Optimization of electrodeposition parameters to improve composite hardness of nickel coatings on brass substrate for varying film thicknesses and applied indentation loads

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***Abstract*—In this investigation, nickel coatings were electrodeposited on brass substrate. The effects of electrodeposition process parameters such as, current density and deposition time (coatings thickness), on surface morphology and composite hardness values were studied. The value of the measured composite hardness by Vickers microindentation technique of the selected "hard film on soft substrate" composite system type depends on the applied indentation loads. For this reason, the microindentation loads are also included in the analysis. According to the experiment plan obtained by Design-Expert software, nickel coating has been produced on the brass cathode using galvanostatic regime (DC) with magnetic stirring of the electrolyte. The nickel sulphamate electrolyte with saccharine additive was used for Ni electrodeposition. Then, response surface methodology (RSM) was used to establish an adequate mathematical model. Subsequently, a mathematical model was developed to weight the effects of each input parameters (coating thickness, current density and indentation load) on the output parameter (composite hardness) of electrodeposited nickel coatings on brass substrate. According to the obtained results, the coating thickness and indentation load greatly influenced resulting composite hardness. On the other hand, coating current density primarily influenced microstructure and surface roughness. The topographic modification of the Ni coating surface depending on the post-treatment (mechanical and chemical) after deposition was studied using AFM microscopy.**

***Index Terms*— electrodeposition; composite hardness; RSM; AFM; optimization; nickel coating.**

I. Introduction

THIN metallic coatings are often used for fabrication of different microelectronic and micromechanical devices. Thin coatings and bulk substrates constitute a composite system which mechanical properties depend not only on material characteristics of constituent materials but also on the mechanical interaction between the two such as the adhesion strength, residual stress, toughness and elastic-plastic properties [1-3]. In general, strong adhesion of the coating to the substrate is desired because it results in improved mechanical properties of the composite system. Additionally, reduction of the residual stress is paramount to prevent spontaneous delamination of the coating due to micro-crack growth between the thin coating and the bulk substrate [3].

Nickel (Ni) is one of the most common metals used to synthesize composite electrochemical coatings (CECs). It is characterized by superior corrosion and wear resistance, and enhanced mechanical and tribological properties [4]. Nickel coatings attract a huge attention from both scientific and technological communities owing to their unique properties, such as excellent friction coefficient during the wear testing of LIGA (lithographic) fabrication micro-rotors [5]. Ni alloys such as Co-Ni possess the high aspect ratio (HAR) during electrodeposition process and excellent magnetic and electrochemical properties [6].

Main methods of Ni thin film synthesis include: electrodeposition (ED), electroless plating (EL), physical vapour deposition (PVD), chemical vapour deposition (CVD), thermal spray and RF sputtering [1]. An interesting approach used for growing both pure Ni coatings and Ni alloys is electrochemical deposition technique. Conventional electrodeposition (ED) or new emulsion supercritical ED technique are very suitable ways to obtain nickel of desired characteristics suitable for application in above mentioned purposes [7, 8]. A common problem that exists during electrodeposition of Ni coatings is formation of hydrogen during ED process. The formation of hydrogen may create several pinholes on the coating [8], but the problem is solved by the adding surfactants (organic additives).

The most common electroplating solution for electrodeposition of Ni coatings met in the literature consists of nickel sulfate, nickel chloride, boric acid, saccharine and 1,4-butynediol [8]. In addition to the sulfate electrolyte, sulphamate electrolyte is also used [9]. Deposition parameters affect many properties of the electroplated material both during and after synthesis. By altering the synthesis parameters such as type of electrolyte and substrate, mixing condition, deposition time, applied current regime and density, post-deposition treatment, etc. we can control the grain size and microstructure of Ni coatings resulting in strengthened and hardened films with little or no loss in coating ductility.

Indentation testing is a reliable method for evaluation of material mechanical properties [3]. However, it cannot be

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applied directly for characterization of thin films due to plastic deformation of the sample during the indentation process [9, 10]. For this reason, indentation method is applied to measure composite hardness (thin film on bulk substrate). Various mathematical models have been developed to calculate thin film microhardness based on the directly measured composite hardness of the film [11-14].

The Response Surface Methodology (RSM) is the most insightful method of evaluating a factorial experiment performance [15, 16]. The aim of this paper, in addition to synthesis of excellent quality Ni coatings on brass by the ED method and microindentation characterization of the material, is also to design an optimal experiment (DoE) according to RSM (Response Surface Methodology) [15-20]. Modification of the coating structure after deposition is another contribution of this paper.

