

The properties of chromium electrodeposited with programmed currents. Part II. Reversing current

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The electrodeposition of chromium in programmed reversing current (RC), was investigated in the regime of high cathodic current density (77 A dm^{-2}) and anodic current density (55 A dm^{-2}). The ratio of the cathodic and anodic time (60 : 1) was used. Chromium was deposited on a steel substrate from a chromic–sulphuric acid solution, during one hour. Anode and cathode were suited in a system of parallel plates. Basic properties of deposits, like thickness, morphology, microhardness, brightness were examined. Surface distribution of the deposits was obtained from the measurements of the thicknesses of the deposits (between 32 and 67 μm). A ferromagnetic non-destructive method was used in the measurements. Based on the results, graphic models of deposit surface distribution were made. Two ranges of the thickness could be seen on the model (range 1 – average thickness 35.1 μm and range 2 – average thickness 57.81 μm). These results were statistically analysed by columns, rows and by the whole surface. For the whole specimens, the average thickness was 45.39 μm with a coefficient of variation of 0.2582. The basic properties of the deposits did not change with a variation of the thickness. Because of this, the coatings deposited with the reversing current could be much more considered reliable in wear and corrosion protection systems than ones deposited by direct current.

Keywords: electrodeposition of chromium, programmed reversing current, properties of deposits, thickness, morphology, microhardness, brightness, distribution of deposits, modelling.

The chromium deposits obtained in the regime of direct current with high current densities have many faults. These faults are the appearance of the cracks and protrusions, coarse and burned deposits at the edge of the electrode, internal stress and also, a low level of current efficiency. The given defects limit the use of these deposits for the protection against systems aggressive gases at high temperatures and pressures.^{1–3}

Chromium electrodeposition at a periodically changing rate (reversing current) can be used for the intensification of the deposition process, increasing of the uniform current distribution on the macroprofile, and improving the properties of

the electrodeposited chromium.⁴⁻⁶ Programmed deposition by the reversing current is characterised with the application of computer procedure and control of the process. The basic work programme consists of two sequences: 1 – anodic etching of the basic metal, 2 – chromium deposition by reversing current.⁷

The reversing current wave is characterised by the cathodic current density and the anodic current density, as well as by the cathodic time of deposition and the anodic time of dissolution. The same average current density can be achieved in different ways, changing the shape of the current–voltage wave.⁴ Specific characteristic of chromium deposition by reversing current must be taken in consideration. The main characteristic of this process is the significant difference between the anodic and the cathodic current efficiency. The solution of this problem can be found by increasing the duration of the cathodic polarisation or by decreasing the anodic current.^{8,9}

The purpose of this paper was the examination of programmed electrodeposition chromium with the reversing current of the low frequency. Special attention was given to the surface distribution of the deposits and its effect on other properties of the coatings.

EXPERIMENTAL

The experimental procedure was the same as in the previous paper.¹⁰ The only difference compared to the previous paper was the determination of reflection (Fig. 1).

Two different location on the surface of the specimens were chosen for measurements reflection (Fig. 1). The circular measurement area had a diameter of 2.5 cm.

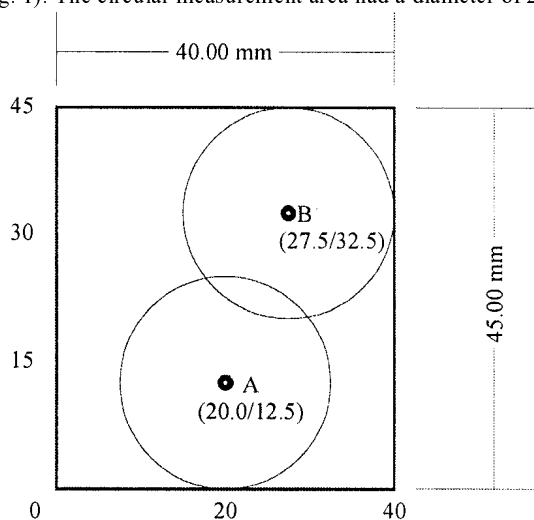


Fig. 1. Graphic model of the location on the specimens for reflection measurement.

