

Passivation of galvanized steel in a solution based on cerium and lanthanum compounds

E.A. Zheludkova,¹ A.A. Abrashov,¹* V.A. Sukhorukova,¹
N.S. Grigoryan,¹ A.V. Sundukova,¹ O.Yu. Grafov²
and T.A. Vagramyan¹

¹Mendeleev University of Chemical Technology, Russia, Moscow, Miusskaya sq., 9,
125047 Moscow, Russian Federation

²A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy
of Sciences, Leninsky pr. 31, 119071 Moscow, Russian Federation

*E-mail: abrashov.a.a@muctr.ru

Abstract

A technology has been developed to replace highly toxic chromate plating processes by depositing protective conversion coatings in a solution containing ions of rare-earth metals on galvanized surfaces. The compositions of the solutions were developed and optimized, and the physicochemical and mechanical properties of the protective coatings on zinc formed in these solutions as an alternative to chromate coatings were studied. A new comprehensive method for assessing the self-healing ability of conversion coatings was developed. The addition of lanthanum nitrate to a cerium-containing solution for zinc passivation was shown to increase the protective ability of the resulting coatings when the ratio of cerium to lanthanum ions in the solution is 2:1 at a total concentration of rare-earth metals in the solution of 3 g/L. It was shown that the protective ability increased due to a decrease in the number and diameter of pores in the coatings. It was found that in the course of self-healing in cerium-lanthanum containing coatings newly formed on damaged areas, the proportion of Ce³⁺ compounds increases. It has been found that addition of sodium pyrophosphate to the solution for the formation of passivating conversion cerium-containing coatings doubles the service life and increases the solution stability fivefold.

Received: March 22, 2024. Published: April 28, 2024

doi: [10.17675/2305-6894-2024-13-2-7](https://doi.org/10.17675/2305-6894-2024-13-2-7)

Keywords: corrosion protection, conversion coatings, surface treatment, chromate-free passivation, rare-earth metals.

Introduction

Until now, the method most widely used for enhancing the corrosion resistance of zinc coatings still involves their passivation in solutions based on hexavalent chromium compounds, despite the serious drawback of this process, namely, the high toxicity of the solutions used. Leakage of chromating solutions into the environment (for example, due to accidents), the chromates they contain cause significant environmental damage. Passivating

chromate coatings also contain toxic Cr(VI) compounds. For example, chromated parts of modern cars can contain up to 200 mg/m² of hexavalent chromium [1–3].

Currently, the majority of developed countries have adopted laws regulating the maximum permissible concentrations of Cr(VI) in drinking water, reservoirs, and wastewater, which limit or completely prohibit the use of Cr(VI) compounds in mechanical engineering and electronics [4–7].

Along with high protective ability, conversion chromate films are advantageous due to their ability to self-heal, which significantly extends the service life of metal structures [8, 9].

A drawback of chromate coatings is their low thermal resistance: on heating to temperatures of 160°C and above, their protective ability sharply deteriorates, which is unacceptable for parts that operate, for example, in the engine compartment or in other “hot spots” of the car.

Passivation in solutions based on compounds of less toxic trivalent chromium are not widely used in practical application, since the resulting passivation films fail to meet the requirements for mechanical strength, protective ability, and self-healing [10, 11].

Since the environmental requirements for mechanical engineering and electronics products in the Russian Federation are becoming increasingly stringent, the use of toxic compounds of metals such as nickel, cobalt, and chromium for the formation of protective and decorative coatings on metal surfaces is limited; therefore, the development of processes for producing conversion protective coatings on zinc that do not contain compounds of these metals is an urgent scientific and engineering challenge.

According to published data, coatings formed in solutions that contain environmentally safer compounds of rare-earth metals (REMs) instead of chromate ions [12–17] can be a promising alternative to chromate coatings.

Experimental

Galvanized plates of cold-rolled steel 08ps were used as samples for applying passivating coatings. Steel samples were galvanized in a weakly acidic electrolyte with the following composition: ZnCl₂ 60–120 g/L; NH₄Cl 200–220 g/L; H₃BO₃ 20 g/L; TsKN-3 30 ml/L ($i_c=2.0$ A/dm²; $t=20^\circ\text{C}$; pH 4.5–6.0). The thickness of the zinc coatings was 10 ± 0.2 μm. The protective ability (PA) of coatings was determined as required by GOST 9.302-88 by the drop method using a 5% solution of lead acetate. According to this method, the protective ability of a coating was estimated as the time (in seconds) until the emergence of (black) zinc corrosion products under the drop.

Corrosion tests of galvanized samples passivated in the developed solutions, including those with a paint coating applied on top of the passivating layer, was carried out in an Ascott S450iP salt fog chamber (UK) in accordance with the international standard ASTM B117 and GOST 9.401-2018. The depth of corrosion propagation from the notch was estimated immediately after the end of the corrosion tests.

Polarization measurements were carried out using an Autolab PGT302N potentiostat in potentiodynamic mode in 3% NaCl solution at a scan rate of 0.5 mV/s. Galvanized steel samples with the coatings were used as the working electrodes. The electrode potentials were measured relative to the silver chloride electrode. Their values were recalculated to the SHE. A graphite electrode was used as the auxiliary electrode. To determine the corrosion potential E_{corr} and the corrosion current density i_{corr} , the Tafel extrapolation method was used.

The thickness of the films formed was determined by the ellipsometric method using a SENreasech 4.0 ellipsometer (SENTECH, Germany).

X-Ray photoelectron spectroscopy (XPS) studies were carried out on an OMICRON ESPa+ spectrometer (Germany) with an aluminum anode equipped with an AlK α XM1000 monochromatic X-ray source (with a radiation energy of 1486.6 eV and a power of 252 W). To eliminate the local charge on the analyzed surface, a CN-10 charge neutralizer was used with an emission current of 4 μ A and a beam energy of 1 eV. The transmittance energy of the analyzer was 50 eV for the panoramic spectrum and 20 eV for individual spectra of elements.

