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Short Communication

Study of Electrodeposited Ni-TiAlN Composite Films

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A study results of electrodeposited Ni-TiAlN composite films is reported. The composite film was electrodeposited from electrolyte solution of 0.38 M Ni2SO4.6H2O, 0.17 M NiCl2.6H2O and 0.49 M H3BO3 adding with various electrodeposition current from 2 mA to 4 mA and TiN and AlN powder from 2 gr/lit to 8 gr/lit. The morphology and compositions were characterized by using SEM/EDS while the crystal structure was characterized by XRD. The results show that the morphology and structure of composite films were influenced by electrodeposition parameters such as electrodeposition current and nitride particle concentration. The evolution of surface morphology and structure was occured as the electrodeposition current and nitride particles concentration were increased. The smoothest and uniform film surface was achieved at high electrodeposition current. However, the agglomeration and initialy spalling film were occured at high nitride particles concentration. Structure analysis of the films revealed the presence of TiN and AlN crystalline in the composite film.

Keywords: Electrodeposition, Ni-TiAlN composite film, tungsten carbide, morphology, composition, structure.

1. INTRODUCTION

Development of thin coating or film onto a material is a method to protect the material from external influencies such wear and corrosion. The wear is occured due to the mechanic interaction between two or more materials cause a friction while the corrosion is due to chemical interaction between material and corrosive ions. The rate of wear and corrosion can be prominent at high temperature operation. In thin fim development, electrodeposition is a method to develop a film onto a material or substrate that work based on the electrochemical process. Electrodeposition is a film growth process onto a material through the electrochemical reduction from an electrolyte solution [1]. In the process, the charges are transfered between electrode rod surface and ionic solution or electrolyte under applied potential or current. Electrolyte is liquid solution containing ionic species in either water or non-aqueous solvent [2,3]. The process is easy to control, low working temperature and produces various films on various substrates. The characteristics of composite films were influenced by electrodeposition parameters such curent density, partikel concentration, stirer speed, pH etc.

In general, the optimum performance of film onto a material can be achieved by combining two or more different type elements in form of composite. For example, nickel (Ni) as an engineering material is commonly used to protect a material from oxidation. Nickel (Ni) films have been widely used to protect materials from wear and corrosion due to high density and less porosity. However, nickel is a ductile material and its performance in protecting material from wear is low especially at high temperature operation. Therefore, nickel can be combined by hard partickel such as nitride and carbide to optimize its performance.

The development of electrodeposited nickel-nitride composite films or coatings onto a substrates have provided better corrosion and wear resistance and hardness than pure-nickel films [2-4]. By embeding nitride compund particles into the Ni films, then the wear and corrosion rate can be reduced. One of nitride compound is TiAlN film that was suitable for dry high speed cutting applications due to excellent resistance to micro-abrasion and high temperature oxidation [5,6].

The electrodeposition of Ni-TiAlN composite films has been investigated to determine the proper electrodeposition parameters [7]. In this paper, the analysis on the effect of electrodeposition current and nitride compound partikel concentration on the composition, surface morphology and structure of composite film is reported.

2. EXPERIMENT

The potensiostat/Gavanostat Edaq controlled by personal computer with Echem software package was used for the electrodeposition experiment. The electrodeposition process was performed at various electrodeposition current from 2 mA to 4 mA and various concentration of TiN and AlN powder from 2 to 8 gr/lit. All experiments were conducted for 15 minutes. Tungsten carbide drill rod with dia. 1 mm as the substrate was used as working electrode while Platinum (Pt) and $AgCl_2$ were used as counter and reference electrode, respectively. Before electrodepositing, the tungsten carbide rods were rinsed in aquades and ultrasonically cleaned in alcohol 70% for 10 minutes and then dried on the hotplate. The electrolyte solution consists of 0.38 M Ni2SO4.6H2O, 0.17 M NiCl2.6H2O and 0.49 M H3BO3 mixed with TiN and AlN powder by using double-destiled aquades and then magneticaly stirered for about 24 hours. Surface morphologies and structure of composite film were analyzed by using SEM (Jeol, JED-2300) and XRD (Shimadzu-7000), respectively.

3. RESULTS AND DISCUSSION

3.1. Effect of electrodeposition current on morphology

The influence of the electrodeposition current on surface morphology is shown in figure 1. The surface morphology became rougher and bigger grain size but not compact as the electrodeposition current is increased from 2 mA to 3 mA. The surface morphology become smoother as further increasing electrodeposition current up to 4 mA. The nitride particles can be entrapped in Ni metal matrix by electrophoresis and the process rate is low at low current density which cause low nitride particle content in the film thus pavor for Ni growth and result rough film surface [3]. As the current density is increased then the grain is refined. However, it is not further refined as the current density is further increased. Thus an apropriate electrodeposition current is required to produce a compact and smooth film surface morphology.

