
Effect of ZnO on electrodeposition and properties of black chromium coatings

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Black chromium coatings suitable for protection against corrosion were electrodeposited from a Cr(VI) bath containing Limeda SCh-1 additive and ZnO. The effect of ZnO on the cathodic process of black chromium electrodeposition as well as the morphology and corrosion resistance of the coatings were examined. It is supposed that Zn(II) hydroxide compounds are formed in an alkaline near-cathode layer during cathodic polarization alongside Cr(III) compounds. According to XPS data, the black chromium coating includes hydroxide Zn(II) compounds in the surface layer and oxide compounds in its deep. The specific features of the corrosion-electrochemical behaviour of the deposits containing Zn(II) compounds are attributed to the surface morphology peculiarities.

Key words: black chromium coating, electrodeposition, morphology, corrosion resistance

INTRODUCTION

Electrodeposition of black coatings such as black zinc, black nickel and black chromium provides for satisfactory properties that may easily be controlled by operating conditions. Black chromium is unique in its excellent durability.

Black chromium coatings always contain impurities of hydrogen, oxygen and other elements derived from the electrolyte [1–3]. In most cases their content is in the order of 45 to 50 wt.%. The properties of the deposits are considerably altered by the presence of these impurities and determined by their chemical and physical nature.

In previous investigations [2–4] it has been found that certain organic compounds added to the electrolyte or adsorbed on the electrode surface greatly influence the properties of black chromium coatings. Using some additives, it was intended to prepare electrodeposited black chromium coatings without pinhole or crack defects.

The purpose of the study was to determine the effect of ZnO on the cathodic process of black chromium electrodeposition and to examine the corrosion-electrochemical behaviour of the coatings as well as their composition and structure.

EXPERIMENTAL

The base electrolyte used for black chromium electrodeposition was prepared with analytical grade re-

agents. Black chromium coatings were electrodeposited from the solutions containing $200 \text{ g} \cdot \text{l}^{-1} \text{CrO}_3 + 5.0 \text{ g} \cdot \text{l}^{-1}$ Limeda SCh-1 additive [5] and $10\text{--}20 \text{ g} \cdot \text{l}^{-1}$ ZnO introduced into the electrolyte. The coatings were deposited from two types of solutions. Solution No 1 contained $200 \text{ g} \cdot \text{l}^{-1}$ of CrO_3 and $5.0 \text{ g} \cdot \text{l}^{-1}$ Limeda SCh-1 additive. Solution No 2 was prepared by adding $20 \text{ g} \cdot \text{l}^{-1}$ of ZnO to solution No 1.

Black chromium was electrodeposited on steel containing 99.4% of iron (Steel-3) and on nickel-plating ($10 \mu\text{m}$) samples. The steel cathode was mechanically polished, degreased with magnesium oxide, rinsed thoroughly, activated in dilute (1:1) hydrochloric acid and then rinsed with deionized water. The cathode was displaced to the nickel-plating cell or immediately to the chromium-plating cell. A bath of a volume of 1 litre with two vertical anodes and cathode between them was maintained at a constant temperature. The current density during plating was $30 \text{ A} \cdot \text{dm}^{-2}$ and the temperature was $20 \text{ }^\circ\text{C}$. A current density of $30 \text{ A} \cdot \text{dm}^{-2}$ was selected as a compromise between efficiency and deposit quality.

The quality of the black chromium deposits was assessed visually, as well as by means of optical microscopy. High quality deposit was defined as a coating of good appearance without grey or rainbow tone.

The polarization measurements were conducted in a three-electrode electrochemical cell using a PI-50-1 potentiostat under potential dynamic conditions with a potential scan rate of $1.0 \text{ mV} \cdot \text{s}^{-1}$ at a tem-

perature of 20 °C. The Ag/AgCl electrode in a saturated potassium chloride solution was used as reference and a platinum plate as an auxiliary electrode. The anodic polarization measurements of black chromium coatings were taken in 3% NaCl solution with a potential scan rate of 2 mV · s⁻¹.

