Effect of Temperature on Electrodeposited Nickel Nitride Composite Coatings

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Abstract. In the present study, the effect of temperature during electrodeposition of Ni-TiN/\(\text{Si}_3\text{N}_4\) composite coatings have been studied. The electrodeposition process was carried out for 15 minutes with a current density of 2.5 mA/cm\(^2\). A potentiostat system completed by an electrochemical cell with three electrodes was used for the experiment. Pt wire as the counter electrode, AgCl as the reference electrode and tungsten carbide (WC) as the working electrode. The electrolyte solution used consisted of 0.17 M NiCl\(_2\).6H\(_2\)O, 0.38 M Ni\(_2\)SO\(_4\).6H\(_2\)O, 6 g/L TiN, 6 g/L AlN, 0.6 g/L Si\(_3\)N\(_4\), 40 g/L H\(_3\)BO\(_3\) and 0.6 g/L Sodium Dodecyl Sulfate (SDS). In this study, the temperature variations used were 35°C, 40°C and 45°C. The samples were characterized by using SEM, EDS, XRD and hardness test. The results show that the high electrodeposition temperature produce the smoother morphology and Ni grain refinement and lead to the increase in coating hardness.

1. Introduction

Temperature is one of the important parameters in deposition process since it influences the structure and the surface morphology of deposited coating on substrate (Aguilera et al., 2019, Kalkabay et al., 2019). In electrodeposition process, the temperature influence on the adsorption mechanism on boric acid over the electrode (Santos et al., 2007). Temperature rise increase the desorption mechanism leading an increase of the hydrogen reaction. The stronger temperature causes lower nonuniformity of crystal growth (Bograchev&Davydov, 2019). The increasing of electrodeposition temperature affect the grain size and grain orientations (Jinlong et al., 2016).

The widespread applications of electrodeposited nickel coating especially in wear and corrosion exposing depend on its mechanical properties. To improve nickel mechanical properties, addition of reinforcement particles or compound can increase the hardness and corrosion resistance (Waware et al., 2017). The incorporated particles in nickel matrix also change the morphology, crystal orientation and crystal size of coating (Kartal et al., 2017). The electrodeposition process involve the mechanism of particles or ions transport, reaction and diffusion which are function of temperature (Hao et al., 2019). The mechanism may considered for the fundamental understanding in electrodeposition morphology.

Electrodeposition of nickel nitride composite coating at room temperature has been carried out to study the structure and mechanical properties (Budi et al., 2018). It was reported that some holes and crack were observed on the coating surface and might contributed to lower hardness. Thus in this
work, an experimental investigation was conducted by electrodeposition of nickel nitride composite coating at various electrolyte temperature.

2. Experiment

Experimental equipment setting is presented in Figure 1 consisting of a potensiotstat system, power supply, magnetic hot plate stirrer (Nesco) and electrochemical cell. Ni-TiN/Si$_3$N$_4$ composite coatings have been electrodeposited by using potensiotstat for 15 minutes at various electrolyte temperature of 35, 40 and 45$^\circ$C and fixed current density of about 2.5 mA/cm$^2$. Three electrodes used in electrochemical cell were a platinum (Pt) wire as counter electrode, AgCl wire as reference electrode and tungsten carbide (WC) bar (0.42x0.42x3.82) cm as working electrode or substrate. The electrolyte was made from aqueous solution (distilled water) containing 0.17 M NiCl$_2$.6H$_2$O, 0.38 M Ni$_2$SO$_4$.6H$_2$O, 6 g/L TiN, 6 g/L AlN, 0.6 g/L Si$_3$N$_4$, 40 g/L H$_3$BO$_3$ and 0.6 g/L Sodium Dodecyl Sulfate (SDS) (from Sigma Aldrich). During electrodeposition process, the electrolyte solution was stirred with a magnetic stirrer. Before electrodeposition the substrate surface was polished by using 400-1500 mesh paper sand and cleaned ultrasonically in 96% alcohol solution and finally dried on hot plate. The surface morphology and chemical composition of the samples were investigated by using a Scan Electron Microscopy (Jeol JED-2300) with Energy Dispersive X-Ray Spectroscopy (EDS). The crystal structure of samples were investigated by using X-Ray Diffraction (XRD) Panalytical Empyrean Philips with Cu-K$_\alpha$ radiation source ($\lambda=1.54$ Å). The coatings hardness was tested by using Vickers Hardness Tester (HV-1000).

