

Investigation of the Inhibiting Effect of Cerium Ions on the Corrosion Behavior of OC404 Stainless Steel in Sulfuric Acid Medium

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Abstract: The inhibiting effect of Ce⁴⁺ ions, introduced in the form of Ce(SO₄)₂, on the corrosion electrochemical behavior of stainless steel OC404, has been studied in sulfuric acid corrosion medium (0.05 M H₂SO₄).

On the basis of the obtained data on the values of the density of the corrosion current (i_{corr}), evaluated using the dependences E- $\lg i$, both in inhibited and uninhibited corrosion medium, the degree of corrosion protection in the presence of the inhibitor was calculated, as well as the fraction of surface coverage (Q) the electrode surface with inhibitor. These studies were carried out with samples of non-treated thermally steel (SS) and thermally treated steel (SS_{tt}). The cathodic reaction of reduction of the oxidative component of the medium Ce⁴⁺ was found to be the basic driving force of the conjugated anodic process, leading to a transition of SS_{tt} from active into passive state. Thereupon an option is created to form an efficient protective film of phase type on the SS_{tt} surface reaching a degree of inhibition efficiency of about 98 %.

In order to elucidate the nature of the inhibiting action of cerium ions the influence of the value of the equilibrium oxidation-reduction potential of the Ce⁴⁺/Ce³⁺ ion pair was investigated as well as that of the exchange current of the oxidation-reduction process upon the processes of passivation of the studied steel.

The obtained results give the reason to classify the cerium ions as cathode type of inhibitor having oxidative action.

Keywords: Corrosion, sulfuric acid medium, stainless steel, Ce⁴⁺/Ce³⁺ ion pair.

1. INTRODUCTION

The use of OC404 type of stainless steels (SS) for the production of catalytic converters for exhaust gas purification, containing NO_x, SO_x, CO, hydrocarbons etc., which are evolved in the processes of burning in internal combustion engines (ICE) as well as in other combustion systems, is based on their suitable physical-mechanical and physical-chemical properties [1,2]. The modifying of their surfaces with oxides of rare earth metals and other elements (Ce, La, Y, Zr, Al etc.) is connected with the specific functions of these oxides as "supports" of additionally deposited on them actual catalytically active systems (Pt, Rh, Pd, different kinds of spinels etc.) as well as with their stabilizing effect in regard to preserving the specific working surface area of the catalytic converters in case of exploitation at high temperature [3,4].

In our previous investigation it was shown that, electrochemically deposited layers of CeO₂ and Al₂O₃ on SS lead to a substantial improvement of the stability to corrosion of the steel in oxidative (0.1 N HNO₃) [5,6] and non-oxidative (0.1 N H₂SO₄) [7-9] aggressive media. This

established positive effect was explained by their stabilizing influence on the passive state of the steel, as a result of the action of cerium oxides, and in particular as efficient cathodic coating [5,9], as well as by the ascertained occurrence of a cathodic depolarization process of reduction of CeO₂ to Ce₂O₃, instead of the depolarizing reaction of hydrogen evolution in 0.1 N H₂SO₄ [9].

As the Ce₂O₃ being formed is chemically unstable and it is being dissolved in acidic media [10], the amount of CeO₂, which has been transformed into Ce₂O₃ on the surface of SS, with the increasing time interval of in aggressive medium, is decreasing at the expense of enriching the medium with Ce³⁺ ions.

A strong impression in the course of these investigations was made by the fact, that even upon reaching a degree of complete dissolution of the CeO₂ layer (absence of Ce upon XPS scanning of the SS surface), the stationary corrosion potential (E_{st}) of SS remained more positive than E_{st} of steel not coated with CeO₂. This effect, as well as the available literature data on the inhibitory influence of Ce⁴⁺ and Ce³⁺ ions in the course of corrosion of various kinds of steel and aluminum in neutral media, including media containing chlorine ions [10-19] gave us the reason to suppose that in addition to the protective effect of the CeO₂ layers deposited electrochemically by us we should probably add also the inhibitory action of cerium ions, transferred into the corrosion medium. Obviously most of the rare earth ionic

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inhibitors were used in neutral or approximately neutral media. The corrosion inhibition of rare earth ions in strong acidic medium was less studied. Recently the synergistic effect of Ce^{4+} /organic compounds mixtures for cold-rolled steel corrosion inhibition in 1.0 M H_2SO_4 media were also investigated [20-25].

In view of these considerations the aim of the present study was to observe the influence of cerium ions as corrosion inhibitor of OC404 stainless steel in non-oxidizing medium of 0.05 M H_2SO_4 .

2. EXPERIMENTAL DETAILS

2.1. Specimens

The test specimens used in this study were prepared using a sheet of OC404 type stainless steel 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 specimens were investigated before (SS) and after thermal treatment ($\text{SS}_{\text{t.t.}}$) at 450 °C for 2h in air.

2.2. Solutions

The model aggressive solution (0.05 M H_2SO_4) was prepared by dilution of analytical grade 98 % H_2SO_4 ("Merck") with distilled water. In order to evaluate the inhibitory effect of Ce^{4+} salt, variable concentrations of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ from 0.1 to 1500 ppm were added to 0.05 M H_2SO_4 .

2.3. Electrochemical (Corrosion) Characterizations

The stationary corrosion potential (E_{st}) of the samples under investigation was determined by direct measurement of the dependence "E_{st}-time" at open circuit vs mercurous sulfate reference electrode (MSE), ($E_{\text{Hg}}/\text{Hg}_2\text{SO}_4 = 0.640 \text{ V vs SHE}$) after exposure of the samples in corrosion medium in the absence and in the presence of Ce^{4+} ions. In the latter case the effect of the temperature of the corrosion medium was also studied within the temperature interval 25 ÷ 100 °C.

After being kept in the corrosion medium for a definite time, the specimens were taken out, rinsed carefully with distilled water several times. The treated specimens were dried in air at room temperature before the XPS and SEM investigations.

The electrochemical (anodic and cathodic) behavior of the samples (10 x 10 x 0.05 mm) was studied in a standard three-electrode thermostatted cell (100 ml volume). The working electrode had the form of a square of dimensions 10 mm x 10 mm and working area of 1 cm^2 . The non-working surface of the electrode was isolated using a suitable lacquer, resistant to acids. A counter electrode, representing a platinum plate (10 x 10 x 0.6 mm), and the same MSE reference electrode were used. All potentials in the text are related to MSE electrode. The anodic and cathodic polarization curves were obtained using a 273 EG&G potentiostat/galvanostat (Germany) and computer-aided processing of the results according to an "Echem" program, with a potential sweeping rate of 10 mV/s within a range of potentials varying from -1.100 to +1.100 V. The potentiodynamic curves were obtained starting from the stationary corrosion potential (E_{st}) in anodic and in cathodic direction. The time interval for reaching the stationary

corrosion potential (E_{st}) is up to 100 minutes. For plotting each anodic or cathodic curve we used a separate electrode (identical with the previous one). All the potentiodynamic electrochemical experiments were carried out at least in triplicate.

