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Cerium treatments for temporary protection of electroplated steel

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Abstract

The present work aims at evaluating the corrosion performance of a cerium immersion treatment on zinc electroplated. For comparison, zinc coatings pretreated with a commercial chromate treatment were also examined. The corrosion behaviour of pretreated zinc surfaces under immersion in sodium chloride was investigated by potentiodynamic polarization to evaluate the effect of cerium on the oxygen reduction reaction. The influence of immersion time, temperature of cerium solutions, stirring influence, cerium concentrations, cerium salt, pH of the solution and oxidation state of cerium are also investigated. Scanning electron microscopy (SEM) and X-ray energy dispersive spectroscopy (EDS) were used to characterize the sample surfaces after treatments. In order to compare the corrosion performance of cerium pretreated samples, an accelerated test in a humid chamber was carried out. The results indicate that the cerium film formed on the zinc surfaces markedly suppressed the cathodic process. The accelerated corrosion test shows that white rust formation is delayed although the protection given by this treatment is less efficient than with commercial chromate treatments.
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Keywords: Electroplated steel; Cerium; White rust; Potentiodynamic polarization; SEM

1. Introduction

Currently, chromates are widely used in anticorrosive pretreatments of a large number of metals and alloys. However, hexavalent chromium presents very high toxicity and has a bad environmental impact. For this reason, an intense research effort is being undertaken to replace chromates by more environmentally friendly compounds. Therefore, cerium salts were tested as corrosion inhibitors for different metallic alloys. Hinton and coworkers found that cerium was effective in reducing the corrosion rate of metallic substrates by inhibiting the cathodic reaction [1–4] Previous papers [5–11] studied the lanthanide inhibitor effect on aluminium and its alloys. By immersion in cerium salt solutions, the aluminium dissolution and the associated hydrogen evolution generate a local increase of pH which leads to localized precipitation of cerium-hydrated oxides.

In this paper, the studied substrates are zinc-coated steel. Zinc is widely used as a protective coating to prevent corrosion of steel. Since zinc is more electronegative than iron, it offers sacrificial protection to steel in corrosive media. For these industrial zinc-coated substrates, it is important to delay or avoid the "white rust" formation during storage in humid atmospheres. Currently, to obtain this protection during a few months, passivation by chromates is used as a posttreatment. However, due to increased environmental concerns and legislation limiting the use of Cr^{6+}, new alternatives must be used.

Zinc coatings can be deposited by different ways: electroplating, hot dip galvanization, metallization. When applied by electroplating, the coating is pure zinc. Surface analysis of electroplated zinc (EP) steel gives evidence that the surface after air exposure is always oxidized by a zinc oxide layer to a depth of more than 100 Å [12].

The present work aims at forming cerium films on zinc surfaces by immersion in cerium salts solutions in order to replace chromate treatments for the temporary protection

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of zinc-electrocoated steel. The influence of the experimental conditions (temperature, immersion time, concentration, pH, stirring and H_2O_2 concentration) is studied. The stirring influence is an important industrial factor because in a coil line, the sheets are coated at speeds of up to 200 m/min.

The modified surfaces were characterized by scanning electron microscopy/X-ray energy dispersive spectroscopy (SEM/EDS). The corrosion behaviour of the pretreated substrates under immersion in sodium chloride was investigated using cathodic polarization curves.

To compare the corrosion performance of a cerium pretreatment to a chromate treatment on EP steel, an accelerated test in a humidity chamber was performed.

2. Experimental method

2.1. Materials and samples preparation

Solutions of analytical grade Ce(III) reagents were used for samples preparation.

The 0.1 M NaCl solution was prepared by diluting analytical grade NaCl. The different oxygenation ratios of the 0.1 M NaCl solution were obtained by bubbling oxygen, nitrogen or compressed air into the solution. The amount of dissolved oxygen in the NaCl solution was about 40 ppm, 8 ppm and lower than 1 ppm for oxygenated, aerated and deoxygenated solutions, respectively, evaluated by means of a consort Z621 oximeter.

The zinc electrocoated steel sheets were prepared by Cockerill Sambre Arcelor (Belgium). The average zinc thickness is 4–5 μm. The dimensions of the substrate plates were 70×50×1 mm. Before the cerium treatment, EP steel was degreased using ethanol. The edges of the panels were coated with a varnish in order to avoid steel contact with the solutions. To reactivate the surface of the sample, the zinc EP steel plates were etched by immersion in HCl 7,5% during 30 s, rinsed with deionised water and finally with ethanol.

For comparison, a commercial chromate treatment is also used. The samples were immersed for 5 s in an aqueous Okemcoat solution (80% Okemcoat/20% water), rinsed with water and dried for 5 min. All the samples were submitted to the electrochemical test after preparation.

2.1.1. Treatment of zinc-coated steel in Ce(III) solutions

Immediately after etching, a "standard" treatment was applied which consisted in a 30-min immersion in a 0.01 M Ce(NO₃)₃.6H₂O (pH 5.5) solution at room temperature with stirring.

