

SILICATE COATINGS FILLED WITH ZINC POWDER AND GRAPHENE NANOPLATES FOR STEEL CORROSION PROTECTION

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Abstract: The method is proposed to protect the carbon steel from corrosion by silicate coatings filled with powdered zinc and graphene nanoplates obtained by thermal splitting of graphite. The conditions for steel pre-treatment in an alkaline solution containing citrate ions and a nonionic surfactant, for the production of potassium liquid glass composition with the addition of zinc and graphene powders are selected. It is shown that coatings 70–80 μm thick, cured at room temperature for three days and containing 80–90 wt. % zinc, 7–12 wt. % silicon dioxide and 0.2 wt. % carbon have the highest adhesion, water resistance and protective ability. The study of steel corrosion in 3.5% NaCl solution using methods of voltammetry and the dependence of open circuit potential on the test duration showed that silicate coatings filled with zinc and graphene provide cathodic polarization of steel and protect it from corrosion better than twice as thick coatings obtained by hot galvanizing. Graphene nanoplates enhance the contact of zinc particles with each other and with steel, promoting its cathodic polarization. Using scanning electron microscopy and X-ray spectral microanalysis, it has been shown that zinc corrosion products fill the pores of the near-surface layer of coatings, enhancing their protective ability.

Keywords: steel, silicate coatings, zinc, graphene nanoplates, corrosion, cathodic polarization, pore healing.

Introduction

Carbon steels are wide-spread materials used in mechanical engineering, energetics, and production of tools, pipelines, building fittings due to their high strength, resiliency and relative cheapness. The main drawback of these steels is low corrosion resistance.

It is known [1] that direct losses are caused by corrosion of metal products in the developed countries amounting to 3–4% of the gross domestic product. However, corrosion can also cause emergency situations during the operation of boilers, engines, bridges, etc. Approximately 25–30% of these losses could be avoided in the case of effective anti-corrosion protection technologies currently available.

Modern methods of protecting metals from corrosion can be classified as follows: 1) alloying metals and production of corrosion-resistant alloys; 2) adding corrosion inhibitors into the corrosive environment; 3) depositing barrier and insulating coatings that prevent metal contact with a corrosive environment; 4) shifting the protected metal potential either to the cathode region to reduce the corrosion rate, or to the anode region to convert the metal to a passive state [1–3].

The most versatile is the corrosion protection method using polymer, inorganic (based on chromates, phosphates, oxides, silicates, etc.) or metal coatings [1, 4]. The latter are able to avoid the contact of a substrate with the corrosive environment, and to provide electrochemical protection of the base metal due to its cathodic polarization as well. Of particular interest are composite coatings capable of simultaneously implementing a combined electrochemical and passive protection, which release the corrosion inhibitor or contain a self-healing agent [3–5].

Until today, zinc is the most common material for obtaining cathodic protective coatings on steel [2, 6]. Metallic zinc coatings are usually obtained by electrochemical deposition from solutions or hot-dip galvanizing in zinc melt. Specially equipped workshops and significant energy amounts are required in these cases. Another way of cathodic protection of steel against corrosion is the application of composite coatings consisting of an organic or inorganic polymer matrix and Zn powder filler [3–5]. Inorganic silicate matrix coatings obtained by sol-gel method are especially promising, because they are more environmentally friendly, cheaper and more stable to operate as compared to traditional polymerization products of acrylates, urethanes or oligomers containing epoxy groups.

The corrosion protection effectiveness of compact zinc coatings is determined by their thickness and strongly depends on the presence of pores and cracks. To ensure reliable cathodic protection by composite zinc-rich coatings, it is necessary to provide electrical contacts of metal filler particles with each other and with the protected substrate [7, 8]. In such composites, the quota of zinc powder should be at least 60–70 wt. % [9], and the requirements for adhesive and cohesive strength of coatings are especially high. A rise of zinc content in coatings leads to an increase in the number of ohmic contacts between metal particles and the electrical conductivity of the composites. However, at the same time, mechanical properties of coatings may deteriorate. When the filler content exceeds 96–97 wt. % the polymer matrix loses its strength and the protective ability of coatings decreases.

It is possible to create a network of interconnected particles without increasing the quota of zinc powder in the matrix by introducing additional conductive filler [7, 10] or using lamellar zinc particles instead of spherical ones. So, zinc lamellar coatings are known, which include zinc flakes, sometimes with the addition of aluminum flakes in an amount up to 10 wt. % [11, 12]. Carbon nanomaterials, in particular, graphene nanoplates are promising conductive fillers for composite zinc-rich coatings [13, 14].

