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The Effect of Cerium Pre-Treatment on the Corrosion Resistance of Steel Sheets[1]

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Abstract—The steel samples have been coated with cerium layer by cathodic electrolytic deposition from the $Ce(NO_3)_3{\cdot}6H_2O$ solution in aqueous ethyleneglycol in the presence of hydrogen peroxide. The influence of the coating parameters (cathodic current density, pH, cerium concentration, hydrogen peroxide concentration, temperature, and treatment duration) on the surface properties; the optimum conditions of the formation of corrosion preventing coating have been elucidated. Hydrogen peroxide concentration and pH are the major factors influencing the deposition process. The corrosion resistance has been further enhanced after treatment with $Na_3PO_4{\cdot}12H_2O$ solution. The cerium-coated samples have been subsequently coated by cathodic electrostatic deposition from the colloidal solution of the paint. The coated materials have been subjected to mechanical testing (hardness, impact, cross cut, bending, and cupping tests), and their structure has been visualized by electron microscopy. The cerium coating has been found to improve the steel corrosion resistance by 15%.

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Various coatings are used to prevent metals and alloys corrosion. One of the popular methods to form the protective coating is the metal treatment in the chromate bath [1]. This method suffers from a significant drawback, the toxicity and carcinogenicity of Cr(VI) compounds; therefore, the coatings based on other compounds have been intensively studied. The compounds of rare earth metals, in particular, these of cerium, have demonstrated attractive protection properties in combination with environmental safety, and are thus considered promising for practical applications [2–5].

In order to form cerium-containing protective coating, the methods of laser evaporation [6], chemical vapor deposition, sol-gel treatment, immersion [7–15], and electrodeposition [16–20] have been used. The electrodeposition approach is considered the most prospective due to the low process temperature, efficiently controlled thickness of the protective layer, and low cost. In particular, the enhanced corrosion resistance has been observed after such treatment in the cases of aluminum alloys [21], zinc [3, 5–8], iron (steels) [9, 11, 12], and magnesium [22].

It has been reported that the post-treatment with $NH_4H_2PO_4$ solution (up to 10 min at 85°C) significantly enhances the corrosion resistance of the cerium-coated aluminum alloy [23]. The report on the significant role of H_2O_2 in the electrodeposition of the cerium-containing coating is available [24]. In order to deeply investigate the reported effects, this work aimed to elucidate the influence of the cerium-based coating on the corrosion resistance of the painted carbon steel, used in the automotive industry. The protective layer was formed by electrolytic deposition from cerium(III) nitrate solution in aqueous ethyleneglycol, in the presence of hydrogen peroxide.

Acidic surface activation. We found that the cerium-containing coating deposition was accelerated in the case of priory treatment of the steel sheet with 1 wt % solution of sulfuric acid (besides the alkaline cleaning, that was performed as usual). At the surface that was only cleaned with alkali and then cerium-coated, the lighter colored spots and nodules were observed; whereas in the case of additional acidic treatment the final surface was deeply orange. The analysis of surface morphology revealed that the additional acidic treatment decreased the overall coating thickness, and fewer of surface cracks were

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[1] The text was submitted by the authors in English.

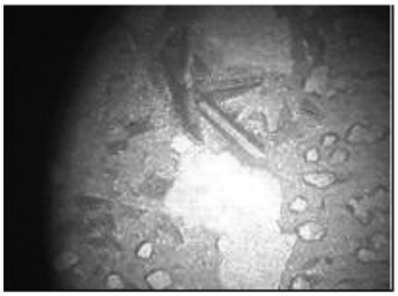

Fig. 1. Cerium oxide layer cracking upon drying (2.4 μm layer thickness, optical microscope).

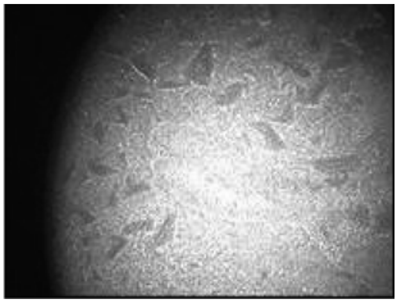

Fig. 2. Cerium-containing coating obtained at current density of 10 A/dm^2 during 40 s (optical microscope).

observed. Without the acidic pre-treatment, the cerium-containing coatings sometimes peeled off the surface. Furthermore, our tests demonstrated that the salt fog performance was also enhanced in the case of acidic pre-treatment.

The observed effects were likely due to acidic dissolution of the oxides at the steel surface, thus, the surface was activated, and the cathodic deposition was more efficient.

