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Corrosion Behavior of Stainless Steels Modified by Cerium Oxides Layers

Emilia Stoyanova and Dimitar Stoychev
Institute of Physical Chemistry, Bulgarian Academy of Sciences
Bulgaria

1. Introduction

The modifying of the surface, which involves altering only the surface layers of a material, is becoming increasingly important with the aim to enhance the corrosion resistance of many kinds of materials. The advantage of this approach lies in the fact that the natural physical and mechanical properties of the material are retained, while at the same time the corrosion resistance is increased. It is well known that electroplated zinc coating is employed as active galvanic protection for low and middle-content alloyed steels (Almeida et al.,1998; Hagans & Hass, 1994; Kudryavtsev, 1979; Lainer, 1984; Zaki, 1988). However, zinc is a highly reactive element, and therefore high corrosion rates of this coating are observed in cases of indoor and outdoor exposures. For this reason a post-treatment is needed to increase the lifetime of zinc coatings. This kind of treatment is applied in the current industrial practice to prolong the lifetime of zinc coatings and the steel substrates, respectively. This treatment consists of immersion in a chemical bath, which forms a conversion layer over the plated zinc. The so formed layer is a dielectric passive film with high corrosion resistance and it is also a better surface for paint adherence (Zaki, 1988). The main problem with the traditionally applied post-treatment procedures is the presence of Cr^{6+} salts that are considered to be carcinogenic substances, which are known to be very harmful to human health and environment (Schafer & Stock, 2005) and whose use is forbidden by European regulations (Hagans & Hass, 1994).

Molybdates, tungstates, permanganates and vanadates, including chromium-like components, were the first chemical elements to be tested as hexavalent chromium substitutes (Almeida et al., 1998a, 1998b; Korobov et al, 1998; Schafer & Stock, 2005; Wilcox & Gabe, 1987; Wilcox et al., 1988). Recently many alternative coatings have been developed, based on zirconium and titanium salts (Barbucci et al., 1998; Hinton, 1991), cobalt salts (Barbucci et al., 1998; Gonzalez et al., 2001) and organic conductive polymers (Gonzalez et al., 2001; Hosseini et al., 2006). The use of salts of rare-earth metals as the main component in the electrolytes, developed for the formation of cerium, lanthanum and other oxide protective films is also a very promising alternative to the chromate films and it is one of the advanced contemporary methods for corrosion protection of metals and alloys (Bethencourt et al., 1998; Crossland et al., 1998; Davenport et al., 1991; Fahrenholtz et al., 2002; Forsyth et al., 2002; Hinton, 1983, 1992; Hosseini et al., 2007; Liu & Li , 2000; Montemor et al., 2002; Montemor & Ferreira, 2008; Pardo et al., 2006; Wang et al., 1997). However, some aspects of

the preparation and of the corrosion behavior of these coatings are not quite clear yet and their practical utilization is still uncertain. In order to find an attractive alternative to Cr^{6+} conversion coating, several treatment procedures that should manifest both efficient anti-corrosive behavior as well as an optimal benefit/cost ratio, and mainly insignificant environmental impact, have yet to be developed. It has been found out that cerium species can be successfully applied to protect zinc from corrosion (Aramaki, 2001, 2002; Arenas et al., 2003, 2004; Ferreira et al., 2004; Otero et al., 1996, 1998; Wang et al., 2004; Virtanen et al., 1997), aluminum and aluminum containing alloys (Aldykiewicz et al., 1995; Amelinckx et al., 2006; Arnott et al., 1989; Davenport et al., 1991; Mansfeld et al., 1989,1991, 1995; Pardo et al., 2006; Zheludkevich et al., 2006; Di Maggio et al., 1997; Lukanova et al.. 2008), stainless steels (Breslin et al., 1997; Lu & Ives, 1993, 1995), magnesium containing alloys (Arenas et al., 2002; Liu et al., 2001) even SiC/Al metal matrix composites. All these can be used to reduce the rate of general corrosion, pitting and crevice corrosion as well as stress corrosion (Breslin et al., 1997; Lu & Ives, 1993, 1995). The oxide films of rare-earth elements and refractory compounds can be formed mostly by means of chemical or electrochemical methods (Amelinckx et al., 2006a, 2006b; Avramova et al., 2005; Balasubramanian et al., 1999; Di Maggio et al., 1997; Marinova et al., 2006; Montemor et al., 2001, 2002; Schmidt et al., 1997; Stefanov et al., 2000a, 2000b, 2004a, 2004b; Stoychev et al., 2000, 2003, 2004; Tsanev et al., 2008; Tyuliev et al., 2002; Valov et al., 2002; Zheludkevich et al., 2005). It is supposed that cerium oxide/ hydroxide formation is the main reason for the corrosion protection property of cerium compounds. In spite of the growing number of investigations during the last years, focused on the mechanisms via which the oxides of rare-earth metals (mainly cerium oxides) lead to improvement of the corrosion stability of the systems "oxide(s)/protected metal", still a series of issues remain problematic. The first hypotheses in this respect have been put forward by Hinton (Hinton & Wilson, 1989; Hinton, 1992). He supposed in his early works that the cathodic reactions (reduction of oxygen and evolution of hydrogen) lead to alkalization of the near-to-the-electrode layer, which in its turn results in precipitation of the oxide of the rare-earth element, respectively in formation of protective film on the electrode surface.

The modern technologies for surface treatment, aimed at modifying the surface composition and structure of metals and alloys, including stainless steels, are becoming more and more important instruments for improving their stability to corrosion and for attributing the desired outside appearance and/or functional properties. Wang and coworkers (Wang et al., 2004) have studied the corrosion resistance of stainless steel SS304 after immersion treatment in electrolytes, containing Ce^{3+} ions, $KMnO_4$ and sulfuric acid. The obtained experimental results prove the considerable increase in the corrosion stability of steel in 3.5% NaCl solution. The corrosion potential of the steel, treated by immersion, has more positive values than that of the non-treated steel, while the potential of pitting formation is also shifted in the positive direction, which is the criterion for weakening the tendency of the studied steel to undergo pitting formation. It has also been observed that the values of the current of complete passivation are decreased by one order of magnitude. As far as the cathodic reaction is concerned, the cerium conversion coatings blocked the matrix steel, which caused the reduction of the oxygen and protons to take place at a higher over-potential and the cathodic reaction was inhibited. The analysis of the chemical state of cerium in the conversion film indicated that the prevailing amount of cerium is in trivalent state. Aldykiewicz and coworkers (Aldykiewicz et al, 1996) have investigated the influence

of cerium oxide, deposited on aluminum alloys and they ascertained that the trivalent cerium is oxidized to tetravalent by the oxygen dissolved in the electrolyte, which leads to precipitation/formation of non-soluble CeO_2 on the cathodic sections of the electrode surface. Montemor and coworkers (Montemor et al., 2001, 2002) studied the effect of the composition of the electrolytes (based on $Ce(NO_3)_3$ and the regime of preparing conversion layers on galvanized (zinc coated) steel. The increase in the thickness of the cerium conversion films in the process of formation leads to their enrichment in Ce^{4+}. According to the same authors the conversion films, formed in $La(NO_3)_3$, are more efficient in view of anticorrosion protection, compared to those formed in electrolytes, containing $Ce(NO_3)_3$ and $Y(NO_3)_3$ (Montemor et al, 2002). The mechanism, involved in such a process of reducing the corrosion rate of the substrate, may be related to precipitation of cerium oxides and hydroxides in the vicinity of the anodic areas. These precipitates reduce the cathodic activity and hinder the transfer of electrons from the anodic to the cathodic spots.

The mechanism of zinc corrosion inhibition, when zinc is treated in solutions of $Ce(NO)_3$, has been studied by Aramaki (Aramaki, 2001a, 2001b, 2002a; 2002b). He established the formation of hydrated or hydroxylated Ce-rich layer. This process, in its turn, leads to the formation of Ce_2O_3 on the electrode/the protected surface, respectively to inhibition of the cathodic reactions of the corrosion process in solutions of NaCl. The work by Lu and Ives (Lu & Ives, 1995) has been extended further to study the effect of cerium salt solution treatment. Rotating disk assemblies were employed to monitor the cathodic electrode process and its inhibition by cerium salt treatment on austenitic stainless steels in a solution simulating sea water. The reduction of oxygen and hydrogen cations on both kinds of non-treated steels has been shown to be controlled by mass transfer processes in the solution. Cerium treatment effectively inhibits the cathodic reduction of oxygen, which is controlled primarily by charge transfer on the electrode. The over-potential for cathodic reduction of hydrogen cations is increased after the cerium treatment and the electrode reaction is controlled both by the mass transfer process in solution and by the charge transfer on the electrode. As a result of inhibition of the electrode processes, cerium improves the localized corrosion resistance, and in particular the crevice corrosion resistance, of stainless steels.

The electrochemical behavior of stainless steels - SS304 and 316L, following various cerium and cerium/molybdenum prereatment steps, was studied aiming at gaining more information on the process, by which cerium and molybdenum can modify the properties of passive film formed on stainless steels (Breslin et al, 1997). The coatings were analyzed by electrochemical impedance spectroscopy and X-ray photoelectron spectroscopy in order to identify the cerium species, which play the main role in the promotion of the passivation behavior. The pre-treatment step, denoted as $Ce(CH_3CO_2)_3$ and $CeCl_3$, involved immersion treatment of the electrodes in the $Ce(CH_3CO_2)_3$ solution for 1 h and then in the $CeCl_3$ solution for one additional hour at approximately 92◦C. Regardless of the nature of the cerium salt, no changes in the rate of the cathodic reduction reaction could be observed. The increase in the corrosion potential (E_{corr}). is mainly due to the decrease in the passive current density, suggesting that treatment in cerium solutions does not affect the rate of the cathodic reaction, but rather reduces the rate of the passive film dissolution. However a significant lowering of the oxygen reduction current could be observed, following the electrodeposition of small amount of cerium onto the electrode surface. Thus, it appears that efficient

formation of cerium hydroxide/oxide does not occur upon immersion of electrodes at elevated temperatures in cerium solutions. It was possible to observe a yellow colored film indicative of cerium in the 4^+ oxidation state on the surface of the stainless steel, following a 24-h immersion time interval in the $Ce(NO)_3$ solution at room temperature. Breslin and coworkers (Breslin et al, 1997) proved that the treatment of SS304 in cerium-salt solutions gave rise to an increase in the value of the pitting potential E_{pit}, with the greatest increase resulting from immersion in $CeCl_3$ at 90-95^{o}C for 30 min, followed by immersion in $Ce(NO)_3$ solution at 90-95^{o}C for additional 60 min time interval. The enhanced resistance to the onset of pitting, according to these authors, could be due to the dissolution of surface MnS inclusions during the immersion in the chloride-containing solution and possibly chromium enrichment of the passive film during treatment in the sodium nitrate solution, which is highly oxidizing. The presence of cerium in the solution seemed to have only a minor effect on E_{pit}. The survey of the various mechanisms, proposed in the current literature, indicates that the role of rare-earth elements as inhibitors of corrosion and as protective coatings is not completely elucidated. It is accepted that their presence leads to improvement of the corrosion stability of metals and alloys and therefore they are a promising alternative, in conformity with the requirements for protection of the environment prohibiting the conventional Cr^{6+} conversion treatment.

