

## ELECTRODEPOSITION OF CHROMOXIDE COATINGS FROM ELECTROLYTES MODIFIED WITH $\text{SiO}_2 \cdot n\text{H}_2\text{O}$

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To increase the corrosion resistance of stainless steel from local types of corrosion, chromium oxide coatings obtained from electrolytes modified with  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  were applied to its surface. It has been established that the coatings obtained from the electrolyte with the addition of  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  are continuous, without cracks, and finely crystalline compared to the coating obtained from the base electrolyte. Elemental analysis did not show the presence of silicon in the composition of the coating obtained from the modified  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  electrolyte, however, it showed the presence of a larger amount of chromium compared to the coating obtained from the base electrolyte. On the polarization curves, there is a complication of the release of hydrogen at the cathode and oxygen at the anode, which indicates a decrease in the electrical conductivity of the obtained coatings. The results obtained make it possible to recommend the use of  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  additives to the electrolyte to obtain chromium oxide coatings on steel with enhanced corrosion protection properties.

### INTRODUCTION

Alloys based on iron, nickel and chromium are widely used in industry, instrumentation and medical technology. However, power engineering requires high-quality alloys with a unique combination of chemical and phase composition, surface micro- and nanostructure, as well as sufficient hardness, wear resistance, and heat resistance [1-3]. Stainless steels are highly resistant to corrosion; however, under harsh conditions, this characteristic is improved by additional passivation, the formation of oxide films of a special composition and structure. This protective film is usually formed as a result of the interaction of the surface layer of steel with oxygen, acids and salts. Special requirements are often placed on the composition of the oxide film, such as corrosion resistance, high temperature oxidation resistance, and the like [4, 5].

The high demand for coatings with increased resistance to highly corrosive environments is a consequence of the growing demand for a safe service life of industrial facilities. Electrodeposition of composite oxide coatings is a valuable new surface intensification technology that allows co-deposition of inorganic and organic particles in coatings to improve surface properties. Such coatings have excellent properties of abrasion resistance, corrosion resistance and high temperature oxidation resistance, and the like [6-9]. In metal matrix composite coatings, different concentrations of second phase reinforcement (oxides, carbides, metal particles, etc.) are used to obtain specific properties [10].

Compared with other types of electroplated black plating, black chrome plating has excellent wear resistance, hardness and durability. The chromium oxide coating is considered to be stable at high temperatures, which demonstrates high selectivity of solar radiation, since black chrome has a low light reflectance [11-15]. In terms of corrosion resistance, chromium oxide

coatings are not inferior to the properties of electrolytic chromium deposits. Studies show that black chrome coatings are highly resistant to a wide range of oxidizing and reducing environments [16]. The deposition of a coating with the inclusion of a dispersed phase makes it possible to reduce the required deposit thickness while improving the physicochemical properties. Modification of such coatings with  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  particles can lead to a decrease in the crystal size and an increase in microhardness, wear resistance, and high-temperature oxidation resistance [17-20].

### MATERIALS AND METHODS

The electrodeposition of chromium oxide coatings was carried out from an electrolyte of the following composition, g/L:  $\text{CrO}_3$  – 150...250;  $\text{H}_3\text{BO}_3$  – 15...20;  $\text{NaNO}_3$  – 4...5;  $\text{Ba(OH)}_2$  – 1...2;  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  – 5...20. As a substrate, AISI 304 steel was used with a composition, %: C – 0.08; Cr – 19.14; Ni – 10.73; Si – 0.58; Mn – 0.19; Fe – 69.28, which had the form of rectangular plates with a total working surface area of 4 cm<sup>2</sup>. A platinum wire was used as the anode.

