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Determination of Modulus of Elasticity, Nanohardness and Residual Stresses in Brush-plated Gold and Silver Coatings on Copper Substrate

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In the current study the investigated brush-plated gold coatings are generally used for repairing the commutators of generators and sliding contacts made in most cases of copper. Considering the cost, gold is sometimes replaced by silver in manufacturing electronic components.

Nickel-hardened gold and silver coatings were brush plated from a commercial SIFCO Dalic Solution (Gold Hard Alloy), Code SPS 5370, and Silver Hard Heavy Build, Code SPS 3080, on unclosed thin-walled copper ring substrates.

The magnitudes of the modulus of elasticity and of nanohardness of the coatings were obtained by instrumented indentation using the MTS Nano Indenter XR® and the Micromaterials Nano Test system pendulum-type nanohardness tester. Residual stresses in the coatings were calculated from the curvature changes of the substrates and they represented tensile stresses. Relaxation of residual stresses was observed. An equation for approximation of the change of residual stresses was applied assuming that the dependence of residual stresses on relaxation time is linear-fractional. The values of residual stresses in the gold and silver coatings decreased considerably, during the first weeks in particular. The equation for approximation of the change of residual stresses allows to predict the finishing residual stresses in the coating for the exploitation period within the limits of measurement uncertainty.

The surface morphology and microstructure of the coatings was studied by means of scanning electron microscopy (SEM).

Keywords: brush-plating, gold and silver coatings, nanohardness, modulus of elasticity, residual stress, stress relaxation.

1. INTRODUCTION

One of the methods of electrodeposition is brush-plating (selective plating, contact plating, swab plating), which is known as a slow method applied primarily in cases where the areas to be coated are small and somewhat unique [1, 2]. When brush-plating is applied, localized areas are plated, using an anode and a porous dielectric cover on the anode adapted to be wet by the plating solution and moved over the workpiece. This process is up to 60 times faster than tank plating and has made reductions in the amount of deposited materials possible.

Brush-plated gold and silver coatings are mainly used for decorative (e.g. copper domes of churches, adornments, etc) or electric applications. Today, nickel-hardened gold layers are used in electric and electronic equipment, as contacts for high-reliability separable connectors, switches and in other applications, where hardness and resistance to mechanical wear are key properties for achieving reasonable service life in compliance with reliability standards. Considering the cost, gold is sometimes replaced by silver in manufacturing electronic components.

In this study the investigated coatings are mainly used for repairing of the commutators of generators and sliding contacts made in most cases of copper. The laying of the coating, however, is accompanied by generation of residual stresses in it. Residual stresses are in many cases high and may cause significant shape changes or contribute to damage development (cracking, delamination due to poor bonding between the coating and substrate), which determines the stability, reliability and lifetime of the coated parts. Thus, accurate measurement and prediction of residual stresses is important for the understanding and ultimate control of delamination and cracking of coatings.

In paper [3 – 5] a discrete deformation method was elaborated for measuring the slit increment of an unclosed ring strip substrate with slipping edges and a unilateral coating. For coating the outer surface, the substrate is fixed to a mandrel, which makes free slipping of the edges as well as instantaneous deformation of the coated substrate possible. The coated substrate with certain coating thickness is released from the mandrel, and the slit increment (bending deflection) of the substrate is measured as the experimental parameter. In such a substrate, the coating is deposited at uniform rotation speed and the brush (holding the solution) is continuously fed with drops of the electrolyte from a cylindrical separatory funnel, which guarantees a constant pressure of the brush on the cathode and a relatively homogeneous temperature of the deposition process.

In the present study residual stresses were investigated in gold and silver coatings, plated with different current densities, and their relaxation depending on time. The microstructure of the studied coatings was investigated by means of scanning electron microscopy (SEM) in Zeiss EVO MA-15.

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2. EVALUATION OF RESIDUAL STRESSES IN THE COATING

The equation used is based on Brenner and Senderoff's concept [6], where the substrate is examined as the beam with slipping ends (see Fig. 1). In this study the equation is modified to account for biaxial stresses and the shell shape of the substrate which is taken into consideration by a coefficient [3 – 5, 7].

