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Influence of calcination of stainless steel OC4004 covered with alumina or ceria carrier layers on their passive state in different acid media

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A comparative investigation has been carried out on the corrosion behaviour of thermally treated stainless steel (SS) OC4004 covered with Al_2O_3 or Ce_2O_3-CeO_2 layers (systems $Al_2O_3/SS_{(t.t.)}$ and Ce_2O_3-$CeO_2/SS_{(t.t.)}$) electrodeposited on in solutions of 0.1 N HNO_3 and 0.1 N H_2SO_4. It has been established that in NO_3^- containing medium $SS_{(t.t.)}$ tends to self-passivation. The thermal treatment of the system Al_2O_3/SS eliminates the protective effect of the electrodeposited Al_2O_3 layer in the corrosion media investigated due to its mechanical cracking and the formation of galvanic Al_2O_3/Fe pairs. Electrodeposited ceria strongly enhances the corrosion resistance of the system Ce_2O_3-CeO_2/SS both before and after thermal treatment. The protective effect of the Ce_2O_3-CeO_2 layers is found to be due to the enrichment of Cr in the passive film provoked by these layers as well as to effective cathodes causing a shift of the steady state potential in the system Ce_2O_3-$CeO_2/SS_{(t.t.)}$ in a positive direction.

Key words: stainless steel, electrodeposited Al_2O_3 and Ce_2O_3-CeO_2, corrosion protection.

INTRODUCTION

The use of stainless steels in high temperature regimes and aggressive media can lead to a decrease in their corrosion resistance due to the formation and prevailing dissolution of the appearing chromium carbides. Such conditions arise, e.g., during the preparation (calcination) and exploitation of catalytic steel converters for neutralization of NO_x, CO, hydrocarbons, etc. evolving from engines and power plants, etc. It is important to characterize their anode (corrosion) behaviour in aggressive media the more so as there may be mixture of nitric, sulphur and/or oxides in the converters, depending on the nature of the chemical compounds to be purified. Interacting with the evolving water vapour, these oxides may produce relatively high acid concentration. In this connection, the occurrence of a corrosion attack on the steel substrates is quite probable. As a result, negative effects may be observed in two directions: (i) strength characteristics deterioration of the steel construction and (ii) formation of chemical compounds in addition to the catalytically active ones, which being present as oxides, hydroxides etc. can decreased the catalytic effect of the catalysts and, in the most unfavourable case, act as catalytic poisons. In this connection, it is important to investigate the temperature effect on the corrosion behaviour of construction stainless steels used in converters and in this respect the role of additionally deposited aluminium or cerium oxides coatings.

The purpose of the present work was to investtigate the effect of thermal treatment on the corrosion behaviour of stainless steel OC4004 covered with electrodeposited Al_2O_3 or Ce_2O_3-CeO_2 in strongly aggressive nitric or sulphuric acid media.

EXPERIMENTAL

The test specimens (10×10 mm) used in this study were prepared from a sheet of OC 4004 type stainless steel (SS) with a thickness of 50 μm. The composition of the steel in wt.% was: 20.0% Cr, 5.0% Al, 0.02% C, and balanced Fe.

The Al_2O_3 and Ce_2O_3-CeO_2 layers were deposited electrochemically on the specimens from non-aqueous electrolytes, whose compositions and regimes are described in [1–3]. The thickness of the deposited layers was ~1 μm. The layers were investtigated after calcinations (thermal treatment) at 450ºC for 2 h in air.

The chemical composition and the oxidation state of the elements on the surfaces being formed (heat-treated and/or subjected to anodic polarization) were studied using X-ray photoelectron spectroscopy (XPS) after a preliminary 5 min bombardment of the surfaces with Ar^+. The XPS studies were performed in an Escalab II system (England) with Al K_α radiation ($h\nu$ = 1486.6 eV) and total instrumental resolution of ~1 eV. The vacuum in the chamber was 10^{-7} Pa. The binding energy (BE) was

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referred to the C1s line (of adventitious carbon) at 285.0 eV. The element concentrations were evaluated based on the integrated peak areas after a Shirley-type linear background subtraction using theoretical Scofield's photoionization cross-sections.

