EFFECT OF COATING THICKNESS ON CORROSION BEHAVIOR OF ELECTROLESS QUATERNARY NICKEL ALLOY DEPOSIT IN 3.5 wt% NaCl SOLUTIONS

M. Zaimi[1] and K. Noda[2]

[1]Faculty of Manufacturing Engineering,
Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya,
76100 Durian Tunggal, Melaka, Malaysia.

[2]Department of Materials Science and Engineering,
Shibaura Insitute of Technology, 3-7-5 Toyosu, 135-8548, Tokyo Japan.

Email: *[1]mdzaimi@utem.edu.my; [2]knoda@sic.shibaura-it.ac.jp

ABSTRACT: Metal additive can be added into electroless Ni-P alloy matrix to improve various characteristic, particularly corrosion resistance. Previous studies show that the decreases plating bath pH, increases the phosphorous content in the nickel alloy coatings, improving the corrosion resistance in 3.5 wt% NaCl solutions. However, the true effect of various plating bath pH on corrosion resistance of the nickel alloy is need to be study due to its effect on deposition rate. In this study, electroless quaternary nickel alloy is deposited on pure iron coupon with copper and zinc as metal additive in the plating bath solution. The deposition is done at various plating bath pH and producing approximately the same thickness to verify the plating bath pH effect. The coated coupon is then immersed into 3.5 wt% NaCl solution for anodic polarization curve measurements. From the results, the nickel alloy deposited at similar thickness exhibit almost identical corrosion potential, hence, similar corrosion resistance regardless the effect plating pH on the nickel alloy composition.

KEYWORDS: *Electroless Nickel Deposition, Ternary Alloy, Quaternary Alloy, Corrosion and Electrochemical Measurement*

1.0 INTRODUCTION

Electroless nickel (EN) alloy deposition method is widely applied in various industries such as chemical, automobile and electronics due to superior plating capability compare to other methods [1]. Nickel alloy can be deposited on any type and shape of substrate without using external current such as electro deposition [1]. Furthermore, the addition of other metal additives in electroless nickel plating bath can produce ternary and quaternary nickel alloy [2]. The addition of copper or zinc into the nickel deposit matrix has significant effect on the alloy properties, especially corrosion resistance [3, 4]. An increase of the plating bath pH in electroless nickel alloy plating bath solution decreased the phosphorous content as well as the metal additives such as copper and zinc content [5]. Furthermore, changes in plating bath pH also produced different nickel alloy with different crystallinity [6]. The inclusion of zinc and copper ion in an electroless nickel plating bath has a significant effect on the electrochemical behavior of electroless nickel alloy deposit in 3.5 wt% NaCl solution [6]. High phosphorous content in the Ni-P alloy provides a higher corrosion resistance than low phosphorous content by exhibiting wider passive areas [6].

However, all electroless nickel alloy deposits previous studies, were produced at fixed deposition times [5, 6]. It is still unclear whether the thickness of the nickel alloy's deposit has an effect on its surface crystallinity and electrochemical behavior in NaCl solution or not. It is crucial to investigate and compare the properties of various type of electroless nickel alloy deposits produced at similar thickness in order to determine which coating is superior in terms of corrosion resistance performance. In this study, electroless nickel alloy deposits deposited at approximately 5 μm thickness from in various types of plating bath solutions are compared. The thickness of the deposits was confirmed using EDX line analysis. The surface of the nickel alloy deposits was analyzed using XRD analysis to investigate the surface crystallinity. Anodic polarization measurement of each nickel alloy type is conducted to study the corrosion resistance behavior in 3.5 wt% NaCl solution.

2.0 EXPERIMENTAL METHOD

The Fe 99.5% is used as a substrate for this study. The substrate first undergoes pretreatment, which includes degreasing, cleaning and etching using ethanol, distilled water and diluted hydrochloric acid respectively. The etched substrate is then rinsed with distilled water before immersing into plating bath solution, as shown in Table 1. Electroless nickel alloy is deposited on the substrate until approximately 5 μm thickness. Deposition time of the electroless nickel alloy deposition reaction required to achieve the desired thickness is determined by using the deposition rate in the previous study [6].

