Preliminary Study on High-Temperature Oxidation of Ni-AlN-TiN/Si3N4 Electrodeposition Composite Coatings

E Budi¹,², C Tandri¹, N Darsono³, A W Andiani¹, M Fajrin¹, W Indrasari¹, I Sugihartono¹, and T B Prayitno¹
¹Department of Physics, Faculty of Mathematics and Science, Universitas Negeri Jakarta
Jl. Rawamangun Muka, Jakarta 13220, Indonesia
²Department of Physics Education, Faculty of Mathematics and Science, Universitas Negeri Jakarta
Jl. Rawamangun Muka, Jakarta 13220, Indonesia
³Research Center for Metallurgy and Material, Indonesian Institute of Science (LIPI), Building 470, Kawasan Puspiptek Serpong, Tangerang Selatan, Indonesia
Email: esmarbudi@unj.ac.id, chintyatandri99@gmail.com

Abstract. High-temperature oxidation is a serious problem for several materials during their application in aggressive environments, such as high temperatures, high-speed machining, and corrosive environments. This research was conducted to analyze the effect of high-temperature oxidation on the surface morphology of the Ni-AlN-TiN/Si3N4 composite coating. The coatings were electrodeposited at a current of 5 mA for 15 minutes and various electrodeposition temperatures of 35°C, 40°C, and 45°C. This composite coating was formed on tungsten carbide substrates with the electrolyte solution consisting of 6 g/L AlN, 6 g/L TiN, 40 g/L H3BO3, 0.6 g/L Si3N4, 0.17 M NiCl².6H2O, 0.38 M NiSO4.6H2O, and 0.6 g/L Sodium Dodecyl Sulfate. The high-temperature oxidation process was carried out at a temperature of 700°C for 2 hours in the furnace. The surface morphology was characterized by using Scanning Electron Microscopy (SEM). The results showed that the surface morphology of the Ni-AlN-TiN/Si3N4 composite coating deposited at a temperature of 40°C had a scaled growth, reduced cracks, and reduced pore. It was due to the effect of high-temperature treatment.

1. Introduction
High-temperature oxidation is a type of oxidation process at high temperatures that can extend a corrosion site. High-temperature oxidation resistance played an essential role in selecting materials used for construction, from gas turbines to heating furnaces. The types of high-temperature corrosion that usually caused problems in industrial equipments, including oxidation, sulfidation, carburizing, nitriding, halogen attack corrosion, and salt melt corrosion [1]. The high-temperature oxidation process in metals is a diffusion process where diffusion will depend on the diffusion coefficient and increase due to high temperatures. High-temperature oxidation was a severe problem for several materials during their application in aggressive environments, such as high temperature, high-speed machining, and corrosive environments. Oxidative damage of metals during high-temperature used in aggressive environments caused severe losses every year [2]. This is an especially case that material at temperatures up to 800°C and in various oxidizing atmospheres, such as conditions containing H2O, O2 or CO2 [3].
High-temperature oxidation resistance is a crucial parameter for optimizing coating performance. In Tribology, high-temperature conditions are associated with high-speed dry machining operations. In these conditions, oxidation may occur due to diffuse out of the coating element and reacts with oxygen (O2) to form an oxide coating on the surface coating [4]. Surface modification with coatings has become...
an important step to improve surface properties such as wear, corrosion, and oxidation. Various conventional techniques have been used to deposit the desired materials onto the substrate to achieve surface modification [5]. The coatings could protect the substrate by providing a barrier between the metal and the environment or through the presence of corrosion-inhibiting chemicals within it [6].

Ni electrodeposited coatings have been widely used in various applications due to their unique combination of properties such as wear resistance, corrosion resistance, nonmagnetism, and uniformity of coating thickness. Electrodeposition is a low-temperature process used to fabricate nanocomposite coatings in a single step without secondary treatment. The nickel matrix prepared by electrodeposition has a unique high density, minimum porosity and has been extensively studied [7]. The nickel matrix has also been widely used in the chemical, mechanical and electronic industries because of its wear, corrosion, and oxidation resistance [8]. Nickel metal (Ni) with its alloys is widely used as a matrix metal in composite coatings because of its good ductility and corrosion resistance. The crystal structure of nickel is FCC with a melting point of 1455°C provided its high thermal stability [9]. Nickel corrosion resistance occurs due to forming a passive oxide coating on its surface which acts as a protector against the corrosive environment.

