The properties of chromium electrodeposited with programmed currents. Part I. Direct current

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The electrodeposition of chromium in programmed direct current (DC) was investigated in the regime of high current density (77 A dm⁻²). Chromium was deposited in a system of plane-parallel electrodes in chromic-sulphuric acid solution, on specimens of steel, during one hour. The basic properties of deposits, the appearance, thickness, morphology, microhardness and brightness were investigated. Thicknesses of the coatings (between 28 and 82 μm) were measured at 36 points on the surface of the specimens by the non-destructive ferromagnetic method. Based on these results, graphic models of the surface distribution of the deposits were made. Three ranges of thickness could be seen on the model (range 1 – average thickness 29.87 μm, range 2 – average thickness 42.0 μm and range 3 – thickness 67.87 μm). For the whole specimens, the average thickness was 50.8 μm with a coefficient of variation of 0.3281. The basic properties of the coating, morphology and brightness changed depending on the deposit thickness being very different at different points of one and the same specimen. For this reason these chromium deposits should not be considered reliable protection against aggressive gases at high pressures and temperature of systems from corrosion, wear and erosion.

Keywords: electrodeposition of chromium, programmed direct current, properties of the deposits, thickness, morphology, microhardness, brightness, distribution of the deposits on the surface, modelling.

Programmed electrodeposition is process controlled and led by a computer. The computer controls the electrodeposition by regulation of basic input parameters within limited values. The basic program has three sequence. The first is pretreatment of the surface, the second is electrodeposition and the third is the final treatment. The input parameters are: solution temperature, cathodic and anodic current, time of treatment, free-time between operation, concentration and volume of solution, etc.¹,²

The properties of chromium deposits are primarily determined by the current density and solution temperature. By variation of these two parameters matt-gray, bright or milk deposit can be achieved.³,⁴ Together with chromium, hydrogen
develops on the cathode. This makes the current efficiency lower (between 10 and 15 % for chromic–sulphuric acid solution).\(^5,6\) The deposition rate increases with increasing current density, which results in an increase of the current efficiency and, consequently, a change of the properties and throwing power of the deposits.\(^7,8\)

The purpose of this work was the examination of programmed electrodeposition of chromium with DC. Special regard was given to the surface distribution of the deposits and its effect on others properties of the coating. The results obtained in the present study will be of reference value for the results obtained in reversing current regime.

**EXPERIMENTAL**

The specimens used in the experiments were in the form of plates (dimensions: \(0.5 \times 0.8 \times 0.025\) \(\text{dm}\)). The specimens were placed vertically in the bath and point 42.5 was on the bottom of the bath. Chromium was deposited on the working area of 0.18 \(\text{dm}^2\) (0.4 - 0.45 \(\text{dm}^2\)). The steel specimens contained 0.28 % C, 0.10 % Si, 0.40 % Mn, 3.1 % Cr, 1.1 % Ni, 0.1 % V and 0.45 % Mo.

All specimens were mechanically polished. Specimens on which the morphology was observed were electropolished in a phosphoric–sulphuric–chromic acid solution (60 \(\text{g dm}^{-3}\) \(\text{H}_3\text{PO}_4\), 50 \(\text{g dm}^{-3}\) \(\text{H}_2\text{SO}_4\), 50 \(\text{g dm}^{-3}\) \(\text{CrO}_3\)).

The basic surface treatment prior to plating was an acetone degrease. The part of the surface on which it was not intended to deposit chromium was protected by vinylplast. The specimens were electrolytically cleaned in an alkaline solution (30 \(\text{g dm}^{-3}\) \(\text{NaOH}\), 35 \(\text{g dm}^{-3}\) \(\text{Na}_3\text{PO}_4\), 30 \(\text{g dm}^{-3}\) \(\text{Na}_2\text{CO}_3\)) for 2 min, at a current density of 20 \(\text{A dm}^{-2}\) at a temperature of 65 °C. The specimens were then etched from 30 to 60 s in a 20 % \(\text{H}_2\text{SO}_4\) solution. Between these operations the surface of the specimens was rinsed in running cold water.

