Synthesis of Ni-TiN/Si$_3$N$_4$ nanocomposite layers using the electrodeposition method

H Nasbey*, E Budi, L Kusumawati, W Indrasari, I Sugihartono and T B Prayitno

Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Jakarta, Jl. Rawamangun Muka, Jakarta Timur, Indonesia

*hadinasbey@unj.ac.id

Abstract. In an effort to find the best technique for coating metals, the synthesis of the Ni-TiN/Si$_3$N$_4$ nanocomposite layers was carried out. The coating process is carried out using the electrodeposition method. In the electrodeposition process, tungsten carbide (WC) is used as the working electrode. The WC is immersed in the electrolytic solution and is electrified for 5 mA for 15 minutes. During the deposition process, the temperature of the solution is maintained at 35 °C using a hot disc. The crystal structure and phase changes formed in the WC are characterized using X-ray diffraction (XRD). The surface morphology of the layer is investigated by scanning electron microscopy (SEM). Based on the results of the characterization, the size of the Ni-TiN crystal is approximately 488.91 Å. The Si$_3$N$_4$ phase is not detected because it is amorphous. The thickness of the layer formed is approximately 805 nm. This simple technique can be used to produce nanocomposite coatings useful for protecting metals from corrosion.

1. Introduction

The need for metallic coating using nanocomposites has become important recently. The application of this coating is applied in various research fields such as photovoltaics [1], catalysts [2,3], sensors [4,5], antibacterial [6], and anti-corrosion [7-9]. Composite coating techniques are generally used to increase the strength of metals and protect against corrosion. In addition, it can also improve the mechanical properties of metals such as hardness level and optical properties [10]. This technique is generally applied to machine tools with high-speed operations (drilling, cutting and grinding) or at high temperatures. The composite coating can be carried out by various methods such as electrodeposition, evaporation, sputtering, ion plating with an arc, physical vapor deposition, and chemical vapor deposition.

The electrodeposition coating method has advantages over other coating methods, including low-cost processes, uniformly formed layers, better adhesion to metals, does not require large electrical voltages, can increase resistance from metal to corrosion and make metals shiny. In the electrodeposition process, the composite that will be used as a coating is dissolved in an electrolytic medium, the working metal is electrified using direct current so that the electrochemical coating process occurs.

In this paper, the results of the deposition of Ni-TiN/ Si$_3$N$_4$ nanocomposite layers on the surface of a tungsten carbide (WC) substrate using the electrodeposition method is explained. During the deposition process, the temperature of the electrolyte is maintained at 35 °C. The crystal structure, phase change, surface morphology, layer thickness were analyzed using XRD and SEM.
2. Experiment
The schematic diagram of the experimental setup for Ni-TiN/Si3N4 nanocomposite coating process using the electrodeposition method is shown by figure 1. In the experiment, electrodeposition takes place in vessels called electrolysis cells. In the process, three electrodes are used, which is the platinum (Pt) as a counter electrode, AgCl wire as a reference electrode, and the tungsten carbide (WC) as a reference electrode. The dimensions of the tungsten carbide used are approximately 0.42 x 0.42 x 3.82 cm³. During the electrolysis process, the electrolysis cell is placed on a magnetic hot plate stirrer so that the temperature of the solution can be maintained at 35 °C. In addition, the magnetic stirrer is used to mix the electrolyte solution homogeneously. The deposition process takes 15 minutes with a current density of 2.5 mA/cm². Electrolyte solution made up to 5 ml composed of NiCl₂·6H₂O 0.17 M, Ni₂SO₄·6H₂O 0.38 M, TiN 6 g/L, AlN 6 g/L, Si₃N₄ 0.6 g/L, H₃BO₃ 40 g/L and Sodium Dodecyl Sulfate 0.6 g/L. The electrolyte solution is diluted with 5 ml of H₂O. In order to form a perfectly homogeneous solution, the electrolyte solution is stirred for 24 hours using a magnetic stirrer.

![Schematic diagram of the experimental setup](image)

**Figure 1.** A schematic diagram of the experimental setup for Ni-TiN/Si3N4 nanocomposite coating process.

The surface morphology and the chemical composition of the layers formed were evaluated using scanning electron microscopy (SEM - Jeol JED-2300) with energy dispersive X-ray spectroscopy (EDS). X-ray diffraction (XRD) (Panalytical Empyrean Philips with radiation source Cu-Kα, λ = 1.54 Å) is used to analyze the crystal structure of the layer formed. In addition, the hardness of the layers formed was tested using Vickers Hardness Tester (HV-1000).