The spectra were recorded using an Argus hemispherical detector-analyzer. The pressure in the analyzer chamber did not exceed 10^{-9} mbar. All spectra were accumulated no less than three times. The fluctuation of the peak positions did not exceed ± 0.3 eV. The positions of the spectra were standardized relative to the C1s peak of hydrocarbon contaminants from the atmosphere with a maximum at 285 eV. The spectra were separated into components after subtracting the background determined by the Shirley method [18]. In the quantitative analysis, the Scofield sensitivity coefficients [19] were used, which were corrected by analyzing salts with a known composition and the mean free paths of the electrons located on these shells.

To estimate the thermal stability of the coatings, they were subjected to thermal shock by heating in a ShS-80-01 SPU drying oven for 1 hour at temperatures of 160°C, 200°C and 250°C followed by cooling in air. After this procedure, the protective ability of the coatings was determined.

The structure and number of pores in the passivating coatings were determined using 2D and 3D images of the sample surface obtained with a LEXT-OSL 4100 confocal laser microscope (Olympus Corporation, Japan). Abrasion resistance was studied on a modified Taber Elcometer 5135 rotational abrasion meter (UK) measuring the number of rotations of the felt disk that resulted in a fixed decrease in the thickness of the coatings and their PA. The adhesion of paintwork to a galvanized surface was determined by the tear-off method using a PosiTest AT digital adhesiometer (USA) and, according to GOST 9.032-74, by determining the depth of corrosion propagation from a notch.

The self-healing ability of conversion coatings was estimated using a comprehensive technique developed by us. It involved examining the presence of zinc corrosion products after accelerated self-healing tests (24 hours in 0.003 M sodium chloride solution) in defects with various specified and reproducible areas that were created on the surface of

passivated samples (in the form of scratches or imprints of a Vickers diamond pyramid). According to the technique, the criteria by which the self-healing ability of coatings was estimated included: the appearance of defects in SEM images, variation of geometric dimensions, and variation in the cerium content in damaged areas of the coating compared to the original composition. The geometric dimensions of defects (indents) were measured using a SuperView W1 optical profilometer (CHOTEST, China), while the appearance and elemental composition were estimated using a Thermo Fisher Scientific Quattro C scanning electron microscope before and after accelerated tests.

Results and Discussion

Given the published data and the results of previous work on the formation of cerium-containing coatings carried out by the authors, solutions containing cerium ions, which were added as nitrate salt $[\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$, and hydrogen peroxide (H_2O_2) as the oxidizer [12, 14, 20–22] were chosen as the base solutions.

Studies on the dependence of the appearance and protective ability of cerium-containing coatings on the concentration of the main components in conversion solutions revealed that homogeneous continuous coatings with the maximum protective capacity are formed on the surface of galvanized products (15–20 s in the express drop method) in the concentration range of 3–5 g/L Ce^{3+} (9–15 g/L cerium nitrate) and 5–15 ml/L 37% H_2O_2 .

The parameters of the passivating processes are presented in Table 1. Coatings with the highest values of protective ability are formed after keeping for 40–60 s the in acid passivating solutions where partial dissolution of the zinc coating occurs, which is required for the formation of the conversion layer. The optimal range of durations of passivation in the developed solution was determined by the protective ability of the cerium-containing coatings formed. If galvanized products are kept in a cerium-containing solution for more than 60 s, the uniformity of the coatings is violated and the protective characteristics deteriorate. It has been found that coatings with the maximum protective ability are formed after drying at a temperature of 40–80°C for 10–15 minutes.

Table 1. Parameters of the passivating process.

Parameter	Cerium-containing solution
Solution pH	2.5–3.5
Solution temperature, °C	40–50
Process duration, s	30–60
Drying temperature, °C	40–80

It has been found that addition of 0.7–1.5 g/L boric acid to a cerium-containing passivating solution facilitates the enhancement of the protective ability of the coatings

being formed and stable maintenance of the solution pH at a level of 3.0–3.3, which made it possible to reduce the frequency of adjusting the solution acidity.

The feasibility of improving the protective characteristics of coatings by adding to the cerium-containing solution, along with cerium ions, ions of other rare-earth metals, for example La^{3+} or Y^{3+} , was examined. The best result was achieved when La^{3+} ions were added to the solution at a constant total concentration of rare-earth metal ions in the solution equal to 3 g/L. It was found that addition of 0.8–1.2 g/L La^{3+} to the solution almost doubles the protective effect (from 60 to 110 s according to the express drop method).

Studies using a laser confocal microscope showed that the protective ability of coatings formed in solutions containing La^{3+} is enhanced due to a decrease in the number and diameter of pores in the coatings (Figure 1). A pore-free coating with a thickness of 120 nm is formed in the solution containing 0.75 g/L La^{3+} .

