

Corrosion stability of stainless steel, modified electrochemically with Ce₂O₃–CeO₂ films, in 3.5% NaCl media

D. Guergova¹, E. Stoyanova¹, D. Stoychev^{1*}, I. Avramova², G. Atanasova², P. Stefanov²

¹Rostislav Kaischew Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

²Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

Received August 12, 2010; accepted October 25, 2010

This work is focused on the study of corrosion-protection ability of the thin ceria film, formed electrochemically on OC404 stainless steel (SS) in non-aqueous electrolytes. The influence of changes in the surface concentration of Ce₂O₃–CeO₂ on the corrosion behaviour of OC404 stainless steel in 3.5% NaCl was investigated prior to the thermal treatment as well as after it. A shift of corrosion potential in positive direction was found via polarization curve recording, as well as via decrease in the corrosion current, respectively decrease in the corrosion rate (enhancement of the corrosion protection) in the presence of ceria oxide films.

The data, acquired by AFM and XPS, are in a good agreement with these results. On the basis of the obtained results we can conclude that the presence of Ce₂O₃–CeO₂ film results in passivation and re-passivation of the steel surface and a slowdown in the pitting corrosion in an aggressive media. These conclusions are explained by the strong polarization influence of the Ce₂O₃–CeO₂ layers on the conjugated depolarization cathodic reaction of reduction of the dissolved oxygen.

Key words: corrosion protection, polarization, electrodeposited Ce₂O₃–CeO₂ thin films.

INTRODUCTION

The option to use representatives of the rare-earth element group (Ce, La, Sm, Y) for the protection of Al, Fe and Zn articles against corrosion in aqueous solutions was studied for the first time by Hinton and coauthors at the beginning of the eighties of the 20th century [1–5]. According to the literature sources, the surface modification of stainless steels in particular [6–15], and the other metal alloys using rare-earth elements, leads to improvement of their resistance to corrosion in aqueous media, containing chloride ions, [16–19]. The increased corrosion stability is due to the formation of thin oxide films (whose protective action is associated with formation of soluble Ce₂O₃, Ce(OH)₃ and/or insoluble CeO₂ and Ce(OH)₂²⁺ oxides/hydroxides) thus hindering the free diffusion of oxygen and adsorption of the aggressive Cl⁻ ion on the metal surface, leading to acceleration of the pitting formation [19–22].

Our previous works showed that the electrochemical formation of Ce₂O₃–CeO₂ and Al₂O₃ thin oxide films on OC404 stainless steel results in improvement of the passivation processes in media with an oxidizing action (0.1 N HNO₃),

and in prevention of pitting corrosion appearance [23, 24]. The behavior of the above systems was studied in non-oxidizing media (0.1 N H₂SO₄) [25, 26]. Thereupon, it was established that the deposition of Ce₂O₃–CeO₂ oxides has a strongly expressed stabilizing effect on the passive state of SS. This effect is connected with the occurrence of effective reduction cathodic process of the CeO₂, leading to a stable passive state. The oxide presence determines the restoration of the disrupted passive state of the thermally treated steel in an acidic media.

The aim of this investigation was to study the corrosion behavior, respectively the protective effect, of the electrochemically formed (in non-aqueous electrolytes) Ce₂O₃–CeO₂ films on the stainless steel (prior to and after the thermal treatment of the “oxide layer/stainless steel” system) in a 3.5% NaCl solution.

EXPERIMENTAL

The test specimens, used in this study, were prepared from a sheet of OC404 type SS, with a thickness of 50 μm. The composition of the steel in wt. % was 20.0% Cr, 5.0% Al, 0.02% C, the rest being Fe.

The Ce₂O₃–CeO₂ layers were deposited electrochemically on SS from non-aqueous

* To whom all correspondence should be sent:

E-mail: stoychev@ipc.bas.bg

electrolytes – their compositions and regimes are described in [27, 28].

The thickness of the deposited layers was $\sim 1\mu\text{m}$. The layers were investigated upon deposition and upon thermal treatment (t.t.) at 450 C for 2 h in air.

The electrochemical behaviour of the samples (10 mm x 10 mm) was studied in a naturally aerated 3.5% NaCl aggressive media (pH = 6.5) at a room temperature in a standard three-electrode thermostatted cell (100 ml volume). A counter electrode, comprising a platinum plate (10 x 10 x 0.6 mm), and a calomel reference electrode (SCE), ($E_{\text{Hg}/\text{Hg}_2\text{Cl}_2} = +0.240\text{ V vs. SHE}$), were used. All potentials in the text are related to SCE. The anodic and cathodic potentiodynamic polarization curves were obtained using a 273 EG&G potentiostat/galvanostat (Germany), with a potential sweeping rate of 10 mV/s within the potential range from -1.500 to +1.000 V.

The corrosion potential (E_{corr}), the breakdown potential (E_{pitt}), and the corrosion current density (i_{corr}) of the samples under investigation were determined based on potentiodynamic polarization curves, obtained in 3.5% NaCl solution.

