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INFLUENCE OF AL$(NO_3)_3$ ON THE MORPHOLOGY OF BLACK CHROMIUM COATING ON AISI 304 STEEL

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INTRODUCTION

Stainless steel is one of the most popular construction materials in the energy and manufacturing industry due to its low cost. In aggressive environments, stainless steel lends itself to local types of corrosion, which in just a few days destroy constructions without noticeable structural changes. In many cases, it is hard to identify such a corrosion on early stages of expansion. Generally, it shows up when the construction has already been badly damaged. To increase corrosion resistance and durability of stainless steel it is reasonable to apply black chromium coating on its surface[1,2].

Black chromium coatings represent chromium oxide layers, which, as we have previously investigated, have in their composition CrO_3, Cr_3O_4, Cr_2O_3[3]. The black chromium layers produced by electroplating, in comparison to other types of black coatings, have excellent wear resistance, rigidity and durability. Also, black chromium is thought to be a high temperature coating with high solar selectivity because black chromium has low luminous reflectivity[4,5].

For black chromium coatings, the use of Cr(VI) compounds is not recommended because they are toxic, carcinogenic and can cause irreversible genetic changes. It is not recommended to use Cr(VI) compounds, because of their toxicity, carcinogenicity and possible development of irreversible genetic changes. To overcome these deficiencies, chromium coatings are also prepared from solutions of trivalent chromium salts. These compounds do not

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pose the same risk for humans and environmental health[6]. Unfortunately, the coatings produced in Cr(III) solutions are unsatisfactory, as Cr(III) ions form highly resistant water complexes in aqueous solutions. To reduce this problem, it is possible to use suitable ligands that can form Cr(III) complexes with optimum chemical and electrochemical reactivity[7,8]. However, the corrosion and wear resistance of coatings produced from electrolytes based on trivalent chromium is lower than for coatings produced from electrolytes based on Cr(VI)[9].

1. Analysis of chromium coatings production methods

The study of chromium electrodeposition is of great practical interest, as chromium coatings are used in various industries to give metal parts certain mechanical properties and decorative finishes. Thus, the authors[10] studied the production of chromium coatings from an electrolyte containing 200 g/l CrO_3, 0.2 g/l $NaNO_3$ and 0.2 g/l Na_2SiF_6 protect metal base against local corrosion. The process was carried out at a current density of 10-20 A/dm^2. As a result, it was found that when the sediment thickness rises from 0.9 μm to 1.5 μm, the surface roughness increases. The coatings produced at a current density of 20 A/dm^2 have on their surface a more developed network of cracks than those obtained at 10 A/dm^2. Anode polarization measurements of black chromium coatings have shown that electrodeposition at 10 A/dm^2 reduces the tendency of local corrosion to affect coatings.[11]. This is probably the result of the formation of a thin layer of black chromium on the steel surface.

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[10] Surviliene S., Cesuniene A., Juskenas R. et al. The use of trivalent chromium bath to obtain a solar selective black chromium coating. *Applied Surface Science*. 2014. V.305. P.492-497. DOI: https://doi.org/10.1016/j.apsusc.2014.03.122.

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In the research[12] chromium coatings, based on Cr(VI) and modified with MoS_2 were produced. The increase in the MoS_2 concentration in the electrolyte leads to a decrease in the cathode output by current from 14.84% to 12.19%. As it is shown, the presence of 0.5 g/l MoS_2 in the electrolyte allows to get coatings without cracks. This may be due to the large number of nucleation centers provided by MoS_2 particles temporarily attached to the substrate surface during electrodeposition. In fact, the MoS_2 concentration and surface area will influence the morphology of electrodeposition of chromium coatings, thus affecting the hydrogen release reaction. The elevated concentration of MoS_2 particles on the cathode's surface increased the hydrogen release reaction, which led to a decrease in the number of cathode sites available for nucleation and chromium layer growth. The resistance of coatings produced from modified with MoS_2 electrolytes is 8 times higher than for chromium coatings made without any additions, so it indicates corrosion protection.

