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INFLUENCES OF ELECTROLYTE TYPE AND AGITATION REGIMES ON STRUCTURAL – MECHANICAL PERFORMANCE OF ELECTROLYTICALLY DEPOSITED COPPER COATINGS ON DIFFERENT CATHODES

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Abstract *Composite systems of electrodeposited 10 μm Cu coatings on Cu foils and 30 μm Cu coatings on brass foils were obtainefd in direct current regimes (DC) from electrolytes without/with additives. Different regimes of stirring electrolytes were investigated: stationary, magnetic, and ultrasonic. Also, multilayered Cu coating was successfully obtained by the electrodeposition with periodic ultrasonic/magnetic stirring of basic sulfate electrolyte. A bending test technique was used to assess the adhesive strength to the cathodes. Vickers indentation test machine was used for measuring composite hardness in the micro-range. The adhesion parameters named "the critical reduced depth" and "critical cycle number" for the Cu coatings proved suitable for assessing the adhesion behavior. Composite hardness models of Korsunsky and Chen-Gao were applied in order to calculate an intrinsic hardness of the coatings and for an assessment of adhesion performance. The corrosion resistance of the Cu coatings was investigated using the "static corrosion test." A comparative study showed that the Cu coatings produced in ultrasonic agitation regime or in laminate form have better mechanical properties and better corrosion resistance. It has also been shown that Cu coatings synthesized from electrolyte with additives are structurally superior, but a "soft hardening effect" was observed.*

Keywords: *composite, soft hardening effect, adhesion, critical reduced depth, critical cycle number.*

1. INTRODUCTION

In the field of surface engineering and materials engineering the copper coatings and multilayer copper structures had attracted great interest. Control of the microstructure of these materials in cost-effective manner enables the development of high-performance materials [1]. Among various techniques to enhance coating properties, electrodeposition technique is simple, low-cost, eco-friendly, easy-controlled, and compatible with other deposition techniques, such as: physical vapour deposition (PVD), chemical vapour deposition (CVD), spraying and roll-to roll coating processes [2]. The properties of copper coatings are a key factor that

determines the reliability of interconnections because copper replaced aluminum as the interconnect material in VLSI technology [3]. Ultrasonic-electrodeposition has much attention recently. The ultrasonic-electrodeposition was used for dispersion of the second phase in copper matrix such as SiC nanoparticles [4], for increasing deposition rate, for improved density and uniformity of the coating or enhanced ion diffusivity of electroplating solution [5]. However, the roughness of copper coatings can be increasing with the application of the stronger intensity of ultrasound probe indicating a strong effect of ultrasound on hydrodynamic conditions in the near-electrode layer, which is manifested by the increase of share of the „activation control" in the mixed „activation-diffusion control" of electroplating process [6]. The beneficial impact on the micromechanical properties of copper coatings was shown during electrodeposition with the assistance of the ultrasound bath during mixing of the electrolyte [7-8]. Nowadays, with application of old technique with little modification, it is possible to replace conventional electrodeposition copper coating (ordinary) with new nanostructured coating (ultrasonically) or with superior multilayer (laminate) composite structures.

The surface hardness of the different forms of copper coating can be investigated using continually or discontinually indentation techniques such as: nanoindentation or microindentation hardness techniques with various application types of shape indenter (pyramid, cone, sphere etc.) [9]. However, with application of microindentation technique for very thin coating with an application of loads above some critical value, a substrate (cathode) commences to contribute to a composite hardness. Then, it is necessary to apply corresponding mathematical composite hardness model for a determination of the absolute (or real) hardness of coating [10-14].

