Stirring Effect on Surface Morphology, Structure, and Electrochemical Behavior of Electrodeposited Nickel Film on Copper Substrates

Ferry Budhi Susetyo¹,², Ahmad Faridh¹ and Bambang Soegijono¹,*

¹Dept. Physic, Universitas Indonesia, Depok 16424, Indonesia
²Mechanical Engineering, Universitas Negeri Jakarta, Jakarta 13220, Indonesia

*E-mail: naufal@ui.ac.id

Abstract. Nickel as engineering material has good corrosion resistance properties. Nickel has been deposited on copper surface by electrochemical deposition with various stirring speed. Objective on this research are to observe the effect of stirring on morphology, structure and electrochemical behavior. Electrodeposited nickel film on copper substrates was conducted with various stirring speeds (0 rpm, 75 rpm, and 150 rpm). Surface morphology was observed with Field Emission Scanning Electron Microscope (FE-SEM), structure was identified with X-ray diffraction (XRD), and electrochemical behavior was investigated by potentiodynamic polarization and cyclic voltammetry. Stirring speed effect clearly on the surface morphology, structure and electrochemical behavior. Corrosion potential and corrosion current are changes while the stirring speed is increase.

1. Introduction

Electrodeposited of nickel films has been used widely in many automotive component manufacturer to improve corrosion protection of metal coated [1-3]. Nickel films a applied at automotive component such as handle comp, fuel tank cap, and door handle etc. Chemical properties and Physical properties of metallic materials are strongly influences by surface morphology [4]. Corrosion resistance of material influences by microstructure behavior, such as surface morphology, grain size, and texture [5-7]. These are closely related to the electrodeposition parameters, such as stirring electrolyte during deposition, electrolyte pH, temperature of the electrolyte solution, current density, additive and texture of the substrate [5,8,9].

The texture crystallographic of substrate such as copper influence significantly properties of deposited nanocrystalline nickel [10]. Nickel as engineering material has good corrosion resistance in aqueous aggressive environments [11]. When nickel a deposited on copper surface, it can protect copper surface from uniform corrosion [12]. Therefore, the aims of the present work were to prepare the nickel films on copper substrates using electrodeposited technique at different magnetic stirring speeds. The Nickel films specimens was observed of by Field Emission Scanning Electron Microscope (FE-SEM), X-ray diffraction (XRD), potentiodynamic polarization and cyclic voltammetry.
2. Experimental Methods

Nickel film was prepared from a watts solution consisting of NiSO₄·6H₂O (250 g/L), NiCl₂·6H₂O (40 g/L), and H₃BO₃ (30 g/L). The electrodeposition was carried out using current density of 2 mA/cm² for 120 minutes and the solution was stirring with various speed: 0 rpm, 75 rpm, and 150 rpm. The samples were designated as Ni-0, Ni-75 and Ni-150. Nickel sheet used as anode and copper were used as cathode. Surface of the substrates were polished using silicon carbide (SiC) abrasive papers 500 up to 2000 prior electrodeposition. Observed of the nickel films morphology was using the FE-SEM. The nickel films crystal structure was identified by XRD. The XRD pattern scans with the resolution of 0.01° from 40° up to 80°. To refine the XRD pattern, software Highscore plus were used. For Electrochemical investigation (potentiodynamic polarization, and cyclic voltammetry), Digi-Ivy DY2311 were used, and Ag/AgCl as Reference Electrode (RE) and Platinum wire (Pt) as Counter Electrode (CE). The working area of test samples is 1 cm².

3. Results and Discussion

3.1. Surface Morphology

Surface morphology of samples Ni-0, Ni-75 and Ni-150 was shows in Figure 1. Those images were capture from FE-SEM with magnification 10000X. The grain size with perform stirring speed 75 rpm and 150 rpm (figure 1 (b) and 1 (c)) are bigger than without stirring. The samples without stirring show smooth surface compared to samples with stirring during electrodeposition.

![Figure 1](image-url)
3.2. Structure
The XRD patterns of nickel films with various stirring speeds are shown in figure 2. The entire sample shows peaks of (111), (002), and (022) that represents the nickel film crystallographic orientation. Increased stirring speed during electrodeposition clearly affected the reduction peak of (002). However, the increase intensity peaks of (111) are revealed on all samples. The nickel films with stirring speed 75 rpm show the intensity of (111) peak higher than the other samples. But, it decrease when stirring changes to 150 rpm.

![XRD pattern of electrodeposit nickel film samples with various stirring speed](image)

**Figure 2.** XRD pattern of electrodeposit nickel film samples with various stirring speed

Refinement results with highscore plus software of XRD pattern show that the crystal systems of nickel films are Cubic FCC with Space Group Fm-3m. Sample Ni-75 has smaller density than the other samples. The Ni-75 sample also has micro strain 0.097 % and difference chemical formula with the other samples. The refinement results with Highscore software are shown in Table 1.