The stirring consisted in an up and down motion of the metallic sample into the solution at an average speed of 10 m/min. The sample was then rinsed thoroughly with deionised water and submitted to the electrochemical measurements.

2.2. Surface analysis

A Philips XL 20 Scanning electron microscope equipped with an EDAX energy dispersive X-ray spectrometer was used. For SEM observations and EDS analysis, flat samples of EP steel (before and after cerium treatment) were used.

2.3. Electrochemical measurements

Polarization curves of bare, chromated and cerium-treated EP steel were measured in a 0.1 M NaCl solution using a three electrode arrangement. The working electrode was the material to be studied, the reference is an Ag/AgCl electrode and a platinum disk was used as counter electrode.

All electrochemical measurements were made after 10-min immersion of the sample in the test media, time required for the open-circuit potential to reach a steady-state value. Cathodic polarization measurements were then carried out using a 273 EG and G PAR potentiostat. The scan rate was 100 mV/min. For comparison, the curves of the untreated and chromated zinc coatings were also determinated.

2.4. Anticorrosive behaviour evaluation

The corrosion resistance of the coated steel was studied by submitting the samples to an accelerated test in a humidity chamber. The cycle conditions were:

Step 1   40 °C—100% RH during 8h;
Step 2   23 °C—70% RH during 16 h.

The cycle time (steps 1 and 2) was 24 h, and 10 cycles were performed.

Visual assessments of surface degradation were based on the time of appearance of white rust, the ratio of white rust after each cycle and the time for the first point of red rust to appear.

3. Results

3.1. Surface analysis

SEM micrographs (a) and (b) on Fig. 1 show the bare EP steel morphology. The sample surface is not totally smooth and zones of different depths exist. The deeper zone presents a sheet structure characteristic of the high current density EP steel [13]. The upper zones are composed of squashed sheets. The SEM/EDS analysis shows that the whole surface is covered with zinc. After HCl etching (c), the sheets are corroded and very small pits are visible on the surface. After a "standard" cerium treatment (d), no grains of cerium are visible on the surface but cerium is detected in the EDS spectrum (not shown).
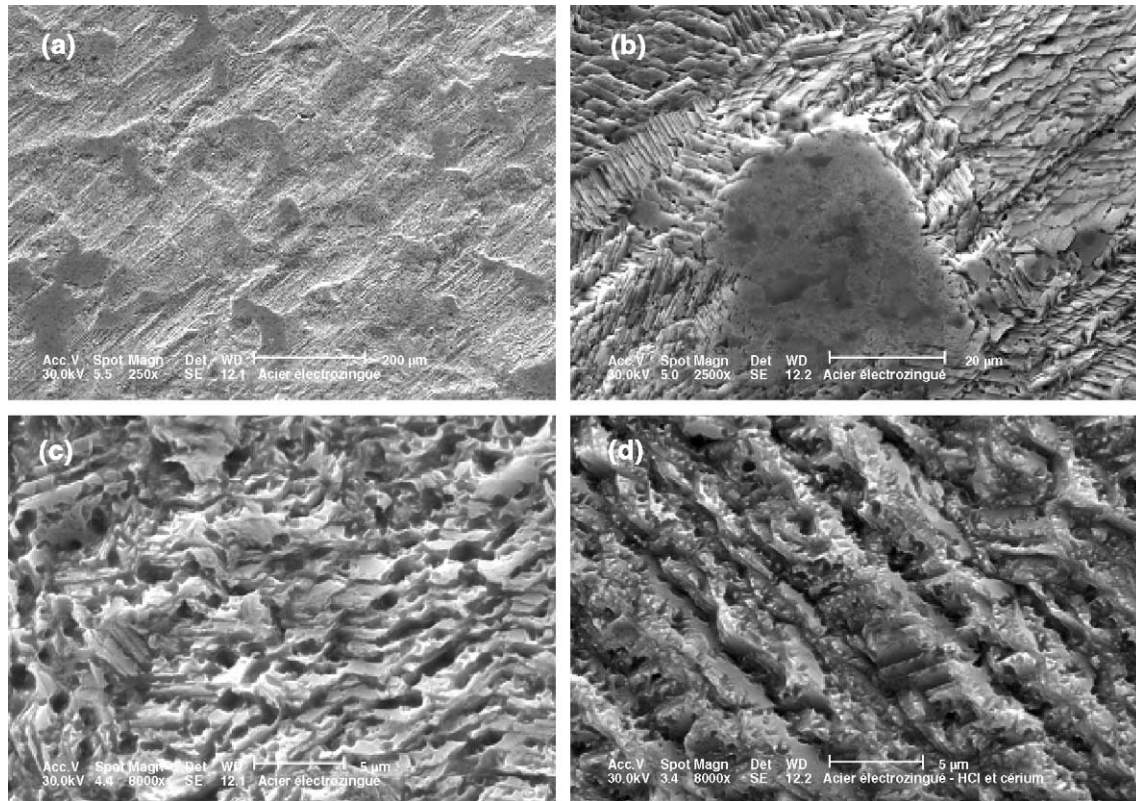
Fig. 1. SEM micrograph of EP steel: (a) bare sample; (b) transition between upper and lower zones on a bare sample; (c) after HCl etching; (d) after a «standard» cerium treatment.

