ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 14, No. 3. 2008

On the Investigation of Residual Stresses in Brush Plated Silver Coatings

Harri LILLE*, Jakub KÕO, Alexander RYABCHIKOV

Department of Structural Mechanics and Engineering, Estonian University of Life Sciences, Kreutzwaldi 5, Tartu 51014, Estonia

Received 31 May 2008; accepted 29 June 2008

In this study residual stresses were determined in a silver coating deposited from a commercial SIFCO Dalic Solution (Silver Hard Heavy Build, Code SPS 3080, silver cyanide 15 % – 17 %, ethylene diamine 5 % – 9 %, pH 11.7) on a brass and on a copper unclosed ring substrate. 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 the thermal expansion of the coating and the substrate materials.

Substrate deformation depending on the coating thickness was examined. The sensitivity of the method was studied and the expanded uncertainties of the computed mean values of residual stresses are presented. Residual stresses in the coating depending on the current density and on the velocity of the cathode were investigated. Residual stresses in coatings represent tensile stresses and their values range from 49 N/mm^2 to 117 N/mm^2 after deposition. The values of residual stresses decrease markedly and they are many times smaller after three months than after deposition.

Keywords: brush-plating, ring strip substrate, silver coating, slit increment, 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].

Electroplated silver coatings have attracted much attention because of their desirable properties such as resistance to oxidation, low electrical resistance and low processing temperature. Presence of residual stresses is typical for all coatings.

To determine residual stresses in brush-plated coatings, a conventional deformation method was used where an unclosed ring strip, which is rotating during deposition, serves as the substrate [3, 4].

In paper [4] 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 momentless deformation of the coated substrate possible. The coated substrate with a certain coating thickness is released from the mandrel, and the slit increment of the substrate is measured as the bending deflection parameter. For this purpose, an experimental system was developed consisting of a set-up for brush plating and a substrate fixer. In such a substrate, the coating is deposited at uniform rotation speed and the brush is continuously fed with drops of the electrolyte from a cylindrical separatory funnel, which guarantees a relatively homogeneous temperature of the deposition process.

In the present study residual stresses were investigated in silver coatings plated with different current densities and velocities of the cathode from the commercial SIFCO Dalic Solution (Silver Hard Heavy Build, Code SPS 3080, silver cyanide 15 % – 17 %, ethylene diamine 5 % – 9 %, pH 11.7). Substrate deformation depending on coating thickness was examined. The sensitivity of the method was also studied and the expanded uncertainties of computed mean values of the residual stresses are presented. Relaxation of residual stresses formed during the brush-plating process is presented as well.

2. EVALUATION OF RESIDUAL STRESSES IN THE COATING

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 [3]. Paper [4] presents a formula for calculating residual stresses where their value changes throughout coating thickness. Assuming that residual stresses are distributed uniformly throughout coating thickness (e.g. in the case of thin coatings within limits of measurement uncertainty), the derivative $d\delta(h)/dh$ was replaced by the δ/h_2 and residual stresses 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, b_1 and b_2 are the width and h_1 and h_2 are the thickness of the substrate and coating, respectively; coefficient

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

the ratio k depends on

*Corresponding author. Tel.: +372-7-313181; fax.: +372-7-313154.
E-mail address: *hlille@eau.ee* (H. Lille)

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

where $\bar{f}_1 = h_1 + \bar{\gamma} h_2$, $\bar{f}_2 = h_1^2 + 2h_1h_2 + \bar{\gamma}h_1^2$,

$\bar{f}_4 = h_1^4 + 4\bar{\gamma}h_1^3h_2 + 6\bar{\gamma}h_1^2h_2^2 + 4\bar{\gamma}h_1h_2^3 + \bar{\gamma}^2h_2^4$,

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

$f_4 = h_1^4 + 4\gamma h_1^3h_2 + 6\gamma h_1^2h_2^2 + 4\gamma h_1h_2^3 + \gamma^2h_2^4$,

$\gamma = E_2 / E_1$,

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

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 thermal correction factor should be introduced

$$\delta^T = 12\pi R_0^2 \frac{\bar{\gamma}(\alpha_2-\alpha_1)(T_0-T)(h_1+h_2)h_1h_2(1+\mu)(1-\mu k)}{\bar{f}_4(1-\mu^2 k)}, \quad (3)$$

where α_1, α_2 are the coefficients of the thermal expansion (CTE) of the substrate and coating, respectively (Table 1).