X-ray Photoelectron Spectroscopy (XPS) using an ESCALAB MK-1 determined the chemical composition of the black chromium deposits. The XPS spectrum lines were recorded at the surface and also at a depth of 10 nm. Argon ion bombardment was required for sublayer etching of the deposits. The vacuum in the analytical chamber was about 10⁻⁸ Pa. The position of spectral lines was determined at a point of maximum within ±0.1 eV. Standards of the relative intensity of photoelectron signals were used for identification of the elements and compounds in the coatings [7]. Surface morphology of the coatings was studied by X-ray spectrometry with a JXA-50A scanning microscope.

Corrosion resistance of the coatings was tested according to the ISO 9497 standard using a neutral salt fog tests. The temperature in the testing chamber was maintained at 35 ± 2 °C and the relative humidity was 97%.

RESULTS AND DISCUSSION

Figure 1 shows that i_{\max} , which characterizes the onset of the cathodic film formation, decreases after addition of ZnO (curves 3 and 4) to the electrolyte. A similar effect of ZnO is observed in the region of the second wave of PC, where Cr(III) → Cr(II) reaction occurs. According to the literature data [8], the pH of a near-cathode layer increases from 0 to 3.0–4.0 and further up to 5.6 during electrolysis. It

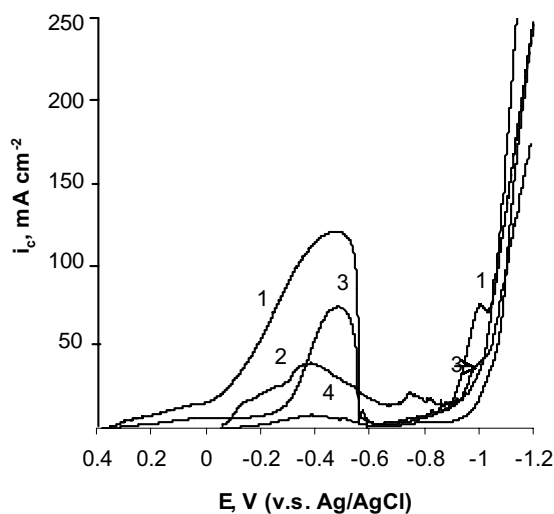


Fig. 1. Polarization curves obtained on Ni-plating (1, 3) and on steel (2, 4) electrodes in basic solution (1, 2) and in solution containing 20 g · l⁻¹ of ZnO (3, 4)

is known that Cr(III) forms aqua-complexes Cr(H₂O)₆³⁺ in an aqueous solution [8]. These complexes have an ability to give dimeric-hydroxo-bridged species at pH 4. In a more alkaline solution (pH > 4), a precipitate usually forms as a Cr(OH)₃(H₂O)₃ compound. The further Cr(III) → Cr(II) reduction leads to an increase in pH in a near-cathode layer [9].

According to the model proposed in [11], concentration profiles of the species involving Cr(VI), Cr(III) and Zn(II) change with pH. On the basis of this model, the species of Zn(CrO₄)_{0.2}(OH)_{1.6} and Zn(OH)₂ may be formed at pH > 4 in an alkaline near-cathode layer, alongside Cr(III) compounds. The formation of Zn(II) hydroxide compounds in the near-cathode layer leads to cathode blocking and to a decrease in i_{\max} . A lowering of the second wave in PC may be attributed to an additional cathode surface blocking with barely soluble Zn(II) compounds embedded simultaneously with Cr(III) compounds (black chromium).

It was observed that the black chromium coatings obtained in a solution containing ZnO are distinguished by a deeper black colour.