3.2. Treatment efficiency and influence of the experimental parameters

The process of zinc corrosion in an oxygenated NaCl solution is a combination of anodic zinc dissolution and cathodic oxygen reduction which is the rate controlling stage. Cerium salts are known as cathodic inhibitors, reducing the rate of the cathodic process.

In order to reveal the cerium treatment efficiency, cathodic polarization curves measurements were performed. Fig. 2 shows the cathodic polarization curves obtained on an etched EP steel sample. The 0.1 M NaCl
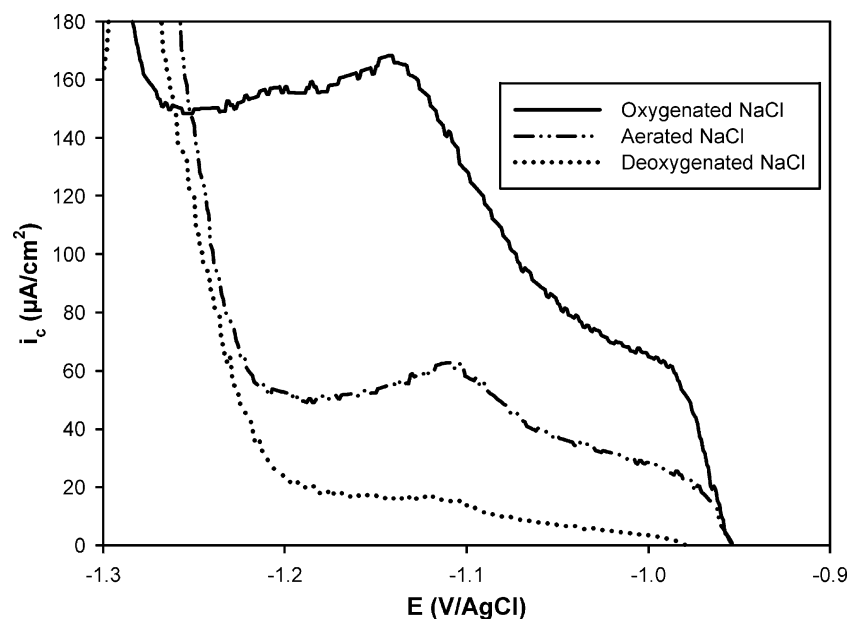

Fig. 2. Cathodic polarization curves of etched EP steel in 0.1 M NaCl at various dissolved oxygen ratios.
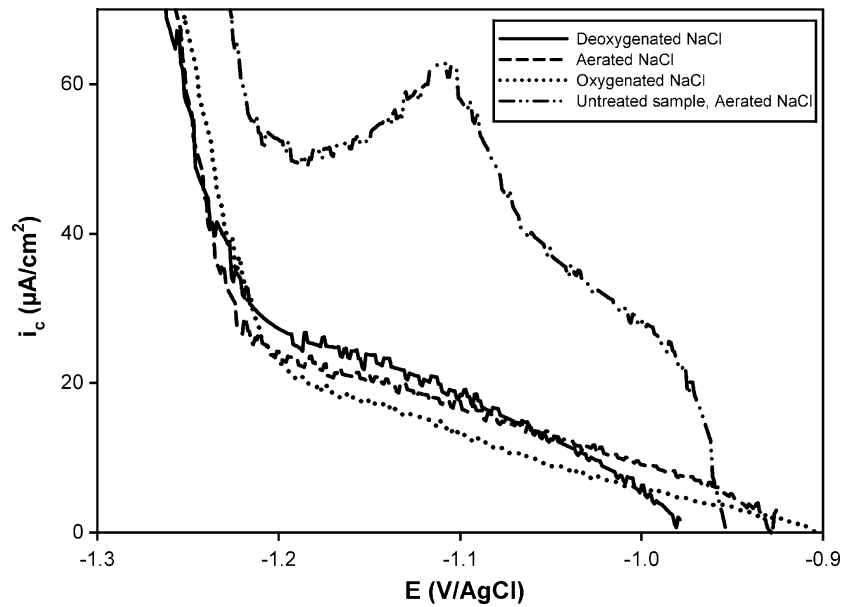
Fig. 3. Cathodic polarization curves of «standard» treated EP steel in (1) oxygenated; (2) aerated; (3) deoxygenated 0.1 M NaCl; (4) untreated sample in aerated 0.1 M NaCl.

electrolytic solution is either deoxygenated (0–1 ppm O_2), aerated (8–10 ppm O_2) or oxygenated (39–41 ppm O_2).

Fig. 3 shows the cathodic polarization curves of a "standard" cerium-treated EP sample. The curves show similar values of cathodic current densities for cerium treated samples at different dissolved oxygen ratios. The cerium film formed during the "standard" treatment inhibits the cathodic oxygen reduction reaction during immersion in the aggressive media, giving corrosion protection to the metallic sample.