It is also possible to obtain chromium coatings from electrolytes modified with Al_2O_3[13] at current densities from. 2 to 5 mA/dm^2. In such conditions, it is possible to obtain coatings with nodule morphology, with the size of nodules increasing with the growth of current density. The thickness of the resulting coatings ranges from 3.7 μm to 10.7 μm. The apparent influence of current density on the number of Al_2O_3 particles in the coating was not observed. It was shown by the authors[14], that Al_2O_3 particles were effectively introduced into the electrodeposited matrix, which allowed to obtain coatings with a finer and compact microstructure. The corrosion rate decreased in 5 times compared to coatings without Al_2O_3.

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Electrodeposition of coatings from trivalent chromium solutions was carried out by pulse electrolysis[15,16,17]. The anode polarization time t_a has been found to be one of the factors necessary to achieve a free from cracks coating; with the reduction of t_a coatings have no cracks and adhesion is improved. The thickness is also decreased[18].

Application of chromium coatings modified with phosphorus shows that chromium forms a stable oxide on the surface and phosphorus increases its amorphous[19]. Both of these effects slow down the corrosion rate in acidic environments.

Composite chrome coatings[20] are successfully applied to steel surface. Addition of boron nitride significantly improved morphology, mechanical properties, corrosion and wear resistance of coatings. The introduction of boron nitride also significantly reduced cracking of the coatings, and provided a more homogeneous surface due to heterogeneous nucleation. Boron nitride in concentrations under 20 g/l increased the hardness of the coating, but after 20 g/l hardness and modulus of elasticity decreased due to agglomeration and reduced adhesion[21].

Kiran G.K. described in his work[22] electrodeposition of perovskite-chromium coatings $MCrO_3$ (M = La, Pr, Nd, Gd, Dy и Y) at constant current density 2,5 mA/cm^2.

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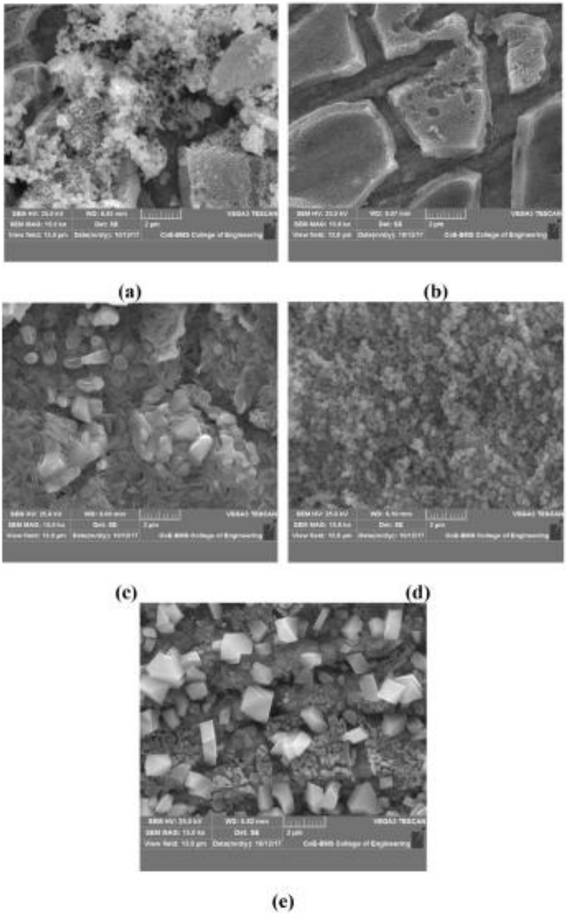

Fig. 1. SEM images of (a) $PrCrO_3$, (b) $NdCrO_3$, (c) $GdCrO_3$, (d) $DyCrO_3$ and (e) $YCrO_3$ – coatings produced as part of the work.[20]

