COMPARISON OF VALUES OF RESIDUAL STRESSES DETERMINED BY VARIOUS METHODS IN HARD NICKEL COATINGS PREPARED BY BRUSH-PLATING IN SULFATE SOLUTION

Lille, H.; Ryabchikov, A.; Kõo, J.; Reitsnik, R.; Veinthal, R.; Mikli, V. & Sergejev, F.

Abstract: Hard nickel coatings were deposited from a sulfate solution onto brass substrates (strips, unclosed rings). The equations used for calculating of residual stresses are based on the conventional curvature method. For comparison, residual stresses were determined by the semi-destructive hole-drilling method and by the X-ray technique. The values of residual stresses determined by mechanical methods and by the X-ray technique were comparable. The surface morphology and microstructure of the coatings was studied by means of scanning electron microscopy (SEM). The values of the modulus of elasticity and micro- and nanohardness of the coatings were obtained.

Keywords: brush-plating, nickel coating, residual stresses, curvature method, hole-drilling, X-ray technique, morphology, microstructure, hardness.

1. INTRODUCTION

Brush-plated hard nickel coatings investigated in the present study are generally used in repair and maintenance [1,2,3,4]. One of the difficulties related to brush-plating is the problem of layer delaminating due to the unfavourable residual stress state. To determinate residual stresses, a conventional curvature method was used, where a coating is deposited on a strip or unclosed ring strip substrate with slipping ends or edges, which deforms without bending during deposition. The change of the axial deformation of the free surface of strip substrate during the manually coating depositing process was measured by a self-temperature compensated strain gauge. The slit increment of the unclosed ring substrate was measured at certain coating thicknesses. The dependence of the deformation parameter on coating thickness was used as experimental information. The experimental results were previously approximated by an analytical expression assuming that the dependence of residual stress on coating thickness is linear-fractional [5].

Residual stresses of the coating on strip substrate were determined by the hole-drilling method. The hole-drilling technique, known as a semi-destructive method, is the most common method for measuring residual stresses and it can be used directly for coated machine parts. This method requires drilling a small hole, typically 1-4 mm in diameter, to a depth approximately equal to its diameter. Residual stresses were also measured by the X-ray technique. Calculation was done according to well-known Bragg’s formula. The values of the modulus of elasticity and micro- and nanohardness of the coatings were obtained by instrumented indentation. The morphology and microstructure of the studied coatings were investigated.
2. EVALUATION OF RESIDUAL STRESSES

Residual stresses in one and the same layer are expressed, according to the general algorithm of layer growing/removing method, as the sum of the initial and the additional stresses \[^6\]. Stresses in the superficial layer are named initial stresses. Additional stresses are understood as the stresses which arise in this layer when subsequent layers are applied. The coated substrate (part) is usually so rigid that residual stresses are practically equal to the initial stresses. The equation used in calculations is based on the Brenner and Senderoff's concept \[^5\], where the substrate is examined as the beam with slipping ends (momentless condition), the equation for the ring substrate is modified to account for biaxial stresses and the shell shape of the substrate which is taken into consideration by an appropriate coefficient \[^5, 8\].

\[\sigma(h) = \frac{-E'_i(h_1 + vh)}{E_1(1-\mu_1)}, \quad \text{where } E'_i = E_i/(1-\mu_i), \quad E_2 = E_2/(1-\mu_2), \quad E_1, E_2 \text{ are the moduli of elasticity, } \mu_1, \mu_2 \text{ are Poisson's ratios for the substrate and the coating, respectively (in this study } \mu_1 = \mu_2 = \mu), \quad R_0 \text{ is the middle radius of the substrate, the coefficient } F = \frac{1-\mu^'k}{\left(1-\mu^'k\right)} \times \frac{2}{\mu^'k} \times \frac{\cos\theta - \cos\beta^*}{\sinh\beta^* - \sin\beta^*}, \quad \text{the ratio } k \text{ depends on } \beta = \sqrt{\frac{3(1-\mu^2)}{R_0^2} \times \frac{f_1}{f_2}}, \quad b \text{ is the width of the substrate}, \quad f_1 = h_1 + vh_2, \quad f_2 = h_2^2 + 2h_1h_2 + vh_2^2, \quad f_3 = h_1^4 + 4vh_1h_2^3 + 6v^2h_2^4 + 4vh_1h_2^3 + v^2h_2^4, \]