The high-temperature oxidation of Ni and Ni-based alloys have become an essential part of the literatures on high-temperature oxidation for the last 50 years. One reason is the number of applications for Ni-based alloys at high temperatures due to neo formation. The NiO system was also of considerable scientific interest, with only one oxide stable at high temperatures [10]. Pure nickel metal does not protect against corrosion through the formation of nanocrystals but the formation of a NiO oxide coating. However, at high temperatures in the range of 700°C - 900°C, the formation of NiO grains, which caused the reduction of Ni to diffuse out through the NiO coating and also the soft nature of nickel at high temperatures can potentially reduce its wear and corrosion resistance. Therefore, adding a complex compound of nitride particles into the nickel coating could maintain wear resistance and corrosion resistance, especially at high temperatures. Several complex particle nitride compounds that can be used were AlN-TiN [11], Si3N4 [13], TiN [14], AlN [15], and ZrN [16].

On-TiN compounds have the ability to form very hard and dense layers with a hardness that can be maintained at high temperatures [17]. The oxidizing behavior of these hard coatings plays a vital role in tool applications as they are frequently exposed to oxidative atmospheres at high temperatures during use as wear and corrosion-resistant coatings [18]. The AlN-TiN coating will start to oxidize at a temperature range of 700°C - 900°C [19][20]. Most ceramic compounds have poor resistance to thermal shock; however, Si3N4 has good resistance to thermal stress, excellent high-temperature strength, and resistance [21][22]. The formation of a super hard coating of AlN-TiN/Si3N4 compound using deposition rules produces a level of diamond hardness with thermal stability at high temperatures. This occurs through a thermodynamic phase segregation mechanism that leads to the spontaneous formation of nanostructures [23]. The nanocomposite formed is stable to grain growth at high temperatures [24].

In this study, a Ni-based system of Ni-AlN-TiN/Si3N4 composite coating was deposited by electrodeposition process. A preliminary study was conducted to investigate the effect of high temperature on the surface coating morphology. The correlation between the electrodeposition process parameters and coating surface morphology after high temperature oxidation treatment was discussed.

2. Method
Ni-AlN-TiN/Si3N4 composite coating was electrodeposited onto Tungsten Carbide (WC) at current 5 MA for 15 minutes and various electrodeposition temperatures of 35°C, 40°C, and 45°C. Before electrodeposition, the substrates were sanded first and washed with soap to remove dirt attached to the substrate. The substrates, then were rinsed with distilled water and alcohol using an ultrasonic cleaner with an electrolyte solution composed of 6 g/L AlN, 6 g/L TiN, 40 g/L H2BO3, 0.6 g/L Si3N4, 0.17 M NiCl2, 6H2O, 0.38 M NiSO4, 6H2O, and 0.6 g/L Sodium Dodecyl Sulfate. All ingredients were mixed in 5 ml of distilled water and stirred for 24 hours using a magnetic stirrer. In this study, three electrodes were used, consisting of AgCl as the reference electrode, put as the supporting electrode, and Tungsten Carbide (WC) as the working electrode. The high-temperature oxidation process was carried by heating
the samples at temperatures of 700°C for 2 hours in the furnace. After the high-temperature oxidation test, the surface morphology of Ni-AlN-TiN/Si3N4 composite coatings was characterized by using Scanning Electron Microscopy (SEM) JEOL-JED 2300 (voltage 15 kV, 1 nA) with a magnification of 500x.

3. Results and discussion

Figure 1. Shows the surface morphology of the Ni-AlN-TiN/Si3N4 electrodeposition composite coating before being given high-temperature oxidation behavior. Based on the results of the characterization, when the temperature is 35°C, the surface of the coating tends to appear with small cracks on the entire surface of the coating. When the temperature increases from 35°C to 40°C, the surface morphology of the coating occurs with large cracks, pores, and agglomeration. At 45°C, the crack disappears, but becomes more porous on the surface of the coating [25].

Figure 1. SEM morphology of Ni-AlN-TiN/Si3N4 composite coating electrodeposited at temperature of (a) 35 ℃ (b) 40 ℃ and (c) 45 ℃ [25].

As the electrodeposition temperature increases, the cracks on the surface of the coating tend to disappear and become smoother, this is in accordance with the previous research that the higher the temperature used in the coating, the smoother the coating [26]. This happens because when the temperature increases to 45°C, the crystal size gets smaller and makes the coating smoother [27]. However, as the temperature increases, the formation of hydrogen gas increases, so that more hydrogen gas diffuses into the coating, causing the coating to be more porous [28]. The addition of temperature at the time of coating will help reduce the morphological cracks of the coating [29]. This happens because the temperature reduces the absorption of hydrogen in the coating, reduces stress, and reduces the tendency towards cracking [30].