Deposited under the same condition these coatings have different morphology with various M in $MCrO_3$. SEM-image in fig. 1 (a) shows a globular morphology, where like $NdCrO_3$ large scales of several micrometers in size are visible, and within these scales tiny crystals are evenly distributed (fig. 1, b). On the other hand, microphotographs of $GdCrO_3$ and $DyCrO_3$ coatings show plate and spherical morphology respectively (fig. 1, c and d). SEM-images of the $YCrO_3$ coating demonstrates an unusual rhomboid morphology (fig. 1, e). Addition of Y_2O_3 in electrolyte allows to receive tight coatings with mass part of yttrium 3.72%[23].

Also, in research[24,25] coatings containing titanium oxides were produced on stainless steel. When titanium dioxide is added to the electrolyte, the morphology becomes more homogeneous and ordered perpendicular to the surface, the size of the plate decreases, and a more compact structure is formed. Electrochemical tests have shown that such coatings increase corrosion resistance and durability of the substrate.

Analyzing this information, we can conclude that chromium coatings are specific in the process of obtaining but required. Application of chromium coatings can solve a number of important technological problems in various industries, particular in the energy industry[26].

However, there is ongoing discussion about the mechanism of black chromium deposition, both from Cr(VI) and from Cr(III) based electrolytes. Discussions on ways to reduce the negative impact of chromium plating electrolytes on workers' health and the environment also continue. Remains as a problem the relatively low efficiency of the process.

The task of this work is electrochemical deposition of black chromium coatings on steel AISI304 and investigation of their composition and morphology. In further work we will study their anticorrosive properties under high temperature conditions and the effects of an aggressive environment on the sample material.

The solution of the claimed problem will increase the service life and the efficiency of use of structural materials used for operation in high temperature conditions in complex technological installations, that require special structural reliability due to the high level of potential danger.

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[24] Штефан В.В., Баламут Н.С., Кануннікова Н.О. Корозійні характеристики сталі 08Х18Н10/Cr·CrO_X·MO_Y (M= Ti, Al, Si). *Colloquium-journal*. 2022. С. 27-30.

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We have expressed suggestion that while chrome coatings are known to be heat-resistant[27] the addition of $Al(NO_3)_3$ will contribute to a significant increase in its operating temperatures.

It is believed that when a certain amount of chromium or aluminium is introduced into a steel composition during the oxidation process on the surface of the workpiece, these elements are capable of forming dense oxide films. These films make it difficult for oxidants to diffuse, thus preventing corrosion of the workpiece during the influence of aggressive environments[28].

2. Materials and methods

Electrolytes, the composition of which is presented in table 1, were used to form the black chromium coating. $Al(NO_3)_3$ crystals were completely dissolved in the electrolyte.

The process was carried out in a two-electrode cell with a working volume of 200 ml with a continuous mixing system. The coating was precipitated on AISI 304 steel the following composition, %: C – 0.08, Cr – 19.14, Ni – 10.73, Si – 0.58, Mn – 0.19, Fe – 69.28; produced by Italinoks Industri (Ukraine) with a rectangular surface area of specimens of 4 cm^2. Platinum wire was used as a counter electrode. The process proceeded at room temperature, at a current density of 50 A/dm^2.

Table 1

Composition of electrolytes for coating deposition

№	**CrO_3**	**$NaNO_3$**	**H_3BO_3**	**$Ba(OH)_2$**	**$Al(NO_3)_3$**
1	2.5	0.06	0.3	0.01	-
2	2.5	0.06	0.3	0.01	0.05
3	2.5	0.06	0.3	0.01	0.1
4	2.5	-	0.3	0.01	0.1

Surface morphology and elemental composition of the resulting coatings was investigated using the scanning electron microscope (SEM) ZEISS EVO 40XVP with the microanalysis system INCA Energy 350 produced by Carl Zeiss (Germany) and Oxford Instruments (England)[29].