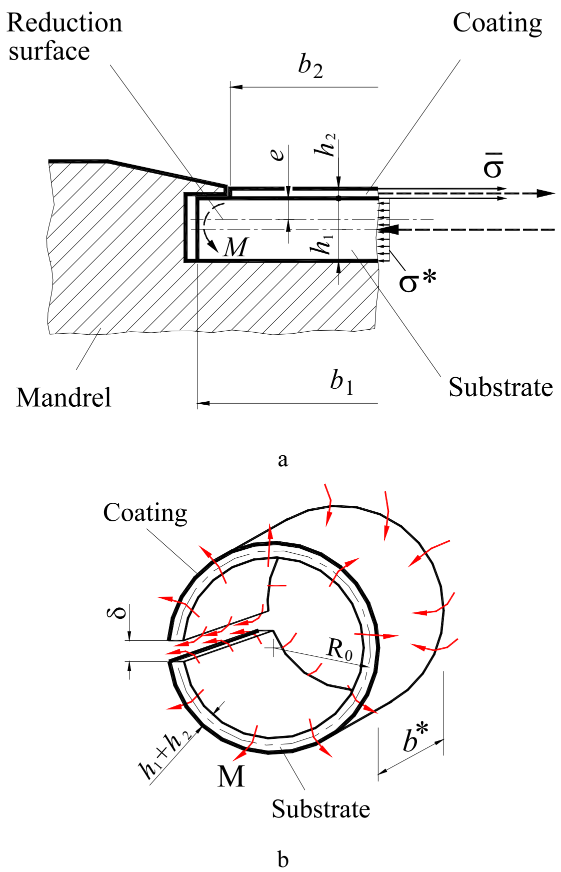


Fig. 1. Fragment of the edge region of a coated ring substrate and formation of the edge moment M generated by the coating (a), geometry of ring substrate and loading by the edge moments (b)

According to the scheme (Fig. 1) the basic formula of bending can be expressed as [4]

$$M = \frac{E_1 b_1 F}{24\pi R_0^2}\frac{\bar{f}_4}{\bar{f}_1}\Delta\delta . \tag{1}$$

Assuming that residual (initial) stresses σ are distributed uniformly throughout coating thickness (as this is the case of a discreet method the results will fluctuate to a great) and the residual stresses in the coating and substrate are expressed from the following equations

$$\bar{\sigma} = \sigma h_1 / \bar{f}_1 ,\ \sigma^* = \sigma h_2 / \bar{f}_1 .$$

The longitudinal force is equal to zero $N_1 + N_2 = 0$, than

$$N_2 = -N_1 = \bar{\sigma} h_2 b_2 . \tag{2}$$

The edge moment and the residual stresses are linked by the equation

$$M = \sigma \frac{b_2 h_2 h_1 (h_1 + h_2)}{2\bar{f}_1} . \tag{3}$$

After solving formulae (1) and (3) jointly and residual stresses are calculated from

$$\sigma = \frac{E_1 b_1 F}{12\pi b_2 R_0^2}\frac{\bar{f}_4 \Delta\delta}{h_1 h_2 (h_1 + h_2)} , \tag{4}$$

where R_0 is the middle radius of the substrate, b_1 and b_2 are the widths and h_1 and h_2 are the thicknesses of the substrate and coating, respectively; $e = \left(h_1^2 - \bar{\gamma} h_2^2\right)/2\bar{f}_1$ is the distance of reduction surface from the interface between the coating and substrate, the coefficient

$$F = \frac{1-\mu^2 k}{\left(1-\mu^2\right)\left(1-\mu k\right)} ,\ \text{where}\ k = \frac{2}{\beta b^*}\frac{\cosh\beta b^* - \cos\beta b^*}{\sinh\beta b^* + \sin\beta b^*} ,$$

the ratio k depends on $\beta = \sqrt[4]{\frac{3\left(1-\mu^2\right)\bar{f}_1^2}{R_0^2 \bar{f}_4}}$, $b^* = \frac{f_1 \bar{f}_4}{\bar{f}_1 f_4} b_1$,

where $\bar{f}_1 = h_1 + \bar{\gamma} h_2$, $\bar{f}_2 = h_1^2 + 2h_1 h_2 + \bar{\gamma} h_1^2$;