II. Experimental

For electrodeposition of fine-grained nickel coatings we chose brass foil (260 1/2 hard, ASTM B36, K&S Engineering, 250 μm thick; composition: 66 % Cu, 34 % Zn) as a substrate (cathode). The surface area of the brass cathode was (2.0 × 1.0) cm^2. The pure Ni anode (rectangular in shape; positioned along the wall of the glass cell) and 500 ml of electrolyte were used. The nickel depositing apparatus is shown in Fig. 1. Prior to deposition, the cathode was mechanically polished and activated in a solution of sulfuric acid.

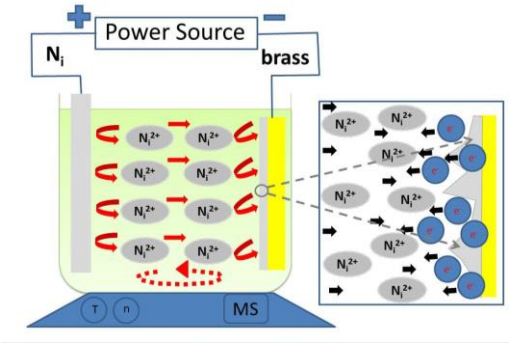

Fig. 1. Schematic presentation of nickel coating electrodeposition on brass substrate from sulphamate electrolyte in DC regime with magnetic stirrer (DC/MS).

Electrodeposition was performed in an open cell type using the direct current galvanostatic regime (DC) from a lab-made sulphamate electrolyte consisting of: 300 g/l Ni $(NH_2SO_3)_2{\cdot}4H_2O$, 30 g/l $NiCl_2{\cdot}6H_2O$, 30 g/l H_3BO_3 and 1 g/l saccharine as the wetting agent, with pH-value and the temperature of the process maintained at 4.20 and 50°C, respectively. The electrolytes were stirred by an application of magnetic stirrer (MS) (300 rpm, Heidolph Instruments GmbH & Co. KG, Schwabach, Germany). The DC/MS electrodeposited regime will be used below in the text.

The current density values were maintained at 10 mA cm^{-2} and 50 mA cm^{-2}. The deposition time was determined according to projected thickness of the coating. Five different coating thicknesses were formed: 2, 5, 10, 20 and 50 μm for each applied current density. Cathodic efficiency of 100% was taken to calculate the deposition time. The thickness was checked across the cross-section using an optical microscope.

The cross-section preparation for characterization was done in a fallowing manner: samples were embedded in a self-curing methyl methacrylate-polymer (Palavit G, Heraeus, Germany) and mechanically polished with different SiC papers (#800 and #1200) and finished with emulsion of alumina powder with different grain size (1-0.3 μm) [21]. Then, rinsing in sodium-carbonate solution and dried in nitrogen flow. The cross-section was prepared in order to validate the thickness of the coating, to observe the adhesion at the coating-substrate interface and to assess the hardness of the coating at the cross-section, see Fig. 2.

The mechanical properties of the composite system and substrate on top side and cross-section were characterized utilizing a Vickers microhardness tester ″Leitz, Kleinharteprufer DURIMET I″ using up to 15 loads ranging from 500 gf (4.9 N) down to 5 gf (0.049 N), see Figs. 2, 3 and 4. Five different loads were selected for optimization (10, 50, 100, 150 and 300 gf). Three indentations were made and the average value of the diagonal was determined by measuring six indentation diagonals, for each load. With the average value of the diagonals, the mean value of the hardness was calculated [9].

The topographic analysis of coatings surface after post-treatment was investigated using an atomic force microscope in the non-contact mode (AFM-Auto Probe CP Research; TM Microscopes-Veeco Instruments, Santa Barbara, CA, USA). The scan area was (20 × 20) μm^2. A histogram analysis of the coatings and bearing rate curve [22, 23] were done by an application of WSxM AFM software [24]. The analysis was performed in order to assess the resistance of the coating and the change in roughness during mechanical treatment and exposure to aggressive reagents such as hydrochloric acid (Fig. 5).

III. Results and Discussion

A. *Indentation on different locations*

The microhardness of Ni coating and influence of the substrate hardness during penetration of indenter is shown to depend on the indentation site. The hardness measured on the cross-section of brass (Fig. 2a) corresponds to the absolute bulk substrate hardness that is used in proportional specimen resistance (*PSR)* model (H_s = 1.41 GPa) [25].