3.2.1. Influence of the pH of the cerium bath

A "standard" cerium treatment is applied to the EP steel samples at various pH which was adjusted by adding nitric acid to the solution. Fig. 4 shows the polarization curves obtained in aerated 0.1 M NaCl. The pH range for the 0.01 M $Ce(NO_3)_3.7H_2O$ solution which leads to cerium film formation with effective blocking of the cathodic corrosion reaction is from 4 to 6.5. At pH values lower than 3, the efficiency of the treatment is slightly decreased.
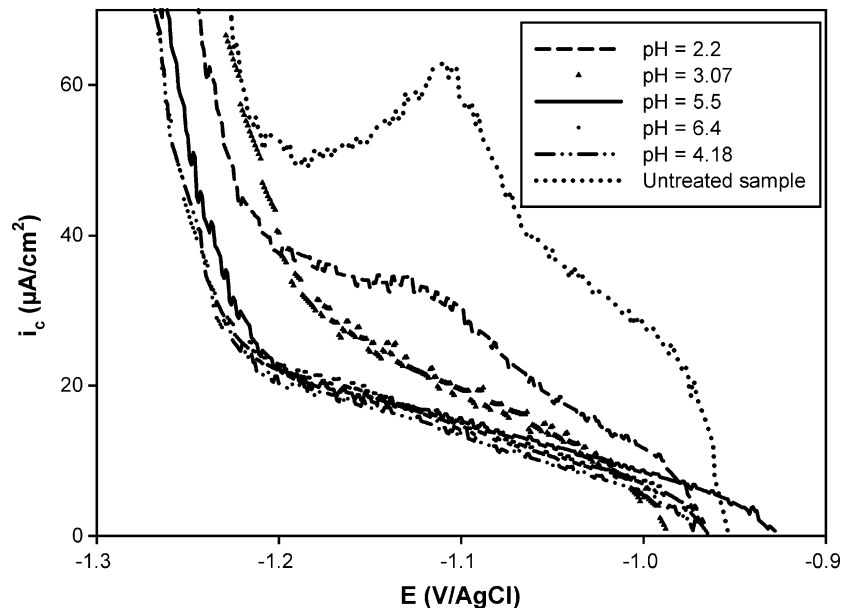

Fig. 4. Cathodic polarization curves in aerated 0.1 M NaCl of «standard» cerium-treated EP steel at various pH.
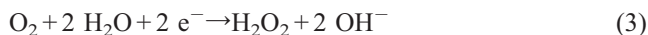
In acidic solutions, zinc has a high solubility and dissolves with formation of Zn^{2+} ions following:

$$Zn \rightarrow Zn^{2+} + 2\ e^- \qquad (1)$$

The associated cathodic reaction is either hydrogen evolution or the two-step oxygen reduction reaction:

$$2\ H^+ + 2\ e^- \rightarrow H_2 \qquad (2)$$

Or

$$O_2 + 2\ H_2O + 2\ e^- \rightarrow H_2O_2 + 2\ OH^- \qquad (3)$$

$$H_2O_2 + 2\ e^- \rightarrow 2\ OH^- \qquad (4)$$

The local pH increase at the surface proximity leads to cerium hydroxide precipitation on the zinc surface:

$$Ce^{3+} + 3\ OH^- \rightarrow Ce(OH)_3 \qquad (5)$$

Or

$$2\ Ce^{3+} + H_2O_2 \rightarrow 2\ Ce^{4+} + 2\ OH^- \qquad (6)$$

$$Ce^{4+} + 4\ OH^- \rightarrow Ce(OH)_4 \qquad (7)$$

At pH values lower than 3, the main cathodic reaction [14] during the cerium film formation is the hydrogen evolution (reaction (2)). The local pH increase near the sample surface leads to the precipitation of Ce(III) compounds on the zinc surface. However, this local pH increase is not sufficient to precipitate a protective cerium film. The local increase of pH is moreover disturbed by stirring.

For higher pH, the oxygen reduction reaction is also a possible associated cathodic reaction. Oxygen reduces with the formation of a hydrogen peroxide intermediate which can oxidize the Ce(III) ions to Ce(IV) ions (reaction (6)). A film containing Ce(III) and Ce(IV) compounds would then be precipitated on the metallic surface. Stirring plays an important role which is discussed in the following paragraph.

3.2.2. Influence of stirring

The aim of this study was not to optimize the stirring but to define whether or not this parameter is significant. For an industrial application, stirring plays an important role since the EP steel is treated at high speeds. Fig. 5 shows the cathodic polarization curves obtained for a "standard" cerium-treated sample and for a sample treated in the same conditions, but without stirring. The cathodic current density obtained for a sample prepared with stirring is lower than that obtained for a simply immersed sample. As discussed above, the predominant cathodic reaction during the cerium film formation under the used working conditions is considered to be the oxygen reduction reaction.