The aim of this work is to obtain composite silicate-matrix coatings filled with zinc and carbon nanomaterial powders for the protection of carbon steel against corrosion, to study their protective ability in 3.5% NaCl water solution and to reveal its mechanism.

Experimental part

Potassium liquid glasses with $\text{SiO}_2/\text{K}_2\text{O}$ molar ratio, or silicate modulus, equal to 3 (PLG-3) and 5 (PLG-5) were prepared by dissolving an amorphous SiO_2 powder (silicon dioxide "Kovelos 35/05", 98 % SiO_2 in dry residue) in a concentrated KOH solution at a temperature of 70 ± 10 °C and stirring. The content of SiO_2 in the liquid glasses was 20 wt.%.

Compositions for obtaining silicate-matrix coatings filled with zinc were prepared by mixing liquid glasses with Zn powder (zinc dust Fine Zink Powder FH 800, Ever Zinc, Ans, Belgium; fineness 2.5–4.5 μm , zinc content 99 wt. %).

Thermally exfoliated graphite (TEG) was used as a carbon filler of the silicate matrix together with zinc. This carbon material consisted of graphene nanoplates obtained by the graphite powder processing in the solution of sodium in the liquid ammonia, followed by the rapid vacuum heating and washing with water [15]. The aqueous suspension of TEG with the addition of dimethyl alkylbenzylammonium chloride as a cationic surfactant was sonicated. This suspension was mixed with the liquid glass containing Zn powder. The concentration and volume of the added TEG suspension was selected in order to obtain about 0.2 wt. % carbon in the solid composite coatings.

The resulting Zn–PLG or Zn–TEG–PLG compositions were applied to the surface of the carbon steel plates (Russia standart – 08KP, EU – DD13, USA – A622DQDS) with a brush in two layers. The first intermediate layer was dried at 20 ± 3 °C for 30 min. The final layer was dried and cured at the same temperature for 24–96 hours. The coating thickness after the drying was 70–80 μm (measurement accuracy 5 μm).

The SiO_2 content in the obtained composite coatings was 7–12 wt. %. The amount of zinc powder was selected so that zinc content in the obtained coatings was 80–90%.

Preliminary preparation of the steel surface included operations of the grinding, degreasing and treatment in the developed aqueous solution, 1 dm³ of which contained 150 g KOH, 120 g of citric acid, and 6 g of the surfactant CAPAO (cocamidopropylamine oxide). Citrate ions ensured the binding of iron ions into soluble complex compounds [16] and the removal of corrosion products, the surfactant was necessary for wetting the steel surface, and the hydroxyl groups adsorbed on its surface provided adhesive interaction with liquid potassium glass. After this treatment, the steel was washed with water and dried at a room temperature.

The adhesion of coatings was measured by applying a grid of scratches with a step of 1 mm, followed by the peeling off with an adhesive tape and measurement of the area of the peeled coating as a percentage of the original one.

The water resistance of composite coatings was assessed by the change in the weight of the samples after their immersion into distilled water for 1 hour and drying at 20 ± 3°C to a constant weight.

The coating porosity was evaluated by the oil absorption technique, based on the measurement of the total volume of pores in the layer available for oil penetration. For this the samples of steel with coatings were dehydrated by drying in the silica gel desiccator and immersed in the mineral oil heated to 150°C ($\rho_{oil} = 0.857 \text{ g/cm}^3$) until the gas evolution stops. The samples extracted from the oil were cooled to room temperature and the excess oil was carefully removed with filter paper. After that, the volume of pores in the sample was calculated using the formula:

$$V = \frac{m_2 - m_1}{\rho_{oil}},$$

where m_1 is the initial mass of the sample; m_2 is the mass of the sample after immersion in the oil. The volume of pores was normalized to the area of each sample.

The protective ability of coatings during their treatment in a 3.5% sodium chloride solution was determined by three methods: a) assessment of the coatings appearance after their treatment for 20–55 days; b) recording of anodic and cathodic polarization curves which illustrate the behavior of coated steel samples in NaCl solution in semilogarithmic coordinates and the analysis of the corrosion diagrams obtained; c) study into the open circuit potential (OCP) evolution of the samples with an increase in the duration of their immersion in the corrosion medium from 1 to 360 hours. For electrochemical studies, we used Autolab PGSTAT204 potentiostat-galvanostat. Polarization curves were recorded in the potentiodynamic mode, potential range from –1.1 V to +0.1 V; sweep rate was 1 mV/s; coated steel samples were used as working electrodes and silver chloride as the reference electrode.