If the indentation is performed on the coating surface, the structural-morphological properties of the coating affect the measurement, and the contribution of the substrate must be taken into account. The measured value of hardness is called composite hardness, H_c. In the case of cross-sectional indentation (Fig. 2b), the measured hardness, $H_{c\text{-}s}$ is constant and equal to the hardness of the bulk material without effects of substrate hardness and morphology of coating surface. Comparative values are shown in Table I. The diagonal size measured on the cross-section of the coating ($d_{c\text{-}s}$) is smaller than on the surface of composite (d), for the same applied load. For the "hard film on soft substrate" composite system type, the cross-sectional hardness value is higher than the composite hardness.

The interfacial indentation [3] hardness test (Figs. 2c and 2d) is a quick way to assess interlayer adhesion strength of the coating to the substrate and indentation toughness

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properties. The interfacial hardness and diagonal interfacial size (d_i) measurement is complex. The problem with this method of measurement is a possible difference in the height of nickel and brass due to the different wear rate of the material when preparing the cross-section. The delamination of the Ni coating did not occur, so the adhesion of the Ni coating for brass substrate is good. For very thin coatings (2, 5, 10 μm), it is not possible to measure hardness on the cross-section, because the Vickers indent size is larger than the projected thickness of the coating.

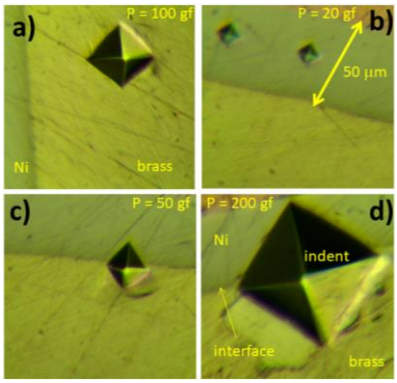

Fig. 2. Indentation on different location of cross-section with variation applied load on Ni/brass composite system: a) indentation on brass substrate, P = 100 gf, b) indentation on Ni coating, P = 20 gf, c) interfacial indentation, P = 50 gf and d) interfacial indentation, P = 200 gf. Nickel coating was obtained in DC/MS electrodeposition regime at 50 mA cm^{-2} current density.

TABLE I
CHANGE IN THE HARDNESS OF THE NICKEL COATING DEPENDING ON THE MEASURING LOCATION

P / gf	d / μm	$d_{c\text{-}s}$ / μm	H_c / GPa	$H_{c\text{-}s}$ / GPa
20	11.08	10.50	2.945	3.278
50	18.88	15.40	2.535	3.810
100	24.90	22.00	2.914	3.734
200	36.50	34.05	2.713	3.117

B. Indentation on the top surface of the Ni coatings on brass substrate

Different load-indentation depth curves can be obtained by changing the coating thickness of Ni coatings and current densities (Fig. 3). It can be seen that the coating thickness is the dominant parameter in the loading indentation process, while current density has very little effect, especially for small coating thicknesses.

The dependencies of the composite hardness (H_c) on the relative indentation depth (*RID*) for the given Ni coatings are shown in Figure 4. The *RID* is defined as a ratio between an indentation depth, h and a coating thickness, δ (*RID* = h /δ), where an indentation depth depends on a diagonal size as h = d /7 [9, 11-14, 21]. The contribution of substrate to composite hardness increases with the increasing *RID* value and applied load P, suggesting that the composite hardness matches the substrate hardness at high *RID* values.

Figure 4 clearly shows three characteristic zones depending on the influence of coating and substrate hardness on the composite hardness: 1) dominant influence of the coatings corresponds to 0.01 < *RID* < 1 (for thick 50 μm coatings), 2) the composite zone corresponds to 0.1 < *RID* < 1 for medium-thick films (10 and 20 μm) and 3) the dominant influence of the substrate is characteristic when *RID* > 1; for thin coatings (2 and 5 μm).

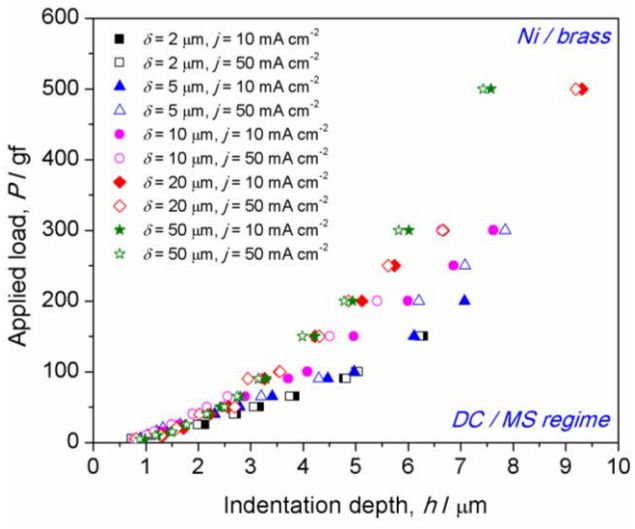

Fig. 3. Load-indentation depth experimental points of different Ni coating thickness electrodeposited on brass substrate in DC/MS regime at two current densities (10 and 50 mA·cm^{-2}).