The chemical composition and the oxidation state of the elements on the surface formed after immersion (for different time intervals) in an aggressive media – for the specimens “upon deposition” and upon thermal treatment, were studied using X-ray photoelectron spectroscopy (XPS). The XPS studies were performed in an Escalab II system (England) with Al K_{α} radiation ($h\nu = 1486.6\text{ eV}$) and total instrumental resolution of $\sim 1\text{ eV}$. The vacuum in the chamber was 10^{-7} Pa . The binding energy (BE) was referred to the C1s line (of adventitious carbon) at 285.0 eV. The element concentrations were evaluated based on the integrated peak areas after Shirley-type of linear background subtraction using theoretical Scofield’s photoionization cross-sections [29].

The atomic force microscope (AFM) used for the surface imaging was a Q-scope 250 (Quesant, USA) with a head, designed for a scan area from 200 nm x 200 nm up to 80 μm x 80 μm . The lateral resolution was approximately 1 nm, and the resolution of the z-axis of approximately the same range. The measurements were performed in the non-contact mode with the following typical scan parameters: a scan rate of 0.5 to 3 Hz, integral and proportional gain in the range between 250 and 400, and image resolution of 300 to 600 dpi.

RESULTS AND DISCUSSION

On the basis of the plotted complete potentiodynamic polarization curves in the range of the potentials from -1.500 to +1.000 V (these are not represented in this work), the basic electrochemical parameters of the corrosion process were determined for the studied systems (Tables 1 and 2). It follows from these results that:

- the cerium oxide films, deposited electrochemically on the stainless steel, create considerable shifts in the SS corrosion potential in a positive direction;
- this shifting grows up with the increase in the concentration of the oxides on the surface of the steel;
- the presence of cerium oxides leads to lowering of the corrosion current;
- the presence of cerium oxides determines a potentials shift of the pitting formation in a positive direction.

Table 1. Electrochemical parameters characterizing the corrosion behaviour of studied systems determined from potentiodynamic polarization curves.

Samples	E_{corr} , V	i_{corr} , A.cm ⁻²	E_{pitt} , V
SS	-0.172	6.0×10^{-7}	-0.065
Ce ₂ O ₃ -CeO ₂ (3.6 at.%)/SS	-0.168	5.1×10^{-7}	-0.054
Ce ₂ O ₃ -CeO ₂ (13.1 at.%)/SS	-0.163	3.0×10^{-7}	0.052
Ce ₂ O ₃ -CeO ₂ (25.7 at.%)/SS	-0.056	6.9×10^{-8}	0.091

Table 2. Electrochemical parameters characterizing the corrosion behaviour of studied systems, after thermal treatment determined from potentiodynamic polarization curves.

Samples	E_{corr} , V	i_{corr} , A.cm ⁻²	E_{pitt} , V
SSt.t.	-1.083	4.6×10^{-6}	-0.003
CeO ₂ -Ce ₂ O ₃ (4.2 at.%)/SSt.t.	-0.300	5.1×10^{-7}	-0.069
CeO ₂ -Ce ₂ O ₃ (11.2 at.%)/SSt.t.	-0.284	1.2×10^{-7}	0.091
CeO ₂ -Ce ₂ O ₃ (29.6 at.%)/SSt.t.	-0.168	1.3×10^{-8}	0.119

The obtained results show also that the thermal treatment of the studied samples causes a substantial change in the corrosion parameters, both, in the case of steel non-covered with cerium oxides, and in the case of the system cerium oxides/steel. As a consequence of the sample thermal treatment, the following is observed:

- E_{corr} of the steel is shifted with more than 0.900 V in the negative direction;
- i_{corr} of the steel is increased with an order of magnitude;
- E_{pitt} of the steel is shifted in the positive direction with more than 60mV, while for the system of CeO₂-Ce₂O₃/SS – with $\sim 120\text{ mV}$.

Thereupon, however, the respective corrosion potentials, which are characteristic for non-treated thermally systems, are not achieved, while the

corrosion currents and potentials of pitting formation are characterized by more favorable values, in terms of corrosion, compared to those, obtained for the non-treated thermally SS, respectively for the Ce₂O₃-CeO₂/SS.

Aiming to evaluate the protective effect of the electrodeposited cerium oxide films, we shall consider in details the anodic and the cathodic polarization curves for the studied systems in some specific zones of potentials, which characterize the occurring anodic and cathodic processes on the steel surface.