The deposition time of electroless nickel alloy deposition is shown in Table 2. The deposited substrate surface is then analyzed using XRD measurement. The nickel alloy coating thickness is confirmed using EDX line analysis of the sample cross section. The electrochemical measurement of the sample is determined using three electrode cells consisting of a working electrode, counter electrode and reference electrode. The sample surface is used as the working electrode while platinum, Pt, and Ag/AgCl/KCl(saturated) are used as counter electrode and reference electrode respectively. The test solution is 3.5 wt% NaCl solutions. In the anodic polarization curve measurement, the measurement started at its natural potential until 1.0 V at a scanning rate of 1 mV/s.

Table 1: Electroless nickel alloy deposition bath condition

Bath composition/condition	**Ni-P**	**Ni-Zn-P**	**Ni-Cu-P**	**Ni-Zn-Cu-P**
Nickel sulphate (M)	0.10	0.10	0.10	0.10
Zinc sulphate (M)		0.01		0.001
Copper sulphate (M)			0.001	0.0005
Sodium hypophosphite (M)	0.10	0.28	0.28	0.28
Trisodium citrate (M)	0.20	0.20	0.20	0.20
Ammonium acetate (M)	0.50	0.50	0.50	0.50
Bath temperature (K)	358	358	358	358
Bath pH	8.50, 9.50	8.50, 9.50	8.50, 9.50	8.50, 9.50
Stir rate (rpm)	500	500	500	500

Table 2: The deposition time of electroless nickel alloy deposition

Alloy type	**Ni-P**		**Ni-Zn-P**		**Ni-Cu-P**		**Ni-Zn-Cu-P**	
Plating bath pH	**8.50**	**9.50**	**8.50**	**9.50**	**8.50**	**9.50**	**8.50**	**9.50**
Deposition time (s)	840	600	8520	2400	990	630	1830	720

3.0 RESULTS AND DISCUSSION

The thickness of the electroless nickel alloy coating on the substrate is shown in Figures 1 to 8 using SEM and EDX line analysis. The thickness of Ni-P coating from pH 8.50 and 9.50 plating bath are approximately 5 μm. However, the thickness of Ni-Cu-P, Ni-Zn-P and Ni-Zn-Cu-P alloy coatings exceed 5 μm, and are between 6 to 10 μm. This shows that the deposition of Ni-P alloy can easily be controlled, but for Ni-Cu-P, Ni-Zn-P and Ni-Zn-Cu-P show otherwise. The addition of copper and zinc ion in an electroless nickel plating bath solution have a different and much more complex reaction mechanism that require further understanding of copper and zinc ion behavior in EN bath [7]. As explained in several articles, copper and zinc cannot be reduced by hypophosphite ion alone and require an activated nickel surface in order to be deposited [7, 8]. Since deposited nickel acts as a catalyst for copper and zinc reduction, the total deposition reactions need to be studied separately.

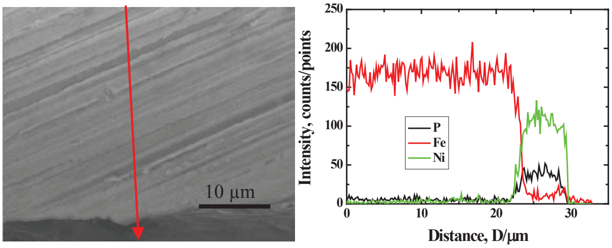

Figure 1: Cross section EDX line analysis of electroless Ni-P alloy deposition from pH 8.50 bath. (a) SEM images, (b) EDX compositions

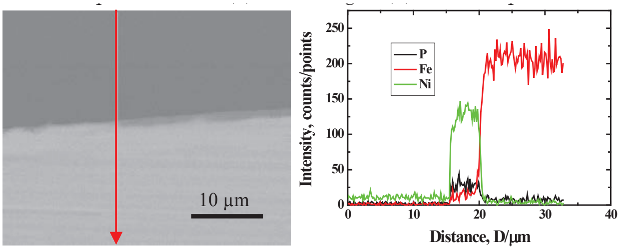

Figure 2: Cross section EDX line analysis of electroless Ni-P alloy deposition from pH 9.50 bath. (a) SEM images, (b) EDX compositions