The morphology and structure of the layers 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 25 kV, I ~ 65 µA. The pressure was of the order of 10^{-6} Torr.

The electrochemical behaviour of the samples was studied in 0.1 N HNO_3 or 0.1 N H_2SO_4 as corrosion media with a standard three-electrode thermostated cell (100 ml volume) at 25ºC. A counter electrode, representing a platinum plate (10×10×0.6 mm), and a mercury sulphate reference electrode ($E_{Hg/Hg_2SO_4} = +0.642$ V vs SHE) were used. All potentials in the text are related to MSE. The anodic and cathodic polarization curves were obtained using a 273 EG&G potentiostat/galvanostat (Germany), with a potential sweeping rate of 10 mV/s within a potential range from −1.150 to + 1.500 V.

The steady-state corrosion potential (E_{st}) of the samples under investigation was also determined by direct measurement after immersing the samples in 0.1 N HNO_3 or 0.1 N H_2SO_4. The following two values of E were determined: E_1 is the potential value, found immediately after the immersion of the samples in the acid; E_{st} is established after a sufficiently long time interval (from a few minutes to several decades of minutes until the moment, when the steady-state corrosion potential change does not exceed 1–3 mV for 5 min).

RESULTS AND DISCUSSION

Figure 1 shows potentiodynamic polarization curves for a thermally treated SS sample in 0.1 N HNO_3 (Fig. 1a) and 0.1 N H_2SO_4 (Fig. 1b).

The anodic behaviour of the steel in 0.1 N HNO_3 is characterized by a region of passive state in the potential zone − 0.750 V to + 0.500 V and by currents of complete passivation (i_{pass} at $E_{c.p.} = +0.500$ V) from about 5.8×10^{-6} to about 4.1×10^{-5} A·cm^{-2}. In the cathode region, at the potential where hydrogen evolution begins, the curve maximum is shifted in a positive direction – from −1.0 V to −0.750 V (at the I, II and III scan – see the insert in Fig. 1a). This effect, which is indicative of a decrease in overpotential of the reaction of hydrogen evolution, is a result of enrichment of the oxide film in several valency states of chromium and the complete disappearance of metal chromium from the surface layer [4, 5].

Simultaneously, at $E = \sim +0.900$ V (see the insert in Fig. 1a), an anodic peak appears which is characteristic of steels with a high chromium content in acid media. This peak is associated with oxidation of Cr^{3+} to Cr^{6+} (formation of anions of chromic acid) according to equation $2Cr^{3+} + 7H_2O = Cr_2O_7^{2-} + 14H^+ + 6e^-$ [6]. After repeated polarization in anodic direction this peak splits, which indicates the appearance of valency states differing from Cr^{6+}.

