Synthesis and characterization of thin copper coatings obtained by sonoelectrodeposition method

Ivana Mladenović, Jelena Lamovec, Stevan Andrić, Miloš Vorkapić, Marko Obradov, DanaVasiljević-Radović, Vesna Radojević and Nebojša D. Nikolić

Abstract—**Influence of an intensity of ultrasonic mixing of electrolyte in a temperature range of 27–37 °C and ultrasonic power intensity in the range of 3.77–18.84 W/cm^2 (10–50 %) on a synthesis of fine-grained copper deposits was examined. Copper coatings were electrodeposited on a brass substrate in direct current (DC) regime with an applied current density of 50 mA·cm^{-2}. The laboratory-made copper sulfate electrolyte was used without or with addition of additives. The variation of temperature under sonoelectrodeposition process and variation mixing intensity of electrolyte were ensured by using an ultrasonic probe. The produced Cu coatings were examined by optical microscope (OM) in order to observe the microstructural modification with variation ultrasonic parameters and for measuring imprints of Vickers indenter. The micro hardness properties of composite systems were characterized using Vickers micro indentation test. The composite hardness models Chicot-Lesage and Chen-Gao were used for the determination the coatings hardness and adhesion evaluation. Application of Atomic Force Microscopy (AFM) technique also confirmed the strong influence of ultrasonic mixing conditions of electrolyte onto change of the microstructure of copper deposits and surface roughness of the coatings. The maximum hardness, good adhesion properties and minimum micro surface roughness was obtained for the fine-grained Cu coating produced with amplitude of 50 % ultrasonic mixing of electrolyte without additives and 30 % for electrolyte with additives.**

***Index Terms*— ultrasonic probe; microindentation; composite system; coatings; adhesion; sonoelectrodeposition.**

I. INTRODUCTION

THE effects of ultrasonic electrolyte mixing can be seen from a few aspects: chemical, mechanical and theirs combination. The chemical effects of ultrasound are due to the “implosion of microbubbles”, generating free hydroxyl radicals [1, 2] with high chemical reactivity, while mechanical effects are caused by “shock waves” formed during symmetric cavitation or by “microyets” formed during asymmetric cavitation [1]. The use of ultrasound in a reaction system provides specific activation based on a physical phenomenon, known as “acoustic cavitation”. Cavitation is caused by a longitudinal sound wave, which results in a change in local pressures and temperatures in the liquid electrolyte [2]. The change in pressure causes the gas bubbles to form and burst, which contributes to electrolyte mixing [3]. The scheme of the mechanism of formation, growth and bursting of bubbles under ultrasound conditions are shown in Fig. 1.

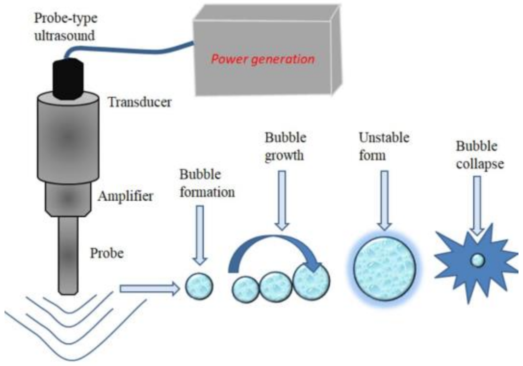


Fig. 1. Schematic presentation of bubble implosion under ultrasonic conditions in electrolyte near cathode surface [3].

Electrodeposition in presence of ultrasound (US-ED) may have effects in terms of: degradation of the reaction, enhanced electrochemical diffusion processes and mass-transport, increase electrochemical rates and current efficiencies, decrease electrode overpotentials [4]. The effects of ultrasonic mixing of electrolyte and influence on the metallic coatings properties have also reported in the literature: change morphology (reduction in grain size or change grain orientation), influence on residual stress, that hence good adhesion and hardness, the increase of brightness has been also observed, etc [4–7]. Ultrasonic deposition (sonoelectrodeposition) is often used in combination with the co-deposition of particles as reinforcement into a metal matrix composite [8].

Using AFM technique, the coating surface roughness was investigated in function of grow rate (applied current density) [9], film thickness (deposition time), variation substrates and mixing conditions [10], as well as variation electrolytes [10, 11].