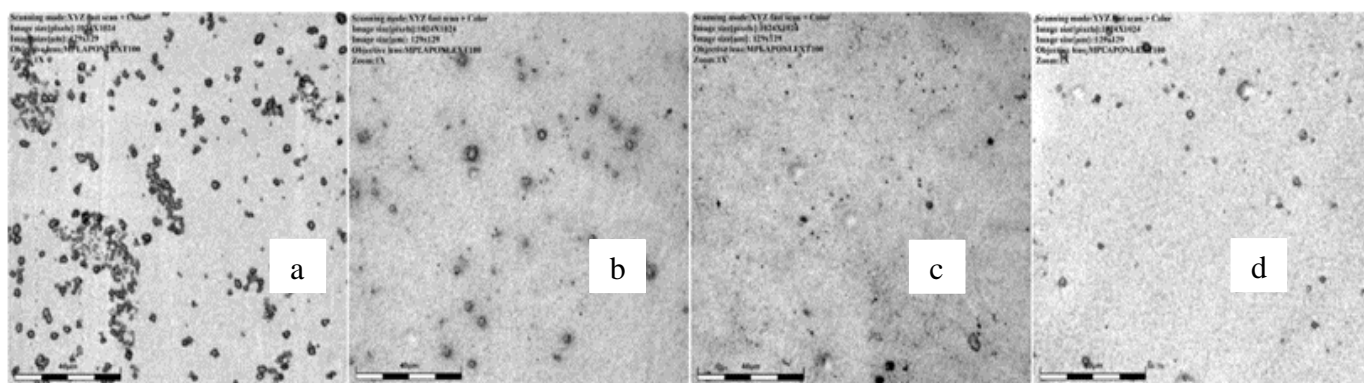


Figure 1. Confocal laser microscopic images of the surface of galvanized samples with coatings formed in solutions without La^{3+} and with $\text{Ce}^{n+}/\text{La}^{3+}$ concentration ratios: a) 1:0; b) 11:1; c) 2:1; d) 11:5. The total content of rare-earth metal ions was 3.0 g/L.

Since hydrogen peroxide is one of the main components of the solution being developed, the stability of the latter was found to be low: the protective characteristics of the coatings formed in these solutions deteriorated from 110 to 25 s after 0.5–2.0 weeks of solution storage.

To increase the solution stability, a number of organic and inorganic inhibitors of hydrogen peroxide decomposition described in the literature, such as saccharin, magnesium sulfate, glycine, and sodium/potassium pyrophosphate, were studied. The change in the content of hydrogen peroxide in conversion solutions during their aging is illustrated in Figure 2.

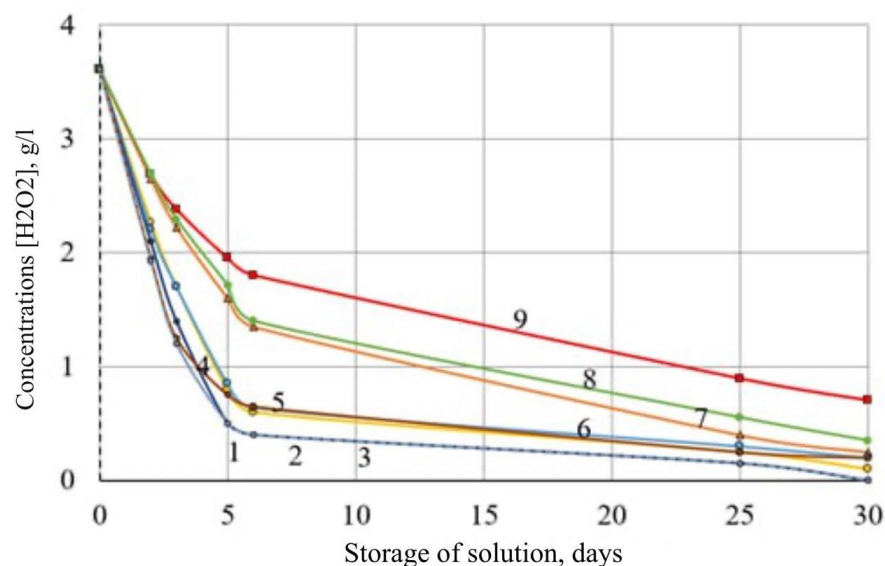
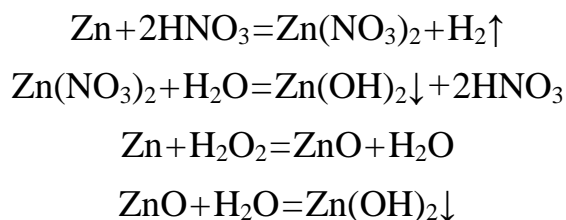


Figure 2. Variation in the H₂O₂ concentration in a cerium-lanthanum-containing solution in the course of aging: 1 – without stabilizer, 2 – MgSO₄ (10 mg/L), 3 – C₂H₅NO₂ (10 mg/L), 4 – C₆H₈O₇ (100 mg/L), 5 – C₇H₅NO₃S (5 mg/L), 6 – C₇H₅NO₃S (20 mg/L), 7 – Na₄P₂O₇ (50 mg/L), 8 – Na₄P₂O₇ (80 mg/L)+Na₄P₂O₇ (10 mg/L), 9 – Na₄P₂O₇ (100 mg/L).

The smallest decrease in the protective ability of coatings and hydrogen peroxide content after 30 days of aging of a solution containing cerium and lanthanum was observed in the presence of sodium or potassium pyrophosphate (up to 100 mg/L). After 25 days of aging the solution without a stabilizer, the peroxide concentration decreased 24-fold. In a solution containing 50–100 mg/L of sodium or potassium pyrophosphate, the concentration of hydrogen peroxide decreased by a factor of 4. It was also found that addition of sodium or potassium pyrophosphate to a cerium-containing solution leads to an enhancement of the protective ability of coatings by ~30% (express drop method), which was not observed with the other tested hydrogen peroxide stabilizers.

Panoramic XPS spectra of cerium-lanthanum-containing coatings revealed the presence of cerium, lanthanum, zinc, and oxygen compounds in the coating. Individual spectra of Ce3d, La3d5, Zn2p3 and O1s showed that the coating consists of hydroxides and oxides of Zn²⁺, Ce⁴⁺, Ce³⁺ and La³⁺ (Figure 3).