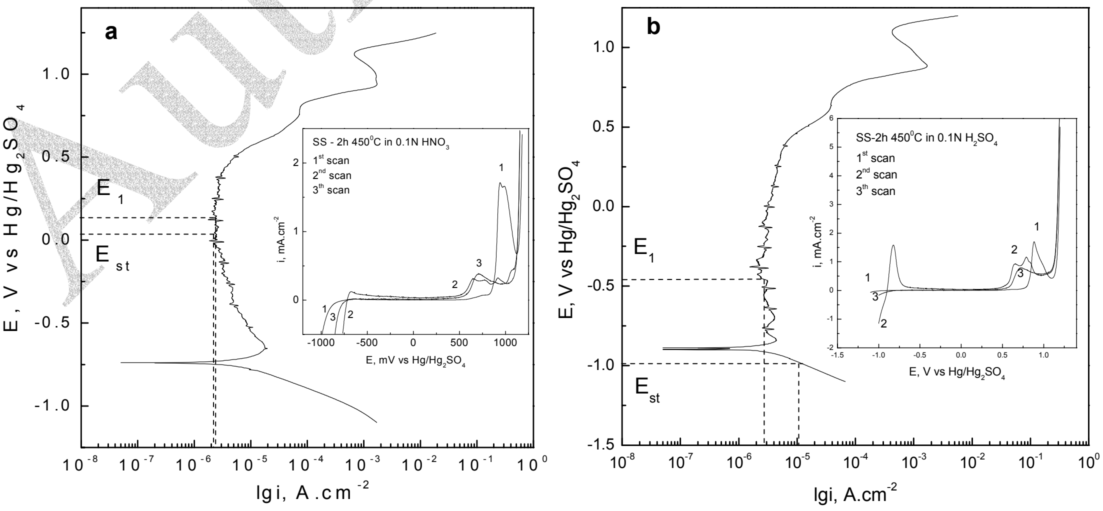

Fig. 1. (a) Potentiodynamic E-lg$i$ curves (i-E curves of scans 1–3, inserted figure) of SS after thermal treatment in 0.1 N HNO_3; (b) in 0.1 N H_2SO_4.

In contrast to the oxidizing affect in 0.1 N HNO_3, in 0.1 N H_2SO_4 an increase in i_{pass} from 1.4×10^{-5} with the first scan to 5.6×10^{-5} $A\cdot cm^{-2}$ with the third scan is observed. In addition, critical currents of passivation appear in the anodic polarization curves after the second scan at $E = \sim -0.800$ V (see the insert in Fig. 1b). Their appearance is associated with the concentration increase, according to Eqn. $Fe - 3e^{-} \rightarrow Fe^{3+}$ [7], of iron in the passive film after the thermal treatment. The changes in shape of the anodic polarization curves (Fig. 1b) are analogous to those found in 0.1 N HNO_3: when E = ~ +0.900 V, peaks characterizing the oxidation of Cr^{3+} to higher valencies appear.

Comparison of the steady state corrosion potentials for heat-treated steel in 0.1 N HNO_3 and 0.1 N H_2SO_4 determined experimentally during the study of the dependences $E-\tau$ (Fig. 2a) shows a difference of about 1 V in their values (in nitric acid $E_{st} = +0.113$ V and in sulphuric acid $E_{st} = -0.976$ V). We assume that this result is due to the oxidative effect of NO_3^{-}. The proceeding of reactions (1) and (2) with potentials of about +0.950 V, vs. NHE (~ +0.280 V vs, Hg/Hg_2SO_4) according to [6–8] is thermodynamically possible:

$$NO_3^{-} + 3H^{+} + 2e^{-} \rightarrow HNO_2 + H_2O$$

$$E^{o}_{H} = +0.940 \text{ V} \qquad \text{vs. NHE} \qquad (1)$$

$$NO_3^{-} + 4H^{+} + 3e^{-} \rightarrow NO + H_2O$$

$$E^{o}_{H} = +0.960 \text{ V} \qquad \text{vs. NHE} \qquad (2)$$

The proceeding of these reactions results in a strongly positive corrosion potential of the medium, which determines the stable passive state of $SS_{(t.t.)}$. Due to this, occurrence of a hydrogen-depolarizing reaction, i.e. conjugated reaction of metal oxidation similar to those occurring in 0.1 N H_2SO_4, is impossible. This specific character of the processes observed in 0.1 N HNO_3 leads to an increase (about 3 times) of the surface concentration of Cr, while the surface concentration of Al drops by about 45% with respect to its values in the passive film of SS not subjected to heat-treatment (Table 1). The changes in surface concentrations of the elements correspond to the surface morphology changes of $SS_{(t.t.)}$ in the two corrosion media (Fig. 3). Obviously, the chemical composition change of the SS surface film resulting from the heating, leads to a change in corrosion behaviour of the steel, which, in the case of 0.1 N HNO_3, is also stabilized by the oxidative effect of the corrosion medium, while in H_2SO_4 such an effect is not observed.

Table 1. Element distribution (in at.%) on the surface layers of SS and thermally treated samples of SS, Al_2O_3/SS, Ce_2O_3-CeO_2/SS after anode polarization in 0.1 N HNO_3 and 0.1 N H_2SO_4 at a potential of +0.500 V.