Ivana Mladenović, Stevan Andrić, Miloš Vorkapić, Marko Obradov, Dana Vasiljević-Radović and Nebojša Nikolić are with the Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11 000 Belgrade, Serbia (e-mail: ivana@nanosys.ihtm.bg.ac.rs), (e-mail: stevan@nanosys.ihtm.bg.ac.rs), (e-mail: worcky@nanosys.ihtm.bg.ac.rs), (e-mail: marko.obradov@nanosys.ihtm.bg.ac.rs), (e-mail: dana@nanosys.ihtm.bg.ac.rs), (e-mail: nnikolic@ihtm.bg.ac.rs).

Jelena Lamovec is with the University of Criminal Investigation and Police Studies, Cara Dušana Street 196, 11 000 Belgrade, Serbia (e-mail: jelena.lamovec@kpu.edu.rs).

Vesna Radojević is with the Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11 000 Beltgrade, Serbia (e-mail: vesnar@tmf.bg.ac.rs).

Hardness and adhesion testing are the most important and widely used methods for assessing the structural and mechanical properties of the composite systems and coatings [12]. If the thickness of the coating is very small, the influence of the substrate must be considered during the coating hardness determination [13] and mathematical composite hardness models are used for this purpose [14–19].

Hence, the present experiment aims here to find the synergistic effects of ultrasound agitation, temperature oscillation, while increasing the power of ultrasonic mixing influence on the roughness, adhesion and micro hardness of copper coatings.

II. COMPOSITE HARDNESS MODELS

Multilayer complex structures such as thin coatings (films) on bulk substrates are often used in fabrication of MEMS devices. A thin coating deposited electrochemically on a conductive substrate can be considered as a composite system. Determination of the hardness of the coating, independent of the influence of the substrate hardness, is not possible in the entire region of the applied indentation loads. For this reason, composite hardness mathematical models are used to estimate the absolute hardness of a thin coating [14–19], and two adequate ones have been selected in this paper. The composite hardness model of Chicot-Lesage (C–L) was found to be suitable for experimental data analysis (for composite hardness values, H_c) and coating hardness determination (H_{coat}) based on our previous research [14–16]. Using this model, it is possible to calculate the absolute value of the coating hardness for each individual indentation load. The model is based on Meyer's law which expresses the variation of the size of the indent (d) in function of the applied load (P) [13]:

$$P = a^{*} \cdot d^{n^{*}} \tag{1}$$

The variation part of the hardness number with load is represented by the factor n^*. Chicot-Lesage adopted the following expression [16]:

$$F\left(\frac{\delta}{d}\right) = \left(\frac{\delta}{d}\right)^{m} = f \quad where\ m = \frac{1}{n^{*}} \tag{2}$$

In equation (2) m is the composite Mayer's index, d is average diagonal size of Vickers indent and δ is coating thickness. The value of m is calculated by a linear regression performed on all the experimental data obtained for a given coating/substrate couple and deduced from the relation [13]:

$$\ln d = m \cdot \ln P + b \tag{3}$$

The composite hardness can be expressed by the following relation [13, 16]:

$$H_C = (1-f) \Big/ \left(1/H_s + f \cdot \left(\frac{1}{H_{coat}} - \frac{1}{H_s}\right)\right) + \\ + f \cdot \left(H_s + f \cdot \left(H_{coat} - H_s\right)\right) \tag{4}$$

Hardness of the film is the positive root of the next equation [13, 16]:

$$\begin{aligned} &A \cdot H_{coat}^{2} + B \cdot H_{coat} + C = 0, \quad with \\ &A = f^{2} \cdot (f-1) \\ &B = \left(-2 \cdot f^{3} + 2 \cdot f^{2} - 1\right) \cdot H_{s} + (1-f) \cdot H_{c} \\ &C = f \cdot H_{c} \cdot H_{s} + f^{2} \cdot (f-1) \cdot H_{s}^{2} \end{aligned} \tag{5}$$

With the known value of m, only the hardness of the films remains to be calculated. The values of composite hardness and substrate hardness (H_s) are the values obtained by measuring on a Vickers tester.