During the formation of a coating in a solution containing cerium and lanthanum (with hydrogen peroxide), the zinc base is partially dissolved, and the solution is alkalinized at the phase boundary. Taking this observation and the XPS results into account, the reactions occurring on the passivated surface can be represented as:



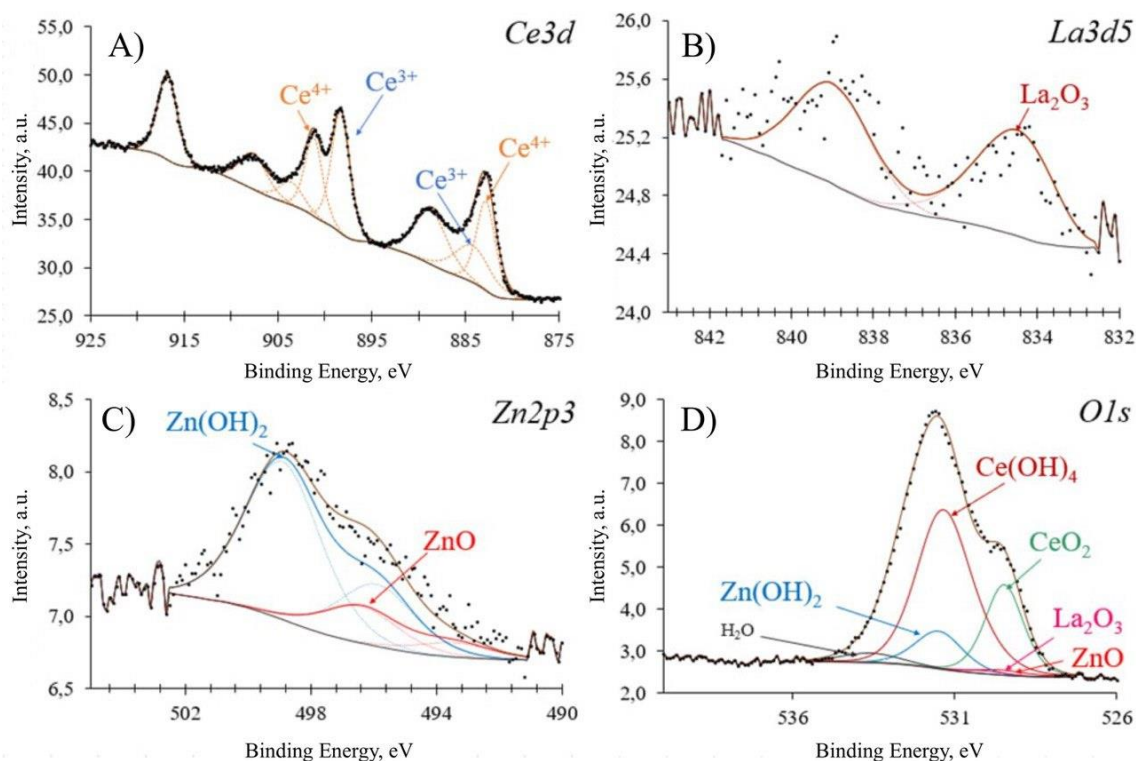
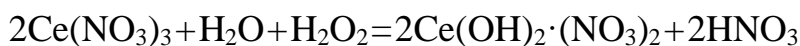
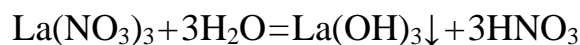
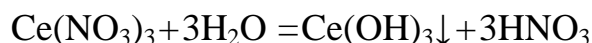
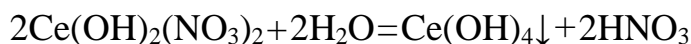


Figure 3. Individual XPS spectra of cerium (A), lanthanum (B), zinc (C) and oxygen (D) in a coating containing cerium and lanthanum.

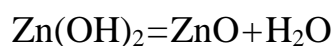
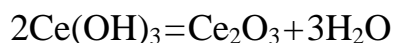
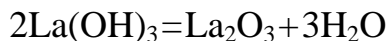
In the presence of hydrogen peroxide in the solution, Ce^{3+} ions are oxidized to Ce^{4+} :



When the pH of hydrate formation at the phase boundary is reached, the Ce^{3+} and La^{3+} salts present in the solution are hydrolyzed to give the corresponding hydroxides:



During subsequent drying, partial dehydration of the coating occurs:



Thus, the coating consists of oxides and hydroxides of zinc, lanthanum, and cerium in various oxidation states.

Using the ellipsometric method, it was determined that the thickness of coatings containing cerium and lanthanum is 110–120 nm, which is significantly less than that of iridescent chromate layers (up to 1000 nm).

The ability of coatings to self-heal was estimated from changes in the appearance and chemical composition of coatings inside defects on the passivated surface of galvanized samples during accelerated self-healing tests. The object of comparison in these experiments was an iridescent chromate coating on the surface of galvanized steel formed in a solution of the TsKN-23 formulation widely used by Russian plants.

Two types of defects were made on the surface of the coatings: (1) scratches with constant width and depth, which were made using a setup with a controllable angle between the diamond indenter edge and the surface of the sample and the pressure force of the indenter on the sample; (2) imprints of a regular tetrahedral Vickers diamond pyramid.

As expected, the images of scratches on samples with a chromate coating before and after 24 hours of testing in 0.003 M NaCl solution obtained under a confocal and scanning electron microscope confirmed the self-healing capability of chromate films: there were no zinc corrosion products in the scratches, and the appearance of the defects was virtually unaltered.

The results of energy dispersive electron microprobe analysis (EMPA) at five points located on lines perpendicular to the scratch showed a significant increase in the chromium content relative to the initial content in the scratch (Table 2).

Table 2. EMPA results, wt.% (chromate coating).

Element	Weight percent, %		Change in elemental composition
	Before testing	After 24 h of testing	
O	3.7	4.8	+30%
Zn	95.1	90.7	–5%
Cr	1.2	4.5	+275%

The results obtained confirm the relevance of the selected criteria for assessing the self-healing ability of conversion coatings.

The self-healing ability of coatings formed in a passivating solution containing cerium and lanthanum at total concentrations of REM ions of 3 g/L and 4 g/L and a ratio of cerium to lanthanum concentrations of 2:1 was revealed. Scratches after corrosion tests in 0.003 M NaCl solution were completely covered with a homogeneous thin layer of the newly formed protective coating; no zinc corrosion products were found in the scratches. The self-healing of coatings formed in a solution with a total REM content of 3 g/L was more pronounced: an increase in the cerium content in a scratch by 31% was observed, which is ~4.4 times greater than the result for a solution with a total REM concentration of 4 g/L.