The adhesion strength of thin coating to the substrate is very important, too. Poor adhesion leads to a reduction in mechanical structural performance [10-12]. Test methods for coating adhesion investigation are very different. Fast tests are often used in the industry, such as: knife, tape-test, pull-off adhesion test, scrape, scratch test and bending test [15]. An adhesion is also a measurable result of some hardness tests made by pencil hardness, gravelometer, impact, mandrel bend or indentation Rockwell technique [16]. However, there is no universal test for adhesion testing of all types of coatings. Most simple tests are not expressed in numerical values or SI units, but are given descriptively, terms like „film failed" or „film passed" [12]. The adhesion investigation for the type of composite system „*soft film on a hard substrate*" was conducted by Chen and Gao through a composite hardness model application of microindentation Vicker's technique on the example of copper films/glass substrate adhesion behavior [10-12]. The bending test jig was applied to investigate the adhesion of the copper coating to the stainless steel substrate using bending method [3]. The bending times or number of cycles before first delamination (air bubble appear on the sample) were recorded as the adhesion criterion of the coating samples. In this investigation the adhesion of the coating to the substrate was measured by bending method using a special automatic bending test designed in our lab. The idea is to compare the values of the adhesion parameter (b) and the values of the critical number of cycles (n). The adhesion parameter (b) or critical reduced depth of indentation was calculated based on composite hardness model applied to experimental value of composite hardness. The adhesion parameter (n) or critical cycle number was obtained by measuring the adhesion through the bending test on home-made devices. In the experimental part of the paper, the construction and fabrication of devices based on the Fused Deposition Modeling (FDM) procedure will be presented [17]. An additive manufacturing technology and biodegradable material (filament based on polylactic acid-PLA) were used for fabricated parts of the adhesion testing device.

2. EXPERIMENTAL

2.1. Synthesis of copper coatings

Copper coatings were produced using the direct current galvanostatic mode (DC regime), DC mode with an application of ultrasound mixing of electrolytes (DC/US regime) and DC mode with an application of magnetic mixing of electrolyte (DC/MS regime) at constant current densities (j = 50 mA·cm^{-2}). For processes of the electrodeposition, the following electrolytes were used: 240 g/l $CuSO_4$ 5 H2O in 60 g/l H_2SO_4, *electrolyte I* and 240 g/l $CuSO_4{\cdot}5H_2O$, 60 g/l H_2SO_4, 0.124 g/l NaCl, 1 g/l PEG 6000 (polyethylene–glycol), 0.0015 g/l MPSA (3–Mercapto–1–propane sulfonic acid), *electrolyte II* [6-8]. Also, multilayered Cu coating was successfully obtained by the electrodeposition with periodic ultrasonic/magnetic stirring of *electrolyte I.* The ultrasonic bath (Bransonic 220 Ultrasonic Cleaner), frequency at 40 kHz, was performed for mixing of electrolyte [8]. The electrolytes were also stirred by an application of magnetic stirrer (MS) (100 rpm, Heidolph Instruments GmbH & Co. KG, Schwabach, Germany).

Table 1. The conditions of electrodeposition applied for a formation of Cu coatings on different substrates from electrolytes *I* and *II*. In all experiments current density was j = 50 mA cm^{-2}.

No.	Name	Regime	Substrate	Thickness, δ (μm)	El.
1.	Ordinary	DC	Brass	30	*II*
2.	Ultrasonically	DC/MS	Brass	30	*II*
3.	Magnetically	DC/US	Brass	30	*II*
4.	Ordinary	DC	Cu	10	*I*
5.	Ultrasonically	DC/US	Cu	10	*I*
6.	Laminate	DC+DC/US	Cu	10	*I*

The cathodes were brass foil (260 1/2 hard, ASTM B36, K&S Engineering, 250 μm thick) and polycrystalline (pc) copper foil (125 μm thick) polished mechanically. The copper plate, cylindrical in shape, was used as anode, polished chemically in acid solution before deposition (HNO_3 : H_2O = 1:1 vol. %). The temperature and pH-values were maintained at 22 ± 0.5 °C, 0.30 (for

electrolyte I) and 0.33 (for *electrolyte II*), respectively. The coating thickness were 10 μm and 30 μm. Deposition area was 2 cm^2. The coating thickness is controlled by the mechanical comparator with electronic reader on display (model: Iskra, type: NP37 (Iskra Avtomatica, Ljubljana, Slovenia) with the accuracy of the vertical shift ±1 μm [7]. All conditions of obtained Cu coatings are summarized in Table 1.

