The influence of Ce³⁺ ions on the corrosion rate of stainless steel in acidic solutions of different pH-values

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The corrosion resistance of AISI 420 stainless steel in 0.1 mol L⁻¹ H₂SO₄ + 0.1 mol L⁻¹ Na₂SO₄ solutions at different pH-values and the inhibiting effect of Ce³⁺ ions was studied using electrochemical polarization methods. The results reveal decreasing of the corrosion rate with an increasing the pH of the solution, which demonstrates the progressive protective character of the inhibitor used. At pH lower than 3.33, the corrosion inhibition was most probably a result of the competitive adsorption of Ce³⁺ with H⁺ ions on the cathodic sites of the electrode surface, and it was found to be dependent on the relative concentration of H⁺/Ce³⁺. The peroxide generated from the oxygen reduction reaction at pH 3.33 was found to be capable oxidize trivalent cerium (Ce) to the tetravalent state. As obtained hydroxide precipitates act as diffusion barrier hindering the corrosion processes, whereafter a spontaneous passivity occurs on the steel surface at this pH.

Keywords: acid corrosion; green corrosion inhibitor; stainless steel; cerium; electrochemical techniques

Introduction

Using inhibitors in an aggressive media enables corrosion protection and is of highly technological importance (1, 2). The inhibition effect depends mostly on surface adsorption and/or chemical bonding. In the past years, organic molecules which contain heteroatoms, (e.g., sulfur, oxygen, and nitrogen) and/or π electron sources (e.g., double and triple bonds) have been enforced as effective corrosion inhibitors (3, 4). Like organic molecules with different heteroatoms, polymers were also found to act as effective inhibitors. Different polyamines such as polyaminoquinones, polydiphenylamines, or polyaniline were found to have good inhibition properties (5).

While the inhibition effect of many organic molecules and polymers is very well understood in acid media, much less is known about the inhibition efficiencies of metal cations. Drazic and Vorkapic found that Cd²⁺, Mn²⁺, and Zn²⁺ inhibit corrosion of an iron in 0.25 M H₂SO₄ through the inhibition of the hydrogen evolution reaction (6). The inhibitive effect of these cations was explained as the underpotential deposition of these metals ad-atoms on the iron. Furthermore, the inhibition of the iron in the 0.5 M H₂SO₄ was investigated through the adsorption of Zn²⁺, Mn²⁺, and Ce⁴⁺ ions (7).

Chromium (VI) compounds have been widely applied as corrosion inhibitors in the past (8). In spite of their broad industrial applications and high inhibition efficiency, chromates possess high toxicity and are slowly being phased out of use (9). Recently, rare-earth metals were found as a green alternative to the chromium species not only because of their high effectiveness but also due to the null toxicity (9, 10). Cerium (Ce) salts in particular have been used successfully as corrosion inhibitors on different metals and alloys (11–15). Lu and Ives showed that the corrosion rate of AISI 314 in NaCl solution decrease by using Ce salts through the formation of a CeO₂ passive layer (16). Moreover, Arenas et al. attempted to establish the pitting-resistance of tinplate in chloride solutions by using Ce salts as inhibitors. In this sense, a preferential precipitation was found regarding distribution of the cathodic area on the surface of the material (17). Also a combination of four rare-earth chlorides was evaluated for the corrosion inhibition of aluminum alloy. In this study, the best mixture composed of 72% Ce and 28% praseodymium (Pr)/lanthanum (La) ions was found to work the best. Individually, La, Pr, and neodymium show varying levels of corrosion inhibition activity, all of which are inferior to that of Ce (18).

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The aim of the present study is to disclose the inhibition effect of Ce$^{3+}$ ions on the corrosion rate of stainless steel in acidic solutions. H$_2$SO$_4$ is widely used as inorganic acid at various concentrations; accordingly, corrosion resistance of AISI stainless steel was evaluated in H$_2$SO$_4$ solutions at different pH-values (0.9, 1.25, 2.33, and 3.33) using potentiodynamic polarization methods.

