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ANALYSIS ON MECHANICAL AND MICROSTRUCTURAL PROPERTIES OF ELECTRODEPOSITED Ni-TiN-ALN/Si_3N_4 COMPOSITE COATINGS

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Abstract

The parameter such as reinforced particles plays a role in controlling the microstructure and eventually influences the mechanical properties of the composite coating. The microstructure strength of composite coating come from phase combination of the matrix and its reinforcement. This study described the effect of the electrodeposition process parameters of Si_3N_4 particle concentration on the Ni-TiN-AlN/Si_3N_4 composite coatings. Therefore, the experiment was performed by varying Si_3N_4 particles concentration in range of 0.2, 0.4 and 0.6 g/L in electrodeposition process. The coating morphology and crystal structure were characterized by mean of Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD), respectively while the coating microhardness was tested by using Vickers hardness test. The calculations were performed to analyze the coating stress from XRD data and presented its relation with the coating microhardness. The analysis results displayed that the uniform surface morphology of composite with the evolution of nitride particle aggregation was observed at various S_3N_4 particles concentration. In general, the uniformity morphology was due to the refinement of Ni crystallite size. The crystal structure was noticed prominently by Ni, TiN and AlN grains while Si_3N_4 grain was not observed due to its amorphous nature. In general, the increase of composite microhardness, as increasing Si_3N_4 concentration was attributed by the reducing Ni crystallite size lead to the increase of coating residual stress.

Keywords: nickel, nitride, composite, coating, electrodeposition, concentration, morphology, structure, stress, microhardness.

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1. Introduction

Development of nickel (Ni) alloy as a thin coating has been obtained significantly since it had good ductility and high corrosion resistance leading to its wide applications [1]. The incorporation of some inert particles such as TiN, AlN, TiC etc, into the nickel as the matrix coating in composite system, evidently has improved its mechanical, corrosion and tribology properties [2–5].

For the mechanical properties especially the coating hardness, the improvement was reported about 10 GPa or below. It is still low value compare to other coating systems.

Number of efforts was performed to enhance the coating properties including by incorporating amorphous phases from inert particle such as silicone-nitride (Si_3N_4). The incorporation of silicone-nitride has received a wide attention in composite technology as a reinforced particle due to its high mechanical strength, wear and corrosion resistance [6–8]. Si_3N_4 nanoparticle incorporation changed the microstructure of composite by filling the crevice and micron hole of composite matrix [9]. Another investigation was reported in developing TiN/Si_3N_4 nanocrystalline coating with the high hardness of 50 GPa due to the spinodal phase segregation which the nanocrystalline of TiN was covered by about monolayer of interfacial Si_3N_4 amorphous phase [10].

Other efforts in improving coating properties were obtained by using an appropriate coating deposition method. Until now, the electrodeposition is an attractive method to develop a hard coating including nickel based composite coating [2]. The coating properties such as structure, morphology and hardness also were easy and effective to be controlled by process parameters such as particle concentration, during the process. The particle concentration influenced to the deposition rate, particle content, crystal growth and grain refine was well as the agglomeration and sedimentation effect [11].

The incorporation of nitride particles as crystalline and amorphous phase within the nickel composite coating was important to be investigated in order to further improve the hardness and the wear resistance of the coating. The formation of nanostructure is a key to improve the coating hardness [12]. However, in the coating system, the stress exists at interface between coating layer and substrate surface due to their different thermal expansion or crystal orientation and may contribute to the coating hardness [13–16]. Furthermore, in the composite coating system, the strength interaction between matrix and reinforced particles is also a key to the residual stress [13, 17].

In this study, the $Ni\text{-}TiN\text{-}AlN/Si_3N_4$ composite coatings were developed by using electrodeposition process at various Si_3N_4 particle concentration. The study of the effect Si_3N_4 particle concentration in the electrodeposition process on the coating microstructure is presented. The analysis on the coating stress and its impact to the coating hardness is described.

