
Protective cerium-containing sol-gel coatings on hot-dip galvanized steel

A.A. Abrashov,* A.V. Sundukova, O.V. Zhilina,
N.N. Gavrilova and O.A. Shloma

D. Mendeleev University of Chemical Technology of Russia, Miusskaya sq. 9, 125047
Moscow, Russian Federation
**E-mail: abrashov.a.a@muctr.ru*

Abstract

Due to the high toxicity of chromating solutions that contain highly toxic hexavalent chromium compounds and the conversion coatings formed in these solutions, most countries have adopted laws restricting or completely banning the use of Cr(VI) compounds in engineering and electronics products. This publication deals with the development of a process for application of protective sol-gel cerium-containing coatings on the surface of galvanized steel. The compositions of solutions for the deposition of self-sufficient protective/decorative or adhesive coatings have been optimized, and the physicochemical and mechanical properties of the coatings that can potentially be employed instead of toxic chromate coatings have been studied. It has been found that sol-gel coatings formed in an alkaline sol of cerium dioxide (pH 9.5–10) at 4–6 mm/min sample withdrawal rate feature the highest protective ability. Subsequent heat treatment of cerium-containing sol-gel coatings at a temperature of 300°C has been shown to enhance the protective characteristics. It has been shown that at the optimum rate of withdrawing a sample from the sol, coatings with a thickness of 100–120 nm are formed. It has been established that the time before the appearance of the first white corrosion spots on the cerium-containing coatings studied is 70 h, which matches the 72 h period established by the ISO 9227 standard for iridescent chromate coatings. Taking into account the results obtained, this technology can be used to obtain functional coatings with protective properties on the surface of galvanized steel. They can be used as protective and decorative coatings in automotive, machine building, instrumentation, aircraft, shipbuilding, chemical and petrochemical and other industries.

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Introduction

Chromate treatment is used to improve the corrosion resistance of electroplated protective zinc coatings and aluminum surfaces. The resulting conversion chromate films inhibit corrosion processes on the surface of these metals and, in addition, can self-heal if the integrity of the film is damaged mechanically [1].

Due to the high toxicity of chromating solutions that contain highly toxic hexavalent chromium compounds, and the conversion coatings formed in such solutions which also contain up to 200 mg/m^2 of Cr^{6+}, the majority of developed countries have adopted laws that restrict or completely prohibit the use of Cr(VI) in mechanical engineering and electronics products [2–9].

Yet another significant drawback of chromate treatment processes is the low thermal stability of the resulting coatings under thermal shock: heating to 160°C or more sharply reduces their protective ability, which is unacceptable for parts that operate, for example, in the engine compartment or in other hot locations in a car. Moreover, as a result of thermal shock, chromate films lose their self-healing ability [3, 10].

Molybdate [11–13], vanadate [14, 15], silicon- [16–18], titanium-, or zirconium-containing coatings [19–22] can be used to replace the chromating process to obtain protective and decorative coatings on galvanized steel. However, the protective ability of molybdate and vanadate coatings is significantly inferior to that of chromate layers, while silicon- and titanium-containing coatings are not yet widely used in practice.

The alternatives to chromates as corrosion inhibitors for galvanized steel reported in publications include salts of rare-earth metals, in particular cerium and lanthanum, which are environmentally safe and fairly efficient corrosion inhibitors of metals such as aluminum, zinc, and magnesium [3, 10, 23–27].

The sol-gel method occupies a special place among the methods for applying corrosion-resistant coatings and allows oxide-metallic (ceramic) coatings to be created on any metal. The deposition of sol-gel films on various surfaces can be used to prevent their degradation and protect them against high-temperature and electrochemical corrosion, destruction due to the action of light, atmosphere and moisture, natural aging, etc., and modify their properties or impart new ones [28–33]. The use of the energy-saving and cost-effective sol-gel technology for the synthesis of protective/decorative hybrid coatings whose operational and technical properties comply with the world standards makes it possible to create protective coatings of the surfaces of non-ferrous metals, with characteristics not inferior to those of chromate layers.