The programmed computer controlling the process contained regulation of anodic etching and chromium electrodeposition. The basic input parameters are given in Table I.

TABLE I. Programmed basic input parameters chromium plating bath in the RC regime

No	Parameters of electrolysis	Sequence I Anodic etching substrate	Sequence II Deposition chromium
1	Anodic current density/ $A\ dm^{-2}$	55	55
2	Cathodic current density/ $A\ dm^{-2}$		77
3	Anodic time/s	45	2
4	Cathodic time/s		120
5	Temperature/ $^{\circ}C$	50–1	50–1

RESULTS AND DISCUSSION

The deposits of chromium obtained by a RC regime with a high cathodic current density ($77\ A\ dm^{-2}$) are smooth and matt-gray.

On the basis of thickness measurements of the specimens, in 6 rows and 6 columns, a graphic model was made. The graphic model of the surface deposit distribution is presented in Fig. 2. The specimens longitude and specimens latitude are presented on the ordinate and abscissa, respectively.

On the basis of the results from Fig. 2, Fig. 3 can be derived as in the previous paper.¹⁰

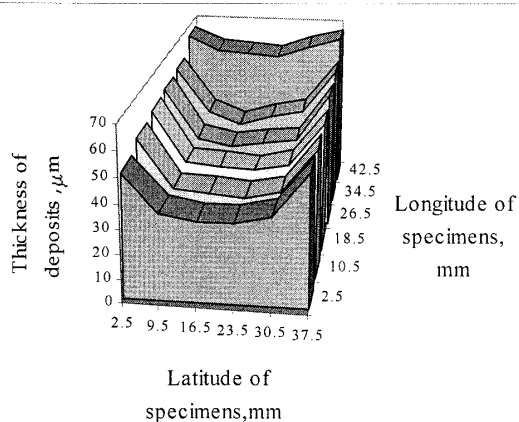


Fig. 2. Latitude profile of the thickness of the deposit in different rows of measurement.

Two ranges of surface deposit distribution can be seen from the graphical model (Fig. 3). Range 1, where the thickness of the deposits ranged between 30 and 40 mm and range 2 with thicknesses ranging from 40 to 60 mm with excessive corner thicknesses over 60 mm. The first range is limited by the line with the mark 40, which means that this line connects the points on the surface with thickness 40 mm. The second range is divided into two sections with the same thicknesses of the coatings (60 mm).

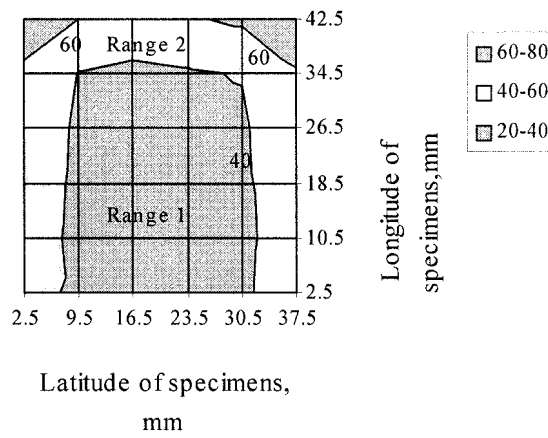


Fig. 3. Graphical model of deposits surface distribution (electrodeposition in the RC regime with $j_c = 77 \text{ A dm}^{-2}$; $j_a = 55 \text{ A dm}^{-2}$, $t_c = 120 \text{ s}$; $t_a = 2 \text{ s}$; at a solution temperature 50°C). Range 1 – thickness from 30 to 40 mm; range 2 – thickness from 40 to 60 mm.

The statistical analysis of the measured thicknesses is given in Table II. On the basis of the statistical results shown in Table II and the profile of the specimens latitude (Fig. 2), and specimens longitude (Fig. 4), it can be concluded that a more uniform chromium deposit is obtained in the RC regime than in the DC regime.