As the derivative of the deformation parameter (its values fluctuating to a great extent) in the calculation equations is presented in accordance with coating thickness, residual stresses were calculated assuming that the dependence of residual stress on coating thickness is linear-fractional \[^5\]

\[\sigma(h) = \frac{h_2 + h}{h_1 + vh}, \quad (3)\]

where \(\sigma_0\) is the initial value of residual stress, \(h_2\) is the final coating thickness, \(c\) is the dimensionless parameter.

Taking into account relation (3), the following equation is obtained from expressions (1) and (2) for approximation of the measured deformation and slit increment

\[\varepsilon(h) = \frac{\sigma_0}{E_1'} \int \frac{h_2 + h}{(h_1 + vh)}dh, \quad (4)\]

\[\delta(h) = \frac{24\pi R_0^2 \sigma_0}{E_1'} f_1 \int \frac{h_1 + h}{(h_1 + vh)}\left[\varepsilon(h) + h\right]dh. \quad (5)\]

where \(\varepsilon = (h_2^2 - vh^2)/2f_1\) is the distance of reduction surface from the interface between the coating and the substrate.

The purpose was to find the unknown constants, i.e. the initial value of the initial stress \(\sigma_0\) and the dimensionless parameter \(c\), so that measured deformation \(\varepsilon(h)\) and slit increment \(\delta(h)\) can be approximated in the best way. This problem was solved by using the regression function genfit (\(v_x, v_y, v_g, F\)) of the mathematical program Mathcad 14.0 \[^9\].

Assuming that residual (initial) stresses \(\sigma\) are distributed uniformly throughout the coating thickness, residual stresses in the coating are expressed by the following equations \[^8\]

\[\sigma = -E'_i(h_1 + vh)\Delta \varepsilon/h_2 \quad (6)\]

\[\sigma = \frac{E_1 F}{12\pi R_0^2} f_4 \Delta \delta \frac{h_1h_2}{h_1 + h_2} \quad (7)\]
where \(\Delta\varepsilon, \Delta\delta\) are the mean values of the measured deformation and slit increment.

As the experimental data for the strip substrate were obtained at elevated deposition temperature, then for comparison of residual stresses to those obtained by the hole-drilling and the X-ray techniques, thermal correction should be introduced by the following equation \([6]\)

\[
\sigma_2^T(h) = E_2\varepsilon h_1 \Delta T \frac{\alpha_1 - \alpha_2}{h_1 + \nu h_2},
\]

where \(\alpha_1\) and \(\alpha_2\) are the coefficients of the linear expansion of the substrate and the coating, respectively, and \(\Delta T\) is the difference between room temperature and deposition temperature.

Residual stresses were measured by X-ray technique at the Moscow Institute for Roentgen Optics \([10,11]\). The deformation of the crystal lattice \(\varepsilon = (d - d_0)/d_0\) causes a displacement of the center of gravity of the diffraction peak which can be expressed by the following equation

\[
\varepsilon = -\Delta\theta \cot \theta_c,
\]

where \(\Delta\theta = \theta_c - \theta_{0c}\).

The sum of the principal stresses \((\sigma_1 + \sigma_2)\) is determined according to Hooke’s law by the following formula

\[
\sigma_1 + \sigma_2 = -E_2\varepsilon/\mu = (E_2/\mu_2)(\theta_c - \theta_{0c})\cot \theta_c.
\]

For the determination of the stresses \(\sigma_\phi\) in the desired direction \(x\), the \(\sin^2\psi\) method was applied. According to this method, measurements are made at 3 – 6 tilts of \(\psi\). Further, the coordinate of the center of gravity of the diffraction peak \(\theta_i\) is determined for every \(\psi\) tilt. Using the least-square method the linear dependence of \(\varepsilon\) on \(\sin^2\psi\) is obtained by the following formula

\[
\varepsilon = b_0 + b_1 \sin^2\psi,
\]

where \(b_0\) and \(b_1\) are the regression parameters. The stresses \(\sigma_\phi\) were calculated from the slope of this line as

\[
\sigma_\phi = b_1 E_2/(1 + \mu).
\]

Residual stresses in the nickel coating deposited onto a strip substrate were determined by the hole-drilling method whereby residual stresses were calculated from the measured relieved strains using the specialized computer program \(H\)-DRILL \([12]\). As coating thickness was relatively small for integral approach, it was assumed that residual stresses were distributed uniformly throughout coating thickness.

