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THE EFFECT OF PULSE PARAMETERS IN ELECTRO DEPOSITION OF COPPER-ALUMINA NANO COMPOSITES

Setareh Golroh, Saeed Reza Allahkaram[*] and Morteza Mohammadalipour

School of Metallurgy and Materials Engineering, University College of Engineering, University of Tehran, P.O.Box: 11155-4563, Tehran, Iran

ABSTRACT

In this study copper-nano alumina composite coatings were pulse plated on copper substrate aimed at the improvement of properties like finer grain size, more hardness, higher wear and corrosion resistance. The inclusion of hard particles such as alumina in a metal matrix leads to higher mechanical properties. In this investigation, pulsed electro deposited coatings has been analyzed from a sulfuric acid bath. Pulse duty cycle of 5% and 10% at frequencies 10Hz, 50Hz and 100Hz were employed. The influences of pulse parameters on the thickness, grain size, alumina content, hardness and corrosion resistance of coating were studied. Finally, the optimum conditions in order to achieve higher coating properties in accordance with more current efficiency were obtained.

Keywords: Pulse plating, Electrocodeposition, Composite coating, Nano particle, alumina

INTRODUCTION

Traditional method of electro deposition is DC plating. This has been modified by the use of current interruption or even current reversal termed as pulsed electro deposition. In DC plating, only the current or potential can be varied. However, in pulse plating method, many variables such as pulse duration, pulse duty cycle and pulse current could be changed in order to obtain better deposited layer. Pulse plating improves the deposit properties such as hardness, plating thickness, finer grain size and corrosion resistance [1]. Generally, in electrocodeposition techniques for producing a metal or compound, a driving force in the form of potential or current is applied to the electrode. Modern electronics allows one to make use of these parameters as a function of time. This permits a number of possible ways of varying the conditions [2]. Four important parameters are of primary importance in pulse plating. They are:

Peak current density (i_p), average current density (i_a), pulse length (*on time*) and pulse pause (*off time*).The sum of the on and off times constitute one pulse cycle. The duty cycle is defined as Eq. (1) and the average current density

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[*] e-mail: akaram@ut.ac.ir, Tel/fax: +982161114108

under pulse plating conditions is defined as Eq. (2).

$$duty.cycle = \frac{on.time}{on.time + off.time} \times 100\%. \tag{1}$$

$$i_{ave} = \frac{t_{on} i_p}{t_{on} + t_{off}} = duty.cycle \times i_p. \tag{2}$$

In this approach, DC and PC electroplating were used in order to achieve copper/ nano-alumina composite deposits. The coating properties obtained by these two methods were compared and finally the optimum pulse parameters were characterized.

EXPERIMENTAL PROCEDURE

Copper-alumina nano composites were deposited from an acidic copper sulfate bath. The basic composition of electrolyte and deposition parameters is given in *Table 1*. Before the electroplating process, the electrolyte was under ultrasonic waves for 30 minutes and during the process it was magnetically stirred at a speed of about 300 rpm in order to keep the nano particles in suspension. Copper plates of 1×1cm^2 area were used as working electrodes and prior to the electrocodeposition were ground using 800 grade silicon carbide papers and degreased with Uniclean 675 solution. The surfaces of cathodes were activated in 10% sulfuric acid solution. Copper plates of 2×3cm^2 area were used as anode. A Potentiostat model ZCM761 (ZAG Chemie Co) was used for DC plating and a rectifier model RCTP50V50A was used for pulse plating. The pulse plating parameters were changed according to *Table 2*.