2.4. Chemical Characterizations

The chemical composition and the oxidation state of the elements on the surface being formed (before and after heat-treated) were studied using X-ray photoelectron spectroscopy (XPS). The XPS studies were performed in a VG Escalab II system with Al K_α radiation ($h\nu = 1486.6 \text{ eV}$) and total instrumental resolution of ~ 1 eV. The vacuum in the chamber was 10^{-8} Pa. The binding energy (BE) was referred to the C1s line (of adventitious carbon) at 285.0 eV. The elemental concentrations were evaluated based on the integrated peak areas after Shirley-type of linear background subtraction using theoretical Scofield's photo-ionization cross-sections.

2.5. Structure Characterizations

Microstructure and morphology of the SS surface before and after the treatment were examined by scanning electron microscopy, using a JEOL JSM 6390 electron microscope (Japan), equipped with an ultrahigh resolution scanning system in a regime of secondary electron image (SEI). The accelerating voltage was 20 kV.

3. RESULTS AND DISCUSSION

3.1. Chronopotentiometric Studies of SS and $\text{SS}_{\text{t.t.}}$ in 0.05 M H_2SO_4

The measurement of the stationary corrosion potential (E_{st}) for SS and $\text{SS}_{\text{t.t.}}$ in 0.05 M H_2SO_4 at open circuit shows that for the non-treated thermally steel $E_{\text{st}} = \sim -0.300 \text{ V}$, while for the thermally treated sample $E_{\text{st}} = \sim -0.980 \text{ V}$.

The shifting of E_{st} in positive direction (Fig. 1) and establishing values with about 300 mV more positive than its value at the moment of immersing the SS sample into 0.05 M H_2SO_4 solution ($E_{\text{in}} = -0.600 \text{ V}$) is due to re-organizing the composition and the structure of the native passive film on SS. A series of studies on similar types of stainless steels proved that such a change of E_{st} is due to the tendency of self-passivation of such steels, determining definite changes in the natural passive film [26]. As it is seen from Table 1, upon immersion into sulfuric acid medium it is enriched in chromium and the ratio Cr/Fe is strongly changed in favor of the chromium. At the same time the Al content is substantially decreased.

The analysis of the XPS spectra of the same samples (the total concentrations of the elements, listed in Table 1) shows (see also detailed data in Table 2 and Fig. 2 – the spectra, respectively), that iron is contained in the native film in the form of Fe^0 (39.3%) as well as Fe^{3+} (60.7%); the chromium is in the form of metal (39.7%) as well as ions Cr^{3+} (39%) and Cr^{6+} (21.3%), and the aluminum is in the form of Al^{3+} ions (100%). After exposure of the samples to 0.05 M H_2SO_4 solutions (50 h), the ratio between elemental iron and the oxides of iron grows up considerably in favor of the elemental iron. The ratio of Cr^{3+} to metallic chromium is increasing about four times, while the Cr^{6+} ions vanish.

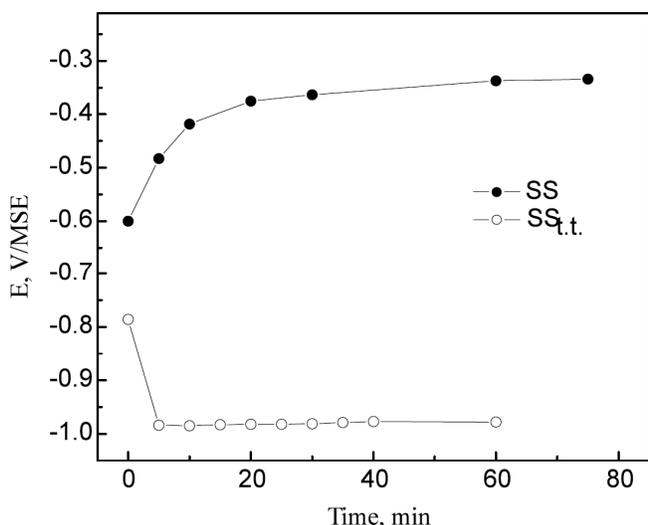


Fig. (1). Open circuit potential vs time curves of SS and SS_{t.t.} in 0.05 M H₂SO₄.

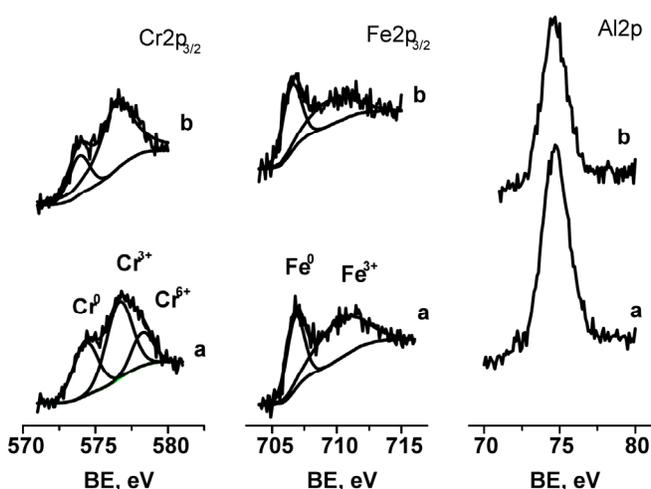


Fig. (2). Cr_{2p_{3/2}}, Fe_{2p_{3/2}} and Al_{2p} X-ray photoelectron spectra of SS (a) and SS_{t.t.} after 50 h immersion in 0.05 M H₂SO₄ (b) (The chemical states of the elements are indicated).

Table 1. Distribution of the Elements (in at. %) on the Surface of SS and SS_{t.t.} Samples Before and After 50 h Time Interval of Immersion in 0.05 M H₂SO₄

Samples	O, at. %	Fe, at. %	Cr, at. %	Al, at. %	Ce, at. %	Cr/Fe, %	Al/Fe, %	Al/Cr, %	E _{st} , V
SS	58.3	3.1	3.4	35.2	–	1.09	11.35	10.35	–
SS 50 h in 0.05 M H ₂ SO ₄	66.8	2.7	3.9	26.6	–	1.44	9.85	6.82	-0.209
SS _{t.t.}	64.9	7.2	7.0	20.9	–	0.97	2.90	2.99	–
SS _{t.t.} 50 h in 0.05 M H ₂ SO ₄	65.4	9.1	12.2	13.3	–	1.34	1.46	1.09	-0.300

Table 2. Amounts of the Constituent Elements in the Respective Chemical State on the Surface of Stainless Steel Evaluated by XPS

Samples	Fe ⁰	Fe ³⁺	Cr ⁰	Cr ³⁺	Cr ⁶⁺	Al ⁰	Al ³⁺
SS	39.3	60.7	39.7	39.0	21.3	0	100
SS after 50 h immersion in 0.05 M H ₂ SO ₄	50.8	49.2	21.2	78.8	0	0	100