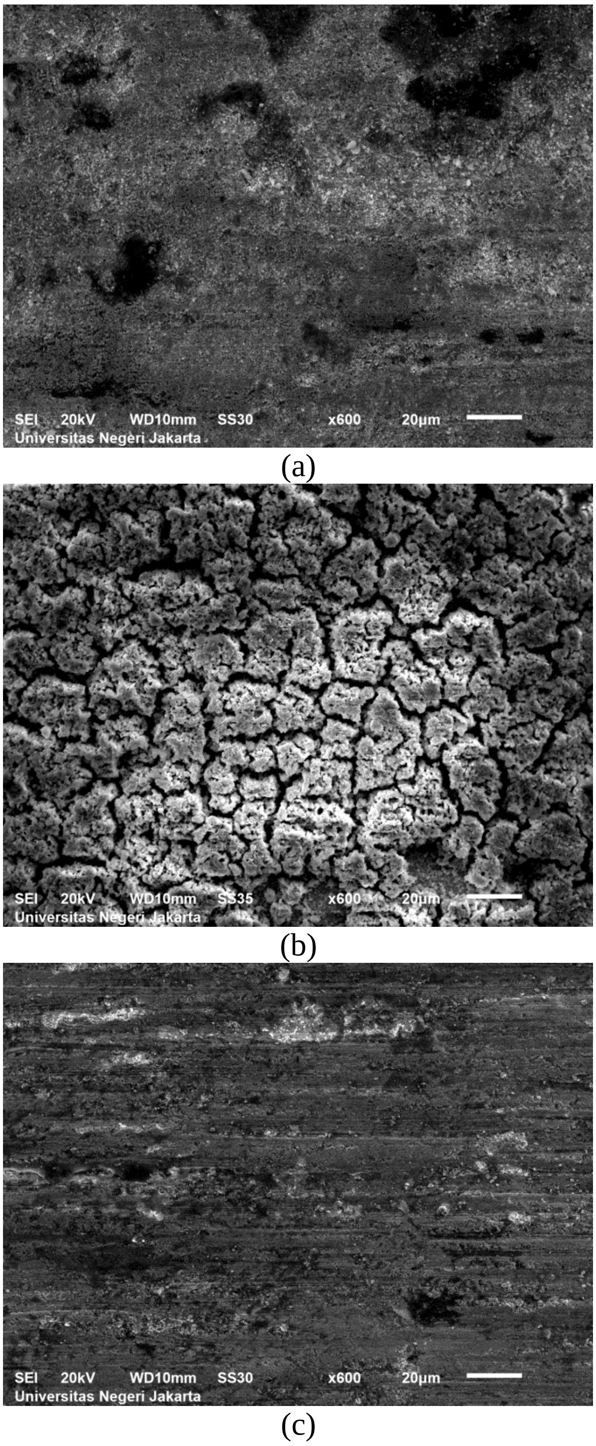
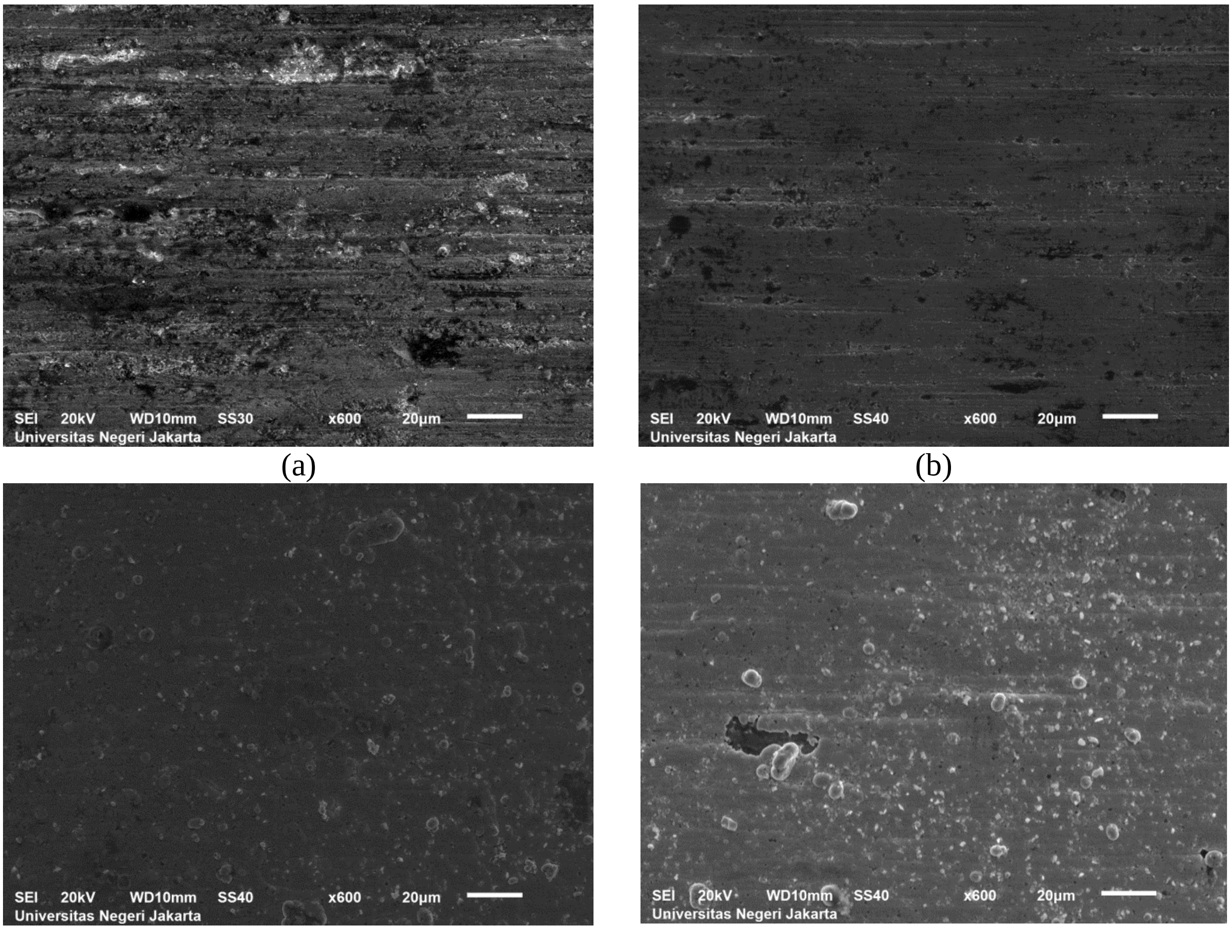