SEM images of the surface of coatings and their cross-sections were obtained using electron microscopes LEO 1420 and LEO 1455VP. X-ray spectral microanalysis of the samples was carried out using energy-dispersive nitrogen-free spectrometer Aztec Energy Advanced X-Max 80 scanning electron microscope (Oxford Instruments, UK). The spectra were recorded for at least 300 s. Quantitative analysis was carried out using software calculation of spectra based on the comparison with reference samples and the level of bremsstrahlung.

Results and discussion

Effect of composition and curing time of coatings on their adhesion, water resistance and porosity

The research data on the effect of coatings composition and their curing time on the adhesion of coatings to steel showed that the adhesion of coatings based on low modulus PGL-3 is higher as compared with this characteristic of coatings obtained from the PGL-5 with high modulus. The increase in curing time of coatings from 24 to 96 hours causes a slight rise of the adhesion. The addition of TEG into the silicate matrix containing zinc filler causes a decrease in the adhesion of coatings. Nevertheless, the adhesion of coatings based on the PLG-3 matrix filled both with zinc

and TEG cured for 96 h, is rather high. Thus, the area of peeled off coating is about 7–10 %, that is down by 5–7 times from the coatings based on the PLG-5.

One of the criteria for evaluating the protective ability of composite coatings in a liquid corrosive medium is their water resistance. Just applied silicate coatings dissolve in water, but lose this ability upon curing owing to the silicate polymerization [17]. Therefore, it was important to choose the duration of curing of the coatings sufficient for the loss of solubility in water.

Curves in Fig. 1 are illustrative of changes in the weight of steel samples covered with silicate coatings after their treatment within one hour in water as a function of curing time. As a result of partial dissolution of the silicate matrix, the weight of coatings decreases by 1.5–4.8% depending on the coatings composition and the curing time. The most significant change in the solubility and an appropriate rise in the water resistance of coatings occur in the first 48 hours of curing in air at a room temperature. Further, the curing process slows down and after 72 hours the mass of samples almost does not change after their treatment in water.

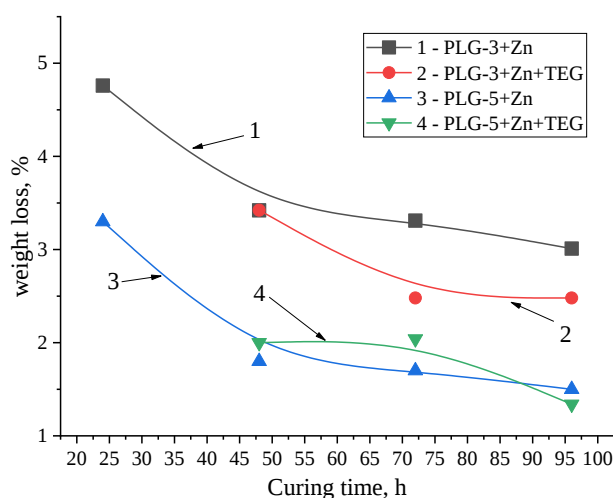


Fig. 1. Weight loss of coatings (%) after 1 hour water immersion depending on the curing time:

1 – PLG-3 + Zn, 2 – PLG-5 + Zn, 3 – PLG-3 + Zn + TEG, 4 – PLG-5 + Zn + TEG

Coatings based on high modulus PLG-5 filled with zinc are more water resistant as compared to PLG-3 + Zn coatings. The addition of TEG into PLG-5 + Zn coatings does not practically affect their water resistance. However, in the case of PLG-3 + Zn coatings, the addition of TEG results in a slight increase in water resistance. The weight loss in water testing of coatings based on silicate matrix filled with both zinc and TEG after their curing for 72 hours does not exceed 2.5%. It does not change with increasing curing time up to 96 hours.

The porosity estimation technique used in the work provides a measurement of the total volume of pores and cracks in coatings available for the penetration of the heated oil (Table). Corrosion of zinc in the coating and iron in the substrate occurs primarily in these pores and cracks. Experimental data are indicative that the porosity of coatings based on low modulus PGL-3 matrix filled with zinc or Zn + TEG is 1.5 times lower compared with their analogues obtained using high modulus liquid glass PGL-5. The main reason for this difference is the presence of cracks in the latter coatings. The addition of TEG in the silicate coatings filled with zinc either does not affect the total pore volume or, in the case of a PLG-3 matrix, reduces it by about 10%.