Meanwhile, Figure 2. Shows the surface morphology of the Ni-AlN-TiN/Si3N4 electrodeposition composite coating after being given high-temperature oxidation behavior. Based on the characterization results, the morphology of the coating showed the presence of scale growth on the surface of the coating, reduced cracks, and reduced pore. The growth of scale on the coating is a characteristic of oxidation [31] and indicates that a protective oxide coating has deposited the above surface coating after high-temperature oxidation [32]. The pores on the coating surface are reduced because the pores have been oxidized on exposure to high temperatures [33].
The 10th National Physics Seminar (SNF 2021)
Journal of Physics: Conference Series 2019 (2021) 012067
doi:10.1088/1742-6596/2019/1/012067

Figure 2. SEM morphology of Ni-AlN-TiN/Si₃N₄ composite coating electrodeposited at a temperature of (a) 35°C (b) 40°C and (c) 45°C. All sample were exposed at temperature of 700°C for 2 hours within air condition.

The nickel surface is morphologically porous due to the kinetics of electrochemical deposition, nucleation, and crystal growth [33], and the pores will oxidize on exposure to high temperatures [34]. Higher resistance to high-temperature oxidation is obtained with the Ni composite coating embedded by TiN or AlN particles. However, its properties depend on the fraction of embedded particles. The good corrosion resistance of the Ni-TiN composite coating is overcome by the presence of TiN particles in the coating, which eliminates intergranular dots [35]. Since the Ni coating with a rough surface becomes potentially susceptible to reacting with corrosive elements, the co-deposition of AlN from the nickel composite coating causes a fine morphology of the nanostructured layer, which efficiently prevents corrosive elements from entering the coating [36]. Si₃N₄ particles also play a role in refining the grains of the Ni composite layer, which causes lower corrosion rates [13].

4. Conclusion
In summary, the morphology of the Ni-AlN-TiN/Si₃N₄ coating showed the presence of scale growth on the surface of the coating, reduced cracks, and reduced pore after the high temperature oxidation process treatment at 700°C.

Acknowledgments
The authors gratefully acknowledge research facilities support from the Laboratory of Material Physics, Physics and Physics Education Programs, Faculty of Mathematics and Science, Universitas Negeri Jakarta and Laboratory of Research Center for Metallurgy and Material, Indonesian Institute of Science (LIPI). This research was financially supported by Kemenristek with contract No. 1/E4.1/DSD/LPPM/2021.

References
[1] Fontana MG, Greene ND. Corrosion engineering Singapore. McGraw-Hill Book Company. 1987.
[2] Gunthner M, Kraus T, Dierdorf A, Decker D, Krenkel W, Motz G. Advanced Coatings on the Basis of Si(C) N Precursors for Protection of Steel Against Oxidation, Journal of the European Ceramic Society, 29: p. 2061-68. 2009.
[3] Pond RB, Shifler DA. High Temperature Corrosion Related Failures: ASM Handbook. 2002.
[4] Joshi A, Hu HS. Oxidation Behavior of Titanium-Aluminium Nitrides, Surface and Coatings Technology. p. 499-507. 1995.
[5] Jagielski J, Khanna AS, Kucinski J, Mishra DS, Racolta P, Sioshansi P, et al. Effect of chromium nitride coating on the corrosion and wear resistance of stainless steel, Applied Surface Science, 156: p. 47–64. 2000.
[6] Gray JE, Luan B. Protective coatings on magnesium and its alloy: a critical review, *J. Alloys Compd.*, **336**: p. 88. 2002.

[7] Aruna ST, Bindu CN, Selvi VE, Grips VK, Rajam KS. Synthesis and properties of electrodeposited Ni/Cora nanocomposite coatings, *Surf. Coat. Technol.*, **200**: p. 6871. 2006.

[8] Harvested A, Janssen LJ. Electrochemical codeposition of inert particles in a metallic matrix, *J. Apple. Electrochem.*, **40**: p. 519-27. 1995.

[9] Xi FF, Liu C, Wang F, Wu MH, Wang JD, Fua HL, et al. Preparation and characterization of Nano Ni–TiN coatings deposited by ultrasonic electrodeposition, *Journal of Alloys and Compounds*, **490**: p. 431-435. 2010.

[10] Haugsrud R. *High Temperatur Oxidation of Ni-20 wt.% Cu from 700 to 1100°C*, p. 55. 2001.

[11] Khrais SK, Lin YJ. Wear mechanisms and tool performance of TiAlN PVD coated inserts during machining of AISI 4140 steel, *Wear*, **262**: p. 64-9. 2007.

[12] Yoon SY, Kim JK, Kim KH. A comparative study of the tribological behavior of TiN and TiAlN coatings prepared by arc ion plating technique, *Surface and Coatings Technology*, **161**: p. 237-42. 2002.

[13] Khazrayie MA, Aghdam AR. Si3N4/Ni nanocomposite formed by electroplating: Effect of average size of nanoparticulates, *Trans. Nonferrous Met. Soc.*, **201**: p. 1017-23. 2010.

