Electrodeposited Ni-TiAlN Composite Coating on Tungsten Carbide: Effect of Surfactant Concentration on Physical and Mechanical Properties

E Budi¹,²*, Y Ermaditha¹, I Sugihartono¹, D Syafindra¹ and M Fajrin³

¹ Physics Program, Faculty of Mathematics and Science, Universitas Negeri Jakarta, Jl. Rawamangun Muka I, Jakarta 13220, Indonesia
² Physics Education Program, Faculty of Mathematics and Science, Universitas Negeri Jakarta, Jl. Rawamangun Muka I, Jakarta 13220, Indonesia
³ Material Physics Laboratory, Faculty of Mathematics and Science, Universitas Negeri Jakarta, Jl. Rawamangun Muka I, Jakarta 13220, Indonesia

*esmarbudi@unj.ac.id

Abstract. The effects of concentration of Sodium Dodecyl Sulfate (C₁₂H₂₅NaSO₄) as surfactant on structure and hardness of electrodeposited Ni-TiAlN composite coating has been investigated. The composites were deposited at fixed current of 3 mA, 12 V for 15 minutes. The electrolyte consists of 0.49 mol/l H₃BO₃, 0.17 M NiCl₂6H₂O, 0.38 M NiSO₄6H₂O, 2 gr/lit AlN and 2 gr/lit TiN. The concentration of Sodium Dodecyl Sulfate (SDS) was varied into 0.2, 0.4 and 0.6 gr/lit. The electrodes used were Pt wire as counter electrode, silver (Ag) wire as reference electrode and tungsten carbide (WC) rod as working electrode. The surface morphology and composition of composites were characterized by using Scanning Electron Microscopy (SEM) dan Energy Dispersive Spectroscopy (EDS), respectively. The crystal structure of composites was characterized by using X-Ray Diffraction (XRD) and the hardness was tested by using hardness Vickers tester. The results showed that a fewer agglomeration was formed on the composite surface for SDS concentration of 0.4 gr/lit. However, the increase of SDS concentration lead to the decrease of crystal size and increase the hardness of composite.

1. Introduction

Hard nitride particle-reinforced nickel (Ni) based-composite coating deposited by electrode position has been widely developed due high hardness, wear and corrosion resistance [1, 2]. The improvement is contributed by incorporation of hard particle that is uniformly distributed as a second phase of composite in nickel metal matrix thus it possess high hardness and good wear and corrosion resistant [3]. Nitride particles such as TiN, AlN and TiAlN are common ceramic material and have high hardness and wear resistance. Therefore these particles are widely used as reinforcement particle in nickel matrix composite coating [4-6].

The mechanical properties (e.g. hardness) of electrodeposited composite coating is influenced by electrode position parameters through controlling physical properties (e.g. morphology and structure) of composite. The electrode position parameters that influences the composite properties include electrode position current, particle and electrolyte concentration, surfactant and etc. [1, 7].
The control of physical properties of electrodeposited composite can be done by adding surfactant into electrolyte. Since the hard particle compound tend to agglomerate within the electrolyte thus it is needed to be dispersed by using surfactant [8]. Sodium Dedocyl Sulfate (SDS) is an anionic surfactant that can reduce surface tension of particle [9]. The objective of this experiment is to investigate the effect of surfactant concentration on physical and mechanical properties of Ni-TiAlN composite coating.

2. Experiment

The composites were deposited at fixed current of 3 mA, 12 V for 15 minutes. The electrolyte consists of 0.49 mol/l H$_3$BO$_3$, 0.17 M NiCl$_2$6H$_2$O, 0.38 M NiSO$_4$6H$_2$O, 2 gr/lit AlN and 2 gr/lit TiN. The concentration of Sodium Dodecyl Sulfate (SDS) was varied into 0.2, 0.4 and 0.6 gr/lit. The electrodes used were Pt wire as counter electrode, silver (Ag) wire as reference electrode and tungsten carbide (WC) rod as working electrode. The surface morphology and composition of composites were characterized by using Scanning Electron Microscopy (SEM) dan Energy Dispersive Spectroscopy (EDS) of Jeol, JED-2300, respectively. The crystal structure of composites was characterized by using X-Ray Diffraction (XRD) of Panalytical Empyrean Philips with Cu-$K\alpha$ radiation source ($\lambda=$1.54 Å) and the hardness was tested by using micro hardness Vickers tester HV-1000.