For the evaluation of the adhesion properties of thin films and absolute film hardness, Chen–Gao (C–G) model was chosen [17–19]. This method introduces the composite hardness as the function of the critical reduced depth beyond which the material will have no effect on the measured hardness. The critical reduced depth, represents ratio between the radius of the plastic zone beneath the indentation and indentation depth [12, 17–19]. The large value of the critical reduced depth corresponds to good adhesion, while low values indicate poor adhesion of the films. The correlation between composite hardness value H_c and the critical reduced depth b are found as [12, 17–19]:

$$H_c = H_s + \left[\frac{(n+1) \cdot \delta}{n \cdot b \cdot h}\right] \cdot (H_{coat} - H_s) \tag{6}$$

H_s and H_{coat} are the hardness of the substrate and of the film, respectively, δ is film thickness, h is indentation depth, n is the power index and b is the critical reduced depth. The convenient value of n is found to be 1.8 for “soft film on hard substrate” and $n = 1.2$ for “hard film on soft substrate” [12, 17–19]. It is first necessary to perform the fitting of the composite hardness depending on the depth of indentation according to the model shown in the equation (7) [18]:

$$H_c = A + B \cdot \frac{1}{h} + C \cdot \frac{1}{h^{n+1}} \tag{7}$$

A, B and C are fitting parameters, and h is indentation depth. Indentation depth can be calculated as 1/7 of diagonal size. Then coating hardness can be expressed as [18]:

$$H_{coat} = A \pm \sqrt[n]{\frac{\left[n \cdot |B| / (n+1)\right]^{n+1}}{n \cdot |C|}} \tag{8}$$

The equation used to estimate adhesion properties coating/substrate composite system has the following form [12]:

$$H_c = \frac{7 \cdot (n+1) \cdot \left(H_s - H_{coat}\right)}{n \cdot b} \cdot \frac{\delta}{d} \tag{9}$$

III. EXPERIMENTAL

A. *Preparation of electrolyte and samples*

Copper was electrodeposited from an aqueous solution of copper sulfate and sulfuric acid without (electrolyte I) and with added additives (electrolyte II). The composition of the electrolytes used in experiments is given in Table 1. Three different additives were used for electrolyte II: polyethylene glycol (PEG, molecular weight 6000), Na-3-mercapto-1-propane sulfonic acid (MPSA) and NaCl, based on the suggested recipe found in the reference [20]. The volume of the electrolyte for all experiment was 100 ml. Brass foil, ½ hard, (ASTM B36, K&S Engineering), 250 µm thick was us as cathode. Pure copper foil, cylindrical shape, was used as anode (see Fig. 2).

TABLE I
COMPOSITION OF THE ELECTROLYTES

Electrolyte I	g/l	Electrolyte II	g/l
$CuSO_4 \cdot 5\ H_2O$ H_2SO_4	240 60	$CuSO_4 \cdot 5H_2O$ H_2SO_4 PEG 6000 MPSA NaCl	240 60 1 0.0015 0.1240

An ultrasonic cleaner (model HD 2200 Bandelin / Germany) of 20 kHz ± 500 Hz frequency (f_s) equipped with a standard sonotrode (probe of 13 mm tip diameter), with power (I) of 200 W in continuous mode was used for sonication and mixing of electrolyte. In general, power intensity I_i (power irradiance) represents power, I, distributed over surface area, S (sonotrode tipe surface) as shown as $I_i = I / S$ [W/cm^2]. The temperature change, T_i, of the electrolytes was observed during the operation of the ultrasound probe with the variation of the amplitude range, P_i. The temperature change of the electrolyte was measured every 5 minutes (see Table II). Electrochemical deposition was performed under DC galvanostatic mode. The current density values were maintained at 50 mA·cm^{-2}; deposition time was fixed at 15 minutes and coating thickness was calculated according to Faraday's law.

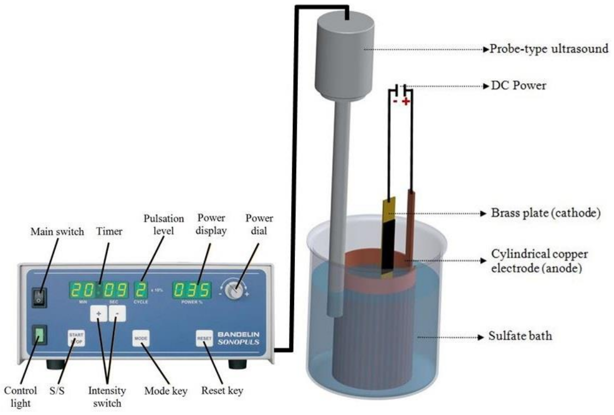


Fig. 2. Experimental setup for a sonoelectrochemical deposition process.

