eProceedings Chemistry 4 (2019) 46-52

eISSN 2550-1453 http://eproceedings.chemistry.utm.my/

Electroless nickel-phosphorus plating (KFJ-20) on copper and iron substrates

Rawaida Liyana Razalli[a], Che Rozid Mamat[a]*, Aishah Abdul Jalil[b], Siti Nur Aisyah Jalaluddin[a]

[a]*Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia*
[b]*School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia*
**Corresponding Author: che@kimia.fs.utm.my*

Article history:
Received 22 June 2019
Accepted 19 July 2019

GRAPHICAL ABSTRACT

Process of plating copper substrate in KFJ-20 (EN)

ABSTRACT

Electroless Nickel (EN) plating is an autocatalytic method, a chemical reduction of a nickel ion in an aqueous solution with the presence of reducing agent that contain sodium hypophosphite (SHP) and where the deposition occurs without the use of electric current. The electroless Ni-P needs to be deposit onto copper but due to passivity of the metal, pretreatment and activation of copper surface need to be carried out. Thus, the optimum operation condition of Ni-P bath, palladium activator and deposition rate of Ni–P were studied. There are two substrates chosen for this study, namely iron and copper, to be coated by nickel. The source of Nickel is from KFJ-20 (Uyemura, Japan). KAT-450 activator which contained the palladium was used to generate active sites on the copper surface and also assist the nickel to deposit on copper substrate. Before undergo plating process, the iron and copper substrate undergo pre-treatment process such as cleaning, soft-etching, acid dipping and activation. Ni-P deposited on iron and copper substrate in order to distinguish the effectiveness of palladium as an activator. The optimum deposition condition was found to be on iron substrate at pH 7.5 while copper substrate at pH 5 with 3 min dipping time in activator, 20 min deposition time and 98.0 ˚C bath temperature. This indicate that palladium activation (KAT-450) is a good activator that can deposit nickel onto copper substrate. We also observed the deposition of nickel in a uniformly nodular and no cracking on the surface by field emission scanning electron microscope (FESEM).

Keywords: Electroless plating, nickel-phosphorous, copper, iron

© 2019 Dept. of Chemistry, UTM. All rights reserved

1. INTRODUCTION

EN plating is known as an autocatalytic method or chemical reduction of a nickel ion in an aqueous solution which contained a reducing agent and the subsequent deposition of the metal without the use of electric current. The thin film nickel deposition can be carried out through the oxidation of a chemical compound (reducing agent) that present in the solution itself. The reducing agent is used to supply an internal current and the most common reducing agent used in EN process is sodium hypophosphate (SHP). EN helps to improve the physical state of the surface material for copper or other metal in which it gives high hardness, excellent corrosion and wear resistance, thickness uniformity and good lubricity [1]. The equation below is the of deposition reaction that involve anodic and cathodic reaction [2].

Anodic reaction

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H^+ + 2e^- \quad (1)$$

Cathodic reactions

$$H_2PO_2^- + 2H^+ + e^- \rightarrow P + 2H_2O \quad (2)$$

$$2H^+ + 2e^- \rightarrow H^2 \quad (3)$$

$$Ni^{2+} + 2e^- \rightarrow Ni \quad (4)$$

Numbers of research works have reported in attempt to improve the corrosion resistance of metal using EN plating. However, there is some limitation for EN, for instance, it cannot be deposited onto copper substrate due to the properties of copper (passive metal). Hence, KAT-450 which contained the palladium have been used to generate active sites on the copper surface for hypophosphite oxidation and assist the nickel to deposit on copper substrate. Even KFJ-20 have an excellent property and been utilized widely in EN application, it cannot provide a nice deposition because the electroless plating process itself is unstable. Its stability fully depends on the substrate material, the pretreatment process, the type of solution used and the pH and temperature during plating [3]. Thus, capability of nickel to deposit on copper substrate at optimum conditions need to be focused in this study. This research will emphasize on applying palladium activation pre-treatment method on copper surface and optimizing the parameters such as pH, concentration and temperature of the bath in order to get the optimum deposition rate of EN plating.