3. Results and discussion

3.1. Surface morphology and composition

The experimental result on SEM image of surface morphology of Ni-TiAlN composite coating at various SDS surfactant concentration is shown in Figure 1. In general, the greater the SDS surfactant concentration, the greater inhibited TiN and AlN aggregation in the electrolyte. The aggregation appears on the composite surface at SDS concentration of 0.2 gr/lit and it disappears at SDS concentration of 0.4 gr/lit. However, the aggregation appears again at further increasing SDS concentration up to 0.6 gr/lit.

![Figure 1](image.png)

*Figure 1. Surface morphology Ni-TiAlN composite coating deposited at SDS surfactant concentration of (a) 0.2 gr/lit.*
The EDS composition of Ni-TiAlN composite coatings at various SDS concentration are shown in Figure 2. It shows that metal element particle of Al tend to increase while Ti element tend to decrease as SDS concentration is increased. It seem that the SDS surfactant is more reactive to the electronegative elements (Al) than Electropositive element (Ti). As a result more Al is deposited in the composite while Ti is loosely absorbed and lead to the Ni grain growth.

Figure 1 (Cont.). Surface morphology Ni-TiAlN composite coating deposited at SDS surfactant concentration of (b) 0.4 gr/lit and (c) 0.6 gr/lit.
Figure 2. EDS analysis of Ni-TiAlN composite coatings at SDS concentration of (a) 0.2 gr/lit, (b) 0.4 gr/lit, (c) 0.6 gr/lit.
One of the major functions of surfactant is to provide the stability of the colloid and disperse the particle in the electrolyte [9]. Without surfactant, the particles may agglomerate due to polar and ionic surface forces. The surfactant can control adatom and kinetically delay the particle segregation due to cluster attachment onto the surface. The reduce agglomeration is due to the diminished strength of interfacial Coulomb interactions that causes the minimization of local dipole moments. It is known that the increase of particles concentration may accelerate the effect of agglomeration and subsequent gravitational sedimentation [10]. In this study, it seems that the sedimentation effects appear at further increasing in surfactant concentration up to 0.6 gr/lit.

3.2. Crystal structure

XRD spectrum of Ni-TiAlN composite coating in varying SDS concentration is shown in Figure 3.

![Figure 3. XRD spectrum of Ni-TiAlN composite coating deposited at SDS concentration of 0.2 gr/lit, 0.4 gr/lit and 0.6 gr/lit.](image)

From the calculation result, it is shown that, generally, the crystal size of composite is about 4 nm and it tend to decrease as increasing in SDS concentration.

Ni grains are shown by the diffraction peaks at 2-theta of 44.33° and 51.72° which correspond to the (111) and (002) crystal plane, respectively. TiN grains are displayed by the peaks at 35.51° and 75.63° which correspond to the (111) and (222), respectively. AlN grains are identified by peaks at 31.23°, 47.90°, 63.97°, 65.57°, 76.82° and 83.46 which correspond to (010), (012), (013), (020), (222) and (014), respectively. The intensity of Ni (111) and Ni (222) peaks show a tendency to increase as the SDS concentration is increased. Meanwhile, the intensity of TiN (111) and AlN (012) peaks tend to decrease as the SDS concentration is increased.

The surfactant changes the (hkl) surface energy of particles thus influences the crystal structure [9]. The increase of SDS concentration may increase the cathodic reactivity of the surfactant thus the nitride particles are more easily embedded on the substrate [11]. Increase of embedded particles on the substrate improve the nucleation site number and perturbs the crystal growth of Ni-metal matrix and consequently reduces the crystallite size [12] as can be seen in XRD spectrum result.

3.3. Hardness

The hardness test result is shown in Table 1. It suggests that the increases of SDS concentration enhances the composite hardness. The reason may be contradictly different by other explanation [13]. The increasing composite hardness is due to the interaction between nickel matrix with reinforced nitride particles (TiN and AlN) which improves upon the SDS surfactant addition as the surfactant increases the tension between matrix and reinforced particles. The SDS surfactant may promote the ionization of
TiN (and AlN) particles and facilitate their adsorption and deposition on the substrate [7]. Thus it may cause the increase of hardness.

**Table 1.** Experimental result of Vickers hardness test of Ni-TiAlN composite coating at various SDS concentration.

| No | SDS concentration (gr/lit) | HVN (kg/mm$^2$) |
|----|----------------------------|-----------------|
| 1  | 0.2                        | 2355.07         |
| 2  | 0.4                        | 2415.40         |
| 3  | 0.6                        | 2520.20         |

**Figure 4.** Vickers hardness indentation on surface of Ni-TiAlN composite coating deposited at SDS concentration of 0.2 gr/lit, 0.4 gr/lit and 0.6 gr/lit.
Figure 4 (Cont.), Vickers hardness indentation on surface of Ni-TiAlN composite coating deposited at SDS concentration of 0.2 gr/lit, 0.4 gr/lit and 0.6 gr/lit.

