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## Original articles

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## Characterization of the properties of thin $\text{Al}_2\text{O}_3$ films formed on structural steel by the sol-gel method

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### Abstract

The sol-gel method was used to obtain single and double layer oxide-aluminium films on the surface of 08kp structural steel for protection against corrosion. The sol-gel system was prepared according to the Yoldas method by hydrolytic polycondensation of aluminium isopropoxide in the presence of acetic acid at a temperature of 85–90 °C. The pH, size, and zeta potential of boehmite particles were measured, and the corrosion behaviour of steel in the resulting colloids was studied. At room temperature, a boehmite hydrogel layer was applied by immersing the steel samples in a gel, incubating them in the gel, and drying them in the presence of ammonia vapour for the suppression of corrosion. Heat treatment at 500 °C in an air atmosphere was used for the decomposition of boehmite with the formation of alumina and for the fixation of the film on the surface of the substrate. A second film layer was applied in a similar manner on top of a fully formed first layer.

The surface morphology of the obtained films was studied by scanning electron and atomic force microscopy. Electrochemical research methods - potentiometry, voltammetry, and electrochemical impedance spectroscopy were used for a comparative study of the anticorrosion properties of single and double layer aluminium oxide coatings on steel in a 3.5% sodium chloride solution. It was shown that the coatings obtained according to the described scheme have good adhesion to the steel surface. Compared with the control sample, coated steel electrodes were characterized by a shift in the stationary potential by more than 0.6 V, and the onset of active electrochemical oxidation by more than 1 V in the positive direction. The kinetics of the anode and cathode processes changed, leading to a decrease in the corrosion current by more than two orders of magnitude.

The application of the method of electrochemical impedance spectroscopy allowed establishing a 2.5-hour high anticorrosive efficiency of a double layer oxide-aluminium coating on steel in a solution of sodium chloride.

**Keywords:** sol-gel method, alumina, films, deposition, structural steel, corrosion.

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## 1. Introduction

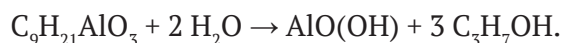
Structural steels, including low-carbon ones, are known to be one of the most popular structural metals. At the same time, they are characterized by low corrosion resistance, therefore products require effective corrosion protection, which can be provided, in particular, by oxide (ceramic) coatings. Ceramic coatings (SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and others) are of great practical interest, since they possess high chemical-thermal stability and therefore are usually deposited on metals for the improvement of their characteristics in high-temperature aggressive environments [1-5]. In aqueous solutions, these coatings usually have high electrochemical potentials and are cathode coatings; therefore, they can only perform their functions if they do not have pores, cracks, and form a physical barrier for the penetration of the solution to the steel substrate [6].

Various methods can be used for the deposition of oxide coatings on a metal base – chemical or physical vapour deposition, plasma deposition, electrophoresis, sol-gel deposition [7–12]. The sol-gel method of producing oxide films on metals, based on controlled hydrolytic polycondensation of organic or inorganic compounds of metals and/or silicon is of great interest [2, 13–15]. Moreover, the properties of the deposited layers are determined by both the size and shape of the synthesized particles, and their chemical nature. Thin films of aluminium oxide Al<sub>2</sub>O<sub>3</sub> are characterized by their excellent dielectric properties and high thermal and chemical stability, and therefore are promising materials for study [16]. However, with the deposition of coating, for example, on low alloy steel, problems associated with the corrosive action of the sol-gel system on the substrate during film formation occur (the stage of immersion in a colloidal solution and drying of the layer), shrinkage of the film during drying, and heat fixing [17]. This leads to a deterioration in the adhesion of the coating to the substrate, the penetration of solutions through the through pores of the coating to the metal/film interface. Multilayer Al<sub>2</sub>O<sub>3</sub> films are characterized by more reliable protective properties [6]. The methods of deposition the layers and, accordingly, the protective effects can vary significantly. This work presents the results of comparative studies of the properties of protective single layer and double layer Al<sub>2</sub>O<sub>3</sub> coatings obtained on 08kp low alloy steel by the sol-gel method using the Yoldas process.