Table 1:– Electrolyte composition and deposition conditions

Materials and Conditions	DC method	PC method
Metal ($CuSO_4.5H_2O$) [M	0.8	0.2
H_2SO_4 [M]	0.56	0.2
pH	1	1.5
Temperature [ºC]	Room temperature	

Table 2. – Pulse plating parameters

t_{on}[ms]	t_{off} [ms]	Pulse frequency [Hz]	Duty cycle [%]
5	95	10	5
10	90		10
1	19	50	5
2	18		10
0.5	9.5	100	5
1	9		10

The surface morphology and microstructure of the coatings were investigated using a Cam. Scan. MV2300 model scanning electron microscope (SEM). The particle content in the films was determined by energy dispersive X-ray analysis (EDX).The Vickers micro hardness of the films was determined by applying 10grf force as described in ASTM E 384-05 a. Polarization curves in electrolytes were recorded at a scan rate of 10 mVs^{-1}. All polarization scans were performed by changing the potential from 0V down to -1V and then anodically to +1V and back to the starting potential.

RESULTS AND DISCUSSION

Metallurgical Inspections.

The effects of pulse parameters were investigated and a comparison was made between DC and PC electrodeposited coatings. The surface morphology of films plated with DC and PC method is shown in *Fig.1*. As it is seen, the surface morphology of the copper films is not homogeneous and made up of relatively large grains in DC method. In the case of PC plated coatings, the surface morphology of coatings was significantly altered due to applying pulses during coating process. According to the electro crystallization as discussed by Denny Thiemig et al., the grain size and growth mode is defined by the interplay of nucleation and growth [3]. In the case of PC experiments, the number of atoms deposited during one cathodic cycle is defined by t_{on} and i_p. Furthermore, sorption process occurring during pulse pause may influence nucleation and growth in the following cathodic pulse cycle. Note that the cathodic pulse current density in PC method is comparable to the average current density in DC plating [3]. The visual inspection of SEM micrographs of *Fig.1* shows that the finest most homogeneous surface morphology is at 100 Hz frequency and 5% duty cycle (*Fig. 1d*). The cross-sectional micrographs of coatings are shown in *Fig 2*. As it is seen, the thickness of coatings applied by PC method ranged from 48.7 to78.2 µm, whereas the coating thickness of DC plated coating is about 10.2 µm.

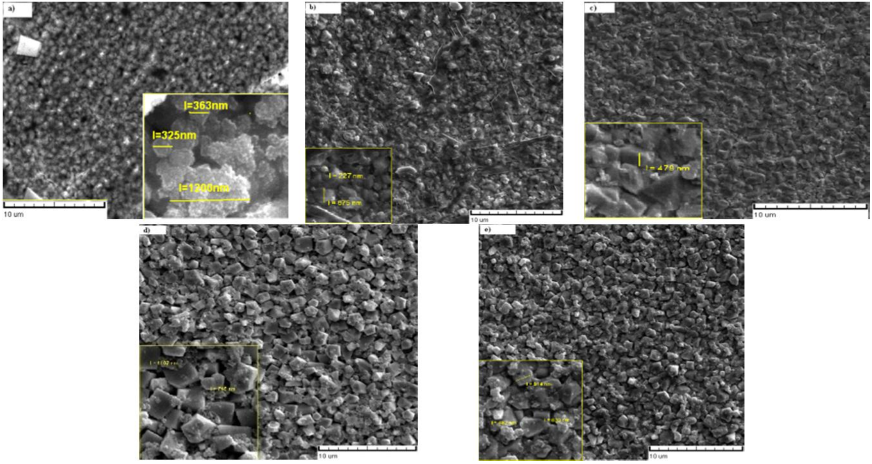

Fig.1 – Surface morphology of composite coatings (×5000): a –Applied by DC method at i=10 mA.cm^{-2}; b– PC method at frequency=10Hz, Duty cycle=5%; c – PC method at frequency=50Hz, Duty cycle=5%; d – PC method at frequency=100Hz, Duty cycle=5%; e –PC method at frequency=10Hz, Duty cycle=10%

Also, the DC plated coating is incoherent (*Fig. 2a*) while all the layers that are deposited by PC method are coherent (*Fig. 2b to 2d*). The maximum coating thickness is obtained at 5% duty cycle and 100Hz frequency.