4. Conclusions
The Ni-TiAlN composite coatings were successfully prepared by electrodeposition with varying Sodium Dodecyl Sulfate (SDS) surfactant. The SEM/EDS results indicate the increase of aggregation as the increase of SDS concentration. The Al element is more reactive with SDS surfactant and as a result Al is more absorbed by substrate than Ti. The XRD and hardness test results indicate the reduction of crystallite size of composite lead the improve of its hardness. Thus it is concluded that the electrodeposition at high SDS concentration is the best parameters for the preparation of Ni-TiAlN composite coating is the higher.

Acknowledgments
The authors gratefully acknowledge research facilities support from Laboratorium of Material Physics, Physics and Physics Education Programs, Faculty of Mathematics and Science, Universitas Negeri Jakarta. This research was financially supported by BLU FMIPA UNJ with contract No. 24/SPK/Penelitian/6.FMIPA/2017 and DIKTI-Ministry of Education with contract No. 7/SP2H/DRPM/LPPM-UNJ/IV/2017.

References
[1] Jiang M, Ma C, Xia F F and Zhang Y 2016 Application of artificial neural networks to predict the hardness of Ni–TiN nanocoatings fabricated by pulse electrodeposition Surface & Coatings Technology 286 p. 191–196.
[2] Xia F F, Liu C, Wang F, Wu M H, Wang J D, Fua H L and Wang J X 2010 Preparation and characterization of Nano Ni–TiN coatings deposited by ultrasonic electrodeposition Journal of Alloys and Compounds 490 p. 431–435.
[3] Shi, Lei, Sun C, Gao P, Zhou F and Liu W 2006 Mechanical properties and wear and corrosion resistance of electrodeposited Ni–Co/SiC nanocomposite coating Applied Surface Science 252 p. 3591–3599.
[4] Xia F F, Yue W, Wang J, Liu C, Wang F and Lia Y 2015 Synthesis of Ni–TiN composite nanocoatings by magnetic pulse current deposition Ceramics International 41 p. 11445–11448.
[5] Xia F F, Xu H, Liu C, Wang J, Ding J and Ma C 2013 Microstructures of Ni–AlN composite coatings prepared by pulse electrodeposition technology Applied Surface Science 271 p. 7–11.
[6] Budi E, Muarief, Khasanah M, Permatasari A L, Sugihartono I, Fahdiran R and Budi A S 2017 Crystal Structure and Corrosion of Electrodeposited Ni-TiAlN Composite Coatings J. Tech. Soc. Sci. 1(2).

[7] Wu M, Jia W and Lv P 2017 Electrodepositing Ni-TiN nanocomposite layers with applying action of ultrasonic waves Procedia Engineering 174 p. 717 – 723.

[8] Chen L, Wang L, Zeng Z and Zhang J 2006 Effect of surfactant on the electrodeposition and wear resistance of Ni–Al2O3 composite coatings Materials Science and Engineering A 434 p. 319–325.

[9] Heinz H, Pramanik C, Heinz O, Ding Y, Mishra R, Marchon D, Flatt R J, Lopis I E, Llop J, Moya S and Ziolo R F 2017 Nanoparticle decoration with surfactants: Molecular interactions, assembly, and applications Surface Science Reports 72 p. 1–58.

[10] ZHU Xu-bei, CAI Chao, ZHENG Guo-qu, ZHANG Zhao and LI Jin-feng 2011 Electrodeposition and corrosion behavior of nanostructured Ni-TiN composite films /Trans Nonferrous Met. Soc. China 21 p. 2216−2224.

[11] Sudagar J, Lian J and Sha W 2013 Electroless nickel, alloy, composite and nano coatings – A critical review Journal of Alloys and Compounds 571 p. 183–204.

[12] Ramesh Bapu G N K R and Jayakrishnan S 2012 Development and characterization of electrodeposited Nickel–Titanium Carbo Nitride (TiCN) metal matrix nanocomposite deposit Surface & Coatings Technology 206 p. 2330–2336.

[13] Nordina M N, Asari N, Mahaidin A A, Shad K M and Aziz N M A N A 2016 Immobilization of Bromoresol Purple in Inorganic-Organic Sol-Gel Thin Film with Presence of anionic and non-ionic surfactants Procedia Chemistry 19 p. 275 – 282.