[14] Veprek, Reiprich S. *A Concept for The Design of Novel Superhard Coatings*, **268**: p. 64-71. 1995.

[15] Aal AA, Bahgat M, Radwan M. Nanostructured Ni-AlN composite coatings, *Surf. Coatings Technol.*, **201**: p. 2910-918. 2006.

[16] Erdemir A, Eryilmaz OL, Urgen M, Kazmanli K, Mehta N, Prorok B. *Tribology of Nanostructured and Composite Coatings*. 2006.

[17] Veprek S, Haussmann M, Reiprich S, Shizhi L, Dian J. Novel Thermodynamically Stable and Oxidation Resistant Superhard Coating Materials, *Surface and Coating Technology*, **86-87**: p. 394-401. 1996.

[18] Derflinger VH, Schutze A, Ante M. Mechanical and structural properties of various alloyed TiAlN-based hard coatings, *Surf. Coat Technol.*, **200**: p. 4693. 2006.

[19] Joshi A, Hu HS. *Surf. Coat. Technol.*, **76**: p. 499-507. 1995.

[20] Chen L, Paulitsch J, Du Y, Mayrhofer PH. Thermal stability and oxidation resistance of Ti–Al–N coatings, *Surf. Coat. Technol.*, **206**: p. 2954-960. 2012.

[21] Pehlke RD, Elliott JF. High-Temperature Thermodynamics of the Silicon, Nitrogen, Silicon Nitride System, *Trans. AIIME*, **215**: p. 781-85. 1959.

[22] Croft WJ, Cutler IB. Review of Silicon Nitride, *ONR Report*. 1973.

[23] Holubar P, Jilek M, Sima M. Present and possible future applications of superhard nanocomposite coatings, *Surface and Coatings Technology*, **133-134**: p. 145-51. 2000.

[24] Veprek S, Jilek M. Superhard nanocomposite coatings. From basic science toward industrialization, *Pure Appl. Chem.*, **74**: p. 475-81. 2002.

[25] Andiani AW, Budi E, Sugihartono I. Pembentukan Lapisan Komposit Ni-TiN-AlN/Si3N4 Menggunakan Metode Elektrodeposisi dengan Variasi Temperatur, *Prosiding Seminar Nasional Fisika*, p. 145-48. 2019.

[26] Sadiku A, Sadiku ER, Ojo OI, Akanji OL, Biotidara OF. Influence of Operation Parameters on Metal Deposition in Bright Nickel-plating Process, *Port. Electrochim. Acta*, **29**: p. 91-100. 2011.

[27] Sen R, Das S, Das K. The effect of bath temperature on the crystallite size and microstructure of Ni–CeO2 nanocomposite coating, *Material Characterization*, p. 257-262. 2011.

[28] Lazic MS, Simovic K, Miskovic S, Kicevic D. The Influence of the Deposition Parameter on the Porosity of Thin Alumina Films on Steel, *Serbian Chemistry Society*, p. 239-249. 2004.
[29] Lu W, Guang P, Li K, Yan P, Yan B. Effect of Bath Temperature on the Microstructural Properties of Electrodeposited Nanocrystalline FeCo Films, *International Journal of Electrochemical Science*, p. 2354 - 364.2013.

[30] Kumar S, Pande S, Verma P. Factor Effecting Electro-Deposition Process, *International Journal of Current Engineering and Technology*, p. 2347 – 5161. 2015.

[31] Talbot D. Corrosion Science and Technology New York, *CRC Press*. 1998.

[32] Sugiarti E, Zaini KA, Sundawa R, Wang Y, Ohnuki S, Hayashi S. Influence of Oxidation Temperature on The Oxide Scale Formation of NiCoCrAl Coatings, *Journal of Physics*, p. 817. 2017.

[33] Kamaraj AB, Shresta H, Speck E, Sundaram M. Experimental Study on the Porosity of Electrochemical Nickel Deposits, *Procedia Manuf*, p. 478-85. 2017.

[34] Bei ZX, Chao C, Qu ZG, Zhao Z, Feng LJ. Electrodeposition and corrosion behavior of nanostructured Ni-TiN composite films, *Transactions of Nonferrous Metals Society of China*, p. 2216-24. 2011.

[35] Xia FF, Liu C, Wang F, Wu MH, Wang JD, Fu HL, et al. Preparation and characterization of Nano Ni–TiN coatings deposited by ultrasonic electrodeposition, *Journal of Alloys and Compounds*, p. 431-35. 2010.

[36] Ma C, Yu W, Jiang M, Cui W, Xia F. Jet pulse electrodeposition and characterization of Ni–AlN nanocoatings in presence of ultrasound, *Ceramics International*, 44: p. 5163-170. 2018.