The spectra recorded on the surface and in the deep (10 nm) of the coating show a shift to lower values of the binding energy peak in the deep of the deposit. According to literature data [6, 7, 10], a binding energy peak Cr 2p_{3/2} of metallic Cr is 274.4 ± 0.2 eV, Cr₂O₃ – 576.8 ± 0.2 eV, Cr(OH)₃ · nH₂O – 577.9 eV and CrO₃ – 579.4 ± 0.8 eV. The binding energy peak of O 1s (about 531 eV) may be attributed to the oxygen in an adsorbed aqueous group, which resembles OH⁻ groups, and a peak about 530 eV – to bonds between oxygen and chromium in Cr₂O₃. Therefore, the data obtained allow supposing that the superficial layer of black chromium consists of Cr(OH)₃, CrOOH and a small impurity of CrF₃ (due to Lameda SCh-1 additive). Moreover, the oxygen and different impurities from the electrolyte may be adsorbed on the surface as well. After surface sputtering with argon ion bombardment, the values of the chromium peaks coincide with those of standard Cr₂O₃ [7]. Thus, it is reasonable to assume that the inner layer of the black chromium deposit consists of Cr₂O₃ with a small impurity of CrF₃. Test 3 (in Table 1) obtained in the electrolyte containing 20 g · l⁻¹ ZnO shows a binding energy peak of Zn 2p_{3/2} in the both superficial and inner layers of the deposit. Comparing these data with the values of binding energy of Zn 2p_{3/2} for pure chemical compounds such as ZnO (1021.7 eV ± ± 0.3), Zn(OH)₂ (1022.7 eV), ZnCrO₄ (1021.1 eV) and ZnF₂ (1022.2 eV), one can suppose that there is a mixture of some of these compounds in the superficial layer. It is possible that the inner layer

Table 1. Data of XP spectroscopy (Cr 2p_{3/2}, Zn 2p_{3/2}, O 1s, F 1s) recorded on the surface and in the deep (10 nm) of deposits obtained in basic solution (1) and in solution containing ZnO: 10 g · l⁻¹ (2), 20 g · l⁻¹ (3)

Test No	Depth nm	Element peak	Binding energy E, eV	Element wt. %	Compounds
1	0	Cr 2p _{3/2}	577.9	45.74	CrOOH, Cr(OH) ₃ , CrF ₃
	0	O 1s	531.0	52.38	
	0	F 1s	683.7	1.88	
	10	Cr 2p _{3/2}	576.9	62.57	Cr ₂ O ₃ , CrF ₃
		O 1s	530.0	36.52	
		F 1s	684.1	0.91	
2	0	Cr 2p _{3/2}	577.5	44.14	CrOOH, Cr(OH) ₃ , CrF ₃
	0	O 1s	531.0	52.14	
	0	F 1s	683.7	3.72	
	0	Zn 2p _{3/2}	–	0	Cr ₂ O ₃ , CrF ₃
	10	Cr 2p _{3/2}	576.5	61.19	
		O 1s	530.2	37.36	
3	0	Cr 2p _{3/2}	577.5	45.83	CrOOH, Cr(OH) ₃ , CrF ₃ , ZnOH, ZnF ₂
	0	O 1s	530.9	49.24	
	0	F 1s	683.3	2.34	
	0	Zn 2p _{3/2}	1019.4	2.59	Cr ₂ O ₃ , CrF ₃ , ZnO
	10	Cr 2p _{3/2}	576.4	58.16	
		O 1s	529.8	39.50	
		F 1s	684.9	1.39	
		Zn 2p _{3/2}	1021.4	0.95	

of this coating contains a small amount of ZnO, as was confirmed by the coincidence of the Zn 2p_{3/2} peaks.

A comparison of the morphology of the deposits obtained in the electrolytes of the both types shows differences in the surface structure (Fig. 2). The morpho-

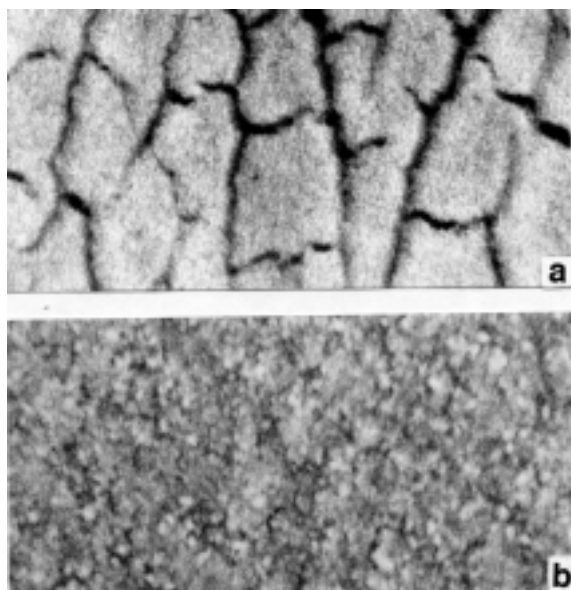


Fig. 2. Micrographs of black chromium coatings deposited at 30 A · dm⁻² in basic solution (a) and in solution containing 20 g · l⁻¹ of ZnO (b). × 6000

logy of the amorphous coatings changes from a close-packed structure with a network of microcracks (in the basic electrolyte) to a granular structure without microcracks (in the electrolyte with ZnO).