At the same time it is known that thin films of Ce_2O_3-CeO_2, have also an important functional designation for the manufacture of catalytic converters, where ceria is widely used in such kind of catalytic processes as a reducible oxide support material in emission control catalysis for the purification of exhaust gases from various combustion systems (Trovarelli, 1996). In the so called "three-way automotive catalysis", for example, the reducibility of ceria contributes to oxygen storage/release capability, which plays an important role in the oxidation of CO and hydrocarbons catalyzed on the surface of precious metal particles (Bunluesin et al, 1997). It is because of their specific interactions with oxygen that the cerium oxides are included in the support layers (Al_2O_3, ZrO_2, etc.) of the proper catalytically active components of the converters (noble metals like Pt, Ro, Pd and others) and they participate directly in the decontamination of exhaust gases (reduction of NO_x, oxidation of CO and hydrocarbons, etc.) originating from internal combustion engines (Mcnamara, 2000). In this connection it is important to point out that during the process of operation the main construction elements of the catalytic converters, which are made of stainless steel (Lox et al, 1995; Nonnenmann, 1989) (for example steel OC 404), are subjected simultaneously to over-heating and at the same time to the aggressive action of the nitrogen oxides, being liberated in the course of the processes of combustion, of sulfur oxides, of water vapor and incompletely oxidized hydrocarbons etc. (respectively resulting in formation of HNO_3, H_2SO_4 etc). In this respect and in the light of the data available in the literature about the protective action of the cerium oxides and hydroxides, it is essential to know what is the intimate mechanism of their anti-corrosion action and to what extent they could contribute, in particular, to the prolongation of the exploitation life-time of the catalytic converters, made of stainless steel.

Our studies on the protective effect of mixed Ce_2O_3-CeO_2 films electrochemically deposited on stainless steel OC 404 (SS) in model media of 0.1N HNO_3 and 0.1N H_2SO_4 (Nikolova et al., 2006a, 2006b, 2008; Stoyanova et al., 2006a, 2006b, 2010), have shown that these films in their nature are in fact cathodic coatings. The influence of the change in the concentration of

Ce in the oxide films has been studied in regard to the corrosion potential of the steel in the same corrosion medium. Thereupon it was found out that the increase in the surface concentration of Ce in the oxide films results in a gradual shift of the corrosion potential of steel in the positive direction - from the zone characteristic of anodic dissolution to the zone of deep passivity – defined by the anodic potentiodynamic curve. Moreover it has been proved that there occurs a cathodic reaction of reduction of the electrochemically active CeO_2 – one of the components of the electrodeposited mixed Ce_2O_3-CeO_2 film.

The present work discusses a hypothesis, aimed at elucidation of the question: how the change in the surface concentration of Ce in the mixed Ce_2O_3-CeO_2 oxide film electrodeposited on OC 404 steel influences the processes of anodic passivity of the studied steel, respectively the values of the potentials of complete passivation and the potentials of pitting formation, as well as the current density in passive state, determining the corrosion behavior of the steel under consideration. As far as the oxide of Ce^{3+} (i.e. Ce_2O_3) is chemically unstable and it is dissolved in sulfuric acid medium (Achmetov, 1988) the investigations carried out in ref.(Guergova et al, 2011) established an effective inhibitory action of the cerium ions (Ce^{3+}, Ce^{4+}), passing over from the system Ce_2O_3-CeO_2/SS into the corrosion medium. A possible inhibitory interaction has been supposed to occur on the surface of the steel.

2. Experimental

2.1 Specimen preparation and structure characterization

The stainless steel (SS) samples (SS type OC 404 containing 20% Cr, 5.0% Al, 0.02% C, the rest being Fe) were 10x10 mm plates of steel foil, 50 μm thick. The deposition of the films was carried out in a working electrolyte consisting of absolute ethanol saturated with 2.3 M LiCl and 0.3 M $CeCl_3x7H_2O$ salts. The cathodic deposition was performed in a galvanostatic regime at current density of 0.1mA.cm^{-2}. The deposition time interval was 60 min. Platinum coated titanium mesh was used as counter electrode (anode). It was situated symmetrically around the working electrode and its surface was chosen specially to ensure a low anode polarization, which hindered Cl^- oxidation. Because of the relatively low equivalent conductance of the working electrolyte (χ - 1.10^{-2} Ω^{-1} cm^{-1}), it becomes warmed up during the electrolysis. For this reason, the electrochemical measurements were carried out in a specially constructed electrochemical cell. The cell was kept at a constant temperature of 5–7^{o}C by circulation of cooling water. The obtained CeO_2-Ce_2O_3 coatings had a thickness of 1μm (Avramova et al., 2005; Stefanov et al., 2004). The system CeO_2-Ce_2O_3/SS was investigated prior to and after thermal treatment (t.t.) at 450°C for 2 h in air. The model aggressive solution (0.1N 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 lanthanide salt, variable concentrations of $Ce(SO_4)_2.4H_2O$ from 0.1 to 1500 ppm were added to 0.1N H_2SO_4.

The morphology and structure of the samples was examined by scanning electron microscopy using a JEOL JSM 6390 electron microscope (Japan) equipped with ultrahigh resolution scanning system (ASID-3D) in regimes of secondary electron image (SEI) and back scattered electrons (BEC) image. The pressure was of the order of 10^{-4} Pa.

2.2 Chemical characterization

The chemical composition and state of the surfaces being formed was studied using X-ray photoelectron spectroscopy (XPS). The XPS studies were performed on an Escalab MkII system (England) with Al K_∞ radiation ($h\nu$ = 1486.6 eV) and total instrumental resolution of ~ 1 eV. The pressure in the chamber was 10^{-8} Pa. The binding energy (BE) was referred to the C1s line (of the adventitious carbon) at 285.0 eV. The element concentrations were evaluated from the integrated peak areas after Shirley-type of linear background subtraction using theoretical Scofield`s photoionization cross-sections.

2.3 Electrochemical (corrosion) characterization

The electrochemical behaviour of the samples (plates 10 x 10 x 0.05mm) was studied in a standard three-electrode thermostated cell (100 ml volume). The model corrosion medium was 0.1 N H_2SO_4 ("p.a." Merck) after deaeration with additionally purified argon at 25°C. A counter electrode, representing a platinum plate (10x10x0.6mm), and a mercury/mercurous sulfate reference electrode (MSE), ($E_{Hg/Hg2SO4}$= +0.642V versus 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 and computer-aided processing of the results according to an "Echem" programme, with a potential sweeping rate of 10 mV/s within a potential range from –1.500 to +1.500V. The recording of the potentiodynamic curves was carried out starting from the stationary corrosion potential (E_{st}), measured in the absence of external current (at open circuit) in the anode and cathode directions. We used a separate electrode for each recorded curve. The stationary corrosion potential of the samples under investigation was determined by direct measurement of the function "E_{st}–time" at open circuit (with respect to the same reference electrode) after immersing the samples in 0.1 N H_2SO_4 in the absence and in the presence of Ce^{4+}. The E_{st} was established after a sufficiently long time interval - from few minutes to several decades of minutes until the moment, when the corrosion potential change did not exceed 1-3mV for 5 min.

3. Theoretical background

It is known that one of the basic approaches to promote the corrosion resistance of alloys is to enhance their passivity. It has been established that upon introducing a new component with higher inclination to passive state into the metal or into the alloy, it transfers this property to the main metal or to the alloy. The formation of a system, which is more stable to corrosion (i.e more easily passivated system) could be achieved through promoting the effectiveness of the cathodic process. At first glance this is a self-contradictory statement, however it can be easily explained in the following way. It can be seen from the corrosion diagram, represented in Fig. 1, that if the anodic potentiodynamic curve of the alloy remains one and the same, the rate of corrosion can be changed considerably at the expense of the changing effectiveness of the occurring cathodic process. It is important to note that in the case of non-passivating systems (i.e. systems characterized by anodic behavior until point B of the anodic curve) the corrosion rate is always increasing with the increase in the cathodic efficiency (for example the transition from cathodic curve K_1 to K_2 in Fig.1). In the cases when the corrosion systems are passivating ones and the anodic polarization curve is not a monotonous dependence between the potential and the current and when there exists a

region of potentials somewhere between the passivation potential (E_p) and the potential of transpassivity (E_t) (or the potential of pitting formation (E_{pit})), in which the increase of the effectiveness of the cathodic process is leading not to enhancement but rather to abatement of the corrosion rate (for example in the course of the transition from one cathodic process K_2 to another one K_3) one can observe a system more stable to corrosion (easily passivating system). Obviously in this case of minimal corrosion currents there will appear a cross-point between the anodic and the cathodic curves of the corrosion diagram within the zone of stable passive state. Under these conditions it is quite possible that a smaller corrosion current is corresponding to a more efficient cathodic process in comparison to the system displaying a lower cathodic efficiency (if we exclude the conditions where the potential of the system is reaching the value of the potential of transpassivation and the potential of pitting formation - K_4). Therefore one can conclude that during the occurring of an efficient cathodic process the system will pass over spontaneously to a stable passive state and it will be corroding at a much lower rate, corresponding to the current of complete passivation. The stationary corrosion potential of such a system will be more positive than the potential of complete passivation (E_{cp}) and at the same time more negative than the potential of break through the passive film and the potential of transpassivation. In this way the rate of corrosion can be reduced to a considerable extent by the correct use of the phenomenon "passivation".