2. Material and method

$Ni\text{-}TiN\text{-}AlN/Si_3N_4$ composite coatings were developed by electrodeposition in electrolyte bath that consist of 0.17 M $NiCl_2{\cdot}6H_2O$, 0,38 M $Ni_2SO_4{\cdot}6H_2O$, 0.49 M H_3BO_3, 1.2 g/L *Sodium Dodecyl Sulfate* (SDS), 4 g/L TiN and 4 g/L AlN (Sigma Aldrich). The process flow of the experiment is presented in **Fig. 1**.

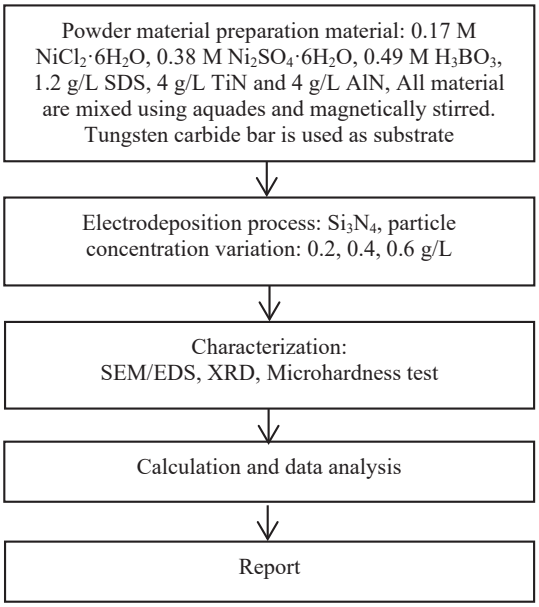


Fig. 1. Process flow of the experiment

The electrodeposition process was done at fixed current density of 2 mA/cm^2 and various of Si_3N_4 concentration of 0.2, 0.4 and 0.6 g/L. The electrolyte was dissolved by using aquades and stirred by using magnetic stirrer for 24 hours. Before the electrodeposition process, the (4×4×38) mm substrate of tungsten carbide bar were polished by using sand paper of 150–2000 mesh and then washed by using detergent and subsequently dried on hot plate. Finally, the substrate bars were cleaned by using ultrasonic cleaner in 96 % alcohol. The electrodeposition was conducted for about 15 minutes by using potensiostat system. Three electrodes used were Pt (PAR RDE 0021) and Ag/AgCl wires (Princeton K0265) as counter and reference, respectively. During the process, the electrolyte was magnetically stirred at speed of 850 RPM. The samples were characterized by Scanning Electron Microscopy (SEM) JEOL-JED 2300, X-Ray Diffractometer (XRD) Shimadzu 7000 (Cu Kα, λ = 1.54 Å, 40 kV, 30 mA) and Micro Vickers hardness tester Leco LM 800AT.

The crystallite size (D), lattice strain (ε), internal stress (S) and residual stress (σ) of composite coating was calculated by using following equations (1)–(4) [13, 17]:

$$D = \frac{k\lambda}{\beta\cos\theta}, \tag{1}$$

$$\varepsilon = \frac{\beta}{4\tan\theta}, \tag{2}$$

$$S = \left(\frac{K}{D}\right)^{1/2}\left(\frac{I_{111}}{I_{111}+I_{002}}\right)^{1/2}, \tag{3}$$

$$\sigma = S\left(\frac{E}{1-\nu}\right)^{1/2}, \tag{4}$$

with k is a constant (= 0.9), λ is wave length for Cu (= 1.54 Å), β is Full Width at Half Maximum (FWHM), θ is diffraction angle, K is a constant (= 2.5) accommodate for the difference in surface and grain boundary energy, E is elastic modulus (= 303 GPa), ν is Poisson ratio (= 0.24), D is crystallite size and I_{hkl} is the integrated intensity of the (hkl) diffraction peaks to consider the effect of anisotropic elastic modulus. S and σ parameters account for the effect of grain size and its crystallographic orientation.