[27] Edy J.E., McMurray H.N., Lammers K.R., deVooys A.C.A. Kinetics of corrosion-driven cathodic disbondment on organic coated trivalent chromium metal-oxide-carbide coatings on steel. *Corrosion Science*. 2019. V. 157. P. 51-61. DOI: https://doi.org/10.1016/j.corsci.2019.04.037.

[28] Shtefan V.V., Kanunnikova N.A. Oxidation of AISI 304 Steel in Al– and Ti-Containing Solutions. *Protection of Metals and Physical Chemistry of Surfaces*. 2020.V. 56. P. 379-384. DOI: https://doi.org/10.1134/S2070205120020239.

[29] Shtefan V., Kanunnikova N., Pilipenko A., Pancheva H. Corrosion Behavior of AISI 304 Steel in Acid Solutions. *Materials Today: Proceedings*. 2019. V. 6. P. 150-157. DOI: https://doi.org/10.1016/j.matpr.2018.10.088.

The image of the surface was obtained by recording secondary electrons (SE) by scanning the electron beam over the surface. Secondary radiation was excited by irradiating the samples with a beam of electrons with an energy of 15-20 keV. SMARTSEM software environment was used for image processing[30].

3. Results and discussing

Morphology of the resulting coatings. The resulting coatings are matt black[31]. An example of the appearance of formed coatings is given in fig. 2. Visual examination of the samples did not reveal any damage to the integrity of the layers.

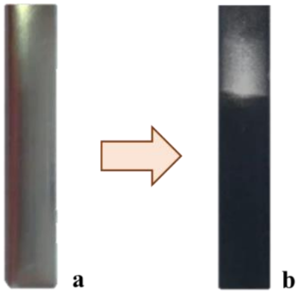

Fig. 2. The appearance of steel AISI 304 samples before (a) and after applying black chromium (b)

Figure 3 shows microphotographs of the AISI304 steel surface with coatings derived from electrolytes № 1-4 (table. 1). The images show that cracks in the layers, obtained from aluminium-modified electrolytes, are larger. Also, when considering photo (b) and (c) fig. 3 it can also be observed that areas of the coating, bounded by cracks, in a sample, formed in an electrolyte with the addition of 0.1 mol/l $Al(NO_3)_3$, have a bigger size than a black chromium coating precipitated from an electrolyte with the addition of 0.05 mol/l $Al(NO_3)_3$. When comparing images (a), (b) and (c) fig. 3, it can also be

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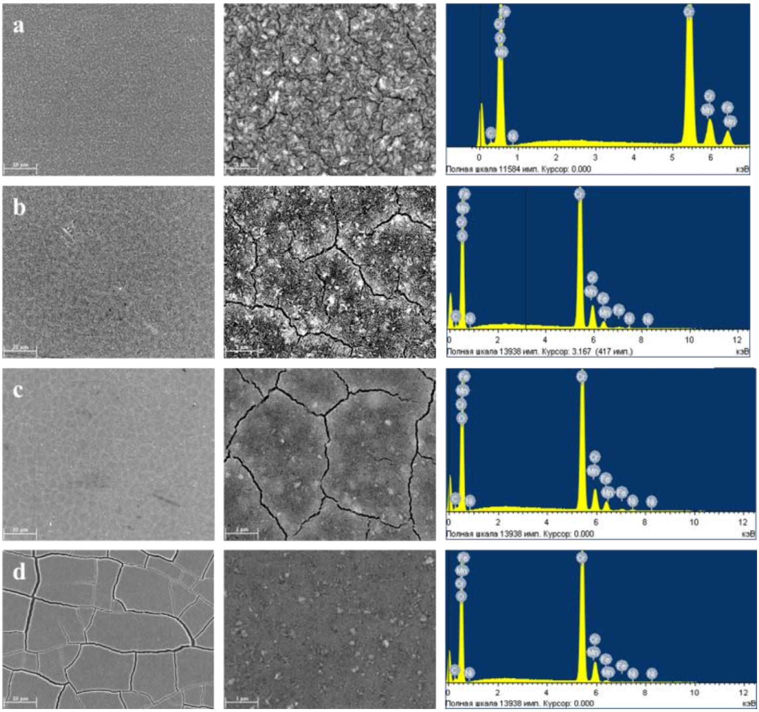