TABLE II
THE PARAMETERS OF THE SONOELECTRODEPOSITION

No.	P_i / %	electrolyte	t_i / min	T_i / °C
1	10	I	1	28.8
			5	29.7
			10	30.4
			15	32.2
3	30	I	1	28.3
			5	29.6
			10	30.6
			15	35
5	50	I	1	28.9
			5	30.9
			10	33.2
			15	37.2
3'	30	II	1	27
			5	28.1
			10	30.5
			15	31.5

B. *Optical microscopy*

The structural properties of Cu coatings were examined by optical microscope (OM)–model Motic AE-2000 MET. A metallographic microscope–Carl Zeiss Epival Interphako was used to measure the diagonal size of Vickers indents.

C. *Topography of the Cu coatings*

The surface topography and roughness of the Cu coatings were examined using atomic force microscope (AFM, TM Microscopes-Vecco) in the contact mode. The values of the arithmetic average of the absolute roughness parameters (R_a) of the surface height deviation, were measured from the mean image data plane, using free software Gwyddion [21]. The values of R_a roughness parameter, calculated as average from three independent measurements at different locations of one sample of copper surface obtained by the DC regime with variation of ultrasonic intensity mixing and electrolyte composition. The scanned area was 20 µm^2 in contact mode.

D. *Mechanical characterization*

The mechanical properties of the composite systems were characterized using Vickers microhardness tester "Leitz, Kleinharteprufer DURIMET I" with loads ranging from 2.452 N down to 0.049 N. Three indentations were made at each indentation load from which the average diagonal and composite hardness could be calculated.

IV. RESULT AND DISCUSSION

A. *Structural characterization of the Cu coatings*

Fig. 3 shows morphologies of the Cu coatings obtained using sonoelectrodeposition method with ultrasonic amplitude at 10 % (Fig. 3a), 30 % (Fig. 3b), 50 % (Fig. 3c) from electrolyte I.

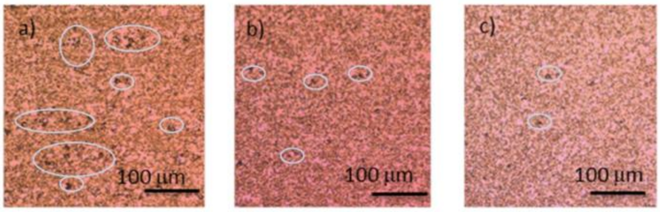


Fig. 3. Microscopic images of Cu coatings obtained in sonoelectrodeposition regime on a brass substrate from electrolyte I. The sonoelectrodeposition parameters are: j = 50 mA·cm^{-2}, t = 15 min, δ = 16.61 µm, T_{av} = 31.6 °C and f_s = 20 kHz with variation of the amplitude range of ultrasonic mixing: a) P_i = 10 %, b) P_i = 30 % and c) P_i = 50 %.

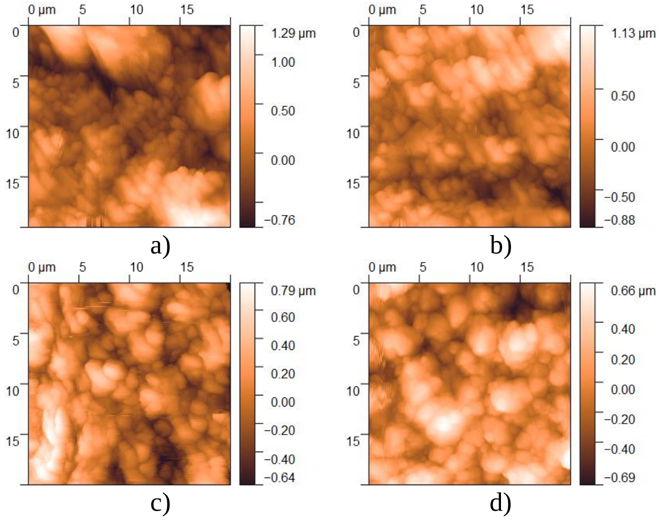
The smaller number of different size of cavitation holes were observed (Fig. 3a). It has been observed that the number of holes decreases with increasing intensity of ultrasonic mixing of the electrolyte (Figs. 3b and 3c). The bursting of large gas bubbles caused by the mixing of electrolytes at the low intensity, leads to the formation of micro cavities on the surface of the coating (Fig. 1).