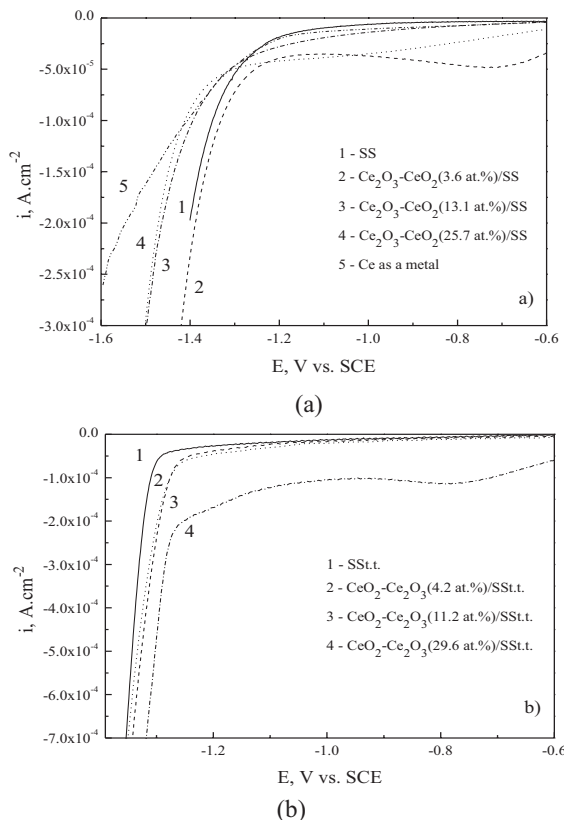


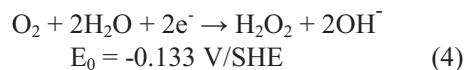
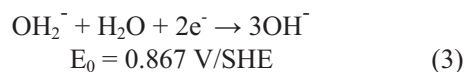
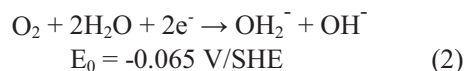
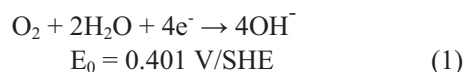
Fig. 1. Characteristic part of cathodic potentiodynamic polarization curves for the SS OC404 with Ce oxides surface modification, before (a) and after thermal treatment (b), obtained in 3.5% NaCl.

Fig. 1 illustrates the cathodic polarization curves, obtained in 3.5% NaCl solution, for stainless steel SS OC404 and for the systems of Ce₂O₃-CeO₂/SS before (a) and after thermal treatment (b). Fig. 1a represents the potentiodynamic curves for SS (curve 1) and for SS with various concentrations of the cerium oxide films, deposited on it electrochemically (curves 2-4). For comparison curve 5 was also plotted, characterizing the rate of the cathodic reduction process on metallic cerium.

It was necessary to carry out the investigation of the possible changes in the surface composition and the electrochemical (corrosion) behavior of the studied systems as a function of the duration of the thermal treatment in view of their application as supports of the catalytically active systems. These systems are calcinated (treated at high temperature) to undergo the respective transformations of the active phase or of the support, as well as in a number of other cases, in which it is possible to use SS, modified superficially with cerium oxide at high temperatures, and in the presence of chloride ions in the working environment [30, 31].

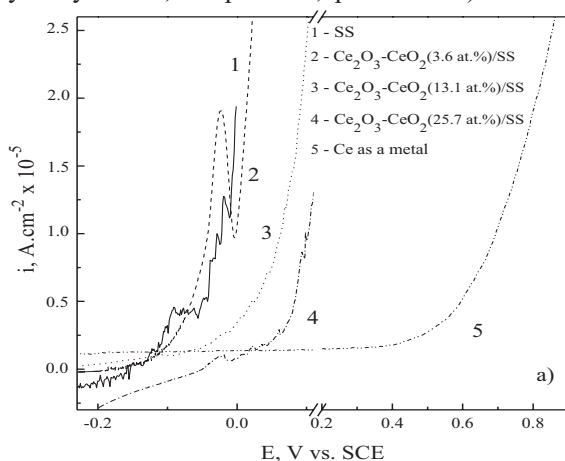
Fig. 1a clearly shows that the increase in the surface concentration of the cerium oxides in the case of non-treated thermally steel samples determines the increase in the reduction overpotential of the oxygen, dissolved in the corrosion medium. Such increase is inherent to this reaction in a native passive film on stainless steel, growing to values, close to those inherent to the metallic cerium. (In this case it is important to notice that the surface of the metallic Ce is always covered with a relatively thick layer of cerium oxides due to the extremely high affinity of Ce to oxygen [32]).

As reported in a study of Klaper et al. [33 and references therein] on the electrochemical reduction of oxygen in neutral and alkaline solutions, this process gives rise to formation of OH⁻ groups, following a four-electron pathway (Eq. (1)), or it can yield OH⁻ via hydrogen peroxide following a two-electron pathway (Eqs. (2) and (3)), or it can produce H₂O₂ as a final reduction product (Eq. (4)).