Table 1. Constants of the materials

Constant	Substrate		Coating
	Brass [5]	Copper [5]	Silver [6]
Modulus of elasticity E [10^5 N/mm^2]	1.14	1.10	0.76
CTE α [10^{-5}1/°C]	2.05	1.65	1.96
Density [gf/cm^3]	8.50	8.94	10.5

The presented method allows to determine the mean values of residual stresses in thin coatings, assuming that they are constant throughout coating thickness. It can be used when the slit increment depending on coating thickness is linear. To establish this, were a series of specimens coated with different coating thickness, and the slit increment depending on coating thickness was approximated by a linear relation.

It was observed that residual stresses decrease with time. An equation for approximation of the change of residual stresses calculated from the 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) [7]

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

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 the change of residual stress depending on time is reduced to finding of adequate constants. The constants should be determined so that the slit increment and the calculated residual stresses are approximated in the best way. This problem is solved by using the program *Mathcad2001i Professional* with the regression function *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

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

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 [8]. 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 $a_0 = 0$, $a_1 = 183.38$.

Dispersions and covariations of the values of parameters a_0 and a_1 can be calculated according to the formulas presented in [8]. Solution yields: $s^2(a_0) = 0.02$, $s^2(a_1) = 188.58$, $s^2(a_0a_1) = 1.781$, $s^2 = 0.047$.

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

$$u^2(\delta_i) = \frac{s^2}{\Delta}\left\{\left(\frac{\partial\delta_i}{\partial a_0}\right)^2 \Delta_{11} + \left(\frac{\partial\delta_i}{\partial a_1}\right)^2 \Delta_{22} + 2\frac{\partial\delta_i}{\partial a_0}\frac{\partial\delta_i}{\partial a_1}\Delta_{12}\right\}. \quad (6)$$

As all equations were composed using the mean results of the 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

$$w_c^2(\bar{\delta}) = \frac{u^2(b_2)}{b_2^2} + \frac{u^2(d)}{d^2} + \frac{u^2(g)}{g^2} , \quad (7)$$

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

$$w_c(\delta) = \sqrt{w^2(\delta_i) + w_c^2(\bar{\delta}_i)} , \quad (8)$$

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

Expanded uncertainty in case of 95 % degree of confidence is

$$U = 2 w_c(\delta) . \quad (9)$$

As a result expanded uncertainty of 16.3 % was obtained. 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

Strips with dimensions (11.9 × 96.0 × 0.19) mm and (11.9 × 96.0 × 0.09) mm used as the substrate were cut from a rolled brass (62 % – 65 % Cu [5]) and copper ribbon. Copper and brass strips are used to increase the 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 set-up (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.

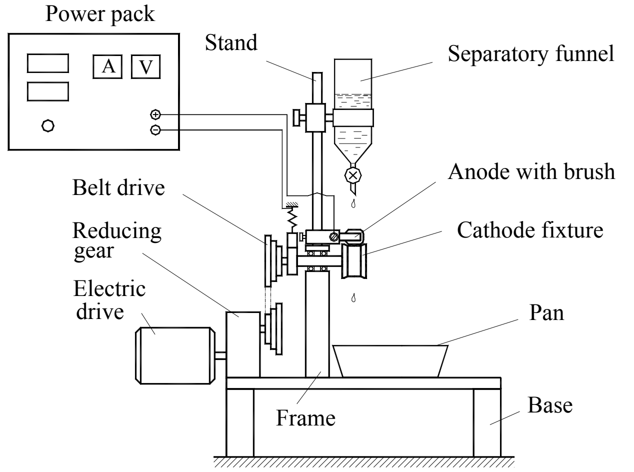

Fig. 1. Set-up for deposition of ring substrate

An anode made of special-grade heat-resistant graphite with a cotton batting was attached to the set-up and fed from a separatory funnel by drops (15 – 20 drops per minute) at ambient temperature. The ratio of anode surface to the surface to be coated was 1 : 8.

At the beginning of deposition the temperature of the substrate rose from room temperature to $\Delta T = 1\,°C – 12\,°C$ (depending on current density). The temperature of the substrate was measured immediately after deposition when the substrate was still on the cathode fixture. Deposition time was chosen considering desired coating thickness.