Stirring is able to regenerate the dissolved oxygen concentration near the sample. In order to confirm the importance of the dissolved oxygen ratio in the cerium solution for the treatment, EP steel samples were treated by immersion in 0.01 M $Ce(NO_3)_3.7H_2O$ (pH 5.5) solutions either aerated or oxygenated (Fig. 6). The oxygenated cerium solution gives rise to a cerium layer formation with better corrosion resistance, showing the importance of the dissolved oxygen ratio in the cerium solution.
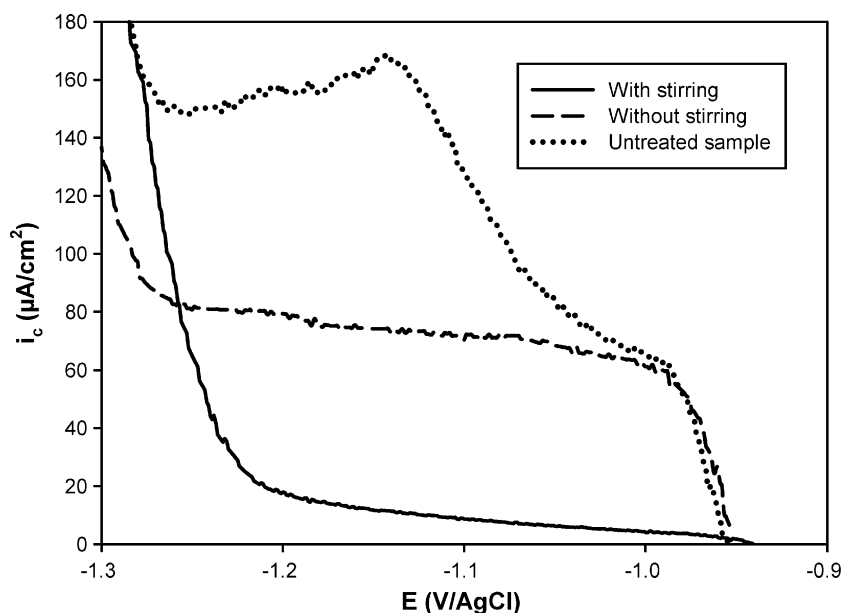

Fig. 5. Cathodic polarization curves of «standard» cerium-treated EP steel in oxygenated 0.1 M NaCl with and without stirring.
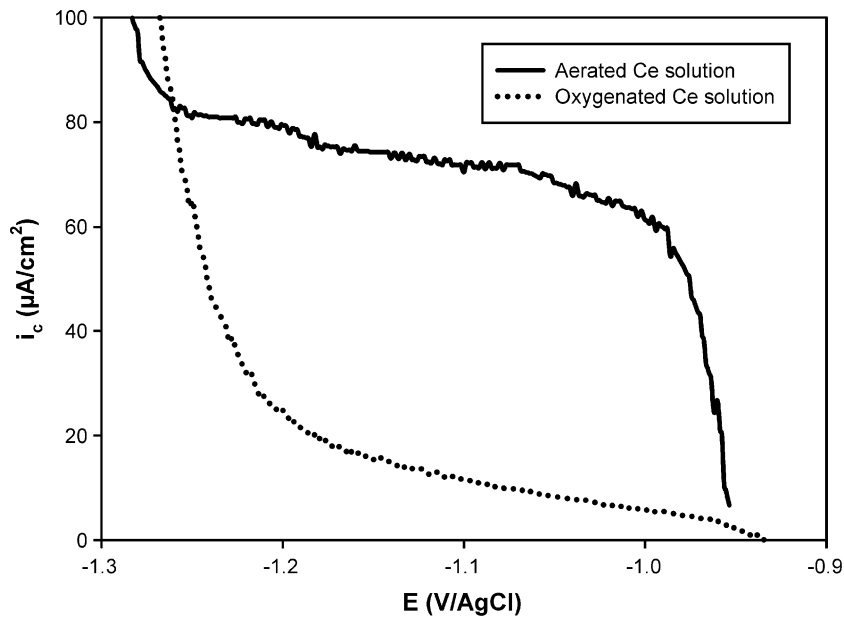
Fig. 6. Cathodic polarization curves in oxygenated 0.1 M NaCl of EP steel treated by immersion without stirring in an oxygenated or aerated 0.01 M $Ce(NO_3)_3$ solution.

Without stirring, the hydrogen peroxide intermediate formed in the first step of the oxygen reaction may react with the Ce(III) cations following reaction (6) to form Ce(IV) cations which precipitate on the zinc surface according to reaction (7). As discussed below, the films mainly composed of Ce(IV) oxides/hydroxides are less efficient for blocking the cathodic corrosion reaction.

The positive effect of stirring could be explained by the change in the kinetics of the oxygen reduction reaction, avoiding hydrogen peroxide formation and leading to the formation of a colourless cerium film thus probably mainly composed of Ce(III) oxides and hydroxides.