Figure 1. SEM analysis on surface morphology of Ni-TiAlN composite film at TiN and AlN concentration of 2 gr/lit and electrodeposition current of (a) 2 mA, (b) 3 mA (c) 4 mA.

The evolution of crystal grain depend on the nucleation and grain growth velocity. The finer crystal grain is due to high nucleation velocity and low grain growth velocity. At relatively low current density, the existence of particle lead to the high nucleation velocity and low crystal growth velocity cause the formation of nano crystal grains. On the other hands, at relatively high current density, the electro-gravitation between the substrate (cathode) and nickel ion (Ni^{+2}) is increased lead to the increase of nitride particle content in the composite films [8]. At high current density, much hydrogen is generated on the cathode surface thus increase the absorption and co-deposition of some insoluble material such as nickel hydroxide at the active nucleation and then cause inhibit the grain growth [9]

3.2. Effect of nitride particle concentration on morphology

The influence of TiN and AlN concentrations on the surface morphology of Ni-TiAlN composite films is shown in Figure 2.



(a) (b)

(c) (d)

Figure 2. SEM analysis on surface morphology of Ni-TiAlN composite film at TiN and AlN particle concentration of (a) 2 gr/lit, (b) 4 gr/lit, (c) 6 gr/lit and (d) 8 gr/lit.

The surface morphologies of composite films are fine as the concentration of TiN and AlN are increased from 2 gr/lit to 4 gr/lit. However as the concentration of TiN and AlN are further increased to 8 gr/lit, the film morphology become rough indicated by forming aglomeration onto the surface. The film delamination is also observed.

The nitride particle addition into the nickel-based composite films restrained the grain growth and accelerate the nucleation of nickel crystals cause the formation a fine film surface. As the concentration of nitride particles are increased in the electrolyte solution, the nitride contents in composite film increase and the composite film morphology should refine. However, at further increasing particle concentration, the agglomeration effect and subsequent gravitational sedimentation is occured cause the decrease of particle content in the film and rough surface morpholog formation [3]. It is obseved that irrespectively to the value of applied current density, the nitride particle content in the film increases to a certain maximum limit as the nitride particle concentration is increased but the content decrease after further increasing in nitride particle concentration [10]. The nitride particle addition stimulate the agglomeration of nickel particles grain of different sizes and propagate vertically in the film surface [2].

Film delamination may be due to the co-deposition of hydrogen during electrodeposition proess that takes place in aqueous electrolyte solution as a side-reaction accompanied with the metal ion reduction at the cathode and subsequently accumulate in the interface of film-substrate as the voids [11]. In this study, the effect is prominent at high nitride particle concentration.