2. EXPERIMENTAL

The experiment was divided into three main stages. The first stage was focused on the preparation of pre-treatment solutions, nickel strike solution and KFJ-20. The pre-treatment solutions prepared were C-4000 (cleaning solution), soft etching, pre-dipping, and acid dipping. In the second stage, the copper substrate was undergoing plating test. The sample (copper substrate) was cut into 5 cm × 5 cm sized. It started with the pre-treatments first, continue with palladium activation by dipping in KAT-450 for 3 min and lastly, plating in KFJ-20 for 20 min with the condition of 98.0 ℃ and 200 rpm of the KFJ-20 bath. The deposition speed of nickel layer was calculated and recorded. Variable parameters such as pH, temperature, plating time of KFJ-20 and KAT-450 activator dipping time being tested in this research. Table 1 shows the chemical composition of pre-treatment process. Later, in stage three, the copper substrate with and without nickel strike activation were characterized to study the surface morphology of the substrate by using FESEM.

Table 1. Operating conditions for pre-treatment process

Stage	Chemical
Cleaner	C-4000T
Soft etching	$Na_2S_2O_8$ 100 g/L 98% H_2SO_4 10 g/L
Pre-dip	98% H_2SO_4 30 g/L
Acid dipping	98% H_2SO_4 100 g/L
Activation	KAT-450 100 mL/L

3. RESULTS AND DISCUSSION

3.1. Effect of KAT-450 Activator Dipping Time on Plating

Activation is a vital step to ensure the electroless nickel deposition can take place on a copper surface. According to Huh et al. (2015), the number of palladium (Pd) nanoparticles increased with increase Pd activation time [4]. The weight of iron substrate increased after being plated, showing that nickel from KFJ-20 bath was deposited on iron with aid of KAT-450 activator. Figure 1 shows the plot of activator dipping time versus deposition rate on (a) iron and (b) copper plate. From the plot, there are no specific increase/decrease trend of deposition rate by increasing the activator dipping time. However, the plot shows the optimum deposition rate at 2 min and 3 min of activator dipping time with 14.97 and 13.76 micron/h while the lowest deposition rate was shown at 4 min of activator dipping with 6.94 micron/h. This meant that a larger quantity of Pd nanoparticles did not result to have a good deposition rate.

Figure 1 (b) shows deposition of nickel on copper substrate. The optimum deposition with 10.95 micron/h observed at min 4 while lowest deposition rate occurred at min 2. From the plot, the copper substrate showed an opposite result against the iron substrate with optimum deposition at 4 min activator dipping time. As we know, copper is a noble metal than iron. Thus, the reaction of palladium to take place on the copper substrate was slower compared to an iron substrate.

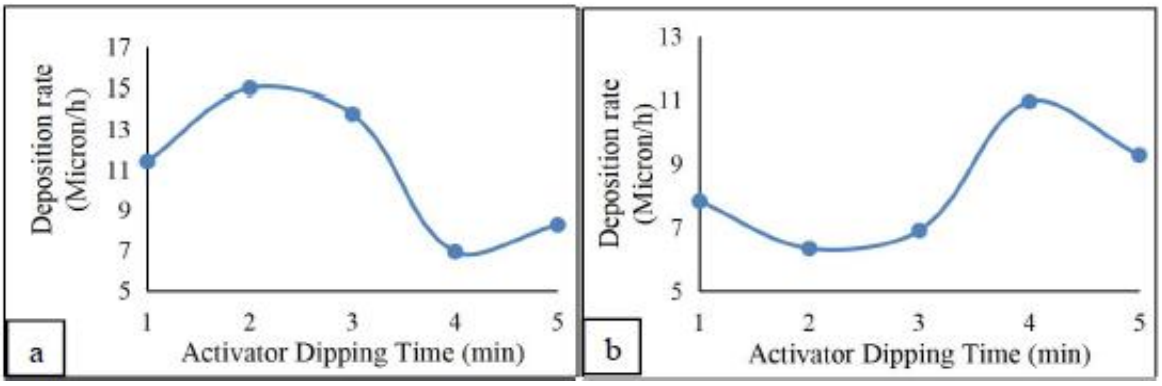

Figure 1. Graph of activator dipping time versus deposition rate on (a) iron and (b) copper plate

3.2. Effect of KFJ-20 Bath Deposition Time on Plating

In EN plating, the deposition time of plating is one of the important parameters that can change the deposition rate of the substrate. For the optimization of deposition time, both copper and iron substrates were used. The deposition rate of nickel on iron substrate is shown in Figure 2 (a). A trend was observed where the deposition rate decreased from 20 min until 40 min for both with and without KAT-450. Further increase deposition time to 60 min slowly increased the deposition rate. However, it cannot guarantee that the nickel deposition stable if deposition time increase to 70 min. It can be concluded that the best deposition time for iron without KAT-450 is at 20 min with 16.10 micron/h and for iron substrate with KAT-450 is at 20 min with 13.35 micro/h.

