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RELAXATION OF RESIDUAL STRESSES IN BRUSH-PLATED GOLD COATING

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Abstract: *In this study residual stresses were determined in a gold coating deposited from a commercial SIFCO Dalic Solution (Gold (Hard Alloy), Code SPS 5370) on copper and brass substrates with different thicknesses. The calculation formula is extended Stoney's formula which takes into consideration the real shape of the substrate, and the difference between the elasticity moduli and the coefficient of thermal expansion of the coating and the substrate materials.*
Residual stresses in coatings represent significant tensile stresses and their maximum values are higher than the values of stresses in coatings obtained in a bath solution. The values of residual stresses decrease markedly and after nine months they are many times smaller than after deposition. The sensitivity of the method was studied and the expanded uncertainties of the computed mean values of the residual stresses are presented. Substrate deformation depending on coating thickness is examined.
Keywords: brush-plating, ring strip substrate, coating, slit increment, residual stress, stress relaxation

1. INTRODUCTION

Electroplated gold coatings have attracted much attention because of their desirable properties such as resistance to oxidation, low electrical resistance, overall chemical inertness and low processing temperature.
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]. In general, this method only needs a power pack, a number of solutions and brush tools to conduct the brush-plating process. This process has many advantages, such as portability and flexibility and it is usually employed at ambient temperature. However, two major problems have hindered this method to be extensively applied in industry, namely, high labour intensity and low labour productivity plus unstable quality of brushed deposits.
Presence of residual stresses is typical of all coatings. To determine residual stresses in brush-plated coatings, a conventional deformation method was used where an unclosed ring strip serves as the substrate [3,4,5]. The substrate is fixed to a mandrel, which makes free slipping of the edges as well as momentless deformation of the coated substrate possible. The slit increment of the substrate is measured as successive layers of the coating are deposited and the ring is free from the mandrel. The calculation formula is extended Stoney's formula which takes into consideration the real shape of the substrate, and the difference of the elasticity moduli of the coating and the substrate materials.
In this study residual stresses were determined in a hard gold coating deposited from a commercial SIFCO Dalic Solution (Gold (Hard Alloy), Code SPS 5370) on copper and brass substrates with different thicknesses. Study was made of substrate deformation depending on coating thickness. The sensitivity of the method was also analyzed and the expanded

uncertainties of the computed mean values of residual stresses were determined. Relaxation of residual stresses formed during the brush-plating process is presented.

2. EVALUATION OF RESIDUAL STRESSES IN COATINGS

The presented equation is different from the formula, obtained according to the scheme of the beam, by the coefficient which takes into consideration the real shape of the substrate [4]. Paper [5] presents a formula for calculating residual stresses where their value changes throughout coating thickness. Assuming that residual stresses are uniformly distributed throughout coating thickness (it can be used when the slit increment depending on coating thickness is linear), they are calculated from

$$\sigma = \frac{E_1 F}{12\pi R_0^2}\frac{b_1}{b_2}\left(\frac{\bar{f}_4}{\bar{f}_2 h_2} + 3\bar{\gamma}\frac{\bar{f}_2}{\bar{f}_1}\right)\delta, \qquad (1)$$

where E_1, E_2 are the moduli of elasticity of the substrate and coating, respectively. Poisson's ratio for the substrate and for the coating are assumed to be the same ($\mu_1 = \mu_2 = \mu$), R_0 is the middle radius of the substrate: coefficient

$$F = \frac{1-\mu^2 k}{\left(1-\mu^2\right)\left(1-\mu k\right)},$$

where $k = \dfrac{2}{\beta b^*}\dfrac{\cosh\beta b^* - \cos\beta b^*}{\sinh\beta b^* + \sin\beta b^*}$,