## 2. Experimental

### 2.1. Production of the sol-gel system

The boehmite dispersion was prepared from aluminium isopropoxide (AIPO), Acros organics, 98 %, in accordance with the Yoldas process [18]. AIPO was dissolved in hot (85–90 °C) distilled water with continuous stirring. During dissolution, the AIPO hydrolysis reaction proceeded with the formation of boehmite sol AlO(OH):



Peptization of the obtained particles was carried out for about 24 h at a temperature of 85–90 °C using acetic acid (chemically pure). The molar ratio of the components of the reaction mixture AIPO/N<sub>2</sub>O/acid was 1/100/0.15. A sol-gel transition with the formation of a translucent gel was observed after ~12 h of the incubation of the solution at the indicated temperature. Physicochemical characteristics of colloidal systems were determined using a Kellymeter pH-009 (I) (Kelly Union Electronics, Hong Kong) pH meter and a Zetasizer Nano particle size and zeta potential analyser (Malvern Instruments Ltd., the UK).

### 2.2. Preparation of 08kp steel samples

The coating was applied to 08kp carbon structural steel (composition, %: Fe ~98 %, C 0.05–0.11; Si up to 0.03; P up to 0.035; As up to 0.08; S up to 0.04; Mn 0.25–0.5; Ni up to 0.25; Cr up to 0.1; up to 0.25 [19]). Samples were degreased in acetone, then in an alkaline solution at a temperature of 70–75 °C for 30 min, washed with hot water and dried.

### 2.3. Deposition of coating

Samples were immersed in boehmite gel, incubated in it for 3 min, and then removed. The boehmite hydrogel layer was dried in an air-ammonia medium at room temperature [17]. Afterwards, the sample with a dried film was heat treated in an air atmosphere at a temperature of 500 °C for 1 h. In order to obtain a double layer coating, a second layer was applied over the thermofixed first layer, dried and heat treated, in the same manner as the first layer. According to the literature data [7, 13, 20, 21], as a result of heat treatments at a specified temperature, boehmite decomposes with the formation  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The introduced organic anions also decompose into CO<sub>2</sub> and H<sub>2</sub>O.

#### 2.4. Investigation of properties of $Al_2O_3$ coatings

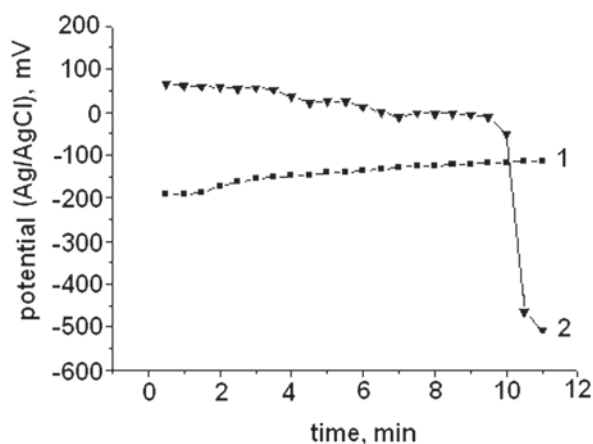
The morphology of the  $Al_2O_3$  coatings was studied by electron scanning microscopy, SEM (scanning electron microscope Vega 3 SBH, Tescan, Czech Republic) and atomic force microscopy, AFM (scanning atomic force microscope SOLVER 47 PRO, “NT-MDT”, Russian Federation)

The corrosion properties of the metal/oxide system ( $Al_2O_3$ ) were studied in a 3.5% aqueous NaCl solution at a temperature of  $25 \pm 1$  °C. Potentiometric and voltammetric studies were carried out in a three-electrode electrochemical cell using a PI 50-Pro-3 pulse potentiostat with automatic data recording and PS Pack2 software (OOO “Elins”, Russian Federation). The reference electrode was a saturated silver chloride electrode, the loop electrode was Pt. The method of electrochemical impedance spectroscopy was used for the evaluation of the protective properties of the coating at an open circuit potential, the cell voltage was 10 mV, the frequency range of the alternating current was  $10^{-2}$ – $10^6$  Hz, the counter electrode was Pt/Pt-black. The studies were carried out using a Solartron SI 1260A impedance and amplitude-phase characteristics analyser (Solartron Analytical, the UK), and ZPlot and ZView2 software packages.