Samples	in 0.1 N HNO_3 at $E_{c.p.}$ = +0.500 V				
	O, at. %	Fe, at. %	Cr, at. %	Al, at. %	Ce, at. %
SS	62.0	1.7	3.1	33.2	-
SS (t.t.)	67.7	2.7	9.4	20.2	-
Al_2O_3 /SS (t.t.)	59.3	1.3	0.8	38.6	-
Ce_2O_3-CeO_2/SS(t.t.)	61.3	7.0	8.8	17.0	5.9
	in 0.1 N H_2SO_4 at $E_{c.p.}$= +0.500 V				
SS (t.t.)	62.8	2.3	6.1	28.8	-
Ce_2O_3-CeO_2/SS(t.t.)	60.0	0.9	6.7	30.8	1.6

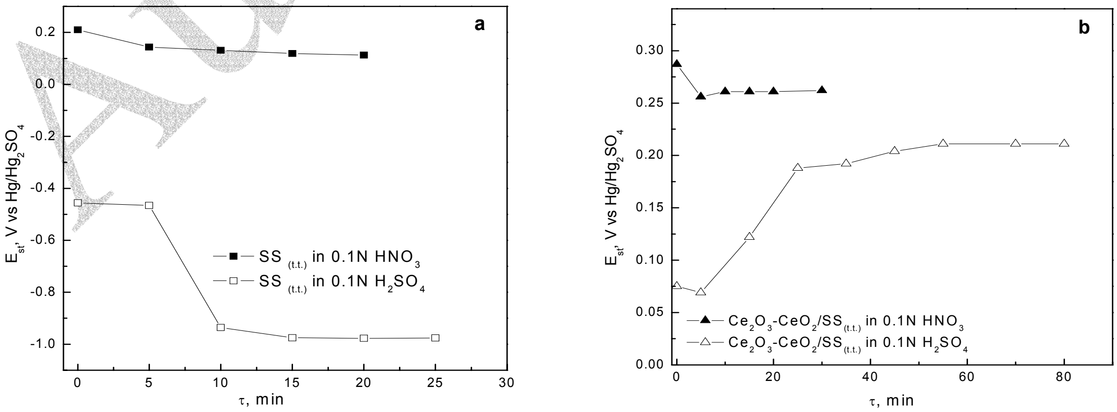

Fig. 2. Open circuit stationary potential (E_{st}) vs. time for: (a) $SS_{(t.t.)}$; (b) Ce_2O_3-CeO_2/$SS_{(t.t.)}$ in different acid media.

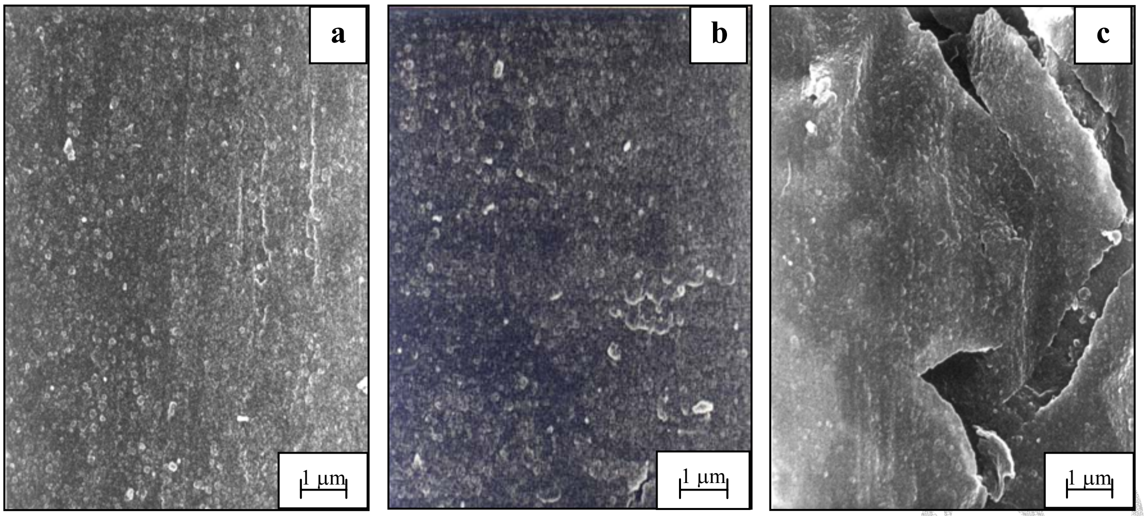

Fig. 3. SEM micrographs of the surface after thermal treatment of: (a) SS; (b) SS in 0.1 N HNO_3 at $E_{st} = +0.113$ V; (c) SS in 0.1 N H_2SO_4 at $E_{st} = -0.976$ V.