For SS_{t.t.} the corrosion potential at the moment of immersion into 0.05 M H₂SO₄ solution ($E_{in} = -0.780$ V), is more negative with ~180 mV compared to the potential for the non-treated thermally steel (Fig. 1). The establishment of unchanging with the course of time potential E_{st} (~-0.980 V) in this case becomes much more rapid (after ~ 5 min). The registered significantly more negative values of E_{st} for SS_{t.t.}, in our opinion, are owing to the strong cracking of the native passive on the SS surface (Fig. 3). Most probably the reason for this loss of the passivity feature of the stainless steel surface is some revealed sections on the surface, determining several times higher concentration of iron-containing agglomerates (active anodic sections) in the surface layer (Table 1). Obviously their amount starts to be dominating in the value of E_{st} for SS_{t.t.} (E_{st} for pure iron, measured by us in 0.05 M H₂SO₄, is ~-0.912 V).

Both the composition (Table 1) and the state of the elements in the surface layer of SS_{t.t.} are strongly different (see detailed data in Table 3 and Fig. 4 – the spectra, respectively) compared to those for SS. After the thermal treatment of the steel samples all the three components, included in the composition of the steel (Fe, Cr, Al) in its surface layer, are present only in their oxide state. After 50 h of exposure to sulfuric acid medium the surface layer is modified and the iron is registered both in the form of Fe⁰ and Fe³⁺ (at a ratio 48.2% to 51.8%); the registered chromium is in the form of Cr⁰ and Cr³⁺ (at a ratio 18.7% to 81.3%), while the detected aluminum is in the form of Al⁰ and Al³⁺ (at a ratio 28.3% to 71.7%). These results are in accordance with the microscope observations of the samples of thermally treated steel prior to and after their exposure to 0.05 M H₂SO₄, showing the development of total corrosion and the appearance of pitting corrosion as a consequence of disruption of the passive state of the thermally treated steel (Fig. 5).

3.2. Chronopotentiometric Studies of SS and SS_{t.t.} in 0.05 M H₂SO₄, Containing Ce⁴⁺ Ions

Fig. (6) illustrates the analogous E-τ dependencies at open circuit, obtained upon immersion of SS and SS_{t.t.} in

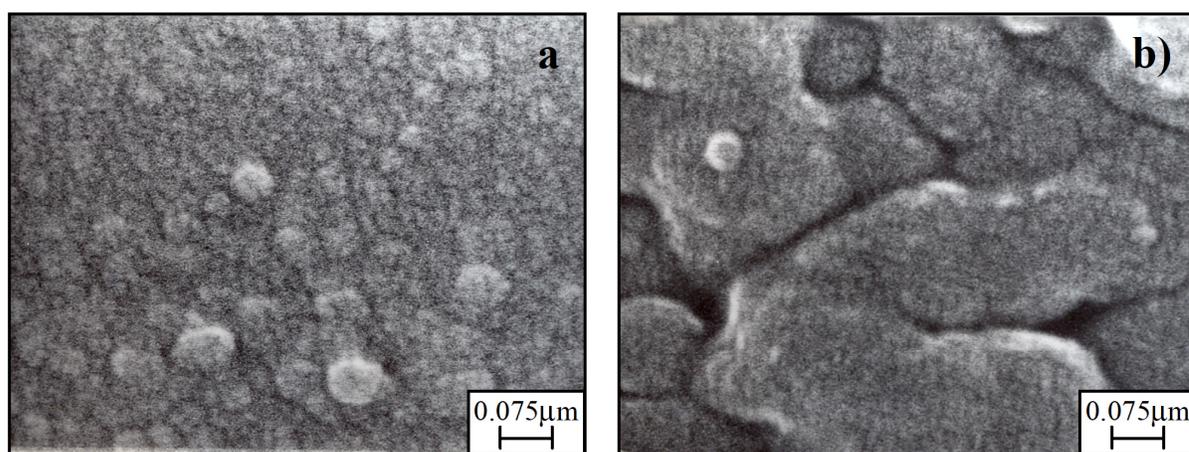


Fig. (3). SEM images of stainless steel before (a) and after thermal treatment (b).

Table 3. Amounts of the Constituent Elements in the Respective Chemical State on the Surface of Thermally Treated Stainless Steel Evaluated by XPS

Samples	Fe ⁰	Fe ³⁺	Cr ⁰	Cr ³⁺	Al ⁰	Al ³⁺
SS _{tt}	0	100	0	100	0	100
SS _{tt} after 50 h immersion in 0.05 M H ₂ SO ₄	48.2	51.8	18.7	81.3	28.3	71.7

0.05 M H₂SO₄ solution, to which various concentrations of Ce⁴⁺ have been added.

For the non-treated thermally steel (Fig. 6a) the change in E_{st} at concentrations ranging up to about 0.3 ppm Ce⁴⁺ ions is relatively small. Upon increasing further the concentration a considerable shift of E_{st} in positive direction is being registered. At concentrations about 115 ppm E_{st} reaches values $\sim +0.510$ V. Upon further increase in the concentration of Ce⁴⁺ in 0.05 M H₂SO₄ E_{st} is changing only slightly and at concentration 1000 ppm the shift in positive direction reaches a value of 0.570 V. E_{st} practically does not change further at the next concentration values.

The strong shift in E_{st} in positive direction (from -0.942 V up to -0.286 V) in the case of thermally treated steel (Fig. 6b) is realized at relatively low concentrations of Ce⁴⁺ (0.3 ppm). Upon increasing the concentration of Ce⁴⁺ in 0.05 M H₂SO₄ further (from 0.3 to 0.9 ppm) E_{st} varies to a

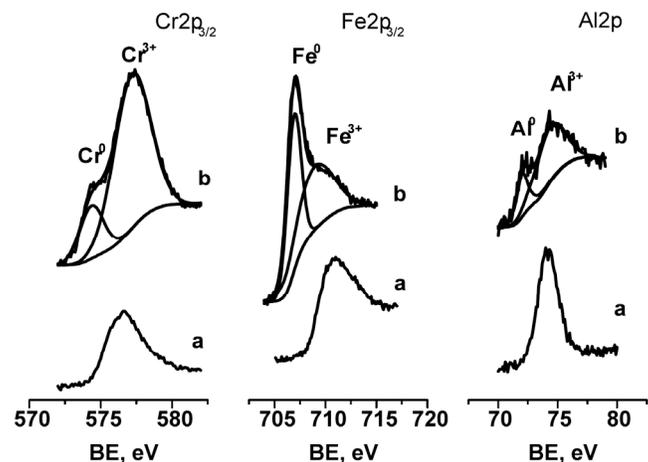


Fig. (4). Cr_{2p_{3/2}}, Fe_{2p_{3/2}} and Al_{2p} X-ray photoelectron spectra of SS_{tt}. (a) and SS_{tt} after 50h immersion in 0.05 M H₂SO₄ (b).