2.2. Realization of lab-made bending test machine for adhesion evaluation using additive technology

The photography of our lab-made device for testing of copper coatings on various metal and flexible substrates on non-standard test machine is shown in Figure 1. Certain elements of the prototype were realized on a 3D printer (WANHAO Duplicator i3Plus, desktop printer ID: SHBST15080055732341YER-3, China). The basic parameters of device are: build volume 200 × 200 × 180 mm; layer resolution 0.1-0.4 mm; print speed 10-100 mm s^{-1} and extruder temperature 240°C-260°C. The following parameters were used during the fabrication of PLA elements: 1) printing nozzle temperature of 215°C, 2) build plate temperature of 60 °C, 3) print speed of 50 mm s^{-1}, 4) travel speed of 70 mm s^{-1}, and 5) infill orientation 90/-45/0/+45 and the 100% infill.

In this technical solution, a bipolar stepper motor NEMA 17HS4401 is used as a power unit with a 1.80 angular pitch, holding torque of 40 N·cm, and 1.7 A of phase current. The stepper motor provides precise positioning of the timing belt. It is computer controlled via a microcontroller board connected to a stepper motor driver. The test parameters for cyclic adhesion test were the following: maximal number of cycles (n_{max} = 1000), speed of rotation of step motors (w = 500 o·min^{-1}), the pulling force (F_c = 21 N), speed of timing belt (v = 9 m·s^{-1}) and dimension of sample was 110 × 10 mm^2 with coating deposition area of 50 × 4 mm^2 [7].

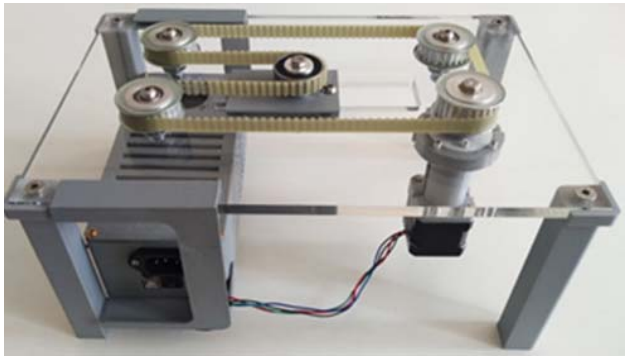

Figure 1. Appearance of the designed device for testing the adhesion by cyclic bending: real photography view.

2.3. Examination of the compactness of the copper coatings

The corrosion property and compactness of copper coatings obtained galvanostatic in different applied regimes and deposition times were investigated using static corrosion test. The nitric acid (20% HNO_3) was selected as a corrosion medium, based on reference [3]. The experiment is based on weight losses of the copper samples in static corrosion test using acid solution. The corrosion start time of the sample (beginning of the etching reaction) is the moment when the first bubbles of gas (H_2) appear on the copper surface. The beginning of the reaction and the appearance of bubbles on the sample is shown in Figure 2.

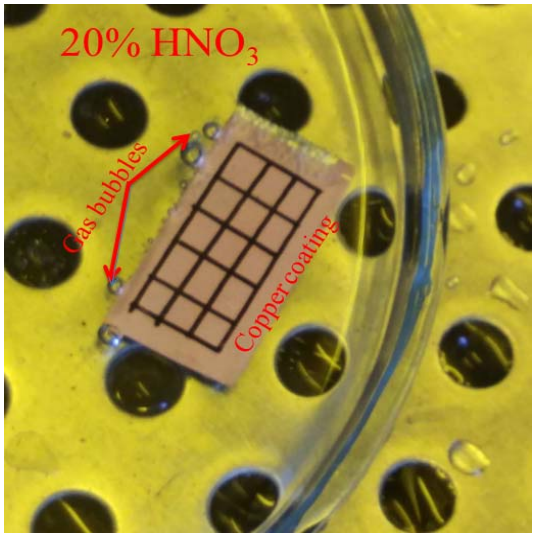

Figure 2. The appearance of the first gas bubbles as an indicator of the start of the reaction (etching start time).