Table 1

The composition of electrolytes for the deposition of chromium oxide coatings

Component	Electrolyte number and concentration of components, g/L	
	1	2
$\text{CrO}_3$	150...250	150...250
$\text{H}_3\text{BO}_3$	15...20	15...20
$\text{Ba(OH)}_2$	1...2	1...2
$\text{NaNO}_3$	4...5	4...5
$\text{SiO}_2 \cdot n\text{H}_2\text{O}$	–	5...20

The process was carried out at a current density of 40...50 A/dm<sup>2</sup> for 20...40 min with continuous convection at a temperature of 18...25 °C.

The surface morphology and elemental composition of the resulting coatings were studied using a ZEISS EVO 40XVP scanning electron microscope (SEM) with an INCA Energy 350 microanalysis system manufactured by Carl Zeiss (Germany) and Oxford Instruments (England). The surface image was obtained by detecting secondary electrons (SE) by scanning the electron beam over the surface. The secondary radiation was excited by irradiating the samples with an electron beam with an energy of 15...20 keV. The SMARTSEM software environment was used for image processing.

Anticorrosion properties were studied on samples without and with chromium oxide coatings after 1 h exposure in 3% NaCl solution. The change in the potential of the sample (E) was evaluated with respect to the silver chloride electrode, and its value was listed to normal hydrogen electrode. The polarization curves were

recorded from a stationary potential set for an hour using the IPC-Pro potential. A platinum grid served as the counter electrode.

## RESULTS AND DISCUSSIONS

In this work, coatings were deposited from chromium-containing electrolytes modified with  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  (Table 1). The resulting chromium oxide coatings have a black matte color (Fig. 1) and are strongly adhered to the base.

The surface morphology and structure of the coating will have a significant impact on the corrosion behavior, determined by the level of porosity and defects.

Earlier [21], by changing the parameters of nonstationary electrolysis, we established changes in the morphology of chromium oxide coatings on steel.

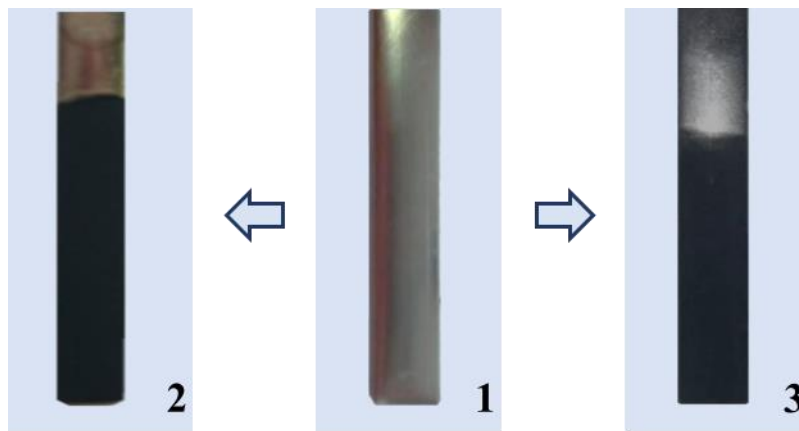


Fig. 1. Surface of samples of AISI 304 steel without coating (1) and with coatings obtained from basic (2), modified  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  (3) electrolytes