$\bar{f}_4 = h_1^4 + 4\bar{\gamma} h_1^3 h_2 + 6\bar{\gamma} h_1^2 h_2^2 + 4\bar{\gamma} h_1 h_2^3 + \bar{\gamma}^2 h_2^4$;

$\bar{\gamma} = E_2 b_2 / E_1 b_1$, $f_1 = h_1 + \gamma h_2$;

$f_4 = h_1^4 + 4\gamma h_1^3 h_2 + 6\gamma h_1^2 h_2^2 + 4\gamma h_1 h_2^3 + \gamma^2 h_2^4$; $\gamma = E_2 / E_1$;

E_1, E_2 are the moduli of elasticity of the substrate and coating, respectively. Poisson's ratio for the substrate and coating are assumed to be the same ($\mu_1 = \mu_2 = \mu$), $\Delta\delta$ is the measured slit increment.

Calculation shows that higher deposition temperature causes temperature stresses whose role in residual stresses is not significant [5].

It was observed that residual stresses decreased with time. An equation for approximation of the change of residual stresses, calculated from experimental data, can be developed assuming that the dependence of residual stress on relaxation time is linear-fractional (equilateral hyperbola with the asymptote parallel to the coordinate axes) [8]

$$\sigma(t) = b\left(\sigma - \sigma_j\right)/\left(at + b\right) + \sigma_f , \tag{5}$$

where σ is the calculated residual (initial) stress of a freshly plated coating, $t = 0$), σ_f is the calculated finishing stress, t is relaxation time (days), and a and b are constants.

Thus, determination of the change of residual stress depending on time is reduced to finding adequate constants. The constants should be determined so that calculated residual stresses are approximated in the best way by minimizing the square of the error (least square regression). This problem was solved by using the program Mathcad2001i Professional with the regression function *genfit* (vx, vy, vg, *F*) [9].

The magnitudes of the modulus of elasticity of the coatings were obtained by instrumented indentation using the MTS Nano Indenter XR® and the Micromaterials Nano Test system pendulum-type nanohardness tester according to the equation

$$\frac{1}{E^*} = \frac{1-\mu_2^2}{E_2} + \frac{1-\mu'^2}{E'} , \tag{6}$$

where $E' = 11.43\times10^5$ N/mm^2 and $\mu' = 0.07$ are modulus of elasticity and Poisson's ratio of CVD diamond indenter, respectively [10]; μ_2 is Poisson's ratio of the coating which is assumed to be same as that of pure cold and silver (see Table 1), E^* and E_2 are the measured and the calculated moduli of elasticity of the coating materials.

3. RESULTS

The effect of current density on residual stresses was studied using a series of specimens (minimum of eight specimens in one series) and mean values were employed. Coatings with a thickness of 3.0 µm to 3.9 µm (gold) and of 10.2 µm to 11.9 µm (silver) were deposited at different current densities (0.15 A/cm^2 to 0.35 A/cm^2, with the interval 0.05 A/cm^2) on copper substrates ($11.4 \times 96.0 \times 0.17$ mm, $11.8 \times 96.0 \times 0.17$ mm, 99.9 % Cu [11]) at the cathode velocity of 0.39 m/sec.

The coated surface of the substrate was polished to the roughness $R_a = 0.062$ µm. The plating technology is described in [4, 5].

Microhardness obtained for gold and silver coatings as soft coatings are (0.39 – 1.00) GPa, (0.39 – 1.86) GPa, respectively. According to literature data [12], silver coating has to some degree higher microhardness than gold coatings. However the results of our nanohardness experiments are the contrary.