3.3. Effect of electrodeposition current on structure

The effect of electrodeposition current on crystal sructure of Ni-TiAlN composite films are shown in Figure 3. The XRD peak of TiN and AlN tend to decrease, indicating grain refinement as electrodeposition current is increased from 2 mA to 3 mA. However, the peak of TiN and AlN increase as further increasing in electrodeposition current up to 4 mA, indicating crystal growth. The peaks at 35.73^0 and 48.36^0 correspond to TiN (111) and AlN (102) peaks, respectively while the peak at 77.1^0 corresponds to Ni (220) peak [2,3,4,12,13,14]. In general, there is a tendency of TiN peaks and AlN peak decreases slightly as the electrodeposition current was increased from 2 mA to 4 mA.

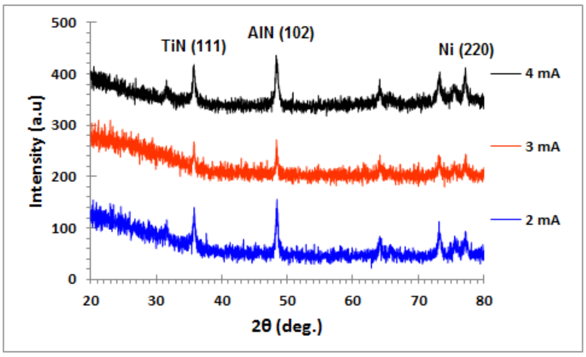


Figure 3. XRD analysis on structure of Ni-TiAlN composite film at electrodeposition current of (a) 2 mA, (b) 3 mA and (c) 4 mA.

Two important electrodeposition parameters that governing the particle content within the composite film are current density and particle concentration [15]. Current density control the particle flux to the subtrate (cathode) and may increase the probability of particle entrapped in the nickel growing crystal. In general, the various electrodeposition current do not influence the crystal orientation. AlN crystal peak is higher than TiN crystal indicating AlN crystal size is larger than TiN crystal size. A particle group could be embbed into the metal matirix when the attraction between the particle group and electrode is stronger than the removing force on the electrode [4,16]. In electrochemical process, a smaller nitride particle group has higher adsorption ability on the electrode than that of larger nitride particle group due to larger reactive area.

3.4. Efect of nitride particles concentration on structure

The effect of TiN and AlN particles on structure are shown in Figure 4. The peak of TiN decreased and broadened as TiN particle concentration is increased, indicating grain refinement. The peak at 44.6^0 , 52.1^0 and 76.6^0 correspond to (111), (200) and (220) Ni. The peak at 35.7^0 and 48.3^0 correspond to TiN (111) and AlN (102) peak, respectively [4,12,13,14,17]. In general, there is a tendency of TiN peaks decreases while AlN peak increases as the nitride concentration increases from 4 gr/lit to 8 gr/lit.

The addition of nitride stimulate the agglomeration of nickel particle of different size in the composite surface and it start propagate vertically on the surface cause a rough surface [2]. When the nitrides particle concentration in the electrolyte solution are increased then the nitride fraction in the coating increases and the increase of peak nitride intensities were observed.

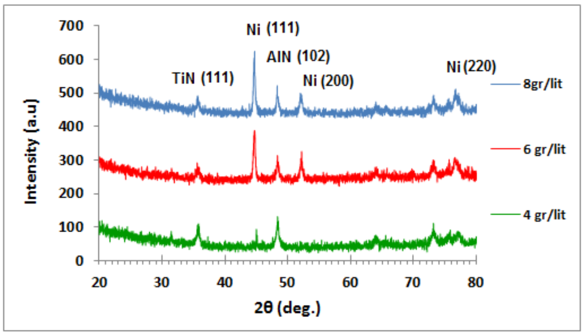


Figure 4. XRD analysis on structure of Ni-TiAlN composite film at TiN and AlN particle concentration of (a) 4 gr/lit, (b) 6 gr/lit and (c) 8 gr/lit.

4. CONCLUSIONS

The effect of various electrodeposition currents and nitride particles concentrations on surface morphology and structure of Ni-TiAlN films have been studied. The evolution of surface morphology and structure was occured as the electrodeposition current and nitride particles concentration were increased. The smoothest and uniform film surface was achieved at high electrodeposition current.

However, the agglomeration and initialy spalling film were occured at high nitride particles concentration. At high electrodeposition current and particle concentration, TiN crystal peaks tend to decrease slightly while AlN crystal peak increase as the nitride particles concentration is increased. AlN crystal peak is higher than TiN crystal indicating AlN crystal size is larger than TiN crystal size.

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