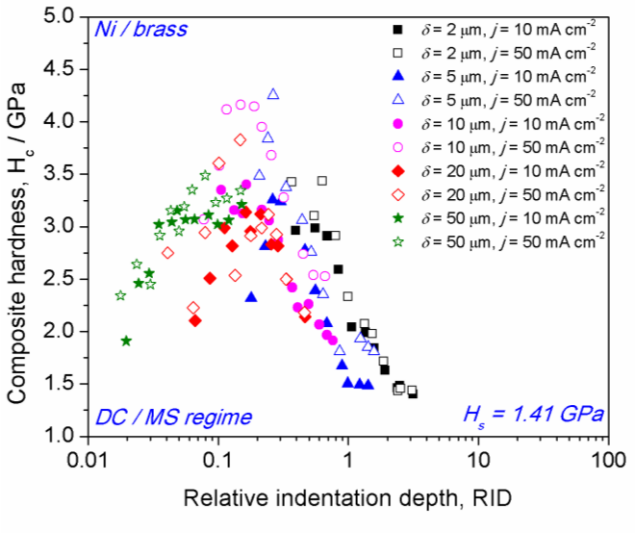

Fig. 4. The dependencies of the composite hardness (H_c) on the RID for the Ni coatings electrodeposited on the brass from the sulphamate electrolyte.

Figure 4 also shows a characteristic turning point, corresponding to a value of *RID* of 0.14. For the *RID* values smaller than 0.14, the measured composite hardness corresponds closely to the hardness of the coating. By crossing this critical point, the value of hardness decreases, which indicates the contribution of the softer substrate below. The Ni coatings obtained with a higher current density (50 mA·cm^{-2}) appeared harder than those deposited with 10 mA·cm^{-2}. For hard coating on soft substrate composite systems, with increasing the relative indentation depth (0.1 ≤ *RID* ≤ 1), the composite hardness H_c decreases until the hardness of the substrate is reached as shown on Fig.4 (H_s = 1.41 GPa).

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C. Modification of Ni surface after deposition by mechanical and chemical treatments

Stochastically roughened of metallic thin coatings can be obtained with various methods including dry etching, wet chemical etching or mechanical treatment (abrasion). Depending on the applied method, different surface profiles are obtained with microstructural modifications of surface coatings. The goals of this work were to explore the correlations between the AFM-based and treatment method for samples with different roughness and therefore different areas. For example, the difference in mechanical properties on the cross-section and the surface of the coating is one of the consequences of the treatment (mechanical). The roughness of each of the samples was determined using AFM topographic measurements. Figures 5 present the 3D AFM images of Ni / brass systems obtained at 50 mA·cm^2 (left) and histograms (right) with different treatment: mechanical (Figs. 5 a, b), chemical (Figs. 5 c, d) and no-treatment (Figs. 5 e, f).

Comparing the topography of nickel coatings, mechanical treated (Fig. 5a) and chemical treated coating (Fig. 5c) have similar roughness and stochastically nodular topography. Ni coating with mechanical treatment (Fig. 5a) can be observed to have a rather irregular surface with distributed nodular surface features. Deep channels as a result of sanding and scratching the surface were observed, too. From the values of the arithmetic average of the absolute roughness parameter (R_a) of the surfaces presented in Fig. 5, it could be observed that the roughness increases for Ni coatings including either chemical or mechanical treatment relative to non-treated coating (R_a = 28.68 nm for no-treated, R_a = 82.43 for chemical and R_a = 78.14 for mechanical treated coatings).