The change in surface within the imprints of a regular tetrahedral Vickers diamond pyramid was studied on samples with cerium-lanthanum-containing and chromate coatings before and after accelerated tests in 0.003 M NaCl solution for 24 and 72 hours.

At the deepest points of the indents (2.5 μm or 9.4 μm deep) on the chromate-coated sample, formation of nuclei of zinc corrosion products was observed after 24 hours of corrosion testing. They increased in size after 72 hours, while the appearance of the side walls of pyramidal indents remained unchanged (Figure 4a). EMPA results for chromate-coated samples after accelerated self-healing tests showed an increase in the chromium content by 300% at the deepest point of the indents (2.5 μm or 9.4 μm deep); the zinc content decreased slightly in both cases (Figure 4a).

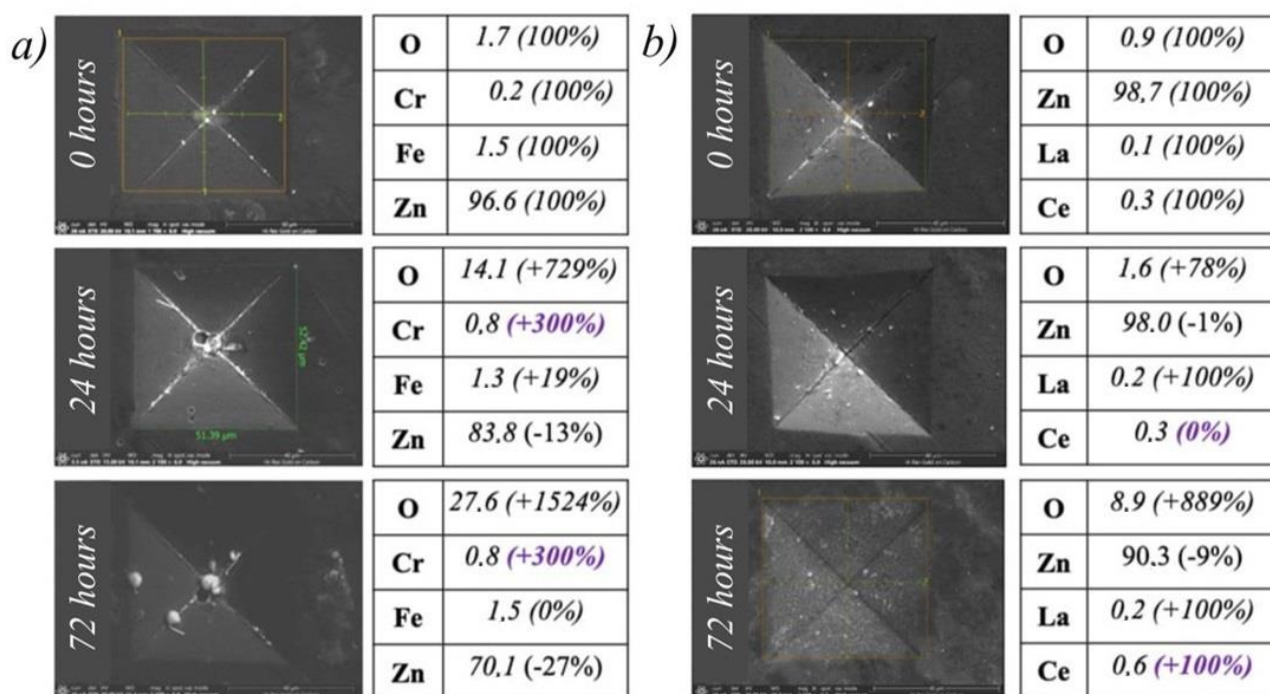


Figure 4. SEM images of Vickers pyramid indents on samples with chromate (a) and cerium-lanthanum-containing (b) coatings and EMPA results (wt.%) at the bottom point of the indent before and after testing in a 0.003 M NaCl solution.

The appearance of indents with various depths on a sample with a coating containing cerium and lanthanum did not change within 24 hours of testing, similarly to the cross-sectional profile of the scratch, which indicates the presence of a protective barrier film on their surfaces. The EMPA results showed a sharp increase in the cerium content (+800% of the initial composition at the studied point) with constant zinc content values at the lowest point of the indent with a depth of 2.5 μm . At a point located in the center of the side face of the indent, the REM content increased after 24 hours of testing, but not so significantly (+8% cerium). After 72 hours of exposure to the corrosive NaCl solution, the 2.5 μm deep indent began to be partially filled with zinc corrosion products. The cross-

sectional profile reflects similar changes in the surface of the sample and the indent that occur as a result of chemical interaction with the medium. In an indent with a depth of 9.4 μm , the concentration of cerium and lanthanum increased by 100% of the initial composition at the test point only after 72 hours of accelerated testing (Figure 4b).

After 24 hours of corrosion testing of chromate-coated samples, the average chromium content over the entire area of indents with a depth of 2.5 μm and 9.4 μm increased by 78% and 90%, respectively. After 24 hours of corrosion testing of samples with a coating containing cerium and lanthanum, the average cerium content over the entire area of the indent with a depth of 2.5 μm increased by 40%, while it did not change in the indent with a depth of 9.4 μm . Thus, the deeper indent was not covered by the protective cerium-lanthanum film after 24 hours of testing. However, after 72 hours of testing, the average cerium content over the entire indent area with a depth of 9.4 μm increased by 30%, while the oxygen content increased by 144%. The zinc content did not increase at any stages of studying the composition of indents with various depths.