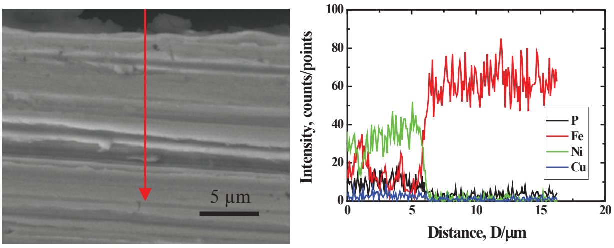

Figure 3: Cross section EDX line analysis of electroless Ni-Cu-P alloy deposition from pH 8.50 bath. (a) SEM images, (b) EDX compositions

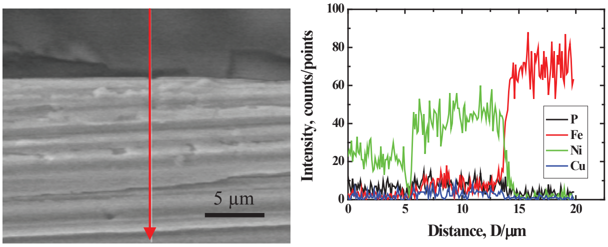

Figure 4: Cross section EDX line analysis of electroless Ni-Cu-P alloy deposition from pH 9.50 bath. (a) SEM images, (b) EDX compositions

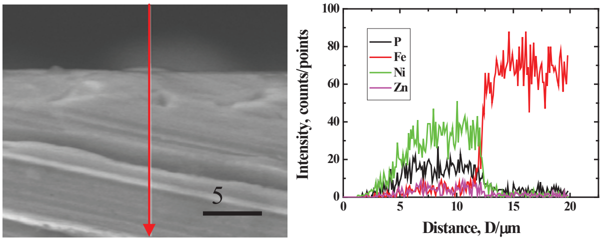

Figure 5: Cross section EDX line analysis of electroless Ni-Zn-P alloy deposition from pH 8.50 bath. (a) SEM images, (b) EDX compositions

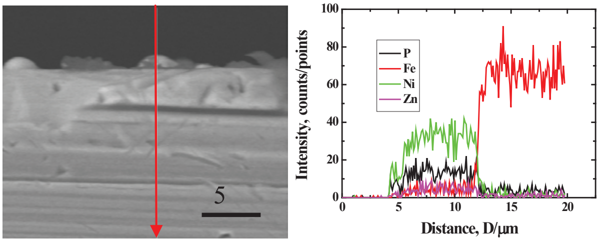

Figure 6: Cross section EDX line analysis of electroless Ni-Zn-P alloy deposition from pH 9.50 bath. (a) SEM images, (b) EDX compositions

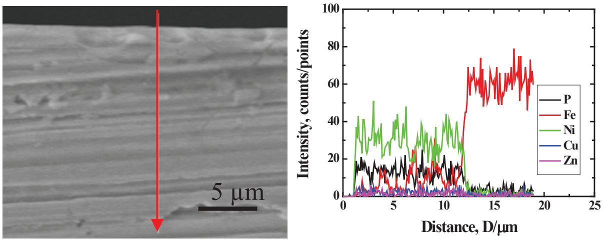

Figure 7: Cross section EDX line analysis of electroless Ni-Zn-Cu-P alloy deposition from pH 8.50 bath. (a) SEM images, (b) EDX compositions

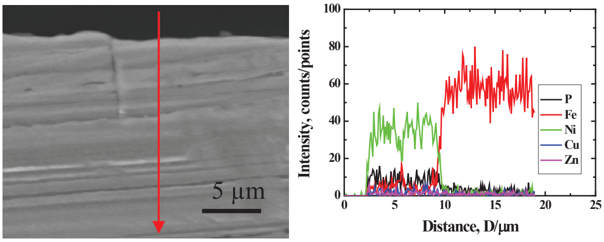

Figure 8: Cross section EDX line analysis of electroless Ni-Zn-Cu-P alloy deposition from pH 8.50 bath. (a) SEM images, (b) EDX compositions

Each electroless nickel alloy deposit XRD measurement result is shown in Figure 9. Both Ni-P deposits from pH 8.50 and 9.50 plating baths have similar thickness and show different crystallinity, where at pH 9.50, Ni-P shows a higher and sharper peak than at pH 8.50. This reveals that the crystallinity of Ni-P alloy does not decrease as suggested by Zaimi and Noda [6], rather the effect may be caused by the increase in coating thickness. Hence, it can be proven that the addition of phosphorous will decrease the Ni-P alloy crystallinity.