the ratio k depends on

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

where $\bar{f}_1 = h_1 + \bar{\gamma} h_2$, $\bar{f}_2 = h_1^2 + 2h_1 h_2 + \bar{\gamma} h_1^2$, $\bar{f}_4 = h_1^4 + 4\bar{\gamma} h_1^3 h_2 + 6\bar{\gamma} h_1^2 h_2^2 + 4\bar{\gamma} h_1 h_2^3 + \bar{\gamma}^2 h_2^4$, $\bar{\gamma} = E_2 b_2 / E_1 b_1$, $f_1 = h_1 + \gamma h_2$, $f_4 = h_1^4 + 4\gamma h_1^3 h_2 + 6\gamma h_1^2 h_2^2 + 4\gamma h_1 h_2^3 + \gamma^2 h_2^4$ and $\gamma = E_2 / E_1$,

$$\delta = \bar{\delta} + \delta^T, \qquad (2)$$

where $\bar{\delta}$ is the measured slit increment.

When determining the values of residual stresses at the deposition temperature T, which is different from the ambient temperature T_0 at which the increment of the slit is measured, the following correction should be introduced

$$\delta^T = 12\pi R_0^2 \frac{\bar{\gamma}(\alpha_2-\alpha_1)(T_0-T)(h_1+h_2)h_1 h_2 (1+\mu)(1-\mu k)}{\bar{f}_4\left(1-\mu^2 k\right)}, \qquad (3)$$

where α_1, α_2 are the coefficients of the thermal expansion (CTE) of the substrate and coating, respectively.

Table 1. Constants of the materials used

Parameter	Substrate		Coating
	Copper [6]	Brass [6]	Gold [7]
Modulus of elasticity $E\times10^5$ [N/mm^2]	1.10	1.14	0.80
Poisson's ratio	0.34	0.34	0.44
CTE $\alpha\times10^{-5}$ [1/°C]	1.65	2.05	1.44
Density [gf/cm^3]	8.94	8.50	19.3

To determine the relation between the increment of the slit and coating thickness, two series (No3 and No4) of substrates (30 specimens each were coated) and experimental data were approximated using linear function.

There was observed, that residual stresses decrease over 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 asymptotic parallel to the coordinate axes) [8]

$$\sigma(t) = \left(a\left(\sigma_0 - \sigma_f\right)\right)/\left(bt + a\right) + \sigma_f, \qquad (4)$$

where σ_0 is residual stress at the end of deposition (t = 0), σ_f is remaining residual stress, t is relaxation time (days), a and b are constants.

Thus, determination of the slope of the approximation line and of the change of residual stress depending on time is reduced to the finding of adequate constants. This problem can be solved using the program *Mathcad2001i Professional* with the regression functions *genfit* (*vx*, *vy*, *F*).

3. ANALYSIS OF UNCERTAINTIES OF MEASURED PARAMETER VALUES

In order to evaluate uncertainties of measurement, the linear regression analysis was applied. Experimental data was approximated with a formula

$$\delta_i = a_0 + a_1 h_i \ , \qquad (5)$$

where δ_i is slit increment, h_i is coating thickness, $i = 1\ldots J$.

The fundamentals of evaluating uncertainties using linear regression are described in [9].

Estimation of parameters a_0 and a_1 of Eq. 5 based on measured data is reduced to solve the system of normal equations. Solution yields a_0= 0, a_1 = 361.44 for specimens of series No3 and a_0= 0, a_1 = 80.48 for specimens of series No4.

Dispersions and covariations of the values of parameters a_0 and a_1 can be calculated according to the formulas presented in [9]. Solution yields for specimens of series No3: $s^2(a_0)$ =2.03·10^{-3}, $s^2(a_1)$ =225.89, $s^2(a_0 a_1)$ =-0.60, s^2 = 0.012 and for specimens of series No4: $s^2(a_0)$ =2.84·10^{-4}, $s^2(a_1)$ = 14.06, $s^2(a_0 a_1)$ = -0.06, s^2 = 2.01·10^{-3}.