![Figure 1](image1.png)

**Figure 1.** Experimental equipment setting for electrodeposition of nickel nitride composite coating.

3. Results and Discussion

3.1. Surface Morphology and composition

The morphology of composite coating characterized by the SEM is presented in Figure 2. The image confirms the compact surface at higher electrodeposition temperature while the EDS analysis is presented in Figure 3. It confirms the existence of Ni, Ti, Si and N elements within the coating indicating the formation of Ni-TiN/Si$_3$N$_4$ composite coating. The coating surface formation is controlled by nucleation and crystal growth process (Aguilera et al., 2019). The initial nucleation provides new grains and followed by the secondary nucleation that brings another new grains and defect structural. While the crystal growth occur after the grain reach a critical size (radius). In this study, the crystal growth was occurred at temperature of 35 $^\circ$C and it became larger as temperature was increased. It was observed that the separation between grains were large.
However at further higher temperature, the grains become more compact with some holes and large grains agglomeration are observed on the surface. It seems that the nucleation and diffusion increase as the temperature is increased. The electrodeposition morphology depends on the competition between the ion transport in the electrolyte, electrochemical reaction kinetics and surface self-diffusion (Hao et al., 2019). High electrochemical reaction and diffusion lead to uniform and smooth morphology. It was reported that the first stage in the formation of electrodeposition morphology was particles nucleation on the substrate (Aguilera et al., 2019). However this stage also involved hydroxyl ions production and hydrogen formation at substrate surface. The gas production rate increased as increasing the electrodeposition temperature and it might cause some holes formation on the surface.

Based on EDS data in Table 1, the atomic percentage of Ni and Ti elements decreased while Si element increased as the electrodeposition temperature was increased. Thus, in this study, the increase of nucleation rate might be due to prominently the increase of Si element deposited on the substrate. The increase and the decrease of metal element in electrodeposition process might be due to agglomeration and collision effect (Li & Zhang, 2018).
Figure 2. SEM image of Ni-TiN/Si$_3$N$_4$ composite coatings electrodeposited at temperature of (a) 35°C (b) 40°C and (c) 45°C

Figure 3. EDS composition of Ni-TiN/Si$_3$N$_4$ composite coatings electrodeposited at temperature of (a) 35°C (b) 40°C and (c) 45°C
Table 1. EDS analysis on Ni-TiN/Si$_3$N$_4$ composite coating at various electrodeposition temperature

| Element | % Mass |
|---------|--------|
| Ni      | 14.82  |
|         | 13.9   |
|         | 7.42   |
| Ti      | 0.73   |
|         | 1.09   |
|         | 0.14   |
| Si      | 1.05   |
|         | 1.87   |
|         | 2.24   |

3.2. Crystal structure
The XRD data shows that the Ni-TiN, TiN and Ni peaks intensity are observed while Si$_3$N$_4$ peak is not revealed indicating its amorphous nature (Budi et al., 2018; Das et al., 2016). The TiN high sharp peaks indicate the high crystalline quality. TiN(111), TiN (011) and TiN (031) planes are located at $2\theta = 31.28^0$, $35.42^0$ and $63.64^0$, respectively while Ni (111) and Ni (002) planes are located at $2\theta = 44.36^0$ and $51.72^0$, respectively. The crystallite size is calculated by using Scherrer’s equation and generally, TiN crystal sizes are larger than Ni. The average Ni crystal size decreased from about 30-35 nm to below about 30 nm as the electrodeposition temperature was increased up to 45°C. The decrease of Ni crystal size at high temperature lead to the finer surface morphology as presented in Figure 2(c). The Ni crystal refinement is indicated by the diffraction peak broadening due to dominantly the incorporation of Si$_3$N$_4$ particles. The inclusion of Si$_3$N$_4$ particles and TiN particles provides nucleation site that inhibit the Ni crystal growth (Li & Zhang, 2018).
Figure 4. XRD spectrum pattern of Ni-TiN/Si$_3$N$_4$ composite coatings electrodeposited at temperature of (a) 35°C (b) 40°C and (c) 45°C.