B. *The roughness analysis of the Cu coatings*

The AFM surface areas of Cu coatings produced under different conditions are shown in Fig. 4. The average values of the roughness parameters (R_a) obtained by application of *Gwyddion* free software are given in Table III. The average roughness can be calculated as:

$$R_a = \frac{1}{N_x \cdot N_y} \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \left| z(i,j) - z_{mean} \right| \qquad (10)$$

where N_x and N_y are the number of scaning points on the x-axis and y-axis; $z(i, j)$ is the height of the (i, j) measuring point, z_{mean} is the mean hight of all measuring points [22].



a) b)

c) d)

Fig. 4. 2D-AFM images of copper deposits prepared on brass substrate obtained in DC-US regime. The sonoelectrodeposition parameters are: j = 50 mA·cm^{-2}, t = 15 min, δ = 16.61 µm, T_{av} = 31.6 °C and f_s = 20 kHz with variation of the amplitude range of ultrasonic mixing: a) P_i = 10 %, b) P_i = 30 % and c) P_i = 50 % for electrolyte I and d) P_i = 30 % for electrolyte II.

Based on the results in Table III and Fig.4, a decrease in the roughness of the Cu coating from electrolyte I was observed with increasing mixing intensity (Fig. 4a–c).

The copper coating obtained from the electrolyte with additives and 30 % applied ultrasound amplitude hads minimal roughness (see Fig. 4d).

TABLE III
THE VALUES OF ROUGHNESS PARAMETER FOR SONOELECTRODEPOSITION COPPER COATINGS WITH VARIATION ULTRASONIC AMPLITUDE AND ELECTROLYTE

No.	P_i %	electrolyte	R_a / nm
1	10 %	I	270
3	30 %	I	230
5	50 %	I	180
3’	30 %	II	148.8

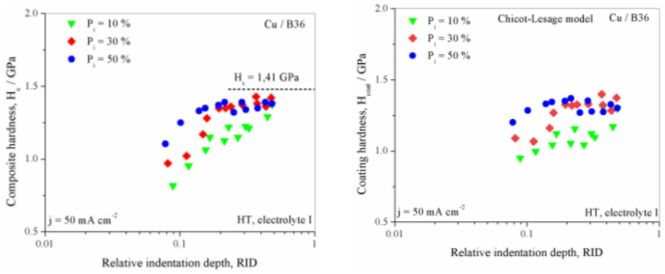
C. *Composite hardness of copper coatings/brass systems.*

The average values of the indent diagonal d (in µm), were calculated from several independent measurements on every specimen for different applied loads P (in N). The absolute substrate hardness and composite hardness values, H_c (in GPa) were calculated using the formula [23]:

$$H_c = 0.01854 \cdot P \cdot d^{-2} \qquad (11)$$

where 0.01854 is a constant, geometrical factor for the Vickers indenter.

Fig. 5 shows the variation in composite hardness values with relative indentation depth (h/δ =RID), where h is indentation depth ($h = d/7$) for copper coatings deposited from electrolyte I with change applied ultrasonic amplitude percent.



a) b)

Fig. 5. Variation hardness vs. relative indentation depth for the copper coatings deposited on brass substrates with variation ultrasonic mixing of electrolyte: a) composite hardness and b) hardness of the coating calculated according to Chicot-Lesage model. The current density and deposition time were 50 mA·cm^{-2} and 15 min. Electrolyte I was used.

The effect of changing the intensity of the ultrasonic mixing of the electrolytes is reflected in the change values of the composite system hardness and the coating hardness. An increase in composite hardness with increasing electrolyte mixing was observed. The maximum value of the composite hardness was obtained for the copper coating deposited with the 50 % ultrasound mixing electrolyte (Fig. 5a) and the minimum value for the 10 %. The results of the calculated coating microhardness according to the C-L model more clearly indicate the influence of the applied ultrasound mixing condition on the microstructure and the hardness of the coating, and the highest coating microhardness value was obtained for the 50 % ultrasound amplitude settings (Fig. 5b). For shallow indentation penetration depth ($0.1 \leq$ RID ≤ 1), it was found that the response was that of the coating and substrate together. Based on the results from: Fig. 3c), Table III (sample 5), Fig. 4c and Fig. 5a,b conclude that a 50 % ultrasound amplitude is an optimal condition for copper ultrasonic deposition from electrolyte I.