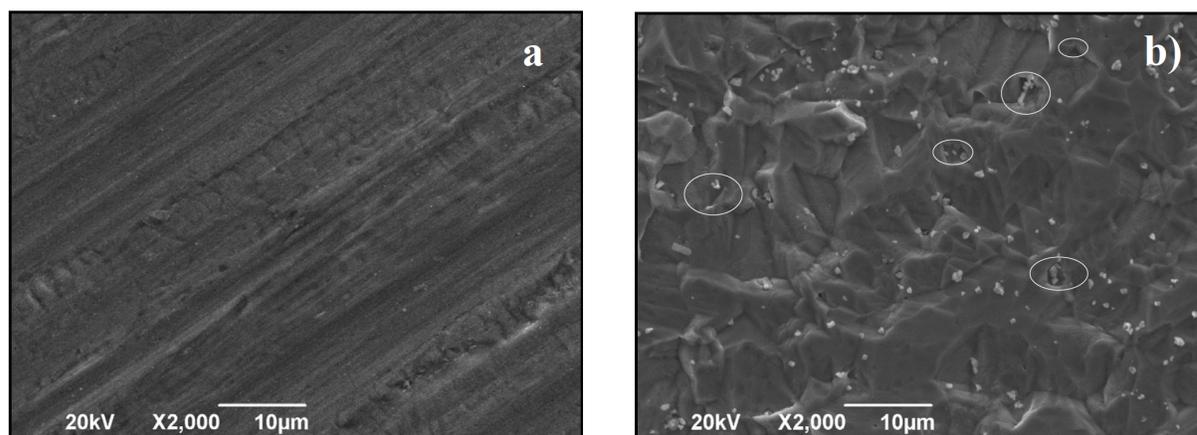


Fig. (5). SEM images of thermally treated stainless steel before (a) and after immersion 50 h in 0.05 M H₂SO₄ (b).

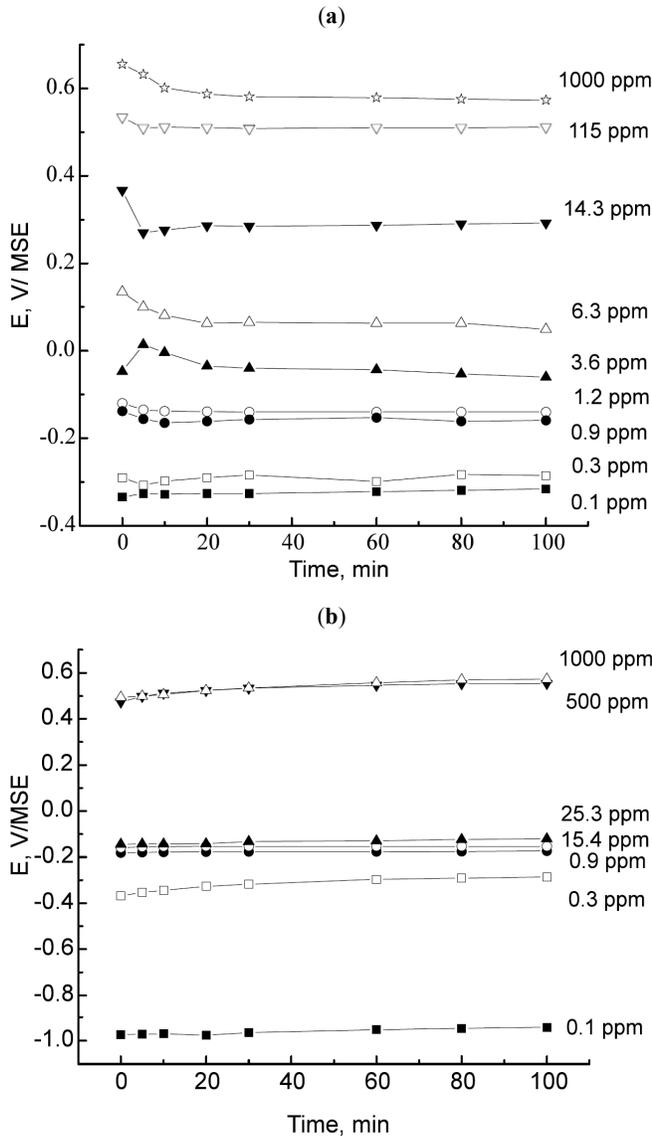


Fig. (6). Evolution of the open-circuit potential for SS and SS_{t.t.} at different concentrations of Ce⁴⁺ in 0.05 M H₂SO₄.

considerably smaller degree, while in the interval 0.9-25.3 ppm this shift in positive direction is quite small.

The obtained results show that upon increasing the Ce⁴⁺ concentration in the corrosion medium the E_{st} for SS is shifting in a certain proportional dependence varying from ~-0.316V up to ~+0.570 V. For SS_{t.t.} this shifting has a jump-like course – it jumps from -0.942 V (at Ce⁴⁺ ions concentration 0.1 ppm) to -0.175 V (at Ce⁴⁺ ions concentration 0.9 ppm). In the next step of 20 – 30 times increase in the concentration of Ce⁴⁺ ions (15.4-25.3 ppm) preservation of E_{st}, is registered whereupon it reaches values ~-0.150 - -0.120 V. Further follows 20-50 times increase in the concentration of Ce⁴⁺ ions (500-1000 ppm) and E_{st} is shifting strongly in positive direction and it acquires now values of ~+0.510 - +0.570 V, which are characteristic of E_{st} for the non-treated thermally steel at the same inhibitor concentration.