This works deals with a study on the physicochemical properties of anticorrosion sol-gel CeO_2 coatings on the surface of galvanized steel.

Experimental

Hot-dip galvanized steel plates 3×3 cm in size were used as the samples.

Highly dispersed particles of cerium dioxide were obtained by chemical precipitation followed by peptization. Ammonia solution (2 mol/L) was added to a dilute $Ce(NO_3)_3$ solution with constant stirring by means of a magnetic stirrer to a ratio of $[Ce^{3+}]:[NH_4^+] = [1]:[4]$.

$$Ce^{3+} + 3OH^- = Ce(OH)_3 \tag{1}$$

Then the precipitate was stirred for 1.5 h.

$$4Ce(OH)_3 + O_2 = 4CeO_2 + 6H_2O \tag{2}$$

The resulting precipitate was washed by decantation. Further, distilled water was added to the resulting precipitate and treated ultrasonically for 3–4 min at a working frequency of 22 kHz. Solutions of HNO_3, NH_4OH, and $Ce(NO_3)_3$ were used as the peptizing agents. After adding the peptizing agent, the resulting system was treated ultrasonically for 3–4 min at a working frequency of 22 kHz. The process scheme is shown in Figure 1.

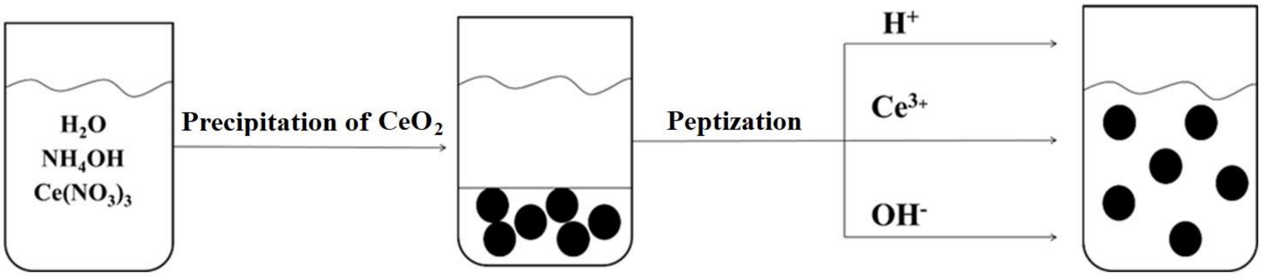

Figure 1. Stages of the synthesis of cerium dioxide hydrosol by the peptization method.

To obtain cerium-containing coatings, a zinc sample was immersed for 20 min at room temperature in the cerium dioxide hydrosol thus prepared. After that, the sample was withdrawn at a rate ranging from 1 to 30 mm/min. The samples were subsequently dried for 60 minutes at 70°C. To improve the quality of the coating, the samples were further subjected to heat treatment in the temperature range from 100°C to 400°C.

The size and shape of the particles of the hydrosol thus obtained were examined using the images taken on a LEO 912AB OMEGA transmission electron microscope (Carl Zeiss) at the Transmission Electron Microscopy Center for Collective Use of the Moscow State University. Samples were prepared by applying 1–2 μL of the sol to a Formvar-coated copper grid (d = 3.05 mm), which was then air-dried. Images were analyzed and particle size distribution histograms were plotted using Image Pro-10 software.

The protective ability of the coatings was determined by the drop method according to GOST 9.302-88 using a 5% solution of lead acetate. According to this method, the protective ability of the coating was evaluated as the time (in seconds) before the appearance of zinc corrosion products, which manifested itself as a change in the color from gray to black on the surface area under the drop.

Surface roughness was studied using an OLYMPUS LEXT4100 confocal laser microscope.

To determine the coating thickness using a Sentech SEN research 4.0 SER 800 ellipsometer with a fast monochromator, the ellipsometric parameters Ψ and Δ were measured as a function of the wavelength in the spectral range from 240 to 1000 nm at a goniometer angle of 70°. The calculated result was considered valid if the parameters of the physical model matched the mathematical model and were within the established error limits [34].