The differences in the surface morphology should be taken into account when the corrosion resistance of the coatings is compared. The polarization behaviour of the black chromium deposited on steel and Ni-plating substrates is shown in Fig. 3. As is well

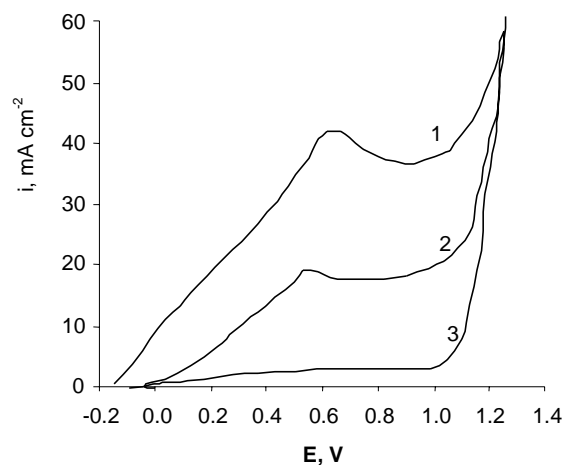


Fig. 3. Anodic behaviour of black chromium coatings (2 μm) in NaCl (3%) solution. Deposits were obtained in basic solution (1, 2) and in solution containing 20 g · l⁻¹ of ZnO (3) on steel (1) and Ni-plating (2, 3) substrates

known, Cl⁻ ions retard oxide formation. During anodic polarization of pure black chromium, the anodic process dramatically accelerates up to about 0.5 V (curves 1 and 2). The anodic current density (i_a) is much lower for the deposit containing ZnO (curve 3) in comparison with i_a for pure black chromium deposits (curves 1 and 2). One can see that the limiting current of the anodic process recorded for the deposit obtained on the steel substrate (curve 1) is about twice as high as that obtained on the Ni-plated substrate (curve 2). From the anodic behaviour of the deposits and their structures, one can see that the anodic limiting current is higher for the deposits with a network of microcracks (curve 2) than for the grain structure without them (curve 3). According to [12], during anodic polarization the excess hydrogen is removed from the coating and causes additional cracklings of the coating. It may be supposed that the anodic current contributes to the dissolution of the substrate through cracks and pores of the coating. Apparently, as a result of the support dissolution, the formation of chloride and some hydroxide compounds occurs.

It should be noted that the conventional voltammetric measurements do not provide information concerning corrosion dynamics. An attempt has been made to compare the results of voltammetric measurements with the data determined in the corrosion chamber. Figure 4 shows the results of accelerated corrosion testing. The black chromium samples were submitted to a salt spray test and evaluated by a rating number following the ISO 4540 standard. Table 2 shows the rating of coatings subjected to the corrosion test [13]. Figure 4 shows that the deposits of the both types (with and with-

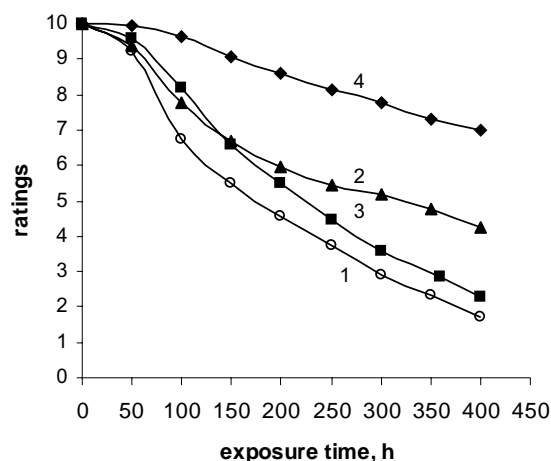


Fig. 4. Corrosion behaviour of black chromium coatings in corrosion chamber. Deposits (2 μm) were obtained in basic solution (1, 2) and in solution containing 20 $\text{g} \cdot \text{l}^{-1}$ of ZnO (3, 4) on steel (1, 3) and Ni-plating (2, 4) substrates

