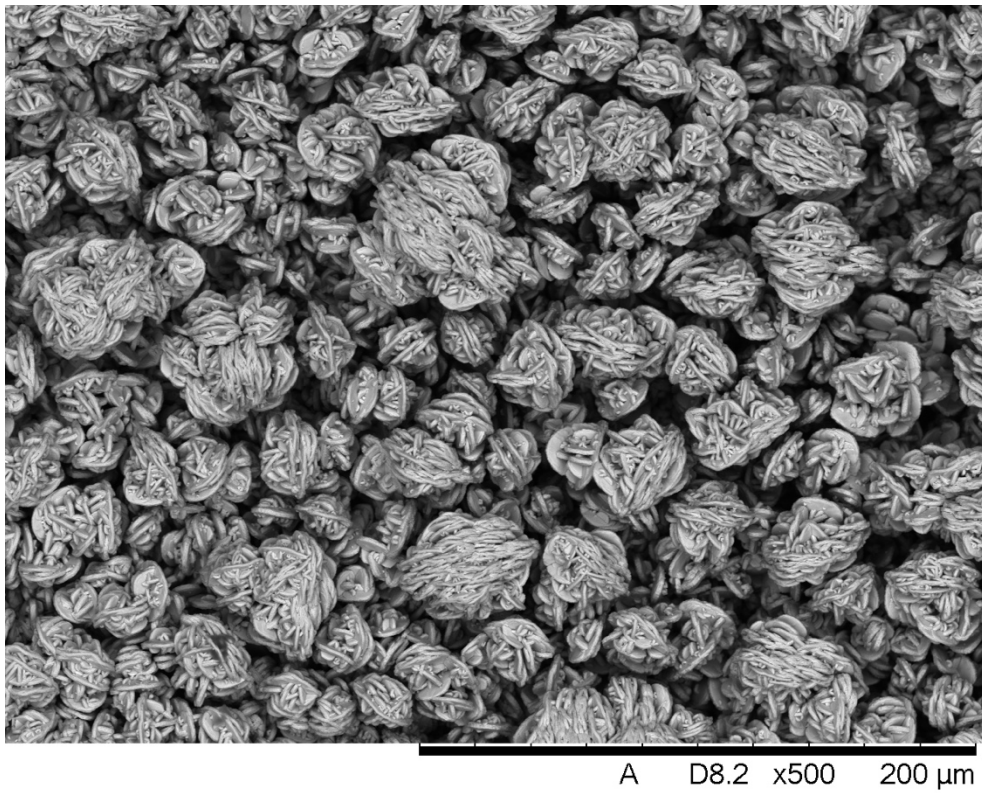


Figure 5-13d SEM photo of 30 min electroplating sample surface(500)



Figure 5-14a SEM photo of 10 min electroplating sample surface(4000)