The programmed computer-controlled process consisted of the regulation of the anodic etching and of the chromium electrodeposition. The basic input parameters are given in Table 1. A personnel computer and additional equipment maintained the basic input parameters within the limited values.

**TABLE 1. Basic input parameters in the chromium plating bath in the DC regime**

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameters of electrolysis</th>
<th>Sequence I</th>
<th>Sequence II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Anodic etching of the substrate</td>
<td>Chromium deposition</td>
</tr>
<tr>
<td>1</td>
<td>Anodic current density/ (\text{A dm}^{-2})</td>
<td>55</td>
<td>77</td>
</tr>
<tr>
<td>2</td>
<td>Cathodic current density/ (\text{A dm}^{-2})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Anodic time/ s</td>
<td>45</td>
<td>3600</td>
</tr>
<tr>
<td>4</td>
<td>Cathodic time/ s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Temperature/°C</td>
<td>50 – 1</td>
<td>50 – 1</td>
</tr>
</tbody>
</table>

The programmed anodic etching and the chromium electrodeposition were performed in chromic–sulphuric acid solution (250 \(\text{g dm}^{-3}\) \(\text{CrO}_3\), 2.5 \(\text{g dm}^{-3}\) \(\text{H}_2\text{SO}_4\)). Insoluble anodes were used, the lead alloy contained 10 % tin. The anode and cathode were situated 5 cm apart.

After deposition the specimens were rinsed in running cold and hot water, and then dried in a hot air current.

The thickness of the deposit was measured by a magnetic method (Deminiton 3000). The thickness of the deposit was measured at 36 points on the surface of specimens, as is shown in Fig. 1a. The method of measurement with 6 rows and 6 columns was used.
Fig 1. Graphic model of the positions for measurement on the specimens: a – for thickness; b – for reflection; c – for microhardness.

The reflection of the deposit was measured by a spectrophotometer (Beckman UV 5240). Three different locations on the surface of the specimens were chosen for the reflection measurements (Fig. 1b). The circular measurement area had a diameter of 2.5 cm. The hardness of each specimen was determined by an average of nine measurements. The selection was made with a net (Fig. 1c). A Vickers tester with a load of 100 g (Durtment) was used for the hardness measurements. Surface morphology was examined by optical microscopy (Metaplan Leitz).

RESULTS AND DISCUSSION

The chromium coatings deposited in the programmed DC regime with 77 A dm⁻² at a solution temperature 50 °C were bright, with a pronounced edge effect. Visible rough and burnt deposits were visible on the surface at the edges, especially on the lower edge and on the corners.

The distribution of the thickness of the deposits is presented in Fig. 2. A pronounced edge effect can be seen in the latitude profile. The last row (longitude 42.5 mm) has a deformed profile and the highest values of the deposit thickness.
The longitude profiles are presented in columns in Fig. 3 and as can be seen they are non-uniform. The columns at latitudes 2.5 mm and 37.5 mm, along the side edges have thicknesses from 60 to 80 mm. The middle columns at latitudes 16.5 mm and 23.5 mm have thicknesses from 28 to 70 mm. The largest values of the thickness were measured on the lower edge (the last value in the columns). The ratio between the minimum thickness and the maximum thickness in the middle columns is 2.4. Statistical analysis of the measured deposits thickness was made. The analysis included determination of the interval of variation ($I$), the average thickness ($\overline{\delta}$), the standard deviation ($\sigma\delta$) and the coefficient variation ($cv$). According to this, the latitude profiles are non-uniform. The average thickness of the points belonging to
row with longitude 2.5 mm was $\bar{d} = 45.33$ mm and the corresponding value for the row with longitude 42.5 mm was $\bar{d} = 72.33$ mm.

The biggest interval of variation ($I$) existed between the points belonging to the row with longitude 2.5 mm and the row with longitude 42.5 mm:

$$I = d_{\text{max}} - d_{\text{min}} = 82 - 28 = 54 \text{ mm} \quad (1)$$

On the basis of the results from Fig. 2, Fig. 4 can be derived, assuming a linear change of the thickness of the deposit between two neighbours points.