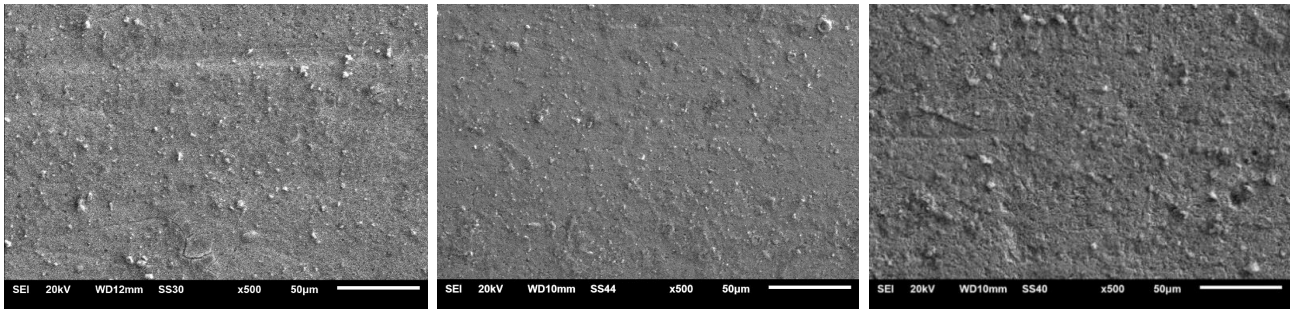
3. Results and discussion

SEM surface morphology of Ni-TiN-AlN/Si_3N_4 composite coatings at different Si_3N_4 particles concentration is shown in **Fig. 2**. The uniformly coating surface with few nitride particles was appeared to aggregate to a certain extent on the coating surface. It was observed that the aggregation effect increased with the increase of Si_3N_4 particle concentration due to the nature of nitride compound deposition within the nickel metal matrix composite and the effect was accompanied by sedimentation effect. Both effects increased as the particles concentration was increased and aligned to previous results [9–11]. Some holes also were observed on the coating surface indicating the porous nature of nickel oxide surface morphology [18–20]. Air or gas bubble may accumulate during deposition and often block crystal growth causing pores on the surface coating. The water molecule resulted from reaction of hydrogen and the oxygen of nickel oxide was desorbed from the surface into the gaseous phase and left the pores formation on the surface.

Fig. 3 shows XRD spectra of Ni-TiN-AlN/Si_3N_4 composite coating deposited at different Si_3N_4 particles concentration. It revealed that the coatings display intensity of cubic Ni (111) and Ni (200) (ICDD 00-004-0850), hexagonal AlN (100), AlN (102), AlN (004), AlN (104) (ICDD 01-070-2543) and cubic TiN (111), TiN (311) (ICDD 01-087-0631). While Si_3N_4 phase did not appear due to its amorphous and non-electrochemical activity nature caused not participating in crystallization process [9, 21]. This result indicated the successfully formation of nickel-nitride composite coating.

The most significant effect of the increase of Si_3N_4 concentration up to 0.6 g/L was the inhibit on Ni (111) and Ni (200) crystal growth but it promoted the crystal growth of AlN (100),

AlN (102), TiN (311) and TiN (111). The crystal size calculation by using Scherrer formula (1) is shown in **Fig. 4**. The result showed that the average of crystal size of Ni (111) and Ni (200) decreased to about 0.5 Å as the Si_3N_4 concentration is increased up to 0.6 g/L. In this study, the decrease of Ni crystal size at high Si_3N_4 particles concentration indicated Ni crystal refinement was occurred due to the increase of TiN and AlN crystals size. Meanwhile, the formation of amorphous phase of Si_3N_4 particles provided the obstacles for nickel grain growth and promoted the increase of nucleation rate of nitride particles. It also was confirmed that the grain refinement of Ni metal matrix was attributed by Si_3N_4 particles as inhibitor for Ni crystal growth [9]. The similar result was also shown by Cu metal matrix [22]. The grain refinement rate increased with the increase of incorporated particles content.