The deposited layer parameters. After the coating with cerium oxide, the steel sheet became orange, the color depth being dependent on the formed layer thickness. The thickness of cerium oxide film was of 0.3 to 4 μm, depending on the deposition time, current density, and other process parameters. The surface color revealed the presence of hydrated cerium(IV) compounds [25]. It was found that the 1.5–2 μm thick cerium oxide layer was less cracked upon drying than the thicker layer (>2.4 μm) (Fig. 1).

Electrolysis bath pH. Our experiments revealed that at when pH of the near-surface cathodic layer was below 1.2, the soluble (at least partially) cerium substances were formed, and the protective coating was not continuous. Moreover, there were some evidences that at pH < 1.2 the steel sheet oxidation occurred instead of cerium compounds deposition. At pH > 1.3, the cerium hydroxide precipitate was formed throughout the whole bath volume; the coating formed under that conditions was characterized by the indefinite composition and morphology as well as by numerous defects. Therefore, pH = 1.2–1.3 was found to be optimal for the electrolytic deposition of cerium-containing coating onto the steel surface.

Cerium salt concentration. In our experiments we varied the cerium salt concentration in the electrolysis bath in the 0.01–0.04 mol/L range with the step of 0.01 mol/L. At 0.01 mol/L of the cerium salt, the formed coating was too thin, did not cover the steel plate completely, and was partially washed off with water. On the contrary, at 0.04 mol/L of cerium, the obtained coating was too thick, and numerous defects (pores and cracks) were observed in the deposited layer. In the both cases, the corrosion resistance of the coating was not satisfactory. The optimal concentration of the cerium salt was found to be of 0.02 mol/L: the so formed coating covered the whole plate surface and was not cracked.

Cathodic current density. The cathodic current density was varied in the range of 1 to 30 A/dm^2. At below 6 A/dm^2, the cerium oxide coating was not obtained at all. With increasing current density, the surface of the formed film became more heterogeneous, large cracks and peeling zones were observed (see an example in Fig. 2). The surface defects revealed at high current density were due to local inhomogeneities of the cathode surface leading to non-even hydrogen release and film deposition. The cracks and peeling the coating off the steel surface decreased the coating corrosion resistance. The best protective properties were observed in the case of coating formed at the current density of 6 A/dm^2.

Deposition time. Time of electrodeposition was varied in between 20 s and 180 s. The optimal time to obtain the coating of desired thickness was found to be of 40 s. Shorter deposition time led to too thin, discontinuous coating (Fig. 3), whereas at longer deposition time the formed layer was peeled off. In the course of deposition, the color intensity was increasing during the first 105±5 s, and did not change later.

Temperature of the electrolysis bath. We did not find any noticeable effect of the deposition temperature on the microstructure and the electrochemical properties of the deposited cerium-containing film (in the range of 18–40°C. However, the determined corrosion-protective properties of the

Fig. 3. Cerium-containing coating obtained by deposition during 20 s (optical microscope).

obtained samples were the best in the case of bath temperature of 29°C, being noticeably poorer in the case of warmer or cooler electrolysis bath. The decrease of the protective properties upon heating of the bath was likely due to cerium oxide crystallization: the polycrystalline film should have had poorer corrosion protection performance.

Solvent. Cerium nitrate could be introduced into the electrolysis bath in the form of solution in water or in different alcohols, including polyols. The steel plates treated by aqueous cerium nitrate solution did not pass the salt fog test. In some cases, the addition of an alcohol enhanced the protective properties of the obtained coating. The solutions in aqueous ethyleneglycol were selected for detailed studied, as they showed up the properties optimal for electrodeposition (in terms of viscosity and surface tension). The ethyleneglycol/water mass ratio was varies from 30 : 70 to 60 : 40, the optimal composition was found to be of 50 : 50 by mass. The observed effect of ethyleneglycol was seemingly due to formation of smaller cerium oxide particles and thus the denser protective coating. The detailed study of mechanism leading to formation of smaller particles of cerium oxide in the presence of ethyleneglycol was out of the scope of this work.

Hydrogen peroxide concentration. The introducetion of hydrogen peroxide activated some side processes connected with cerium oxide deposition, in particular, conversion of hydroxides to oxides and peroxides, in other words, decrease of the hydroxyl groups in the material. In turn, that led to less adhesion of the particles and, thus, to formation of more homogeneous and dense protective layer. Indeed, we found that the addition of hydrogen peroxide to the electrolysis bath medium decreased the subsequent cracking of the layer upon drying; hence, one of the general drawbacks of the solution methods of alloys coating was eliminated. We found that the optimal concentration of H_2O_2 was of 1–1.4 vol %: at lower concentration, the positive effect of the peroxide was not noticeable, whereas at higher concentration, hydrogen peroxide passivated the steel surface thus preventing cerium oxide deposition.