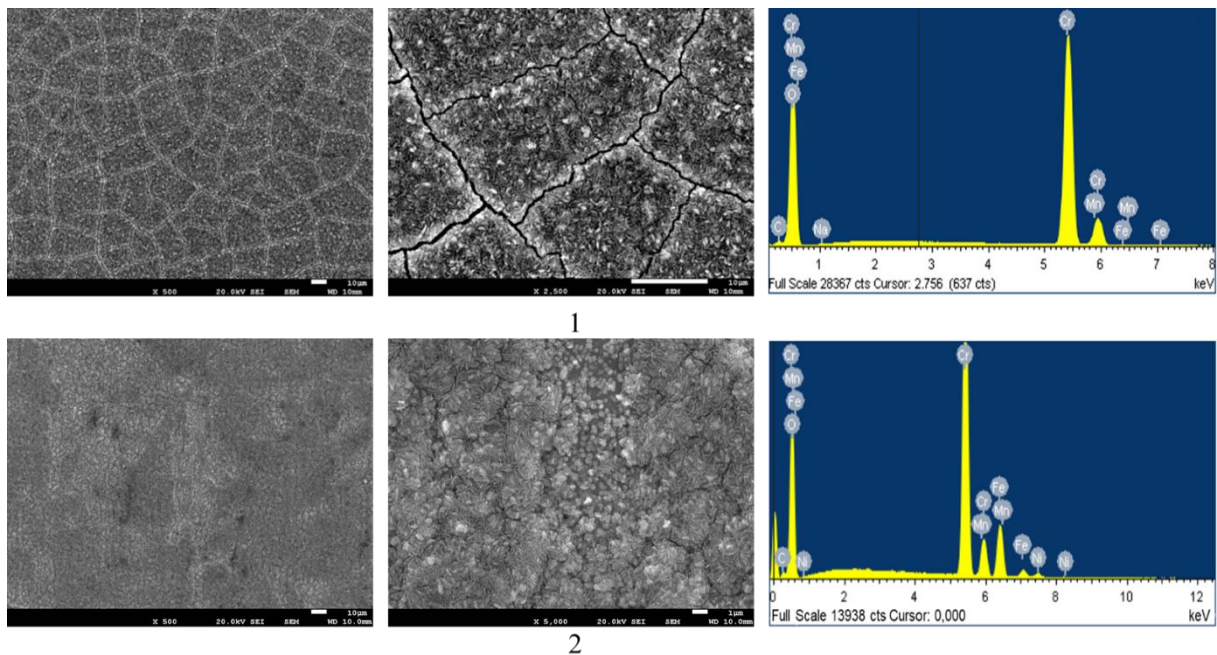


Fig. 2. SEM images and EDX – surface spectra of coatings obtained from base (1) and modified  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  (2) electrolyte

