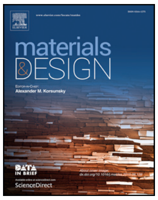
Materials and Design 107 (2016) 74–81

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes



Gradient electrodeposition of Ni-Cu-W(alumina) nanocomposite coating

M.H. Allahyarzadeh, M. Aliofkhazraei *, A.R. Sabour Rouhaghdam, V. Torabinejad

Department of Materials Engineering, Faculty of Engineering, Tarbiat Modares University, Tehran, P.O. Box: 14115-143, Iran

ARTICLE INFO

Article history:
Received 7 March 2016
Received in revised form 26 May 2016
Accepted 6 June 2016
Available online xxxx

Keywords:
Ni-Cu-W-Al_2O_3
Nanocomposite
Functionally graded
Hydrophobic

ABSTRACT

Ni-Cu-W-alumina nanocomposite coatings with functionally graded structure were electrodeposited using a continuous variation of duty cycle/frequency within eight stages. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were employed for microstructure and elemental analysis, respectively. The atomic force microscopy (AFM) and profilometry analyses were used to investigate the roughness of coatings. Results showed copper and alumina contents increased, while nickel and tungsten contents decreased toward the surface with a continuous drop in duty cycle. Continuous variation of pulse frequency showed a different manner, however; as it was found less effective than duty cycle. The observed contact angle demonstrated that the produced coatings have hydrophobic properties owing to their hierarchical morphology. In addition, the pin-on-disk wear test results indicated that the predominant controlling wear mechanism might be described as the abrasive wear created by the abrasive grooves.

1. Introduction

Nickel–tungsten alloys is considered as a promising candidate for environmentally friendly replacement of hard chromium because of its satisfactory properties and appearance [1]. Ni-W coatings are of interest because of their proper characteristics such as premium hardness and wear resistance [2–4], desirable anti-corrosion properties [5], electro-catalytic features [6], etc. These coatings can be applied by different techniques such as magnetron sputtering [7], electroless [8], and electrodeposition [9,10] methods. In electrodeposition method, it is possible to utilize direct current, pulse current, and pulse-reverse current. It is reported that coatings with proper mechanical properties can be obtained by the use of pulse currents [11]. Pulse plating also provides fabrication of novel structures such as functionally graded [12] and multilayer structures. By controlling and adjusting pulse parameters, namely the duty cycle and frequency, it is possible to control the structure and properties of deposited coatings in a more precise and efficient manner.

Regarding the electrodeposition of nanocomposite coatings, it is stated that ceramic particles (i.e. Al_2O_3) in the composite coatings degrade the adhesion of coating to the substrate [13–15]; therefore, their wear resistance significantly declines. To avoid this, coatings with low content of reinforcement particles at the coating/substrate interface and high content at top of the surface are recommended. These coatings are known as functionally graded coatings (FGC). Functionally graded materials are a kind of new engineering materials, in which some characteristics such as chemical composition and structure gradually change toward the surface, resulting in a change in the material properties [16].

Regarding the electrodeposition of FG coatings Wang et al. [17] fabricated Ni/SiC gradient deposit with continuous distribution of the SiC content from 0 to 30 vol.% By the method of increasing SiC concentration gradually and controlling the deposition conditions. Ni-P gradient electrodeposits with a graded variation of P content and phase structure as a function of coating thickness were conducted in a single plating bath through the control of current density [18]. Lari-baghal et al. electrodeposited the functionally grain size and SiC content graded Ni-Co/SiC coating using gradual increase in current density during electroplating. Their findings exhibited better bonding toughness and higher wear resistance of FG Ni-Co/SiC coating in comparison to uniform nanostructured coatings [19]. Ni-Al_2O_3 nanocomposite coatings with gradient structure were also pulse electrodeposited by continuous variation of pulse duty cycle and frequency through five layers. Alumina nano-particles gradually increase with decrease in pulse duty cycle, and consequently the microhardness increase as a function coating thickness [20]. Ni-W-(α-alumina) nanocomposite coatings with gradual increase in tungsten and alumina contents were deposited in our previous work. Pulse duty cycle decreasing and frequency increasing separately employed in order to obtain functionally graded coatings in eight steps. Also, results showed the more pronounced effect of duty cycle increasing in comparison with pulse frequency variations [21].

In this study, in a nickel-copper-tungsten ternary system, we are trying to fabricate Ni-Cu-W-alumina FG coatings using pulse electrodeposition so that the amount of copper and alumina content increased gradually, simultaneous with the drop in nickel and tungsten contents

---

* Corresponding author.
E-mail addresses: maliofkh@gmail.com, khazraei@modares.ac.ir (M. Aliofkhazraei).

http://dx.doi.org/10.1016/j.matdes.2016.06.019
0264-1275/

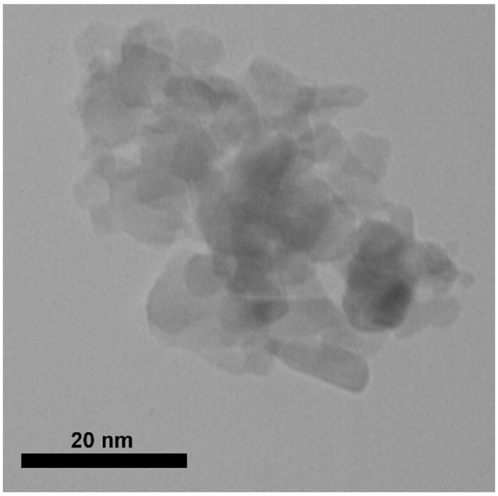


Fig. 1. TEM image of alumina nanoparticles used in FG-NC coatings.

along the coating thickness. For this purpose, stepwise variation of pulse parameters has been employed in eight steps. Since the commonly dominant factor affecting the corrosion properties of Ni-W alloys is crack density [22], this study was also conducted to investigate whether introducing copper is an efficient way to reduce the cracking of Ni-W structure. However, visual survey showed that the density of crack reduced, the cracks are also evident in the Ni-W after introducing copper.