![Diagram](image)

**Fig. 4.** Graphic model of the surface deposit distribution (electrodepositions in the DC regime with 77 A dm$^{-2}$ at a solution temperature 50 °C). Range 1 – thickness from 20 to 30 mm; range 2 – thickness from 30 to 50 mm; range 3 – thickness from 50 to 70 mm.

The specimens latitude is presented on the abscissa and the specimens longitude is presented on the ordinate. The distribution of the deposit on the surface was determined in three ranges of thicknesses. The first range is limited by a line marking 30, which means that this line connects the points on the surface with thickness 30 mm. The first range contained thicknesses from 20 to 30 mm. The second range is limited by lines marking 30 and 50. The third range is limited by lines marking 50 and 70. The thickness on the corners was over 70 mm.

Statistical analysis of measured thicknesses is given in Table II. Range 1 with the smallest $\bar{d} = 29.87$ mm was uniform with fine grains.

Range 2 has middle thickness $\bar{d} = 42$ mm, larger grains and excessive cracks. Range 3 is the edge and the deposits were rough and burnt.

Investigation of the morphology was performed by optical microscopy. The finest structure with small grains and few cracks was observed in the first range (Fig. 5a). Bigger grain with larger cracks was observed in the second range (Fig.
5b). The morphology of the edges of the specimens is presented in Fig. 5c, from which it can be seen that the deposits in range 3 are rough and burnt. Especially burnt deposits could be seen on the lower corners (Fig. 5d).

**TABLE II. Results of the statistical analysis of the measured thickness**

<table>
<thead>
<tr>
<th></th>
<th>Average thickness/ mm</th>
<th>Standard deviation of the thickness/ mm</th>
<th>Coefficient of variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range 1</td>
<td>29.87</td>
<td>1.55</td>
<td>0.0518</td>
</tr>
<tr>
<td>Range 2</td>
<td>42</td>
<td>4.32</td>
<td>0.1031</td>
</tr>
<tr>
<td>Range 3</td>
<td>67.87</td>
<td>5.26</td>
<td>0.0776</td>
</tr>
<tr>
<td>Whole surface of the specimens</td>
<td>50.80</td>
<td>16.68</td>
<td>0.3281</td>
</tr>
</tbody>
</table>

Fig. 5. Morphology of the deposits in different ranges of thickness (electrodeposition in the DC regime with 77 A dm⁻² at a solution temperature 50 °C). Magnification 640 ×. a) Range 1 – thickness from 20 to 30 mm; b) range 2 – thickness from 30 to 50 mm; c) range 3 – thickness from 50 to 70 mm; d) corner – thickness 82 mm.

Reflection from the surface of the deposits was measured at three location on the specimens (Fig. 1b). The total and diffuse reflection was measured and their difference is the mirror reflection. The mirror reflection is an indicator of the surface brightness. A reflective spectrophotometer in the visible wavelength range (from 400 to 700 nm) was used for the measurements. Nine curves are presented in Fig. 6. The
top three curves show the total reflection at all three location on the specimens. The three curves in the middle represent the diffuse reflection and the last three curves the mirror reflection at all three location on the specimens. As can be seen from Fig. 6, there is a difference in the reflection at different points of the specimen due to the differences in the surface morphology. Obviously, these results are only qualitative, because there are different morphologies in each region under consideration.

![Graph showing reflection of chromium deposits dependence on wavelength](image)

**Fig. 6.** Reflection of chromium deposits dependence on wavelength in the visible range (electrodepositions in the DC regime with 77 A dm⁻² at a solution temperature 50 °C) D-a, D-b, D-c diffuse reflection at locations A, B and C; T-a, T-b, T-c total reflection at locations, A, B and C; R-a, R-b, R-c – mirror reflection at locations A, B, and C (Fig. 1b).

The results of the microhardness measurements are presented in Table III. The measurements were performed at nine selected points on the surface. It seems that the microhardness at the different points depends on the deposit thickness, being higher with increasing thickness.