| Parameter               | Samples         |
|-------------------------|-----------------|
| Crystal System          | Cubic FCC       |
| Space Group             | Fm-3m           |
| a=b=c (Å)               | 3.5284          |
| V (Å³)                  | 43.928          |
| density (g cm⁻³)        | 8.87            |
| Crystallite size (nm)   | 2791.34         |
| Micro strain (%)        | 0.000           |
| Chemical formula        | Ni 4.00         |
| Rwp (%)                 | 8.54            |
| GOF                     | 1.59            |
| Ni-0                    | Cubic FCC       |
| Fm-3m                   | 3.5284          |
| 43.917                  |
| 8.06                    |
| 2791.34                 |
| 0.097                   |
| Ni 3.99                 |
| 8.06                    |
| 2791.34                 |
| 0.000                   |
| Ni 4.00                 |
| 8.43                    |
| 1.49                    |
3.3. Electrochemical Behavior

To determine the corrosion behavior of nickel coated to copper, potentiodynamic polarization test is used for examination. In order to deep explore corrosion behavior, potentiodynamic polarization measurements was employed to observe nickel film in 3.5 % NaCl solution. The results of potentiodynamic polarization test are shown in Table 2.

| Sample | I_{Corrosion} (A) | E_{Corrosion}(V) | Corrosion Rate (mmpy) |
|--------|-------------------|-----------------|------------------------|
| Ni-0   | 1.22E-05          | -0.898          | 0.131                  |
| Ni-75  | 1.55E-05          | -0.851          | 0.167                  |
| Ni-150 | 1.78E-05          | -0.850          | 0.192                  |

Figure 3 shows of the potentiodynamic polarization behavior of nickel film deposited on copper substrat with various stirring speed in a 3.5% NaCl. Nickel film of all samples has showed behavior an active to passive and trans passive. The passive layer was form on the nickel surface is one of the key that affected the nickel films corrosion behavior [7]. Passive region shown on figure 3 are difference to each sample. Nickel film with no stirring has higher passive region than nickel film with stirring. Figure 3 also shows that nickel film with stirring has shifted to positive corrosion potential (E_{corrosion}) than nickel film with no stirring. Sample with no stirring (Ni-0) resulting smaller corrosion current and corrosion rate than the other samples (table 2).

![Figure 3. Potentiodynamic polarization curve in 3.5% NaCl solution at a scan rate 0.05 mV/s.](image)

Cyclic voltammetry characteristic of the samples were performed with scan rate 0.05mV/S at 100 mL 3.5% NaCl solution and showed in Figure 4. Cyclic voltammetry are characterized generally by the presence of anodic and cathodic peaks in the respective area, which are related to the dissolution and reduction of metallic ion [13]. Cyclic voltammetry of nickel film are shown in Figure 4, and it can be seen that swept of the potential is forward direction increase in the cathodic current and resulting difference cathodic peaks of samples. This current increment are due to reduction nickel film (Ni^{2+}/Ni) with simultaneous evolution of hydrogen as shown in equation (1).

\[ \text{Ni}^{2+} + 2e^- \rightarrow \text{Ni} \]  

(1)
On reverse sweep in direction of anodic region resulting potential around -0.65 V for oxidation peak attributed to the nickel film dissolution of as shown in equation (2).

\[ Ni \rightarrow Ni^{2+} + 2e^- \]  

(2)

Figure 4. Cyclic voltammetry curve investigated in 3.5% NaCl

4. Conclusions
The Nickel film deposit on copper substrate has been carried out successfully. The stirring speed influenced on the grain size, structure parameter and electrochemical behavior. Increasing the stirring speed clearly affected the reduction peak of (002). The electrochemical investigation shows that Ni-0 sample possessed the best corrosion resistance. The corrosion potential for samples Ni-75 and Ni-150 samples shift to more positive potential value than Ni-0 sample.

Acknowledgement
The authors gratefully acknowledge with the financial supports from the Universitas Indonesia under grant PITTA, No. 2239/UN2.R3.1/HKPO5.00/2018.

References
[1] Bazzaoui M, Martins JI, Bazzaoui EA, and Albourine A 2012 App. Surf. Sci. 258 7968
[2] Lampke T, Dietrich D, Leopold A, Alisch G, and Wielage B 2008 Surf. Coat. Technol. 202 3967
[3] Snyder DL 1997 Metal Finishing 95 29
[4] Tan L, Ren X, Sridharan K, and Allen TR 2008 Corros. Sci. 50 3056
[5] Zhao H, Liu L, Zhu J, Tang Y, Hu W 2007 Mater. Lett. 61 1605
[6] Zamanzad-Ghavidel MR, Raeissi K, and Saatchi A 2009 Mater. Lett. 63 1807
[7] Nasirpour F, Sanaeian MR, Samardak AS, Sukovatitsina EV, Ognev AV, Chebotkevich LA, Hosseini MG, and Abdolmaleki M 2014 App. Surf. Sci. 292 795
[8] Jinlong L, Tongxiang L, and Chen W 2016 Journal of Solid State Chemistry 240 109
[9] Wasekar NP, Haridoss P, Seshadri SK, and Sundararajan G 2016 Surf. Coat. Technol. 291 130
[10] Ebrahimi F, and Ahmed Z 2002 Mater. Charact. 49 373
[11] Guiñón-Pina V, Igual-Muñoz A, Garcia-Anton J 2009 Corros. Sci. 51 2406
[12] Zhang W, Yu Z, Chen Z, and Li M 2012 Mater. Lett. 67 327
[13] Nath P, Sahu DK, and Mallik A 2016 Surf. Coat. Technol. 307 772