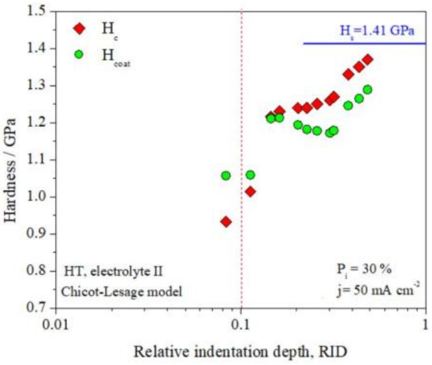


Fig. 6. Variation hardness vs. relative indentation depth for the copper coatings deposited on brass substrates with applied 30 % amplitude of ultrasonic mixing of electrolyte II. Red points are composite hardness values and green points are values for hardness of the coating calculated according Chicot-Lesage model. The current density and deposition time were: 50 mA·cm^{-2} and 15 min.

The composite hardness response has a growing tendency with increasing applied indentation load or relative indentation depth (see Fig. 6). The hardness of the coating is lower than the composite hardness in the composite region so it is confirmed that the system belongs „soft film-hard substrate“ composite system type.

Based on the results from: Fig. 4d, Table III (sample 3') and Fig. 6 conclude that a 30 % ultrasound amplitude (3.77 W/cm^2) is an optimal condition for copper ultrasonic deposition from electrolyte II.

D. Determination the copper coatings hardness and adhesion

Absolute hardness of the brass substrate, H_s, necessary to calculate the absolute hardness of the coating, is 1.41 GPa, according to our previous measurements [25].

The results of calculated film hardness according to the Chen–Gao model for the system ED Cu film on brass as the substrate were given in Table IV. Fitting of experimental datas (Fig. 7) were done in Matlab using the *cftool* command.

Films obtained with optimal condition of ultrasonic mixing appear harder than others deposited (sample No. 5). Copper coatings deposited from electrolyte with additives show lower hardness value then same coatings from electrolyte I.

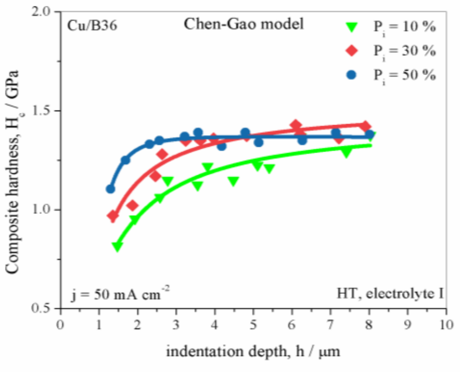


Fig. 7. The dependencies of the composite hardness of the Cu coatings, H_c on indentation depth, h calculated by Eq. (7) for various ultrasound mixing amplitude of electrolyte I.

TABLE IV

THE RESULTS OF CALCULATED FILM HARDNESS ACCORDING CHEN–GAO MODEL AND FITTING PARAMETERS (*A*, *B*, *C*) WITH ROOT MEAN SQUARE ERROR (*RMSE*)

No.	H_{coat}	*A*	*B*	*C*	*RMSE*
1	1.381	1.446	-7.20	-55.2	0.005
3	1.399	1.527	-5.46	-12.3	0.050
5	1.466	1.494	-1.52	-54.1	0.021
3'	1.357	1.412	-4.13	-43.0	0.038

The increase in hardness of electrodeposits obtained with ultrasonic agitation has been associated with the production of deposits with a fine grain size and higher grain-packing density [24]. Equation (9) was used to calculate the critical reduced depth b for the system of thin ED Cu films on the brass as the substrate. The value of the parameter n in the CG model can be 1.2 or 1.8, for soft films 1.8 is taken [12, 17-19].

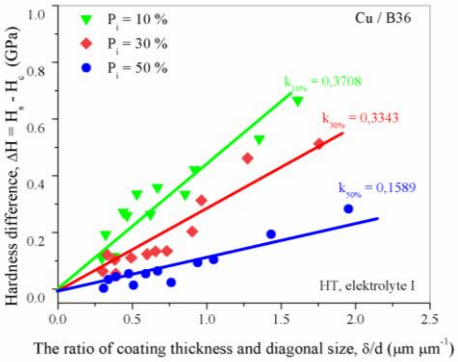


Fig. 8. Hardness difference vs. ratio between the film thickness and the indentation diagonal for copper films on the brass as a substrate. The slope value, k, ED Cu films (electrolyte I) for different ultrasonic mixing amplitude % is shown.