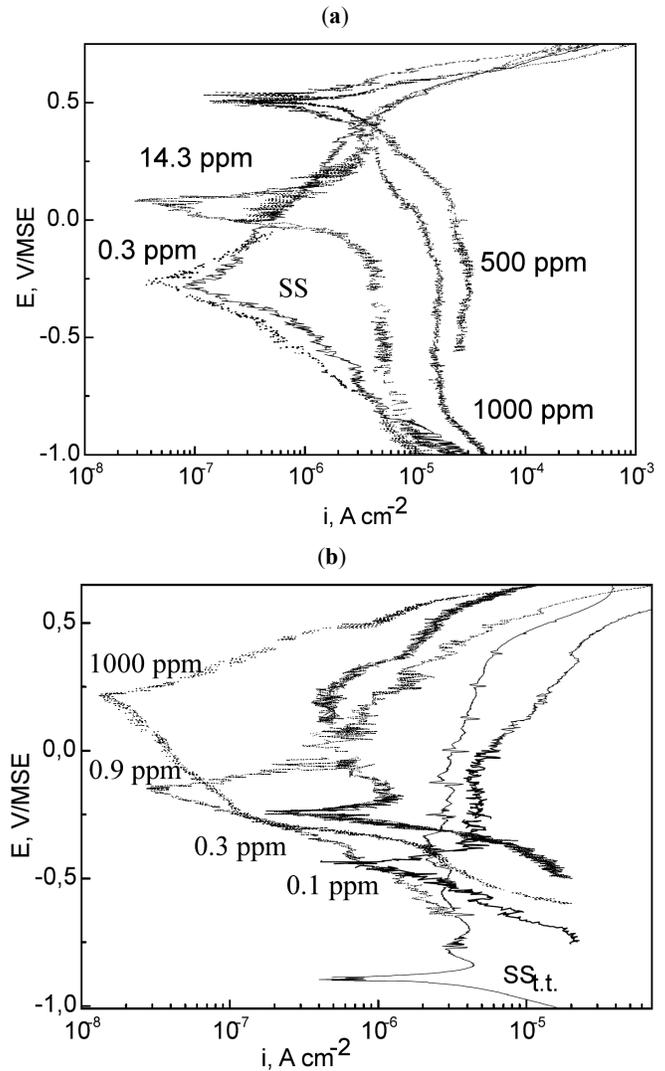


Fig. (7). Potentiodynamic E-|gi curves of SS (a) and SS_{t.t.} (b) at different concentrations of Ce⁴⁺ in 0.05 M H₂SO₄.

3.3. Potentiodynamic Measurements of SS and SS_{t.t.} in 0.05 M H₂SO₄, Containing Ce⁴⁺ Ions

The potentiodynamic curves, obtained for SS in the presence of Ce⁴⁺ ions in the corrosion medium (Fig. 7a) show that the ions shift substantially its corrosion potential (E_{corr}) in the positive direction – from ~-0.285 V to ~+0.510 V – upon increasing the inhibitor concentration from 0.3 to 1000 ppm. It is important to point out that the values for E_{corr}, obtained by means of extrapolation of the anodic and cathodic potentiodynamic curves in the presence of Ce⁴⁺, were juxtaposed with the values of E_{st} (Fig. 6a), determined on the basis of the E-τ dependences (regime of open circuit) finding good coincidence. At the same time the changes in the corrosion current density (i_{corr}) in the presence of Ce⁴⁺ are insignificant – they remain close in value to the passive state current of the steel in the absence of Ce⁴⁺. Obviously in the case of non-treated thermally steel the inhibiting action of Ce⁴⁺ ions is expressed only in a strong shift in the corrosion potential in positive direction (Table 4). One can observe,

however, that at Ce^{4+} concentrations 500-1000 ppm the measured values for i_{corr} are higher – this is an effect, on which we shall comment further below.

In the case of thermally treated steel ($\text{SS}_{\text{t.t.}}$) (Fig. 7b) the increase in the inhibitor concentration in the corrosion medium leads to a substantial decrease in the corrosion current intensity - from $\sim 1.5 \times 10^{-6}$ (in the absence of Ce^{4+}) to $\sim 3.2 \times 10^{-8} \text{ A}\cdot\text{cm}^{-2}$ (at concentration of $\text{Ce}^{4+} \sim 0.9$ ppm). Upon further increase in the concentration of Ce^{4+} ions in the corrosion medium from ~ 0.9 ppm (which can be accepted to be “critical value”) up to 1000 ppm, however, the change in the corrosion rate is insignificant. Also in this case, with the increase in the concentration of cerium ions, the corrosion potential is shifting strongly in positive direction (from $\sim -0.900 \text{ V}$ to $\sim +0.212 \text{ V}$), whereupon its values at all concentrations of Ce^{4+} are more positive than the potential of complete passivation and more negative than the potential of depassivation of the steel for the entire interval of studied Ce^{4+} concentrations. The lower values of E_{corr} determined from the respective cathodic and anodic curves at concentrations 500-1000 ppm, in comparison to E_{st} obtained at open circuit, can be associated with reaching a stable passive state of $\text{SS}_{\text{t.t.}}$ at concentrations ~ 1 -15 ppm. The reasons for such a supposition become obvious from the results, represented in Fig. (6b). It can be seen that within the interval of concentrations 0.9-25.3 ppm the established values of E_{st} practically coincide with E_{st} measured for the samples of non-treated thermally steel at concentrations ~ 1 ppm (Fig. 6a).

At the same time we should note also the fact that at Ce^{4+} concentrations up to 0.9 ppm in the corrosion medium (Fig. 7b) the anodic potentiodynamic curves for the $\text{SS}_{\text{t.t.}}$ samples are analogous to those in absence of inhibitor (a passivity zone is observed). Upon increasing the concentration of the inhibitor up to 1000 ppm the anodic branch of the curve is changing. The reason for this change is the fact that the equilibrium oxidation – reduction potential of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ couple is reached, which enables the oxidation reaction of Ce^{3+} to Ce^{4+} . The justification of this statement is based on the analogous course of the cathodic and anodic curves, obtained with Pt electrode during our investigation, which is especially focused on the oxidation –reduction reaction of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ ion pair in sulfuric acid medium at 1000 ppm Ce^{4+} concentration - for example Figs. (7b,11).

The obtained results give us the reason to draw the conclusion that in the case of thermally treated steel the presence of cerium ions (acting as an oxidative inhibitor) determines both the strong shift of E_{corr} in positive direction, as well as the change in the character of corrosion – from corrosion in active state into corrosion under conditions of anode passivity. Obviously the cerium ions shift the total potential of the corrosion system in positive direction to potentials, characteristic for the passive state for the anodic process. In our opinion this effect is most probably owing to promoting the effectivity of the cathodic depolarization process involving not only H^+ (H_3O^+) reduction but also Ce^{4+} reduction.

3.4. Estimation of the Inhibiting Effect of Ce^{4+} Ions

Table 4 lists the electrochemical kinetic parameters: corrosion current density (i_{corr}), corrosion potential (E_{corr})

and degree of inhibition efficiency (Z , %), characterizing the corrosion process in the presence and in the absence of cerium ions, determined on the basis of the results represented in Fig. (7). The degree of inhibition efficiency has been calculated on the basis of the equation:

$$Z\% = (i_{\text{corr}}^0 - i_{\text{corr}}) / i_{\text{corr}}^0 \times 100 \quad (1)$$

where i_{corr}^0 and i_{corr} are the values of the corrosion current density in the absence and in the presence of cerium ions.

It is seen from the table that upon increasing the concentration of Ce^{4+} ions in the corrosion medium in the case of samples of thermally treated steel the degree of inhibition efficiency reaches values of $\sim 38\%$ (0.1 ppm Ce^{4+}) up to $\sim 98\%$ (0.9 ppm Ce^{4+}), whereupon the further increase in the concentration of Ce^{4+} practically does not change the degree of inhibition efficiency. At the same time the Ce^{4+} ions determine an insignificant decrease in the corrosion currents, respectively the relatively lower values of the degree of protection with non-treated thermally steel. In this case the inhibiting effect of the Ce^{4+} ions is registered at comparatively low concentrations (up to ~ 14.3 ppm), whereupon a consecutive increase in their concentration in the corrosion medium leads even to a certain increase in the corrosion current of SS, respectively to the so called “negative inhibiting effect”.