### 3. Results and discussion

#### 3.1. Corrosion behaviour of steel in boehmite hydrogel

As a result of the hydrolysis of aluminium isopropoxide, the boehmite dispersion had the following characteristics: pH = 8, average particle



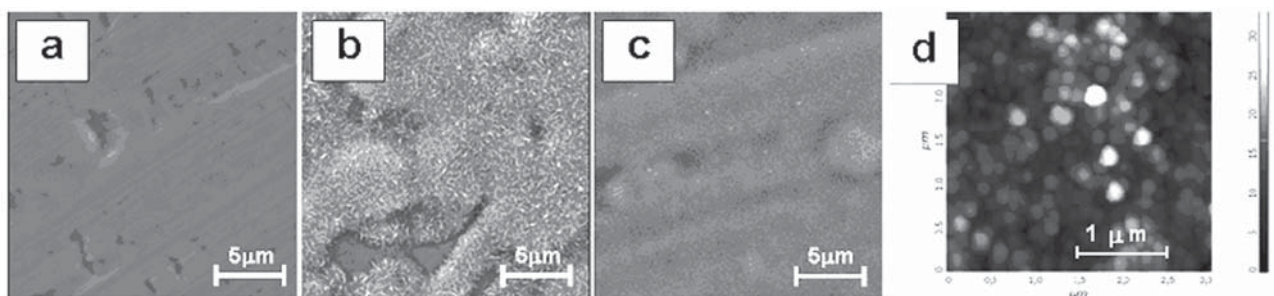
**Fig. 1.** Change in the potential of 08kp steel samples in colloidal systems without a peptizer (1) and with  $CH_3COOH$  (2) Temperature 23 °C

size of 1234 nm, zeta potential of 0.4–0.6 mV. For the peptization of boehmite particles and sol-gel transition according to the Yoldas process, acetic acid was introduced. As a result, the obtained colloidal solution had a pH of 5, an average particle size of 300 nm, and a zeta potential of 32–35 mV. At pH = 8, alloys with a high iron content were sufficiently corrosion-resistant, however with increasing acidity, the risk of developing a corrosion process increased. The change in the potential of steel samples in the initial dispersion and  $AlO(OH)$  hydrogel is shown in Fig. 1. A multidirectional change of the stationary potential  $E_{st}$  was observed due to the difference in the hydrogen ion exponent of colloidal systems. In a slightly alkaline solution, a gradual refinement of the potential occurs, while in a slightly acidic solution, a gradual decrease in the value of  $E_{st}$  during the first 10 min and an abrupt decrease after 11–12 min of immersion were revealed. Probably, such changes in the steel potential also occur in a thin wet boehmite layer even after its extraction from the colloid, as a result of which signs of the development of a corrosion process appeared, specifically a staining of the layer, which is characteristic of Fe (III) compounds. It was found that this process negatively affects the adhesion of the coating to the substrate, and it can be eliminated by drying the hydrogel layer in an air-ammonia medium [17].

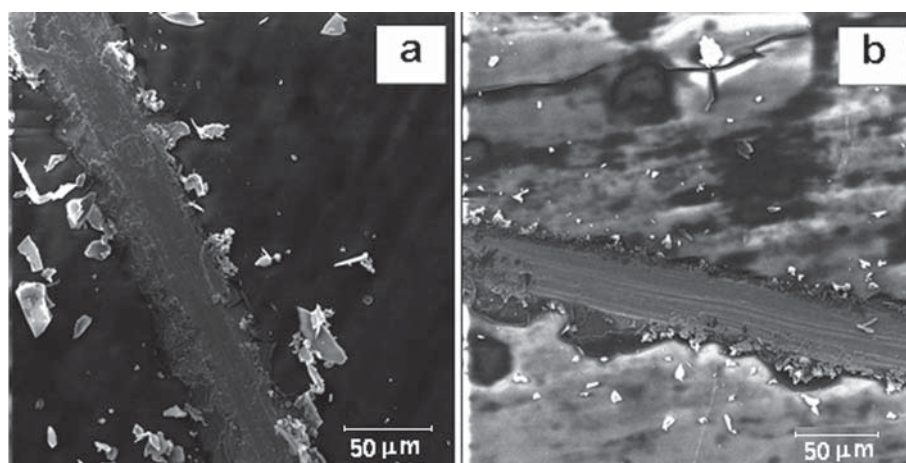
#### 3.2. Morphology of $Al_2O_3$ -coatings

