Mechanical and Tribological Properties of Pulse and Direct Current Electrodeposited Ni-TiO₂ Nano Composite Coatings

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Abstract

Ni-TiO₂ nano composite coatings were fabricated using pulse current electrodeposition technique at 100 Hz pulse frequency with a constant 50% pulse duty cycles and reference was taken with respect to the direct current (dc) electrodeposition. The properties of the composite coatings were investigated by using SEM, XRD, Wear test and Vicker's microhardness test. Pulse electrodeposited composite has exhibited enhancement of (111), (220), and (311) diffraction lines with an attenuation of (200) line. The results demonstrated that the microhardness of composite coatings under pulse condition was significantly improved than that of pure nickel coating as well as dc electrodeposited Ni-TiO₂ composite coatings. Wear tracks have shown the less plastic deformation in pulse plated composite. Coefficient of friction was also found to be lower in pulse plated composite coatings as compared to dc plated composite coatings.

Keywords: Composite coatings, Pulse electrodeposition, Microhardness, Wear

1. Introduction

Incorporation of the second phase fine particles into the metallic matrix during electro- or electroless plating process is known as composite electrodeposition. These fine particles include hard oxides (Al₂O₃, TiO₂, SiO₂, ZrO₂, Cr₂O₃ etc.); carbides (SiC, WC, TiC, etc.); nitrides (Si₃N₄, BN, AlN, TiN etc.); solid lubricants (PTFE, graphite, MoS₂, BaF₂, WS₂ etc.); and others include diamond, whiskers, flakes, nano rods or nano wires, nano tubes, etc. Codeposition of hard nano sized ceramics particles into the metal matrix has stimulated scientific and technological interests due to the superior mechanical properties of the composite coatings over pure metallic coatings. Recently, many researches have been carried out in order to maximize the nano particles incorporation and their homogeneous distribution into the metal matrix¹⁻⁵). Since, homogeneous distribution of nano particles leads to improvement in mechanical pro-

perties, tribological properties, corrosion resistance, anti-oxidation, as well as microhardness⁶⁻¹⁰). Metal matrix composite coatings containing TiO₂ particles exhibit interesting photocatalytic behavior accompanied by improved mechanical properties¹¹⁻¹⁴). The researches related to Ni-TiO₂ composite coatings have demonstrated that the codeposition percentage of nano titania particles is difficult to control quantitatively, mainly due to agglomeration¹⁵).

Over the past decades, vast amount of researches have been conducted on the electrodeposition techniques and consequently, the electro-fabrication process developed from direct current to the pulse current techniques. Compared to direct current electrodeposition, pulse current can allow higher current density, finer grains as well as higher incorporation of nano particles^{1,16}). In addition, pulse current has three independent variables; pulse frequency (f), pulse duty cycles (γ), and peak current density (I_p). Pulse frequency corresponds to the reciprocal of the total time period at a cycle (i.e. T_{on} + T_{off}). Duty cycle is expressed in percentages as the

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ratio of pulse ON to the total time period of a cycle.

$$\text{i.e. Duty Cycle } (\gamma) = T_{\text{on}} / (T_{\text{on}} + T_{\text{off}})$$

In practice, pulse plating usually involves a duty cycles of 5% or greater and T_{on} ranges from μs to ms. Pulse current will deposit metal at the same rate as does in dc plating, provided the average current density equals to the latter.

Pulse plating allows higher peak current which enhances the adatoms population and nucleation rate during T_{on} . Pulse current can affect the electro-crystallization mechanism and controls the physical and mechanical properties of the electrodeposited metal¹⁷⁾. It is interesting to note that the enhancement of coating properties by using pulse current method is not always associated with the influence of pulse current on particles codeposition process. Comparing the hardness of composite coating with that of the pure nickel coating as a function of grain size, it reveals that decreasing the grain size has the most significant effect on hardness of the coating rather than nano particles¹⁸⁾. Abdel Aal¹⁹⁾ has reported the four different mechanisms of strengthening of polycrystalline metals and alloys that describes: a) grain refinement strengthening from Hall-Petch relationship, b) dispersion strengthening due to Orowan mechanism, c) solid-solution strengthening, and d) crystal orientation.

In this present paper, Ni-TiO₂ composite coatings were fabricated by using pulse current electrodeposition technique and the surface morphology, crystallite orientation, microstructures, microhardness, and wear-friction behavior of the composite coatings were investigated as the prime mechanical properties of the metal matrix composites.

2. Experimental

All electroplating experiments were conducted in a 1000 ml glass beaker. The plating electrolyte was made using nickel sulfamate (Purity $\geq 90\%$, Samchun pure chemical Co., Korea) of which concentration and compositions are listed in Table 1. Pure nickel balls inside a titanium basket are used as anode while SUS 304 stainless steel sheet of exposed area $2\text{ cm} \times 3\text{ cm}$ was used as cathode. Cathode was ultrasonically cleaned for 5 minutes before plating. Cathode and anode were placed vertically in electrolytic bath and were separated about 5 cm apart from each other.