Fig. 3. SEM images and EDX spectra of black chromium coatings formed in: a) non-modified electrolyte and electrolyte with addition of: b) 0.05 mol/l $Al(NO_3)_3$; c) 0.1 mol/l $Al(NO_3)_3$; d) 0.1 mol/l $Al(NO_3)_3$ without $NaNO_3$

seen that layers obtained from aluminium-added electrolytes have a more compact crystalline structure.

The coating formed in the electrolyte with the addition of 0.1 mol/l $Al(NO_3)_3$ and without the addition of $NaNO_3$ (fig. 3) has the biggest cracks of all the referenced samples. The crystal structure of the coating is similar to that of the specimen in fig. 3 (c) (0.1 mol/l $Al(NO_3)_3$) with the addition of $NaNO_3$.

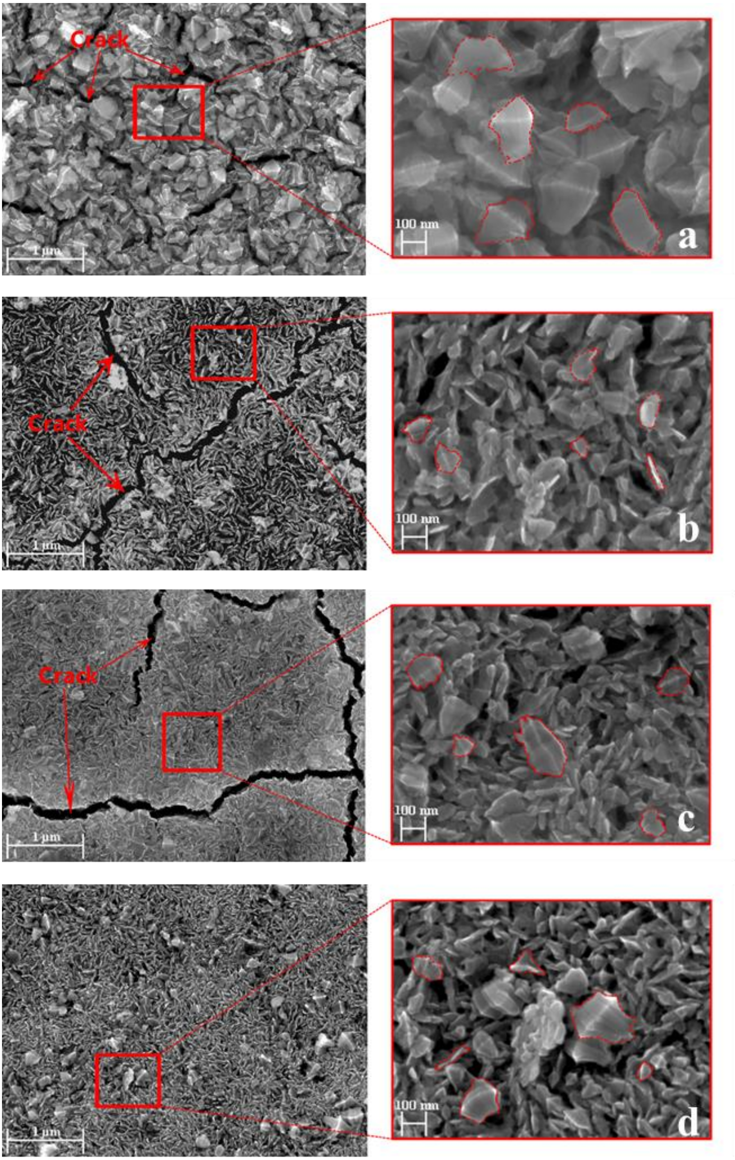

Fig. 4. SEM images of black chromium coatings formed in:
a) non-modified electrolyte and electrolyte with addition of: b) 0.05 mol/l $Al(NO_3)_3$; c) 0.1 mol/l $Al(NO_3)_3$; d) 0.1 mol/l $Al(NO_3)_3$ without $NaNO_3$