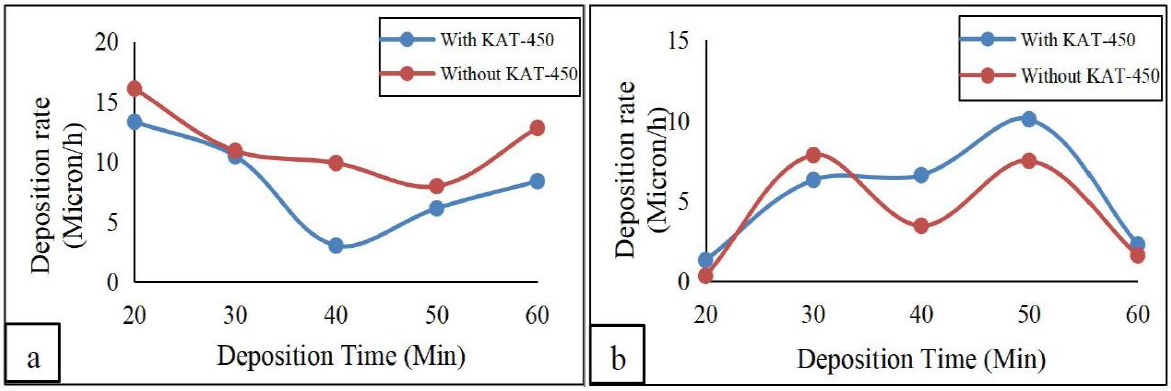

Figure 2. Deposition rate graph of (a) iron plate and (b) copper plate versus deposition time

Based on Figure 2 (b), the result for copper substrate is unusual where there is no exact trend showing the increasing or decreasing of the deposition rate. The minimum deposition rate on copper for both with and without KAT-450 are at 20 min where there was only a thin layer of nickel deposited on copper. During the plating process, we observed that the reaction on the copper surface will start about 5 to 10 min after the copper substrate was dipped into the nickel bath. This probably caused by the surface of copper is not completely activate and the nickel cannot directly interact with the copper. Highest deposition rate was observed at 50 min by addition of KAT-450 with 10.11 micron/h followed by deposition rate at 30 minutes. However, 50 min deposition time is too time consuming. Hence, we considered 30 min as the optimum deposition time in which with addition of KAT-450 and without activation produced 6.33 micron/h and 7.88 micron/h, respectively. During plating process around 50 to 60 min, the bath solution turned cloudy indicate the nickel in the solution itself start to form small flakes instead of only form the layer of nickel on the metal substrate. It showed that the nickel bath is unstable at 50 to 60 min of plating, so we believe that Uyemura's technique or method to maintain 20 min as deposition time is the best.

3.3. Effect of pH Value in KFJ-20 Bath on Deposition Rate

The plating test of iron and copper substrate in different pH value of nickel bath was conducted to determine the trend of deposition rate of the nickel layer onto copper substrate. The copper substrate has undergone plating test with eight different pH values as shown in Figure 3.

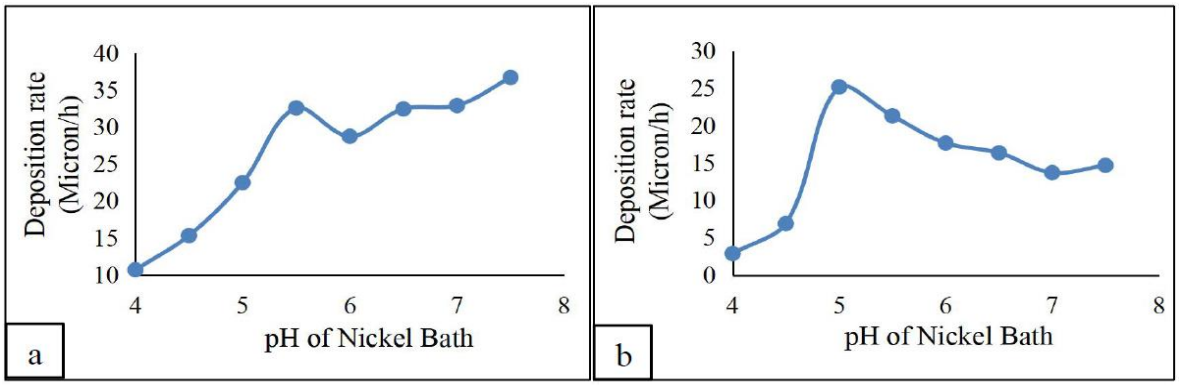

Figure 3. Graph of deposition rate of (a) iron and (b) copper plate versus pH nickel bath