TABLE II. Results of statistical analysis of the measured thickness

	Average thickness/mm	Standard deviation of the thickness/mm	Coefficient variation
Range 1	35.45	3.13	0.0882
Range 2	57.81	4.61	0.0795
Whole surface of the specimens	45.39	11.73	0.2582

The greater part of the surface of the specimen is range 1 with $\bar{d} = 34.45 \text{ mm}$, $sd = 3.13 \text{ mm}$ and $cv = 0.0882$. This part of the surface causes a more uniform profile along the latitude of the specimen, excluding the last row with longitude 42.5 mm . This row belongs to the lower edge of the specimen, which was closer to the bottom of the cell during the deposition. Taking into consideration the analysis of the longitude profile, it can be concluded that the profiles of the average four columns are more compact than the profile of the specimens in the DC regime. There is a larger value of the thickness on the lower edge. Range 2 includes columns along the side edges and the lower row with values: $\bar{d} = 57.81 \text{ mm}$, $sd = 4.61 \text{ mm}$ and $cv = 0.0795$. The ratio between the average thickness of range 2 and range 1 is 1.63. This ratio of the average thickness in the DC regime was 2.27.

The biggest interval of variation was in this case:

$$I = d_{\max} - d_{\min} = 67 - 32 = 35 \text{ mm} \quad (1)$$

which is considerably lower than in the DC regime.

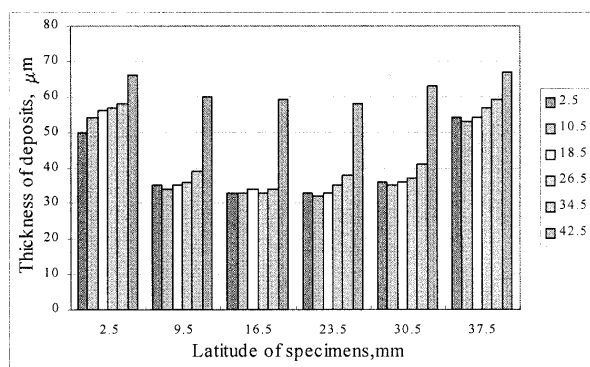


Fig. 4. Longitude profiles of the thickness of the deposits in different columns measurement.

Taking in a consideration that for the deposits in the DC regime $cv = 0.3281$ and for the deposits in the RC regime $cv = 0.2582$, including all the facts mentioned above, it can be concluded that the deposits in the RC regime show more uniformly the surface of the specimens. This is in accordance with earlier examination of chromium deposits in the RC regime given in the literature.^{11,12} This examination was in range the high frequency (from 1200 to 1900 Hz), and the deposits were smooth with uniform current distribution on the macroprofile.

The morphology of the deposits was investigated by means of optical microscopy. The morphology of deposits was found qualitatively the same over the whole surface of the specimens. The deposit had fine grains without cracks. The morphology of range 1 and range 2 (Fig. 5a and Fig. 5b) was identical. A model for the crystallization under RC conditions was given in the literature.¹³

The throwing power of the chromium plating bath is very poor. Electrodeposition in the DC regime with the high current density gives the non-uniform coating.