In the absence of external polarization (open circuit), oxidation of Fe ($Fe = Fe^{2+} + 2e^-$) proceeds in sulphuric acid at –0.976 V on the significantly increased (due to cracking of the passive film on SS) number of local anodic regions of the electrode surface. As a result of the anodic process of Fe self-dissolution, its surface concentration decreases from 7.2 at.% to 1.3 at.% (Table 2).

Table 2. Element distribution (in at.%) on the surface layers of SS, $SS_{(t.t.)}$, respectively Ce_2O_3-$CeO_2/SS_{(t.t.)}$ without corrosion treatment and at open circuit in 0.1 N H_2SO_4.

Samples	O, at. %	Fe, at. %	Cr, at. %	Al, at. %	Ce, at. %
SS	58.3	3.1	3.4	35.2	-
SS (t.t.)	64.9	7.2	7.0	20.9	-
Ce_2O_3-CeO_2/SS(t.t.)	68.9	0.0	3.6	6.8	20.7
	at open circuit potential (E_{st})				
SS (t.t.)	65.4	1.3	6.4	26.9	-
Ce_2O_3-CeO_2/SS(t.t.)	81.4	6.4	3.3	7.4	1.5

The application of anodic polarization ($E_{c.p.}$ = +0.500 V) results in formation of a passive film containing Fe^{3+}, Cr^{3+} and Al^{3+}, most probably as an Al^{3+}-containing spinel of the type $Fe^{2+}(Fe^{3+}, Cr^{3+})_2O_4$ [7]. In this case, a Cr^{3+}:Fe^{3+} ratio of about 3 is attained.

Comparison of the data from XPS analyses on the concentration change of the elements in the surface film shows that in 0.1 N H_2SO_4, changes in the concentrations of Cr and Fe, i.e. the Cr/Fe ratio, appear with both E_{st} and $E_{c.p.}$. The values registered are 5.1 for an open circuit and 2.7 for $E_{c.p.}$ = +0.500 V. Irrespective of the enhanced Cr content in the surface film, the steady state corrosion potential of $SS_{(t.t.)}$ is strongly shifted in the negative direction, as a result of which the steel demonstrates corrosion with hydrogen depolarization. Our opinion is that this is due to the significant cracking as a result of the thermal treatment.

Figure 4 shows the potentiodynamic curves for the systems Al_2O_3/SS and Ce_2O_3-CeO_2/SS after heat treatment in 0.1 N HNO_3 (Fig. 4a) and 0.1 N H_2SO_4 (Fig. 1b). Comparison of the E_{corr} values determined by the intersecting point of the anodic and cathodic polarization curves for the system Al_2O_3/SS(t.t.) with the E_{st} values measured on the $E-\tau$ curves of the real corrosion process shows, after attaining a steady-state value of the corrosion potential, a strong shift of E_{st} in negative direction, i.e. from $E_{corr} = -0.714$ V to $E_{st} = -0.755$ V in 0.1 N HNO_3 and from $E_{corr} = -0.860$ V to $E_{st} = -0.972$ V in 0.1 N H_2SO_4. The SEM data are in agreement with these results (Fig. 5), which means that, as a result of heating, the Al_2O_3 film has cracked and the steel substrate has partially lost its coating, this leading to the appearance of microgalvanic Al_2O_3/Fe pairs. This unfavourable effect is responsible for the more negative E_{st} values found (Figs. 4a and 4b) for the Al_2O_3/SS system in both corrosion media.