Table. The volume of pores and cracks in silicate coatings filled with zinc and TEG measured by the oil absorption

Sample	Pore volume $\cdot 10^6$, dm^3/cm^2
PLG-3 + Zn	$1,1 \pm 0,2$
PLG-5 + Zn	$1,5 \pm 0,2$
PLG-3 + Zn + TEG	$1,0 \pm 0,3$
PLG-5 + Zn + TEG	$1,5 \pm 0,4$

Corrosion study

The change in the appearance of coatings on steel after their treatment in 3.5% NaCl solution was evaluated. In the case of steel corrosion, red-brown spots of iron oxidation products appear on the surface of the samples. Corrosion of zinc filler causes the appearance of white spots of poorly soluble zinc compounds. Such observations made it possible to choose a coating thickness of about 80 μm . Thinner coatings did not protect steel from corrosion irrespective of their composition and the curing time. A further increase in the thickness of the coatings did not provide an increase in their protective ability, but sharply worsened their adhesion and often led to the appearance of cracks and corrosion of iron through them.

In the absence of the silicate coating, the entire surface of the steel after 20 days of testing is covered with a red-brown bloom. In the case of PLG-5 coatings containing zinc or zinc together with TEG, no traces of iron corrosion after treatment in NaCl solution are observed even if the curing time does not exceed 24 hours. However, white zinc corrosion spots form on the surface of these coatings. The curing time of 24 h is not sufficient for PLG-3 coatings with zinc, and after 20 days of testing in a corrosive medium, not only white, but also red-brown spots of zinc and iron corrosion products, respectively, appear on their surface. When the duration of the curing of these coatings is increased to 72–96 h, traces of iron corrosion begin to appear only after 48–52 days of testing. At the addition of TEG into these coatings the corrosion of iron becomes noticeable only after 55 days of testing, while white spots of zinc corrosion products in the silicate matrix appear much earlier. These data allow us to conclude that, firstly, silicate coatings containing both zinc and TEG have a better protective ability, and secondly, zinc corrosion products are formed in the pores of these coatings and healing them.

Fig. 2 shows the polarization cathode and anode curves of the samples with silicate coatings in comparison with the corrosion diagrams of bare steel or steel containing coatings obtained by electrochemical zinc deposition or hot dip galvanizing.

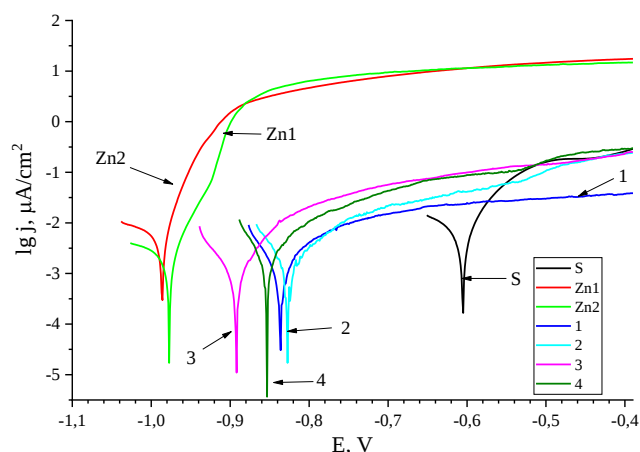


Fig. 2. Corrosion diagrams of the steel protected by zinc or silicate zinc-rich coatings in 3.5% NaCl solution:

S – initial steel; Zn1 – electrochemical zinc coating, 40 μm thick;
 Zn2 – hot dip galvanized zinc coating, $150 \pm 15 \mu\text{m}$ thick;
 1 – PLG-3 + Zn; 2– PLG-5 + Zn; 3– PLG-3 + Zn + TEG; 4 – PLG-5 + Zn + TEG

The corrosion potential of the steel covered by any zinc-containing coating, regardless of its origin, is in the region of more negative values compared to the potential of the bare steel, which indicates the cathodic polarization of steel. The most noticeable shift of the corrosion potential to negative values by 0.38 V is observed in the case of steel with traditional zinc coatings obtained by electrochemical deposition or hot dip galvanizing. The studied silicate zinc-rich coatings have a corrosion potential of 0.23–0.29 V less than that of steel. The cathodic polarization of steel is most pronounced in the case of PLG-3 silicate coatings containing zinc together with TEG. The value of the corrosion potential shift decreases in the series PLG-3 + Zn + TEG; PLG-5 + Zn + TEG; PLG-3 + Zn; PLG-5 + Zn.