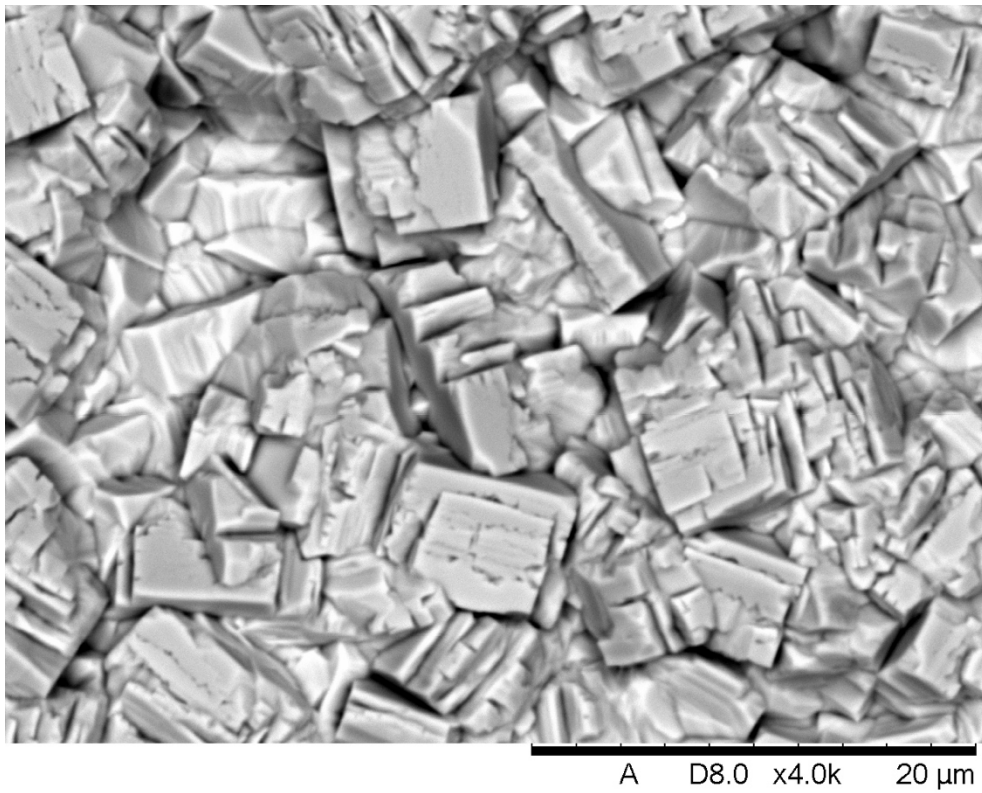


Figure 5-14b SEM photo of 15 min electroplating sample surface(4000)

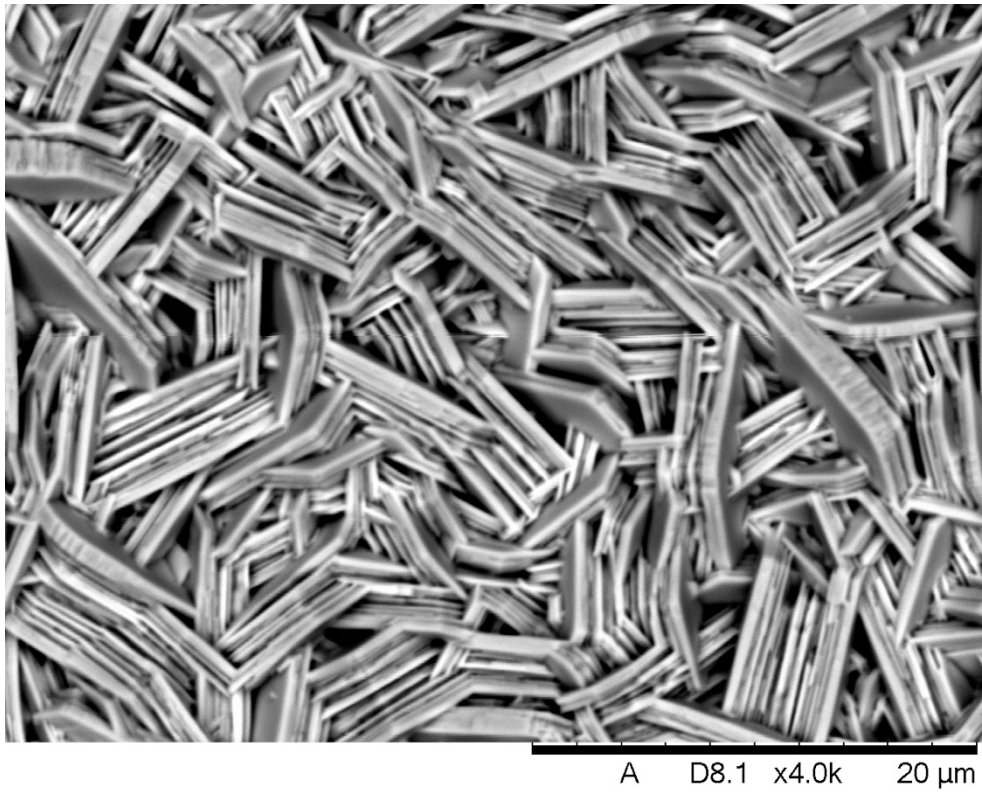


Figure 5-14c SEM photo of 20 min electroplating sample surface(4000)