Figure 4 also shows the potentiodynamic curves for the system Ce_2O_3-CeO_2/SS after thermal treatment in 0.1 N HNO_3 (Fig. 4a) and in 0.1 N H_2SO_4 (Fig. 4b). Comparison of these data with the steady-state corrosion potentials of the heat-treated system Ce_2O_3-CeO_2/SS (Fig. 2b) and $SS_{(t.t.)}$ (Fig. 2a) shows their shift in the positive direction by about 150 mV in 0.1 N HNO_3 and 1 V in 0.1 N H_2SO_4. Hence, the cerium oxides film formed on steel substrates considerably improves their corrosion resistance in sulphuric acid medium, the corrosion process being shifted (E_{st}) from the zone of mixed control (water reduction and metal oxidation) to the zone of stable passivity (Figs. 1b and 4b).

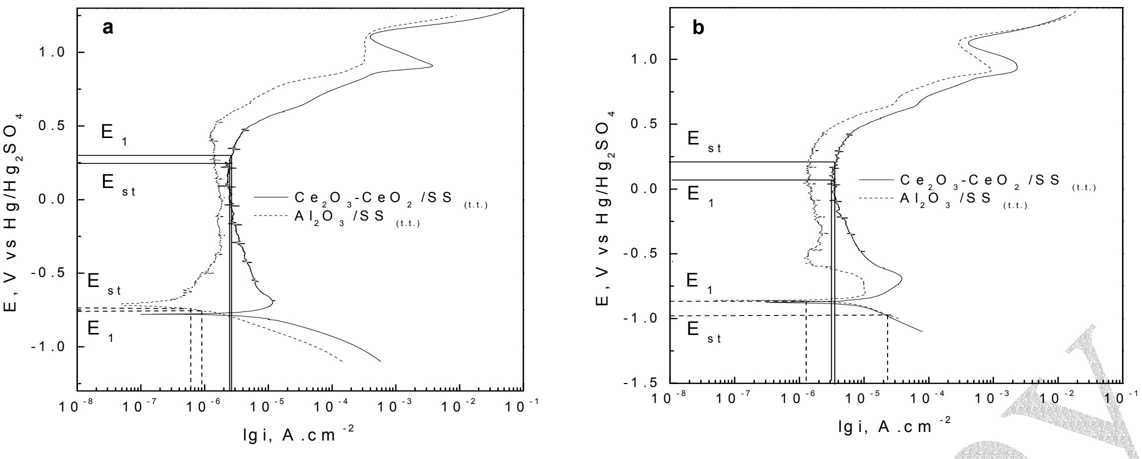

Fig. 4. Potentiodynamic E-lgi curves for the systems Al_2O_3/SS and Ce_2O_3-CeO_2/SS after thermal treatment: (a) in 0.1 N HNO_3; (b) in 0.1 N H_2SO_4.

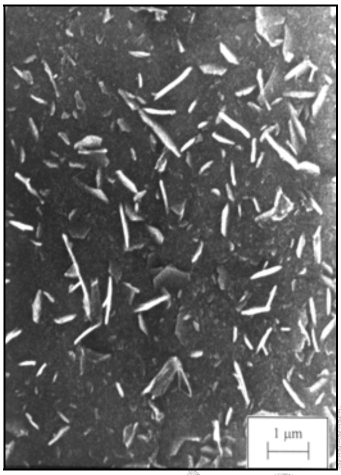

Fig. 5. SEM micrographs of Al_2O_3/SS after thermal treatment.

The results obtained permit concluding that in 0.1 N HNO_3, Ce_2O_3-CeO_2 has an additive protective effect along with that of the medium component NO_3^-. In 0.1 N H_2SO_4 the cerium oxide layers characterized by $E = \sim +1.7$ V [9] act as effective cathodes ensuring the restoration of the steel passive state as a result of the shift of $E_{st} = -0.976$ V for $SS_{(t.t.)}$ to $E_{st} = +0.211$ V for the system Ce_2O_3-$CeO_2/SS_{(t.t.)}$.