Average size of about 30 nm Degussa TiO₂ powder was ultrasonically dispersed in electrolytic bath and

Table 1. Electrolytic bath composition and operating conditions

Ni(NH ₂ SO ₃) ₂ (g/l)	300
NiCl ₂ (g/l)	10
H ₃ BO ₃ (g/l)	40
TiO ₂ (g/l)	20
CTAB (g/l)	0.3
Temperature (°C)	50
pH	4
Current type	dc and pulse
Average current density (mA/cm ²)	80
Stirring rate (rpm)	250
Pulse Frequency (Hz)	100

stirred for about 24 hrs before electrodeposition. Pulse current with average current density 80 mA/cm², pulse frequency 100 Hz with constant duty cycle of 50% were used as pulse parameters during electrodeposition process. After the electrodeposition, the samples were cleaned in running distilled water followed by ultrasonic cleaning for 5 minutes in order to remove loosely adsorbed nano particles and then subjected for further analysis. Microstructures, phase compositions, mechanical and tribological properties such as wear, friction, and microhardness were evaluated by SEM (JSM-6400, JEOL, Tokyo, Japan), XRD (Rigaku DMAX 2200, X-Ray diffractometer, Japan), wear (Plint TE77 tribometer, UK) and Vickers microhardness (Buehler Ltd., USA). Vickers microhardness test was carried out by applying 0.98 N loads for 10 seconds at ten different places of the cross-sections of a sample and the values were averaged. Wear-friction measurements were performed by using ball on plate bidirectional sliding wear method by applying 2 N loads for 10 minutes with the frequencies of 10 Hz at room temperature. Si₃N₄ ball (SN101C) of specific diameter 12.7 mm was used as counterpart during the test.

The crystallites size of nickel matrix were determined by using the (200) diffraction peak broadening according to the Scherrer's equation,

$$D = \frac{0.94\lambda}{B \cos \theta}$$

Where θ is the diffraction angle, λ is the wavelength of X-ray radiation and B is the full-width-half-maxima (FWHM) of the peak. The FWHM of the peaks were estimated after background correction and subtracting the instrumental line broadening, which was calculated using a standard nickel random

oriented powder according to the Warren equation,

$$B^2 = B_M^2 - B_S^2$$

Where, B_M is the measured diffraction FWHM peak and B_S the broadening of Ni standard powder sample.

3. Results and Discussion

3.1 Micro-structural and morphological analysis of deposit

The XRD patterns of pure nickel and Ni-TiO₂ composite coatings are shown in Fig. 1. Nickel coating is clearly observed to be preferentially orientated in the (100) plane direction (Fig. 1(A)). This crystal orientation is in accordance with the SEM surface morphology of the nickel coating prepared at dc plating condition (Fig. 2A). It is clear that the pure nickel coating has a rather regular surface and consists of pyramidal and polyhedral crystals with pronounced (100) planes of a cubic system. Pulse electrodeposited pure nickel has shown reduced preferred orientation with finer surface structure (Fig. 2(B)). Ni-TiO₂ composite coatings prepared at dc condition has retained some preferred orientation of (100) direction (Fig. 1(C)), but rather a random grain orientation. In accordance with this random orientation, the SEM surface morphology of Ni-TiO₂ composite coating does not exhibit the regular symmetry of pure Ni, but formed a variety of morphological structures (Fig. 2(C)). As evidence from the Fig. 1(D), pulse electrodeposited Ni-TiO₂

Fig. 1. XRD spectra of pure nickel and Ni-TiO₂ composite coatings; (A) pure nickel by dc plating, (B) pure nickel by pulse plating, (C) Ni-TiO₂ composite by dc plating, (D) Ni-TiO₂ composite by pulse plating.

Fig. 2. SEM micrographs of the surface morphologies of; (A) pure nickel by dc plating, (B) Pure nickel by pulse plating, (C) Ni-TiO₂ composite by dc plating, (D) Ni-TiO₂ composite by pulse plating.

has shown the pronounced increase in (111), (220), and (311) diffraction lines with an attenuation of (200) line. Moreover, the structure became more compact with some pile up of grains, which may be caused by the agglomeration of nano-titania particles during the co-deposition process (Fig. 2(D)). In the case of Ni matrix, the incorporation of nano particles significantly modifies the crystal growth orientation and corresponding surface morphology. It is assumed that co-deposition of nano particles changes or influences the process of electrocrystallization of Ni, and as a result, changes the crystal orientation and morphology of the matrix surface²⁰. In addition, the nano particles may act as the nucleation sites and as a detriment to crystal growth²¹, accordingly, nickel-titania composites have more compact structures with smaller grain sizes.