Combined dispersion of approximation line is described by the equation of the second range

$$u^2(\delta_i) = \frac{s^2}{\Delta}\left\{\left(\frac{\partial \delta_i}{\partial a_0}\right)^2 \Delta_{11} + \left(\frac{\partial \delta_i}{\partial a_1}\right)^2 \Delta_{22} + 2\frac{\partial \delta_i}{\partial a_0}\frac{\partial \delta_i}{\partial a_1}\Delta_{12}\right\}$$

As all equations were composed using the mean results of experiments, then the uncertainty of measurement for a single experiment was not taken into account.

Uncertainty of measurement for a single experiment is calculated as a relative combined uncertainty [9]

$$w_c^2(\bar{\delta}) = \frac{u^2(b_2)}{b_2^2} + \frac{u^2(d)}{d^2} + \frac{u^2(g)}{g^2} \, ,$$

where b_2 is width of the coating, d is specimen's weight and g is density of the coating material.

The relative combined uncertainty of measurement taking into account uncertainty of measurement within a single experiment series yield

$$w_c(\delta) = \sqrt{w^2(\delta_i) + w_c^2(\bar{\delta}_i)} \ , \qquad (6)$$

where $w^2(\delta_i) = u^2(\delta_i)/\delta$.

Expanded uncertainty in case of 95% degree of confidence is

$$U = 2\, w_c(\delta) \, . \qquad (7)$$

As a result expanded uncertainty of 15.2% and 8.0% was obtained for specimens of series No3 and No4, respectively.

Experimental data representing the dependence of slit increment on coating thickness, approximation line, upper and lower limits of confidence level (dashed lines) are indicated in Fig. 2.

4. EXPERIMENTAL PROCEDURE

In this study residual stresses were determined in a hard gold (23 carats, Au 95.8 wt%, Ni 4.2 wt%) coating deposited from a commercial SIFCO Dalic Solution (Cold Hard Alloy, Code SPS 5370, Coldpotassium cyanide 5-9%, Ethylene diamine 5-9%, Nickel cyanide, pH 8.4) on copper and brass substrate with different thickness.

The strips of four series with the dimensions: No1 - 11.8×96.0×0.125 mm; No2 - 11.8×96.0×0.30 mm; No3 - 11.9× 96.0×0.19 mm and No4 -11.9×96.0×0.39 mm were cut from a rolled copper and brass (62–65%Cu) ribbon [6]. Copper and brass were chosen as the substrate material to attain higher sensitivity of the method. Before deposition of the substrate, its edges were filed, one side of the surface was polished and cleaned and the substrate was then rolled to form a ring with an inner diameter of 30.5 mm. The thickness and the slit (the mean value measured on two flank sides of the plane) of the substrate were measured to 0.01 mm. The substrate was weighed on the Sartorius Balance BA61 (readability 0.0001 g), placed into the fixture and fixed to the setup (Fig. 1). Further, it was electrocleaned by forward polarity with a voltage of 10 V for about 0.5 minutes (cleaning solution Code SCM 4100, sodium hydroxide 3-4%) and rinsed.

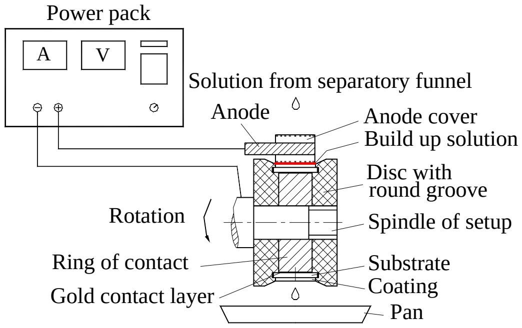

Fig.1. Deposition of the gold coating on the ring substrate with free slipping of the edges.

An anode made of special-grade heat-resistant graphite (to ensure the ratio 1:8 of anode surface to the surface to be coated) with a cotton batting was attached to the setup and fed from a separatory funnel by drops (15-20 drops per minute at temperature 20^{o}C) (Fig.1). The coating was deposited onto the area (width ~ 10.6mm) of the rotating substrate under the following conditions: velocity of the cathode ~11 m/min, current density 15A/dm^2, temperature of deposition 24 ^{o}C.