Reduced modulus of elasticity was calculated by equation \([13]\)

\[
E_{\text{red}} = \frac{1}{E_1 + \frac{h_1}{E_2}}.
\]

### 3. EXPERIMENTAL PROCEDURE

Strips and rings were cut from a rolled brass ribbon \((E_1=112\ GPa,\ \mu_1=0.34,\ \alpha_1=2.05\times10^{-5},\ 62–65%\ Cu\ \)\([13]\)). The dimensions of the strips were \((22\times70\times0.95)\ mm\) with a coated length of 51 mm and the dimensions of the rings were \((11.4\times96.0\times0.94)\ mm\) with a middle radius of \(R_0=15.12\ mm\). The substrate was prepared for the deposition process and the coated surface of the substrate was polished to roughness \(R_a=0.062\ \mu\m\).

A pure nickel coating with the elastic coefficients \(E_2=163\ GPa\) (determined in the coatings on the strip substrate by four-point bending) and \(\mu_2=0.31,\ \alpha_2=1.33\times10^{-5}\ \)\([14]\) was deposited from the electrolyte with the following composition: \(\text{NiSO}_4\times7\text{H}_2\text{O},\ 350\ \text{g/litre};\ \text{HCOOH},\ 60\ \text{g/litre};\ \text{MgSO}_4\times7\text{H}_2\text{O},\ 10\ \text{g/litre};\ \)gravity \(1.19\pm0.01\ \text{g/cm}^3,\ \text{pH}=1.57\text{-}1.63\) (determined at \(20^\circ\C\)).

The experimental measuring system presented in \([6,14]\) was used for deposition of the coating. It allows continuous measurement and recording of deformations and temperature during the coating process. The stylus was swabbed over the area where the coating was to be deposited.

For coating the outer surface, the ring substrate was 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 a certain coating thickness was...
released from the mandrel, and the slit increment of the substrate was measured. The plating technology is described in details by Lille et al.\cite{5}.

Residual stresses in the nickel coating on the strip substrate were determined by the hole-drilling method. The procedure for determination of residual stresses is described in the standard ASTM 837-08\cite{15}. Surface preparation for strain gauge rosette bonding was carried out according to the instruction bulletin B-129\cite{16}. As the thin substrate was deformed before hole-drilling, it was then cast into a mortar cradle to avoid additional deformations caused by the drilling process (Fig. 1).

![Fig. 1. Mortar cradle for fixing and positioning of the strip substrate, and bonded strain gauge rosette.](image)

The precision high-speed milling guide Vishay model RS-200\cite{17}, powered by air compression of 3.0 bar, was accurately centred with an alignment set-up over the drilling target on the rosette and a hole with a diameter of 1.75 mm was drilled through the geometric centre of the rosette (Fig. 2).

![Fig. 2. Installed strain gauge rosette and the drilled hole.](image)

The blind hole was only drilled through the studied coating. Strain gauge rosettes of type EA-06-062RE-120 were bonded onto the middle region of each specimen with the glue Z70, wired and connected to the Vishay Strain Indicator and Recorder Model P3.

As the coating thickness of the brush-plated Ni coating was too small for application of the integral method, a hole was drilled with one step equal to the coating thickness of 40 μm. Hard metal end mills coated with a highly wear resistant PVD coating (AlCrNi) were used for drilling a hole and the orbiting of the end mill was applied.

The residual stresses were measured by the X-ray technique on specimens with different final thicknesses of the coating. The specimen prepared for measurement of residual stresses by the X-ray technique is shown in Fig. 3.

