Crystal Structure and Corrosion of Electrodeposited Ni-TiAIN Composite Coatings

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Abstract. An investigation has been done to study the influence of various stirrer speed, electrodeposition current and substrate on the crystal structure and corrosion of electrodeposited Ni-TiAlN composite coating. To study the influence of stirrer speed, the composites were deposited on tungsten carbide substrate at various stirrer speed of low (1235 rpm), medium (1995 rpm) and high (2446 rpm) at fixed current while to study the effect of electrodeposition current, the composites were deposited on tungsten carbide at various current of 2, 3 and 4 mA at fixed stirrer speed. Other composites were deposited at various substrate of brass, steel (HSS) and galvanic metal substrates at fixed electrodeposition current and stirrer speed. The crystal structure of composites was characterized by using XRD spectrum analysis and the corrosion rate of the composites is better at high electrodeposition current and low stirrer speed. It shows that the crystalization and corrosion rate of the coating on brass substrate are better than others.

1. Introduction

Electrodeposition is a technique to develop a thin coating based on the electrochemical process. The electrodeposition technique, especially electroplating, uses electric current to deposit metal particles onto the substrate through autocatalytic reduction process. Electrodeposition has advantages including the coating quality especially in the physical and mechanical properties. The technique is suitable for alloy and composite deposition with a good particle dispersion through agitation control [1-3]. Agitation process through stirring of the electrolyte solution is desirable since it improve ion transport to the substrate and decrease the diffusion layer thickness.

Nickel-nitride composite films such as Ni-TiN, Ni-AlN or Ni-TiAlN is one of the composite coatings for mechanical and electrical application [4-10]. It showed that all the composite properties are controlled by electrodeposition parameter such as current density, particle concentration, stirerrer speed, temperature, pH etc.

In film or thin coating development, the adhesion strength between coating and substrate is very important since it control the coating performance. The strong bonding is influenced by the material and the substrate surface finish since the nucleation rate on the subtrate differs from

different substrate-coating types and conditions [3,11]. It is known that the bonding between coating and substrate determine the coating properties and it is influenced by its crystallography orientation.

The coating is also functionalised as surface material protection especially metal from corrosion [12]. The nitride particle content in the composite coating can improve the mechanical and corrosion resistance [5-7,13].

In this paper, the influence of different current, substrates and stirrer speed on the crystal structure and corrosion resistance of electrodeposited Ni-TiAlN composite coatings are studied.

2. Electrodeposition of Ni-TiAlN Composite Coating

The Ni-TiAlN composite coatings were prepared by electrodeposition in aquaous bath (0.38 M Ni₂SO4.6H₂O, 0.17 M NiCl₂.6H₂O and 0.49 M H₃BO₃) contaning nitride (~ 0.3 µm size TiN and 100 nm size AlN) particles powder at room temperature. The eletrodeposition process was performed by Edaq potensiostat that controlled by Echem software package. Platinum (Pt) and AgCl₂ wire was used as counter and reference electrode, respectively (Figure 1). The first investigation was performed by varying substrate material types such as brass, HSS and galvanic at constant current of 3 mA. The second experiment was performed by varying magnetic stirer speed of of low (1235 rpm), medium (1995 rpm) and high (2446 rpm). An experiment of electrodeposited Ni-TiAlN composite coating also was performed by using simple developed electrochemical cell with two electrodes system. The experiment was performed by varying electrodeposition current.



Magnetic stirrer bar

Fig. 1. Electrodeposition experiment set up

The crystal structure of the samples were analized by using X-Ray Diffraction spectrum that performed on Shimadzu 7000 instrument using Cu K α radiation (λ =1,54060Å). The operating target voltage was 40 kV and the current was 30 mA.

The average of crystal diameter size (D) was calculated by using Scherrer equation as follows [4]:

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

Where K is grain factor (K = 0.89), λ is the x-ray wave length ($\lambda_{Cu} = 1.5406$ Å), β is the width at half height of the diffraction peak (FWHM) and θ is the Bragg angle.

Parameter	Value	
Current (mA)	2,3,4	
Stirer speed (rpm)	1235 , 1995 , 2446	

WC, Galvanic, Brass, HSS

Table 1. Electrodeposition parameters for Ni-TiAlN composite ccoating

The corrosion test was performed by mass loss method where the samples were immersed into chemical acid solution. The samples mass before and after immersion were measured by using analytic balance.

3. Results and discussion

3.1. Crystal structure of composite at various electrodeposition current.

Substrate material

The crystal structure of Ni-TiAlN composite coating at various electrodeposition current are shown in Figure 2.



Fig. 2. XRD spectrum of Ni-TiAIN composite coating at various electrodeposition process.

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The peaks at 44.62⁰, 51.88⁰ and 76.58⁰ correspond to Ni (111), Ni (200) and Ni (220) peaks. The calculated average of diameter size of Ni grains was approximately 40 nm. The intensity of Ni (111) and Ni (200) peaks tend to decrease as increasing current from 2 mA to 3 mA. However, Ni (111) is back again increasing as further increasing current up to 4 mA. The decrease of Ni (111) and Ni (200) peaks are sugested due to the decrease of mean size of Ni crystals [4] while the increase of Ni (111) peak at higher current might be due to accelerate the reduction process and Ni crystal growth [5].