According to the model Chen–Gao (C–G) in Fig. 7 and Fig. 8 the values of slope, k (its value is used to calculate the critical reduction depth, b) for ED Cu films on brass deposited with different ultrasonic amplitude (10, 30 and 50 %) were shown. It was noted higher value of the slope, k, for the sample deposited at lower ultrasound intensity values.

The slopes values, k, (from Fig.7) and the absolute hardness values of the film (from Table IV) were used for the calculation the critical reduction depth, *b*, the calculated values are shown in the Table V.

TABLE V
THE RESULTS OF CALCULATED CRITICAL REDUCTION DEPTH, ACCORDING TO CHEN–GAO MODEL

No.	electrolyte	*k*	*b*
1	I	0.3708	2.995
3	I	0.3343	2.736
5	I	0.1589	1.165
3'	II	0.2872	4.777

Comparison of the adhesive strength by the adhesion parameter, *b*, can be noticed that higher value corresponds to the ED Cu films from electrolyte II than ED Cu films from electrolyte I. That means that better adhesion properties have ED Cu film with additives then ED Cu films without additives. When additives are added, more intense ultrasonic mixing power contributes to an increase in the adhesive strength of the substrate film and a better dissolution of the additives in the basic electrolyte. In the case of no additives, the adhesion value is almost unchanged with the variation of the mixing power.

V. CONCLUSION

Based on the microhardness measurements, it was shown that the same film with different structural properties giving different mechanical response depending on the electrochemical parameters during synthesis. The copper films deposited on brass from basic electrolyte have higher composite and film hardness values then sonoelectrodeposited copper films from electrolyte with additives for same deposition parameters and projected thickness.With increasing value of applied amplitude ultrasound mixing of electrolyte I, composite hardness value increasing, too. Adhesion properties is better for copper films from electrolyte II on brass then copper films from electrolyte I, because the values of *b* are larger for system ED Cu (electrolyte II)-brass then ED Cu (electrolyte I-brass). Better adhesion properties shown copper film deposited with a higher mixing condition.

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REFERENCES

[1] L. C. Hagenson, L. K. Doraiswamy, "Comparison of the effects of ultrasound and mechanical agitation on a reacting solid-liquid system," *Chem. Eng. Sci.*, vol. *53*, no. *1*, pp. *131–148*, Apr., 1998.

[2] L. Fathyunes, J. Khalil-Allafi, "Effect of employing ultrasonic waves during pulse electrochemical deposition on the characteristics and biocompatibility of calcium phosphate coatings," *Ultrason. Sonochem.*, vol. *42*, pp. *293–302*, Apr., 2018.

[3] J. M. Costa, A. F. A. Neto, "Ultrasound-assisted electrodeposition and synthesis of alloys and composite materials: A review," *Ultrason. Sonochem.*, vol. *68*, pp. *105193*, Nov., 2020.

[4] C. T. Walker, R. Walker, "Effect of ultrasonic agitation on some properties of electrodeposits," *Electrodeposition Surf. Treat.*, vol. *1*, no. *6*, pp. *457–469*, Jul., 1973.

[5] A. K. Behera, A. Mallik, "Ultrasound assisted electroplating of nano-composite thin film of Cu matrix with electrochemically in-house synthesized few layer graphene nano-sheets as reinforcement," *J. Alloys Compd.*, vol. *750*,, pp. *587–98*, Mar., 2018.

[6] Y. Niu, J. Wei, Y. Yang, J. Hu, Z. Yu, "Influence of microstructure on the wear mechanism of multilayered Ni coating deposited by ultrasound-assisted electrodeposition," *Surf. Coat. Technol.*, vol. *210*, pp. *21–27*, Oct., 2012.

[7] A. Mallik, B. C. Ray, "Residual stress and nanomechanical properties of sonoelectrodeposited Cu films," *Surf. Eng.*, vol. *27*, no. *7*, pp. *551–556*, Aug., 2011.