In order to elucidate the weaker inhibiting effect of Ce^{4+} in the case of corrosion of non-treated thermally steel, we determined the charge on its surface, comparing its stationary corrosion potential ($E_{\text{st}} = -0.285 \text{ V}$) with the potential at zero point on Fe ($E_{\text{zp}} = -1.040 \text{ V}$ versus MSE), as it should be done in such cases [27]. Based on the expression:

$$E = E_{\text{corr}} - E_{\text{zp}} \quad (2)$$

One obtains the value for the related corrosion potential, characterizing the charge of the steel surface, equal to $+0.755 \text{ V}$. Obviously in the case under consideration the steel is charged positively in regard to the corrosion medium and the adsorption of cations or positively charged complexes will be hampered. This “negative” effect will grow stronger with the increase in the positive charge of steel upon increasing the concentration of Ce^{4+} ions in the corrosion medium (Fig. 6a). This is one of the possible explanations for the lower inhibiting efficiency of Ce^{4+} in the corrosion of non-treated thermally SS in $0.05 \text{ M H}_2\text{SO}_4$. Moreover, it should be taken into account that the studied SS has a well-expressed ability to self-passivation, i.e. to acquire a thick passive film on the surface, which has decisive influence on its corrosion behavior [28].

As it was noted above, upon disrupting the integrity of the passive film as a result of the thermal treatment, there appear «bare» sections of the steel surface, which leads to strongly negative value of E_{st} and change in the value of the charge on the steel surface from $+0.755 \text{ V}$ to $+0.140 \text{ V}$, in accordance with equation (2). This decrease in the positive electric charge of the steel will facilitate to a certain extent the adsorption of Ce^{4+} , thus explaining the higher efficiency of the cation-active inhibitor for $\text{SS}_{\text{t.t.}}$. The obtained results give us the reason to suppose that in case of disruption of the passive film on the steel surface this will lead to a change in

the character of adsorption of cerium ions on the thermally treated steel.

In this connection it is logical to assume that in the case of SS samples (continuous passive film) between the inhibitor and the oxidized surface there exist mainly Van-der Waals forces of interaction (physical adsorption), while in the case of SS_{t.t.} (disrupted passive film) in addition to the electrostatic forces there can appear also chemisorption interaction. The latter forces will characterize the interaction between the non-covered with passive film sections on the steel surface (the active bare iron zones, where the charge is -1.040 V) and the cerium ions. At the same time, within the range of potentials, where oxidation processes are taking place ($\text{Me} - \text{ne}^- \rightarrow \text{Me}^{n+}$), the respective conjugated reaction $\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}$ will be occurring too, which will lead to formation of Ce^{3+} hydroxide compounds of the type $\text{Ce}(\text{OH})^{2+}$ and $\text{Ce}(\text{OH})_2^+$ [29]. The latter can form protective layer on the steel surface. They can block the bare iron sections, which also will exert influence in the direction of shifting of E_{st} of SS_{t.t.} in positive direction and decrease in i_{corr} .

Confirmation of such concepts about the physical nature of the Ce^{4+} adsorption on SS is given by the characteristic course of the dependence of E_{st} on the temperature of the corrosion medium (Fig. 8). On the other hand the insignificant change in the curve $E_{\text{st}} - T$ for SS_{t.t.} within the entire studied temperature interval is evidence for efficient adsorption process on SS_{t.t.}. The obtained data about the increase in the efficiency of the inhibiting action with the increase in the concentration of Ce^{4+} in the corrosion medium for the thermally treated steel (Table 4) supposes an interconnection between the inhibitor concentration and the degree of surface coverage, Q , following the equation (3) [27]:

$$Q = (i_{\text{corr}}^0 - i_{\text{corr}}) / i_{\text{corr}}^0 \quad (3)$$

where i_{corr}^0 and i_{corr} are respectively the corrosion current density obtained by extrapolation of anodic and cathodic potentiodynamic curves in the absence and in the presence of various concentrations of the inhibitor in the corrosion medium.

On the basis of the obtained data about the fraction of surface coverage of steel electrode as a function of the concentration of the inhibitor, one can accept that the adsorption process obeys Langmuir's isotherm. According to this isotherm the interconnection between the fraction of surface coverage and the concentration of the inhibitor is the following:

$$Q = KC / (1 + KC) \quad (4)$$

respectively

$$C/Q = 1/K + C \quad (5)$$

where K is the adsorption constant and C is the concentration of the inhibitor. The dependence C/Q as a function of C for the thermally treated steel is represented in Fig. (9). It is seen that the experimental data describe a linear dependence, whereupon the coefficient of the linear regression and the slope of the straight line of this dependence approach a value of 1, which proves the validity of Langmuir's isotherm in our case.

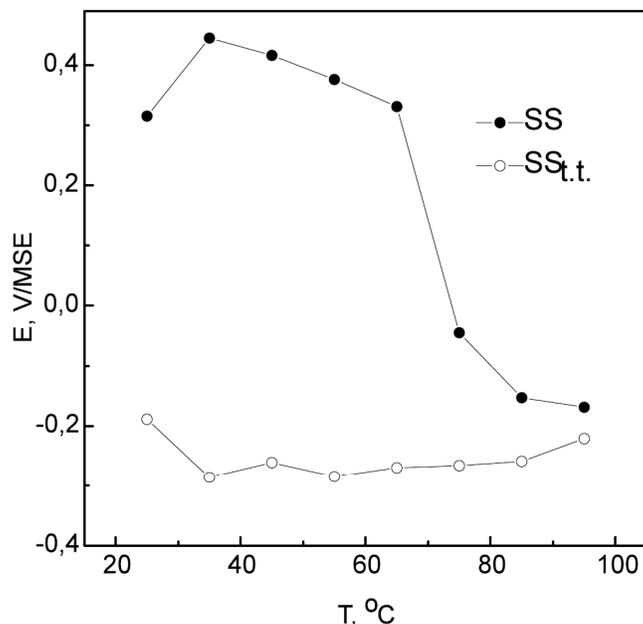


Fig. (8). E_{st} versus temperature for SS and SS_{t.t.} in 0.05 M H_2SO_4 in the presence of Ce^{4+} ions.