3. Results
Figure 2 shows the results of the evaluation of the Ni-TiN/Si₃N₄ layer formed by the electrodeposition process using SEM. The layer formed has a distance between the coarse grains and an agglomerate formed over the entire surface of the layer.
Figure 2. The results of the SEM characterization of the Ni-TiN/Si$_3$N$_4$ layers at 35 °C.

Table 1 presents the results of the analysis of the chemical composition of the layers formed using EDS. Nickel (Ni) is the element with the highest percentage compared to Ti, N and Si. Indeed, nickel (Ni) is the matrix of the layers and has the highest concentration in the electrolyte solution. Whereas the elements Ti, N and Si are reinforcing materials for the layers.

Table 1. The results of the EDS characterization of the Ni-TiN/Si$_3$N$_4$ layers at 35 °C.

| Element | Elemental mass composition (%) | Composition of atomic element amount (%) |
|---------|--------------------------------|----------------------------------------|
| N       | 10,82                          | 17,84                                  |
| O       | 45,12                          | 65,11                                  |
| Si      | 1,28                           | 1,05                                   |
| Ti      | 1,51                           | 0,73                                   |
| Ni      | 37,70                          | 14,82                                  |
| W       | 3,58                           | 0,45                                   |

Figure 3 shows a cross section of tungsten carbide which has been coated with a layer. Clearly visible layer formed by the electroplating process.

Figure 3. The cross section of tungsten carbide with the Ni-TiN/Si$_3$N$_4$ coated layers.
The thickness of the layer is calculated using the ratio of weight, area and density. The thickness of the layer formed is approximately 805 nm. The thickness of the layer is confirmed by the results of figure 3.

Figure 4 shows the X-ray diffraction (XRD) results of the layer formed. The highest diffraction peaks are the phase of nickel nitride and titanium, each being at $2\theta = 31.34^\circ$, $2\theta = 48.02^\circ$ and $2\theta = 48.07^\circ$. This shows that the nickel-titanium nitride phase has a high level of atomic order. Based on the results of the characterization, the size of the Ni-TiN crystal is approximately 488.91 Å.

![Figure 4. The results of the XRD characterization of the Ni-TiN/Si$_3$N$_4$ layers at 35 °C.](image)

4. Discussion
The Ni-TiN/Si$_3$N$_4$ nanocomposite layer formed by the electroplating process is proven by the results of SEM-EDS and XRD. A very large layer thickness formed around 805 nm is possible due to the length of the electroplating process. By developing rapid electrodeposition methods, it is possible to maintained the morphology, composition and structure. The process also can obtain smaller thicknesses. This simple technique can be used to produce nanocomposite coatings useful for protecting metals from corrosion.

5. Conclusion
The Ni-TiN / Si$_3$N$_4$ nanocomposite layer can be formed by the electroplating process. The layer formed is clearly shown by the results of the analysis using SEM, EDS and XRD. The thickness of the layer formed can be controlled during electroplating process.

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.

References
[1] Wang J, Ball J, Barea E, Abate A, Alexander J, Huang J, Saliba M, Sero I, Bisquert J, Snaith H, Nicholas R 2014 *Nano letter* **14** 724-730
[2] Smazna S, Shree S, Polonskyi O, Lamaka S, Baum M, Zheludkevich M, Faupel F, Adelung R, Mishra Y 2019 *Journal of Env. Chem. Eng.* **7** 103016
[3] Li G, Gray K 2007 *Chemical Physics* **339** 173-187
[4] Felix S, Kollu P and Grace A 2017 *Material Research Innovations* 1358507
[5] An K, Jeong S, Hwang H and Lee Y 2004 *Advance Materials* **16** 1005-1009
[6] Kung M, Tai M, Lin P, Wu D, Wu W, Yeh B, Hung H, Kuo C, Chen Y, Hsieh S, Hsieh S 2017 *Colloids and Surfaces B: Biointerfaces* **155** 399-407
[7] Xu-bei Z, Chao C, Guo-qu Z, Zhao Z, Jin-feng L 2011 *Trans. Nonferrous Met. Soc. China* **21** 2216-2224
[8] Zhang W, Li B, Ji C 2019 *Ceramics Int.* **45** 14015-14028
[9] Xia F, Wu M, Wang F, Jia Z, Wang A 2009 *Current Applied Physics* **9** 44-47
[10] Muarif, Budi E, Sugiartono I 2015 *Physics National Seminar IV* 81-84