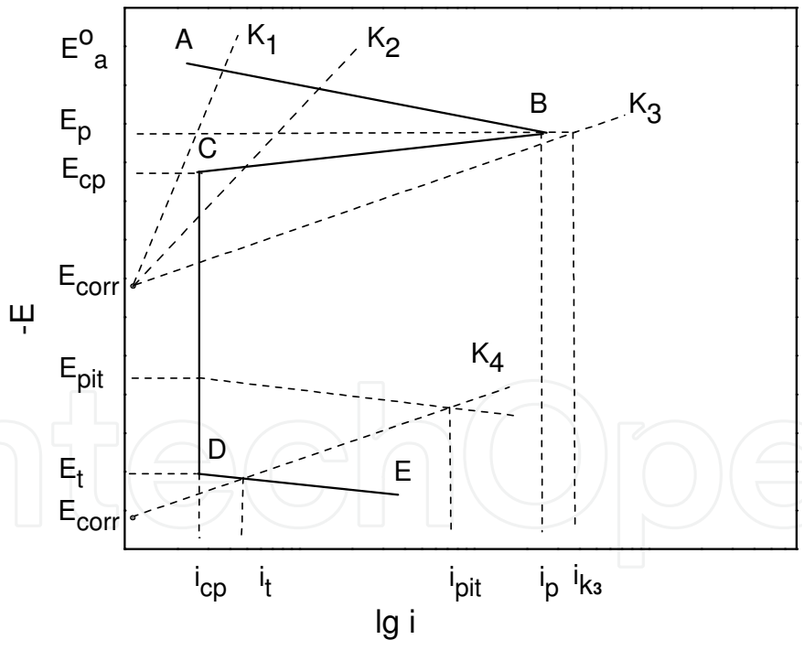


Fig. 1. Schematic polarization diagram explaining the action of the effective cathodic coatings on the steel corrosion: $i_{p,}$ i_{cp}., i_{pit}, i_t- respectively currents of initial passivation, complete passivation, pitting formation and corrosion in transpassive state.

So, in order to create a system stable to corrosion and to decrease the rate of corrosion, it is necessary to find a way to promote the cathodic effectiveness (for example as it is in this specific case of investigations, carried out by us, to modify the steel surface with CeO_2-Ce_2O_3

oxides as cathodic coating). This theoretical approach has been used in this work, with a view to explain the obtained results, in view of stabilization and restoration of the passive state of OC 404 steel as a consequence of electrochemical formation of the surface CeO_2-Ce_2O_3 layers. We agree with the assumption that for a similar type of modified systems there exists only one passive state of the system (even without applying any external anodic current). Or, in other words, the result is a spontaneously self-passivating system and if in some way it is being led away from its passive state (for example in the case of cathodic polarization or by exerting a mechanical impact), after the termination of the external effect, again the system will pass over to its passive state.

As a matter of fact the increase in the effectiveness of the cathodic process is connected with the character of the cathodic process. The dilemma is whether the promotion of the cathodic efficiency is due only to the process of hydrogen depolarization, on the cerium oxide cathodic coating (in case of steel corrosion in acidic medium) or it is possible that there exists another cathodic process, owing to the oxidative properties of the electrochemically active CeO_2.

Figure 2 represents an example of a corrosion diagram, illustrating the changes in the behavior of the corrosion system upon increasing the surface concentration of the effective cathodic coating (for example in the case of modifying the steel surface with cerium oxides). It follows from the diagram that the shift in the corrosion potential of the system is associated with the increase in the concentration of the cathodic depolarizer (the cerium oxides), which will facilitate the transition from active state into passive state of the system, under the conditions of disturbed passivity. At concentration of the cerium oxides, corresponding to the cathodic curve C_1 (Fig. 2), the rate of dissolution of the steel will

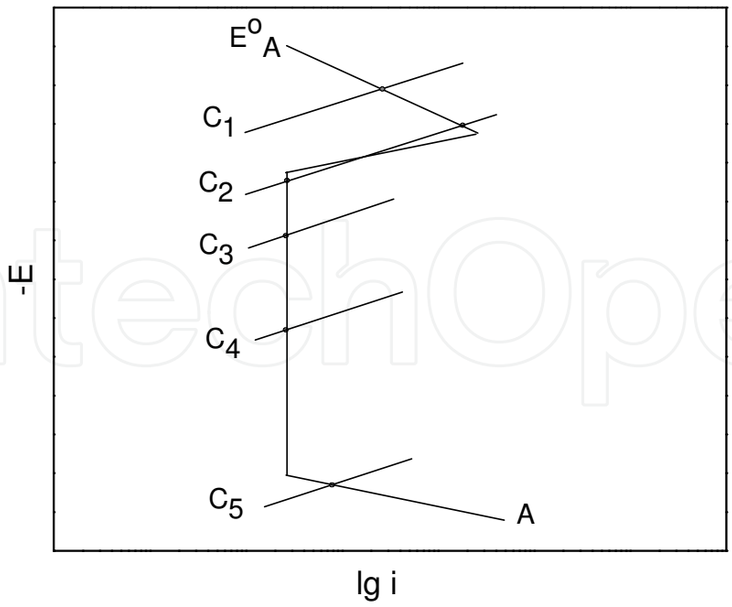


Fig. 2. Schematic polarization diagram illustraiting the influence of the effective cathodic coating on the steel corrosion, respective cathodic curves : c_1, c_2, c_3, c_4, c_5 in case of increasing the surface concentration of cerium oxides.

become commensurable with that of the pure steel. At concentration of the cerium oxides, corresponding to the cathodic curve C_2 it is possible to establish two corrosion potentials of the steel, located respectively in the passive and active regions of dissolution of the anodic potentiodynamic curve. At the higher concentrations of the cerium oxides, represented in the corrosion diagram by means of the respective cathodic potentiodynamic curves of the system cerium oxides/steel - C_3 and C_4, the steel is characterized by a stable passive state and under these conditions the rate of corrosion of the steel is no longer dependent on the surface concentration of the cerium oxides. The influence of the further increase in the concentration of the cerium oxides can be illustrated through the corrosion diagram by means of the cathodic curve C_5 – the rate of steel corrosion will grow up due to the fact that the stationary corrosion potential of the steel will be shifted to the region of transpassivity (Tomashov & Chernova, 1963; 1993). The experimental results, obtained by us, confirm these theoretical concepts.

4. Experimental results and discussion

4.1 Potentiodynamic polarization studies

Figure 3 shows a typical experimentally obtained corrosion diagram E-lg i, illustrating the kinetics of the cathodic and anodic processes on the studied steel in the absence of electrochemically deposited cerium oxides film (the curves 2) and after the deposition of thin oxide films with different surface concentrations of Ce (curves 3-5).

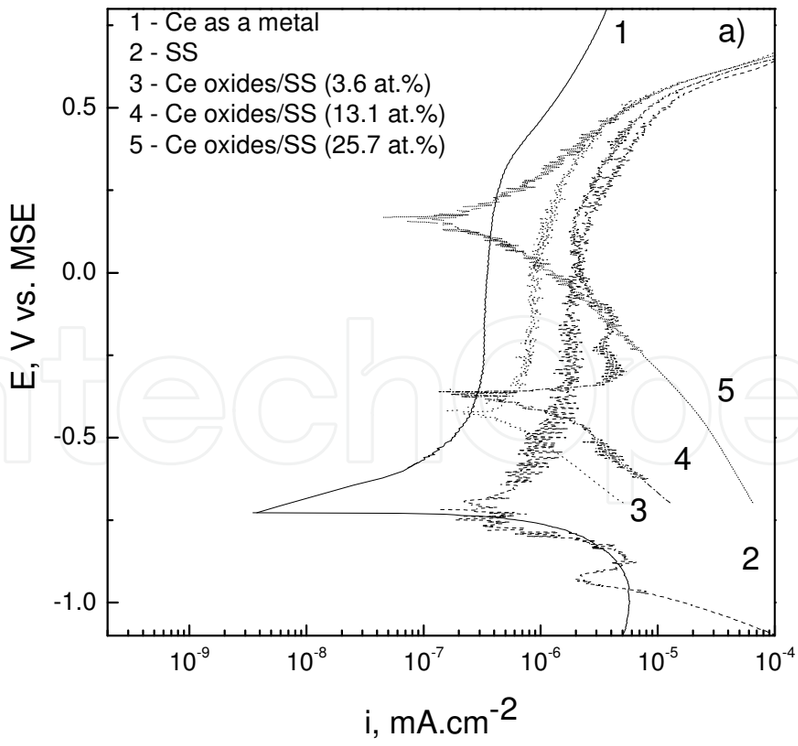


Fig. 3a. Potentiodynamic E–lgi curves for Ce (1), for SS (2) and for the systems CeO_2-Ce_2O_3/SS containing different concentrations of Ce (3-5), obtained in 0.1 N H_2SO_4.

The plotting of the model polarization curves enabled us to follow the changes in E_{corr} , estimated on the basis of the cross-point of the anodic polarization curve of the studied steel (SS) with the cathodic polarization curves of the studied systems, having different surface concentrations of Ce (ranging from 4% up to 30%). Such an approach of considering the partial polarization curves allows us to make the connection between the occurring anodic and cathodic corrosion processes, localizing the cathodic reaction on the rich in cerium zones on the electrode surface. For the sake of comparison the figure represents also the anodic and cathodic potentiodynamic curves of the metallic Ce (curves1). It follows from Fig. 3a that with the increase in the surface concentration of Ce (curves 3-5) the values of the corrosion potential E_{corr} are shifted strongly in the positive direction - from ~ –0.900V (for the non-coated with cerium oxides steel) up to ~ + 0.160 V. Obviously for the non-coated with CeO_2-Ce_2O_3 steel surface the cathodic depolarizing reaction, occurring at voltage ~ –0.900V, is connected with the evolution of hydrogen. As far as the respective cathodic branches of the potentiodynamic curves of the system Ce_2O_3-CeO_2/ SS are concerned, they are also shifted strongly in positive direction in the zone of passivity of the investigated steel.

The slope of the cathodic Taffel's curves grows up considerably from 0.250V up to 0.319 V with the increase in the surface concentration of cerium (Table 1). The change in the slope of these curves confirms the supposition about the occurring of another cathodic reaction, different from that of hydrogen evolution on the heterogeneous electrode surface.

SS				
Samples	**E_{corr}, V**	**i_{corr}, mA.cm^{-2}**	**$i_{c.p,}$ mA.cm^{-2}**	**b, V**
SS non-covered with cerium oxides	-0.890	2.24 x 10^{-7}	1.89 x 10^{-6}	0.107
SS covered with 3.6 at. % cerium oxides	- 0.432	2.85 x 10^{-7}	9.10 x 10^{-7}	0.250
SS covered with 13.1 at. % cerium oxides	- 0.371	2.93 x 10^{-7}	3.63 x 10^{-6}	0.276
SS covered with 25.7 at. % cerium oxides	+0.161	1.36 x 10^{-7}	-	0.319
	$SS_{t.t.}$			
Samples	**E_{corr}, V**	**i_{corr}, mA.cm^{-2}**	**$i_{c.p.}$, mA.cm^{-2}**	**b, V**
SS non-covered with cerium oxides	- 0.975	1.74 x 10^{-7}	3.21 x 10^{-6}	0.074
SS covered with 4.2 at. % cerium oxides	- 0.486	7.96 x 10^{-7}	2.96 x 10^{-6}	0.151
SS covered with 20.7 at. % cerium oxides	- 0.269	7.98 x 10^{-8}	1.33 x 10^{-6}	0.176
SS covered with 29.6 at. % cerium oxides	+ 0.090	8.19 x 10^{-7}	-	0.304

Table 1. Electrochemical characteristics of coated steel before and after thermal treatment compared to bare steel.