The morphology of the initial and heat-treated steel surface, as well as a single layer  $Al_2O_3$  coating deposited on steel is shown in Fig. 2. On SEM images, it is seen that the coating is thin and the initial structure of the substrate is visible. The film is impermeable to atmospheric oxygen, and iron oxidation products were not formed. The AFM image of the coating (Fig. 2d) showed that the aluminium oxide particles were uniform in size and shape, and their size did not exceed 200 nm.

The differences between single and double layer coatings, both in appearance and in relation to scratching, are shown in Fig. 3. As can be seen, the second coating layer was unevenly deposited on the previous layer. However, higher adhesion to the substrate and ductility of the coating were obvious.



**Fig. 2.** SEM-images of the initial (a) and thermally oxidized (b) surface of the steel, steel with an aluminium oxide coating (c); AFM image of the coating (d)



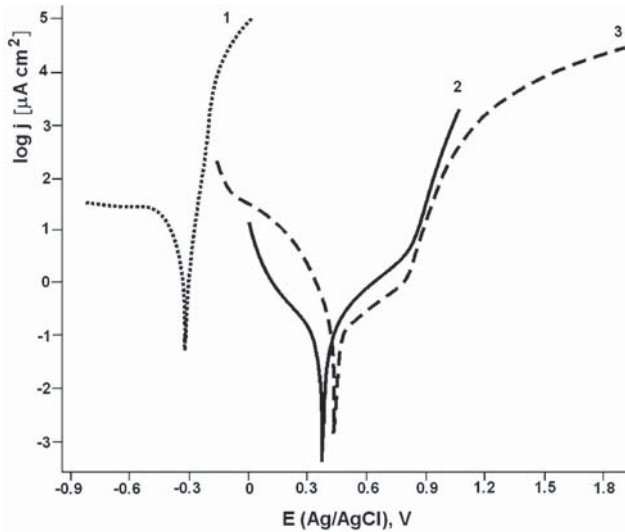
**Fig. 3.** SEM image of a scratch applied to a single layer (a) and double layer (b) aluminium oxide coating on steel

### 3.3. Corrosion behaviour of steel in a sodium chloride solution

The voltammetry and electrochemical impedance spectroscopy are highly informative electrochemical methods for studying the corrosion behaviour of metals in electrically conductive media [22, 23]. The corrosion diagrams (Evans diagrams) of the initial 08kp steel sample and samples with a single and double layer coating are shown in Fig. 4. The aluminium oxide films formed on the steel surface altered the corrosion-electrochemical behaviour of the metal, studied in a 3.5 % NaCl solution. As can be seen, the coating contributed to the shift of the stationary potential of the electrode in the positive direction by more than 600 mV, it changed the nature of the anodic and cathodic processes that occurred at the electrode|electrolyte interface. An analysis of the Evans diagram for an uncoated steel electrode showed that the corrosion process proceeds with a cathodic velocity control (due to the occurrence of the oxygen diffusion-limited current, the restoration of which provides the cathodic depolarization of the electrode).

Aluminium oxide has dielectric properties, and the film can isolate the surface of the metal from the electrolyte. Due to this, the active electrochemical oxidation of the film-coated steel was shifted by more than 1 V in the positive direction in comparison with the control sample. The change in the kinetics of the anodic and cathodic processes together led to a decrease in the corrosion current by more than two orders of magnitude. The electrode with a double layer coating has a slightly more positive stationary potential, but the nature of the polarization curves of electrodes with single and double layer coatings was similar.