Based on own data and on other authors data, we can make the important conclusion that for stainless steels and iron-chromium alloys, the mechanism and kinetics of oxygen reduction strongly depend on the material (chemical composition, surface state), the electrolyte (pH, chemical composition), and the conditions under

which the reaction is taking its course (hydrodynamics, temperature, polarization). These



authors, as well as the authors of the paper [34] pay special attention to the specific type of the stainless

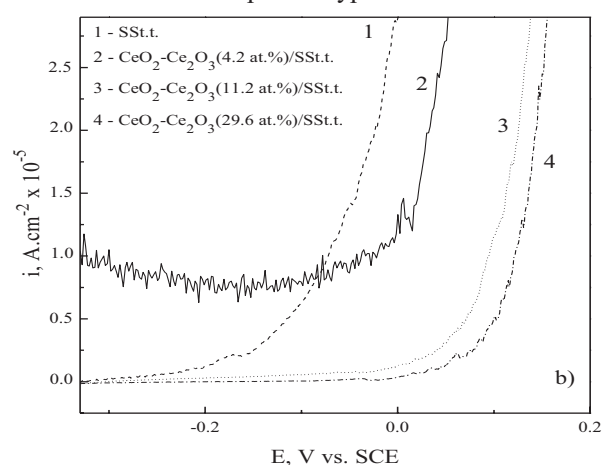


Fig. 2. Characteristic part of anodic potentiodynamic polarization curves for the SS OC404 with Ce oxides surface modification, before (a) and after thermal treatment (b), obtained in 3.5% NaCl.

steel. The presence of passive layers is also a very important factor, affecting the oxygen reduction reaction. Also, as far as localized corrosion of stainless steels is concerned, it preferably occurs within these layers rather than on the metallic surface, and therefore its catalytic activity should be related to the concentration of Fe (II) ions.

In the light of these considerations, the observed differences in the course of the curves 2-4, compared to curve 1 (for the SS non-coated with cerium oxides) in Fig. 1a are obviously due to the different nature of the support, on which the reduction process is occurring. Thereupon, we can clearly outline two zones of potentials (up to and above ~ -1.25 V), in which the nature of the reduction process is changing. Up to -1.25 V the steel surface, modified with cerium ions, determines a depolarizing effect, which (in our opinion) is due to reorganization of the mixed oxide films on the steel surface - see the corresponding peaks of oxidation in curve 2 (at $E = \sim -0.090$ V and at -0.020 V) in Fig. 2a. In the more negative range of potentials ($E < -1.25$ V), which corresponds to the proper zone of cathodic reduction of oxygen, the increase in the concentration of cerium oxides leads to a substantial growth of the overpotential of this reaction, respectively to decrease in its rate. Such impedance of the oxygen reaction, which is a conjugated cathodic reaction during the occurrence of steel corrosion in the $\text{Ce}_2\text{O}_3\text{-CeO}_2/\text{SS}$ system, obviously will lower the rate of the conjugated oxidation reaction, and thus, the total rate of the corrosion process. Besides this, such an inhibition of the cathodic reaction, under the conditions of passivity, is a guarantee for preservation of the

stable passive state of the stainless steel, respectively – for corrosion under conditions of passivity.

In the cases of thermally treated $\text{SS}_{\text{t.t.}}$ and $\text{CeO}_2\text{-Ce}_2\text{O}_3/\text{SS}_{\text{t.t.}}$ samples (Fig. 1b), which are known to have a disrupted surface passive film [26,35], we can observe an increase in the cathode current with about one order of magnitude, for both, the $\text{SS}_{\text{t.t.}}$ and the $\text{CeO}_2\text{-Ce}_2\text{O}_3/\text{SS}_{\text{t.t.}}$ system. At the same time, in the case of $\text{CeO}_2\text{-Ce}_2\text{O}_3/\text{SS}_{\text{t.t.}}$ sample a considerable depolarizing effect is registered (with ~ 0.2 V, in comparison with the $\text{Ce}_2\text{O}_3\text{-CeO}_2/\text{SS}$ system) in regards to the cathodic reaction in the zone of the potentials ($E < -1.25$ V), where the reaction of oxygen reduction is occurring. These results give us the reason to suppose that the occurrence of a second reduction process is also very probable in the thermally treated systems of $\text{Ce}_2\text{O}_3\text{-CeO}_2/\text{SS}_{\text{t.t.}}$ within the zone of potentials < -1.25 V, determining a mixed potential. Taking into account the fact that during the thermal treatment practically the whole amount of cerium oxides is converted into CeO_2 state, i.e. in the form of Ce^{4+} ions (prior to the thermal treatment, for the films “upon deposition”, the cerium oxides in the form of Ce_2O_3 are dominating) [27, 28], it is logical to assume the Ce^{4+} reduction reaction occurrence

$$(\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}).$$

If such a reaction is really occurring, it could cause two effects. On one side it will compete with the first reaction, i.e. it will decrease the rate of the occurring cathodic oxygen reaction, while on the other side it will lead to the formation of Ce^{3+} ions in the aggressive medium, which possess a much more positive potential of oxidation (in view of the

reaction $\text{Ce}^{3+} - e^- \rightarrow \text{Ce}^{4+}$ [36]) than the oxidative potentials of the steel components, respectively those of the natural passive film on it (Fe, Cr, Al), which are being oxidized in the course of its corrosion. Therefore, the presence of cerium oxides on the steel surface will lower the rate of corrosion, since it will lead to restoration of its passive state, disrupted as a result of the thermal treatment, due to the occurrence of an effective cathodic reaction of Ce^{4+} ions reduction ($\text{Ce}^{4+} + e^- \rightarrow \text{Ce}^{3+}$).