The strong shifting of E_{corr} of the steel surface, covered with cerium oxides in the positive direction depending on the surface concentration of cerium could also be associated with the occurrence of another cathodic process. The values of the corrosion potential in the presence of Ce are more positive than the Flade potential and more negative than the potential of transpassivity of the steel under consideration. Therefore we can conclude that even at surface concentration of Ce about 4% the corrosion potential of the steel is shifted in positive direction reaching potentials more positive than the potential of complete passivation. The improvement of the corrosion stability of the steel as a result of the action of the effective cathodic coating is expressed in the stabilization of the passive state of the steel. One can conclude from Figure 3a that the steel samples with electrochemically deposited cerium oxide film will corrode under the conditions of passivity. Thereupon with the increase in the surface concentration of Ce from 0 up to 3.6 at % a tendency is observed – a decrease in the currents of complete passivation ($i_{c.p.}$,see Table 1). At 13.1%concentration of the cerium oxides the current of complete passivation is of the same order with that of the non-covered steel, while at 25,7% concentration as a result of the strong shifting of E_{corr} in positive direction and its approaching the values within the zone of potentials of pitting formation and transpassivity the anodic potentiodynamic curve is not characterized by a well expressed region of passivity. The change in the currents of complete passivation depends to a considerable extent on the composition of the passive film on the steel. Therefore for the system Ce_2O_3-CeO_2/SS we can assume that it will pass over spontaneously into a stable passive state and that it will be dissolved at a much lower rate of corrosion, corresponding to the values of the anodic currents in the passive state (Fig. 3a).

If in one way or another the system is artificially taken out of its state of passivity (for example by means of cathodic polarization or by some mechanical impact), after discontinuing the external impact, it will restore again its passive state, i.e. what we obtain is a spontaneously self-passivating system.

A similar effect, expressed to an even greater extent, is also observed with the samples of thermally treated system Ce_2O_3-CeO_2/$SS_{t.t}$ (Fig. 3b), in which case it was established that as a result of disruption of the integrity of the oxide film the passive state of the steel is disturbed (Guergova et al., 2008) and conditions are created to increase the rates of the total and the local corrosion. The presence of electrochemically deposited cerium oxide film (in a way analogous to that for the samples of non-treated thermally system Ce_2O_3-CeO_2/SS) shifts strongly the corrosion potential of the system in positive direction (see curves 3–5). This effect determines the restoration of the passive state of the steel, disturbed as a result of its thermal treatment. Upon increasing the surface concentration of the cerium one can observe not only shifting of the corrosion potential of the samples in the positive direction, but also a tendency of decrease in the currents of complete passivation. An exception in this respect is observed at very high concentrations of the cerium oxides (≥ ~29%). Obviously in these cases the corrosion potential of the system CeO_2-Ce_2O_3/$SS_{t.t}$, which is still in the process of being established, starts approaching the value of the reversible redox potential of the couple Ce^{4+}/Ce^{3+}, whereupon the reaction of oxidation of Ce^3 to Ce^{4+} is taking place. As a result of this the character of the anodic curve will be changed (Fig. 3b, curve 5) and the determination of the current of complete passivation of the steel based on this curve would be incorrect.

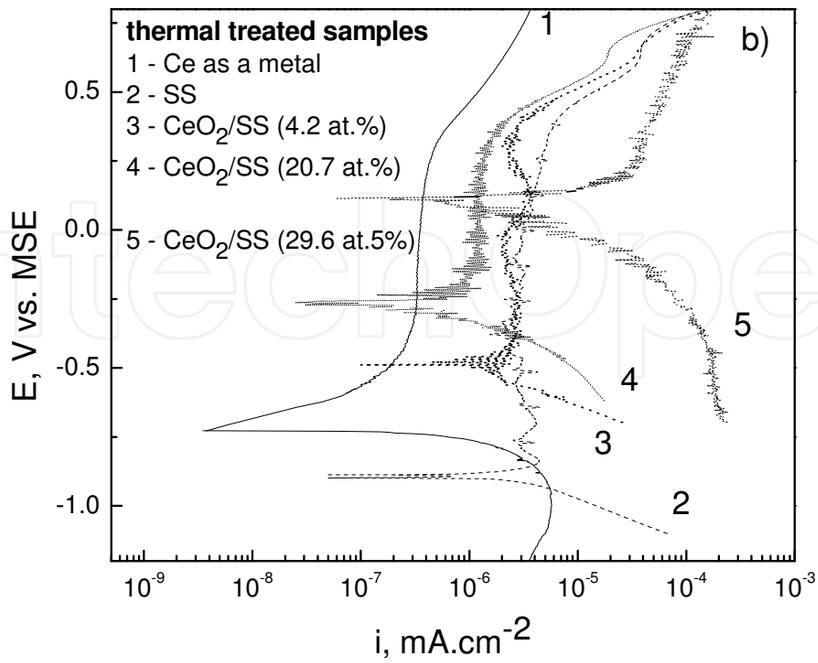


Fig. 3b. Potentiodynamic E–lgi curves for Ce(1), for $SS_{t.t.}$ (2) and for the systems CeO_2-$Ce_2O_3/SS_{t.t.}$ containing different concentrations of Ce (3-5), obtained in 0.1 N H_2SO_4.

4.2 Chronopotentiometric investigation

Fig. 4a and 4b illustrate the altering of the stationary corrosion potentials in the case of open circuit (open circuit potentials) with the SS and $SS_{t.t.}$ samples and with the systems Ce_2O_3-CeO_2/SS and Ce_2O_3-$CeO_2/SS_{t.t.}$ The juxtaposition of the values of the stationary corrosion potentials with the anodic potentiodynamic curves of SS and $SS_{t.t.}$ shows that in the presence of cerium oxide film on the surface of the steel one can observe a strongly manifested tendency to self-assivation. In the cases of non-thermally treated steel its high corrosion resistance and its ability to passivate itself is connected also with the high content of Cr, while the role of the cerium oxides is reduced to promoting the passivation ability and stabilization of its passive state in weakly acidic medium (Stoyanova et al, 2006). In the case of thermally treated steel, however, due to the cracking of the surface passive film, as a result of the thermal treatment its stationary corrosion potential reaches values ($E_{st.}$= -0.975V), characteristic of the corrosion in the active state (Fig. 4b). The disrupted passive state is also a prerequisite for the development of local corrosion in the active anodic sections – pitting and/or inter-crystalline, which is characteristic for this type of steel. It is also seen in Fig. 4b that the electrochemically formed cerium oxide films on the surface of the steel samples lead to strong shifting of the stationary corrosion potential of the steel in the positive direction – to potentials more positive than the potential of complete passivation and more negative than the potential of transpassivity. The established experimental facts unanimously indicate that the electrochemically deposited oxide films on the surface of the steel lead to restoration of its passive state, due to promoted ability of the system to passivate itself under the conditions of the real corrosion process.

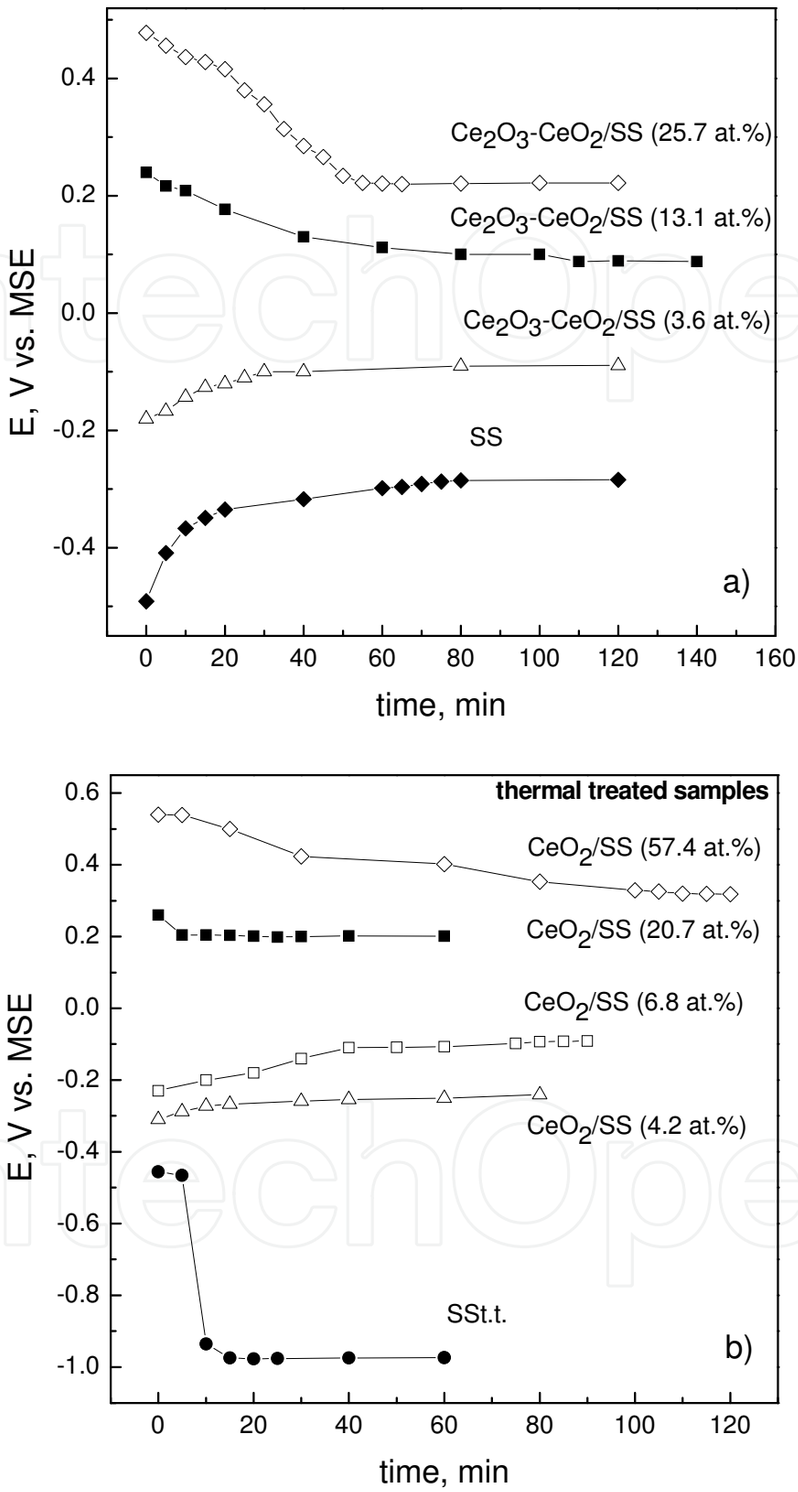


Fig. 4. Open circuit potential vs. time curves for SS (a) and $SS_{t.t.}$(b), as well as for the systems CeO_2-Ce_2O_3/SS (a) and CeO_2-Ce_2O_3/$SS_{t.t.}$(b), containing different concentrations of Ce, obtained in 0.1 N H_2SO_4.