In this experiment, the pH value of the nickel bath was adjusted by using NaOH or 6 M H_2SO_4 solution before plating of copper substrate. As shown in Figure 3 (a), the trend of the deposition rate of nickel layer on the iron substrate increased from pH 4.0 to 5.5 then it drops a little bit and increased until pH 7.5 with the optimum deposition rate of 36.72 micron/h. On the other hand, Figure 3 (b) shows increased in deposition rate from pH 4 to pH 5 with the optimum deposition rate of 25.18 micron/h then the deposition rate keeps decreasing until pH 7.5. At pH more than 5, the nickel bath might be not suitable and unstable for the copper plating process. Hence, pH 5 is chosen as optimum and the best pH condition.

3.4. Effect of KFJ-20 Bath Temperature on Plating

Based on a previous study on the effect of temperature on nickel coating, it was found that there was no apparent reaction at below 50.0 °C [5]. While another study suggests that acid hypophosphite plating solutions need to be operated between 85.0 and 90.0 °C and if the temperature exceeds 90.0 °C, the solution has the tendency to substrate out or even solution decomposition increased [6]. However, too high temperature will cast film formation. In addition, a thick film will reduce the adhesion strength of the coating to the substrate. Therefore, in order to obtain an excellent film, the exact temperature and film thickness should be best selected.

It is expected that by using Pd, the nickel can be deposited on the copper substrate and have a good surface coating. Figure 4 (a) shows the deposition rate of plating on an iron substrate with various temperature. For both condition of the iron substrate with activation and without activation, the results showed the optimum deposition rate occurs at 98.0 °C with production of 14.05 and 16.42 micron/h, respectively. It was observed deposition rate increased from 90.0 to 98.0 °C for both situations and decreased when temperature reaches 100.0 °C. At 100.0 °C, the solution started to evaporate since distilled water was used as the solvent. Figure 4 (b) shows the effect of bath temperature on the deposition rate of copper substrate and the deposition rate increased with increasing of the bath temperature. At 90.0 °C, no nickel deposited on the copper surface for both situations, but the reaction shows increasing in weight of nickel deposit from 92.0 °C to 100.0 °C. The best deposition rate appeared at 100.0°C h with 11.02 micron/h. This shows that the activator successfully deposit nickel on the iron substrate.

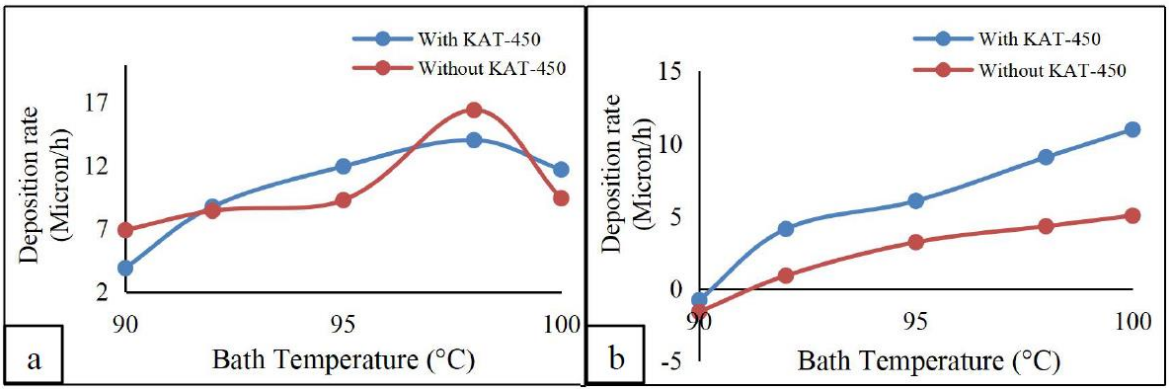

Figure 4. Graph of deposition rate on (a) iron and (b) copper plate vs bath temperature