Thus, it can be concluded that an increase in the $Al(NO_3)_3$ electrolyte contributes to a finer crystalline structure of the sediment layer, but also contributes to an increase

in cracks[32]. The presence of $NaNO_3$ in electrolyte also affects the size of cracks of the coating[33].

According to the microphotographs shown in the fig. 4, it can be seen how the crystalline structure of the layers changes with the including of $Al(NO_3)_3$ to the electrolyte composition. Fig. 4 (a) depicts a coating obtained from electrolyte without addition of $Al(NO_3)_3$. As it is seen, the average grain size is 150-200 nm. Coating specimens formed in electrolytes with the addition of $Al(NO_3)_3$ appear to differ in crystal configuration, and their grain size is about 100 nm.

Thus, it can be concluded that the size of the coating crystals may depend on the presence of $Al(NO_3)_3$ in the composition of the electrolyte, so the addition of its greater amount leads to a reduction in the size of the crystals.

Fig. 4 (d) shows a layer of black chromium formed in the electrolyte with the addition of 0.1 mol/l $Al(NO_3)_3$ and without the addition of $NaNO_3$. The coating has similar to the samples obtained from electrolytes with the addition of $Al(NO_3)_3$, (fig. 4 (b, c)) size and configuration of crystals. But there is the presence in the structure of inclusions of crystals of greater size, visually similar to those that form the structure inherent to the sample (a) on fig. 4. Such inclusions are also typical for coating, obtained from electrolyte with the addition of 0.1 mol/l $Al(NO_3)_3$ (fig. 4 (c)). The size of these inclusions exceeds 100 nm.

Elemental composition. Table 2 shows the elemental composition of the coatings formed in electrolytes with the addition of 0.05 mol/l $Al(NO_3)_3$, 0.1 mol/l $Al(NO_3)_3$ and without the addition of $Al(NO_3)_3$.

When comparing the data in table 2, the atomic part of oxygen in the composition of the coatings formed in modified electrolytes is slightly smaller than in the black chromium layer produced from the non-modified electrolyte. In contrast, the atomic fraction of chromium is correspondingly larger, so that promotes the protective and mechanical properties of the coating, since

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[33] Akhtar K., Khan Z.U., Gul M. et al. Electrodeposition and Characterization of Ni-Al_2O_3 Nanocomposite Coatings on Steel. *Journal of Materials Engineering and Performance*. 2018. V. 27. P. 2827-2837. DOI: https://doi.org/10.1007/s11665-018-3346-2.

chromium is a metal with high hardness and protective properties[34,35]. During the analysis of coating composition, no aluminum was found. However, the effect of the additive on surface morphology is obvious, so the mechanism of modification's influence on the structure of the crystalline layer requires further study.

Table 2

Elemental composition of the resulting coatings

Element (a.p. %)	Coating, obtained from electrolyte with addition of $Al(NO_3)_3$, mol/l			
	0	**0,05**	**0,1**	**0,1 (without $NaNO_3$)**
O	66,10	62,28	63,64	63,35
Cr	33,90	37,71	36,36	36,65

Fig. 5 shows image of the examined coatings, indicating the points at which the SEM analysis was performed. The achieved data and associated estimated oxides are presented in table 3.

The highest melting point among the estimated oxides has the compound Cr_2O_3 (2435°C)[36]. The least heat-resistant oxide is CrO_2. It oxidizes to Cr_2O_3 at 427°C[37]. In addition, this compound exhibits high corrosion resistance. Cr_3O_4 melts at a temperature of 1705°C. The most solid is Cr_2O_3, because its crystal has a hexagonal structure, characteristic of the corundum[38]. CrO_2 has a rutile-type structure and Cr_3O_4 has a spinel-type[39].