The strong shifting of E_{corr} of the steel sample, modified with cerium oxide film, in the positive direction, depending on the surface concentration of cerium, can be attributed to the occurrence of another cathodic process in addition to the reaction of hydrogen evolution. We can assume that the effective cathodic sections of CeO_2-Ce_2O_3 will participate in the occurring cathodic depolarizing reaction according to the equations (1 and 2) given below:

$$CeO_2 + 2H^+ = Ce(OH)_2^{2+} \quad (1)$$

$$2Ce(OH)_2^{2+} + 2e^- = Ce_2O_3 + H_2O + 2H^+ \quad (2)$$

The above indicated reactions occur as a result of the extraordinary oxidation-reduction capability of the couple CeO_2-Ce_2O_3. The occurring of these reactions means that in the course of the corrosion process the surface film will be changing, enriching itself in Ce_2O_3. On the other side, the reactions (3) and (4) will also take place on the anodic sections of the steel surface and the latter one will lead to passivation:

$$Me \rightarrow Me^{n+} + ne \quad (3)$$

$$Me + H_2O \rightarrow Me_2O_n + ne \quad (4)$$

Taking into account the fact that the oxides of Ce^{3+} of the type Ce_2O_3 are soluble in acids, the reaction reported in (Achmetov, 1988) will also occur:

$$Ce_2O_3 + 6H^+ = 2Ce^{3+} + 3H_2O \quad (5)$$

As well as the respective conjugated reaction of oxidation:

$$Ce^{3+} + 2H_2O = Ce(OH)_2^{2+} + 2H^+ + e^- \quad (6)$$

Obviously, the cathodic reaction of reduction of CeO_2, which occurs at the corrosion potentials, established for the systems CeO_2-Ce_2O_3/$SS_{t.t.}$, is the main reason for restoring and preserving the passive state of the thermally treated steel samples (in accordance with equation 4) during their corrosion in solutions of sulfuric acid.

4.3 The inhibiting effect of cerium ions

In connection with the above statements a next step has been made in the investigations, namely studying the influence of the Ce^{3+} and Ce^{4+} ions as components of the corrosion medium (0.1N H_2SO_4) on the anodic behavior of stainless steel. These investigations were provoked by the observed occurrence of cathodic depolarization reaction of Ce^{4+} (CeO_2) reduction, as a result of which the surface concentration of cerium is decreasing and theoretically it should approach zero value (Stoyanova et al., 2010). For this purpose an inverse experiment was carried out at different concentrations of Ce^{4+} ions in the corrosion medium we monitored the changes in the stationary corrosion potential of the thermally treated steel by the chronopotentiometric method. The aim of this experiment was to prove the occurrence of a reversible reaction of reduction of Ce^{4+}: $Ce^{4+} - e \leftrightarrow Ce^{3+}$, (instead of the reaction of hydrogen depolarization), which in its turn creates also the option to form a film (chemically insoluble) of cerium hydroxides/oxides on the active sections of the steel surface.

Figure 5 illustrates the analogous E-τ dependences at open circuit, obtained upon immersion of SS_{tt} in 0.1 N H_2SO_4 solution, to which various concentrations of Ce^{4+} ions have been added. It was important to find out what is the influence of cerium ions on the corrosion behavior of the samples of thermally treated steel, when the character of the corrosion process is changed as a consequence of the thermal treatment of the steel. It should be reminded at this point that the stationary corrosion potentials (E_{st}) of SS and $SS_{t.t.}$in 0.1N H_2SO_4 solution have values for the non-thermally treated steel E_{st}= ~ -0.300 V, while for the thermally treated steel this value is E_{st}= ~ -0.980 V (Fig. 4)). The registered negative values of E_{st} in the absence of cerium ions for the $SS_{t.t.}$ samples, in our opinion, are connected with the strong cracking of the natural passive film on the surface of SS (Fig. 6). The most probable reason for this loss of the "stainless character" of the steel surface are the revealed sections, determining a several times higher concentration of iron-containing agglomerates in the surface layer (Table 2).

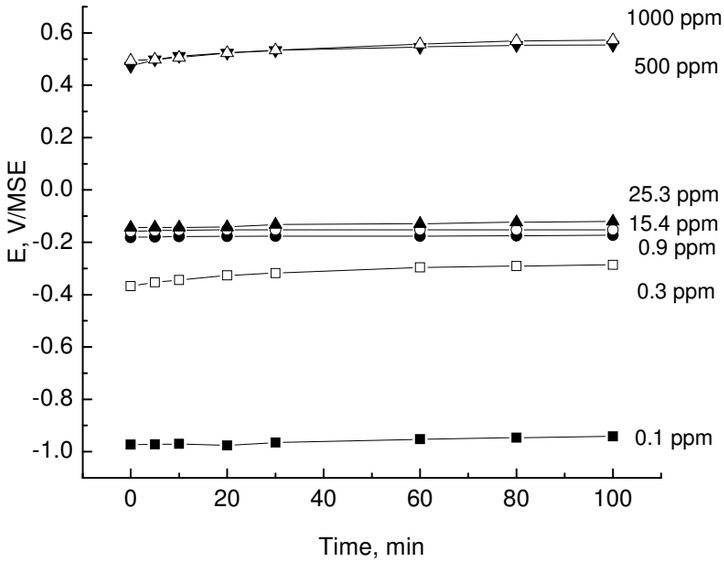


Fig. 5. Evolution of the open-circuit potential for $SS_{t.t.}$ at different concentrations of Ce^{4+} in 0.1 N H_2SO_4 solution.

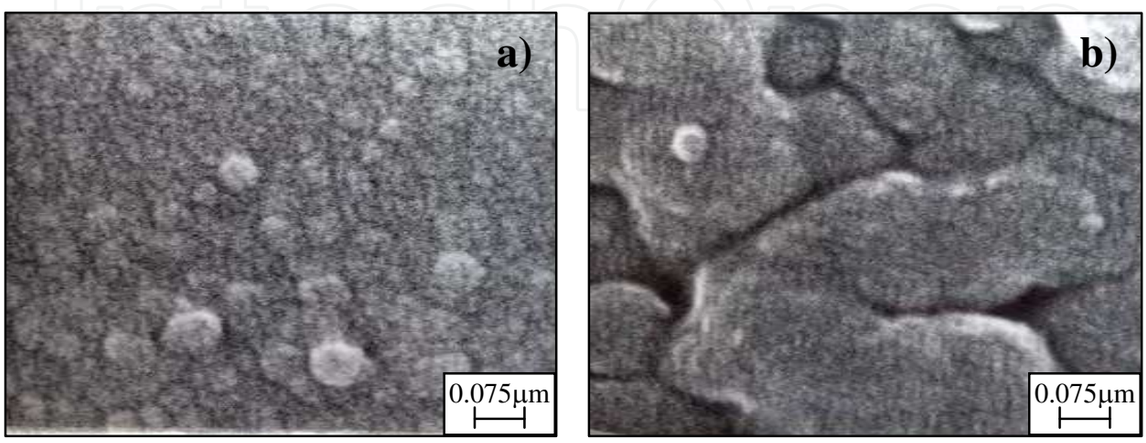


Fig. 6. SEM images of stainless steel before (a) and after thermally treatment (b).

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 50h in 0.1N H_2SO_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	_
$SS_{t.t.}$ 50h in 0.1N H_2SO_4	65.4	9.1	12.2	13.3	-	1.34	1.46	1.09	-0.300

Table 2. Distribution of the elements (in at. %) on the surface SS and $SS_{t.t.}$ before and after 50h immersion in 0.1N H_2SO_4.

For this reason this cycle of investigations has been carried out using samples of thermally treated steel, since the thermal treatment leads to change in the character of the corrosion process of steel. It should be taken into account that such kind of excessive heat treatment happen to take place both in the formation of catalytic converters, as well as in the course of their operation. In the latter case in the presence of cerium ions in the corrosion medium (Fig. 5), one observes a strong shifting of E_{st} in positive direction (from -0.942 V to -0.286 V), even at relatively low concentrations of Ce^{4+} (0.3 ppm) in the corrosion medium. The further increase in the concentration of Ce^{4+} ions (from 0.3 to 0.9 ppm) results in insignificant changes in E_{st} . Thereupon for SS_{tt} this shift jumps from -0.942 V (at Ce^{4+} ions concentration 0.1 ppm) up to -0.175 V (at Ce^{4+} ions concentration ~ 0.9 ppm). In the consecutive 20 – 30 fold increase in the concentration of Ce^{4+} ions (15-25 ppm) a preservation of the E_{st} value is observed, whereupon it manifests values ~ -0.150 - -0.120 V. The consecutive 20-50 fold increase in the concentration of Ce^{4+} ions (500-1000 ppm) leads to strong shifting of E_{st} in positive direction reaching values of about +0.510 - +0.570V.

These results prove that in the case of samples of thermally treated steel non-coated with Ce_2O_3-CeO_2 one observes analogous changes in the stationary corrosion potential of the steel electrode, which have already been registered for the system Ce_2O_3-CeO_2/$SS_{t.t.}$. The juxtaposition of the above-mentioned changes in E_{st} at open circuit (conditions of self-dissolution) with the characteristic zones (corrosion potential, Flade potential, zone of passivity, transpassivity region), defined by the cathodic and anodic potentiodynamic E-lgi polarization curves (conditions of external cathodic and anodic polarization) for SS_{tt} (Fig. 7.) in 0.1 N H_2SO_4 solution not-containing Ce^{4+}, shows the following. The addition of cerium ions causes shifting and establishing stationary corrosion potential (Fig. 7) in the zone of passivity of the steel. Evidently, this effect will lead also to improvement of the passivation ability, respectively to improvement of the stability to corrosion, of the steel in sulfuric acid medium, which is of great importance for the specific case of thermally treated steel, when the inhibitory action of the Ce^{4+} ions eliminates the negative influence of the cracking of the natural passive film on the steel.