The cathodic polarization of steel is more pronounced when TEG is present in zinc-rich silicate coatings. This may indicate an improvement in the conditions for the electric current transit due to the cross-linked network which is formed by contacting zinc and graphene particles, and to their electrical contact with the steel surface.

Corrosion currents in cases of steel covered by silicate zinc-rich and electroplated zinc coatings are of the same order. In the presence of graphene particles in the coatings, the corrosion currents are reduced by a factor of 3–5. This is in accord with the reduced porosity of such coatings. Low corrosion currents in the case of silicate zinc-rich coatings compared to the currents characteristic of even thicker hot dip galvanized zinc coatings may be due to the sealing of pores in the silicate matrix with zinc corrosion products.

The results of research of the OCP evolution for the steel samples covered with silicate zinc-rich coatings at their treatment in 3.5 % NaCl solution are presented in Fig. 3. The initial OCP of all samples has close values of $-(0.92\text{--}1.00)$ V. The lowest potential value is typical for the samples with hot dip galvanized zinc and PLG-3 + Zn + TEG coatings. This value does not change within 360 hours of treatment in the sodium chloride solution.

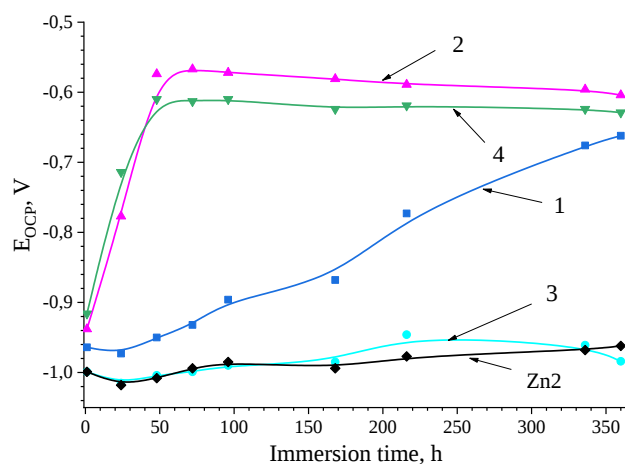


Fig. 3. Open circuit potential evolution of the steel with hot dip galvanized zinc coating (Zn2) and silicate zinc-rich coatings during their treatment in 3.5% NaCl solution:
 1 – PLG-3 + Zn; 2 – PLG-5 + Zn; 3 – PLG-3 + Zn + TEG; 4– PLG-5 + Zn + TEG

The OCP of steel with coatings based on high modulus PLG-5 containing zinc or zinc together with TEG sharply grows to the values of $-(0.57\text{--}0.63)$ V at 48 hours of the treatment, following which it stops changing. This behavior can be explained by the accumulation of zinc corrosion products in the pores and cracks of the silicate matrix and their full sealing by the end of the second

day of testing. The OCP of steel with PLG-3 + Zn coatings slowly grows, but only by 360 h of testing the potential approaches the values typical for samples with coatings based on the PLG-5 matrix. These results confirm the benefits of coatings based on PLG-3 filled with zinc together with TEG.

Morphology and elemental composition of coatings

According to the SEM study, zinc powder consists of spherical 1–4 μm sized particles, (Fig. 4, a). The angular lamellar TEG particles have a widely varied lateral sizes from hundreds of nanometers to 10 μm and the thickness of 15–25 nm (Fig. 4, b). After ultrasonic treatment, the TEG plates are crushed, the fraction of particles with sizes above 2 μm almost disappears (Fig. 4, b, insert). In coatings based on PLG, zinc particles are covered with a silicate shell and they are in close contact with each other (Fig. 4, c, d). The silicate matrix in Fig. 4, c–f, looks like a very thin layer between zinc particles, which differs from them in contrast.