[8] I. Tudela, Y. Zhang, M. Pal, I. Kerr, A. J. Cobley, "Ultrasound-assisted electrodeposition of composite coatings with particles," *Surf. Coat. Technol.*, vol. *259*, no. *C*, pp. *363–373*, Nov., 2014.

[9] K. Hedayati, G. Nabiyouni, "Surface roughness analysis and magnetic property studies of nickel thin films electrodeposited onto rotating disc electrodes," *Appl. Phys. A*, vol. *116*, pp. *1605–1612*, Feb., 2014.

[10] I. O. Mladenović, J. S. Lamovec, V. B. Jović, M. M. Obradov, D. G. Vasiljević-Radović, N. D. Nikolić, V. J. Radojević, "Mechanical characterization of copper coatings electrodeposited onto different substrates with and without ultrasound assistance," *J. Serb. Chem. Soc.*, vol. *84*, no. *7*, pp. *729–741*, Mar., 2019.

[11] L. Bonou, M. Eyraud, R. Denoyel, Y. Massiani, "Influence of additives on Cu electrodeposition mechanisms in acid solution: direct current study supported by non-electrochemical measurements", *Electrochim. Acta*, vol. *47*, no. *26*, pp. *4139–4148*, Oct., 2002.

[12] L. Magagnin, R. Maboudian, C. Carraro, "Adhesion evaluation of immersion plating copper films on silicon by microindentation measurements," *Thin Solid Films*, vol. *434*, no. *1*, pp. *100–105*, Jun., 2003.

[13] J. Lamovec, V. Jović, D. Ranđelović, R. Aleksić, V. Radojević, "Analysis of the composite and film hardness of electrodeposited nickel coatings on different substrates," *Thin Solid Films*, vol. *516*, no. *23*, pp. *8646–8654*, Oct., 2008.

[14] J. Lesage, D. Chicot, A. Pertuz, P. -Y. Jouan, N. Horny, A. Soom, "A model for hardness determination of thin coatings from standard micro-indentation tests,", *Surf. Coat. Technol.*, vol. *200*, no.*1–4* , pp. *886–889*, Oct., 2005.

[15] D. Chicot, J. Lesage, "Absolute hardness of films and coatings", *Thin Solid Films*, vol. *254*, no. *1–2*, pp. *123-130*, Jan., 1995.

[16] J. Lesage, A. Pertuz, D. Chicot, "A New Method to Determine the Hardness of Thin Films," *Revista Matéria*, vol. *9*, no. *1*, pp. *12–19*, Jan. 2004.

[17] M. Chen, J. Gao, "The adhesion of copper films coated on silicon and glass substrates," *Mod. Phys. Lett. B*, vol. *14*, no. *3*, pp. *103–108*, Mar., 2000.

[18] J. L. He, W. Z. Li, H. D. Li, "Hardness measurement of thin films: Separation from composite hardness," *Appl. Phys. Lett.* vol. *69*, no. *10*, pp. *1402–1404*, Jun., 1996.

[19] Q. Hou, J. Gao, S. Li, "Adhesion and its influence on micro-hardness of DLC and SiC films," *Eur. Phys. J. B*, vol. *8*, pp. *493–496*, Apr., 1999.

[20] N. D. Nikolić, Z. Rakočević, K. I. Popov, "Reflection and structural analyses of mirror-bright metal coatings," *J Solid State Electrochem.*, vol. *8*, pp. *526–531*, Dec., 2004.

[21] http://gwyddion.net/

[22] Y. Li, J. Yang, Z. Pan, W. Tong, "Nanoscale pore structure and mechanical property analysis of coal: An insight combining AFM and SEM images," *Fuel*, vol. *260*, pp. *116352*, Jan., 2020.

[23] *Metallic Materials—Vickers Hardness Test—Part 1: Test Method*, ISO 6507-1-2005, International Organization for Standardization: Geneva, Swizterland, 2005.

[24] P. M. Ashokkumar, "*Theoretical and Experimental Sonochemistry Involving Inorganic Systems*", *2011*th ed. New York, US: Springer, 2014.

[25] I. O. Mladenović, N. D. Nikolić, J. S. Lamovec, D. G. Vasiljević-Radović, V. J. Radojević, "Application of the Composite Hardness Models in the Analysis of Mechanical Characteristics of Electrolytically Deposited Copper Coatings: The Effect of the Type of Substrate," *Metals*, vol. *11*, no. *1*, pp. *111*, Jan., 2021.