The recovery of the passive state of SS_{tt}, characterized by disrupted passive film, in our opinion, is brought about also by some other reasons. It is caused by the flow of internal cathodic current (instead of external anodic current), which is determined by the occurring

of a reduction reaction $Ce^{4+} \leftrightarrow Ce^{3+}$ in the redox system Ce^{4+}/ Ce^{3+}. Therefore the Ce^{4+} ions, as component of the corrosion medium, are acting as inhibitor, exerting an oxidative effect. It follows from (Fig. 7), that the increase in the concentration of the inhibitor in the corrosion environment leads to a substantial decrease in the corrosion current - from 1.10^{-6} (at inhibitor concentration of 0.1 ppm) - to $1. 10^{-8}$ A.cm^{-2} (at inhibitor concentration ~0.9 ppm). What is making impression is the fact that the further increase in the concentration of the Ce^{4+} ions in the corrosion medium from ~0.9 ppm (which could be accepted as "critical") up to 1000 ppm influences to a smaller extent the rate of corrosion. It is necessary also to point out that with the increase in the concentration of cerium ions the corrosion potential is shifted in positive direction, whereupon its values remain more positive than the potential of complete passivation and more negative than the potential of depassivation of the steel within the entire interval of studied concentrations – an effect analogous to the one already established for the systems Ce_2O_3-CeO_2/$SS_{t.t.}$in 0.1 N H_2SO_4 solution.

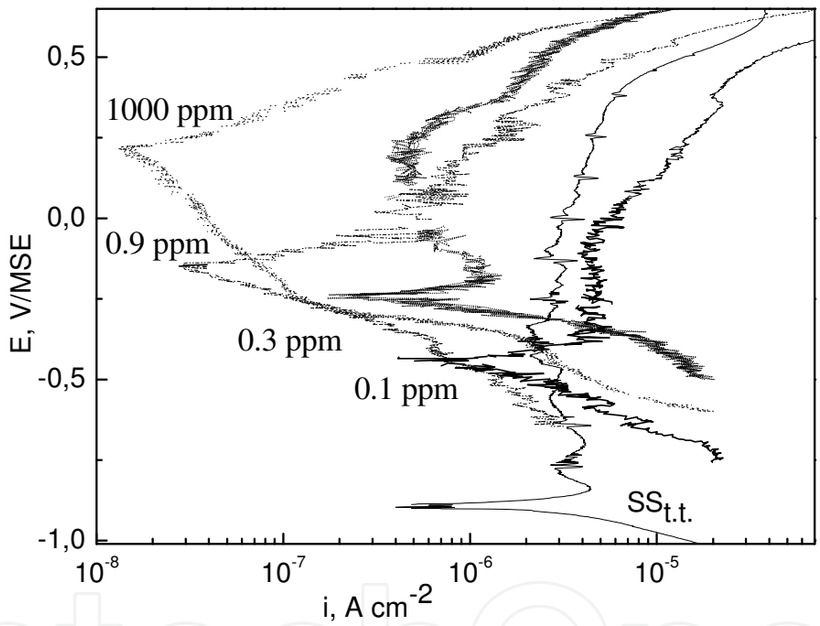


Fig. 7. Potentiodynamic E-lgi curves of $SS_{t.t.}$ at different concentrations of Ce^{4+} in 0.1 N H_2SO_4 solution.

Table 3 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:

$$Z\% = (i^{o}_{corr.} - i_{corr.}) / i^{o}_{corr.} \times 100 \quad (7)$$

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

Samples	E, V	i_{corr}, A m^{-2}	Z, %
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

Table 3. Electrochemical parameters characterizing corrosion behaviour of $SS_{t.t.}$.

It is seen from the table that upon increasing the concentration of Ce^{4+} ions in the corrosion medium the degree of protection reaches values up to 99% for the samples of thermally treated steel. The obtained data about the promotion 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 3) supposes an interconnection between the inhibitor concentration and the degree of surface coverage, Q following the equation (8):

$$Q = (i^{o}_{corr} - i_{corr})/\ i^{o}_{corr} \tag{8}$$

where i^{o}_{corr} 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:

$$Q = KC.(1+KC), \text{ and respectively:} \tag{9}$$

$$C/Q = 1/K + C \tag{10}$$

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. 8. 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.

The constant K in the equation (9) is connected with the standard free energy of adsorption (Δ G) in accordance with the equation:

$$K = (1/55.5) \exp (-\Delta DG\ ^{o}_{ads} / RT) \tag{11}$$

The value of K, determined graphically based on the plot of the dependence C/Q as a function of C, is $44{,}6 \times 10^{6} M^{-1}$, while the value of ($-\Delta G^{o}_{ads}$) amounts to 10.35 κ call.mol^{-1}.The relatively low value of ΔG^{o}_{ads}, is indicative of electrostatic forces of interaction between the ions of the inhibitor and the steel surface. Or in other words the interaction of the inhibitor with the surface of the thermally treated steel has physical nature. On the basis of the obtained electrochemical corrosion data from the potentiodynamic curves in the presence

and in the absence of inhibitor and judging from the measurements of the stationary corrosion potential of the steel, depending on the concentration of the inhibitor at open circuit we could suppose that under the conditions of internal anodic polarization in the presence of inhibitor the nature of the passive layers remains the same as in the case of external anodic polarization. As far as we can judge the specific action of the inhibitor is manifested in the formation of an adsorption layer, which is transformed into bulk phase, on the active anodic sections of the surface of the metal. In view of the XPS analyses (Guergova, 2011) after 500-hour interval of staying of the thermally treated steel in the aggressive medium in the presence of Ce^{4+} ions (25 ppm), on the surface of the studied film in the region of the Ce3d XPS band one can observe the appearance of a certain amount of cerium (1.5 at. %) in the form of Ce_2O_3. The cerium is most probably incorporated into the surface film as a result of the stay of the steel sample in the inhibited corrosion medium, which leads to its modifying as a consequence of the formation of mixed oxides of the type of cerium aluminates and chromates (Burroughs et al., 1976; Hoang et al., 1993). In support of such hypotheses comes the absence of visible corrosion damages on the surface of $SS_{t.t.}$ exposed for 500 h in 0.1N H_2SO_4 solution in the presence of Ce^{4+} ions (Fig. 9). 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 proceeding of reduction of Ce^{4+} into Ce^{3+}. In order to investigate the kinetics of reduction of the Ce^{4+} ions to Ce^{3+}, in the region of potentials, characteristic of the passive state of the steel under consideration, we plotted the anodic and the cathodic potentiodynamic curves, characterizing the behavior of the oxidative-reductive couple Ce^{4+}/Ce^{3+} at various concentrations of Ce^{4+} in 0.1 N H_2SO_4 solution, on an inert support of platinum (Fig. 10). Such an approach (Tomashov & Chernova, 1965), to our mind, enables the complete elucidation of the mechanism of inhibitory action of the cerium ions. It allows direct juxtaposition of the changes in the values of the corrosion potentials (respectively the corrosion currents) of the steel in their presence with the values of the reversible redox potentials (respectively the exchange currents) of the couple Ce^{4+}/ Ce^{3+} at comparable concentration levels.

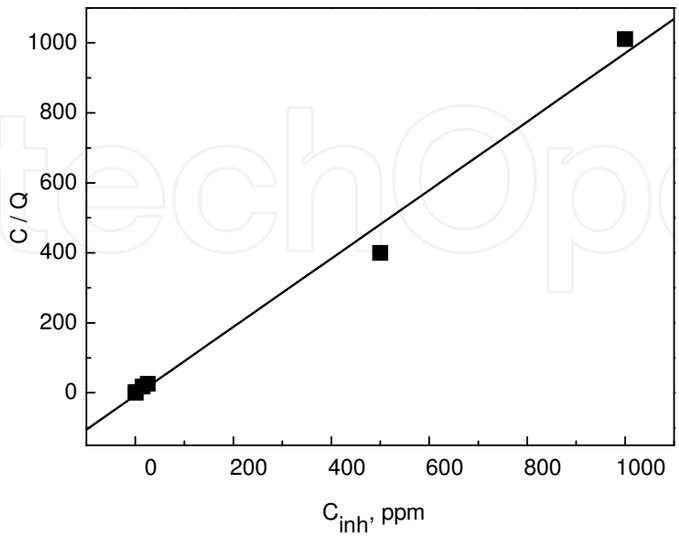


Fig. 8. Langmuir adsorption plots for $SS_{t.t.}$ in 0.1 N H_2SO_4 solution at different concentrations of Ce^{4+} ions.

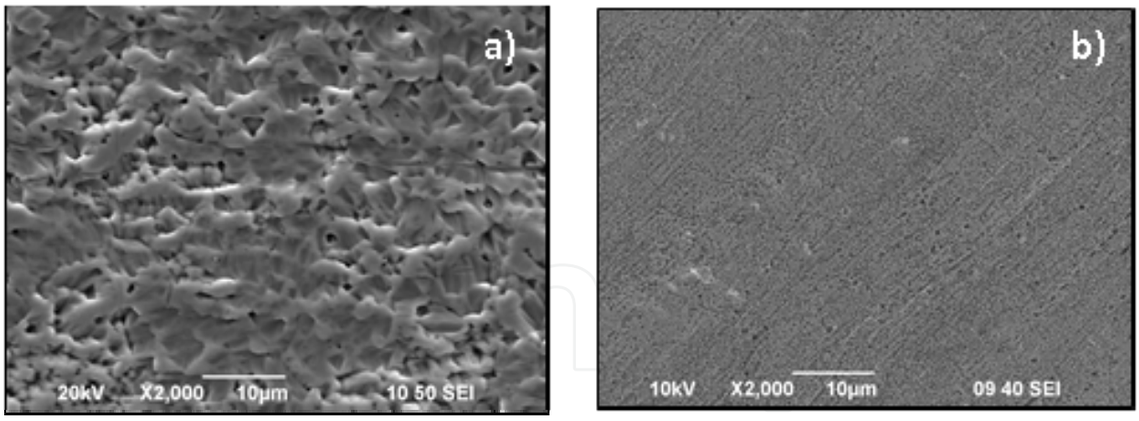


Fig. 9. SEM images on thermally treated stainless steel after 500 h immersion in 0.1 N H_2SO_4 without Ce^{4+}(a) and in the same media with 25 ppm Ce^{4+} (b).

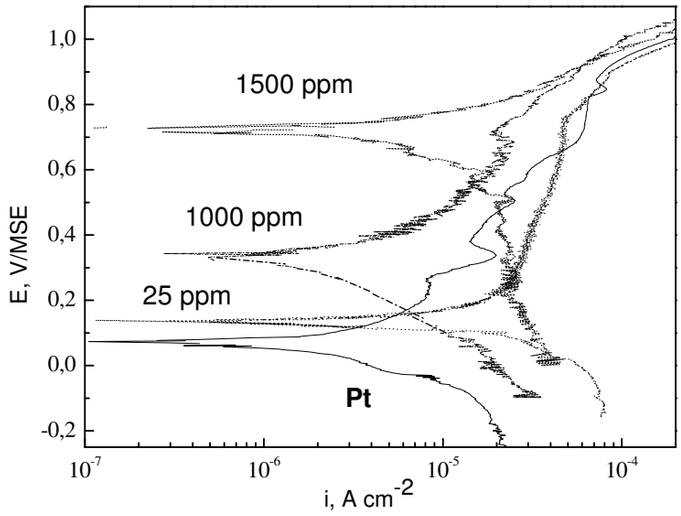


Fig. 10. Potentiodynamic E-lgi curves of Pt at different concentrations of Ce^{4+} in 0.1 N H_2SO_4 solution.