Experimental

Electrochemical measurements were carried out at room temperature using three electrodes cell and potentiostat Jaisle IMP 88 PC-R. The working electrode was the material under study (AISI 420 stainless steel, composition in wt%: C, 0.21; S, 0.031; Si, 0.45; Cr, 13.3; Ni, 0.15; Cu, 0.47; Fe, balance) with a cross-sectional area of 1 cm$^2$ exposed to the solution. The reference electrode was a saturated calomel electrode connected to the cell by a salt-bridge and a Luggin capillary, and a counter electrode consisting of platinum foil.

The potentiodynamic polarization curves were performed in aqueous mixtures of 0.1 mol L$^{-1}$ H$_2$SO$_4$ + 0.1 mol L$^{-1}$ Na$_2$SO$_4$ (pH = 0.9, 1.25, 2.33, 3.33) without and with 0.01 mol L$^{-1}$ Ce(NO$_3$)$_3$ as the inhibitor. The test solutions were prepared from analytically graded reagents (Aldrich chemicals) and distilled water. The electrolytes tested were not deaerated. Prior to the polarization measurements, the samples were wet abraded with silicon carbide papers up to 1200 grit, then polished with diamond paste to 1 µm finish, washed in distilled water, and degreased with acetone. After cathodic reduction of the air-formed oxides at $-1000$ mVSCE for 10 minutes, the specimens were put at open-circuit potential for 5 minutes and then polarization measurements performed in the anodic direction from $-800$ mV$_{SCE}$ to 800 mV$_{SCE}$ with a sweep rate of 5 mV/s. The linear polarization region of the polarization curves (over-voltage lower than ±20 mV) was used to calculate polarization resistance ($R_p$). Each experiment was repeated at least three times in order to check the reproducibility.

Results and discussion

The polarization behavior of stainless-steel electrodes in 0.1 mol L$^{-1}$ H$_2$SO$_4$ + 0.1 mol L$^{-1}$ Na$_2$SO$_4$ solutions of pH 0.9, 1.25, 2.33, and 3.33 is shown from the curves represented in Figure 1a, and the effect of 0.01 mol L$^{-1}$ Ce$^{3+}$ added as corrosion inhibitor to each pH is depicted in Figure 1b. Electrochemical parameters (i.e., corrosion current densities ($i_{corr}$), corrosion potentials ($E_{corr}$), and polarization resistances ($R_p$)) were calculated and tabulated in Table 1.

Inspection of the polarization curves in the pH ranging from 0.90 to 2.33 reveals that the decrease in the H$^+$ activity as well as addition of Ce$^{3+}$ ions, shifted the cathodic branches to lower current density values without affecting the cathodic Tafel line slopes (Figure 1a and 1b). Therefore, the presence of Ce$^{3+}$ ions in the electrolyte did not change the cathodic process that controls the corrosion mechanism. This compound inhibits the rate of hydrogen evolution reaction without affecting its mechanism only by blocking the transmission of H$^+$ ions and electrons between the cathodic area and solution. Notably, an increase in both Tafel constants was found at pH 3.33, which could have been due to an increase in the energy barrier for anodic steel dissolution, the
hydrogen proton discharge, and the oxygen reduction (diffusion-controlled reactions), while almost complete prevention of dissolution was attained by the added inhibitor.

In the anodic region, an active–passive transition was observed in all uninhibited solutions. The maximum current that was achieved at the transition point, termed as the critical current density ($i_{crit}$), decreased from 10.9 mA cm$^{-2}$ to 2.0 mA cm$^{-2}$ when pH increased from 0.9 to 3.33, respectively. This current density is required for the formation of a sufficiently high surface concentration of metal cations such that the nucleation and growth of surface passive film can proceed. In the case of stainless steel, the passive film is based on Fe(II) and Cr(III) hydroxides/oxides, which occurs more easily at higher pH. In test solutions (pH = 0.9, 1.25, 2.33) where Ce$^{3+}$ was added as the inhibitor, we found lower $i_{crit}$ at the anodic active–passive transition, while at pH 3.33 the spontaneous passivation was observed.