3.2.3. Influence of the cerium oxidation state

By the addition of oxygen peroxide to the cerium solution, the oxidation state of the cerium can be varied from (III) to (IV) following reaction (6). The films obtained were yellow–orange coloured, indicating that the film contains a higher Ce(IV) ratio than the "standard" cerium-treated ones.
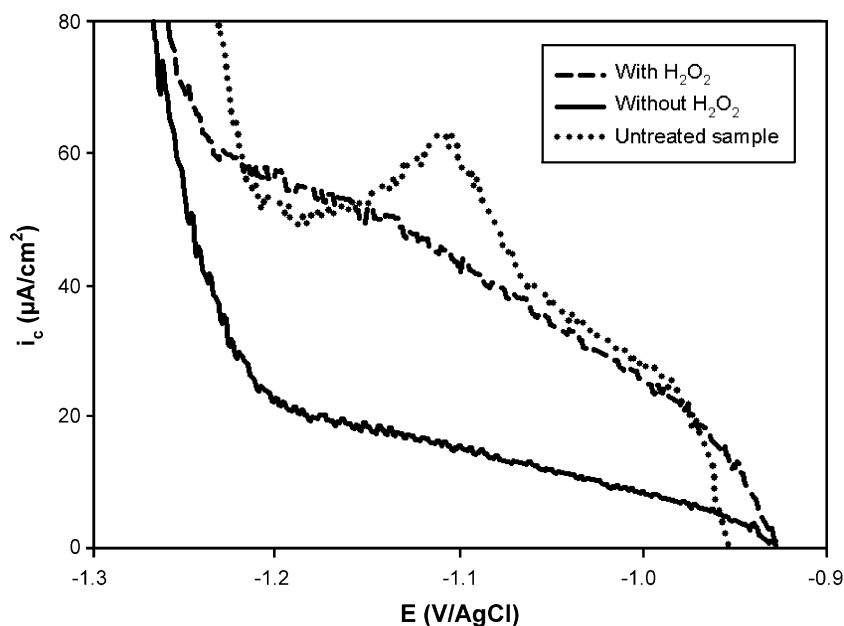

Fig. 7. Cathodic polarization curves in aerated 0.1 M NaCl of EP steel with and without hydrogen peroxide in the $Ce(NO_3)_3$ solution.
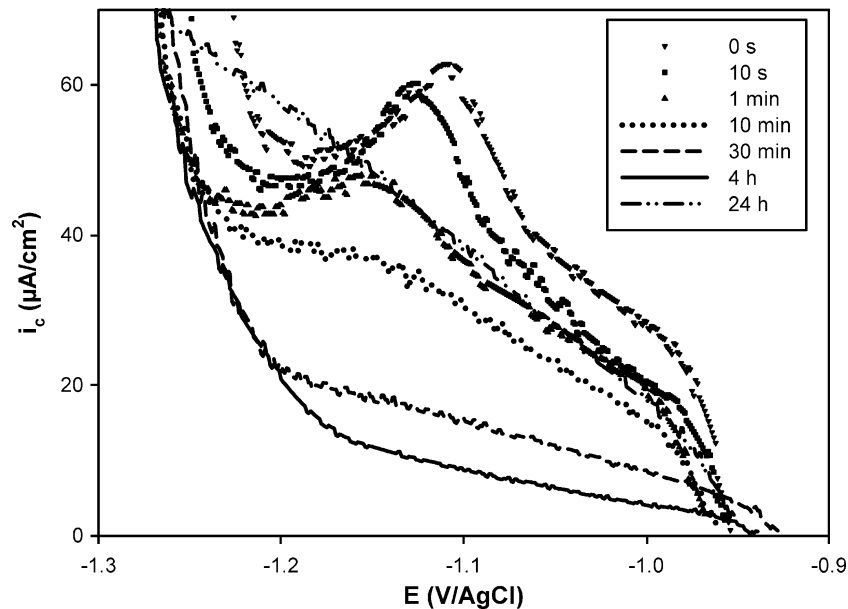
Fig. 8. Cathodic polarization curves in aerated 0.1 M NaCl. EP steel treated for (1) 0 s, (2) 10 s, (3) 1 min, (4) 10 min, (5) 30 min, (6) 4 h, (7) 24 h in the 0.01 M Ce(NO$_3$)$_3$ with stirring.

Fig. 7 shows the cathodic polarization curves in a 0.1 M aerated NaCl solution. This result confirms that Ce(IV) treatment is less effective on zinc in blocking the oxygen reduction reaction [16].

3.2.4. Immersion time effect

"Standard" cerium treatments were made using various immersion times at 10 s, 1 min, 10 min, 30 min, 4 h and 24 h. The treatment efficiency increased with immersion time in the cerium solution up to 4 h, as shown in Fig. 8. Immersion times shorter than 30 min produce a cerium film with poor corrosion protection properties. Under the

investigated conditions, the sample treated during 4 h presents the best result, although the 30 min treated sample shows a marked inhibition of the cathodic corrosion reaction and offers a better time/efficiency compromise for an industrial application. Short immersion times lead to uniform surface film formation [15,16].