Phosphate post-treatment. The sealing of deposited coating is generally accompanied with the expansion of the material grains and the particles aggregation. The salt fog test demonstrated that temperature and duration of the phosphate post-treatment significantly altered the corrosion resistance of the cerium oxide coating. In the course of post-treatment, the surface morphology was changed as well as its composition, in particular, Ce(IV) was partially converted to Ce(III),

Mechanical properties of steel after the salt fog testing[a, b]

Sample	Number of tests	Impact (40 and 60 lb)	Adhesion	Hardness (Percoz)	Cupping (mm)	Bending
With cerium-containing coating, phosphate post-treatment	10	+	Class 10	327	8	+
With cerium-containing coating, without phosphate post-treatment	5	+	–	–[c]	6.5	5
Without cerium-containing coating, phosphate post-treatment	5	+	+	320	8	+
Reference (untreated steel)	5	+	+	>270	>7.5	+

[a] "+" Test passed; "–" test not passed. [b] Salt fog testing duration was of 1000 h in the case of samples without cerium-containing coating, of 1144 h in the case of samples with cerium-containing coating; the reference steel was not subjected to salt fog testing. [c] Could not be assessed due to surface roughness.

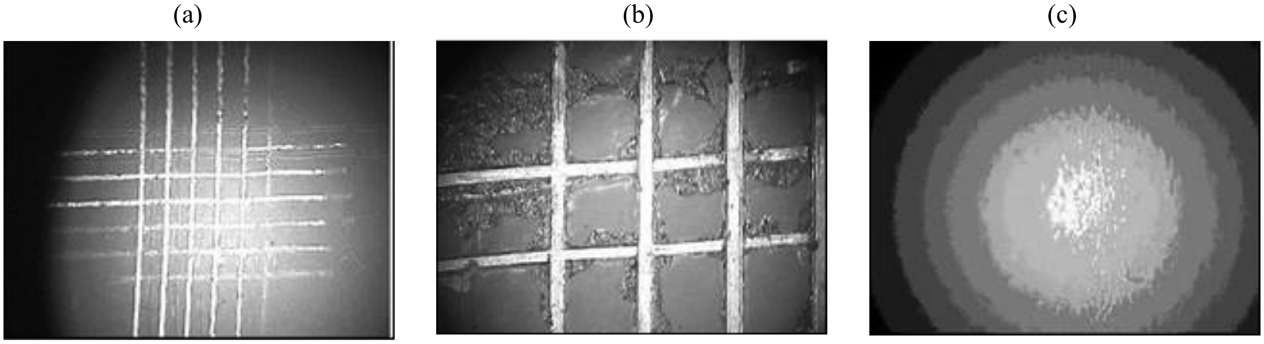

Fig. 4. (a) A sample after having passed the adhesion test (class 10); (b) a sample not passed the adhesion test (class 2); (c) a sample after cupping test (8 mm). (Optical microscope).

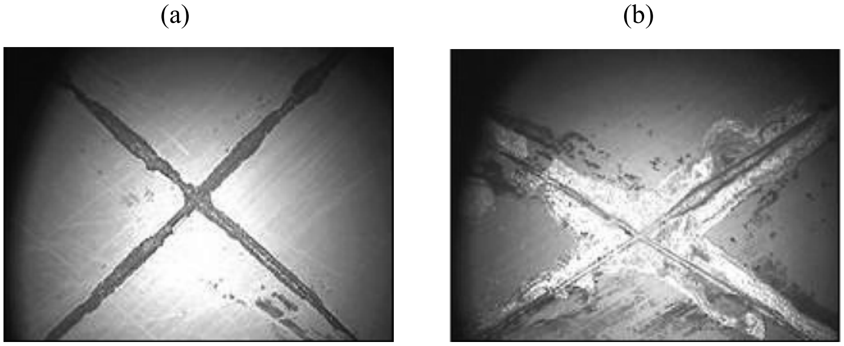

Fig. 5. Cerium-containing (a) and phosphate (b) coatings after the salt fog testing (optical microscope).

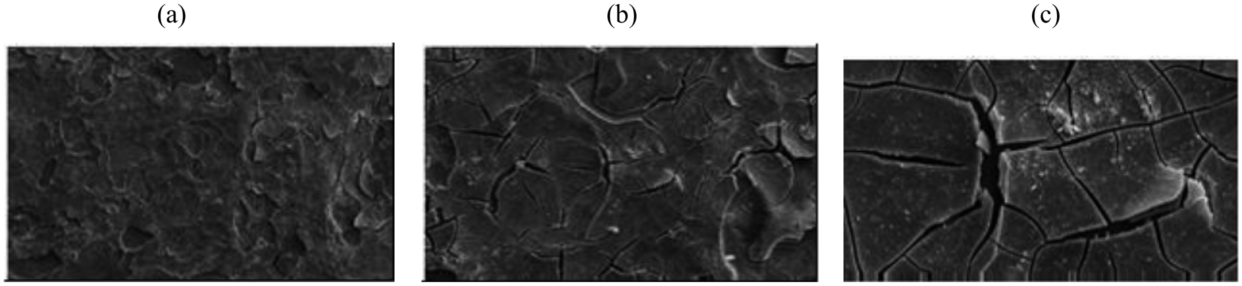

Fig. 6. The general view of cerium-containing coating (a), a region with small cracks (b), and a region with larger crack (c). SEM, note the scale difference between the figures (a)–(c).