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[36] Kharissova O. V., Torres-Martínez L. M., Kharisov B. I. Handbook of Nanomaterials and Nanocomposites for Energy and Environmental Applications. Springer Nature Switzerland AG 2021. 3786 p. DOI: https://doi.org/10.1007/978-3-030-36268-3

[37] Патент на винахід 119022 Україна, МПК C25D 11/34. Спосіб електрохімічного оксидування нержавіючої сталі / В.В. Штефан, Н.О. Кануннікова, Н.С. Баламут, О.В. Кобзєв; заявник та власник патенту НТУ «ХПІ». № a2018 07699; заявл. 09.07.2018; опубл. 10.04.2019; Бюл. № 7.

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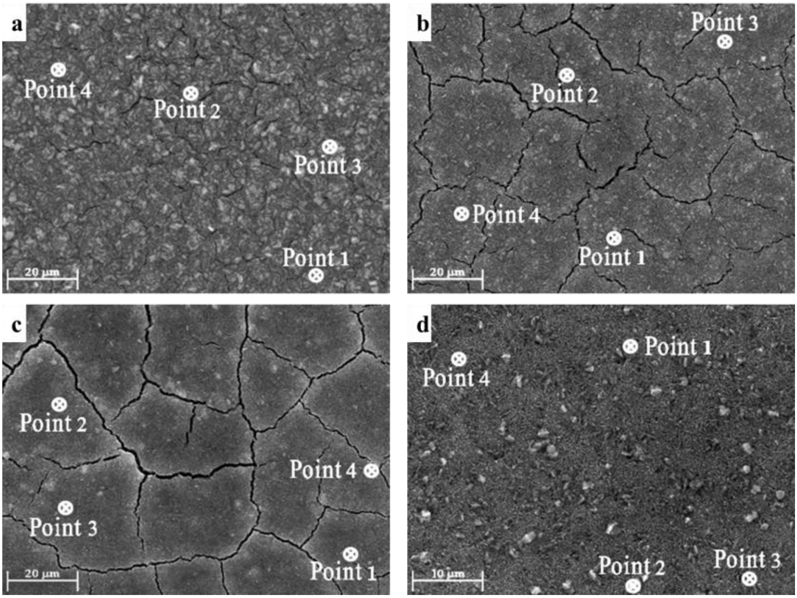

Fig. 5. Image of the coatings samples obtained from the a) non-modified electrolyte and electrolyte with addition of: b) 0.05 mol/l $Al(NO_3)_3$; c) 0.1 mol/l $Al(NO_3)_3$; d) 0.1 mol/l $Al(NO_3)_3$ without $NaNO_3$, according to the results of the SEM analysis at four points (shown in table 3)

For a coating sample precipitated from an electrolyte with the addition of 0.05 mol/l $Al(NO_3)_3$, it is most likely that CrO_2 oxide forms a coating near cracks (fig. 5 (b)). Cr_2O_3 and Cr_3O_4, on the contrary, form the crystalline layer on areas far from cracks. This observation suggests the conclusion that the resulting coating consists mainly of Cr_2O_3 and Cr_3O_4. The conclusion that CrO_2 oxide is present near cracks is also valid for a coating obtained from non-modified electrolyte. It is also confirmed with the data of layer composition of sample, formed in electrolyte without $Al(NO_3)_3$ in point 2.

Similarly, the analysis of the elemental composition found that the surface of the sample formed in the electrolyte with the addition of 0.1 mol/l $Al(NO_3)_3$ probably consists of Cr_2O_3 and CrO_2. Chromium oxide (III) appears mainly within crack-limited areas (in the pictures on fig. 5 (c) areas with a predominance in Cr_2O_3 are most likely to have a darker color). CrO_2 predominates in cracks and more lighter areas. So, it can be assumed that the coating of the sample formed in the electrolyte with the addition of 0.1 mol/l $Al(NO_3)_3$ consists mainly of Cr_2O_3 with some CrO_2 included.