Corrosion tests were carried out using an Ascott S450iP salt spray chamber in accordance with the ASTM B117 international standard [35]. The depth of corrosion propagation from the notch was evaluated immediately after the end of the tests. The samples were washed with water and dried with filter paper. The paint coating (PC) was then carefully separated from the surface of the sample using a knife blade held at an angle to the interface between the coating and the painted surface. The PC was softened with a special Elcon S® paint remover according to the usage instructions and then peeled off from the sample by carefully lifting the coating with a knife blade or spatula without damaging the area adjacent to the notch.

The depth of corrosion propagation was measured at no less than six points evenly distributed along the notch. The depth of propagation of corrosion from the notch was determined as the average value calculated taking into account the maximum damage every 10 mm of the notch line (ISO 9227). Concurrently, the width of under-film corrosion was estimated according to the ASTM D 1654-08 standard, and a score from 0 to 10 was assigned (the higher the score, the higher the protective ability [36, 37]).

Results and Discussion

To determine the size and shape of the particles in the cerium dioxide hydrosols obtained, microscopic studies were carried out by transmission electron microscopy.

Figure 2 shows micrographs of cerium dioxide hydrosol particles obtained using a LEO 912AB OMEGA electron microscope. Analysis of the images indicates that the shape of the particles is close to spherical. The shape of the rings in the electron diffraction pattern indicates a relatively high degree of crystallinity of the particles.

Based on the statistical processing of the microphotographs, histograms of the size distribution of cerium dioxide particles were plotted (Figure 3).

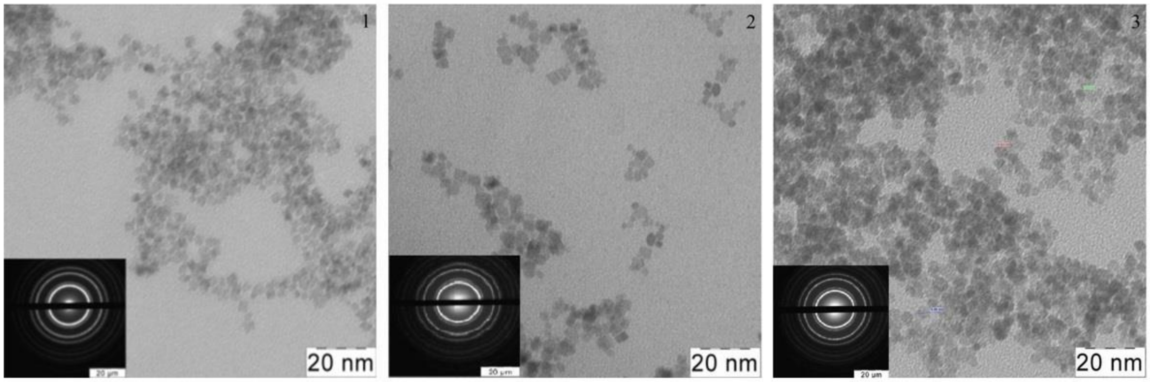

Figure 2. Images of the particles of cerium dioxide hydrosol obtained by stabilization with: 1 – $NH_3 \cdot H_2O$, 2 – HNO_3, 3 – $Ce(NO_3)_3$.

Figure 3 shows that the particle size of cerium dioxide ranges from 1.8 to 8.5 nm. The number average values of particle sizes according to transmission electron microscopy data and the main physicochemical properties of CeO_2 hydrosols are displayed in Table 1.

Table 1. Physicochemical properties of cerium dioxide hydrosols.

Stabilizer **Characteristic**	**Ce^{3+}**	**OH^-**	**H^+**
[stabilizer]:[CeO_2] ratio	[1]:[0.02]	[1]:[1.2]	[1]:[0.4]
Probable diameter of hydrosol particles, nm	5	3.8	4.4
Concentration, mass %	0.8	0.4	0.37
pH	4.4–5.0	9.5–10.0	2.2–2.3

Based on published data, several options for applying a cerium-containing coating by the sol-gel method were suggested: onto a substrate at an angle of 45°, onto a rotating substrate, withdrawal at a certain rate, and immersion. The first two methods are technically challenging and require special equipment. As a result, withdrawal of a sample out of the sol at a certain rate and immersion were chosen. Since the immersion method is technically the simplest, it was used in the first experiments.