As can be seen from Table 1, the corrosion current density increased with increasing of the acidity of the sulphuric acid solution. During an active dissolution of steel at corrosion potential, the two reactions oppose each other, i.e., metal dissolution and cathodic reduction of H$^+$ ion as follows:

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (1)$$

$$2\text{H}_3\text{O}^+ + 2e^- \rightarrow \text{H}_2 + 2\text{H}_2\text{O} \quad (2)$$

If the concentration of hydrogen ions in the acid increases then, according to Equation (2), the reversible potential, $E_r$, becomes more positive:

$$E_r/V = 0 - 0.0591 \log \text{pH} \quad (3)$$

Furthermore, the exchange current also increases, while the Tafel slope of the polarization curve remains unchanged. Thus the polarization curve of the hydrogen ion reduction reaction is displaced parallel to itself in order to initiate at a more positive reversible potential and larger exchange current density. According to Equation (1), the anodic reaction is not affected by the change of the pH. Thus the increase in hydrogen ion concentration causes the anodic and cathodic polarization curves to intersect at a more positive corrosion potential, $E_{corr}$, and the corrosion current increases. $E_{corr}$ was found to change with the pH-values as can be seen from Figure 2. The slope of the resulting straight line is about $-0.060 \text{V/pH}$, which suggests that the electrochemical reaction controlling the corrosion potential is characterized by a H$^+$ and e$^-$ ratio of unity. The process is evidently cathode limited, and the corrosion potential is close to the reversible potential for the anodic process.

The polarization resistance ($R_p$), which is inversely proportional to the corrosion current density according to the Stern–Geary equation, decreases with decreasing pH (Table 1).

**Influence of Ce ions**

Since the process is cathode limited, it is possible to slow it down by inhibiting the rate of hydrogen evolution. Addition of the Ce$^{3+}$ ions as the inhibitor or increasing the pH of the electrolyte has the same impact, i.e., the reduction of the exchange current density of hydrogen evolution which can be seen as a change in $i_{corr}$. Moreover, the difference between the

Table 1. Electrochemical parameters of stainless steel in 0.1 mol L$^{-1}$ H$_2$SO$_4 + 0.1$ mol L$^{-1}$ Na$_2$SO$_4$ solutions of different pH-values without and with 0.01 mol L$^{-1}$ Ce$^{3+}$ (aq).

| pH | $E_{corr}$/mV SCE | $E_{corr}$/mV SCE with Ce$^{3+}$ | $i_{corr}$/mA cm$^{-2}$ | $i_{corr}$/mA cm$^{-2}$ with Ce$^{3+}$ | $R_p$/Ω cm$^2$ | $R_p$/Ω cm$^2$ with Ce$^{3+}$ | IE($i_{corr}$) (%) | IE($R_p$) (%) |
|----|------------------|-------------------------------|------------------------|--------------------------------------|----------------|-----------------------------|------------------|--------------|
| 0.90 | -521            | -495                           | 0.70                   | 0.65                                 | 80             | 88                          | 7                | 10           |
| 1.25 | -550            | -545                           | 0.60                   | 0.50                                 | 93             | 114                         | 17               | 18           |
| 2.33 | -617            | -580                           | 0.40                   | 0.25                                 | 190            | 355                         | 38               | 46           |
| 3.33 | -595            | -500                           | 0.07                   | –                                    | –              | –                           | –                | –            |

Figure 2. Variation of corrosion potential with pH.
corrosion current densities and the polarization resistances was noticed when the Ce$^{3+}$ was added to the electrolyte. Table 1 shows the values of inhibition efficiency (IE) obtained from the corrosion current density IE($i_{corr}$) and from the polarization resistance IE($R_p$). The IE (%) was calculated using the following equations:

\[
IE \left( i_{corr} \right) = \frac{i_{corr} - i_{corr,\text{inh}}}{i_{corr}} \times 100 \quad \text{and} \quad IE \left( R_p \right) = \frac{R_p,\text{inh} - R_p}{R_p,\text{inh}} \times 100
\]

where $i_{corr}$ and $i_{corr,\text{inh}}$ are the corrosion current densities without and with an inhibitor, $R_p$ and $R_p,\text{inh}$ are the polarization resistances without and with an inhibitor, respectively. As can be seen, the two IE values are in a good agreement at the same pH (Table 1).

