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Synthesis of functionally graded nano Al_2O_3–Ni composite coating by pulse electrodeposition

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ABSTRACT

The main goal of this research is the synthesis of functionally graded nickel–nano Al_2O_3 composite coatings by using pulse deposition in which the amount of the embedded nano alumina particles changes in the cross section of the composite. For producing functionally graded nanocomposite coatings by pulse electrodeposition under ultrasonic agitation, frequency and duty cycle changes can be applied and in this research, the influence of both parameters has been studied. Microstructure of these coatings investigated by SEM, EBSD and XRD methods. By changing the duty cycle from 90% to 10% at different frequency, the microstructure of the coatings did not change significantly. These coatings showed ductile structure with {0 0 1} texture at primary layers and small randomly oriented grains at final layers. The most important factor affecting the microstructure of the nickel matrix was the average current density and incorporation of nano alumina particles does not have significant effect on the microstructure. The optimum condition for production of functionally graded nano Al_2O_3–Ni coating was changing of the duty cycle from 90% to 10% at fixed frequency of 10 Hz.

1. Introduction

Metal matrix composite coatings (MMCs) can show unique physical, mechanical and chemical properties [1–3]. This makes them promising low cost advanced materials which can be produced by means of electrocodeposition. The advantages of the electrochemical fabrication method compared to other coating methods such as physical vapor deposition (PVD), chemical vapor deposition (CVD) and powder metallurgy include more homogenous distribution of particles, reduced waste materials and ability of continuous processing [4]. However, the dispersion of the particles (particularly for nano particles) in a common plating bath can be problematic. In most cases agglomeration and sedimentation of the particles take place which makes successful co-deposition difficult.

Functionally graded material (FGM) is a novel engineering system developed in the mid-1980s in Japan. In these materials some characteristics like composition and structure gradually change, resulting in material properties changes [5]. It is already known that functionally graded materials may reduce delamination and spallation of coatings [5–7]. In the simplest FGMs, two different type of structures change gradually from one to the other. The materials can also change in a discontinuous way in a stepwise gradation. So far graded coatings have been produced by various methods such as PVD, CVD, thermal plasma spray and electrodeposition [7]. By using electroplating method, the graded coatings can easily be manufactured by changing the process variables like the current density, rate of stirring and particle loading in the bath. Examples of such graded coatings include a nickel deposit reinforced with SiC microparticles [5,6,8,9] and Al_2O_3 nanoparticles [7,10,11].

Among these parameters the imposed current is one of the most important ones, having a great influence on particle content in the composite coating and consequently on coating properties [3,4,12]. Different types of currents like direct current (DC), pulsed current (PC) and pulsed reversed current (PRC) have been employed [4,12–18]. PC has been proved to be a useful tool for designing metallic coating properties and a considerable number of theoretical models have been introduced to explain the way pulse current alters the process of electrodeposition [13]. Landolt and Marlot reviewed the effect of PC on microstructure and composition of metallic coatings [13] and recently, many other researchers were employing PC and PRC for production of the composite coatings. Pulsed electrodeposition is employed to produce many different composite coatings like Ni/W–Al_2O_3 [14], Ni–SiC [15] and Ni–TiO_2 [3,12], and results have shown a possible control of particle content in the coating by using PC [3,15,17] or PRC [17] and also enhancement of the uniformity of particle dispersion in the coating. However, the effect of pulse electroplating parameters on

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Table 1
Chemical composition of the bath and the parameters of electrodeposition conditions.

Compositions and conditions	
$NiSO_4{\cdot}6H_2O$	250 g L^{-1}
$NiCl_2{\cdot}6H_2O$	40 g L^{-1}
H_3BO_3	35 g L^{-1}
$C_{12}H_{25}NaO_4S$ (SDS)	0.3 g L^{-1}
Al_2O_3 particle (80 nm)	20 g L^{-1}
Maximum current density	20 A dm^{-2}
Coating thickness (5 layers)	100 μm (each layer 20 μm)
Pulse frequency	1–125 Hz
Pulse duty cycle	10–90%
Stirring speed during electrodeposition	100 rpm + ultrasonic agitation
Temperature	50 ± 2 °C
pH	3.5 ± 0.2

incorporation rate and properties of the coating is not always reported the same. For example, in the case of Ni–Al_2O_3 composite coating, the authors have reported contradictory behaviors by using PC [4,14,18].

The main goal of this research is the synthesis of functionally graded nickel–nano Al_2O_3 composite coatings in which the amount of the embedded nano alumina particles changes in the cross section of the composite. Such composite coatings already were produced by other methods [7,9], but this is the first time that pulse parameters during electrodeposition process will be used to manufacture functionally graded composite coatings.

2. Experimental

A modified Watts Ni bath composition and the electroplating process conditions are presented in Table 1. The solutions were prepared from analytic grade chemicals (Merck) and double distilled water. The pH of the bath was adjusted to value (pH = 3.5 ± 0.1) with $NH_3{\cdot}H_2O$ (10 wt.%) and H_2SO_4 (10 wt.%) solutions.