Table 4. Electrochemical Parameters Characterizing the Corrosion Behavior of SS at Different Concentrations of the Ce^{4+}

Samples	E_{corr} , V	i_{corr} , A cm^{-2}	Z, %
SS without Thermal Treatment			
SS	-0.285	7.5×10^{-8}	-
with 0.3 ppm	-0.235	3.6×10^{-8}	51.7
with 14.3 ppm	-0.023	3.4×10^{-8}	54.5
with 500 ppm	0.503	7.1×10^{-7}	-
with 1000 ppm	0.510	4.1×10^{-7}	-
SS After Thermal Treatment			
SS _{t.t.}	-0.900	1.5×10^{-6}	-
with 0.1 ppm	-0.435	5.8×10^{-7}	37.8
with 0.3 ppm	-0.238	2.2×10^{-7}	86.8
with 0.9 ppm	-0.156	3.2×10^{-8}	98.2
with 1000 ppm	0.212	1.6×10^{-8}	99.4

The constant K in equation (6) is connected with the standard free energy of adsorption (ΔG_{ads}^0) in accordance with the equation:

$$K = (1/55.5) \exp(-\Delta G_{\text{ads}}^0 / RT) \quad (6)$$

The value of K , determined graphically based on the plot of the dependence C/Q as a function of C , is $44.6 \times 10^6 \text{ M}^{-1}$, while the value of $(-\Delta G_{\text{ads}}^0)$ amounts to $10.35 \text{ kJ} \cdot \text{mol}^{-1}$. The relatively low value of ΔG_{ads}^0 , however, is an indication of electrostatic forces of interaction, existing between the ions of the inhibitor and the SS_{t.t.} surface. In spite of this fact the efficiency of the studied inhibitor remains high and practically it does not change with the increase in

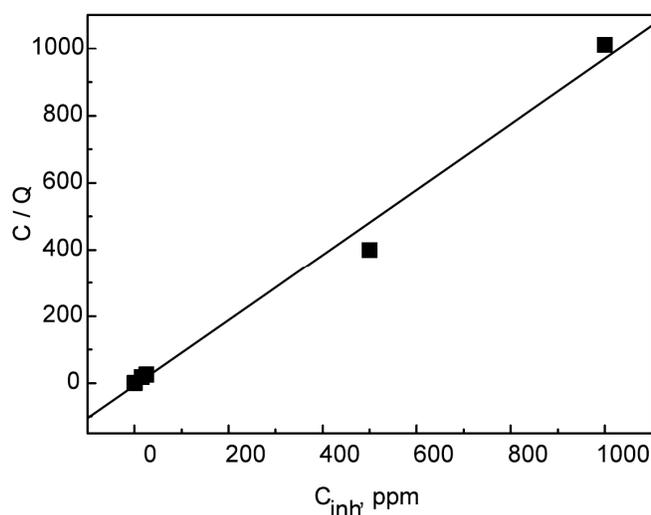


Fig. (9). Langmuir adsorption plots for $SS_{t,t}$ in 0.05 M H_2SO_4 at different concentration of Ce^{4+} ions.

temperature (Fig. 8). In our opinion, the specific action of the inhibitor on $SS_{t,t}$ is manifested in the formation of the adsorption layer, which is being transformed through phase transition (forming Ce_2O_3 , bulk phase, for example), on the active anode (Fe) sections on the surface of the $SS_{t,t}$. Such a supposition is in accordance with the option, found recently by Scott A. Hayes *et al.* [29] to precipitate cerium oxides/hydroxides at much lower pH values than those given in the original Pourbaix.

The results from the XPS studies of the surface composition of $SS_{t,t}$ come as a confirmation of this hypothesis. Considering the XPS analyses, after 500 hours of exposure of the thermally treated steel to the aggressive medium in the presence of Ce^{4+} ions (25.3 ppm), on the surface of the studied steel in the region of Ce3d photoelectron line a certain amount of cerium is registered (1.5 at.%) in the form of Ce_2O_3 . The cerium ions are most probably intercalated inside the surface film as a result of exposure of the steel to the inhibited corrosion medium, which leads to its modifying, as a consequence of formation of mixed oxides of the type of cerium aluminates and

chromates [30, 31]. In support of such a hypothesis comes the fact that no visible corrosion damages are present on the surface of $SS_{t,t}$ exposed for 500 h to 0.05 M H_2SO_4 solution in the presence of Ce^{4+} ions (SEM micrographs in Fig. 10). This modification of the passive film leads to a decrease in the total free energy of the system, respectively to promotion of the stability of the passive film.

Of course from purely electrochemical point of view, the ability of the inhibitor to define strongly positive oxidation-reduction potential of the steel is connected with the occurrence of reduction of Ce^{4+} to Ce^{3+} . In order to establish how the reduction of Ce^{4+} ions to Ce^{3+} is occurring (cathode depolarization reaction of the oxidative component of the corrosion sulfuric acid medium) within the region of potentials, characteristic of the passive state of the studied steel, we plotted the anode and cathode potentiodynamic curves, characterizing the behavior of the oxidation-reduction couple Ce^{4+}/Ce^{3+} at various concentrations of Ce^{4+} on indifferent support of platinum (Fig. 11). Such an approach [28], in our opinion, enables the evaluation of the mechanism of inhibitory action of the cerium ions. It allows direct juxtaposition of the change in the values of the corrosion potential (respectively corrosion current density) of the steel in the presence of cerium ions with the values of the reverse redox potentials (respectively exchange currents) of the couple Ce^{4+}/Ce^{3+} at comparable concentrations.

From the juxtaposition of the obtained results it is seen that with the increase of the concentrations of cerium ions the equilibrium oxidation-reduction potential of the system Ce^{4+}/Ce^{3+} is shifted in positive direction (Fig. 11 and Table 5), in accordance with the equation of Nernst, whereupon practically for all studied concentrations it is placed in the zone of potentials, characteristic of the passive state of steel (Fig. 7b). Thereupon the corrosion potentials of the steel are more negative than the equilibrium oxidation-reduction potentials of the system Ce^{4+}/Ce^{3+} . At the same time the comparison of the corrosion currents for steel in the presence of cerium ions with the exchange currents for the system Ce^{4+}/Ce^{3+} on Pt, at commensurable concentrations of the cerium ions, shows that they are very close to the exchange currents for the system Ce^{4+}/Ce^{3+} . At concentrations of the