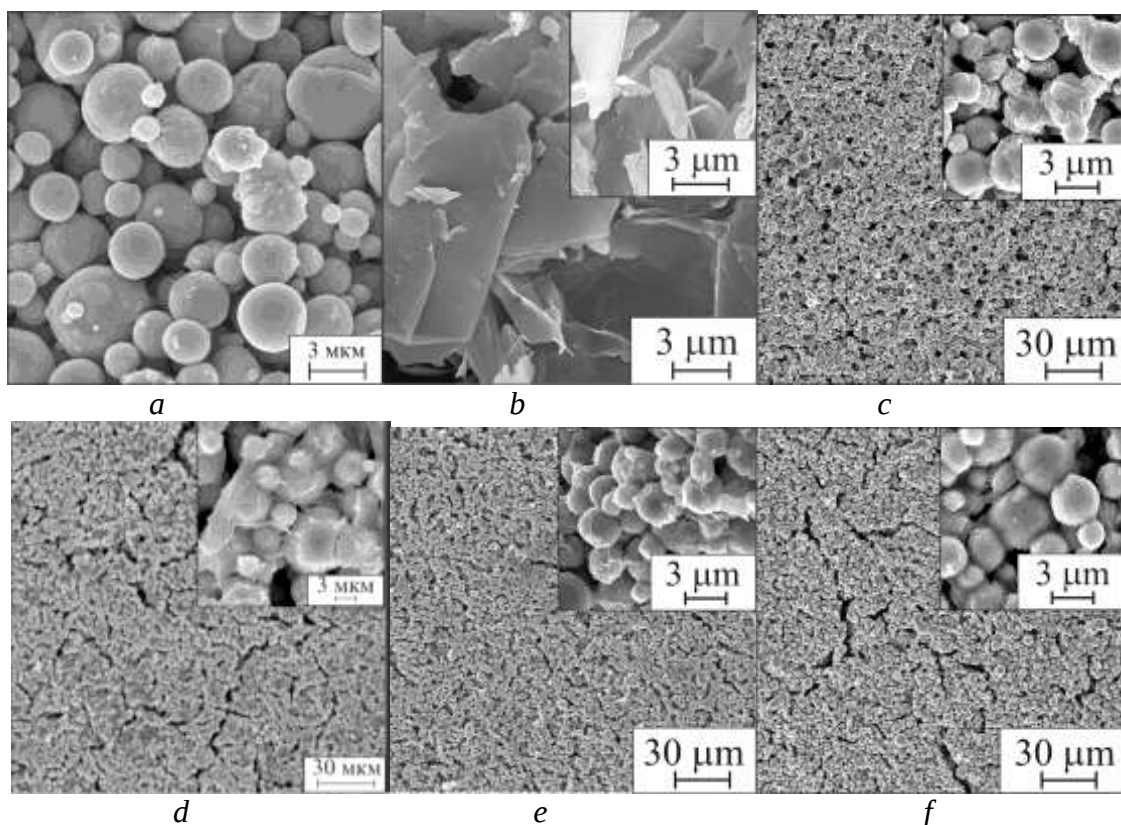


Fig. 4. SEM images of powders (a, b) and composite coatings surfaces (c–f): a – Zn, b – TEG before and after (insert) sonication; c – PLG-3 + Zn; d – PLG-5 + Zn; e – PLG-3 + Zn + TEG; f – PLG-5 + Zn + TEG

Coatings based on PLG-5 have many submicron pores and cracks 10–30 μm long and up to 3 μm wide (see Fig. 4, d and f) unlike coatings based on PLG-3 (see Fig. 4, c and e). The quantity and size of pores and cracks in coatings containing TEG (see Fig. 4, e and f) are much smaller than in their analogues without TEG (see Fig. 4, c and d). Graphene plates create additional contacts between zinc particles. SEM images of the coatings cross-sections testify to the fact that pores and cracks are closed and that they do not penetrate through coatings. Note that the formation of cracks can occur due to the shrinkage of the silicate gel during the curing, which is more significant when using high modulus PGL-5 as a result of their faster curing.

SEM images of the surface of coatings after their treatment in 3.5% NaCl solution for 50 days show that at the initial stages of corrosion the products appear on the surface of zinc particles as spherical nuclei 100–200 nm in size and their loose islands. Further zinc corrosion products form a discontinuous layer of loose and formless aggregates that are significantly less contrast compared to zinc particles (Fig. 5). These aggregates occupy a much larger volume than the original zinc

particles, which ensures the filling of pores and cracks in the silicate matrix with corrosion products.

The effect of coating compaction by corrosion products is especially noticeable in the near-surface layer of coatings, which can be seen in the SEM photographs of the cross-section (Fig. 6, *a*, *b*). As a result, the corrosion resistance of coatings is ensured not only due to the cathodic polarization, but is also caused by the isolation from the external environment. In such coatings, the destruction of the surface compacted layer filled with zinc corrosion products will promote the corrosion of zinc particles in the deeper layers thus providing the pores healing in the damaged area.