The comparison of the obtained results gives evidence that with the increase in the concentration of the cerium ions in 0.1 N H_2SO_4 solution the equilibrium oxidation-reduction potential of the system Ce^{4+}/ Ce^{3+} is shifted in positive direction (Fig.10 and Table 4), in correspondence with the equation of Nernst, whereupon at all the studied concentrations it is located in the zone of potentials, characteristic of the passive state of steel (Fig. 7). 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 juxtaposition of the corrosion currents for the steel in the presence of cerium ions with the exchange currents for the system Ce^{4+}/Ce^{3+}on Pt, at comparable concentration levels of the cerium ions, shows that they have quite close values.

The so obtained data give us the reason to classify the studied oxidation-reduction couple as an inhibitor having an oxidative effect, which does not influence directly the kinetics of the anodic process. Its action is expressed in its participation in the depolarizing reaction of the

corrosion process (i.e. oxidative depolarization), respectively in the establishment of oxidative-reductive potential of the medium more positive than the potential of complete passivation of the steel. This effect, in its turn, defines the value of the stationary corrosion potential of the steel to be more positive than the potential of complete passivation.

Samples	E_o, V	i_o, A cm^{-2}
Pt metal	0.070	2.17 x 10^{-7}
Pt with 0.3 ppm	0.107	8.99 x 10^{-6}
Pt with 25 ppm	0.135	6.35 x 10^{-7}
Pt with 1000 ppm	0.331	6.08 x 10^{-7}
Pt with 1500 ppm	0.722	7.67 x 10^{-7}

Table 4. Reversible redox potentials E_o, and equilibrium currents io, of the system Ce^{4+} /Ce^{3+} on Pt at different concentrations of the Ce^{4+} in the corrosion medium.

In order to prove the integral nature of cerium oxides films as efficient cathodic coating, involved directly in the corrosion process and the role of cerium ions as inhibitors possessing oxidative effect, participating also directly in the corrosion process and leading to the formation of phase layer of cerium oxides on the active cathodic sections of the steel surface, we compared the dependences E-lgi for the systems Ce_2O_3-CeO_2/$SS_{t.t.}$ as well as for the system Ce^{4+}/Ce^{3+}/Pt. – Fig. 11. It is seen in Fig. 11 that the corrosion currents of the systems Ce_2O_3-CeO_2/$SS_{t.t.}$are close in value to the exchange current of the oxidation-reduction current of the couple Ce^{4+}/Ce^{3+} on Pt. The differences between the corrosion potential of the systems Ce_2O_3-CeO_2/$SS_{t.t}$ and of the equilibrium oxidation-reduction potential of the couple Ce^{4+}/Ce^{3+} can be explained by the discrepancies in the surface and bulk phase concentrations of the components.

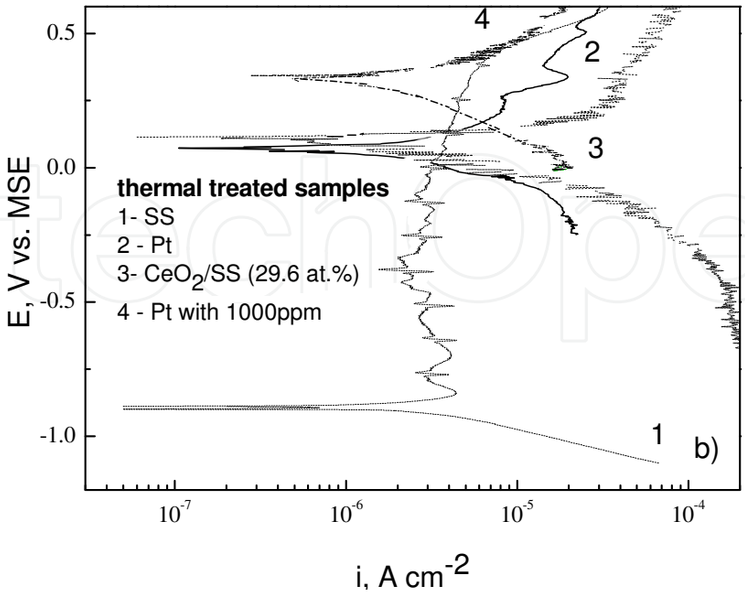


Fig. 11. Potentiodynamic E–lgi curves for $SS_{t.t}$ (1)., for Pt (2) and for the systems CeO_2-Ce_2O_3/Pt (3); Ce^{4+}/Ce^{3+}/Pt (4); obtained in 0.1 N H_2SO_4 solution.

4.4 XPS and SEM results

In confirmation of these results and the conclusions come also the data of the XPS analyses of the samples, having electrochemically deposited cerium oxide films, characterizing the changes in the chemical state and in the composition of the surface film, depending on the time interval of the immersion stay of the samples in $0.1NH_2SO_4$ solution (Stoyanova et al., 2010). Table 5 represents the results for the sample with surface concentration of electrochemically deposited cerium oxide layer 45.1 at.% .It is seen that after 1000 hours of exposure to the corrosion medium the surface concentration of cerium is decreased from 45.1ат.% down to 0.2 at.%. This result is convincing evidence for the occurring of depolarizing reaction involving the participation of the rich in CeO_2 sections of the surface, acting as effective cathodes, in accordance with the equations (1-4). It becomes evident that the presence of cerium oxide film determines the establishment of more positive stationary corrosion potential of the system, due to the proceeding of the reactions 1- 6, the surface passive film will become modified, whereupon its composition, respectively the ratio Cr/Fe, will become different.

Time of exposure, h	E_{st}, V	C, at. %	O, at. %	Al, at. %	Fe, at. %	Cr, at. %	Ce, at. %
as deposited	0.151	15.6	37.6	1.0	0.1	0.6	45.1
18	0.169	50.1	35.7	1.6	0.5	0.4	11.7
200	0.249	64.4	31.5	0	0	0	4.1
250	0.236	63.7	31.5	0	0	0.2	4.6
400	0.239	68.5	27.4	0	0	0	4.1
1000	0.060	31.4	42.9	19.9	0.7	4.9	0.2

Table 5. Concentration of the elements (in at. %) on the surface layers of the system CeO_2-Ce_2O_3/SS after thermal treatment and after corrosion test in 0.1 N H_2SO_4.

In this cycle of experimental runs, using the XPS method, the changes were monitored, occurring in the chemical composition of the passive film of the system CeO_x /SS, during prolonged exposure of the samples in 0.1 N H_2SO_4 solutions (Table 5). The analyses were carried out after the 18th, 200 th, 250 th , 400 th , and 1000 th hour - time intervals of exposure. Within the interval 200-400 hours E_{st} remains practically the same, while after 1000 hours of exposure it is shifted strongly in the negative direction, reaching a value of about ~ +0.060 V. To obtain further information about the influence of ceria on the corrosion behaviour of as-deposited sample we analyzed in depth the Ce3d and O1s XPS spectra. As it has already been discussed in our previous papers (Nikolova et al., 2006; Stoyanova et al, 2006), the Ce3d spectrum is a complex one, due to the fact that the peak is spin-orbital split into a doublet, each doublet showing extra structure due to the effect of the final state. There are 8 peaks assignments in the spectra labelled according to Burroughs (Burroughs et al., 1976), where the peaks V, V^{II}, V^{III} and U, U^{II}, U^{III} refer to the 3d5/2 and 3d3/2 respectively and they are characteristic of Ce(IV) 3d final states. The peaks labelled as V^{I} and U^{I} refer to 3d5/2 and 3d3/2 they are characteristic of Ce(III)3d final state (Fig.12).The literature data make it

obvious that the chemical state of Ce could be evaluated based on the percentage of the area of the u''' peak, located at 916.8 eV with respect to the total Ce3d area. So if the percentage of the u''' peak related to the total Ce3d area varies from 0 to 14%, then the Ce^{4+} percentage related to the total amount of Ce varies from 0 to 100%. In our case the u'''% amounts change as a result of dipping the as-deposited sample into 0.1 N H_2SO_4 solution, so we observed also change in the percentage of Ce^{4+} and Ce^{3+} on the surface (Table 6). The obtained O1s X-ray photoelectron spectra, recorded after different time intervals of exposure, are quite complicated. These spectra had to undergo de-convolution procedure to analyze the contribution of the separate components in them.

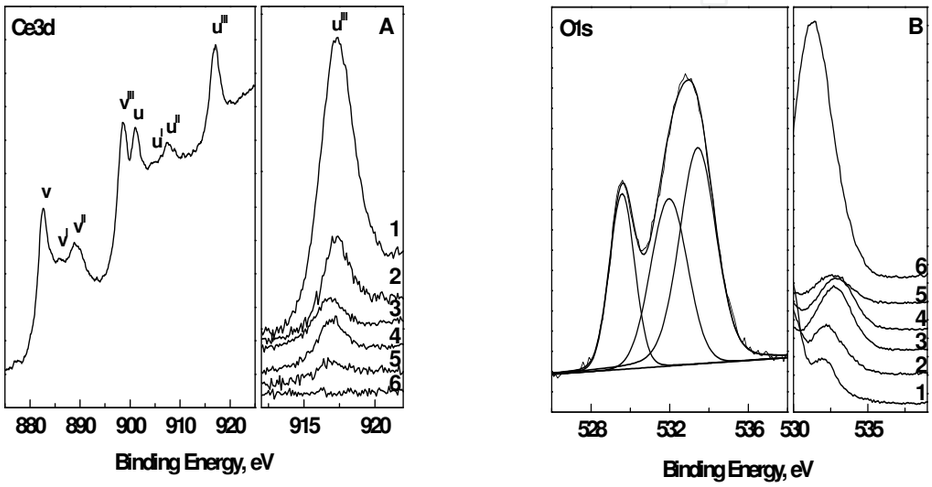


Fig. 12. Ce3d and O1s XPS spectra of CeO_2-Ce_2O_3/SS sample after 250 h exposition to 0.1 N H_2SO_4, Panel A and B correspond to high BE and high BE portion of Ce3d and O1s spectral regions taken at different step of corrosion test. (1) as-deposited; (2) after 18 h ; (3) after 200 h; (4) after 250 h; (5) after 400 h; (6) after 1000 h exposition to 0.1 N H_2SO_4 solution.