2.4. Examination of the real hardness of the Cu coatings

Hardness analysis of the coatings was done by Vickers microindentation test machine. An applied loads were between 0.049 and 2.452 N, and a dwell time of 25 s. Vickers microhardness tester Leitz Kleinert Prufer DURIMET I (Leitz, Oberkochen, Germany) was used for a determination of hardness. The measured Vicker's hardness of coating is defined by Eq. (1) [9]:

$$H_c = 0.01854 \cdot P \cdot d^{-2} \quad (1)$$

In Eq. (1), H_c (in Pa) is a measured or composite hardness, P (in N) is an applied load, and d (in m) is a size of diagonal made in a coating during indentation. Hardness of the substrates was determined by the PSR (Proportional Specimen Resistance) model, Eq. (2) [18]. The parameters a_1 and a_2 correspond to the elastic and plastic properties of the material.

$$\frac{P}{d} = a_1 + a_2 \cdot d \quad (2)$$

For electrolytically produced Cu/brass systems, the Chen-Gao (C–G) composite hardness model [10–12] was used for a determination of the absolute hardness of Cu coatings. This model was employed to evaluate the adhesion of Cu coatings on substrates, too. The following equations were used for the calculations: -equation (3) was used to fit the experimental data; -equation (4) was used to calculated coating hardness value (H_{coat}); -equation (5) was used to calculated adhesion parameter b:

$$H_C = A + B \cdot \frac{1}{h} + C \cdot \frac{1}{h^{m+1}} \quad (3)$$

where A, B and C are fitting parameters, calculated from curve fitting. Indentation depth (h) can be calculated as 1/7 of diagonal size as theoretical value according geometry of indenter [6-8, 10-12]. The value of m (power index) is found to be 1.8 for $H_{coat} < H_s$ ($m \rightarrow 2$; volume law of mixtures applies) or 1.2 ($m \rightarrow 1$; area law of mixtures applies) for $H_{coat} > H_s$ [10-12].

$$H_{coat} = A \pm \sqrt[m]{\frac{\left[m \cdot |B| / (m+1)\right]^{m+1}}{m \cdot |C|}} \quad (4)$$

The value of the adhesion parameter b is determined from the slope of the linear fit of the line $\Delta H = f(\delta/d)$:

$$\Delta H = \left[\frac{7 \cdot (m+1) \cdot (H_s - H_{coat})}{m \cdot b}\right] \cdot \frac{\delta}{d} \quad (5)$$

Model of Korsunsky (K-model) is suitable for the analysis of "*hard film on soft substrate*" composite systems [13-14] such as composite system Cu/Cu. The composite hardness, H_c according to this model, is expressed as equation (6):

$$H_c = H_s + \left[\frac{1}{1 + k' \cdot \left(\frac{d^2}{\delta}\right)}\right] \cdot (H_{coat} - H_s) \quad (6)$$

A dimensionless material parameter k' is related to the composite response mode to indentation.

3. RESULT AND DISCUSSION

3.1. Absolute hardness of cathodes (substrates)

Based on the PSR model, the absolute hardness of the selected cathode materials was estimated. The experimental points were given on Figure 3. By multiplying the value of the slope with the Vicker's constant, the absolute hardness of the substrate is calculated. The hardness of brass was 1.41 GPa [6], and hardness for copper substrate was 0.36 GPa. We can see that the hardness of brass substrate was 3.92 × harder than copper substrate.

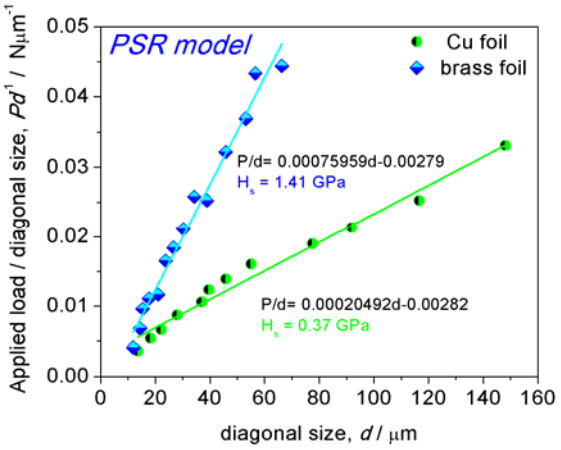

Figure 3. PSR model for calculated absolute hardness values of substrates without coatings.