The reason for putting forward such a hypothesis is the dependence, established by K. Vetter, of the total reaction cathodic overpotential on the $\text{Ce}^{3+}/\text{Ce}^{4+}$ electrode: $\text{Ce}^{3+} \leftrightarrow \text{Ce}^{4+} + e^-$ [37]. Vetter unambiguously proves that the anodic diffusion-limited current density of this reaction is proportional to the concentration of Ce^{3+} , while that of the cathode is proportional to the concentration of Ce^{4+} . Thereupon, these quantities do not depend on the concentrations of other substances, possibly present in the electrolyte. However, at higher potentials and especially in the case of low current densities (i.e. values close to the equilibrium potential) complications occur. Such complications are connected with the parallel occurrence of another electrode reaction (formation of mixed potential, respectively). In these cases oxygen evolution reaction occurs [37]. The author explicitly proves in the same study that the rate of the reaction of the electron transfer in a direction to the cathode is proportional to the concentration of the Ce^{4+} and it does not depend on the Ce^{3+} concentration. This is the reason why in the case of non-treated thermally system of Ce_2O_3 - CeO_2/SS , when only Ce^{3+} ions have passed over to the aggressive medium, there is only one reaction occurring, i.e. the reduction of oxygen, while in the case of non-treated thermally system, simultaneous reduction of Ce^{4+} (CeO_2) and of oxygen can occur. If this reduction occurs at more positive potentials, then it will dominate over the total rate of the cathodic reduction process. Evidence for this statement is supplied by the value of the cathodic current. It is higher with one order of magnitude for the thermally treated systems (Fig. 1b).

Fig. 2 illustrates sections of the anodic polarization curves, obtained in 3.5% NaCl, for stainless steel SS OC404 (curve 1) and for the Ce_2O_3 - CeO_2/SS systems with a different surface content of cerium oxides (from 3.6 up to 29.6 at. %), depending on the time interval of their deposition (from 50 sec up to 80 min) - curves 2, 3, 4, prior to the thermal treatment (Fig. 2a), and after it (Fig. 2b).

It is seen, in view of the obtained results, that in the case of non-treated thermally steel (Fig. 2a, curve 1) two peaks are observable (at $E = \sim -0.090$ V and at $E = -0.020$ V), characterizing the oxidation reactions occurrence, and what follows thereafter (at $E \sim -0.008$ V) is a steep course of the curve, corresponding to the anodic evolution of oxygen via the reaction of $4\text{OH}^- = 2\text{H}_2\text{O} + \text{O}_2 + 4e^-$. At the lowest studied concentration of cerium oxide, deposited on steel (curve 2) up to potentials ~ -0.015 V, a weak depolarizing effect is observed, whereupon the first peak is practically disappearing, while the second one (at $E \sim -0.020$ V) grows stronger. Within the zone of potentials > -0.015 V the presence of cerium oxide film gives rise to the overpotential of the anodic reaction of oxygen evolution. At the next concentration of cerium oxide on the steel (curve 3) a considerably stronger polarizing effect is observed in the zone of the potentials > -0.130 V, while at the maximal studied concentration of cerium oxides (curve 4) the polarizing effect is present even to a greater extent within the entire interval of potentials. Respectively, the current of the reaction of oxygen evolution at each next value of the cerium oxides concentration is decreased substantially.

The action of the cerium oxide layers, deposited on the steel, is analogous also in the case of thermally treated samples (Fig. 2b). Some difference was established only in the case of the lowest concentration of cerium oxides (Fig. 2, curve 2), at which the depolarizing effect is preserved also at potentials > -0.015 V. This is obviously associated with both, the strong cracking of the native passive film on the steel substrate, and the cerium oxide film deposited on it, which leads to a considerable decrease in the corrosion current of the steel, occurring as a result of depassivation ($\sim 7 \cdot 10^{-6}$ A.cm⁻²), before reaching the zone of the anodic oxygen evolution. In the light of this result, it became especially important to find out how the surface modification with cerium oxide film influences the localization of the corrosion process, preceding the evolution of oxygen.

It is important, in this respect, that the corrosion resistance of stainless steels, under the conditions of anodic polarization (in solutions of Cl^- ions) is connected not only with the processes of passivation, but also with the processes, leading to disruption of the integrity of the passive film, and therefore, to the development of local corrosion. From the passive state theory prospective this