When electroplating was finished the substrate with the coating with a desired thickness was removed from the fixture and was rinsed, cleaned, dried and weighed after one hour. The final thickness of the substrate with the coating, the width of the deposited coating and the increment of the slit were measured. The coating thickness estimated from the plating of the current was corrected using a weight, by calculating average coating thickness from the difference in the weight of the specimen before and after deposition. As residual stresses decrease with time due to relaxation, the specimens were placed on a glass pane to allow them to deform freely. The slit increment of the substrate was measured after one day and three days and then with an interval of one week to three months and further with the longer intervals.

5. RESULTS

To determine the relation between the increment of the slit depending on coating thickness, a series of specimens were coated, altogether 34 specimens with coatings with a thickness of 2.3 µm to 18.5 µm. Deposition took place at the current density of 15 A/dm^2 and at the velocity of the cathode of 0.18 m/sec and was plated onto the area (width ~11.0 mm) of the rotating substrate. The experimental data of the slit increment depending on coating thickness are shown in Fig. 2.

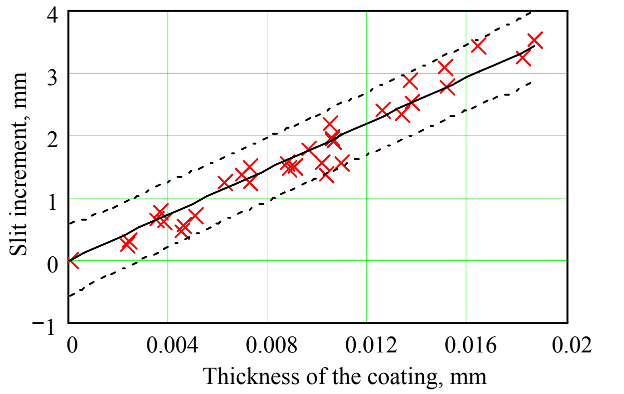

Fig. 2. Experimental values of the slit increment δ, depending on coating thickness h_2 and the line of approximation

The experimental data do not fluctuate to a great extent and remain in the zone with a sufficiently uniform width. The presented method allows to determine the mean values of residual stresses in thin coatings, assuming that they are constant throughout coating thickness. This was demonstrated by the satisfactory approximation of the dispersed experimental data using a linear relation. In order to improve accuracy, one must measure the real moduli of elasticity of plated silver and use the obtained values in estimation of residual stresses.

The mean values of residual stresses calculated from th experimental data (at a coating thickness of 10 µm), depending on time, are presented in Fig. 3. The results show that time affects residual stresses in coatings to a great extent.

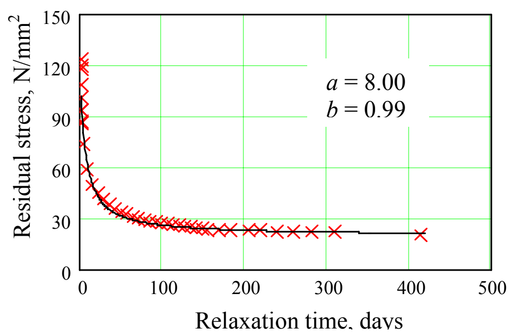

Fig. 3. Residual stresses depending on relaxation time and the curve of approximation

The maximum values of residual stresses were (116.9 ±19.1) N/mm^2 and (117.3 ±19.1) N/mm^2 at deposition temperature of ~24 °C. Calculation shows that higher deposition temperature causes temperature stresses whose role in residual stresses is not significant. The maximum values of residual stresses are reduced through the mechanism of relaxation. Depending on relaxation time, the remaining stress (21.0 N/mm^2 ±3.4 N/mm^2) is then approximately one quarter of maximum stress.

The effect of current density and velocity of the cathode 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

10 μm were deposited at different current densities on brass substrates at the velocity of the cathode 0.39 m/sec. Eight series of experiments were carried out and the obtained mean values of residual stresses are presented in Table 2 and in Fig. 4.