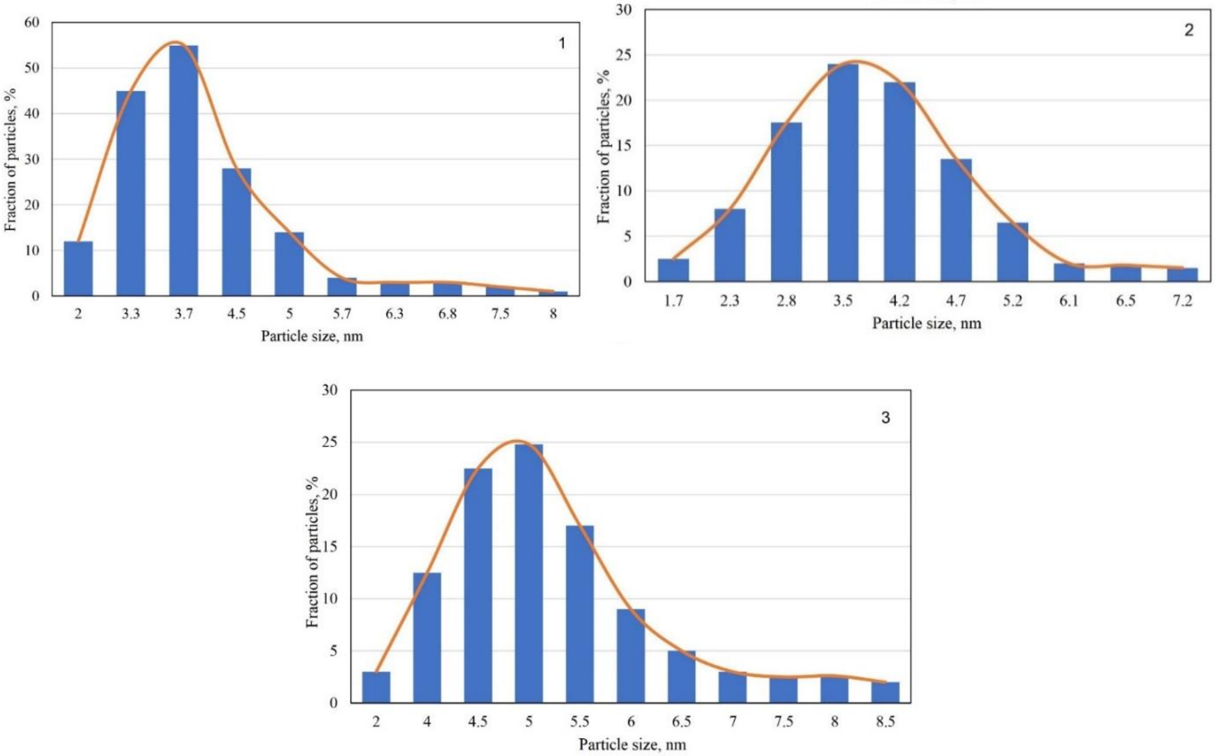

Figure 3. Histograms plotted using data of transmission electron microscopy; distributions of the dimensions of the hydrosol particles obtained by stabilization: 1 – $NH_3 \cdot H_2O$, 2 – HNO_3, 3 – $Ce(NO_3)_3$.

Zinc samples were immersed into sols with various pH values for 5, 10, 15, and 20 min. The samples were subsequently dried for 60 min at 70°C. Further, heat treatment in the range from 100°C to 300°C was carried out to improve the quality of the coatings.

Cerium dioxide films obtained by immersing a sample into an alkaline sol (pH 9.5–10.0) were found to show the highest protective ability. This can be explained by the most probable diameter of hydrosol particles. For the alkaline sol, it is 3.8 nm, the smallest value of the three suggested hydrosols. It can be assumed that the densest CeO_2 film is formed as a result, which is also facilitated by an increase in the heat treatment temperature of the samples to 300°C.