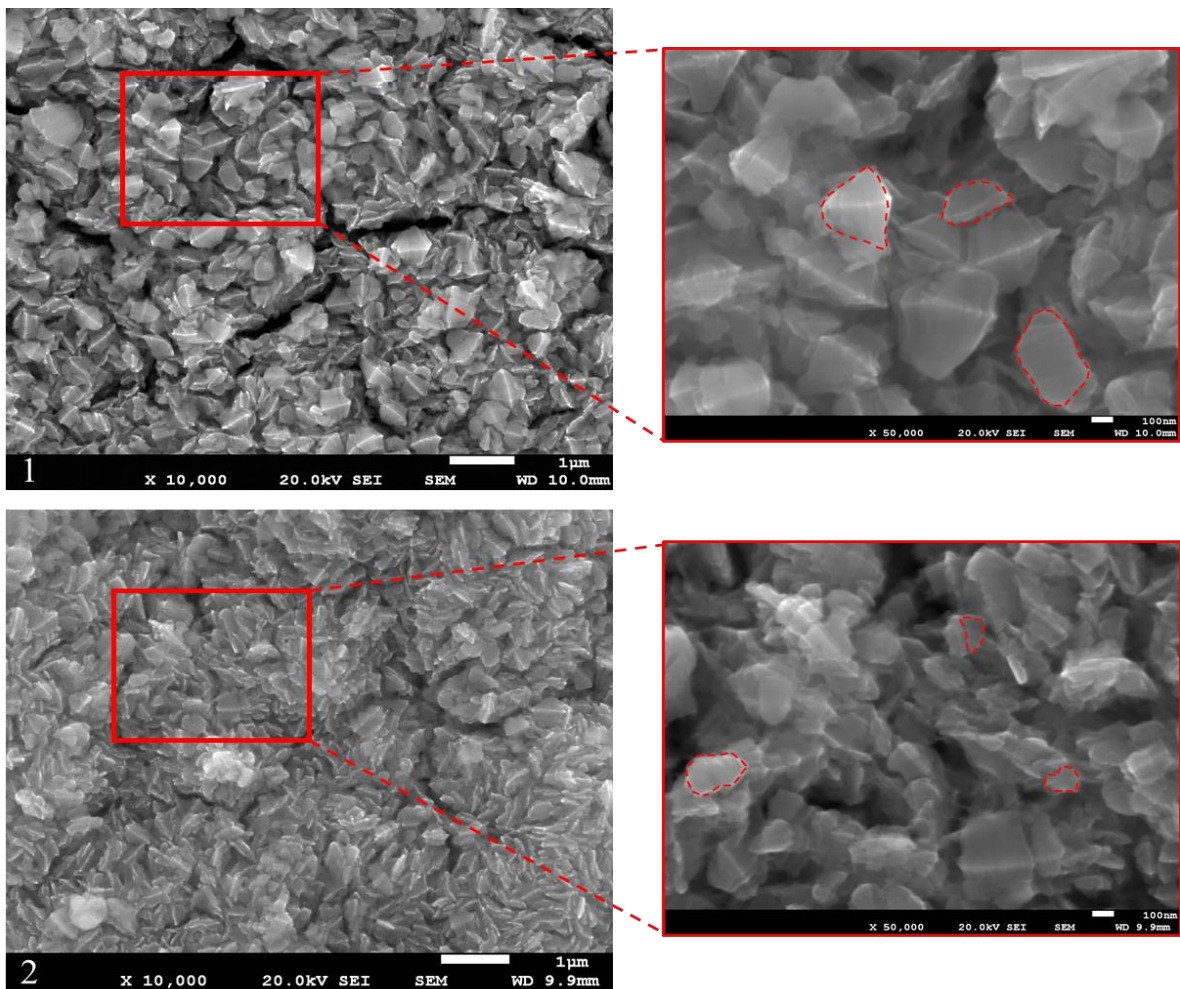


Fig. 3. SEM images of coatings obtained from base (1) and modified  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  (2) electrolyte

Table 2  
Elemental composition of the resulting coatings

Coating derived from electrolyte	Element (mas.%)	
	O	Cr
without $\text{SiO}_2 \cdot n\text{H}_2\text{O}$	66.10	33.90
with $\text{SiO}_2 \cdot n\text{H}_2\text{O}$	59.48	40.52

The coating obtained from the modified electrolyte differs in that there are no cracks on its surface compared to that obtained from the chromium-containing electrolyte without the addition of  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  (Fig. 2). The structure of the coating shown in Fig. 2,2 is more continuous than that shown in Fig. 2,1. The surface of both samples has protrusions in the form of pyramids and other irregularities.

The deposition of modified  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  electrolytes leads to the formation of a finer crystalline structure. On Fig. 3,1 it can be seen that the  $\text{Cr-CrO}_x$  coating consists of crystals 340...500 nm in size (see Fig. 3,1), and the coating obtained from the modified electrolyte has smaller crystals 80...300 nm in size on its surface (see Fig. 3,2). On the surface of both samples, petals of crystals with different orientations are formed.

Using SEM, the presence of oxygen and chromium in large quantities in the obtained coatings was confirmed, which indicates the presence of oxygen-containing chromium compounds. Analyzing the data in Table 2, it is obvious that the proportion of oxygen in the

sample formed from the electrolyte with the addition of  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  is reduced, and the proportion of chromium slightly increased compared to the coating obtained from the base electrolyte. According to the results of the analysis of coatings of the element, silicon was not found, although the morphology changed significantly, which is confirmed by a comparison of micrographs of coatings (see Fig. 3) deposited from an electrolyte with and without the addition of  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ .

Fig. 4 shows micrographs of the surfaces formed from the electrolyte with the addition of  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  with the positions of the points at which the elemental composition was analyzed. Table 3 shows the elemental composition of the chromium oxide layer obtained from the electrolyte modified with  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ . According to the results of the SEM analysis at four points, the probable compounds were calculated (see Table 3). As is known from [22], the most heat-resistant is chromium (III) oxide –  $\text{Cr}_2\text{O}_3$ . Its melting point is 2329 °C. The lowest melting point of the listed substances is demonstrated by  $\text{CrO}_2$  – it decomposes at a temperature of 427 °C to  $\text{Cr}_2\text{O}_3$ . Importantly, it also has high corrosion resistance. The oxide of the composition  $\text{Cr}_3\text{O}_4$  has a melting point of 1705 °C and has a spinel structure. Among all compounds,  $\text{Cr}_2\text{O}_3$  is the hardest, since the  $\text{Cr}_2\text{O}_3$  crystal has a hexagonal corundum-like structure.  $\text{CrO}_2$  crystallizes into a rutile type structure.

Chromium oxide (II) when heated above 100 °C disproportionation reaction occurs with the formation of CrO oxidizes to Cr<sub>2</sub>O<sub>3</sub>, when heated above 700 °C, a Cr<sub>2</sub>O<sub>3</sub> and other products.

Table 3

Elemental composition of the coating obtained from the modified SiO<sub>2</sub>·nH<sub>2</sub>O electrolyte according to the results of the SEM analysis at four points

Point number	Element, mas.%		Probable oxide
	O	Cr	
1	58.34	41.66	Cr <sub>2</sub> O <sub>3</sub>
2	54.01	45.99	CrO
3	64.24	35.76	CrO <sub>2</sub>
4	56.80	43.20	Cr <sub>3</sub> O <sub>4</sub>