3.3. Coating thickness

In this study, the thickness of composite coating was calculated by using equation (Sivasakthi & Sangaranarayanan, 2019) and the result is presented in Table 2:

$$\text{thickness} = \frac{\text{weight of deposition} \times 10^4}{\text{area (cm}^2\text{)} \times \text{density (g cm}^{-3}\text{)}}$$  \hspace{1cm} (1)
**Table 2.** Calculated thickness of Ni-TiN/Si\(_3\)N\(_4\) composite coating at different electrodeposition temperature

| Temperature (°C) | Deposited mass (g) | Thickness (µm) |
|------------------|--------------------|----------------|
| 35               | 0.004              | 0.818          |
| 40               | 0.176              | 36.002         |
| 45               | 0.116              | 23.729         |

It shows that the thickness of composite increases as the electrodeposition temperature is increased from 35°C to 40°C. However, it decreases as the temperature is further increased up to 45°C. The various thickness of coating was attributed by the modulation of grain size and chemical composition (Kurmanaeva et al., 2016). The coating thickness of composite was determined by crystal orientation and grain growth that provided the improvement of crystalline quality (Sivasakthi & Sangaranarayanan, 2019). However, in this study, the improvement of crystalline quality was contributed by TiN and Ni-TiN crystal rather than Ni crystal.

**3.4. Hardness**

The hardness measurement result of Ni-TiN/Si\(_3\)N\(_4\) at various electrodeposition temperature is presented in Table 3. From the measurement it is clear that the hardness increases with increasing in electrodeposition temperature. It was known that the hardness improvement of the metal-based composite system that involved Si\(_3\)N\(_4\) particles was attributed by Si\(_3\)N\(_4\) particles inclusion within the metal matrix composite (Li & Zhang, 2018; Robin et al., 2011). It has been studied that the high hardness of nitride composite system might be contributed by the combination of crystalline-metal nitride/amorphous phase or crystalline nitride/metal phase (Das et al., 2016; Veprek et al., 2007). Therefore, in this study, the high hardness might be contributed by the combination of Ni/TiN or TiN/Si\(_3\)N\(_4\) systems. From grain size calculation, it was clear that the increase of hardness value as increasing in electrodeposition temperature was due to the Ni grain refinement that was caused by the inclusion of Si\(_3\)N\(_4\) and TiN particles in the composite.

**Table 3.** Hardness of Ni-TiN/Si\(_3\)N\(_4\) composite coating at various electrodeposition

| No | Temperature(°C) | Hardness (GPa) |
|----|-----------------|---------------|
| 1  | 35              | 5.65          |
| 2  | 40              | 8.84          |
| 3  | 45              | 8.86          |
4. Conclusion
Ni-TiN/Si$_3$N$_4$ composite coatings were electrodeposited at various electrodeposition temperature. The increase in temperature lead to the smoother surface morphology of coating due to Ni grain refinement. At high electrodeposition temperature, Ni grain refinement lead to the higher coating hardness due to the inclusion Si$_3$N$_4$ and TiN particles.

Acknowledgement
This research financially was supported by Ministry of Research, Technology and Higher Education with contract No. 18/KOMP-UNJ/LPPM-UNJ/V/2019 and No. 18/SP2H/DRPM/LPPM-UNJ/III/2019.

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