<table>
<thead>
<tr>
<th>Microhardness HV₀₁</th>
<th>I column</th>
<th>II column</th>
<th>III column</th>
<th>Average HV₀₁±sd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 row</td>
<td>946</td>
<td>920</td>
<td>933</td>
<td></td>
</tr>
<tr>
<td>2 row</td>
<td>950</td>
<td>946</td>
<td>988</td>
<td></td>
</tr>
<tr>
<td>3 row</td>
<td>946</td>
<td>1003</td>
<td>967</td>
<td>955 – 26</td>
</tr>
</tbody>
</table>

For the whole specimens d = 50.8 nm with a cv = 0.3281. This makes the deposit non-uniform in the distribution of the thickness. Because of the important
variations in the thickness, the morphology and the reflection of the deposits in all three ranges, this kind of protection cannot be taken as reliable under aggressive atmosphere conditions. Also, range 3, with burnt and fragile deposits, is unreliable in systems with high dynamic pressure and precise dimensions. The results of the microhardness measurements (Table III) showed that the hardness is high $HV_{0.1} = 955 - 26$ and stable. According to the literature, bright chromium coatings deposited at temperatures between 50 to 56°C with thickness variations form 30 to 70 μm have stable microhardnesses.

On the basis of these results and the literature, programmes for deposition with reversing current will be proposed. The purpose of these programmes will be obtaining deposits with fine grain, cracks-free structures, free and with a more uniform thickness distribution of the deposits on the surface.

CONCLUSION

Chromium deposited with a programmed DC regime in the range of high current density (77 A dm$^{-2}$) at a temperature of 50°C was bright with a pronounced edge effect.

Graphic models based on the measurement of the thickness of the deposits showed three different ranges of thickness with specific corners (range 1 – average thickness 29.87 μm, range 2 – average thickness 42 μm and range 3 – thickness 67.87 μm).

The morphology and structure was different in the different ranges of the specimen, from fine in range 1 to rough and burnt in range 3. The reflection was different in the different ranges, and decreased from the middle to the edge of the specimens (total reflection from 59.92 % to 56.93 %, mirror reflection from 28.96 to 19.8 %). The microhardness is stable over the whole specimens and has a value of $HV_{0.1} = 955 - 26$.

Statistical analysis was performed to define the coefficient of variation for the whole specimens, 0.3281. The latitude profiles of the thickness of the deposits are non-uniform, and the longitude profiles, presented as columns, are also non-uniform. It was shown that the distribution of the deposit is non-uniform.

ИЗВОД

СВОЈСТВА ЕЛЕКТРОХЕМИЈСКИ ИСТАЛОЖЕНОГ ХРОМА ПРОГРАМИРАНИМ СТРУЈАМА ДЕО ЈЕДНОСМЕРНА СТРУЈА

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Електролитичко таложење хрома у програмираном режиму једносмерне струје испитивано је у области високих густини струје (77 А dm$^{-2}$). Хром је таложен из хром-натрио-сулфатног електролита на узорке од челика, у току једног часа. Електроне су
постављене у систем план-паралелних плоча. Испитивана су основна својства превлачака хрома: изглед, дебљина, морфологија, микротврдина и рефлексија. Дебљина превлачаке (од 28 до 82nm) мерена је на површини узорка на 36 места. Коришћена је иерархија феро-магнетних метода. На основу резултата мерене урађени су графички модели расподеле талога по површини узорка. На моделима су обаче три области дебљина превлачаке (област 1 – средња дебљина 29,87nm, област 2 – средња дебљина 42nm, област 3 – средња дебљина 67,87nm). Испитивањем основних својстава превлачаке (морфологије и рефлексије) утврђено је да се менају по површини превлачаке у зависности од дебљине превлачаке хрома. У средини узорка област 1 структура је замиски (сигнум зрио са танким пресутинама), потом се зрио укрупњава и појављују се веће пресутине област 2, да би на крају у узорка област 3, талог био груб и прегорео, посебно на угловима узорка. Статистичком анализом измерених резултата за дебљину утврђено је да је превлачак хетерогена са великом интервалом варијације (54nm) и кофракцијеном варијације 0,3281. Резултати ових испитивања доводе у питање поузданост ових превлачака хрома у заштити од корозије, ерозије и хабања система који раде са агресивним токсичним на високим температурама и притисцима.

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