![Fig. 3. Strip substrate fixture and the irradiating zone for applying the X-ray technique.](image)

The experiments were carried out with the portative diffractometer DRP-3\cite{11}, based on the \(\sin^2\psi\) method\cite{10}. The residual stresses were determined in the axial and transversal directions using FeKα radiation in the \{311\} reflection of the coating in the middle region, when the coated substrate was placed onto the equipment for deposition.
Young’s modulus and Poisson’s ratio for electrolytic nickel were 179 GPa and \( \mu = 0.3 \), respectively (determined by the nanoindentation method; the lower value was used in calculations, as there were cracks in the coating).

The morphology and microstructure of the studied coatings were investigated by means of scanning electron microscopy (SEM) in \textit{Zeiss EVO MA-15}.

The values of the modulus of elasticity and micro- and nanohardness of the coatings were obtained by instrumented indentation using the \textit{MTS Nano Indenter XR} \cite{MTS} and the \textit{Micromaterials Nano Test system} pendulum-type nanohardness tester.

\section*{4. RESULTS AND DISCUSSION}

The stylus, equipped with a graphite anode wrapped in the absorbent, was swabbed over the area where the coating was to be deposited at a current density of 64 A/dm\(^2\).

According to the deformation readings, coating thickness was divided into 91 equal parts. Thus we had 91 pairs of readings per single experiment. Since all experiments were carried out under similar conditions, the data of the three experiments, 273 readings each, were pooled. Using the computer program \textit{MS Excel} and the calibration results, the experimental data were converted to the axial deformation of the substrate \( \varepsilon \) depending on coating thickness \( h \) (Fig. 4, a).

As is evident, the measured values fluctuate to a great extent. One reason for this phenomenon may be temperature fluctuation during the depositing process. A series of ring substrates (20 specimens) were coated with coatings of different thicknesses, at a cathode velocity of 0.39 m/sec and a current density of 100 A/dm\(^2\). The electrolytic nickel anodes were wrapped in the absorbent recommended by SIFCO Company. The experimental data obtained on the ring substrate fluctuated somewhat less (Fig. 4, b), as the coating is deposited by uniformly rotating speed and the brush is fed continuously by drops of electrolyte from a bottle, which guarantee a relatively homogeneous temperature of the cathode.

The results of approximation by the equations (4) and (5) for strip and for unclosed ring are shown in Fig. 4.

The coated machine parts are usually so rigid that residual stresses in the coatings are practically equal to the initial stresses and in our experiments they were 817 N/mm\(^2\) and 623 N/mm\(^2\) in the elaborated electrolyte nickel coatings.

It is essential to mention that the labor consuming indirect curvature method was applied to determine the initial stresses, which is also suitable to obtain the mean values of residual stresses. It is possible to determine the residual stresses in the coatings on machine parts directly by hole-drilling or by X-ray technique, but the equipment are much more expensive.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Experimental values (a) of the axial deformation \( \varepsilon \) and (b) of slit increment \( \delta \) on the coating thickness \( h \) and the curve of approximation.}
\end{figure}
Dependence of residual stresses on the coating thickness calculated by equation (3) is presented in Fig. 5.

![Graph showing the dependence of residual stresses \( \sigma \) on coating thickness \( h \).](image)

Fig. 5. Dependence of residual stresses \( \sigma \) in the coating of the strips at room temperature (solid line) and in the coating of the unclosed rings (dotted line) on thickness \( h \); \( o \) - stresses were measured in the axial direction of the strip by the X-ray technique.

With the aim of studying the influence of the current density and the cathode velocity on residual stresses, three series (5 specimens in each series) were coated with the same coating thickness of 15 \( \mu \)m at the same cathode velocity of 0.31 m/sec and at different current densities. The mean value of residual stresses was calculated by equation (7).

Residual stresses through coating thickness in the coating on the ring substrate do not change much and remain in the limit of experimental uncertainty, hence using the equation (7) is proper in spite of the relatively thick coating. The results can then be compared to the mean values of residual stresses determined by the hole-drilling method. The values of residual stresses determined by different techniques are summarized in Table 1.