The chemical composition of the surface film of the CeO_2-Ce_2O_3/$SS_{t.t.}$ systems under consideration is shown in Table 5. It is important to note that on the surface of the 'as-deposited" samples, covered with cerium oxide film, we detected also the presence of iron, chromium and aluminum in addition to the cerium. The latter is mainly in the valence state Ce^{4+} i.e. in the form of CeO_2. After 18 hours of exposure to 0.1 N H_2SO_4 solution the chemical composition on the surface of the system has changed. The surface concentration of cerium drops down from 45.1 to 11.7 at. %, whereupon Ce^{3+} appears in the form of $Ce(OH)_3$ and Ce_2O_3. After continuing the exposure further (200-400 hours) one observes evolution of the spectra with respect to cerium and oxygen (Fig.12). The main peak in the spectrum of oxygen, having binding energy of about ~529.5 eV, is attributed to the presence of O^{2-} ions, which exist basically as Ce-O bonds in the crystal lattice of the cerium oxide being formed. The second peak, located at 531.7 eV, is associated with the existence of OH^- groups on the surface, while the presence of a peak at 533 eV shows that there is adsorbed water on the surface of the studied passive films (533 eV) (Hoang et al., 1993; Paparazzo, 1990). It can be seen in the spectra that after exposure of the samples in corrosion medium for 200-400 hours

the respectively detected high-energy peak in the spectrum of oxygen for these samples is growing up initially, while afterwards it decreases its intensity. This effect, in our opinion, is owing to consecutive enrichment and then impoverishment of the surface layer of the film in OH^- groups i.e. adsorbed water molecules (Fig.12, Table 6). The obtained results gives us the reason to draw the conclusion that the surface passive film under these conditions at this stage consists of CeO_2, Ce_2O_3, $Ce(OH)_4$ as well as $CeO(OH)_2$ and $Ce(OH)_3$, whose existence has been ascertained also by some other authors (Huang et al., 2008).

Time of exposure, h	O1s, eV	Percentage of oxygen contribution to the total	Bonds	Ce3d, eV	Percentage of Ce^{4+} to the total Ce
as deposited	529.2 531.4	59 41	Ce-O Ce-OH	883.0	100
18	529.2 531.5 533.2	43 42.5 14.5	Ce-O Ce-OH Others	882.9	85.35
200	529.4 531.9 533.3	21.4 33.6 45	Ce-O Ce-OH Others	882.4	76
250	529.5 531.9 533.4	23 32 45	Ce-O Ce-OH Others	882.5	76
400	529.5 532.1 533.4	23 45 32	Ce-O Ce-OH Others	882.5	76
1000	531.2	100	OH	882.0	-

Table 6. Calculated contribution of oxygen and percentage of Ce^{4+}, depending of the exposure time in 0.1 N H_2SO_4. Types of the chemical bonds and values of binding energy.

After 1000 hours of exposure the quantity of cerium is drastically decreased, as a consequence of the occurring reactions 1-4 and only some insignificant amounts of cerium have been registered in the valence state Ce^{3+}, i.e. in the form of Ce_2O_3. Only a single peak has been detected in the spectrum of oxygen, having a binding energy of 531,2 eV. Chromium, aluminum and iron have also been detected (Table 5). On the basis of the values of their binding energies (Table 5), including also the location of the O1s peak (Fig.12), we can also conclude that they exist in the form of oxides and hydroxides: Cr_2O_3, $Cr(OH)_3$, Fe_2O_3, FeOOH, Al_2O_3 and $Al(OH)_3$. The high concentration of carbon registered in the surface film is owing to the considerable amount of carbonates adsorbed during the thermal treatment in a high-temperature oven.

In support of the conclusions, drawn on the basis of the above results, evidence is also given by the direct SEM observations carried out. It follows from the electron microscopic studies of the samples, exposed to the corrosion medium, that the disruption of the passive state of steel at the initial stages (until the 50th hour) leads to appearance of local corrosion and its

propagation and spreading further to give total corrosion (Fig.13 a,b). For the sake of comparison Fig. 13 shows the same surface in the presence of cerium oxide coating after 50 hours of exposure to the corrosion medium. In this case no corrosion damages can be observed on the surface not only after the 50th hour, but even after 1000 hours of exposure (Fig.13) to the corrosion medium, as a result of its modifying, already discussed above.

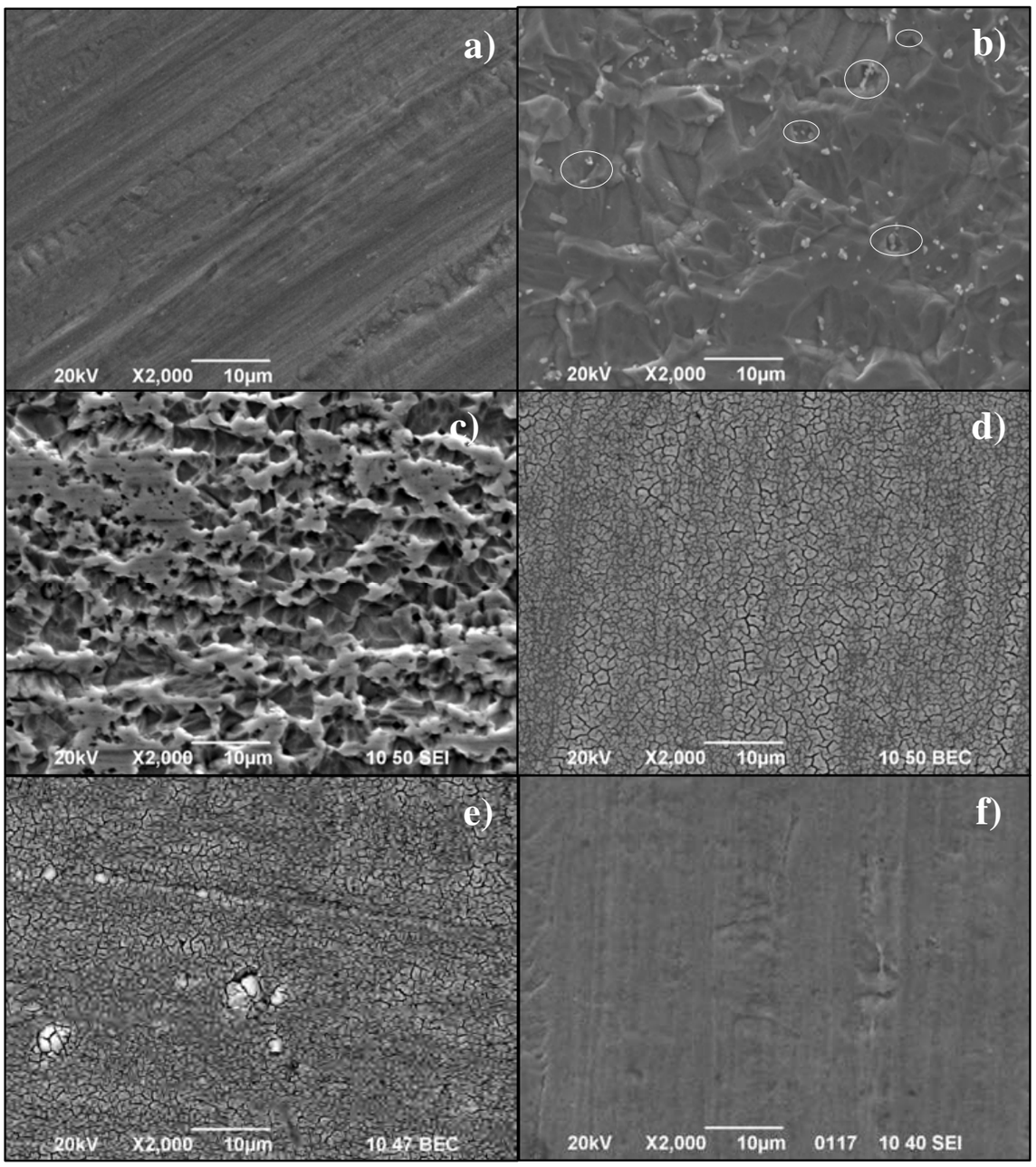


Fig. 13. SEM images for the samples: a) $SS_{t.t.}$; b) $SS_{t.t.}$ after 50 h exposition in 0.1 N H_2SO_4 (O – areas of local corrosion); c) $SS_{t.t.}$ after 1000 h exposition; d) CeO_2-$Ce_2O_3/SS_{t.t.}$; e) CeO_2-$Ce_2O_3/SS_{t.t.}$ after 50 h exposition in 0.1 N H_2SO_4; f) CeO_2-$Ce_2O_3/SS_{t.t.}$ after 1000 h exposition.

5. Conclusions

The above discussed results elucidate the mechanism of action of cerium oxide coatings as effective cathodes and of cerium ions (when they are present as a component of the corrosion medium) – as inhibitor having oxidative action, leading to improvement of the corrosion stability of stainless steels. They explain the improved ability of the steel to undergo passivation, respectively to recover its passive state in cases of disruption of its surface passive film – especially in this specific case, studied by us, i.e. disruption as a result of thermal treatment.

This effect is associated with a strong shifting of the stationary corrosion potential of the steel in positive direction, moving over from potentials, characteristic of corrosion in active state to potentials, located inside the zone of passivity. In this respect, another basic purpose of the investigations was the elucidation of the mechanism of action of the cerium oxides film and in particular collecting experimental evidence for the supposition about the occurring of an efficient depolarization reaction of CeO_2 reduction, resulting in a state of passivity, instead of hydrogen depolarization reaction. For this purpose we considered also the decrease in the surface concentration of Ce in the passive layer under the conditions of the actual corrosion process (self-dissolution) of the stainless steel, by means of XPS, EDS and ICP-AES analyses. A decrease in the surface concentration of CeO_2 (Ce^{4+}) has been observed, which is known to be chemically inert in acidic media. The obtained results prove the occurrence of an effective cathodic process of Ce^{4+} reduction into Ce^{3+} in the surface oxide film. These results elucidate in details the corrosion behavior of the system Ce_2O_3-CeO_2/steel in 0.1N H_2SO_4. They explain the improved ability of self-passivation, respectively the restoration of the passive state of the thermally treated steel in the presence of cerium oxides as components of the modified passive surface film.

It has also been shown that the couple Ce^{4+}/Ce^{3+}, as component (inhibitor) of the corrosion medium, displays analogous action. It is expressed in the occurrence of a reaction of reduction of the oxidative component of the medium - Ce^{4+}, leading to consumption of the electrons removed in the course of oxidation, respectively passivation, of the active anodic sections.

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The book has covered the state-of-the-art technologies, development, and research progress of corrosion studies in a wide range of research and application fields. The authors have contributed their chapters on corrosion characterization and corrosion resistance. The applications of corrosion resistance materials will also bring great values to reader's work at different fields. In addition to traditional corrosion study, the book also contains chapters dealing with energy, fuel cell, daily life materials, corrosion study in green materials, and in semiconductor industry.

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Slavka Krautzeka 83/A
51000 Rijeka, Croatia
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