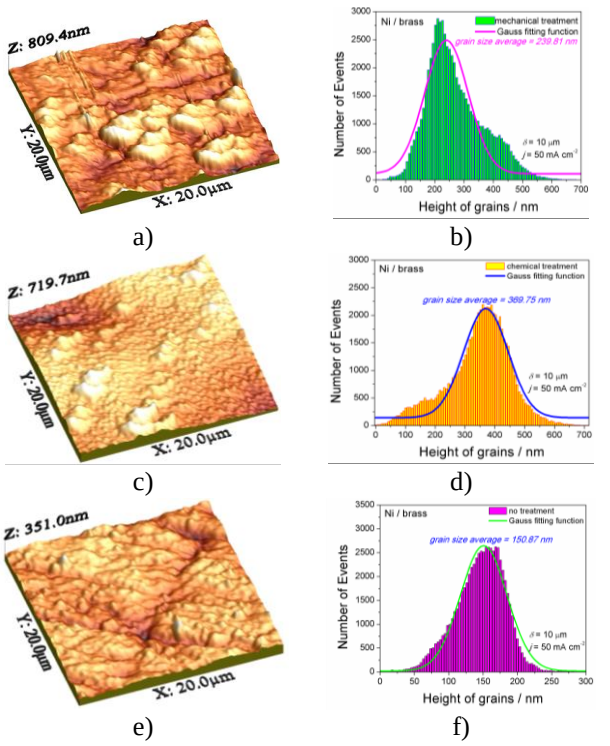

Fig. 5. Examples (20 × 20) µm^2 AFM topographic measurements for a Ni coating (10 µm thick) on brass substrate (left) and corresponding histograms (right) after electrodeposition and roughened surface treatment: a) and b) mechanical; c) and d) chemical; e) and f) no treatment. Ni coatings were obtained by electrodeposition technique in DC/MS regime at a current density of 50 mA cm^{-2} from the sulphamate electrolyte.

Although the topography of the untreated sample and the chemically etched one is very similar, based on the average height of grains obtained via the Gaussian distribution fitting function, it can be seen that the chemically treated sample has higher peaks (369.75 nm). However, mechanical treatment of the surface leads to the suppression of high peaks (Fig. 5b), which results in a reduction of total roughness (239.81 nm), i.e. smoothing of the surface.

Figures 6 show the relationship of bearing ratio (in %) with the grain height (Firestone–Abbott bearing curve, standards DIN4776; STN ISO 13 565-2). The bearing curve is the cumulative probability density function of the surface profile's height which is calculated by integrating the profile of the AFM trace [22]. As can be seen, if the bearing area rate reached 95 %, the order of the corresponding grain height of these treated Ni coatings are mechanical (800 nm) > chemical (700 nm) > no treatment (350 nm), see Fig. 6a.

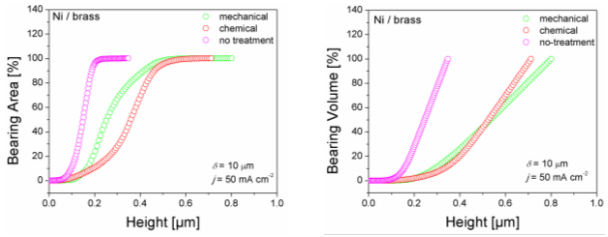

Fig. 6. Bearing ratio curves of Ni coatings on brass substrate with a variation of treatment: a) bearing area and b) bearing volume curve.

With application of post-treatment, the distribution range of nodule sizes shifts to the direction of larger values, see Fig. 6a. It indicated that the Ni coating without any treatment has the finest granule size, comparatively. It suggested that the Ni benefits smooth and fine-grained structure. Bearing flooded volume or bearing area curve indicated that the critical dimension point is 500 nm for peak height (Figs. 6a and 6b) for treated surface.

D. Optimization of composite hardness of Ni/brass systems

Design-Expert 12 (Stat-Ease, US) software and Optimal Design was used for the response methodology to examine correlation between the input variables (coating thickness, current density and applied indentation load) and output parameter (composite hardness). The factors (3 numerical) and factor levels (numerical) are shown in Table II.

TABLE II

INFLUENCE FACTORS ON NI COATING COMPOSITE HARDNESS

Mark	Parameters	Value limit Lower	Value limit Upper	unit
P	Applied indentation loads	10	300	gf
δ	Thickness of the Ni coatings	2	20	µm
j	Current densities	10	50	mA cm^{-2}