<table>
<thead>
<tr>
<th>Average current density, A/dm(^2)</th>
<th>65</th>
<th>70</th>
<th>100</th>
<th>100</th>
<th>130</th>
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</thead>
<tbody>
<tr>
<td>Average working voltage, V</td>
<td>18.0</td>
<td>9.5</td>
<td>11.5</td>
<td>12.0</td>
<td>17.0</td>
</tr>
<tr>
<td>Velocity of the cathode, m/s</td>
<td>manually</td>
<td>0.31</td>
<td>0.39</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td>Deposition temperature, °C</td>
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<td>95</td>
<td>95</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>Coating thickness, mm(\times)10(^{-3})</td>
<td>40</td>
<td>15</td>
<td>14</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Mean residual stresses, ( \sigma ), N/mm(^2)</td>
<td>curvature method</td>
<td>616</td>
<td>756</td>
<td>615</td>
<td>621</td>
</tr>
<tr>
<td></td>
<td>hole-drilling technique</td>
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<td>551±66</td>
<td>551±66</td>
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</tr>
<tr>
<td></td>
<td>X-ray technique</td>
<td>543±295</td>
<td>543±295</td>
<td>543±295</td>
<td>543±295</td>
</tr>
</tbody>
</table>

Table 1. Conditions of electrodeposition and mean values of residual stresses.

The mean values of residual stresses obtained for coatings deposited with two technologies on strip and ring substrates are in the same order within the limit of experimental uncertainty.

It is evident that the values of residual stresses are not directly affected by current density and do not practically depend on cathode velocity.

Residual stresses determined by the hole-drilling technique were somewhat higher than those obtained by curvature method. The reason might be the generation of additional stresses during the drilling process.

Residual stresses determined by the X-ray technique were somewhat lower than those obtained by curvature method, however uncertainties of measurements of stresses constituted half of the mean value.

Coatings structure and morphology is presented in Fig. 6.
Fig. 6. SEM images at the surface and cross-section of samples: (a) and (b) ring substrate; (c) and (d) strip substrate.

Both coatings are thick and built up on 100-300 nm size Ni nanoparticles. Ni coating on the strip substrate was 100 µm and on the ring substrate 30 µm. Due to the high residual stresses Ni coating has vertical cracks in the ring form substrate coating (Fig. 6, a).

Residual stresses in brush plated nickel coatings are usually up to three times as high as the residual stresses in nickel coatings deposited from a similar bath solution \[^{18}\]. It is well known that high values of tensile residual stresses and several cracks in nickel cause a significant reduction in the fatigue strength of the restored machine parts \[^{19}\].

The microhardness obtained for the nickel coatings was 341±16.5 HV\(_{0.025}\) and 395±15.1 HV\(_{0.050}\), respectively in literature (520-580 HV \[^{2}\]); nanohardness (load 50mN) was 5.400±0.342 GPa, and the modulus of elasticity was \(E = 197±18\) GPa. In calculations of residual stresses by the X-ray technique the lower value of the modulus of elasticity was used. The microhardness strongly depends on the grain size, while the value of the modulus of elasticity is affected by the grain size to a small degree \[^{20}\].

5. CONCLUSIONS

The values of residual stresses in the coatings manually deposited on the strip substrate and automatically on the ring substrate determined by the curvature methods were comparable.

Residual stresses determined by the hole-drilling method and by the X-ray technique were in the same range and somewhat lower than those obtained by the curvature method, however comparable within the maximum limit of experimental uncertainty.

As the microstructure of the coatings was fine-grained (Ni nanoparticles), the values of residual stresses were high, which resulted in a number of cracks in places in the coatings, which reduce the lifetime of coated machine parts.

6. ACKNOWLEDGEMENT

This work was supported by the Estonian Ministry of Education and Research (targeted finance project No SF01400091) and the Estonian Science Foundation grant No. 8459.

The electrolyte was elaborated by PhD M. Pille from the Estonian University of Life Sciences.

The residual stresses by the X-ray technique were determined by Dr D. Matveev from the Institute for Roentgen Optics (Moscow).

7. REFERENCES


**ADDITIONAL DATA ABOUT AUTHOR**

Harri Lille, Assoc. Professor, Cand Sc (Phys-Math), Estonian University of Life Sciences, Institute of Forestry and Rural Engineering, Kreutzwaldi 5, Tartu 51014, Estonia, E-mail: harri.lille@emu.ee, Phone: +372 7313181, Fax: +372 7313156.