For long immersion times, the efficiency decreases. This is possibly due to a loss in the film coherence when it reaches a critical thickness. The microcracks in the film allow the continuation of the cathodic and anodic processes leading to an overprecipitation of cerium in some areas of the surface. The film becomes heterogeneous and porous
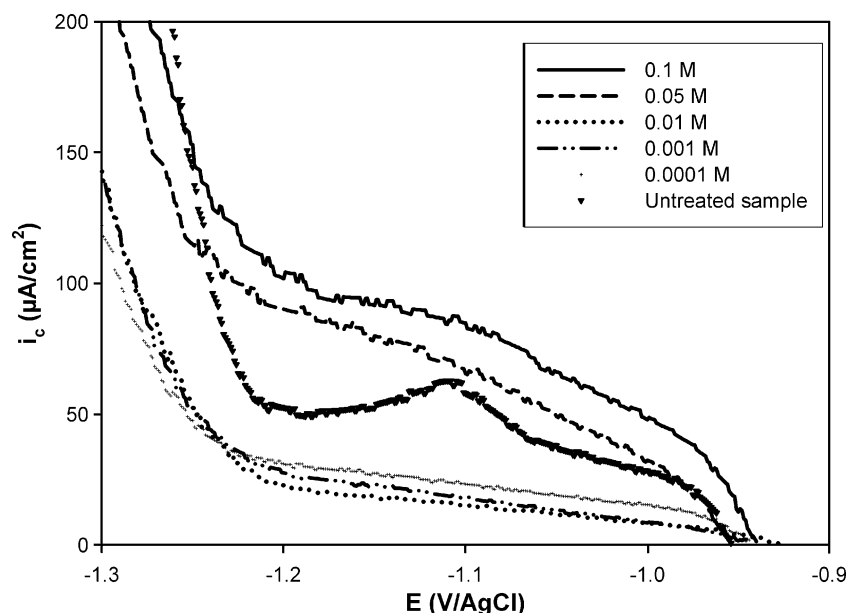

Fig. 9. Cathodic polarization curves in aerated 0.1 M NaCl of «standard» cerium-treated EP steel samples at various cerium concentrations.
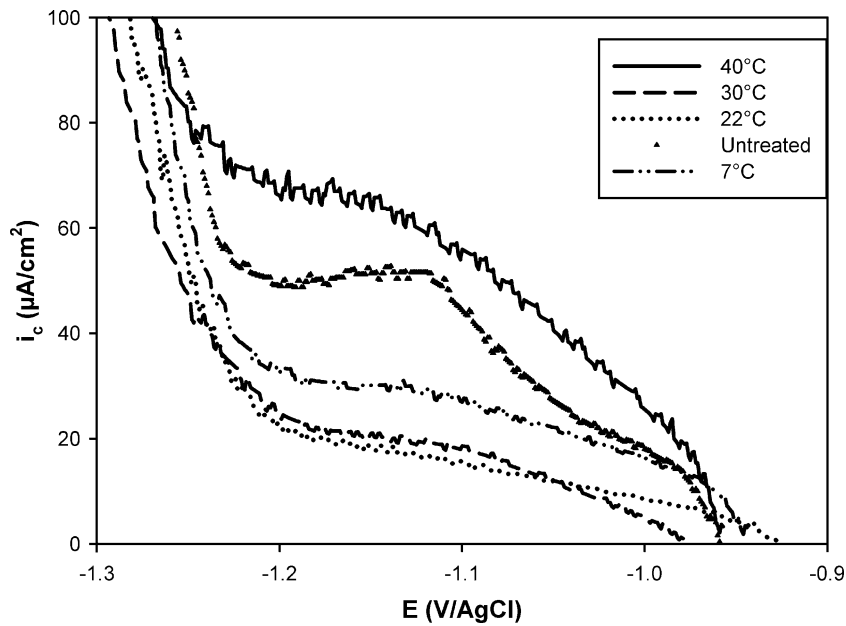
Fig. 10. Cathodic polarization curves in aerated 0.1 M NaCl of «standard» cerium-treated EP steel at various solution temperatures.

and is mainly composed of Ce^{4+} oxides. The treatment efficiency is sensitive to the treatment time. The films are composed of a mixture of Ce^{3+} probably $Ce(OH)_3$ and CeO_2 species with a predominance of Ce^{3+} in the first instants of treatment followed by enrichment in Ce^{4+} [17,18].

3.2.5. Cerium concentration effect

A "standard" cerium treatment was used for the sample preparation with cerium concentrations varying from 0.0001 M to 0.1 M. The best results were obtained with a nitrate cerium concentration of 0.01 M, as shown in Fig. 9. At concentrations up to 0.1 M, a homogeneous passive layer consisting of zinc and cerium oxides was developed. When cerium was present at high concentration, the inhibitor oxidation seemed to become competitive with zinc oxidation. This leads to high cerium oxidation and precipitation with a concurrent zinc oxide. Such behaviour produces an inhomogeneous layer consisting of different zones, some rich in cerium oxides and others poor in cerium oxides with a poor zinc oxide film. The zones poor in cerium oxides could become preferential zones for corrosion attack.