It has been found that cerium-lanthanum-containing and chromate coatings feature the self-healing ability, but it is more pronounced in the latter coating. Both coatings are able to re-passivate defects with a depth of 2.5 μm at the same rate, but the healing rate of defects with a depth of 9.4 μm is smaller for coatings containing cerium and lanthanum: the self-healing ability only begins to manifest itself after 72 hours of testing. The change in the appearance of chromate films and the formation of spherical nuclei on the surface of the indents may be due to the different ductility of the films themselves. The chromate coating is more fragile, so in the depth of the indent, due to its cracking, zinc is exposed, while the oxide coating containing cerium and lanthanum, which is thinner and more ductile, is pressed more deeply by the indenter and its continuity is disrupted to a lesser extent.

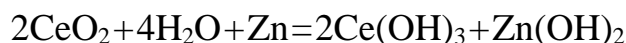
The composition of the coating containing cerium and lanthanum in a scratch was determined before and after 24 hours of accelerated self-healing tests (Table 3).

Table 3. Composition of a coating containing cerium and lanthanum in a scratch before and after accelerated self-healing tests in a 0.003 M NaCl solution.

Name of the peak	Initial composition of coating, at.%, fraction of the total Ce content		Initial composition in scratch, at.%, fraction of the total Ce content		Composition in scratch after testing, at.%, fraction of the total Ce content		
O1s	66.24		69.72		69.34		
Zn2p3	13.72		16.92		13.77		
Ce3d	Ce(IV)	11.90 (84%)	14.17	7.94 (84%)	9.45	9.45 (75%)↓	12.60↑
	Ce(III)	2.27 (16%)		1.51 (16%)		3.15 (25%)↑	
La3d5	5.87		3.91		4.29		

The panoramic XPS spectrum showed a relative increase in the total cerium content in the scratch after accelerated self-healing tests. Along with this, the individual Ce3d spectrum showed that the proportion of Ce³⁺ in the coating in a scratch increased by a factor of 1.2–1.5.

Taking into account the results obtained, the self-healing of defects on a galvanized surface with coatings containing cerium or cerium+lanthanum can be described by the following equations:



Corrosion tests in a salt fog chamber (ASTM B117) showed that the protective ability of coatings containing cerium and lanthanum (85 hours) was comparable to that of the iridescent coatings (100 hours) and superior to colorless chromate coatings (16 hours) (Figure 5). It should be noted that, though the cerium-lanthanum-containing coatings are ~4.2 times thinner than chromate coatings, they are virtually not inferior to the latter in terms of protective and adhesive properties. Ce-containing coatings exhibited a lower protective ability: the time before the appearance of white corrosion foci on them was 35 hours, and therefore they can be recommended for conditions of interpretational storage of products with a galvanized surface.

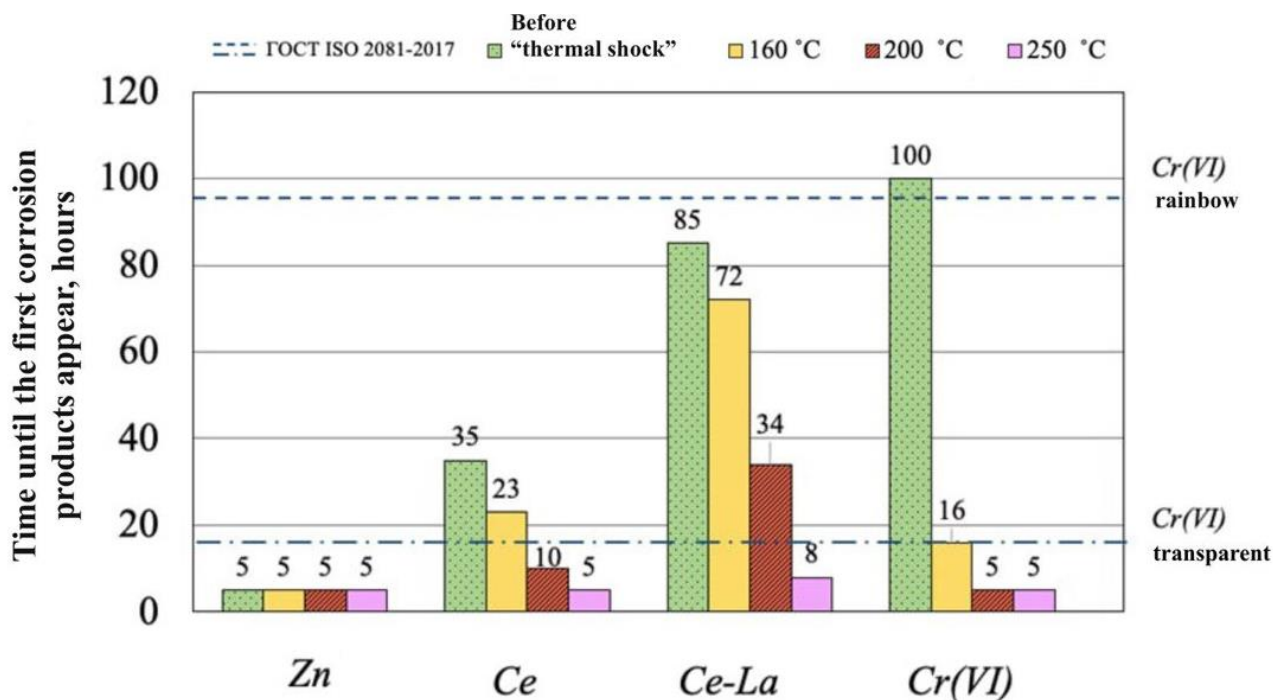


Figure 5. Results of corrosion tests in a salt fog chamber of samples with coatings before and after heat treatment.

To identify the operability of coatings under high temperature conditions (thermal shock), the change in the protective ability of coatings upon heat treatment for 1 hour at temperatures of 160°C, 200°C and 250°C was studied (Figure 5). The developed cerium-lanthanum-containing and cerium-containing coatings can withstand heat treatment at a temperature of 160°C for 1 hour without significant deterioration of protective characteristics. After treatment at a temperature of 200°C, the protective ability of coatings containing cerium and lanthanum decreased by 60%, cerium-containing coatings by 71%, and chromate coatings by 95%.