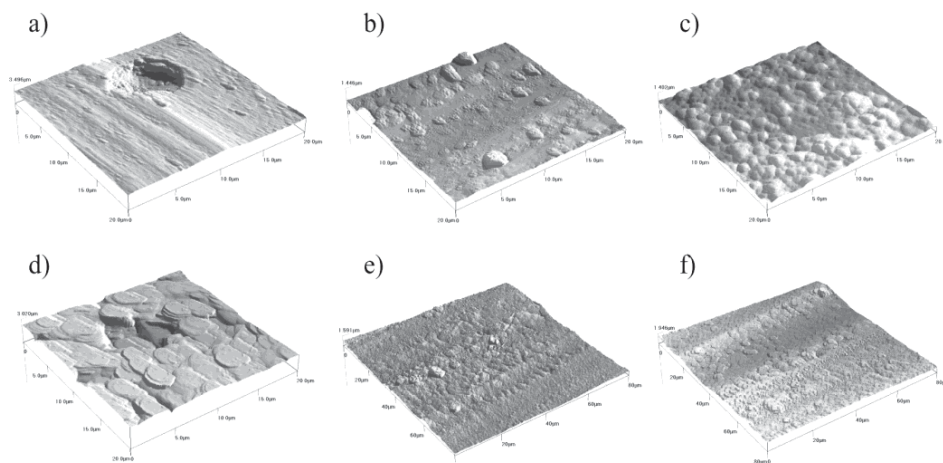


Fig. 3. AFM images for the samples after 5 min at the E_{pitt} in 3.5% NaCl: a) SS; b) $CeO_2-Ce_2O_3(13.1 \text{ at.}\%)/SS$; c) $CeO_2-Ce_2O_3(25.7 \text{ at.}\%)/SS$; d) SSt.t.; e) $CeO_2-Ce_2O_3(4.2 \text{ at.}\%)/SSt.t.$; f) $CeO_2-Ce_2O_3(29.6 \text{ at.}\%)/SSt.t.$.

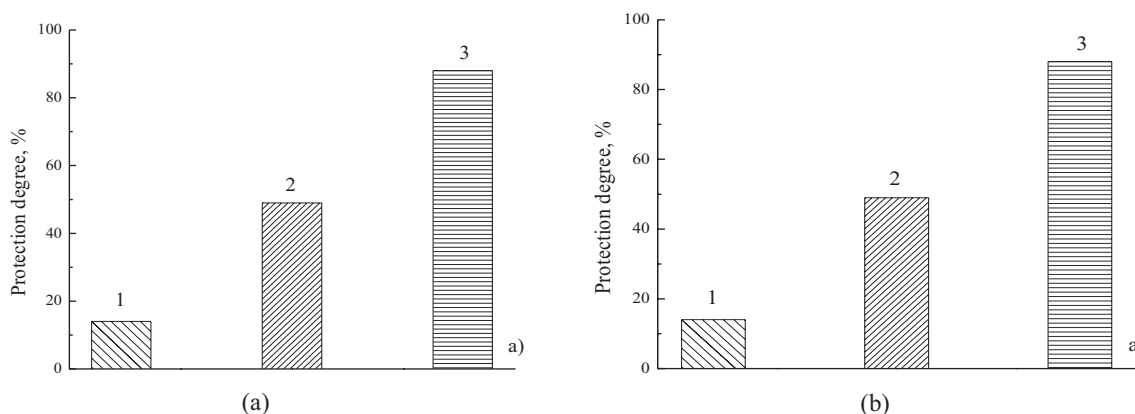


Fig. 4. Protection degree in 3.5% NaCl for different concentrations of $Ce_2O_3-CeO_2$ oxides on SS before (a – 1-3.6 at.%; 2-13.1 at.%; 3-25.7 at.%) and after thermal treatment (b – 1-4.2 at.%; 2-11.2 at.%; 3-29.6 at.%).

phenomenon is associated with the gradual substitution of the oxygen in the passive film with chloride ions or in accordance with the adsorption theory – with substitution of the adsorbed oxygen on the surface with chlorine ions. This process begins upon reaching a definite value of the potential, known as the potential of pitting formation. As a result of its occurrence, the oxide film, protecting the steel surface, can be converted into a soluble metal chloride, resulting in appearance and development of pitting corrosion on separate sections of the surface.

Aiming at investigation of the propensity of the studied steel to pitting corrosion we used the anodic

potentiodynamic curves to estimate the values (Fig. 2a, 2b) of the potentials of pitting formation (E_{pitt}) (Tables 1 and 2). The values of the potentials of pitting formation of samples, having ~5 at. % cerium oxides on the surface (before and after the thermal treatment), are close to that value for the steel itself (Fig. 2a, 2b) (E_{pitt} , Tables 1,2). The further increase in the surface concentration of ceria for the $Ce_2O_3-CeO_2/SS$ system (above ~11.0 at. %) leads to a shift of E_{pitt} with more than ~100 mV in the positive direction. This effect is observed in both, the non-treated thermally steels, and the thermally treated samples. The shifting of E_{pitt} in

Table 3. Distribution of the elements (in at. %) in the surface layers of samples as deposited, thermally treated and after immersion in 3.5% NaCl for the samples corresponding to the curves 3.