3.2 Microhardness

Microhardness of the pure nickel and Ni-TiO₂ composite coatings are shown in Fig. 3. It shows that microhardness of the pulse electrodeposited pure nickel is higher than the dc electrodeposited nickel. Similarly, Ni-TiO₂ composite coatings prepared at pulse condition has shown better microhardness than dc electrodeposited composite coatings. For the metal matrix composite coatings system, the microhardness of Ni-TiO₂ composites are approximately two times higher than that of pure Ni coatings, which can be attributed to the dispersion strengthening mechanism, grain refining effects as well as change in crystalline orientation patterns of nickel matrix. This reveals that

Fig. 3. Effect of pulse current and direct current electrodeposition on the microhardness of pure nickel and Ni-TiO₂ composite coatings.

Fig. 5. Variation of friction coefficients as a function of pulse and dc current electrodeposits.

Fig. 4. SEM micrographs of the worn out surfaces of; (A) pure nickel by dc plating, (B) pure nickel by pulse plating, (C) Ni-TiO₂ composite by dc plating, (D) Ni-TiO₂ composite by pulse plating.

the fine particles dispersed in the nanocrystalline matrix impede the motion of dislocations and thus increase the hardness of the metal matrix composites. The Ni-TiO₂ composite coatings prepared at pulse condition exhibit further increase in hardness than that of pure nickel and dc composite coating. At the same time reduces the plastic deformation of the matrix by grain refining and dispersive strengthening effects (Fig. 4). Thus, overall increase in microhardness of the pulse electrodeposited composite coatings is associated with the dispersion hardening, grain refining and change in crystalline orientation patterns of the nickel matrix.

3.3 Wear and friction

Wear tracks of pure nickel and nickel-titania

composite coatings are shown in Fig. 4. Metallic coatings generally undergo plastic deformations during sliding wear due to the movement of slip planes. As shown in Fig. 4(A), wear tracks of pure nickel coatings prepared from dc electrodeposition, shows typical adhesive type of wear with severe delamination along the sliding direction under the combined stresses of compression and shear. So, heavy plastic deformation occurred. Severe plowing and accumulation of the wear debris further increase the frictional properties of the coating, as evident from the coefficient of friction shown in Fig. 5. In contrast, pulse electrodeposited pure nickel shows some wear resistance properties as indicated by less wear depth and less wear debris. It might be associated with the grain refining effect that cause harder and compact deposit obtained by pulse condition. The wear behaviors of the composite coatings prepared by dc and pulse coatings have shown a mixed mode of adhesive- abrasive wear as shown in Fig. 4(C) & Fig. 4(D) respectively. Pulse deposited composite coating further exhibited wear resistant properties by less deformation as compared dc electrodeposited composites. It might be due to the dispersed nano particles, efficient grain refining effect and change in nickel crystalline orientation pattern from highly ductile (100) plane orientation into the harder nature of deposit, which resists for movement of dislocation planes, as represented by enhancement of (111), (220), and (311) peak reflections as shown in Fig. 1.

3.4 Grain size of composite matrix

The nickel crystallites sizes of pure nickel and Ni-TiO₂ composite coatings as a function of pulse or dc current electrodeposition are shown in Fig. 6. The

Fig. 6. Effect of pulse current and direct current electrodeposition on the nickel crystallites size.

nickel crystallite sizes for (100) plane orientation were calculated by using well-known Scherrer's formula. In order to form smaller or even nano-sized matrix crystals, continuous nucleation of new crystals should occur and this can be achieved by: (a) adding suitable grain refining agents to the electrodeposition bath, (b) adding a reinforcing second phase, and/or (c) applying pulse in the deposition current^{4,13}. The relation between the crystallite size and microhardness can be expressed by Hall-Petch relation, $H = H^0 + kd^{-1/2}$ where k is a constant known as the Hall-Petch stress intensity factor, d crystallite size, H microhardness and H^0 is the hardness of the material. This is based on the concept that grain boundaries act as barriers to the motion of dislocations by forming dislocation pile-ups at grain boundaries, resulting in hard deposits. Embedding of nano particles in the metal matrix perturbs the crystal growth by increasing the number of nucleation sites and consequently a reduction in the crystallite size occurs. Accordingly, our studies have revealed that the effect of pulse current electrodeposition and embedding of TiO₂ particles in the Ni matrix both enhanced to reduce the size of nickel crystallites.

4. Conclusions

Pulse electrodeposition has been found to have pronounced effect on grain refining of nickel coatings and consequently, increase in microhardness was also observed. Microhardness of the pulse electrodeposited Ni-TiO₂ composite has been increased as compared to composite coating fabricated by direct current. XRD patterns show that pulse electrodeposited

composite has exhibited enhancement of (111), (220), and (311) diffraction lines with an attenuation of (200) line. Ni-TiO₂ composite coatings prepared from pulse electrodeposition has shown increased wear resistance properties as compared to conventional direct current electrodeposition. Moreover, coefficient of friction was also found to be lower in the case of pulse composite electrodeposition.

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