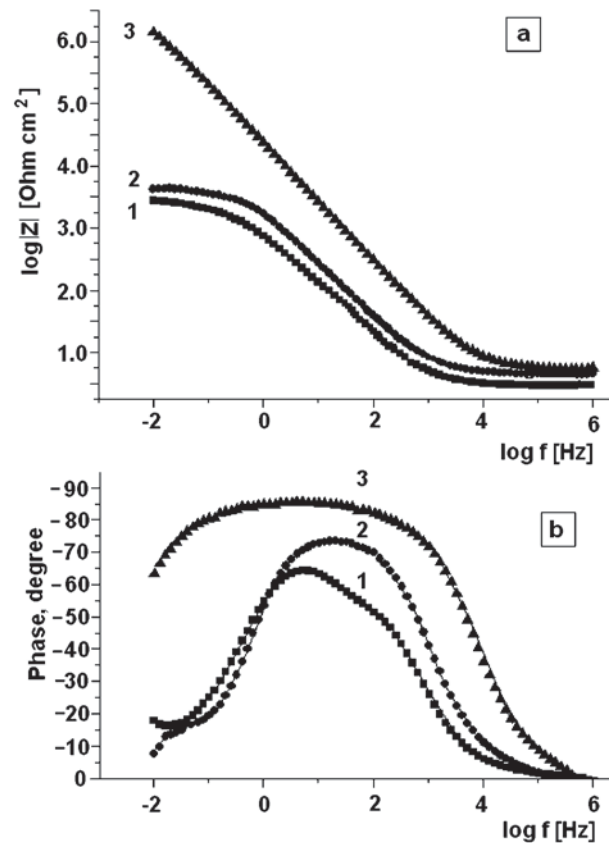
The state of the electrode|electrolyte interface and the changes occurring when the electrolyte penetrated through the pores of the film to the metal surface were studied by the method of electrochemical impedance spectroscopy. The frequency dependences of the impedance module  $|Z|$  and the phase angle (Bode diagram) of 08kp steel samples after 0.5 h incubation in a 3.5 % NaCl solution are shown in Fig. 5. As can be seen, the



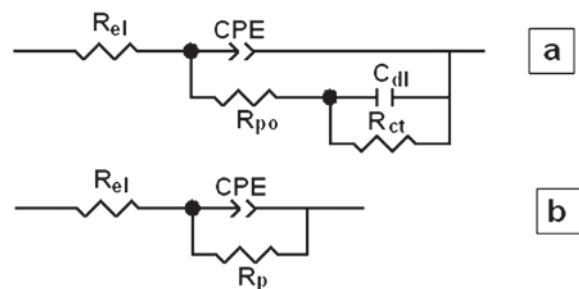
**Fig. 4.** Corrosion diagrams of a steel electrode without a protective coating (1) and with aluminium oxide single layer (2) and double layer (3) coatings

coated electrodes were characterized by higher impedance values and phase angle in comparison with the control sample. An analysis of the low-frequency part of the impedance spectrum showed a much more effective protection of the steel surface with a double layer coating:  $f = 0.01$  Hz  $|Z| > 10^6$  Ohm  $\text{cm}^2$ , while for electrodes with a single layer coating and without coating  $|Z| < 10^4$  Ohm  $\text{cm}^2$ . In addition, the electrode with a double layer coating showed alternating current behaviour close to being purely capacitive (in a wide frequency range, the phase angle value approached  $-90^\circ$ , and the  $\log |Z| - \log f$  dependence was linear).