Table 1. Constants of the substrate and coatings materials

Constant	Substrate [11]	Coating [13]	
	Copper	Gold	Silver
Modulus of elasticity E, 10^5 N/mm^2	1.10	0.843 ±0.194	0.834 ±0.078
Poisson's ratio μ	0.34	0.44	0.37
Density, g/cm^3	8.94	19.3	10.50
Coefficient of thermal expansion α, 10^{-5} 1/deg	1.65	1.42	1.89
Nanohardness of the coating, GPa	–	2.19 ±1.00	1.68 ±0.30

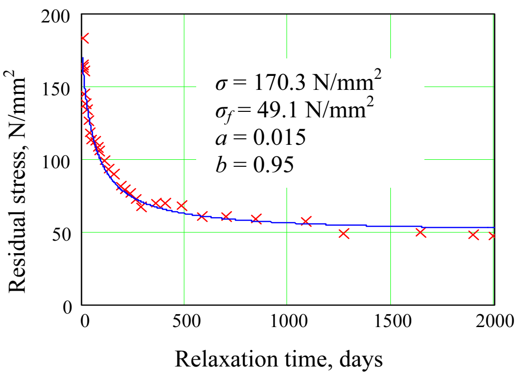


Fig. 2. Residual stresses in the gold coating on a copper substrate depending on time and the line of approximation

The selected particular mean values of measured residual stresses (initial stresses) of freshly plated coatings and relaxed stresses $\sigma(t)$ are presented in Tables 2 and 3 and in Figs. 2 – 5.

The mean values of residual stresses in gold coatings, deposited at current densities 0.15 A/cm^2 on a copper substrate, calculated from the experimental data of eight specimens (at a coating thickness of 2.0 µm), depending on time, are presented in Fig. 2. According to equation (5) calculated residual stress after 1992 days is 49.1 N/mm^2, while measured residual stress is 47.3 N/mm^2. The results show that maximum residual stress was significantly reduced through the mechanism of relaxation, depending on observed relaxation time, about 3.5 times.

Table 2. Electrodeposition parameters and the change of residual stresses of freshly plated gold coatings after six months

Code of the coating		Au20	Au25	Au30	Au35
Current densities, A/cm^2		0.20	0.25	0.30	0.35
Temperature change ΔT, °C		5	5	5	6
Thickness of coatings h_2, mm×10^3		3.0	3.9	3.3	3.5
Measured residual stresses, N/mm^2	σ	187.5 ±13.7	193.6 ±14.1	150.4 ±11.0	154.2 ±11.3
	σ_f	121.2 ±8.8	107.4 ±7.8	72.6 ±5.3	75.8 ±5.5
Calculated residual stresses (eq. 5), N/mm^2	σ	182.2 ±13.3	188.2 ±13.7	145.7 ±10.6	151.0 ±11.0
	σ_f	120.3 ±8.8	110.1 ±8.0	81.0 ±5.9	84.9 ±6.2
Constants	a	0.059	0.16	0.03	0.12
	b	0.90	0.93	0.1	0.26
Relation σ/σ_f	Measured	1.55	1.80	2.07	2.03
	Calculated	1.51	1.71	1.80	1.78

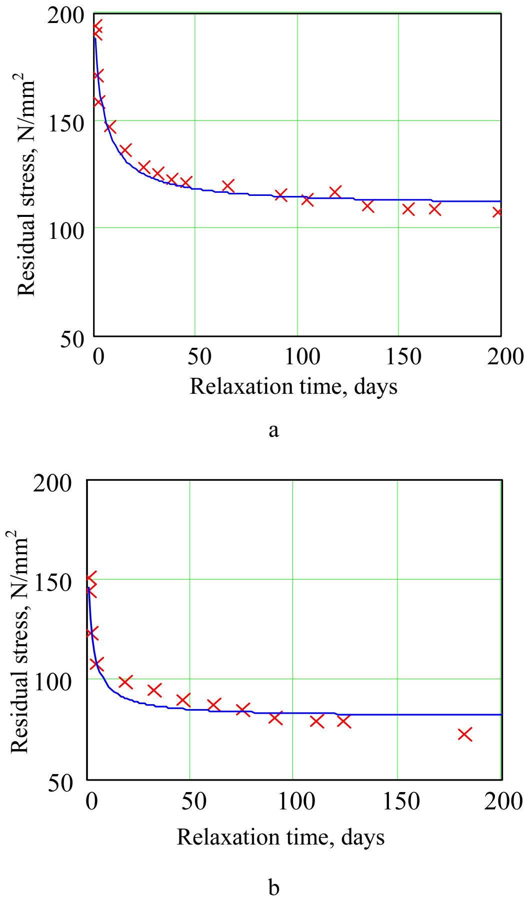


Fig. 3. Residual stresses in gold coatings deposited at various current densities (a – Au25; b – Au30) on a copper substrate depending on relaxation time and the curve of approximation

The mean values of residual stresses in silver coatings, deposited at current densities 0.15 A/cm^2 (at a coating thickness of 10 μm) on brass Fig. 4 and on copper substrates, calculated from the experimental data, depending on time, are presented in Fig. 5.