During electrodeposition proces, the crystal growth of Ni can be inhibited by chemical species [14]. The [100] crystal texture mode is considered if the electrolyte is free from inhibiting chemical process. However, during the process both nickel hydroxide and hydrogen are deposited and partially absorbed on the substrate surface and also ionization of boric acid cause the formation of (220) crystal orientation.

Meanwhile, the peaks at 35.76° and 48.32° correspond to TiN (111) and AlN (102), respectively. The calculated average of diameter size of TiN and AlN grains was approximately 36 nm and 35 nm, respectively. It was showed that TiN grains increase with increasing electrodeposition current from 2 mA to 3 mA. However, it decreases with further increasing current up to 4 mA. The increase of electrodeposition current may lead the increase of the Coulomb force between Ni⁺² ions absorbed on the nitride particles (TiN) and the substrate (cathode) thus increase of nitride particles contents on the substrate [7]. However, at further increasing current, it decreases due to rapid deposition of the Ni metal matrix thus decreases the nitride particles deposited on the composite.

Meanwhile, generally AlN grains decreases with increasing electrodeposition current. It is due to the increase of Ni metal matrix deposition [7]. At high electrodeposition current density, the hydrogen reduction rate is accelerated leads the decrease of nitride deposition in the composite [5].



3.2.Crystal structure composite at various substrate

Fig. 3. Crystal structure of Ni-TiAIN composite coating at substrate of galvanic, HSS and Brass.

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From the XRD analysis, it shows that the crystal structure of Ni-TiAlN composite coating on the brass substrate is better than HSS and Galvanis substrate (Figure 3). The crystal structure of Ni-TiAlN composite coating on brass is indicated by TiN (200) peak at 41.86⁰, Ni (111) peak at 44.22⁰ and AlN (102) peak at 48.88⁰. The crystallization of Ni-TiAlN coating on Brass (Cu-Zn alloy) substrate is due to the crystal coherency between Ni-based coating and Cu-based substrate. It was reported that the crystal coherency exist between Ni coating and Cu substrate [15]. In general, crystal structure of brass is FCC (α -phase) and has similarity with Ni-TiAlN coating.

3.3. Crystal Structure of composite at low stirer speed

From the result of various stirrer speed, it showed that the nitride composition of composite at medium dan high stirrer speed is lack of Ti and Al elements compare with that of low stirrer speed. The crystal structure of Ni-TiAlN composite coating at low stirrer speed is showed in Figure 4.



Fig.4. Crystal structure of Ni-TiAIN composite coating at substrate of WC with low speed stirrer (1235 RPM).

The stirrer speed is utilized to carry the particle effectively to the cathode during the eletrodeposition. However, further increasing in stirrer speed produce the dislodging of the absorbed particle [16]. In high speed of stirrer, the repellent force of substrate surface is dominant [17].

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3.4. Corrosion test

The results of corrosion test for the samples which deposited at various electrodeposition current was shown in Table 2. The samples were immersed into 3.5% NaCl solution for 3 hours. It shows that the rate of mass loss tend to decrease.

Current (mA)	m ₁ (gram)	m ₂ (gram)
0	0.507	0.501
2	0.131	0.129
3	0.151	0.146
4	0.211	0.210

Table 2. Corrosion test result for Ni-TiAIN composite ccoating deposited at various current.

Note: m₁ and m₂ is mass before and after corrosion test, respectively.

The results of corrosion test for the samples which deposited at various substrate was shown in Table 3. The samples were immersed into $0.5 \text{ M H}_2\text{SO}_4$ solution for 6 hours. It shows that brass is more resistant to corrosion than steel and galvanic metal substrates.

Table 3. Corrosion test result for Ni-TiAIN composite ccoating deposited at various substrate

Substrate	m ₁ (gram)	m ₂ (gram)
HSS	0.148	0.108
Galvanic Brass	0.150 0.048	0.138 0.045

Note: m₁ and m₂ is mass before and after corrosion test, respectively.

The better corrosion resistance of the composite coating may be due to the defect size reduction. The nitride particles segregate the corrosive medium and prevent the growing of corrosive pits [13]. The decrease of corrosion rate is due to the decrease of the grain size of composite crystal [18]. In general, the nitride particle size decrease as the increasing electrodeposition current. Ni matrix on a substrate is a cathodic coating which can hinder the contact between substrate and acid solution. When defects or mechanical damages are revealed in the coating, the presence of nitride particles such as TiN and AIN can eliminate the interspaces and enhance the coating density lead the decrease of porosity and eventually improve corrosion resistance [6].

4. Conclusion

Ni-TiAlN composite coatings have been successfully deposited by using electrodeposition technic. The crystal structure of electrodeposited Ni-TiAlN composite coating are influenced by current, stirrer speed and substrates. The crystalization and corrosion resistance of composite coating is higher at high electrodeposition current and low stirrer speed. It is also higher for coating deposited onto brass substrate.

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