The substrate with the coating with a desired thickness was then removed from the mandrel, and was cleaned, dried and weighed. The final thickness of the substrate with the coating and the width of the deposited coating and the increment of the slit were measured. Coating thickness estimated from the quantity of the current was corrected, using a weight, by calculating average coating thickness from the difference in the specimen's weight before and after deposition.

5. RESULTS OF EXPERIMENTS

The experimental data of slit increment depending on coating thickness are shown in Fig. 2.

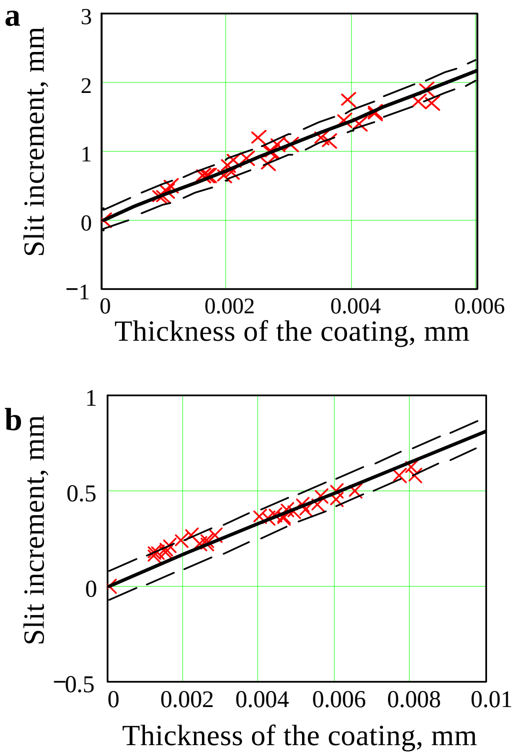

Fig. 2. Experimental values of the slit increment δ, depending on coating thickness h_2, and the line of approximation: (a) specimens of series No3, (b) specimens of series No4.

The experimental data do not fluctuate to a great extent and remain in the zone with sufficiently uniform width. The range of fluctuation of the experimental data depends on the thickness of the substrate. In the case of the thin substrate the limit of confidence is wider.
The presented method allows to determine the mean values of residual stresses in thin coatings assuming that they are constant throughout coating thickness. This is demonstrated by the satisfactory approximation of the dispersed experimental data using linear relation.
The calculated residual stresses (according to Eq. 1 at measuring temperature)

depending on relaxation time are presented in Fig. 3.