The average particle size of the Alumina powder used in the experiment was about 80 nm. Alumina particles were maintained as suspension in an electrolytic bath by using continuous magnetic stirring at rotating speed of 300 rpm for at least 24 h before deposition. The suspension was subsequently agitated by an ultrasonic homogenizer (SONOPULS HD 3200, Bandeline, Germany) for 30 min just prior the electroplating. The frequency of ultrasonic homogenizer was 20 kHz and the ultrasonic power was about 100 W (50% of max. power) with a titanium probe (KE 76, 6 mm tip diameter) for 500 cc of the bath solution.

Copper sheets with an area of 0.785 cm^2 (a circle with 1 cm diameter) on one side was used as the cathode while the other surface of the substrate was covered with a PVC adhesive tape. A high purity (99.99%) nickel plate used as the soluble anode was vertically maintained at 3 cm from the copper sheet. Anode's surface area was chosen approximately six times greater than that of the cathode to ensure that no problem arises from the anodic polarization of nickel. Prior to electroplating, the substrates were mechanically polished to a 0.08–0.12 μm surface finish with emery papers and then sequentially ultrasonically cleaned in acetone for 3 min, washed in distilled water, activated in 1:5 H_2SO_4 for 15 s, washed in distilled water again and then immersed immediately in the plating bath to allow the electrodeposition of the target nanocomposite coatings.

In order to maintain a uniform particle concentration in the bulk solution, two agitation methods were used simultaneously during the electrodeposition process: mechanical agitation by a magnetic stirrer (100 rpm) located at the bottom of the cell and ultrasonic energy by an ultrasonic probe (20 kHz, 20 W) which was directly immersed into the solution and positioned between the working and counter electrodes in such a way that there was no shielding. The probe was immersed deep enough into the bath to avoid foaming. The electrolyte temperature was maintained at 50 ± 2 °C during electrodeposition process. The electrochemical deposition experiments were made using a PGSTAT128N model Autolab potentiostat/galvanostat controlled by the NOVA software. Saturated calomel electrode (SCE) was the reference electrode while the copper and the nickel plates were the working and counter electrodes, respectively.

As mentioned before, for producing functionally graded nanocomposite coatings by pulse electrodeposition, frequency and duty cycle changes can be applied. In this research, the influence of both parameters has been studied. Each of the functionally graded electrodeposited coatings used in this investigation was prepared at 20 A dm^{-2} peak current density and consists of 5 layers manufactured at different pulse conditions. To study a role of duty cycle in production of functionally graded coatings a set of samples was prepared with identical duty cycle changing frequencies: 5, 10, 50 and 100 Hz. In these samples at each frequency the duty cycle has been changed in such a way that 1st, 2nd, 3rd, 4th and 5th layers were deposited with 90, 75, 50, 25 and 10% duty cycles. Details of pulse parameters for these samples are summarized in Table 2.

Also, in order to study a role of frequency in of modification of structure of coatings another set of samples was prepared using different frequencies for each layer (5, 10, 50, 100 and 125 Hz) at different duty cycle as listed in Table 3.

Ultrasonic cleaning of the deposits in distilled water, for 5 min, was followed by the electrolytic codeposition to remove any loosely adsorbed particles. The thickness of the deposited coatings as theoretically calculated by Faraday law was about 100 μm (each layer 20 μm). The thickness of the coatings is calculated neglecting the cathodic reaction that generally reduces the thickness of the composite coatings and so the actual thickness of the deposits was about 90–96 μm.

Table 2
Sample deposition conditions used to investigate fabrication of functionally graded coating by changing duty cycle.

Sample	f (Hz)	θ (%)	T_{off} (ms)	T_{on} (ms)	i_p (A dm^{-2})	i_m (A dm^{-2})
D5	5	90, 75, 50, 25 and 10	20–180	180–20	20	18, 15, 10, 5 and 2
D10	10	90, 75, 50, 25 and 10	10–90	90–10	20	18, 15, 10, 5 and 2
D50	50	90, 75, 50, 25 and 10	2–18	18–2	20	18, 15, 10, 5 and 2
D100	100	90, 75, 50, 25 and 10	1–9	9–1	20	18, 15, 10, 5 and 2

Table 3
Sample deposition conditions used to investigate fabrication of functionally graded coating by changing frequency.

Sample	f (Hz)	θ (%)	T_{off} (ms)	T_{on} (ms)	i_p (A dm^{-2})	i_m (A dm^{-2})
f25	5, 10, 50, 100 and 125	25	150–6	50–2	20	5
f50	5, 10, 50, 100 and 125	50	100–4	100–4	20	10
f75	5, 10, 50, 100 and 125	75	50–2	150–6	20	15
f90	5, 10, 50, 100 and 125	90	20–0.8	180–7.2	20	18

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