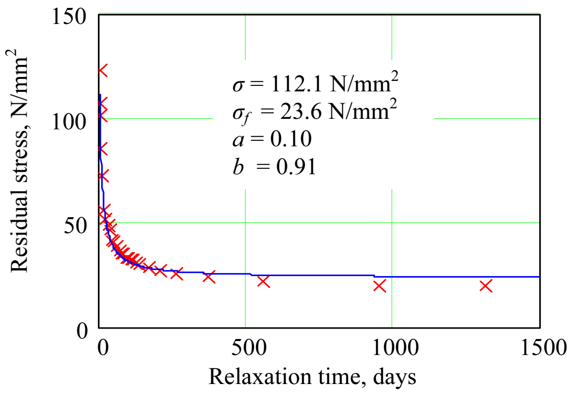


Fig. 4. Residual stresses in silver coating on brass substrate depending on the time and the line of approximation

The results show that time affects residual stresses more in silver coatings than in gold coatings and the largest difference between finishing stress and initial stress is approximately 4.8 fold.

Table 3. Electrodeposition parameters and the change of residual stresses of freshly plated silver coatings after eight months

Coating code		Ag15	Ag20	Ag25	Ag30
Current densities, A/cm^2		0.15	0.20	0.25	0.30
Temperature change ΔT, °C		4	6	8	8
Coatings thickness h_2, mm×10^3		10.2	11.9	11.8	10.6
Measured residual stresses, N/mm^2	σ	95.4 ±15.6	128.8 ±21.0	111.1 ±18.1	108.5 ±17.7
	σ_f	32.5 ±5.3	49.5 ±8.1	37.8 ±6.2	62.1 ±10.1
Calculated residual stresses (eq. 5), N/mm^2	σ	91.7 ±14.9	125.2 ±20.4	107.0 ±17.4	104.8 ±17.1
	σ_f	37.6 ±6.1	55.1 ±9.1	40.5 ±6.6	63.4 ±10.3
Constants	a	0.45	0.13	0.13	0.12
	b	0.89	0.92	0.91	0.96
Relation σ/σ_f	Measured	2.94	2.60	2.94	1.75
	Calculated	2.44	2.27	2.23	1.65

According to equation (5) calculated residual stresses in silver coatings (Ag15) on a copper substrate, based on the data recorded during 32 weeks, 37.6 N/mm^2 are twice lower than initial stresses. Hence they can be regarded as finishing stresses within the limits of measurement uncertainty.