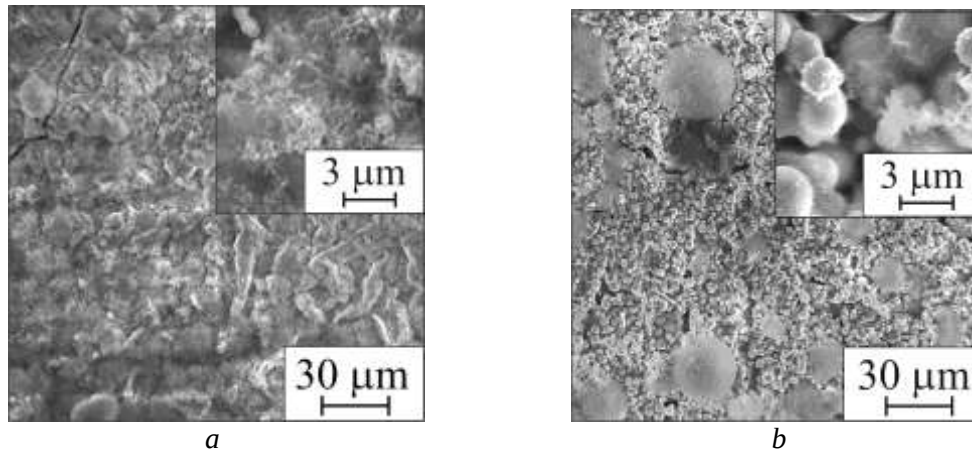


Fig. 5. SEM images of the surface of silicate coatings on steel after their corrosion in 3.5% NaCl solution for 50 days: *a* – PLG-3 + Zn + TEG; *b* – PLG-5 + Zn + TEG

X-ray spectral microanalysis of coatings composition in their near surface layer up to a depth of 13–30 μm (Fig. 6, *c*, *d*) indicates that the treatment in NaCl solution leads to the increase in oxygen content from 9 to 30 wt. % and the reduction of zinc content from 77 to 47 wt. %. This occurs owing to the oxidation of zinc. Up to 5 wt. % sodium atoms and about 7 wt. % chlorine atoms are detected in the near-surface zone of the samples after their corrosion. This fact can indicate the adsorption of NaCl, possibly with the partial replacement of potassium atoms in the silicate matrix by sodium ions. The chlorine atoms found in the silicate matrix can comprise into the products of zinc corrosion.

These results are consistent with the work [18], which revealed that the corrosion product of zinc in sodium chloride solution is $\text{ZnCl}_2 \cdot 4\text{Zn}(\text{OH})_2$.

The iron atoms are present in a quantity of 5 wt. % on the surface of coatings after their corrosion test, but their content inside the coatings is much less than 1%. This fact indicates a slight oxidation of iron at the initial moment of coated steel immersion in a liquid corrosive medium, following which the pores in the coating are sealed, and iron ions available in NaCl solution are adsorbed on its surface.