The increase of plating bath pH on electroless Ni-Cu-P alloy deposition bath increases the coating crystallinity [6]. From Figures 3 and 4, it can be seen that the thickness of Ni-Cu-P from the pH 8.50 bath is lower than that from the respective pH 9.50. Also, the Ni-Cu-P alloy from the pH 9.50 bath has higher crystallinity than the respective alloy from the pH 8.50. Therefore it can be concluded that the increase of plating bath pH in the electroless Ni-Cu-P alloy deposition bath increases the crystallinity of the coating until it reaches a certain thickness. The increase in of Ni-Cu-P alloy crystallinity as plating bath pH increases, is possibly due to the effect of the lowered phosphorous content and the effect of Cu as an EN accelerator. The phosphorous content decreases significantly due to the increase in plating bath pH, furthermore, an increase in deposition rate can also increase the crystallinity of the coating.

The effect of Zn addition in electroless nickel alloy matrix on coating crystallinity can be seen in Figure 9. The peak of Ni-Zn-P alloy deposit produced at bath pH 9.50 has similar intensity than pH 8.50, hence similar crystallinity. The crystallinity of Ni-Zn-P alloy deposit is considered the lowest compare to other nickel alloy deposit. From these results, it can be known that the addition on zinc in nickel alloy deposit decreased the crystallinity of the coating. This is maybe caused disorientation of crystal structure by zinc (hcp) that has not good metal solubility with nickel (fcc) which produced amorphous like structure.

Low crystallinity by zinc addition in electroless Ni-Zn-Cu-P alloy deposit is shown in Figure 9. The crystallinity of Ni-Zn-Cu-P alloy deposit from plating bath pH 9.50 is slightly higher than pH 8.50. The slight increase of crystallinity of the nickel alloy deposit is probably caused by the existence of copper(II) ion in plating bath solution that act as accelerator and stabilizer for electroless nickel deposition reaction [9].

Anodic polarization measurement results of electroless Ni-P alloy deposit from pH 8.50 and pH 9.50 is shown in Figure 10(a). From the results, Ni-P alloy deposit from pH 8.50 plating bath has less noble corrosion potential than pH 9.50. However, Ni-P alloy deposit form pH 8.50 plating bath has wider passive area than pH 9.50. The Ni-P alloy deposit from pH 9.50 shows no passive area. This is due to Ni-P from pH 8.50 has higher phosphorous content than in pH 9.50 which contribute higher corrosion resistance behavior in NaCl solution.

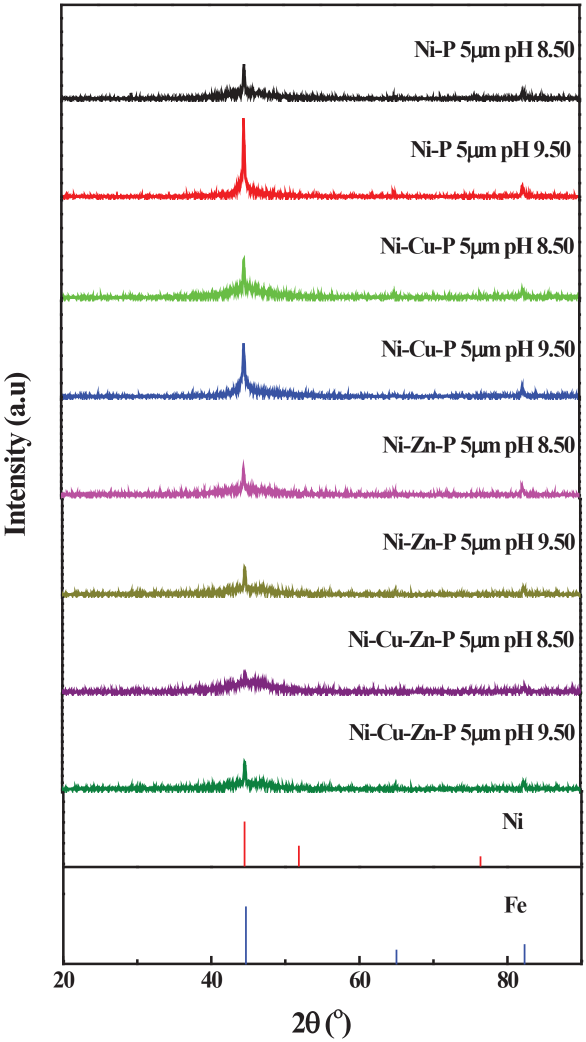

Figure 9: XRD measurement results of electroless Ni alloy deposit from pH 8.50 and 9.50plating bath solutions