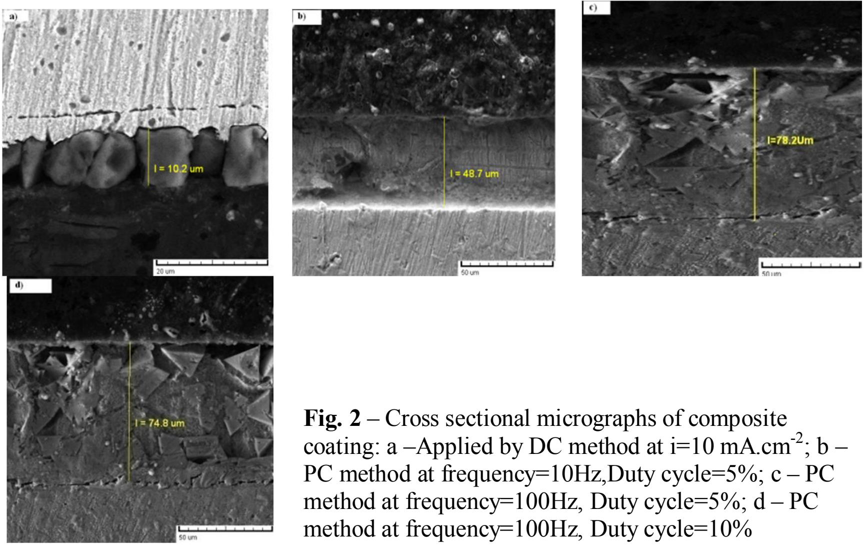

Fig. 2 – Cross sectional micrographs of composite coating: a –Applied by DC method at i=10 $mA.cm^{-2}$; b – PC method at frequency=10Hz,Duty cycle=5%; c – PC method at frequency=100Hz, Duty cycle=5%; d – PC method at frequency=100Hz, Duty cycle=10%

The variation of the amount of embedded alumina nanoparticles in the metal matrix with the pulse frequency and duty cycle is given in *Fig. 3*. In general, the particle content of the coatings increases with decreasing duty cycle and increasing frequency. Shorter on times are beneficial for the particle inclusion at the same duty cycle. The average particle incorporation in copper films ranged from 14.1 to 22.7 wt.% alumina.

Table 3 – Coating thicknesses of the samples in Fig. 2.

Figure	Thickness [µm]
2-a	10.2
2-b	48.7
2-c	78.2
2-d	74.8

The maximum particle incorporation was observed in coating deposited at a duty cycle of 5% at a frequency of 100Hz. Compared to DC plating of $Cu-Al_2O_3$ composites at a current density of 10 $mA.cm^{-2}$ with a particle content of about 13.4 wt%, an enhancement of particle incorporation occurred due to the application of pulses. As the duty cycle decreases and pulse frequency increases, the alumina content of the composite layer increases. So the best final properties are expected at this condition.

The effect of the individual pulse parameters (pulse length, t_{on} and pulse pause, t_{off}) can be summarized by introducing the average plating current density, Eq. (2).Taking into account that the average current density increases with the duty cycle and peak current density, i_p, one can conclude that the incorporation of alumina nanoparticles is favored by low average current densities. The average current density in PC is comparable to the applied current density in DC deposition. Similar to the currently observed dependence, the maximum amount of co-deposited particles in the case of DC deposition was often found in the range of low current densities at which the metal ion reduction changes from charge transfer to mass transport control [3].

HARDNESS AND CORROSION RESISTANCE ANALYSIS.

The hardness of composites is known to be related to the structure of the matrix and the amount and distribution of reinforcing metal oxides particles. The results shown in *Fig. 4* indicate a significant hardness increase in composite films comparing to the substrate. Note that the average micro hardness of the substrate was about 65HV, whereas the values of the composite coating varied between 124 and 156 HV. It means that the presence of alumina nanoparticles leads to about 1.4 times increase of micro hardness. During pulses, a very thin pulsating diffusion layer has been formed leading to an enhanced nucleation rate and surface coverage with denser building up of fine grained deposits. Also note that the micro hardness differs by changing the pulse parameters during the electrodeposition process. For example by increasing the frequency from 10Hz to 100Hz in composite coatings, the micro hardness of coating increased from 149 to 156 HV at duty cycle 5%. Also the shift of diagram by changing the duty cycle percent from 5% to 10% is clearly noticed in *Fig. 4*. The main parameter governing the hardness of the coating in the composite films is the microstructure of the metal films which is changed by the different pulse parameters, as shown in morphological pictures above [4].