Table 3

Elemental composition of coatings obtained from electrolytes with different concentrations of $Al(NO_3)_3$ (shown in fig. 5)

Concentration of $Al(NO_3)_3$ in electrolyte, mol/l	Studied point number	Element (a.p. %)		Probable oxide
		O	Cr	
0	1	59.93	40.07	Cr_2O_3
	2	66.65	33.35	CrO_2
	3	69.29	30.71	Cr_2O_3
	4	65.12	34.88	CrO_2
0,05	1	65.48	34.52	CrO_2
	2	66.87	33.12	CrO_2
	3	60.59	39.41	Cr_2O_3
	4	56.93	43.07	Cr_3O_4
0,1	1	60.26	39.73	Cr_2O_3
	2	60.59	39.40	Cr_2O_3
	3	66.71	33.29	CrO_2
	4	66.21	33.79	CrO_2
0,1 (without $NaNO_3$)	1	62.48	37.52	Cr_2O_3
	2	66.40	33.60	CrO_2
	3	59.71	40.29	Cr_2O_3
	4	59.16	40.84	Cr_2O_3

From the analysis of the elemental composition, it can be concluded that the black chromium layer obtained from the electrolyte with the addition of 0.1 mol/l $Al(NO_3)_3$ and without the addition of $NaNO_3$ probably consists mainly of Cr_2O_3 with CrO_2 inclusion. In microphotographs presented in the fig. 5 (d), Cr_2O_3 oxide looks like small dark crystals, which mainly made the coating, while CrO_2 inclusions are much bigger in size and lighter.

CONCLUSIONS

During the work electrochemically obtained black chromium coatings on steel AISI304 from studied electrolytes. Based on the results of visual inspection, analysis of surface morphology and elemental composition by SEM and EDX, the following conclusions were made:

1. All coatings obtained from the studied electrolytes have a matte black color. During the visual inspection any violation of the coating integrity was not detected.

2. It is obvious that the surface morphology changes with an increase in the concentration of $Al(NO_3)_3$ in the composition of the electrolyte – the coating acquires a finer crystalline structure, but the size of the cracks and the areas limited by them increases.

3. Oxygen and chromium were found in the composition of coating. According to the evaluation of the ratio Cr:O, oxides of the following

composition are proposed: CrO_2, Cr_2O_3, Cr_3O_4. It is likely that these compounds make up a layer of black chromium. No aluminum was found in the coating composition.

4. With the exception from the composition of the electrolyte $NaNO_3$ the cracks have become larger and, accordingly, cover larger areas compared to coatings obtained from electrolytes with the addition of $NaNO_3$. The size of the crystals did not change significantly.

5. The coating formed from the electrolyte without the addition of $NaNO_3$ may consist mainly of Cr_2O_3, with some inclusion of CrO_2.

SUMMARY

The widespread use of stainless steels in the energy industry is explained by its low cost and corrosion resistance in certain environments. Due to the exposure of AISI304 to local types of corrosion, black chromium coatings are applied to the surface, which increases corrosion resistance in aggressive environments. In this study, the influence of $Al(NO_3)_3$ and $NaNO_3$ on the morphology and elemental composition of black chromium coatings was examined. It is found, that the structure of coatings produced from the electrolyte modified by $Al(NO_3)_3$ is finer than that obtained from the non-modified electrolyte. With an increase of the concentration of $Al(NO_3)_3$ in the electrolyte, the size of cracks and areas limited by them increases. The morphology of coatings produced from an electrolyte without the addition of $NaNO_3$ has a similar structure to coatings obtained from electrolytes with the addition of $NaNO_3$, but bigger cracks. Based on the ratio of Cr:O in the coating, oxides of CrO_2, Cr_2O_3, Cr_3O_4 are proposed as most likely to form a black chromium coating.

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