3.5. Analysis of Palladium Concentration in KAT-450

The calibration curve for palladium was constructed by plotting plot of absorbance versus concentration. A linear regression by the least square method was then applied. The value of the determination coefficient shown linearity calibration curve which R^2 = 0.9991. Table 2 shows the concentration and absorbance for standard solution of palladium while Figure 5 shows a plot of absorbance versus concentration. From the plot, the unknown concentration of palladium in the KAT- 450 activator can be determined. The concentration of palladium in KAT-450 is 2.506 mg/L with 0.0657 absorbance after 50x of dilution. In every EN plating process, the amount of activator that being used was 25 mL KAT-450 in 250 mL of distilled water. So, the concentration of palladium in the activator used throughout pre-treatment is 12.53 mg/L with 0.328 absorbance. This product is already commercialized and give a positive deposit on the copper. Hence, the prepared concentration is good enough for the nickel to be deposited on substrate.

3.6. Surface Morphology of Nickel Coatings

In this study, the deposition of Ni layer on the iron and copper substrate with and without activation of KAT-450 were characterized using Field Emission Scanning Electron Microscope (FESEM). FESEM was used to study the surface morphology of the coated and uncoated iron and copper substrate. We use FESEM instead of SEM as FESEM can provide better quality image with high magnification and resolution due to different type of beam gun. SEM used a thermionic beam gun whereas FESEM using an electromagnetic that is superior. Figure 6 presents the morphology of uncoated and coated iron substrate at various magnification. The uncoated iron substrate seems too rough with scratch and imperfections. Thus, surface pre-treatment of the substrates must be done before electrodeposition process in order to remove the contaminants and oxide layer from the substrate surface. The present of this impurities can affect the bonding between coating and substrate resulting in poor adhesion. It was proved that after pre-treatment process, the substrate surface become smoother and cleaner from the larger imperfection in which this enhanced the adhesion of the coating to the substrate [7].

Table 2. Concentration and absorbance for standard solution of palladium

Solution	Concentration (ppm)	Absorbance
Blank	0.000	0.0000
Calibration standard 1	1.052	0.0276
Calibration standard 2	2.061	0.0541
Calibration standard 3	3.084	0.0809
Calibration standard 4	3.965	0.1040
Calibration standard 5	4.940	0.1296

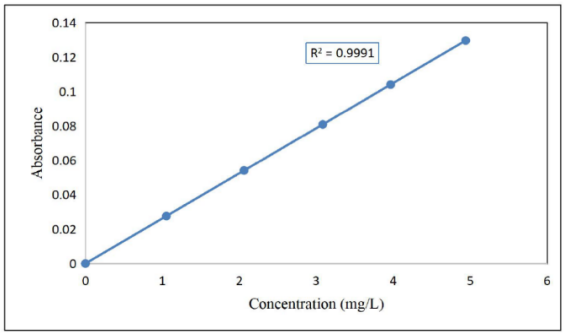

Figure 5. Plot of absorbance versus concentration

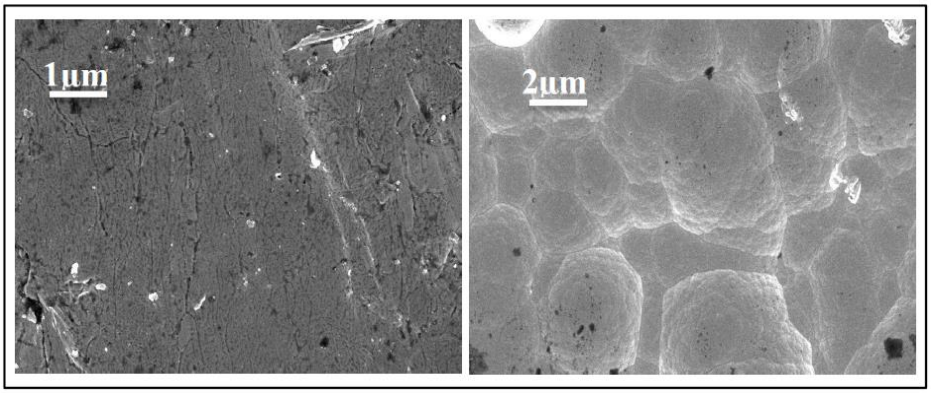

Figure 6. FESEM micrograph of (a) uncoated and (b) coated iron plate at 2500 magnification