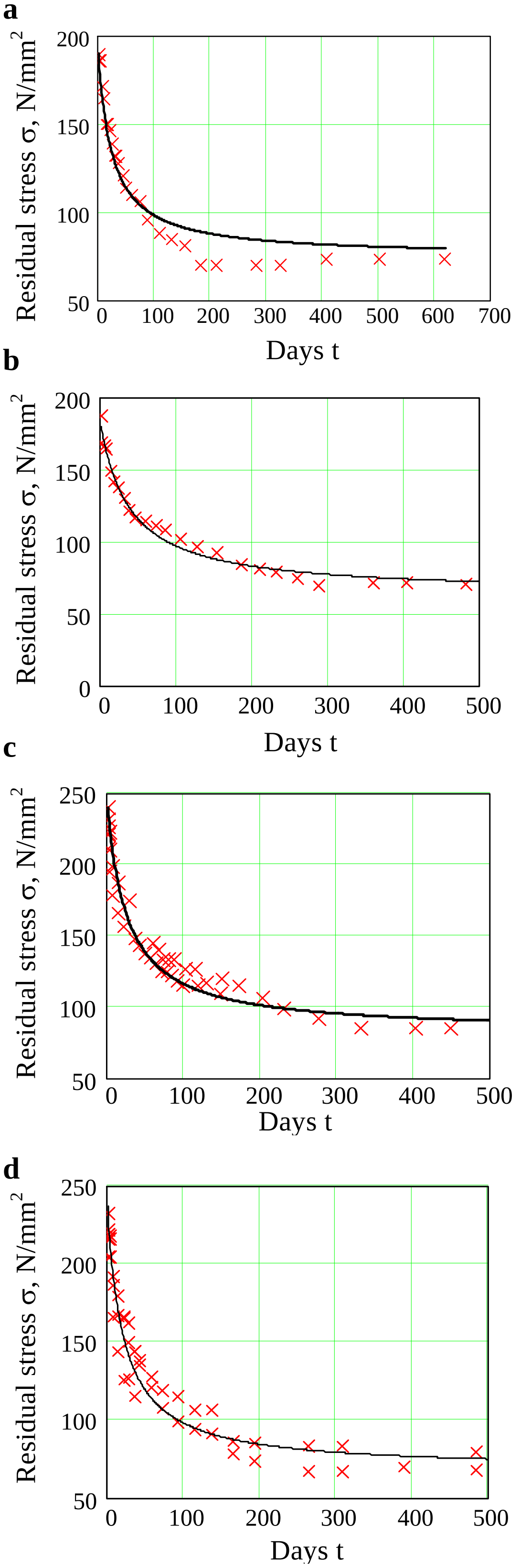

Fig. 3. Calculated values of residual stresses in gold coatings, depending on relaxation time, and the curve of approximation: specimens from series No1(a); No2(b); No3(c); No4(d).

The mean values of five specimens from series No1 and No2 and of nine specimens from series No3 and No4 were used.

The results show that time affects residual stresses in coatings to a great extent. It is evident that approximation of the calculated values of the residual stresses depending on relaxation time, using the presented formula, is satisfactory, where the values of σ_0 and σ_f are the maximum and remaining calculated residual stresses, respectively.

It is evident from the results of the approximation of residual stresses depending on time that the constants are similar for all coatings. Residual stresses calculated after deposition are significant and to some extent smaller on the copper substrate but the remaining stresses are comparable.

Table 2. Data of the substrate with coating and the results of the experiments

Parameter	No. of the specimens series			
	1	2	3	4
Mean thickness of the substrate h_1, mm	0.125	0.30	0.19	0.39
Mean thickness of the coating h_2, μm	2.0	4.3	2.1	5.2
Dimensionless constants a	2.38	2.25	2.38	2.26
b	0.066	0.078	0.088	0.088
Slope			361.4	80.5
Maximums of residual stress σ_0, N/mm^2 at measuring	186± 28	188± 15	240± 36	230± 18
at deposition	187± 28	189± 15	243± 37	233± 19
Remaining residual stresses σ_f, N/mm^2	61± 9	69± 6	83± 13	71± 6
Uncertainty, %	15.2	8.0	15.2	8.0

In our experiments residual stresses did not depend significantly on the substrate or on coating thickness.

6. CONCLUSIONS

Residual stresses in coatings represent significant tensile stresses and their maximum values were 186±28 N/mm^2; 188±15 N/mm^2 and 240±36 N/mm^2; 230±18 N/mm^2 at measuring temperature for gold coatings on the copper and brass substrates, respectively. The obtained values are higher than the values of stresses in coatings obtained in a bath solution [10]. The reason for generation of such high residual stresses in brush-plated coatings is the fact that these coatings have a fine crystalline structure which is due to the high deposition current [11]. Measurement uncertainties are evaluated for the method used and relative expanded uncertainty is 15.2% and 8.0%. Higher deposition temperature causes temperature stresses whose role in residual stresses is not significant. The values of residual stresses decrease markedly, and after nine months they are 61±9 N/mm^2; 69±6 N/mm^2 and 83±13 N/mm^2; 71±6 N/mm^2 for gold coatings on the copper and brass substrate, respectively. In the case of the dimensions of the substrate and the coating thickness used, the slit increment of the substrate depending on coating thickness is linear. This analysis was limited to the data obtained from the experiments described above.

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8. ADDITIONAL DATA

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