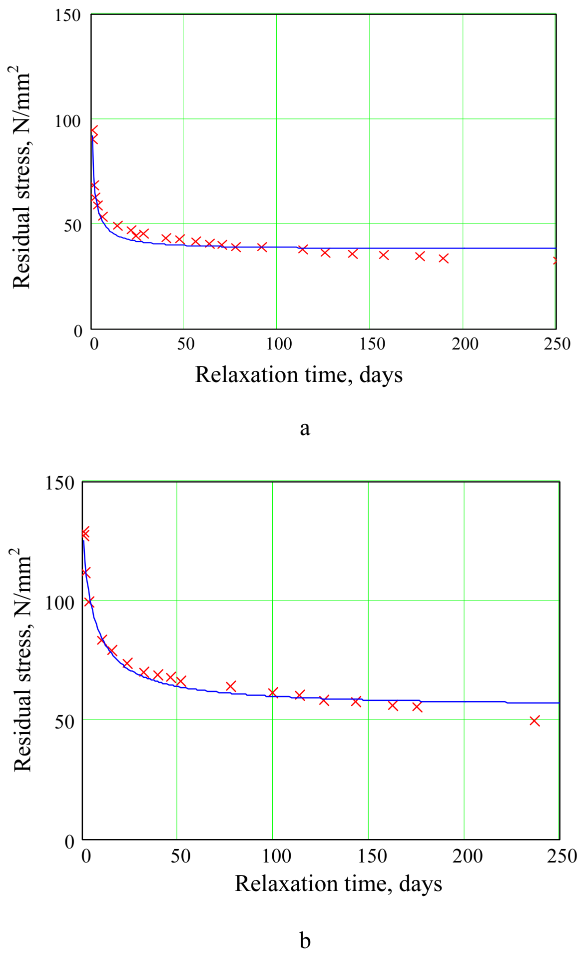


Fig. 5. Residual stresses in silver coatings (a – Ag15, b – Ag20) depending on relaxation time and the curve of approximation

Measurement uncertainties for the presented method were evaluated and expanded uncertainty was about 7.3 % and 16.3 % for gold and silver coatings, respectively [5, 14].

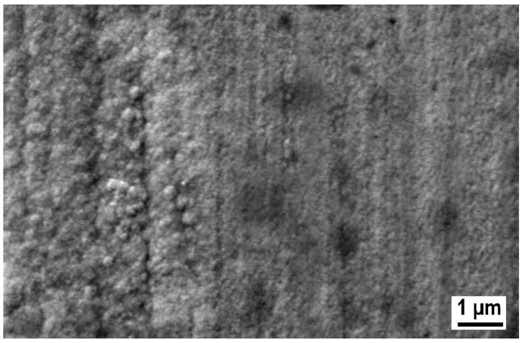
Equation (5) approximated the experimental data satisfactorily and it can be used for prediction of finishing stresses obtained for a smaller number of months.

On the other hand, the equation (5) approximates experimental data obtained for silver coatings better than for gold coatings.

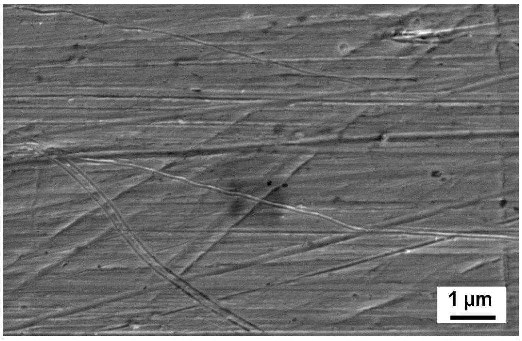
Residual stresses in gold and silver coatings were somewhat lower on a copper substrate than that on a brass substrate [5].

According to literature data [15], residual stresses in thin gold coatings electrodeposited from a tank of a standard electrolyte, at a current density of 0.0030 A/cm^2, and at temperatures of T = 55 °C and T = 70 °C, on one side of a strip steel substrate, determined by the curvature method, vary from 310 N/mm^2 to 510 N/mm^2.

The morphology and the cross-section of the gold and silver coatings are shown in Figs. 6, 7. The brush-plated coating has a fine crystalline structure which is caused by the high deposition current. The coatings have impure of carbon particle from the graphite anode, which can have an effect on the mechanical properties of the coating material.



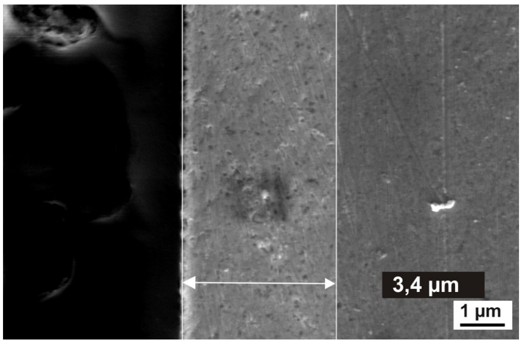
a



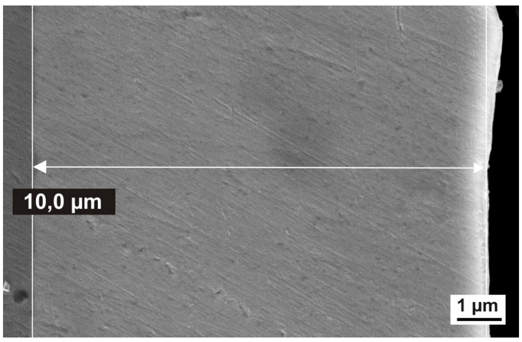
b

Fig. 6. Morphology of the gold (a) and silver (b) coatings that were brush-plated at current density 0.20 A/cm^2 and 0.15 A/cm^2

It is seen, the surface of coatings obtained by brush-plating inhomogeneous fine-grained, and proportions of single grains are various.