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Using data given in Table II, a regression mathematical model was developed to describe the function between the input parameters and measured response values. The relationship enabling a prediction of the composite hardness (H_c) values of the Ni/brass systems in a function of applied variables (indentation load (P), thickness of the coating (δ) and current density (j) is given by Eq. 1:

$$H_c^{-1}=0.3833+0.0534A-0.11191B-0.024C-0.835AB-$$
$$-0.0391AC-0.033BC-0.0433A^2+0.01374B^2+0.0318C^2 \quad (1)$$

where A, B and C represent numerical factors from Table II corresponding to the input variables, i.e. applied load, coating thickness and current density. Figure 7 shows the dependence of H_c values predicted by the RSM based on the regression model generated by coded Eq. 1 for every combination of two input parameters: applied load, coating thickness and current density (Fig. 7a load and thickness; Fig.7c current density and load; Fig. 7e current density and thickness). Each combination has a positive and statistically significant effect on composite hardness as also revealed by the contour lines presented in Figs. 7b, 7d and 7f. The red color corresponds to high values of composite hardness i.e. dominant influence of the coatings ($H_c \rightarrow 3.4$ GPa), yellow and green correspond to the composite zone and the blue indicates the dominant influence of the substrate i.e. composite hardness approaches to the hardness of the substrate ($H_c \rightarrow H_s$).

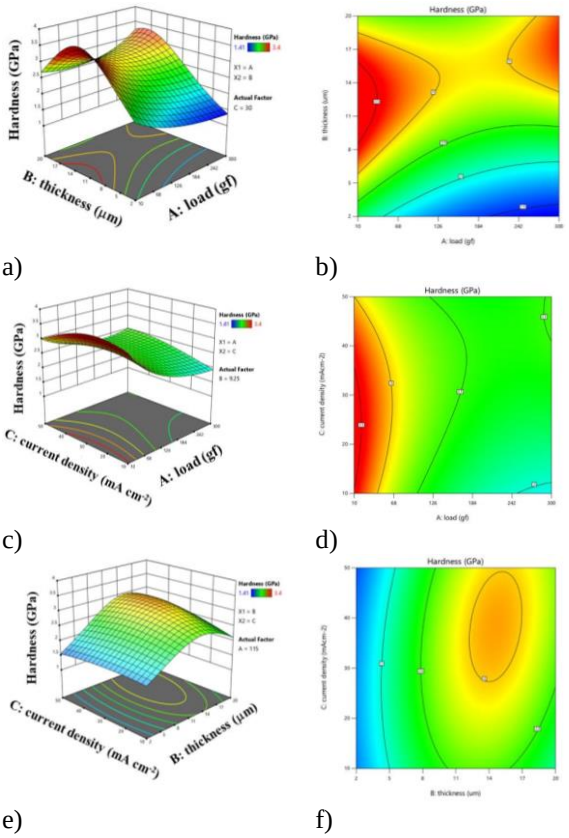

Fig. 7. 3D response surface (left) and contour plot (right) of Ni/brass composite hardness for different coded values: a) and b) of A (indentation load) and B (thickness), c) and d) of A (indentation load) and C (current density), e) and f) for B (thickness) and C (current density).

An increase in current density also indicates an increase in composite hardness value, but for indentation loads corresponding to the "film zone" (up to 50 gf), see Fig. 7d. It can be seen from Fig. 7 that the coating thickness and applied loads have a significant impact on the Ni/brass composite hardness systems. The current density is the least dominant factor in composite hardness change (Figs. 7f).

IV. Conclusion

The parameters suitable for fabrication of hard, compact and uniform Ni coatings on brass substrate were obtained in the direct current regime with magnetic stirring (DC/MS) from lab-made sulphamate electrolyte. Nickel coatings of various thickness were obtained utilizing different current densities. The maximal composite hardness of Ni/brass composite system was achieved for a current density of 50 $mA \cdot cm^{-2}$, 15 μm coating thickness and with applied indentation load of 50 gf (0.49 N).

Two ways of measuring micro hardness are presented: on the cross-section and the top of surface coating. The measured hardness at the cross-section of depth Ni is higher than composite hardness on top surface. Based on the interfacial indentation test, good adhesion between the coating and the substrate was determined, and no delamination occurred.

Stochastically roughened of electrodeposited Ni thin coatings can be obtained with various methods including mechanical and chemical treatment after electrodeposition process. Based on topographic analysis, it has been shown that each additional treatment after electrochemical deposition introduces an increase in stochastic roughness. That means, after deposition, it is not necessary to treat the surface of the coating before micro indentation.

The RSM optimization of operating parameters for the synthesis of the Ni/brass composite system was applied. Analysis of variance confirmed that the proposed regression model is in good agreement with the experimental data, providing a high determination and adjusted determination coefficients. The results suggested that the used adequate micro indentation loads, as well as the synthesis parameters, can directly affect the material mechanical properties such as composite hardness.

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