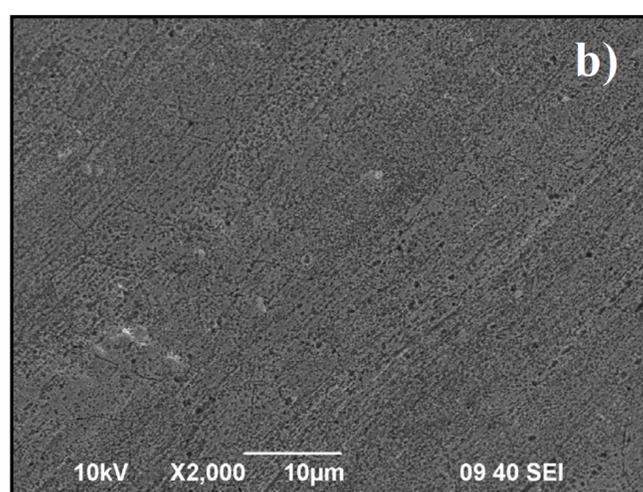
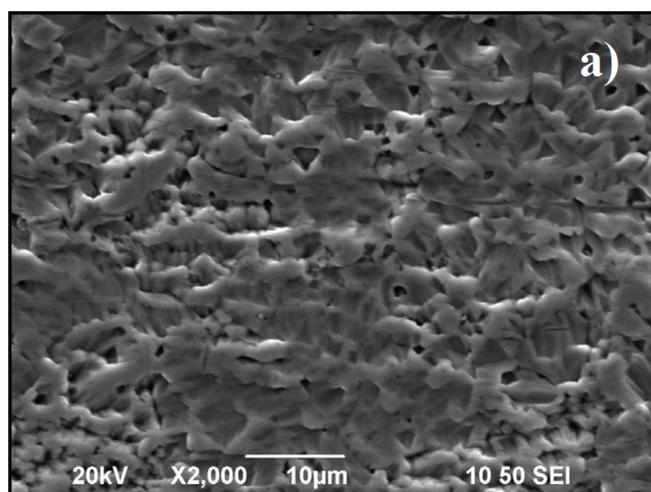


Fig. (10). SEM images on thermally treated stainless steel after 500 h immersion in 0.05 M H_2SO_4 without Ce^{4+} (a) and in the same media with 25.3 ppm Ce^{4+} (b).

inhibitor higher than “the critical value” for $SS_{t.t.}$, however, the corrosion currents of steel are decreased with about half an order of magnitude ($\sim 1 \times 10^{-8} \text{ A.cm}^{-2}$), in comparison with the exchange currents of the oxidation-reduction couple Ce^{4+}/Ce^{3+} . Evidently, the high exchange currents of the oxidation-reduction of the oxidative inhibitor will have favorable influence in case of disruption of the passive state of the steel, as a result of external action, leading to its “self-healing”.

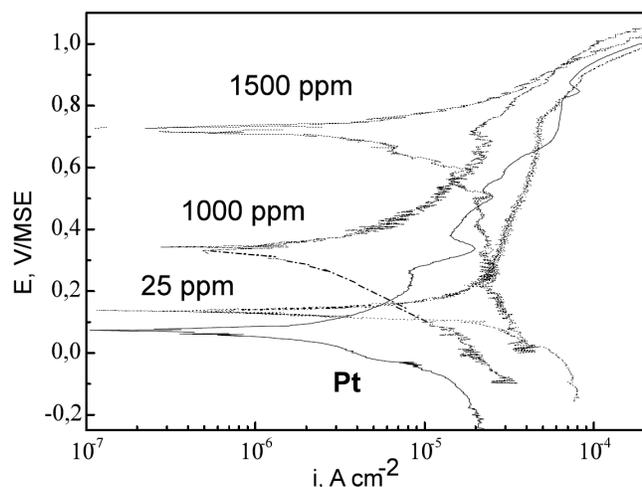


Fig. (11). Potentiodynamic E-Igi curves of Pt at three different concentrations of Ce^{4+} and reference curve (in the absence of inhibitor) in 0.05 M H_2SO_4 .

Table 5. Reversible Redox Potentials E_0 , and Equilibrium Currents i_0 , of the System Ce^{4+}/Ce^{3+} on Pt at Different Concentrations of the Ce^{4+} in the Corrosion Medium

Samples	E_0 , V	i_0 , $A \text{ cm}^{-2}$
Pt metal	0.070	2.17×10^{-7}
Pt with 0.3 ppm	0.107	8.99×10^{-6}
Pt with 25 ppm	0.135	6.35×10^{-7}
Pt with 1000 ppm	0.331	6.08×10^{-7}
Pt with 1500 ppm	0.722	7.67×10^{-7}

The obtained results give the reason to classify the studied oxidation-reduction couple as cathode inhibitor, which does not influence directly the kinetics of the anode process. This determines the proceeding of a cathodic depolarization reaction ($Ce^{4+} + e^- \rightarrow Ce^{3+}$), leading to shifting of the stationary corrosion potential of the system in positive direction reaching values, corresponding to the zone of passivity of the investigated steel, in accordance with the concepts about the so called “oxidative depolarization” [28].

CONCLUSIONS

The obtained results show that the corrosion of the non-treated thermally steel of the type OC404 in sulfuric acid medium occurs at potentials assisting the preservation of the anode passivity, i.e. under conditions of anodic control. The established shifting of the corrosion potential of steel in positive direction upon addition of cerium ions to sulfuric

acid aggressive medium characterizes these ions as cathode type of inhibitor. Thereupon the concentrations have been determined, at which the cerium ions in their role of cathode inhibitor with oxidative action, facilitate efficiently the processes of self-passivation, as a consequence of the decrease in the total free energy of the system and this leads to stabilization of the passive state of the steel.

In the cases when the steel has been treated thermally, as a result of the disruption of the native passive steel and the revealing of sections rich in iron on the surface, the stationary corrosion potential of the steel is shifted with about 0.7 V in negative direction, whereupon the corrosion process is limited by the cathode reaction of hydrogen evolution. Also in this case the addition of cerium ions to the aggressive medium shifts drastically the corrosion potential of the steel in positive direction, whereupon its values, respectively the corrosion currents, are dominated by the redox potentials and by the exchange currents for the couple Ce^{4+}/Ce^{3+} . The obtained results indicate that in the presence of Ce^{4+} ions, which display their property as cathode inhibitor in sulfuric acid medium, the reaction of cathodic evolution of hydrogen in the course of $SS_{t.t.}$ corrosion is no longer a determining factor. It is replaced by the effective cathode reaction of reduction of Ce^{4+} to Ce^{3+} , occurring at much more positive potentials of E_{st} for $SS_{t.t.}$. In the course of this transition a possibility is created to form on the surface of the thermally treated steel an effective protective film of specific phase composition.

The research work carried out on elucidating the influence of cerium ions on the corrosion behavior of SS and $SS_{t.t.}$ supplies information about their specific interaction with the steel surface. The XPS data show that the cerium ions determine a substantial modification of the composition (the concentration and the chemical state of the elements) of the passive film. Thereupon the ratio iron to chromium is changed and especially to aluminum, respectively the ratio between their oxides, in favor of the latter elements, which restores (in the case of $SS_{t.t.}$) and improves (in the case of SS) the passive state, respectively the corrosion stability of the studied steel.

ACKNOWLEDGEMENTS

This paper has been completed with the support of the National Fund for Scientific Investigations under Contract DO 02-242/ TK 01-185. The authors are grateful for the access to the scientific equipment for part of the electrochemical measurements donated to Prof. A. Milchev (Institute of Physical Chemistry, Bulgarian Academy of Sciences) by the Alexander von Humboldt Foundation, Germany.

CONFLICTS OF INTEREST

Declare to none.

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Received: November 11, 2011

Revised: January 15, 2012

Accepted: January 16, 2012

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