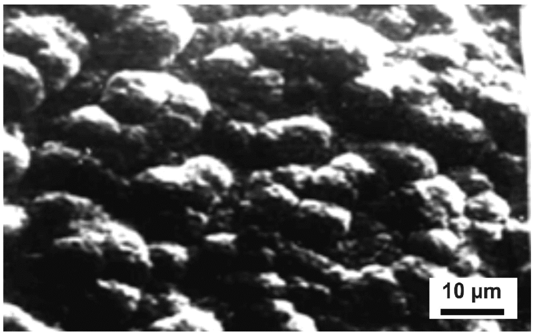


a

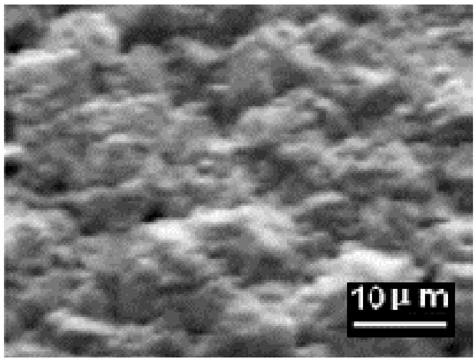


b

Fig. 7. Cross-section of the gold (a) and silver (b) coatings that were brush-plated at current density 0.15 A/cm^2 and 0.20 A/cm^2



a



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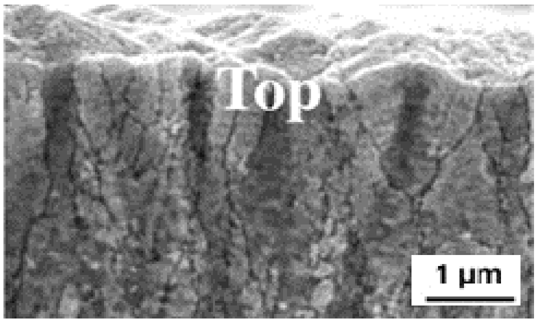

c

Fig. 8. Morphology of the gold (a) and silver (b) coatings and cross section of silver coating (c) that were electroplated in plating bath at 0.0025 A/cm^2 [16], 0.004 A/cm^2 [17] and 0.005 A/cm^2 [18]

4. CONCLUSIONS

1. Residual stresses in freshly plated coatings were high tensile stresses and their calculated mean values ranged from (145.7 ±10.9) N/mm^2 to (188.2 ±13.7) N/mm^2 and from (91.7 ±14.9) N/mm^2 to (125.2 ±20.4) N/mm^2 at measurement temperature for gold and silver, respectively. Higher deposition temperatures caused temperature stresses whose proportion in residual stresses was insignificant, accounting for not more than 2.5 % [5].

2. Residual stresses were not significantly influenced by current densities in our experiments.

3. The values of residual stresses in coatings decreased markedly and after two months they were two times lower for silver coatings and to some degree lower for gold coatings compared to the respective values obtained for freshly plated coatings. Residual stresses stabilized after 1300 and 400 days for gold and silver coatings, respectively.

4. The equation for approximation of the change of residual stresses allows calculation of finishing residual stresses in the coating on the basis of the data obtained during some months within the limits of measurement uncertainty.

5. The values of residual stresses in brush-plated gold coatings obtained from our experiments are higher than those in silver coatings and lower than the respective values of stresses in coatings obtained from a tank solution.