3.2. Absolute hardness of the copper coatings

Figure 4 present fitting curves according to Chen-Gao model for electrodeposited 30 μm thick copper coatings on brass substrate. We can see from Figure 4 and Table 2 that the composite hardness and absolute hardness coating values obtained for the copper coatings in the DC/US regime were larger than those obtained in the DC/MS regime or DC regime.

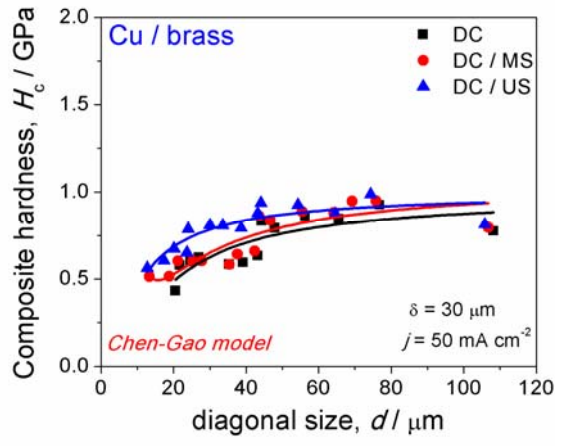

Figure 4. The dependencies of the composite hardness for 30 μm thick copper coatings electrodeposited on the brass substrate with variation current regime, on diagonal size calculated according to Chen–Gao model.

Figure 5 presents fitting curve according to Korsunsky model for electrodeposited 10 μm thick copper coatings on Cu substrate. Two current regimes were used: stationary DC regime without mixing of *electrolyte I* and DC/US regime with application of ultrasonic waves for mixing. The third sample was synthesized in the form of a laminate by deposition in a combination regime (DC+DC/US) with 1 μm thick and with 10 individual layers. The final layer was deposited in DC/US regime. The lowest value of an absolute hardness of Cu coating was shown by the sample deposited in the stationary mode, and the maximum by the laminate form of the coating.

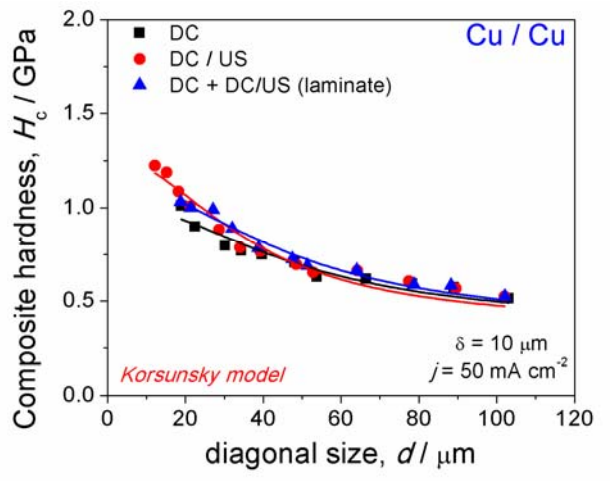

Figure 5. The dependencies of the composite hardness for 10 μm thick copper coatings electrodeposited on the copper substrate with variation current regime, on diagonal size calculated according to Korsunsky model.