and hydrated CeO_2 was transformed into hydrated $CePO_4$). The corrosion resistance of the samples was estimated taking into account the mechanical properties changes after the salt fog testing (see table). The mechanical tests comprised the standard set of steel test (impact, adhesion, hardness, bending, and cupping).

The studied samples were comparable to the reference steel sample after the salt fog testing, hence, the coatings imparted the necessary corrosion resistance. Noteworthily, the tabulated results were obtained after 1144 h of the salt fog testing in the cases of cerium-containing samples, and after only 1000 h of the same testing in the case of cerium-free samples. Therefore, the cerium-containing coating enhanced the corrosion resistance of steel. Some of the mechanical testing results are visualized in Fig. 4.

Cerium-containing layer effect on the coating durability. As seen in Fig. 5, the introduction of the cerium-containing protective layer significantly increased the samples corrosion resistance.

Surface morphology. Figure 6 shows the typical results of the morphology studies of cerium-containing surface formed in the optimal conditions. The regions with smaller cracks (smaller than 1 μm, Fig. 6b) covered about 90% of the surface; areas with larger cracks (thickness of more than 1 μm) were revealed as well (Fig. 6c).

EXPERIMENTAL

Samples preparation. We used carbon steel containing Mn (0.087 wt %), P (0.008 wt %), Si (0.003 wt %), S (0.0044 wt %), C (0.0014 wt %), and Fe. The studied steel plates (50 mm × 50 mm) were priory cleaned by treatment with Ridosol 2960 (Henkel Co). Then, they were degreased by immersing in alkaline aqueous cleaner (Ridoline 1562, Ridosol 550 CF, Henkel Co.) for 135 s at 55–60°C and thoroughly washed with deionized water during 80 s. To clean the surface of the oxides, the samples were immersed in the sulfuric acid solution (1 wt %) for 30 s at 55–60°C. After that, the samples were washed with deionized water again, during 120 s.

Formation of cerium-containing coating. In a typical experiment, the solution for coating was prepared of 8.68 g $Ce(NO_3)_3 \cdot 6H_2O$ (Merck, >98.6%), 480 mL of deionized water, and 480 mL of ethyleneglycol. At the last step, 40 mL of hydrogen peroxide solution (35 wt %) was added and pH was adjusted to 1.2 with nitric acid (Merck, 65%). A precleaned steel plate was used as cathode in the electrolysis process, anode being made of zinc plate with a one-side surface of 50 mm × 50 mm. Continuous current was applied to the electrolyte solution (Munk rectifier, 30 A/dm^2, 600 V). The process parameters were varied as follows: cerium salt concentration, 0.01–0.04 mol/L; pH, 1.2–3.5; temperature, 18–40°C; current density, 1–30 A/dm^2; treatment duration, 20–480 s.

Phosphate post-treatment. Deposition of cerium-containing coating was followe dby phosphate sealing using the $Na_3PO_4 \cdot 12H_2O$ solution (2.5 wt %, pH of about 4.5 [23]). In the experiments, we varied the treatment duration (2, 5, or 10 min) and temperature (60, 70, or 85°C). The unsealed (as-treated) steel plate was used as reference.

Coating adhesion was evaluated using a tape test (3M, Scotch Co. and 3M, Permacel Co.): the tape was pressed onto the dry sample surface, and then removed abruptly. The film was then examined visually and with optical as well as electron microscope.

Electro-coating with organic paint. The 220 V constant voltage of was applied to the steel plate as catode immersed into the bath containing organic paint during 120 s (35±2°C, pH = 5.8–6.2, and paint concentration of 10–20 wt %), the paint was deposited onto the cathode surface in the electrostatic field. Then, the sample was thoroughly washed with deionized water and dried during 20 min at 175°C. The so prepared steel samples were tested according the following standards NES M0007, NES M0140, ISO 2409, JIS K5400, and K5600.

Corrosion resistance test. The samples corrosion resistance was tested in the salt fog (5% NaCl at 35°C) during certain time, the samples were scribed with "X." The samples were visually examined from time to time for premature failure.

CONCLUSIONS

It was demonstrated that the introduction of protective cerium-containing layer significantly enhanced the corrosion resistance of steel. The optimal conditions to obtain the protective coating were elucidated.

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