a *b* *c*

Fig. 2. Scanning Electron Microscopy surface morphology of Ni-TiN-AlN/Si_3N_4 composite coating at Si_3N_4 particles concentration of: *a* – 0.2 g/L; *b* – 0.4 g/L; *c* – 0.6 g/L

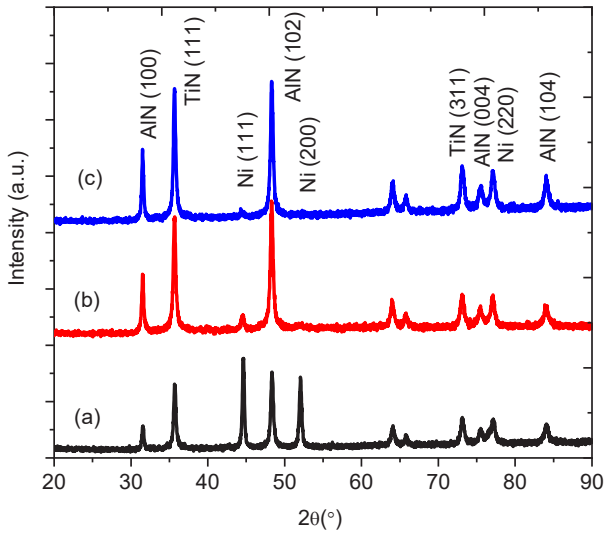


Fig. 3. X-Ray Diffraction spectra of Ni-TiN-AlN/Si_3N_4 composite coating at Si_3N_4 particles concentration of: *a* – 0.2 g/L; *b* – 0.4 g/L; *c* – 0.6 g/L

The lattice strain and its relation with the internal stress between Ni matrix and nitride reinforced particle are calculated by using (2), (3) shown in **Fig. 5**. It shows that the lattice strain and internal stress increase up to about 1.67 GPa and 1.44 GPa, respectively as the Si_3N_4 particles concentration is increased up to 0.6 g/L. The uniformly distribution of Si_3N_4 particles within the Ni matrix cause the evolution of Ni crystal grain preferably (111) orientation, grain refinement and increase the lattice strain due to the increase in the surface free energy [17]. However, the increase of lattice strain at higher Si_3N_4 particles concentration can be due to Si_3N_4 particles agglomeration in the coating matrix [23] lead the increase of the lattice distortion between matrix and particle and misfit dislocation [24]. The agglomeration that causes the increase in strain also can be due to reduction in metal-particle interface. In this study, the particle agglomeration size increases as

the Si_3N_4 particles concentration is increased as shown in **Fig. 2**. The increase of lattice strain induces the increase of the internal stress due to the evolution of crystal grain and orientation that subsequently induce to the coating residual stress [13, 17, 25].

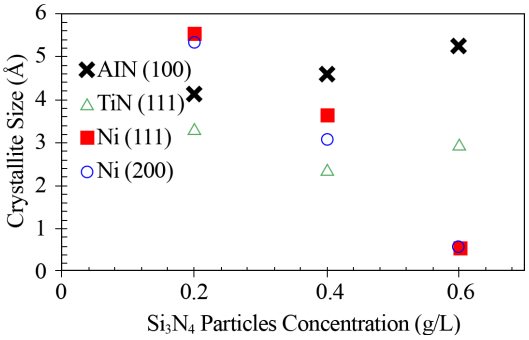


Fig. 4. Crystal size of Ni (111), Ni (200), TiN (111) and AlN (100) of Ni-TiN-AlN/Si_3N_4 composite coating at different Si_3N_4 particles concentration