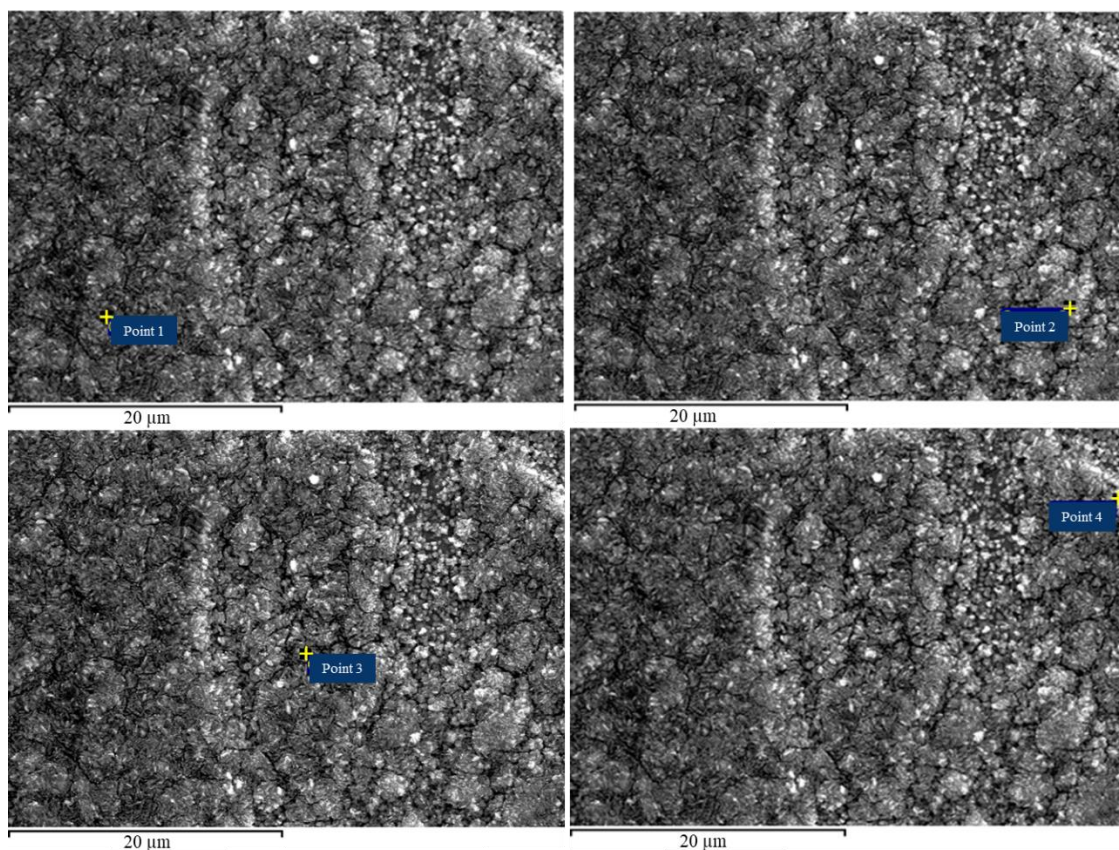


Fig. 4. Micrographs of the coating samples obtained from the electrolyte modified SiO<sub>2</sub>·nH<sub>2</sub>O according to the results of the SEM analysis at four points (according to Table 3)

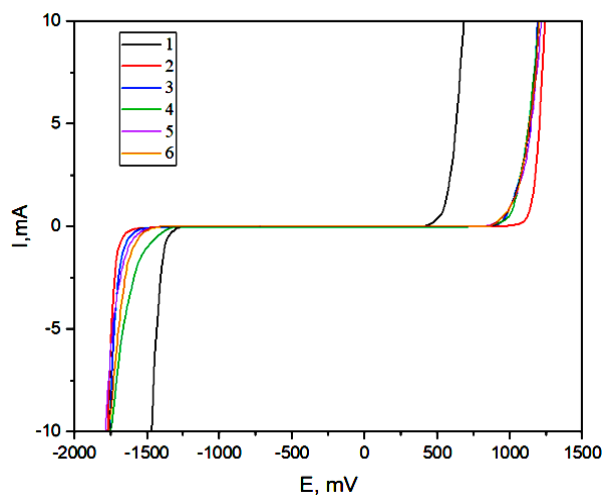


Fig. 5. Polarization curves of steel without (1) and with coatings obtained from base (2) electrolyte and modified SiO<sub>2</sub>·nH<sub>2</sub>O, g/L: 5 (3), 10 (4), 15 (5), 20 (6)

Fig. 5 shows the polarization curves obtained in a 3% NaCl solution. The evolution of hydrogen at the cathode and oxygen at the anode on AISI 304 steel occurs at potentials of – 1390 and 630 mV, respectively. When applying chromium oxide coatings, the processes of evolution of both hydrogen and oxygen become more complicated and proceed at potentials of – 1600...1750 mV for the cathode, 1130...1200 mV for the anode, depending on the concentration of  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  in electrolytes.

Based on these data, it can be concluded that the application of modified chromium oxide  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  coatings contributes to an increase in the shift in the potential for the onset of evolution of both hydrogen and oxygen, so such coatings can be recommended to protect steel from corrosion.

## CONCLUSIONS

It is shown that  $\text{Cr} \cdot \text{CrO}_x$  coatings have cracks, and the introduction of  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  into the electrolyte promotes the formation of a continuous coating. Although silicon was not found in the composition of the coating, the morphology changed significantly, the structure of the coatings obtained from modified  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  electrolytes is more finely crystalline than from what was obtained in the base electrolyte.

The composition of the coatings contains chromium and oxygen in the amount of 40.52 and 59.48%, respectively, which indicates the presence of chromium oxides of different oxidation states. Most likely, these are oxides  $\text{Cr}_2\text{O}_3$ ,  $\text{CrO}$ ,  $\text{CrO}_2$ ,  $\text{Cr}_3\text{O}_4$ .

The polarization curves indicate that the reactions of hydrogen and oxygen evolution are hindered at the cathode and anode, respectively. When applying chromium oxide coatings obtained from electrolytes without and with the modification of  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  on steel, the potential for the onset of hydrogen evolution is shifted by 220...350 mV to the electronegative side, depending on the concentration of  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ . The potential for the onset of oxygen evolution after the deposition of chromium oxide coatings is shifted to the electropositive side by 500...600 mV. The obtained results make it possible to recommend the use of the addition of  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  to the electrolyte to obtain chromium oxide coatings on steel with increased protective properties against corrosion.