Figure 10(b) shows the anodic polarization measurement result of electroless Ni-Cu-P alloy deposit in NaCl solution. From Figure 3 and 4, the thickness of Ni-Cu-P alloy deposit from pH 8.50 and 9.50 are approximately 5.5 μm and 8.8 μm respectively. The corrosion potential of Ni-Cu-P from pH 8.50 bath is much noble than pH 9.50. Both Ni-Cu-P alloy show very narrow passive area compared to Ni-P form pH 8.50 bath. However, in anodic polarization curve measurement result in the earlier work passive area of electroless Ni-Cu-P alloy deposit can be observed [6]. Difference in polarization curves behavior occurred possibly due to the large difference of thickness where the Ni-Cu-P alloy deposition time is much longer compare to Ni-Cu-P alloy deposition time in Table 2 [4]. From these results, it can be suggested that electroless Ni-Cu-P alloy deposit requires thickness more than 8 μm to exhibit better corrosion resistance in NaCl solutions.

From Figure 5 and 6, the thickness of Ni-Zn-P alloy deposit produced from pH 8.50 and pH 9.50 baths are approximately 7.25 μm and 6.25 μm. Anodic polarization curves behavior of electroless Ni-Zn-P alloy deposit in NaCl solutions is shown in Figure 12. The polarization curves of both Ni-Zn-P alloy deposit from pH 8.50 and pH 9.50 plating bath exhibits similar behavior, which, are no passive area and low corrosion potential. This shows that the addition of zinc(II) ion in electroless nickel alloy plating bath solution produced the Ni-Zn-P alloy deposit with low corrosion resistance in 3.5 wt% NaCl solutions compare to Ni-P and Ni-Cu-P alloy deposit.

The thickness of electroless Ni-Zn-Cu-P alloy deposit produced from pH 8.50 and pH 9.50 plating bath shown in Figure 7 and 8 are approximately 10.5 μm and 7.8 μm respectively. Electroless Ni-Zn-Cu-P alloy deposit also shows anodic polarization behavior in NaCl solutions similar to Ni-Zn-P alloy deposit that is shown in Figure 13. The Ni-Zn-Cu-P alloy has lower corrosion potential compare to Ni-Zn-P alloy deposit. The existence of zinc in electroless Ni-Zn-Cu-P alloy deposit matrix decreased the corrosion resistance of the alloy significantly compare to Ni-P and Ni-Cu-P alloy deposit [6]. Although the thickness and phosphorous content of Ni-Zn-Cu-P alloy deposit for pH 8.50 bath are higher than pH 9.50, as potential move towards anodic area, rapid dissolution without passive area can be observed. As a conclusion, high phosphorous content and thickness have no effect on electroless Ni-Zn-Cu-P alloy corrosion resistance performance.

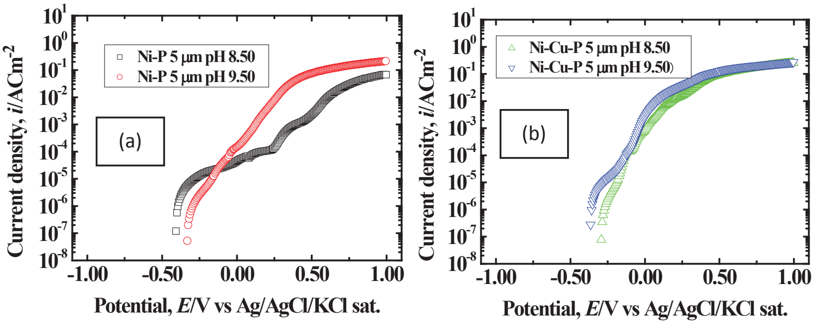

Figure 10: Anodic polarization behavior of electroless Ni alloy deposit in 3.5 wt% NaCl solution. (a) Ni-P (b) Ni-Cu-P