Samples	Time of immersion, h	O, at. %		Fe, at. %		Cr, at. %		Al, at. %		Ce, at. %	
		~25°C	2 h 450°C	~25°C	2 h 450°C	~25°C	2 h 450°C	~25°C	2 h 450°C	~25°C	2 h 450°C
Ce	as deposited	67.6	64.2	0	10.6	1.6	2.4	17.7	11.6	13.1	11.2
oxides/S	after 1 h	74.7	73.9	0	8.4	1.8	2.9	13.4	10.4	10.4	4.4
S	after 2 h	73.6	79.6	0	6.7	3.3	3.4	14.4	7.4	8.7	2.9

the positive direction improves substantially the corrosion stability of the studied systems in regards to the pitting corrosion. The change in E_{pit} determines the suppressed development not only of the pitting corrosion but also of the total corrosion, especially strongly expressed in the case of the thermally treated systems (Fig. 3). The basic reason for it (in our opinion) is the action of the cerium oxides which block the active sections (Fe sections) on the steel surface.

A support to this statement are the AFM observations on the appearance and the development of local corrosion on samples of non-treated and thermally treated steel (Fig. 3a, 3d), polarized anodically for 5 min, at the potential of pitting formation. Pitting spots are seen on the surface of the non-treated thermally samples. Besides that, damages are caused by the local and total corrosion in the thermally treated samples. After the electrodeposition of cerium oxides with different surface concentration at the same potential no appearance of pitting is observed (Fig. 3b, c, e, f). We attribute this to the effect of cerium oxides which modify the surface film and enrich it to chromium oxides (Table 3), blocking effectively the active sites on the steel surface.

The quantitative evaluation of the steel protection by cerium oxide films, based on the data in Tables 1 and 2, is shown in Fig. 4. It presents the dependence of the steel degree of protection on the $\text{Ce}_2\text{O}_3\text{-CeO}_2$ surface concentration, calculated using the formula:

$$\text{IP} = \frac{i_{\text{corr}}^0 - i}{i_{\text{corr}}^0} \times 100,$$

where: i_{corr}^0 and i_{corr} are the corrosion current, taken from the polarization curves, with and without $\text{Ce}_2\text{O}_3\text{-CeO}_2$ on the surface of the working samples. The presence of Ce oxides enables high degree of protection reaching ~90%.

CONCLUSIONS

It was found that the cerium oxide films, formed on OC404 steel, inhibit the oxygen depolarization reaction of the corrosion process. Thereupon, this effect stabilizes the stable passive state of the steel,

under investigation, in 3.5% NaCl solutions, which gives a guarantee for the proceeding of the corrosion under the conditions of a passive state.

It was shown that upon disturbing the steel passive state, as a result of the thermal treatment, the cerium oxide films act as efficient cathodic coating, restoring the passive state of the studied steel. In this case the zone of the potentials, inherent to the passive state, grows wider, being shifted to a positive direction to the potential of the pitting formation. Thus, the corrosion resistance of the studied steel to pitting corrosion is increased.

Acknowledgements: *This paper has been completed with the support of the National Fund for Scientific Investigation under Contract TK 01-185.*

REFERENCES

1. B.R.W. Hinton, D.R. Arnott, N.E. Ryan, *Metals Forum*, **7**, 211 (1984).
2. B.R.W. Hinton, D.R. Arnott, N.E. Ryan, *Asia Pacif. Interfinish 86 Conf.*, Hobart (1986).
3. D.R. Arnott, B.R.W. Hinton, N.E. Ryan, *Mat. Perf.*, August, 42 (1987).
4. B.R.W. Hinton, D.R. Arnott, 21st Annual Technical Meeting of the Int. Metallographic Soc., eds. P.J. Kenny, G.S. Cole, D.O. Norwood, J. Wylie, G.F. Vander Voort (Materials Park, OH: ASM International) 311 (1989).
5. B.R.W. Hinton, *J. Alloys Compd.*, **180**, 15 (1992).
6. F. Mansfeld, S. Lin and H. Shin, *Corrosion*, **45**, 615 (1989).
7. A.J. Devenport, H.S. Isaacs and M.W. Kendig, *Corr. Sci.* **32**, 653 (1989).
8. Y.C. Lu and M.B. Ives, *Corr. Sci.* **34**, 1773 (1993).
9. F. Mansfeld, Y. Wang, *Mat. Sci. & Engineering A* **198**, 51 (1995).
10. A.J. Aldykewicz Jr., H.S. Isaacs and A.J. Davenport, *J. Electrochem. Soc.*, **142**, 3342 (1995).
11. Y.C. Lu and M.B. Ives, *Corr. Sci.*, **37**, 145 (1995).
12. A.J. Aldykewicz Jr., H.S. Isaacs and A.J. Davenport, *J. Electrochem. Soc.*, **143**, 147 (1996).
13. I. Zhitomirsky, A. Petric, *Materials Letters*, **40** (6), 263 (1999).
14. I. Zhitomirsky, A. Petric, *Ceramics International*, **27**, 149 (2001).
15. A. Pardo, M.C. Merino, R. Arrabal, S. Merino, F. Viejo, M. Carboneras, *Surf. Coat. Technol.*, **200**, 2938 (2006).