6. Measured nanohardness of gold coatings is higher than that of silver coatings.

Acknowledgments

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REFERENCES

1. **Rubinstein, M**. Electrochemical Metallizing. Van Norstrand Reinhold Company Inc, New York, 1987: 449 p.
2. **Wu, B., Xu, B., Zhang, B., Lu, Y.** Preparation and Properties of Ni/nano-Al_2O_3 Composite by Automatic Brush plating *Surface and Coating Technology* 201 2007: pp. 6933 – 6939.
3. **Lille, H., Kõo, J.** On the Determination of Residual Stresses in the Deposits Applied by Brush-plating *In: Wiss. Beitr Ingenieurhochsch Zwickau (Sonderheft III. Kolloq. "Eigenspannungen und Oberflächen-verfestigung")* Jg. 8 1982: pp. 116 – 121 (in Russian).
4. **Lille, H., Kõo, J., Ryabchikov, A**. Measurement of Residual Stresses in Different Electrochemical Metallized Coatings *Materials Science* (*Medžiagotyra*) 8 (4) 2002: pp. 417 – 420.
5. **Lille, H., Kõo, J., Pihl, T.** Measurement of Residual Stresses in Brush-plated Gold and Silver Coatings on Thin Gross-cut Ring Substrate *Latvian Journal of Chemistry* (*Latvijas Kimijas Zurnals*) 1 2008: pp. 48 – 54.
6. **Brenner, A, Senderoff, S.** Calculation of Stress in Electrodeposits from the Curvature of Plated Strip *Journal of Research of the National Bureau of Standards* 42 (2) 1949: pp. 89 – 104.
7. **Lille, H., Kõo, J., Gregor, A., Ryabchikov, A., Sergejev, F., Traksmaa, R., Kulu, P.** Comparison of Curvature and X-Ray Methods for Measuring of Residual Stresses in Hard PVD Coatings *Materials Science Forum* 681 2011: pp. 455 – 460. http://dx.doi.org/10.4028/www.scientific.net/MSF.681.455
8. **Virchenko, I. A., Lyashko, I. I., Shvetsov, K. I.** Handbook: Graphs of the Functions. Naukova dumka, Kyev, 1979: 320 p. (in Russian).
9. **Kir'yanov, D.** Mathcad 2011. Manual for Self-tution. BHV-Petersburg, Sankt-Petersburg, 2001, 544 p. (in Russian).
10. **Klein, C., Cardinale, G.** Young's Modulus and Poisson's Ratio of CVD Diamond *Proceedings of SPIE* 1759 1992: pp. 178 – 193.
11. **Rakhshtad, A. G., Brostrem, V. A.** Handbook for Metal-worker. Handbook in Five Volumes. Second Volume. Mashinostroyenie, Moscow, 1976: 720 p. (in Russian).
12. A Handbook. The Properties of Electrodeposited Metals and Alloys. Ed. **William H. Safranek**. American Electro Plasters & Surface Finishers S; 2nd edition, 1986: 550 p.
13. Material property data. http://www.matweb.com/search/ /DataSheet.aspx?MatID=7&ckck=1.
14. **Lille, H., Kõo, J., Ryabchikov, A**. On the Investigation of Residual Stresses in Brush Plated Silver Coatings *Materials Science* (*Medžiagotyra*) 14 (3) 2008: pp. 226 – 229.
15. **Hodge, T. C., Bidstrup-Allen, S. A., Kohl, P. A.** Stress in Thin Film Metallization *IEEE Transaction on Components, Packaging, and Manufacturing Technology Part A* 20 (2) 1997: pp. 241 – 250. http://dx.doi.org/10.1109/95.588580
16. **Bersirova, O., Kublanovsky, V.** The Electrodeposition Conditions of Functional Gold Films for Microelectronics *Materials Science* (*Medžiagotyra*) 10 (4) 2004: pp. 308 – 312.
17. **Baek, C-W., Kim, Y-K., Ahn, Y., Kim, Y-H.** Measurement of the Mechanical Properties of Electroplated Gold Thin Films Using Micromachined Beam Structures *Sensors and Actuators A* 117 2005: pp. 17 – 27.
18. **Bersirova, O., Kublanovsky, V., Anufryiev, L., Rubtsevich, I.** Corrosion Behavior of Electroplated Silver Coatings *Materials Science* (*Medžiagotyra*) 10 (1) 2004: pp. 11 – 14.

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