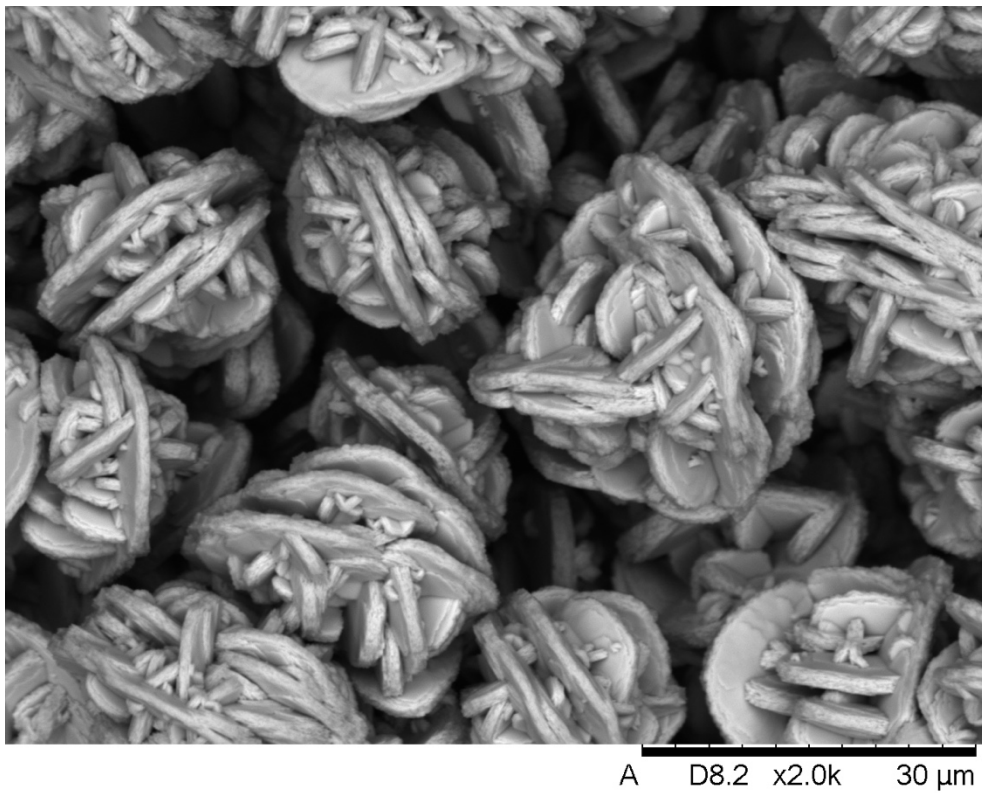
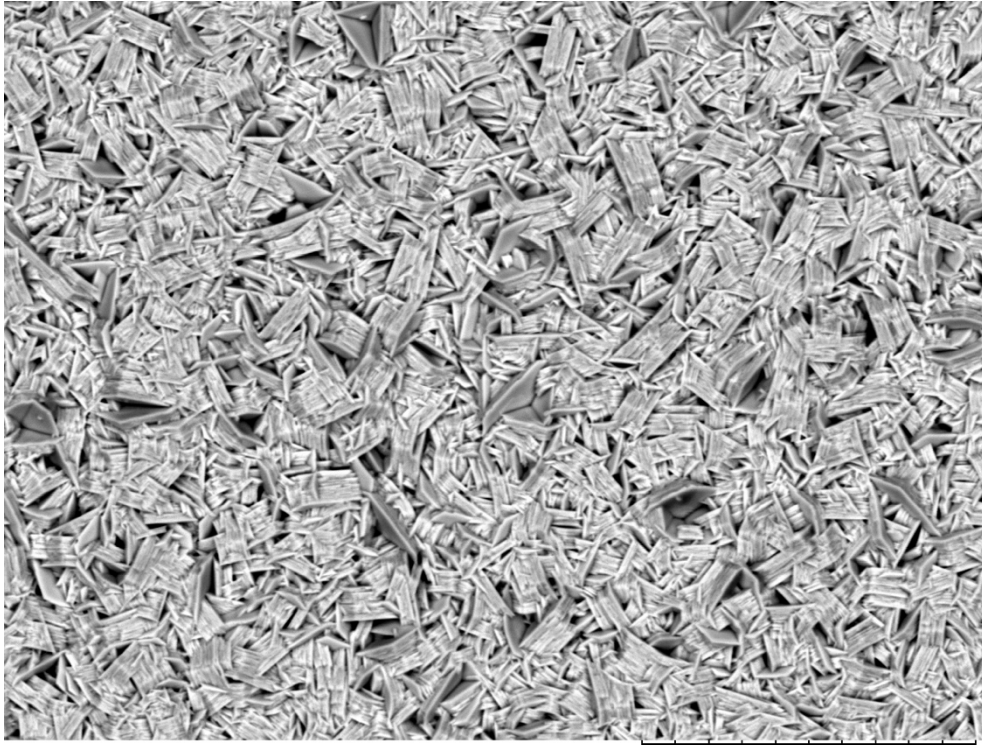


Figure 5-14d SEM photo of 30 min electroplating sample surface(4000)



A D8.1 x2.0k 30 μm
Figure 5-16 SEM photo of electroplated sample surface(2000)

Some original data used in figure5-10, 5-11, 5-12:

Sample number	X (mm)	Y (mm)	Z (mm)	Surface area (dm ²)	Original weight (g)	Electroplated Weight (g)	Weight difference (g)	Average coating thickness(μm)	Current (A)	Current density (A/dm ²)	Approximate Current density(A/dm ²)	Plating Time (min)	Plating Temp. (°C)
1-1	5.86	11.17	12.49	0.05563218	8.5955	8.6239	0.0284	7.14980257	0.1	1.79752079	1.8	15	45
1-2	6.31	11.34	11.87	0.05621218	8.0558	8.0905	0.0347	8.6457134	0.12	2.13476866	2.2	15	45
1-3	5.08	9.55	10.81	0.04133286	7.3825	7.4187	0.0362	12.2663373	0.11	2.6613208	2.7	15	45
2-1	5.94	9.76	12.36	0.05040528	8.721	8.856	0.0135	3.2110763	0.13	2.02266255	2	15	25
2-2	6.06	9.77	12.4	0.05109964	8.4602	8.4779	0.0177	4.4363639	0.12	2.02683361	2	15	30
2-3	6.13	10.15	12.11	0.05187406	7.8206	7.8475	0.0269	6.3624919	0.12	1.97716782	2	15	35
3-1	6.24	9.96	12.39	0.05257368	7.8769	7.9234	0.0465	12.3875769	0.17	3.23355717	3	15	45
3-2	5.81	10.19	11.55	0.04880078	7.6009	7.6342	0.0333	9.55694877	0.12	2.45897709	2.5	15	45
3-3	6.42	10.34	12.16	0.05403688	7.8749	7.9107	0.0358	9.27885844	0.11	2.03564677	2	15	45
4-1	6.31	14	17.11	0.08716882	9.2309	9.2735	0.0426	6.84463384	0.13	1.49135895	1.5	15	45
4-2	6.5	14.58	17	0.090626	10.4509	10.4837	0.0328	5.06900617	0.09	0.99309249	1	15	45
4-3	6.12	13.81	16.71	0.0835095	9.9606	9.979	0.0184	3.08591335	0.04	0.47898742	0.5	15	45
5-1	7.15	13.65	17.18	0.0909883	9.7085	9.7511	0.0426	6.55731182	0.18	1.97827633	2	10	45
5-2	5.95	14.11	16.28	0.08210626	9.1752	9.23	0.0548	9.34772821	0.17	2.07048768	2	15	45
5-3	6.36	11.67	14.17	0.06594126	9.2859	9.3353	0.0494	10.4923192	0.13	1.97145156	2	20	45
6-1	6.59	10.09	12.75	0.05583262	8.4414	8.4577	0.0163	4.08885194	0.11	1.97017442	2	5	45
6-2	6.32	11.42	12.82	0.05992024	8.3949	8.4764	0.0815	19.0495996	0.12	2.00266221	2	30	45
6-3	5.4	10.74	11.93	0.05010924	8.6461	8.791	0.0449	8.54955681	0.1	1.99563993	2	15	40
7-1	6.45	15.04	17.17	0.09319826	10.3093	10.3812	0.0719	9.40940265	0.19	2.03866467	2	15	50
7-2	6.26	10.16	12.54	0.05390168	8.7517	8.7987	0.047	9.63614872	0.11	2.04075272	2	15	55
7-3	6.37	14.24	17.07	0.0885043	9.3095	9.3996	0.0901	10.32820995	0.18	2.03379949	2	15	65

Parts of original data of samples for Tafel test:

Sample number	X (mm)	Y (mm)	Z (mm)	Surface area (dm ²)	Original weight (g)	Electroplated Weight (g)	Weight difference (g)	Average coating thickness(μm)	Current (A)	Current density (A/dm ²)	Approximate Current density(A/dm ²)	Plating Time (min)
11-1	5.82	10.96	12.25	0.05386844	8.5461	8.5717	0.0256	6.65590868	0.08	1.48509962	1.5	15
11-3	5.16	9.57	10.64	0.04122168	7.3392	7.3613	0.0221	7.50876261	0.08	1.94072634	2	15
13-1	6.22	9.98	12.15	0.05178112	7.8438	7.8954	0.0516	13.9566134	0.13	2.51056756	2.5	15
13-2	5.64	9.53	10.29	0.0419697	7.3635	7.3947	0.0312	10.4116729	0.11	2.62093844	2.5	15
14-1	6.23	13.83	16.96	0.0852757	9.193	9.24	0.047	7.71923661	0.17	1.99353391	2	15
14-2	6.32	14.39	16.84	0.08794024	10.4115	10.4753	0.0638	10.1609618	0.18	2.04684454	2	20
14-3	6.04	13.77	16.31	0.08125438	9.9212	10.0075	0.0863	14.8753024	0.16	1.96912462	2	25
15-1	7.15	13.54	16.98	0.08962544	9.652	9.7061	0.0541	8.45410724	0.18	2.00835834	2	15
15-2	5.73	13.58	16.01	0.0773933	8.9468	9.0143	0.0675	12.2152454	0.16	2.06736242	2	20
15-3	6.27	11.45	13.85	0.0634427	9.2208	9.2864	0.0656	14.4818475	0.13	2.04909312	2	25
17-1	6.44	14.92	17.03	0.09196912	10.3026	10.3385	0.0359	5.4670646	0.14	1.52225008	1.5	15
17-3	6.26	14.09	16.91	0.08646438	9.2463	9.2921	0.0458	7.41873801	0.17	1.96612755	2	15