16. Y.C. Lu and M.B. Ives, *Corr. Sci.*, **34**, 1773 (1993).
17. S. Virtanen, M.B. Ives, G.I. Sproule, P. Schmuki, M.J. Graham, *Corr. Sci.*, **39**, 1897 (1997).
19. C.B. Breslin, C. Chem, F. Mansfeld, E. Otero and F.J. Perez, Extended Abstracts of the 189th Meeting of the Electrochemical Society, Paper No.113, Los Angeles, CA (1996).
20. C. Wang, F. Jiang, F. Wang, *Corr. Sci.*, **46**, 75 (2004).
21. M.A. Arenas, J.J. de Damborenea, *Electrochim. Acta* **48**, 3693 (2003).
22. A. Pardo, M.C. Merino, R. Arrabal, F. Viejo, M. Carboneras, J.A. Munoz, *Corr. Sci.*, **48**, 3035 (2006).
23. M.F. Montemor, M.G.S. Ferreira, *Electrochim. Acta*, **52**, 6976 (2007).
24. D. Nikolova, E. Stoyanova, D. Stoychev, P. Stefanov, T. Marinova, *Surf. Coat. Technol.*, **201**, 1559 (2006).
25. D. Guergova, E. Stoyanova, D. Stoychev, G. Atanasova, I. Avramova, P. Stefanov, *Bulg. Chem. Commun.*, **40**, 227 (2008).
26. D. Nickolova, E. Stoyanova, D. Stoychev, I. Avramova, P. Stefanov, *Surf. Coat. Technol.*, **202**, 1876 (2008).
27. E. Stoyanova, D. Guergova, D. Stoychev, I. Avramova, P. Stefanov, *Electrochim. Acta*, **55**, 1725 (2010).
28. P. Stefanov, G. Atanasova, D. Stoychev, I. Valov, Ts. Marinova, Proc. 6th International Conference on Fundamental and Applied Aspects of Physical Chemistry "Physical Chemistry 2002", September 26-28, Belgrad, Yugoslavia, Vol. I, C-16-P, 198 (2002).
29. P. Stefanov, G. Atanasova, D. Stoychev, I. Valov, Ts. Marinova, *Surf. Coat. Technol.* **180**, 446 (2004).
30. J.H. Scofield, *J. Electron Spectrosc. Rel. Phenom.* **8**, 129 (1976).
31. Peter Kritzer, *J. of Supercritical Fluids*, 29,1 (2004).
32. J. Kašpar, P. Fornasiero, M. Graziani, *Catalysis Today*, **50**, 285 (1999).
33. Ya. A. Ugai, Inorganic chemistry, Publ. House "High School", Moscow (1989).
34. H.S. Klapper, J. Goellner, *Corr. Sci.*, **51**, 144 (2009).
35. R. Babic, M. Metikos-Hukovic, Oxygen reduction on stainless steel, *J. Appl. Electrochem.* **23**, 352 (1993).
36. D. Nicolova, E. Stoyanova, D. Stoychev, I. Avramova, P. Stefanov, Nanostructured Materials in Electroplating, Editors: D. Stoychev, E. Valova, I. Krastev, N. Atanassov, St. Kliment Ohridski University Press (2006).
37. N.D. Tomashov, G.P. Chernova, Passivity and Corrosion Protection, (in Russian) Publ. House "Nauka", Moscow (1963).
38. K. Vetter, Elektrochemische kinetik, Springer Verlag (1961), Translated Russian edition, Khimia Publ.H., "Electrode Ce³⁺/Ce⁴⁺", 493&115 (1967).

Корозионна устойчивост на неръждаема стомана, модифицирана електрохимично с Ce₂O₃-CeO₂ филми, в среда от 3,5 % NaCl

Д.Гергова¹, Е.Стоянова¹ Д.Стойчев^{1*}, И.Аврамова², Г.Атанасова², П.Стефанов²

¹Институт по физикохимия "Акад.Р. Кашиев", Българска академия на науките, София 1113, България

²Институт по обща и неорганична химия, Българска академия на науките, София 1113, България

Постъпила на 12 август 2010 г; приета на 25 октомври 2010 г

Работата е посветена на изследването на корозионно-защитната способност на цериево-окисдни филми, които са отложени електрохимично върху неръждаема стомана OC 404 (SS) от неводни електролити. Изследвано е влиянието на промяната на повърхностната концентрация на Ce₂O₃-CeO₂ върху корозионното поведение на SS в корозионно активна среда от 3.5% NaCl преди и след термична обработка на образците. Въз основа на построените поляризационни криви е установено отнемстване на корозионния потенциал на системата в положителна посока, както и понижаване на корозионните токове, респ. скоростта на корозия, когато върху повърхността на стоманата присъстват цериево-окисдни филми. Данните, получени от AFM и XPS анализите, са в добро съответствие с тези резултати.

Въз основа на получените резултати е направен извода, че наличието на Ce₂O₃-CeO₂ слоеве обуславя пасивиране и ре-пасивиране на стоманената повърхност, както и понижаване на питинговата корозия на стоманата. Тези ефекти са обяснени със силното поляризиращо влияние на Ce₂O₃-CeO₂ слоевете върху спрегнатата деполяризираща катодна реакция на редукция на разтворения в корозионната среда кислород.