It was found that the presence of Ce ions retard the rate of reaction relatively to the system without inhibitor having any impact on the mechanism in general. Examination of Pourbaix potential-pH diagram (19) indicates that Ce$^{3+}$ formed insoluble hydroxide and oxides at pH-values in excess of 8. At pH lower than 3, the inhibition was most probably a result of the competitive adsorption of Ce$^{3+}$ with H$^+$ ions on the cathodic sites of electrode surface. Although Ce$^{3+}$ ions are not directly involved in the redox reactions, they provide indirect influence on the electrode phenomenon by blocking the hydrogen evolution reaction. If two substances, H$^+$ and Ce$^{3+}$ compete for the given sites, the adsorption of H$^+$ from the solution is dependent on the relative concentration of H$^+$/Ce$^{3+}$. In accordance, the inhibition efficiency increases with decreasing the concentration of hydrogen ions at constant inhibitor concentration (Table 1).

An associated cathodic reaction at pH 3.33 is also the oxygen reduction. It is well known that oxygen (O$_2$) reduction can proceed in two stages; in the first stage, O$_2$ is reduced to H$_2$O$_2$, while in the second stage, hydrogen peroxide is reduced to water as follows:

\[
O_2 + 2H^+ + 2e^- \rightarrow H_2O_2
\]

\[
H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O
\]

The generated peroxide, an intermediate product of oxygen reduction, can oxidize trivalent Ce to the tetravalent state according to the redox reaction:

\[
2\text{Ce}^{3+} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Ce}^{4+} + 2\text{H}_2\text{O}
\]

in which the standard reaction Gibbs energy is $-32.81$ kJ mol$^{-1}$. $\Delta_rG^\circ$ is negative at 298 K and the reaction proceeds spontaneously. The value of equilibrium constant, $K$, is $5.64 \times 10^3$, and the equilibrium is strongly shifted toward the products. Therefore, it is likely that the Ce$^{4+}$ is formed, after which precipitation occurs according to the reaction:

\[
\text{Ce}^{4+} + 4\text{OH}^- \rightarrow \text{Ce(OH)}_4
\]

Ce(OH)$_4$ precipitates without more difficulty because of very low solubility product. The solubility of Ce (IV) hydroxide layer would be related with pH as follows:

\[
\log [\text{Ce}^{4+}]_{\text{sat}} = 8.3 - 4\ \text{pH}
\]

The value of $K_{sp} = 2 \times 10^{-48}$, used in our calculations, was taken from Reference (20). From Equation (9), it is possible to calculate the concentration of Ce (IV) ions in the solution at pH 3.33, which is $1 \times 10^{-5}$ mol L$^{-1}$. This is in agreement with the findings that the tetravalent Ce forms extremely insoluble hydroxides already at pH about 3 (21). Thereafter, the formed hydroxide of tetravalent Ce is deposited on the cathodic parts providing additional hindering of the corrosion processes, and spontaneous passivity occurs on the steel surface at this pH.

Conclusions

- Corrosion rate of the AISI 420 stainless steel at different pH-values of the H$_2$SO$_4$ solutions was equivalent to hydrogen ions activity.
- Addition of Ce$^{3+}$ ions to the test solutions inhibits the rate of hydrogen evolution reaction without affecting its mechanism.
- At pH lower than 3.33, the inhibition may be explained as a result of the competitive adsorption of Ce$^{3+}$ ions with H$^+$ ions on the cathodic sites of electrode surface.
- The greatest inhibition efficiency was reached at pH 3.33, where generated peroxide was found to oxidize trivalent Ce to the tetravalent state.
- The extremely insoluble Ce$^{4+}$ hydroxide precipitates act as a diffusion barrier hindering the corrosion processes.

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