An increase in the time of exposure of the samples to the cerium dioxide hydrosol leads to an enhancement of the protective ability of the coating. This occurs as a result of the physical adsorption of cerium dioxide on the zinc substrate. In the case of physical adsorption, the CeO_2 particles and the substrate interact by van der Waals forces. During the experiment, adsorption of particles on glass and ceramic vessels was also observed, which confirms the good adsorption capacity of cerium dioxide.

To determine the optimal conditions for applying a cerium dioxide film by immersion, we compared the protective ability of coatings obtained from various sols with subsequent heat treatment at 300°C (Figure 4). The results presented indicate that the films formed by immersion into a sol at pH = 10.00 for 20 min (30 s) feature the highest protective ability.

We studied the effect of the rate of sample withdrawal from the sol on the protective ability. Based on the above data, it can be concluded that the optimal rate of sample withdrawal is 4–6 mm/min. If the rate exceeds 10 mm/min, the protective ability decreases as a result of small adhesive forces between the sample and the gel.

The thickness of the coatings formed was determined using the ellipsometric technique. It was shown that, at the optimum rate of sample withdrawal, coatings with a thickness of 100–120 nm were formed from the sol.

The results of corrosion tests confirm that at a sample withdrawal rate of 4–6 mm/min, the coating that formed was most resistant to corrosion. It is also worthy of note that after heat treatment at 300°C, the samples were least susceptible to corrosion.

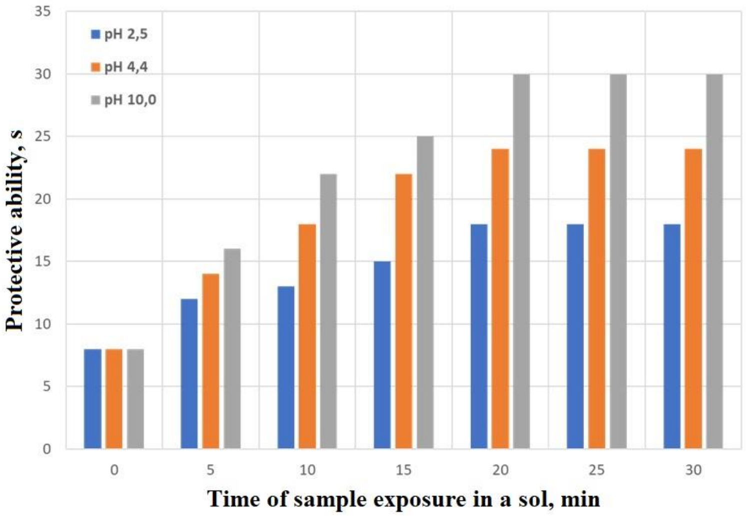

Figure 4. Dependence of the protective ability on the exposure time of the sample in sols with various pH with subsequent heat treatment at a temperature of 300°C.

Corrosion testing (ASTM B117) in a salt spray chamber yielded the time until the first "white" corrosion sites (corrosion of galvanized steel) emerge. It was found that the time until the first sites of white corrosion appeared on the cerium-containing coatings under study was 70 h, which correlates with the value of 72 h set by the ISO 9227 standard for iridescent chromate coatings.

Corrosion testing of zinc samples painted with polyester powder paint with applied sol-gel coatings showed that the developed coatings met the requirements for adhesive layers in what regards the protective ability, since the penetration depth of corrosion under the PC from the notch point for these coatings did not exceed 2.0 mm after 240 h of testing (0.4–0.5 mm). However, in the absence of an adhesive layer, corrosion penetrates by 6.2 mm, while in a chromated zinc coating this value is 0.3–0.6 mm.

Conclusions

We have studied the particles of the cerium dioxide sol and developed a technique for the application of cerium-containing coatings by the sol-gel method.

The optimal rate of withdrawing a sample from the sol was found to be 4–6 mm/min.

The sol-gel coatings formed in an alkaline sol and heat-treated at a temperature of 300°C feature the highest protective ability.

The coatings that we developed can be used as an alternative to the toxic zinc-based chromate coatings.

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