The feasibility of applying the developed passivating coatings to small-galvanized parts in bulk in a drum was tested, and it was found that in this case homogeneous continuous coatings of good quality were also formed. Salt fog corrosion tests (ASTM B117) showed that the protective ability of passivation coatings formed on parts in a drum was 30%, 25%, and 13% lower for cerium-containing, chromate, and cerium-lanthanum coatings, respectively, compared to the protective ability of coatings, which were applied on pendants.

It has been found that the abrasion resistance of coatings containing cerium and lanthanum is superior to that of chromate and cerium-containing coatings. Tests using a modernized rotary abrasion meter showed that over 800 abrasion cycles, the thickness measured on the ellipsometer decreased in the series: Ce–La, Ce, Cr(VI) coatings by 67, 75 and 76%, respectively. This was accompanied by a decrease in protective capacity by 64, 89 and 89%, respectively (Figure 6).

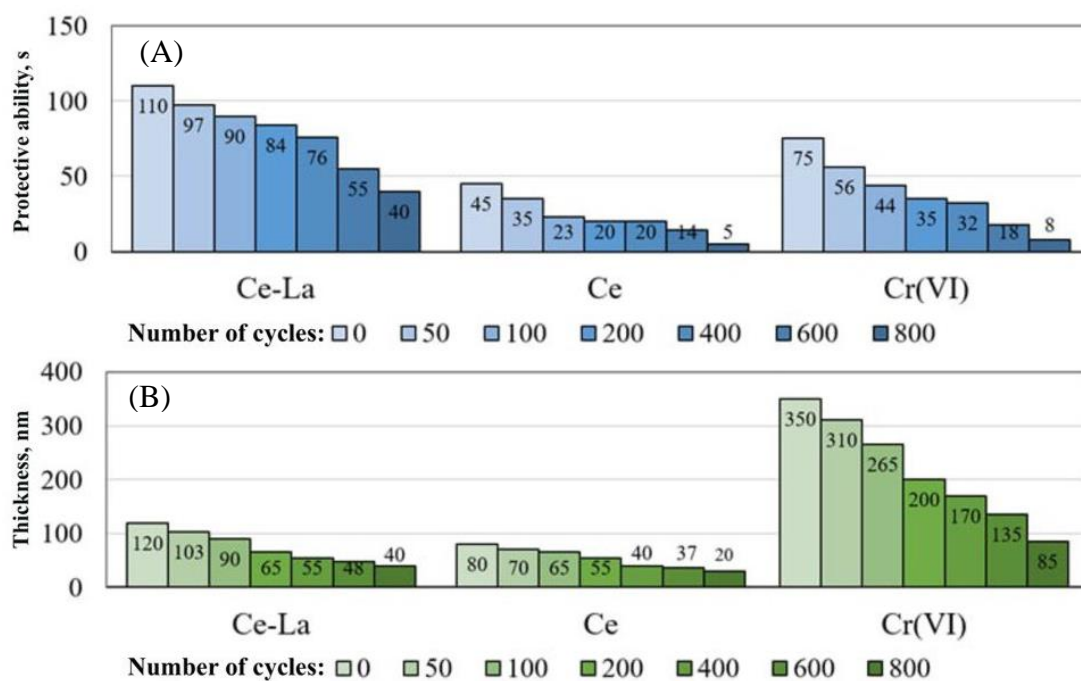


Figure 6. Dependence of the protective ability of the developed coatings (A) and their thickness (B) on the number of abrasion cycles on a felt disk at a load of 3.5 N/cm².

The coatings containing cerium and lanthanum withstand 3 times more abrasion cycles on a felt disk at the same specific pressure on the rotating disk.

Conclusions

1. Based on the results of the study, a passivation production process has been developed, and the composition of the solution and the parameters of galvanized steel treatment in a Ce–La-containing solution have been optimized.
2. A new comprehensive method for assessing the self-healing ability of conversion coatings has been developed.
3. It has been found that cerium- and cerium-lanthanum-containing coatings, like chromate ones, feature a self-healing ability.
4. Inclusion of lanthanum ions in a cerium-containing coating has been shown to increase its thermal stability.
5. The results of this work can be used to create independent protective coatings for corrosion protection of galvanized products instead of highly toxic chromate technologies. They can be applied in car-making, instrumentation, aircraft, shipbuilding, chemical, petrochemical, and other industries.

References

1. S.S. Kerur, S. Bandekar, M.S. Hanagadakar, S.S. Nandi, G.M. Ratnamala and P.G. Hegde, Removal of hexavalent Chromium-Industry treated water and Wastewater: A review, *Mater. Today: Proc.*, 2021, **42**, 1112–1121. doi: [10.1016/j.matpr.2020.12.492](https://doi.org/10.1016/j.matpr.2020.12.492)
2. E.N. Kuzin, Yu.M. Averina, A.Yu. Kurbatov and P.A. Sakharov, Treatment of wastewater from galvanic production using complex coagulant-reducing agents, *Non-ferrous metals*, 2019, no. 10, 91–96 (in Russian). doi: [10.17580/tsm.2019.10.15](https://doi.org/10.17580/tsm.2019.10.15)
3. C.C. Alvarez, M.E.B. Gomez and A.H. Zavala, Hexavalent chromium: Regulation and health effects, *J. Trace Elem. Med. Biol.*, 2021, **65**, 126729. doi: [10.1016/j.jtemb.2021.126729](https://doi.org/10.1016/j.jtemb.2021.126729)
4. Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 “End-of Life Vehicles”, *Off. J. Eur. Communities: Legis.*, 2000, **43**, no. L269, 34–43.
5. Technical regulations of the Eurasian economic community “On the restriction of the use of hazardous substances of electrical and electronic products” (TR EAEU 037/2016) (ap-proved by the Council of the Eurasian Economic Commission on October 18, 2016 (no. 113)).
6. Regulation (EC) no. 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH), Establishing a European Chemicals Agency.
7. Directive 2011/65/EC (RoHS II) of the European Parliament and of the Council of 8 June 2011 on the Restriction of the use of certain hazardous substances in electrical and electronic equipment.