Table 2. Rating of coatings subjected to corrosion test

Area of defect (%)	Rating
0	10
< 0.1	9
0.1–0.25	8
0.25–0.5	7
0.5–1.0	6
1.0–2.5	5
2.5–5.0	4
5–10	3
10–25	2
25–50	1
> 50	0

out ZnO) obtained on the steel substrate (curves 1 and 3) show a greater decrease in corrosion resistance in comparison with the deposits on the Ni-plated substrate (curves 2 and 4). It is possible that hydroxide compounds of Zn(II) adsorbed on the cathode and codeposited with Cr(III) compounds induce a structural modification in the deposits, which are well reflected in the different corrosion behaviour of the black chromium coatings. The data obtained in the corrosion chamber are in good agreement with anodic behaviour of these coatings. We can conclude that ZnO embedded in the electrodeposited black chromium exerts a good effect on corrosion resistance in the presence of chloride ions in the solution (pH about 5.6–7.0), decreasing the corrosion rate.

CONCLUSIONS

A complex study of the electrochemical and corrosion properties, structure and composition of black chromium coatings deposited from Cr(VI) solutions containing ZnO has been performed.

The specific features of the electrochemical behaviour and corrosion of the deposits (as compared to the deposits obtained from the basic electrolytic bath) may be attributed to the peculiarities of surface morphology of the coating containing ZnO.

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References

1. S. Survilienė, E. Matulionis and R. Vishomirskis, *Russian J. of Electrochemistry*, **33** (4), 418 (1997).

2. S. Surviliene, A. Sudavicius, V. Jasulaitiene ir S. Bialozor, *Zashchita metalov*, **34** (4), 402–407 (1998).
3. S. Surviliene, L. Orlovskaja and S. Bialozor, *Surf. Coat. Technol.*, **122**, 235–241 (1999).
4. S. Surviliene, L. Orlovskaja and B. Shebeka, *Chemija* (Vilnius) **11** (1), 9–13 (2000).
5. Pat. 4110 Lt. S. Survilienė.
6. D. Briggs and M. P. Seach (Eds.), *Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*, Wiley, Chichester, UK (1983).
7. C. B. Wagner, W. M. Riggs and L. E. Davis et al., *Handbook of X-Ray Photoelectron Spectroscopy*, Minnesota, (1979).
8. A. J. Falicheva, L. D. Korolova and Ju. H. Shalimov, *Zashchita metallov*, **7** (5), 565–570 (1971).
9. S. Survilienė, *Russ. J. Electrochem.*, **34** (5), 453–458 (1998).
10. A. Cimino, B. A. De Angelio, A. Licketti and G. Minelli, *J. Catalys.*, **45**, 316 (1976).
11. R. Sarmaitis, A. Survila, V. Dikinis and V. P. Stasiukaitis, *Plat. and Surf. Fin.*, **86** (7), 53–57 (1999).
12. V. A. Safonov, L. N. Vykhodtseva, A. A. Edigaryan, A. D. Aliev, E. B. Molodkina, A. I. Danilov, E. N. Lubnin and Yu. M. Polukarov, *Russ. J. Electrochem.*, **37** (2), 148–156 (2001).
13. International Standard ISO 4540, Metallic Coatings Coatings Cathodic to the Substrate, Rating of electroplated test specimens subjected to corrosion tests, 1980.

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ZnO ĮTAKA JUODO CHROMO ELEKTROLITINIAM NUSODINIMUI IR GAUTOS DANGOS SAVYBĖMS

S a n t r a u k a

Pagrindinės juodo chromo dangos nusodintos iš Cr(VI) elektrolito su „Limeda SCh-1“ priedu, į kurį buvo dedama ZnO. Tirta ZnO įtaka katodiniam procesui, juodo chromo dangos struktūrai ir koroziniam atsparumui.

Nustatyta, kad ZnO sumažina Cr(VI) → Cr(III) proceso ribinę srovę ir veikia dangos struktūrą. Dangos morfologijos tyrimai parodė, kad juodo chromo dangų, kurių sudėtyje yra Zn(II) junginių, struktūra smulkiagrūdė be mikroplyšių. Tokių dangų didesnis korozinis atsparumas, kuris gali būti susijęs su dangos struktūros pokyčiais.