Table 2. The results of the absolute hardness of the copper coatings with fitting errors. RMSE–Root mean square error and SE – Standard Error.

regime	Chen-Gao model				
30 μm Cu/brass	A	B	C	RMSE	H_{coat} /GPa
DC	*0.99*	*-11.76*	*368.41*	*0.09*	*0.961*
DC/MS	*1.00*	*-6.73*	*83.78*	*0.06*	*0.953*
DC/US	*1.07*	*-14.06*	*718.78*	*0.08*	*1.043*
regime	Korsunsky model				
10 μm Cu/Cu	*k*	*SE*	H_{coat}/ GPa	*SE*	
DC	2.02E-4	3.94E-4	1.022	0.04	
DC/US	3.69E-4	5.72E-4	1.276	0.05	
DC + DC/US	2.15E-4	2.62E-4	1.296	0.03	

3.3. Adhesion properties of Cu coatings

The adhesion properties of different copper coatings were summarized according to Figures 6 and 7 and Table 3. Based on the values of the slopes of the lines in Figures 6 and 7, the parameter *b* was calculated and shown in Table 3, according to equation (5).

The larger value of the adhesion parameter *b* means the better adhesion of the coating with substrate [10-12]. From Table 3 we can see that the ultrasonic copper coating on brass has better adhesion strength. Although it was expected that the strongest adhesion exists between the same materials (Cu/Cu) the adhesion evaluation through the model did not show this. This behavior can be attributed to the influence of layer thickness and different microstructures of layers (deposition from two different electrolytes) during indentation. But it can be confirmed that the copper coating deposited using ultrasound shows better adhesion performance than the ordinary coating, deposited either on brass or copper substrates. The adhesion bending test results are shown in Table 3, too. This test according to the value of critical cycle number (*n*) indicated that the thinner coating shows a better adhesion behavior [3]. This test also confirmed the better adhesion performance of the sample deposited in DC/US regime on both substrates.

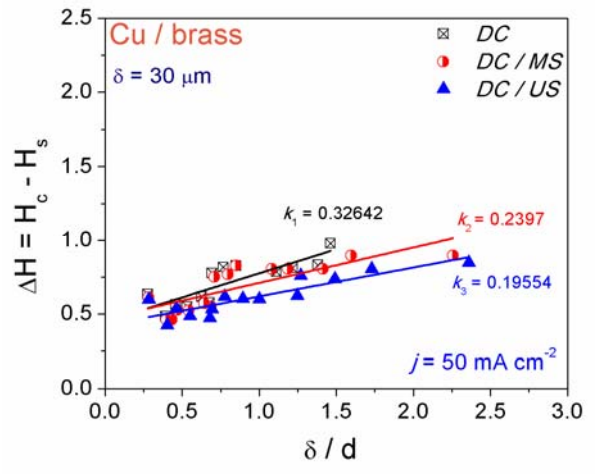

Figure 6. The hardness difference versus ratio between the coating thickness (30 μm) and the diagonal size for the Cu coatings electrodeposited on the brass substrate from *electrolyte II*.

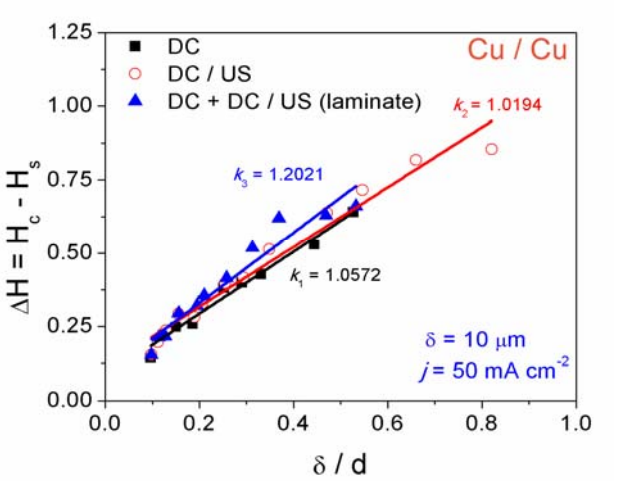

Figure 7. The hardness difference versus ratio between the coating thickness (10 μm) and the diagonal size for the Cu coatings electrodeposited on the copper substrate from *electrolyte I*.