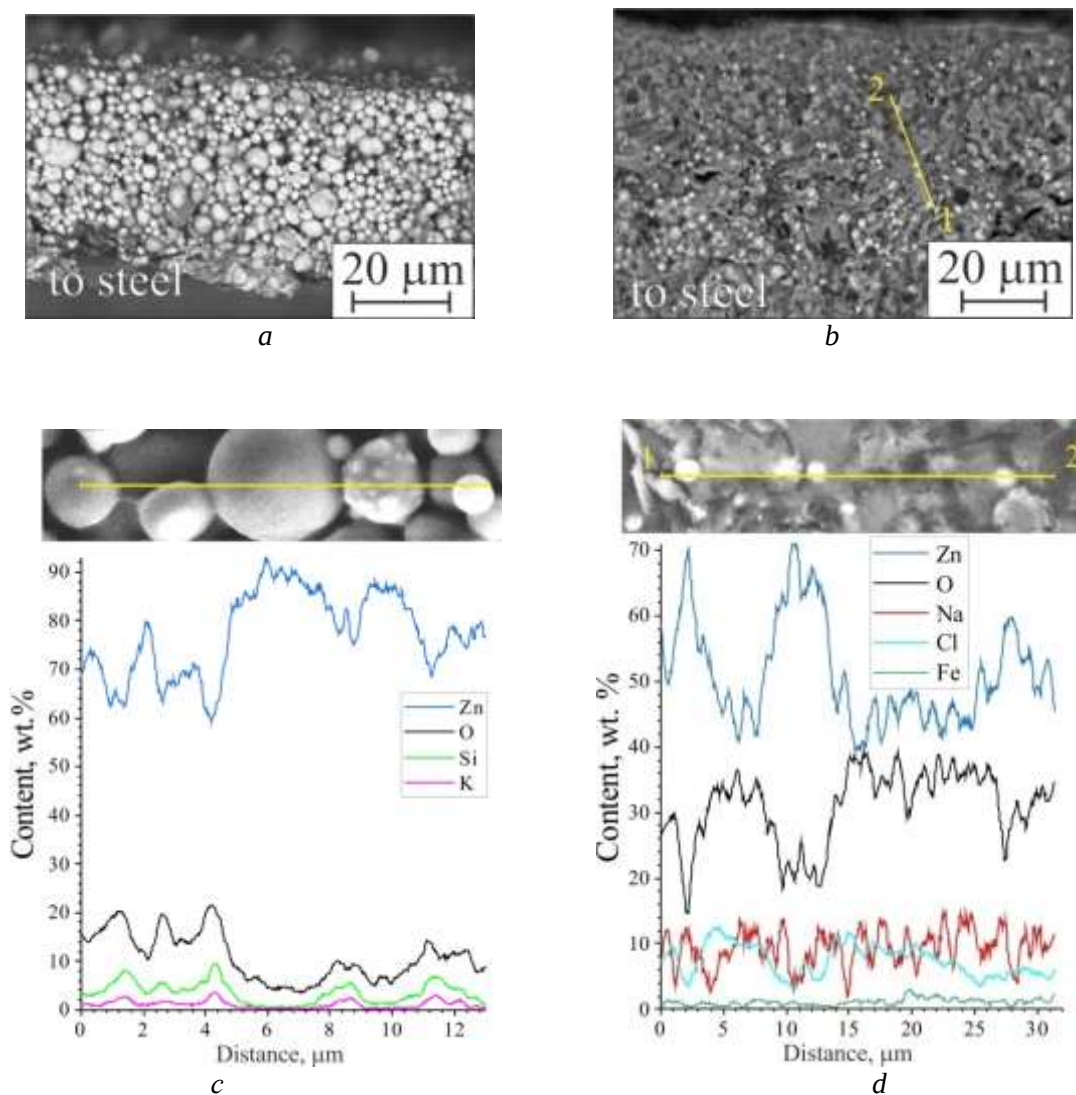


Fig. 6. SEM images of cross-section in PLG-3 + Zn coating (*a, b*) and X-ray spectral microanalysis data on composition (wt. %) across the marked line of cross section (*c, d*):
a, c – original coating; *b, d* – after treatment in 3,5 % NaCl solution for 50 days

Thus, it has been established that the silicate coatings obtained by the sol-gel method from potassium silicate glass with powdery zinc and graphene fillers protect steel from corrosion in sodium chloride solution, providing cathodic polarization of the iron. This effect is more pronounced in the joint presence of zinc powder and graphene nanoplates in the silicate matrix. It is shown that during corrosion the pores in the matrix are filled with sparingly soluble zinc compounds, which enhances the protective properties of the coatings.

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СИЛИКАТНЫЕ ПОКРЫТИЯ С ПОРОШКОВЫМ ЦИНКОМ И НАНОПЛАСТИНАМИ ГРАФЕНА В КАЧЕСТВЕ НАПОЛНИТЕЛЕЙ ДЛЯ ЗАЩИТЫ СТАЛИ ОТ КОРРОЗИИ

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Аннотация: Предложен метод защиты углеродистой стали от коррозии силикатными покрытиями с наполнителями из цинка и нанопластин графена, полученного термическим расщеплением графита. Подобраны условия обработки стали в щелочном растворе, содержащем цитрат-ионы и неионогенный ПАВ, а также получения композиции на основе калиевого жидкого стекла с добавлением порошков цинка и графена. Показано, что наиболее высокую адгезию, водостойкость и защитную способность имеют покрытия толщиной 70–80 мкм, отвержденные при комнатной температуре трое суток и включающие 80–90 масс. % цинка, 7–12 масс. % диоксида кремния и 0,2 масс. % углерода. Изучение коррозии стали в 3,5% растворе NaCl методами вольтамперометрии и зависимости потенциала разомкнутой цепи от длительности испытаний показали, что силикатные покрытия, наполненные цинком и графеном, обеспечивают катодную поляризацию стали и защищают ее от коррозии лучше, чем вдвое более толстые покрытия горячего цинкования. Нанопластины графена улучшают контакт частиц цинка друг с другом и со сталью, обеспечивая ее катодную поляризацию. С использованием сканирующей электронной микроскопии и рентгеновского спектрального микроанализа показано, что продукты коррозии цинка заполняют поры приповерхностного слоя покрытий, усиливая их защитную способность.

Ключевые слова: сталь, силикатные покрытия, цинк, нанопластины графена, коррозия, катодная поляризация, залечивание пор.