Table 2. Conditions of electrodeposition and results

Current density, A/cm^2	Voltage, V	$T - T_0$, °C	Residual stresses, N/mm^2	
			at measuring temperature	at deposition temperature
0.05	5.3	1	48.5 ±7.9	48.6 ±7.9
0.10	6.2	3	105.1 ±17.1	105.4 ±17.2
0.15	6.5	4	115.1 ±18.8	115.5 ±18.8
0.20	7.0	6	115.3 ±18.8	116.0 ±18.9
0.25	7.5	8	115.3 ±18.8	116.1 ±18.9
0.30	8.0	8	110.8 ±18.1	111.4 ±18.2
0.35	8.0	10	111.2 ±18.1	112.3 ±18.3
0.40	9.0	12	114.9 ±18.7	116.1 ±18.9

It is evident that an increase in current density causes higher residual stresses until the current density of 0.15 A/cm^2, and at higher current densities they are practically equal to about 115 N/mm^2.

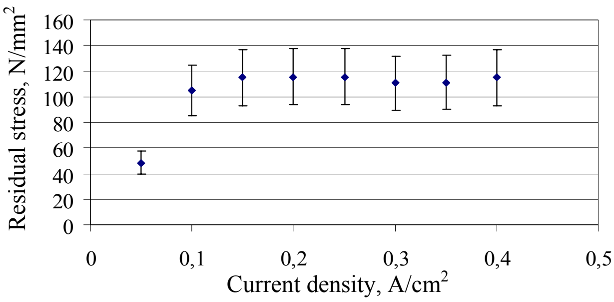

Fig. 4. Residual stresses depending on current density

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. On the other hand, the microstructure can be affected by residual stresses produced during the deposition process [1]. Further research is needed regarding the crystalline structure of coating materials which is formed during brush-plating.

Three series of brass substrates were deposited with a coatings thickness of 10 μm at the current density 0.15 A/cm^2 at different velocities of the cathode. The calculated mean values of residual stresses are practically equal and are presented in Table 3 and in Fig. 5.

Also two series of copper and brass substrate were deposited with a coating thickness of 5 μm at the current density 0.15 A/cm^2 and the velocity of the cathode 0.39 m/sec. The mean values of residual stresses in coatings of (48.7 ±7.9) N/mm^2 and (56.3 ±9.2) N/mm^2 were obtained on a copper and on a brass substrate, respectively. Residual stresses in coatings on the copper substrate were to some extent lower than on the brass substrate.

Table 3. Residual stresses depending on velocity of cathode

Velocity of the cathode, m/s	0.081	0.18	0.39
Residual stresses, N/mm^2	118.0±19.2 118.4±19.3	116.9±19.1 117.3±19.1	117.3±19.1 117.7±19.2

6. CONCLUSIONS

1. The slit increment of the substrate depending on coating thickness for the dimensions of the substrates and the coating thicknesses used is linear.

2. Measurement uncertainties for the method were evaluated and expanded uncertainty was about 16.3 %.

3. Residual stresses in coatings represent significant tensile stresses and their maximum mean values were (116.9 ±19.1) N/mm^2 at measuring temperature and (117.3 ±19.1) N/mm^2 at deposition temperature, respectively. Higher deposition temperatures caused temperature stresses whose role in residual stresses was not significant.

4. The values of residual stresses decreased markedly, and after six months they were (21.0 ±3.4) N/mm^2.

5. Residual stresses were significantly influenced by current density and they increased from (48.5 ±7.9) N/mm^2 to (115.1 ±18.8) N/mm^2 up to the current density 0.15 A/cm^2.

6. The values of residual stresses were not influenced by the velocities of the cathode used.

REFERENCES

1. **Rubinstein, M**. Electrochemical Metallizing. Van Norstrand Reinhold Company Inc., New York, 1987.
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: S. 116 – 121 (in Russian).
4. **Lille, H., Kõo, J., Ryabchikov, A.** Measurement of Residual Stresses in Different Electrochemical Metallized Coatings *Materials Science* (*Medžiagotyra*) 4 2002: pp. 417 – 420.
5. **Rakhshtad, A. G., Brostrem, V. A.** Handbook for Metal-worker. Handbook in Five Volumes. Second Volume. Mashinostroyenie, Moscow, 1976 (in Russian).
6. Material Property Data. http://www.matweb.com/search/DataSheet.aspx?MatID=7&ckck=1.
7. **Virchenko, I. A., Lyashko, I. I., Shvetsov, K. I.** Handbook: Graphs of the Functions. Naukova dumka, Kyev, 1979 (in Russian).
8. **Laaneots, R., Mathiesen, O.** Fundamental of Measurement. Tallinna Raamatutrükikoda, Tallinn, 2002 (in Estonian).