XPS analyses on the element distribution in the surface oxide film of the thermally treated system Ce_2O_3-CeO_2/SS showed Cr_2O_3, Al_2O_3 and Ce_2O_3-CeO_2 as the main film components (Tables 1 and 2). As is evident, after polarizing the system in 0.1 N HNO_3 and 0.1 N H_2SO_4 at $E_{c.p.} = +0.500$ V for 5 min and after immersing the samples in 0.1 N H_2SO_4 for 80 min, the circuit being open, the surface film composition shows considerable changes: (i) The decrease in Ce_2O_3-CeO_2 concentration is much smaller as compared to samples not subjected to thermal treatment [5], due to the transformation of Ce_2O_3 into CeO_2 which does not dissolve in acids [10]; (ii) In the zone of passivity ($E_{c.p.} = +0.500$ V) the concentration of Cr_2O_3 increases in both 0.1 N HNO_3 and 0.1 N H_2SO_4; (iii) In 0.1 N H_2SO_4 the concentration of Cr_2O_3 does practically not change in the presence of real corrosion (open circuit); (iv) The concentration of Al_2O_3 and iron oxides increases.

The concentration change of the elements in the passive film is most probably due to the processes of its modification under the effect of the corrosion medium and the effective cathode coverage of ceria.

CONCLUSIONS

It has been established that in a corrosion medium containing NO_3^-, the heat treatment of stainless steel OC4004 leads to self-passivation.

Thermal treatment of the system Al_2O_3/SS has been shown to eliminate the protective effect of electrodeposited alumina layer in the corrosion media investigated due to its mechanical cracking and the formation of galvanic Al_2O_3/Fe pairs.

Electrodeposited cerium oxides strongly increase the corrosion resistance of the system Ce_2O_3-CeO_2/SS both before and after thermal treatment. This effect is found to be due to the change (increase) in Cr concentration in the modified protective passive film on the surface, i.e. to the Cr/Fe ratio change in this film. This chemical composition change of the surface film is enhanced by thermal treatment. This change leads to a significant shift of E_{st} of the systems in the positive direction up to a value of +0.211 V in sulphuric acid media. These potentials determine the occurrence of the corrosion process under the conditions of stable passivity of the steel. In cases when the passive state of the systems is disturbed, the steel surface parts covered with Ce_2O_3-CeO_2 will begin to act as effective cathodes restoring the passive state.

In addition to the positive role of the enhanced Cr concentration in the surface layer, there will be processes of internal anode polarization due to the electrodeposited Ce_2O_3-CeO_2 layer with its highly positive redox potential. These processes will preserve/restore the passive state of the system under the conditions of real corrosion.

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ВЛИЯНИЕ НА ТЕРМИЧНАТА ОБРАБОТКА НА ЕЛЕКТРООТЛОЖЕНИ АЛУМИНИЕВ И ЦЕРИЕВ ОКСИДИ ВЪРХУ ПАСИВНОТО СЪСТОЯНИЕ НА НЕРЪЖДАЕМА СТОМАНА ОС4004 В КИСЕЛИ СРЕДИ

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(Резюме)

Проведено е сравнително изследване на корозионното поведение на термообработена неръждаема стомана (SS) OC4004 и на електроотложени върху нея Al_2O_3 и Ce_2O_3-CeO_2 слоеве (системите $Al_2O_3/SS_{(t.t.)}$, Ce_2O_3-CeO_2/SS) в разтвори на 0.1 N HNO_3 и 0.1 N H_2SO_4. Установено е, че в корозионна среда, съдържаща NO_3^-, $SS_{(t.t.)}$ проявява склонност към самопасивация. Термообработката на системата Al_2O_3/SS елиминира защитното действие на електроотложения Al_2O_3 слой в изучените корозионни среди, вследствие механичното им напукване и формирането на галванични двойки Al_2O_3/Fe. Електроотложените цериеви оксиди повишават силно корозионната устойчивост на системата Ce_2O_3-CeO_2/SS както преди, така и след термообработка. Установено е, че защитният ефект на Ce_2O_3-CeO_2 слоевете се дължи на предизвиканото от тях повишаване на повърхностната концентрация на Cr в пасивния филм, както и на действието им като ефективни катоди, обуславящи силно отместване на стационарения потенциал на системата Ce_2O_3-$CeO_2/SS_{(t.t.)}$ в положителна посока.