3.2.6. Influence of the temperature of the cerium bath

The EP samples were immersed for 30 min with stirring in a 0.01 M $Ce(NO_3)_3 \cdot 6H_2O$ solution at various temperatures.
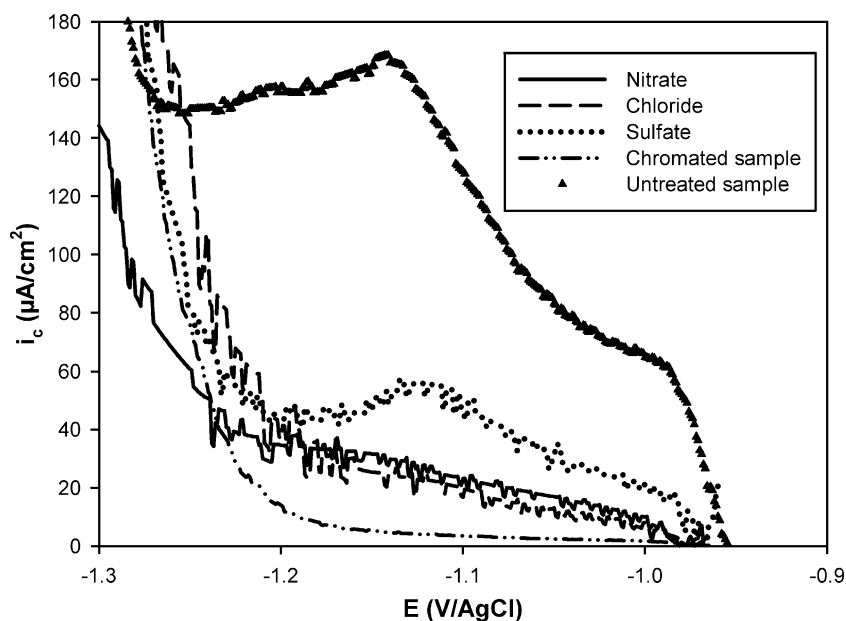

Fig. 11. Cathodic polarization curves in oxygenated 0.1 M NaCl of «standard» cerium-treated EP steel with various cerium salts.

Table 1
Results of the accelerated corrosion test of zinc EP steel

		24 h	48 h	96 h	120 h	144 h	192 h	240 h
Bare EP steel	WR (%)[a]	90	95	97	95	94	90	85
	RR (%)[b]	–	–	3	5	6	10	15
Ce-treated EP steel	WR (%)	25	40	55	58	68	73	86
	RR (%)	–	–	–	–	–	2	2
Chromated EP steel	WR (%)	0	0	0	0	0	0	0

[a] Ratio of white rust covering the sample surface.
[b] Ratio of red rust covering the sample surface.

Fig. 10 shows the obtained cathodic polarization curves in a 0.1M aerated NaCl solution. Neither a decrease nor an increase of the cerium solution temperature seems to be favourable. For temperatures exceeding 40 °C, the cerium treatment is clearly unfavourable. The cathodic current density is higher than that obtained for an untreated sample.

3.2.7. Influence of the nature of the cerium salt

Three cerium salts were investigated, namely, $Ce(NO_3)_3.6H_2O$, $CeCl_3.7H_2O$ and anhydrous $Ce_2(SO_4)_3$. The Ce(III) concentration in the solution is 0.01 M.

Fig. 11 shows that when cerium nitrate and chloride solutions are used for the sample treatment, the films formed on the zinc surface present similar cathodic inhibition efficiencies.

The film obtained on the EP steel sample after treatment in a sulfate solution is less efficient for blocking the oxygen reduction reaction.

The anion plays a role in the cerium film formation and/or composition although this parameter needs to be further investigated.

4. Anticorrosive behaviour evaluation

The results of the accelerated corrosion test in a humid chamber are given in Table 1.

For chromated EP samples, no white rust formation is observed on the sample surfaces at the end of the test (240 h).

On bare EP steel, white rust appears after the first cycle of the test and covers nearly the entire surface of the sample. It develops rapidly and after 96 h, the first red rust point appears. Red rust develops progressively and covers 15% of the surface at the end of the test.

On «standard» cerium-treated EP, white rust apparition is observed after the first cycle of testing. However, the ratio of white rust developed on the surface is lower and its growth slower than for untreated samples. On EP steel, red rust apparition is also delayed and does not develop.

5. Conclusions

The aim of this study carried out in an industrial perspective was to verify the possibility to produce cerium protective films on zinc-coated steels for temporary protection during storage. The different operating parameters were investigated and the best results are given by films formed by a 30-min immersion treatment in a 0.01 M $Ce(NO_3)_3.6H_2O$ solution (pH 5.5) with stirring. This study emphasizes the importance of the stirring and the amount of dissolved oxygen in the 0.01 M $Ce(NO_3)_3.6H_2O$ solution. Stirring is a favourable parameter. This could be explained by a change in the kinetics of the oxygen reduction reaction during the film formation. The H_2O_2 intermediate formation is possibly avoided, and the obtained films are mainly composed of Ce(III) compounds which are more efficient than Ce(IV) films for corrosion protection. While in the industrial process, sheets may be travelling at 200 m/min, there is usually a period where there is a thin film of coating solution on the surface. Oxygen transport through this film is high, so while during immersion there may not be enough time for precipitation reactions occur at the surface, reactions can happen quite quickly out of solution after immersion.

The accelerated corrosion test in a humid chamber shows the protective effect of cerium although cerium treatments are less effective than chromate treatments.

These results are encouraging, and in the future, the possibility of combining cerium with others protection systems will be investigated.

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