Table 3. The results of adhesion properties of copper coatings on different substrates, *b* – critical reduced depth, *n* – critical cycle number.

substrate	δ	regime	el.	*b*	*N*
brass	30	DC	II	14.98	25.5
brass	30	DC/MS	II	18.76	32
brass	30	DC/US	II	20.44	41
copper	10	DC	I	7.07	114
copper	10	DC/US	I	11.53	130
copper	10	DC+DC/US	I	11.36	125

3.4. The compactness of the copper coatings

Figure 8 shows the average weight losses of the electrodeposited copper coatings samples obtained in different current regimes with/without mixing of *electrolyte II* on brass substrate. Figure 9 shows weight losses for Cu coatings deposited on copper substrate from *electrolyte I*. The laminate form of Cu coatings shows the better anticorrosion properties.

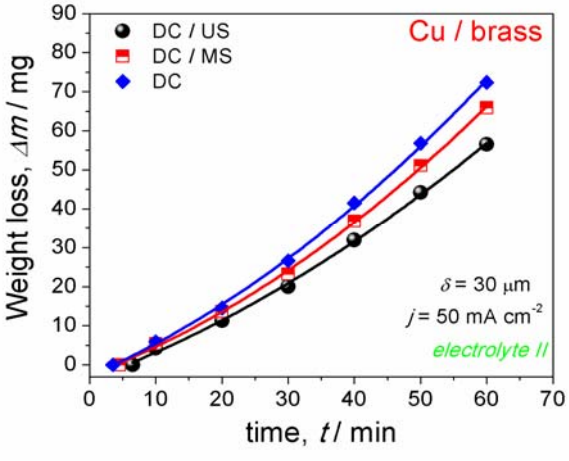

Figure 8. Weight loss of the copper coatings (30 μm) on brass substrates in static corrosion test.

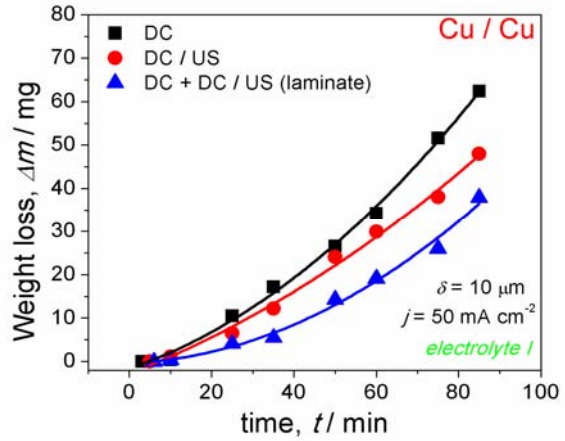

Figure 9. Weight loss of the copper coatings (10 μm) on Cu substrates in static corrosion test.

The first points of the curves are determined by the bubbling time of specimen (see Fig. 2). From Figure 8 we can see that corrosion rate of the DC/US sample is lower than DC/MS and DC samples. Copper coating obtained in stationary regime (DC) have higher corrosion rate than that of the ultrasonic electrodeposited copper coating or DC/MS sample. That means that its anticorrosion feature is worse. For the DC Cu sample, the bubbling time is 3' 27'', for DC/MS is 4' 24'' and for DC/US is 6' 32''. The longer starting time the etching in 20% HNO_3 means the better compactness of samples.

By comparing Figures 8 and 9, it can be concluded that copper samples electrodeposited from *electrolyte II* with additives show greater compactness and more chemical resistance to the HNO_3 acid.

4. CONCLUSION

A copper coating was obtained by different regime of electrodeposition technique: ordinary, magnetic, ultrasonic, and laminate form. The surface coating hardness of copper coating obtained in DC/US regime on brass substrate is 1.04 GPa, better than that in DC regime (0.961GPa) or in DC/MS regime (0.953 GPa). The surface coating hardness of copper coating in combination regime (laminate form) on copper substrate is 1.296 GPa, better than ordinary copper (DC regime). The copper coatings obtained from *electrolyte II* have weaker mechanical properties, but it is more resistant to corrosion and more compact. The adhesion performance of the copper coating obtained in DC/US regime on brass substrate or laminate form of Cu on Cu substrate is better than Cu coatings obtained in DC regime. The corrosion rate of copper coatings from electrolyte with additives is obviously lower.

Acknowledgments

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