2. Materials and methods

Carbon steel specimens were cut as rectangular samples with exposed area of 20 cm^2. Before to electroplating, the specimens were polished up to 600 emery papers. Then, the samples were rinsed with distilled water and degreased with methanol. Finally, they were acid washed and activated with 10% HCl for 10 s. Electrodeposition was conducted in a 200 ml beaker and pure nickel sheet was used as a consumable anode. Electrodeposition was carried out using the pulse current. The variation of pulse parameters during each plating stage was performed by a pulser facility connected to the rectifier. The composition of the electrolyte was 150 g/l nickel sulfate ($NiSO_4 \cdot 6H_2O$), 45 g/l nickel chloride ($NiCl_2 \cdot 6H_2O$), 40 g/l boric acid (H_3BO_3), 20 g/l sodium tungstate ($Na_2WO_4 \cdot 2H_2O$), 73 g/l sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), 10 g/l copper sulfate ($CuSO_4 \cdot 5H_2O$), 20 g/l nano α-alumina, 1 g/l sodium saccharin, and 0.1 g/l sodium dodecyl sulfate (SDS). Fig. 1 shows the TEM image of the utilized alumina nanoparticles. To avoid agglomeration of nano-alumina, the suspension was subsequently agitated by a magnetic stirrer (400 rpm) for 12 h, followed by further agitation with ultrasonic for 30 min (with the power of 160watt and frequency of 20 kHz) just prior to the electroplating. During the plating process, temperature and pH were fixed at 50 °C and 6 ± 0.15, respectively. Besides, the electrolyte was stirred at about 190 ± 10 rpm using a magnetic stirrer, and the solution pH was adjusted using the ammonia or sulfuric acid.

The microstructure of the coating layers was characterized by SEM. Moreover, the elemental analysis of deposited films was performed by energy dispersive X-ray analysis (EDS). Micro-hardness measurements of the coatings were performed on their surface using a Vickers microhardness instrument at an applied load of 25 g for a period of 15 s and the corresponding final values were determined as the average of 5 measurements. Furthermore, the topography and surface profile of the coatings were analyzed using AFM (Ara-A.F.M. Model No.0101/A: Iran). Electrochemical measurements were performed using an EG&G 273A interfaced with a computer. Potentiodynamic polarization was carried out in 3.5 wt.% NaCl solution, in a potential range of −300 mV to +700 mV with respect to OCP with a scan rate of 1 mV/s. For electrochemical measurements, a platinum electrode was used as the counter electrode. Also, the potentials were measured and recorded with respect to a saturated calomel electrode (SCE) as reference electrode. Sliding wear tests were done using a pin-on-disk wear apparatus at room temperature in accordance with the ASTM-G99 standard. The normal load of 40 N with a speed of 8 cm/s was applied with a radius of 10 mm for 400 m of sliding. The used pin was made of alumina. Before the wear test, all contact surfaces were cleaned and then dried. The mass loss and the normalized wear rate were measured by a microbalance with the accuracy of ±50 μg. All samples were subject to wettability test using the deionized water according to D7334 standard. Hamilton syringe (ILS, model: CTC A200 S) was used for pouring the drop. A digital microscopic camera (Dino Lite, model: AM-413ZT) was used to film the drop profile. Wetting angle was measured after 25 s from drop impact with the surface of the coated sample. Table 1 illustrates the deposition conditions for each FG coating.

3. Results and discussion

Figs. 2 and 3 present the SEM images of Ni-Cu-W-Al_2O_3 nanocomposite coatings with functionally graded structures. Fig. 2 demonstrates the FG coatings developed using continuous variation duty cycle in eight layers at the constant frequencies of 100, 450, and 800 Hz at the magnification of 250× and 1000×.

Besides, Fig. 3 shows the FG coatings pulse deposited using the continuous alteration of frequency in eight stages at the fixed duty cycles of 20, 55, and 90% in two magnification levels. Because tungsten is co-deposited with iron-group metals [23,24] through forming complexes such as $[Ni((WO_4)_2(H)_2(Cit)]^{-2}$ on cathode surface, it is expected that with further formation of such products on the cathode surface, tungsten can be more co-deposited on the cathode. Taking into account the lower concentration of tungstate ions and consequently these complexes in the deposition electrolyte, and considering the fact that tungsten could not be deposited solely, as reported elsewhere [25,26], tungsten will be co-deposited under diffusion-control kinetics.

Moreover, from a thermodynamic point of view, copper is nobler than nickel and tungsten and deposits at the less cathodic potentials, at which Ni and W could not deposit. Therefore, during T_{OFF}, copper

Table 1
Conditions for electrodeposition of nanocomposite Ni-Cu-W-Al_2O_3 with FG structure.

Coating no.	Frequency	Time (s)	Duty cycle (%) in							
			1st layer	2nd layer	3rd layer	4th layer	5th layer	6th layer	7th layer	8th layer
FG-NC-100f	100 Hz	1500	90	80	70	60	50	40	30	20
FG-NC-800f	450 Hz	1500	90	80	70	60	50	40	30	20
FG-NC-1500f	800 Hz	1500	90	80	70	60	50	40	30	20
	Duty cycle		Frequency (Hz) in							
FG-NC-11DC	20%	1500	100	200	300	400	500	600	700	800
FG-NC-50DC	55%	1500	100	200	300	400	500	600	700	800
FG-NC-88DC	90%	1500	100	200	300	400	500	600	700	800