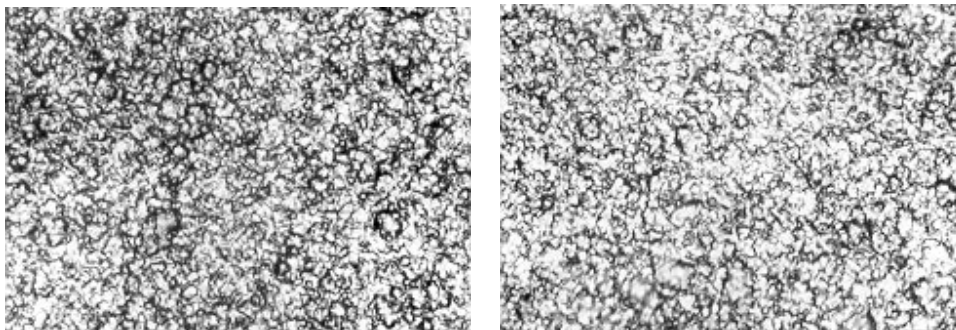


Fig. 5. Morphology of the deposits in different thickness ranges (electrodeposition in the RC regime with $j_c = 77 \text{ A dm}^{-2}$; $j_a = 55 \text{ A dm}^{-2}$; $t_c = 120 \text{ s}$; $t_a = 2 \text{ s}$; at a solution temperature 50°C) a) range 1 – thickness from 30 to 40 mm; b) range 2 – thickness from 40 to 60 mm. Magnification $640\times$.

The applied RC in the electrodeposition results in smooth and more uniformly distributed deposit on the macroprofile. The explanation of this effect is that during the anodic time the regions with the thickest deposit dissolve the most, because over these regions the current density is the highest. During the period of deposition there is an intensive process of hydrogen evolution, during which is hydrogen partially incorporated in the coating. In this way the metastable modification of chromium, β -chromium (hydrid of chromium) is formed. The decomposition of β -chromium enables evolution of the hydrogen and the formation of α -chromium and cracks because of the difference in the structures of these modifications. Under the RC conditions the structurally incorporated hydrogen is oxidized during the anodic period. By applying a sufficiently large value of the ratio Q_a/Q_b (anodic/cathodic charge), the hydrogen content in the coating is minimized, so that β -chromium is not formed and the production of cracks is avoided.

TABLE III. Microhardness of the chromium deposits electrodeposition in RC regime with $j_c = 77 \text{ A dm}^{-2}$; $j_a = 55 \text{ A dm}^{-2}$; $t_c = 120 \text{ s}$; $t_a = 2 \text{ s}$; at a solution temperature 50°C

Microhardness $HV_{0.1}$	I column	II column	III column	Average $HV_{0.1} + sd$
1 row	960	933	996	
2 row	946	974	974	
3 row	1003	996	960	971–24

Usually, the microhardness of the coating deposited in the RC regime is lower than in the DC regime. The results of the measurement, given in Table III, showed that the microhardness of deposits are identical in the RC and the DC regime under the quoted electrodeposition conditions.

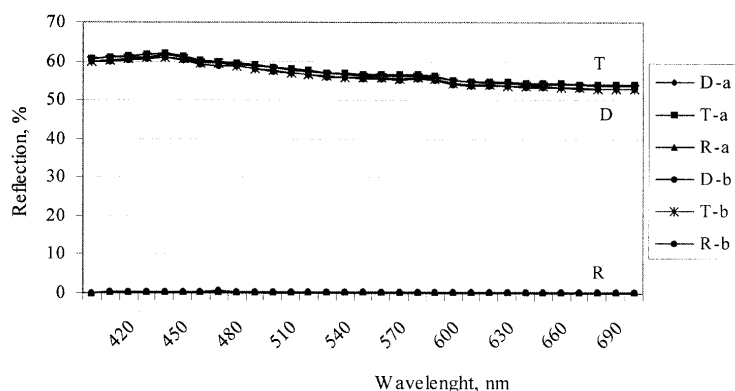


Fig. 6. Reflection of chromium deposits dependence on wavelength in the visible range (electrodepositions in the RC regime with $j_c = 77 \text{ A dm}^{-2}$; $j_a = 55 \text{ A dm}^{-2}$; $t_c = 120 \text{ s}$; $t_a = 2 \text{ s}$; at a solution temperature 50°C). D-a, D-b diffuse reflection at location A and B; T-a, T-b, total reflection at location A and B; R-a, R-b, mirror reflection at location A and B.

Reflection from the surface of the deposits was measured at two locations on the specimens, in the range of the visible wavelength (from 400 to 700 nm). In Fig. 6 six curves of the reflection of the chromium deposits are given. The total reflection has value $Ta = 55.66\%$, $Tb = 54.96\%$ and the diffuse reflection $Da = 55.46\%$, $Db = 54.89\%$. The mirror reflection was zero and the deposit was matt. According to the literature,^{8,9} electrodeposition in the RC regime with a cathodic time of 120 s, gives matt-gray deposits.