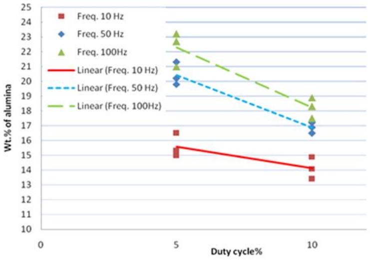

Fig. 3 – Effect of duty cycle and pulse frequency on the alumina content of copper-alumina composites

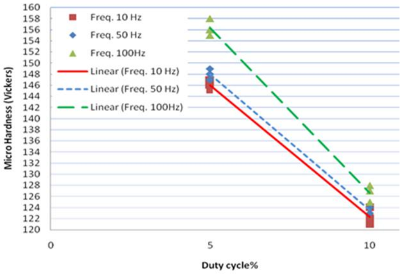

Fig.4 – Effect of pulse duty cycle and frequency on coating micro hardness

In order to determine the corrosion resistance, the polarization curves were compared in coatings. As it is clear in *Fig. 5* and *Fig. 6*, the corrosion current that directly related to the corrosion rate, decreases by increasing pulse frequency and pulse pause length. Increasing the pulse frequency and pulse pause length leads to more homogeneous and finer grain sizes. This leads to more corrosion resistance as expected. This property combined by improved surface hardness in comparison with conventional materials make these composite coatings applicable in a variety of areas.

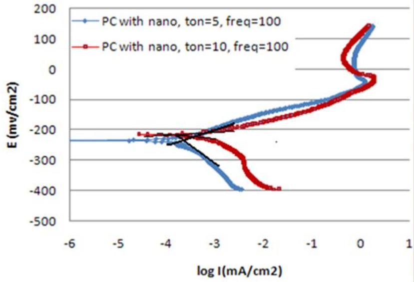

Fig. 5 – Polarization curves for composite coatings in different duty cycles (5% and 10%)

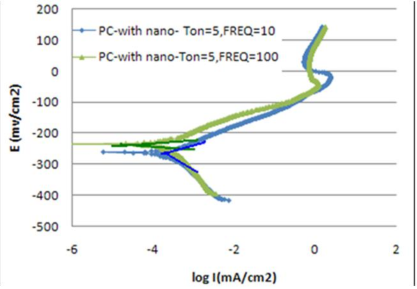

Fig. 6 – Polarization curves for composite coatings in different frequencies (10Hz and 100 Hz).

Sample identity	i_{Corr} (mA.cm^{-2})	E_{Corr} (mV.cm^{-2})	Sample identity	i_{Corr} (mA.cm^{-2})	E_{Corr} (mV.cm^{-2})
5% duty cycle	10^{-4}	-250	10Hz frequency	$10^{-3.8}$	-270
10%duty cycle	$10^{-3.9}$	-220	100Hz frequency	$10^{-4.7}$	-230

CONCLUSION

The influence of pulse duty cycle and pulse frequency during electrocodeposition of copper-alumina composite coatings on surface morphology, coating thickness, alumina content, hardness and corrosion resistance of coatings have been studied. From the obtained data, the following conclusions are made:

1. Comparing DC and PC deposition shows an improvement of the properties of pulse plated coatings in both metallurgical and mechanical properties.

2. Good quality deposits (finer grain size and more homogeneous) in accordance with high hardness and corrosion resistance can be obtained at lower duty cycles and higher frequencies. For example at 5% duty cycle and 100Hz frequency for a peak current density of 10 mA.cm^{-2}.

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