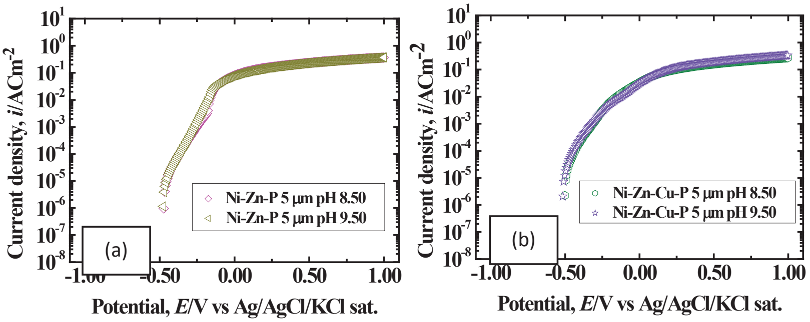

Figure 11: Anodic polarization behavior of electroless Ni-P alloy deposit in 3.5 wt% NaCl solution. (a) Ni-Zn-P (b) Ni-Zn-Cu-P

4.0 CONCLUSION

Composition of electroless nickel alloy deposit and coating thickness has a significant effect on the alloy surface crystallinity. Phosphorous and zinc disorient the crystal structure of nickel deposit matrix, hence produced amorphous like surface. From anodic polarization curve measurements, electroless Ni-P and Ni-Cu-P alloy deposit have effective corrosion resistance in 3.5 wt% NaCl at thickness 5 µm and above. At a thickness from 6 to 10 µm, electroless Ni-Zn-P and Ni-Zn-Cu-P alloy deposit show almost the same anodic polarization behavior despite having different thickness and composition.

ACKNOWLEDGMENTS

The author would like to thanks University Teknikal Malaysia Melaka (UTeM) and Yayasan Pelajaran Mara (YPM) for the Doctorate scholarship. Also, special acknowledgement to Professor Dr. Kazuhiko Noda for the generous guidance during the supervision.

REFERENCES

[1] Glenn O. Mallory and Juan B. Hadju, *Electroless Plating: Fundametals & Applications*, Orlando: American Electroplaters and Surface Finishing Society, 1990.

[2] J. N. Balaraju, V. Ezhil Selvi, V.K. William Grips, K. S. Rajam, “Electrochemical studies on electroless ternary and quaternary Ni-P based alloy”, *Electrochimica Acta*, vol. 52, Issue 3, pp. 1064 -1074, 2006.

[3] E. I. Neacsu, V. Constantin, V. Soare, P. Osiceanu, M. Popa, A. M. Popescu, “Corrosion protection of steel using ZnNiP electroless coatings”, *Recista De Chimie*, vol. 64, Issue 9, pp. 994-999, 2013.

[4] Y. Liu, Q. Zhao, “Study of electroless Ni-Cu-P coatings and their anti-corrosion properties”, *Applied Surface Science,* 228, pp. 57-62, 2004.

[5] M. Zaimi, K. Noda, “Film formation and corrosion behavior of electroless Ni-X-P alloy deposition in 3.5 wt% NaCl aqueous solution”, *The Sixth Japan-China Joint Seminar on Marine Corrosion, Proceedings* no.16, 2012.

[6] M. Zaimi, K. Noda, “Quaternary alloy of Ni-Zn-Cu-P from hypophosphite based electroless deposition method”, *ECS Trans*, vol. 45, Issue 19, pp. 3 – 16, 2013.

[7] B. Veeraraghavan, B. Haran, S. P. Kumaraguru and B. Popov, “Corrosion protection of steel using nonanomalous Ni-Zn-P coatings,” *Journal of Electrochemical Society*, vol. 150, Issue 4, pp. B131-B139, 2003.

[8] X. Gan, K. Zhou, W. Hu, D. Zhang, “Role of additives in electroless copper plating using hypophosphite as reducing agent,” *Surface and Coating Technology*, vol. 206, Issue 15, pp. 3405-3409, 2012.

[9] A. Hung, and K. M. Chen, “Mechanism of hypophosphite-reduced electroless copper plating,” *Journal of Electrochemical Society*, vol. 136, No. 1, pp. 72-75, 1989.