Probably, the single layer coating has a certain number of transverse pores. Therefore, according to the nature of the change, the frequency dependences of the impedance and phase angle of such an electrode and the initial sample were similar. The obtained dependences (Fig. 5a, b, curves 1 and 2) were modelled by a standard equivalent electric circuit (EEC) for a corroding metal with a defective (porous) passive coating [7], shown in Fig. 6a. At the same time, for steel with a double layer coating (Fig. 5a, b, curves 3), EEC for metal with a non-porous coating [24] was applicable, Fig. 6b. In these equivalent electrical circuits:  $R_{el}$  – electrolyte resistance, CPE – constant phase element, reflecting non-ideal coating capacitance,  $R_{po}$  – resistance of the coating/layer of corrosion products,  $C_{dl}$  – the double layer capacitance at the metal|electrolyte interface,



**Fig. 5.** Frequency dependences of the impedance module  $|Z|$  (a) and phase angle (b) of 08kp steel samples after 0.5 h exposure in a 3.5 % NaCl solution: without a coating (1), with an  $\text{Al}_2\text{O}_3$  coating – single layer (2) and double layer (3)



**Fig. 6.** Models of equivalent electrical circuits of corroding metal with a non-conductive coating (a) and metal with an insulating coating (b). Designations of EEC elements are given in the text

$R_{ct}$  – charge transfer resistance,  $R_p$  – resistive component of the  $\text{Al}_2\text{O}_3$ -coating. Impedance  $Z_{CPE}$  is represented by the expression [25, 26]:

$$Z_{CPE} = \frac{1}{Q(j\omega)^n},$$

where  $Q$  – constant CPE element ( $\text{F cm}^{-2} \text{s}^{-(1-n)}$ );  $\omega$  – circular frequency,  $\omega = 2\pi f$  ( $\text{rad s}^{-1}$ );  $j^2 = -1$  and

$n$  – exponent of the CPE element (shows the depression angle, which characterizes the deformation of the capacitive loop in the Nyquist plot). In the case when  $n = 1$ , the CPE element is converted into capacitance.

The calculated EEC parameters for a corroding uncoated steel electrode and for coated electrodes are presented in the Table. From these data, it follows that a thin aluminium oxide film prevented the active development of the corrosion process and the formation of a loose layer of corrosion products. However, probably, due to the presence of transverse pores, within 0.5 h after the start of corrosion tests, the solution had already penetrated to the metal|electrolyte interface. By the end of the test the  $C_{dl}$  and  $R_{ct}$  of the control sample and the sample with a single layer coating had similar values.

The double layer coating was characterized by capacitance values lower by more than an order of magnitude when compared to a single layer

coating and a very high value of the resistive component of the coating, which was associated with a higher thickness of the oxide layer. The value of the exponent  $n > 0.9$ . The study [27] demonstrated that for  $1 > n > 0.9$ , the value of  $Q$  ( $F\ cm^{-2}\ s^{(1-n)}$ ) can be equated to the film (coating) capacitance  $C_f$  ( $F\ cm^{-2}$ ). As can be seen from the Table and Fig. 7, after 2.5 h of contact with a corrosive medium, the sample with a double layer coating increased the capacitance by more than an order of magnitude. This finding indicated the filling of the pore space of the film with electrolyte and the actual termination of the protective effect of the coating. In this case, the alternating current behaviour of such an electrode resembles the behaviour of a single layer electrode.