## REFERENCES

1. V. Shtefan, N. Kanunnikova, A. Pilipenko, H. Pancheva. Corrosion Behavior of AISI 304 Steel in Acid Solutions // *Materials Today: Proceedings*. 2019, N 6, p. 150-157.
2. J.L. Marulanda Arevalo, F.J. Pérez Trujillo, S.I. Castañeda. Aluminum-silicon coatings on austenitic stainless steel (AISI 304 and 317) deposited by chemical vapor deposition in a fluidized bed: Recubrimientos de aluminio-silicio sobre acero inoxidable austenítico AISI 304 Y 317 por deposición química de vapor en lecho fluidizado // *Ingeniería e Investigación*. 2014, N 34, p. 5-10.
3. V.V. Shtefan, B.I. Bairachnyi, G.V. Lisachuk, O.Yu. Smirnova, V.A. Zuyok, R.O. Rud', O.V. Voronina. Corrosion of Aluminum in Contact with Oxidized

Titanium and Zirconium // *Material Science*. 2016, N 51, p. 711-718.

4. V.V. Shtefan, N.O. Kanunnikova, T.Ye. Goncharenko. Analysis of the Structure and Anticorrosion Properties of Oxide Coatings on AISI 304 Steel // *Material Science*. 2021, N 57, p. 248-255.

5. M. Alizadeh, A. Teymuri. Structure, indentation and corrosion characterizations of high-silicon Ni-Si nanocomposite coatings prepared by modified electrodeposition process // *Transactions Nonferrous Metals Society of China*. 2019, N 29, p. 608-616.

6. Патент на корисну модель 147835. Україна, МПК С25D 11/34. Спосіб формування захисних оксидних покриттів на нержавіючій сталі / В.В. Штефан, О.Ю. Смирнова, Н.О. Кануннікова, Н.С. Баламут. Заявник та власник патенту НТУ «ХПІ». № u2020 08156; заявл. 21.12.2020; опубл. 16.06.2021; Бюл. №24.

7. A. Karimzadeha, M. Aliofkhazraeia, F.C. Walsh. A review of electrodeposited Ni-Co alloy and composite coatings: Microstructure, properties and applications // *Surface and Coatings Technology*. 2019, N 327, p. 463-498.

8. G.K. Kiran. Electrodeposition and structural characterization of  $\text{MCrO}_3$  (M = La, Pr, Nd, Gd, Dy, and Y) perovskite oxide coatings on stainless steel substrates // *Materials Chemistry and Physics*. 2021, N 267, p. 124677.

9. В.В. Штефан, Н.О. Кануннікова, Н.С. Баламут. Структура та властивості хромоксидних покриттів, отриманих стаціонарним та нестаціонарним електролізом // *Resource- and energy-saving technologies in the chemical industry: Scientific monograph*. Riga, Latvia: "Baltija Publishing", 2022, 264 p.

10. Z.B. Zheng, Y.G. Zheng. Effects of surface treatments on the corrosion and erosion-corrosion of 304 stainless steel in 3.5% NaCl solution // *Corrosion Science*. 2016, N 112, p. 657-668.

11. V. Klimas, V. Pakštas, I. Vrublevsky, K. Chernyakova, A. Jagminas. Fabrication and Characterization of Anodic Films onto the Type-304 Stainless Steel in Glycerol Electrolyte // *The Journal of Physical Chemistry C*. 2013, N 117, p. 20730-20737.

12. V.V. Shtefan, N.A. Kanunnikova, S.A. Leshchenko, N.S. Balamut. Anodic dissolution of stainless steel in acid solutions // *Записки Таврійського національного університету ім. В.І. Вернадського. Серія «Технічні науки»*. 2019, т. 30(69), №2, ч. 2, с. 136-141.