On the basis of all above mentioned, including the decreased range with thicker deposits relative to the deposits in the DC regime, there is lower cost and energy loss with the desired dimension on the protected element. The average value of the thickness is taken as a measure of the corrosion protection, because the lowest value of the deposit thickness is close to the average value the range 1. Taking in consideration that the deposits of chromium in the RC regime are of small grain size and without the cracks, it can be assumed that the protection is better in the RC than in the DC regime. On the other hand, the measured values of the microhardness of deposits in the DC and in the RC regime are almost the same. Earlier investigations of the resistance to wear and erosion confirmed that, except for the hardness, the structure and the way of the preparation of the surface also have important influence on the results of the investigation.^{2,3} In both cases, the surface was prepared in the way, which means that a better structure and morphology, without rough and coarse deposits is obtained in the RC regime. This can mean that better protection against wear and erosion is obtained with deposits in the RC regime than in the DC regime.

CONCLUSION

Electrodeposition with programmed RC, the following parameters: cathodic current of 77 A dm^{-2} , anodic current of 55 A dm^{-2} , cathodic time 120 s, anodic time 2 s, and a solution temperature 50°C , produced smooth and matt-gray chromium deposits.

The graphic model, based on the measurement of thicknesses of the deposits showed two different ranges of the thickness (range 1 – average thickness 34.45 mm , range 2 – average thickness 57.81 mm).

The chromium deposit had high microhardness $HV_{0.1} = 971 - 24$.

The morphology of the deposits did not depend on the thickness. The structure had fine grain without cracks.

Statistical analysis of the results of the thickness measurements shows that the coefficient of variation is 0.2582, which confirms that the deposits in the RC regime are more uniform than the deposits obtained in the DC regime (77 A dm^{-2}). Latitude and longitude thickness profiles were uniform but the lower edge was thicker. Relation between the average thickness of range 2 and range 1 was 1.63. This relation was smaller than in the case of electrodeposition in the DC regime.

ИЗВОД

СВОЈСТВА ЕЛЕКТРОХЕМИЈСКИ ИСТАЛОЖЕНОГ ХРОМА ПРОГРАМИРАНИМ СТРУЈАМА. ДЕО II. РЕВЕРСНА СТРУЈА

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Електролитичко таложење хрома са програмираном реверсном струјом, испитивано је у режиму високих катодних (77 A dm^{-2}) и анодних густина струје (55 A dm^{-2}). При томе је коришћен однос катодног и анодног времена ($60 : 1$). Хром је таложен на узорке од челика из хроматно-сулфатног електролита у току једног часа. Анода и катода постављене су у систем план-паралелних плоча. Испитивана су основна својства превлака као што су: дебелина, морфологија, микротврдоћа и рефлексација. Дебелина превлаке мерена је неразрађујом феромагнетном методом, у интервалу од 32 до 67 μm . На основу мерења дебелине превлаке добијена је расподела талоба по површини узорка и урађени су графички модели. На моделима уочене су две области дебелине превлаке (област 1 – са средњом дебелином 35,45 μm , област 2 – са средњом дебелином 57,81 μm). Обављена је статистичка анализа резултата мерења дебелина. Анализом измерених вредности дебелине превлаке на целој површини добијен је коефицијент варијације од 0,2582, који одговара равномернијој расподели превлаке по површини, него код превлака таложених са једносмерном струјом. Показано је да се са променом дебелине превлаке нису мењала испитивана основна својства превлака. Структура је ситнозрнаста, без прскотина, а превлаке имају високу тврдоћу (971 $HV_{0.1}$). На основу резултата ових испитивања и ранијих испитивања отпорности према корозији, хабању и ерозији превлака хрома, претпоставља се да ће превлаке хрома таложене са реверсном струјом бити поузданије у заштити од корозије, хабања и ерозије.

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