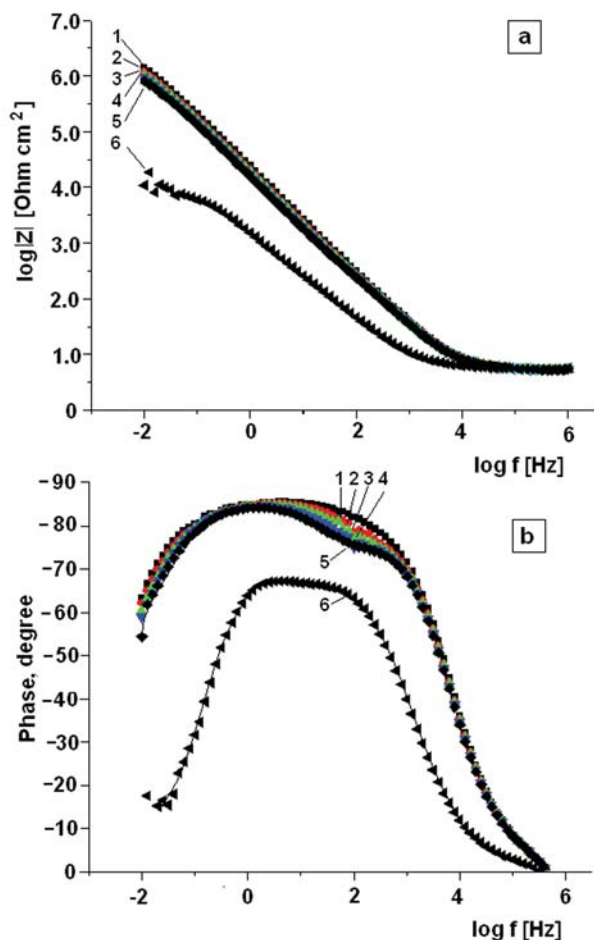
#### 4. Conclusions

Studies have shown the possibility of obtaining aluminium oxide films with satisfactory adhesion to the substrate using the sol-gel method on

**Table.** Parameters of the equivalent electrical circuit of the studied electrodes in 3.5 % sodium chloride solution depending on immersion time

Time, h	$R_{el}$ , Ohm cm <sup>2</sup>	$Q$ , $\mu F\ cm^{-2}\ s^{-(1-n)}$	$n$	$R_{po}$ , kOhm cm <sup>2</sup>	$C_{dl}$ , mF cm <sup>-2</sup>	$R_{ct}$ , kOhm cm <sup>2</sup>	$R_p$ , kOhm cm <sup>2</sup>
Uncoated steel							
0.5	7,2	311,7	0.75	2,80	21.9	3.7	–
1.0	7,3	353,7	0.76	2,52	16.6	1.9	–
1.5	7,2	387,4	0.76	2,28	13.2	1.5	–
2.0	7,2	418,2	0.76	2,14	12.9	1.6	–
2.5	7,2	457,6	0.76	2,06	13.2	1.7	–
3.0	7,2	492,1	0.76	2,06	13.7	1.7	–
Steel with a single layer Al <sub>2</sub> O <sub>3</sub> coating							
0.5	4.5	105.9	0.86	3.96	8.1	1.1	–
1.0	4.5	125.7	0.85	2.86	8.5	1.5	–
1.5	4.4	143.6	0.85	2.42	9.4	1.6	–
2.0	4.4	162.4	0.86	2.18	10.3	1.5	–
2.5	4.5	173.6	0.86	1.86	12.2	1.3	–
3.0	4.6	197.0	0.85	1.87	14.0	1.5	–
Steel with a double layer Al <sub>2</sub> O <sub>3</sub> coating							
0.08	8.5	6.10	0.92				7333
0.5	5.8	7.87	0.93	–	–	–	3994
1.0	5.7	9.29	0.92	–	–	–	3291
1.5	5.7	10.16	0.91	–	–	–	2829
2.0	5.7	11.12	0.90	–	–	–	2514
2.5*	5.6	12.33	0.89	–	–	–	2083
3.0	5.5	146.6	0.78	10.8	2.3	3.5	–

\* this time limits the resistance of the coating to the penetrating effect of the electrolyte



**Fig. 7.** Frequency dependences of the impedance module  $|Z|$  (a) and phase angle (b) of O8kp steel samples with a double layer coating after incubation in 3.5 % NaCl solution for 0.5 h (1); 1.0 h (2); 1.5 h (3); 2.0 h (4); 2.5 h (5) and 3.0 h (6)

low-alloy structural steel. The double layer film creates a physical barrier for the penetration of a corrosive solution to the surface of the metal, the effectiveness of which exceeds 2.5 h. However, the resulting coatings have a higher or lower permeability towards the components of the solution. This was due to the thermal decomposition and removal of the decomposition products of organic anions introduced into the film during the stage of preparation of boehmite hydrogels. Since the critical diameter of the acetic acid molecule is 5.1 Å (the radius is 2.55 Å, respectively) [28], the pore size formed during heat treatment of a hydrogel layer exceeds that of water molecules (1.9 Å [29]) and hydrated  $\text{Cl}^-$  ions (2.28 Å [30]). Partial overlapping of the pores of the first aluminium oxide layer by the deposition

of a second layer resulted in the formation of an effective protective film.

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### Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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