13. E. Husain, A. Abdel Nazeer, J. Alsarraf, K. Al-Awadi, M. Murad, A. Al-Naqi, A. Shekeban. Corrosion behavior of AISI 316 stainless steel coated with modified fluoropolymer in marine condition // *Journal of Coatings Technology and Research*. 2018, N 15(5), p. 945-955.

14. V.V. Shtefan, A.Yu. Smirnova. Electrochemical formation of cerium-containing oxide coatings on titanium // *Russian Journal of Applied Chemistry*. 2013, N 86, p. 1842-1846.

15. V.V. Shtefan, A.Yu. Smirnova. Synthesis of Ce-, Zr-, and Cu-containing oxide coatings on titanium using microarc oxidation // *Russian Journal of Applied Chemistry*. 2015, N 51, p. 1168-1175.

16. В.В. Штефан, Н.С. Баламут, Н.О. Кануннікова. Корозійні характеристики сталі 08X18H10/Cr·CrO<sub>x</sub>·MO<sub>y</sub> (M = Ti, Al, Si) // *Colloquium-journal*. 2022, N 12, p. 27-30.
17. Y. Sun. Corrosion behavior of sediment electrocodeposited Ni-Al<sub>2</sub>O<sub>3</sub> composite coatings // *Materials Chemistry and Physics*. 2014, N 145, p. 476-483.
18. R.M.R. Junqueira A.P. de Andrade Manfridini, C.R. de Oliveira et al. Loureiro. Morphological, chemical and mechanical characteristics of anodic coating on stainless steel // *Surface Engineering*. 2013, N 29, p. 379383.
19. V.V. Shtefan, N.A. Kanunnikova. Oxidation of AISI 304 Steel in Al- and Ti-Containing Solutions // *Protection of Metals and Physical Chemistry of Surfaces*. 2020, N 56, p. 379-384.
20. V. Shtefan, N. Kanunnikova, N. Balamut. Anodic oxidation of AISI 304 steel in acidic solutions // *Proceedings of Odessa Polytechnic University*. 2018, N 3(56), p. 89-94.
21. В.В. Штефан, Н.С. Баламут, Н.О. Кануннікова, О.В. Кобзев, Імпульсний електроліз хромоксидного покриття на нержавіючій сталі // *Вчені записки Таврійського національного університету ім. В.І. Вернадського. Серія «Технічні науки»*. 2022, т. 33(72), №3, с. 92-98.
22. А.И. Волков, И.М. Жареный. *Большой химический справочник*. Минск «Современная школа», 2005, 608 с.

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### ЕЛЕКТРООСАДЖЕННЯ ХРОМОКСИДНИХ ПОКРИТТІВ З ЕЛЕКТРОЛІТІВ, МОДИФІКОВАНИХ SiO<sub>2</sub>·nH<sub>2</sub>O

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Для підвищення корозійної стійкості нержавіючої сталі від локальних видів корозії на її поверхню нанесли хромоксидні покриття, отримані з електролітів, що модифіковані SiO<sub>2</sub>·nH<sub>2</sub>O. Встановлено, що покриття з електроліту з додаванням SiO<sub>2</sub>·nH<sub>2</sub>O є суцільними, без тріщин, та дрібнокристалічними у порівнянні з отриманим покриттям з базового електроліту. Елементний аналіз не показав наявності силіцію у складі покриття, який отриманий з модифікованого SiO<sub>2</sub>·nH<sub>2</sub>O електроліту, проте показав наявність більшої кількості хрому в порівнянні з покриттям, отриманим з базового електроліту. На поляризаційних залежностях спостерігається ускладнення виділення водню на катоді, та кисню на аноді, що свідчить про зниження електропровідності отриманих покриттів. Дані результати дозволяють рекомендувати використання добавки SiO<sub>2</sub>·nH<sub>2</sub>O до електроліту для отримання на сталі хромоксидних покриттів з підвищеними захисними властивостями від корозії.