8. E.A. Zheludkova, A.A. Abrashov, N.S. Grigoryan, N.A. Asnis and T.A. Vagramyan, Cerium-containing solution for chromate-free passivation of zinc coatings, *Prot. Met. Phys. Chem. Surf.*, 2019, **55**, no. 7, 1329–1334. doi: [10.1134/S2070205119070190](https://doi.org/10.1134/S2070205119070190)
9. V.V. Okulov, Environmental technical and economic aspects of the replacement of chromate passivating solutions, *Galvanotekhnika i obrabotka poverkhnosti*, 2005, **13**, no. 2, 35–41 (in Russian).
10. X. Liu, L. Wang, M. Wang, F. Li, J. Gao and J. Li, Dynamic structures and electrochemical behavior during the formation of trivalent chromium-based conversion coating on Zn, *Coatings, Surf. Coat. Technol.*, 2022, **431**, 128041. doi: [10.1016/j.surfcoat.2021.128041](https://doi.org/10.1016/j.surfcoat.2021.128041)
11. S. Hesamedini and A. Bund, Trivalent chromium conversion coatings, *J. Coat. Technol. Res.*, 2019, **16**, 623–641. doi: [10.1007/s11998-019-00210-9](https://doi.org/10.1007/s11998-019-00210-9)
12. A.A. Abrashov, N.S. Grigoryan, N.D. Kondrat'eva, E.A. Zheludkova, V.S. Miroshnikov and D.V. Mazurova, Chromate-free passivation of galvanized steel in solution based on lanthanum nitrate, *Chem. Saf. Sci.*, 2020, **4**, no. 2, 198–211 (in Russian). doi: [10.25514/CHS.2020.2.18014](https://doi.org/10.25514/CHS.2020.2.18014)
13. F. Khast, M. Saybani and A.A.S. Dariani, Effects of copper and manganese cations on cerium-based conversion coating on galvanized steel: Corrosion resistance and microstructure characterizations, *J. Rare Earths*, 2022, **40**, no. 6, 1002–1006. doi: [10.1016/j.jre.2021.07.015](https://doi.org/10.1016/j.jre.2021.07.015)
14. A.A. Abrashov, A.V. Sundukova, N.S. Grigoryan, N.A. Asnis, N.A. Khazanov, T.A. Chudnova and E.A. Zheludkova, Protective conversion coatings based on rare-earth compounds for passivation of galvanized steel, *Int. J. Corros. Scale Inhib.*, 2022, **11**, no. 4, 1749–1762. doi: [10.17675/2305-6894-2022-11-4-22](https://doi.org/10.17675/2305-6894-2022-11-4-22)
15. S. Kőszegi, I. Felhősi, F.H. Kármán and E. Kálmán, Temporary corrosion protection of galvanised steel by coatings containing cerium, yttrium and lanthanum, *Mater. Sci. Forum*, 2005, **474**, 219–224. doi: [10.4028/www.scientific.net/MSF.473-474.219](https://doi.org/10.4028/www.scientific.net/MSF.473-474.219)
16. X. Liu, Passivation effect of rare earth lanthanum on galvanized steel, *Appl. Mech. Mater.*, 2014, **525**, 31–34. doi: [10.4028/www.scientific.net/AMM.525.31](https://doi.org/10.4028/www.scientific.net/AMM.525.31)
17. A.E. Hughes, T.G. Harvey, N. Birbilis, A. Kumar and R.G. Buchheir, Coatings for corrosion prevention based on rare earths, *Rare Earth-Based Corrosion Inhibitors*, 2014, 186–232. doi: [10.1533/9780857093585.186](https://doi.org/10.1533/9780857093585.186)
18. D.A. Shirley, High-resolution X-ray photoemission spectrum of the valence bands of gold. *Phys. Rev. B*, 1972, **5**, 4709–4713. doi: [10.1103/PhysRevB.5.4709](https://doi.org/10.1103/PhysRevB.5.4709)
19. J.H. Scotfield, Hartree-Slater subshell photoionization cross-sections at 1254 and 1487 eV, *J. Electr. Spectr. Relat. Phenom.*, 1976, **8**, 129–137. doi: [10.1016/0368-2048\(76\)80015-1](https://doi.org/10.1016/0368-2048(76)80015-1)
20. A.A. Abrashov, N.S. Grigoryan, T.A. Vagramyan, M.A. Simonova, V.S. Miroshnikov and I.A. Arkhipushkin, Surface passivation of 5556 aluminum alloy in solutions based on cerium nitrate, *Int. J. Corros. Scale Inhib.*, 2021, **10**, no. 1, 132–144. doi: [10.17675/2305-6894-2021-10-1-8](https://doi.org/10.17675/2305-6894-2021-10-1-8)

-
21. A.A. Abrashov, N.S. Grigoryan, M.A. Simonova, T.A. Vagramyan and I.A. Arkhipushkin, Passivation of the surface of AZ31B magnesium alloy in solutions based on salts of rare-earth metals, *Int. J. Corros. Scale Inhib.*, 2021, **10**, no. 3, 961–975. doi: [10.17675/2305-6894-2021-10-3-9](https://doi.org/10.17675/2305-6894-2021-10-3-9)
22. A.A. Abrashov, E.A. Zheludkova, A.A. Petrushina, N.S. Grigoryan, A.V. Sundukova, T.A. Vagramyan and O.Yu. Grafov, Protective conversion nanocoatings for hot-dip galvanized steel, *Theory and Practice of Corrosion Protection*, 2023, **28**, no. 3, 7–17 (in Russian). doi: [10.31615/j.corros.prot.2023.109.3-1](https://doi.org/10.31615/j.corros.prot.2023.109.3-1)