The coated iron nickel was produced with deposition of Ni-P in 20 min at pH 7.5. The iron substrate exhibits a smooth and compact surface, which is very different compared to surface of uncoated iron substrate. A uniform distribution of small nickel particles disperses on the iron substrate with spherical like structures was observed. In magnification of 2500x, the coated iron showed the continuation deposition of nickel stacking on the iron substrate surface in which a new nickel layer form on the old deposited nickel layer. Further increased of pH in nickel bath not only increased the size of old particles, it also increased the thickness of the nickel film on the substrate.

For the uncoated copper substrate, there were dislocation or imperfection of crystal and the dark spot is not fully disappeared even after undergoing pre-treatment process to remove the impurities. Further study for pre-treatment of copper substrate might be needed in order to get a clean surface before undergo plating process to get the best adhesion of nickel on the copper substrate. The surface morphology of electroless Ni-P coating deposited on the copper substrate for 20 min at pH 5 with 25.18 micron/h is shown in Figure 7 (b). It can be seen that the Ni-P coating was compact, and uniformly covered the copper substrate surface, and there were no obvious defects such as pores or cracks on the coating surface. The Ni-P coating deposited for 60 min showed a spherical nodular-like structure, which looks similar to that deposited on the iron substrate at pH 7.5 with a higher deposition rate with 36.72 micron/h (Figure 6). However, the structure on the iron substrate looks more compact compared to the structure on the copper substrate surface. Thus, when the deposition rate is higher meaning that the mass of the nickel substrate is more uniform and looks thick under the microscope. Moreover, the Ni-P crystals cell size deposited on the copper substrate surface appeared larger than that deposited on the iron substrate. The black part and dark spot are not the defects as it also presents from the uncoated metal surface.

4. CONCLUSION

The focus in this research is to deposit electroless Ni-P plating on the copper substrate by using palladium activation technique. The operating parameter including the dipping time of KAT-450 activator, temperature, and a deposition time of electroless Ni-P, was investigated. Sulphuric acid was diluted in a few conditions and used for soft etching, pre-dipping and acid dipping. It is a pretreatment process for the copper substrate. The electroless Ni-P bath or KFJ-20 bath solution is also prepared according to the optimum condition. The copper substrate was optimized at different temperature and deposition time of the bath solution. Besides copper, the iron substrate also used to compare the effectiveness of palladium activator, deposition speed and surface morphologies. The best value of temperature for the copper substrate is at range 92.0 ˚C to 98.0 ˚C and the best value of deposition time is at range 20 min to 30 min at pH 5. While the optimum condition for iron substrate is at 90.0 ˚C to 98.0 ˚C, 20 min of dipping time and at pH 7.5. Surface morphologies by FESEM revealed the spherical particles of copper were deposited on the iron and copper substrate. The observation of surface morphology on the iron and copper substrate also revealed that the number of the nodular-shape particles will increase and thicker with increased deposition speed. From the result, the nickel is deposit on both copper substrate that undergoes with and without the activation (KAT-450) because electrons could be transferred via the conductive Cu. However, the copper substrate with activation shows a higher deposition rate compared to without palladium activation.

REFERENCES

[1] Zhang, H. Z., Zou, H., Lin, J., Tang, B., Surf. Rev. Lett. 21, 200-206 (2014).
[2] Mainier, F., Fonseca, M. C., Tavares, S., Pardal, J. M., J. Mater. Sci. Chem. Eng. 12-20 (2013).
[3] Hanim, M. A. A., Mater. Sci. Mater. Eng. 3, 220-229 (2017).
[4] Huh, S. H., Choi, S. H., Shin, A. S., Jeong, G. H., Ham, S. J., Kim, K. S., Circ. Wor. 41, 137-146 (2015).
[5] Shao, Z., Guo, J., Liu, P., Anti-Corros Method M. 63, 256-261 (2016).
[6] Mallory, G. O., Electroless Plating: Fundamentals and Applications, American Electroplaters and Surface Finishers Society, Orlando, FL, 1990, pp. 57-99,
[7] Isa, N. N. C., Mohd, Y., Zaki, M. H. M., Mohamad, S. A. S., Int. J. Electrochem. Sci. 12, 6010-6021 (2017).