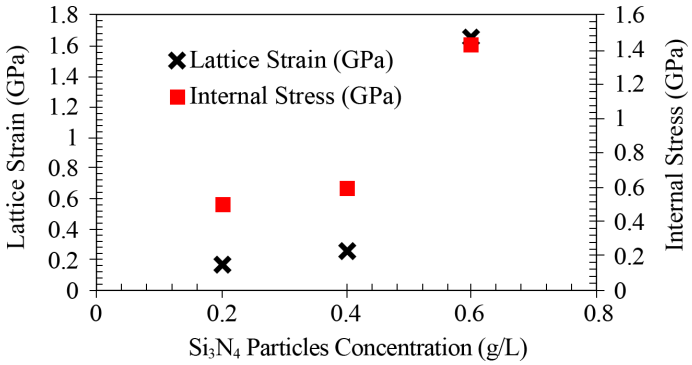


Fig. 5. Lattice strain and Internal Stress of Ni-TiN-AlN/Si_3N_4 composite coating at different Si_3N_4 particles concentration

The microhardness of Ni-TiN-AlN/Si_3N_4 composite coatings at different Si_3N_4 particle concentration and its relation with residual stress that calculated by using equation (4) is presented in **Fig. 6**.

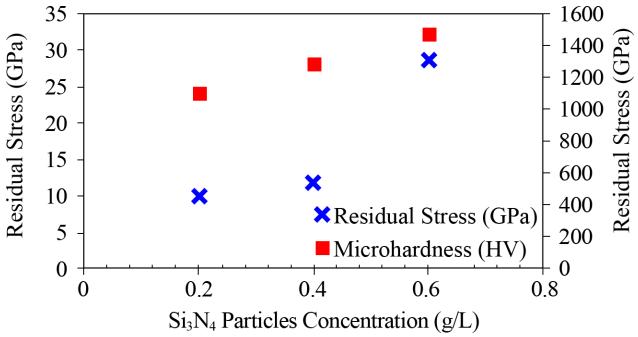


Fig. 6. Microhardness and Residual Stress of Ni-TiN-AlN/Si_3N_4 composite coating at different Si_3N_4 particles concentration

It was noticed that the microhardness and residual stress of composite coating increase up to 1400 HV and 28.67 GPa, respectively as the Si_3N_4 particle concentration was increased up to 0.6 g/L. The improvement in the microhardness was provided by composite strengthening that govern the hardness due to the combination of grain refinement and dispersion strengthening [25]. Although, it is also influenced by solid solution strengthening and crystal orientation, however

both effects are weak. In this study, the increase of Si_3N_4 particle concentration reduced the Ni crystal size resulting the increase of composite microhardness. The increase of microhardness also was caused by the TiN, AlN and Si_3N_4 particles that act as nuclei and nucleation site in the composite that restricted the Ni crystal growth. This was consistent with previously report [22] that the increase of coating hardness was due to dispersion-strengthening and grain refinement simultaneously. In this study, the amorphous phase of Si_3N_4 particles promoted the nickel grain refinement and caused the increase in residual stress and microhardness.

Based on this study result, it is shown that the nickel grain refinement and the increase of stress were attributed to the microhardness of the nickel composite coating. It is known that the high coating hardness is addressed to the fine-crystallite and crystallographic orientation [13]. The later strengthening is related to the coating stress that is influenced by particle concentration. At high temperature exposure, the coating stress may be released leading to the decrease of the coating hardness [10]. Further development on nickel composite coating can be focused to enhance the microstructure properties through others process parameter and post-deposition treatment.

4. Conclusions

In this work, the influence of Si_3N_4 particles concentration on the microstructure and microhardness of Ni-TiN-AlN/Si_3N_4 composite coatings were investigated. Generally, the finer and uniform morphology was revealed due to the decrease of nickel crystal size as the increase of Si_3N_4 particles concentration up to 0.6 g/L. Crystal structure of composite coatings were consisted of Ni, TiN and AlN grains indicating the composite coating was successfully formed with Si_3N_4 peaks were not revealed due to its amorphous nature. The increase of the microhardness and residual stress of Ni-based composite coatings up to about 1400 HV and was attributed by the decrease of nickel crystal size down to about 0.5 Å and the increase of residual stress that were facilitated by the increase of nitride particle concentration. about 0.5 Å as the Si_3N_4 concentration is increased up to 0.6 g/L.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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Data availability

Manuscript has associated data in a data repository.

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