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Article

Inhibition of Steel Corrosion in NaCl Solutions by Samarium

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Neste trabalho o efeito do Samário sobre o comportamento corrosivo de diferentes aços em soluções de NaCl + Sm (III) tem sido estudado por métodos eletroquímicos. Os resultados permitem avaliar a eficiência do Samário como um inibidor da corrosão através dos parâmetros cinéticos da reação de redução do oxigênio e do comportamento eletroquímico dos aços. O comportamento observado depende da natureza do aço e do fenômeno de inibição e tem sido associado à modificação da superfície devido à formação de uma camada de hidróxido de Samário, o que foi confirmado por estudos de EDS.

In this research the effect of samarium on the corrosion behavior of different steels in NaCl + Sm (III) solutions is studied by electrochemical methods. The results allow the evaluation of the efficiency of samarium as a corrosion inhibitor by the kinetic parameters of the oxygen reduction reaction and the electrochemical behavior of the steels. The behavior observed depends on the nature of the steel, and the inhibition phenomenon is associated with a surface modification due to a hydroxy-samarium compound layer formed at the steel surface, as confirmed by EDS studies.

Keywords: *corrosion, inhibition, samarium, conversion coatings*

Introduction

Rare earth metal salts have shown to be very effective corrosion inhibitors for aluminium and aluminum alloys[1-4]. It is assumed that this inhibition is produced by a protective rare earth oxide film at the surface.

On this basis rare earth conversion coatings have been developed for corrosion protection. Cerium conversion coatings for aluminium alloys have been obtained by immersion in Ce (III) solutions and have proven to provide significant corrosion protection against exposure to NaCl solution[3-5]. The degree of protection is strongly dependent on the time of immersion in the rare earth metal salt solution and to achieve significant protection immersion times of some hours are required, which of course is commercially unattractive. The conversion coating may also be formed electrolytically by cathodic polarization. This procedure would allow the reduction of the time needed for the film formation, but its industrial utilization has not been reported.

In previous researches we studied the inhibitory effect of samarium on the oxygen reduction reaction on Pt in a weakly acidic solution[6], and on the anodic corrosion behavior of steels treated by immersion in a samarium solution[7,8]: samarium changes the electrochemical parameters of the oxygen reduction reaction and shifts the steel corrosion potential towards more anodic potentials. Since the oxygen reduction is the main reaction involved in corrosion processes, and as the corrosion potential is related to the corrosion feasibility, it is possible that samarium may act as a corrosion inhibitor of steels in aqueous solutions. Previous research on the utilization of samarium as a corrosion inhibitor of steels is not known.

Here, we study the efficiency of samarium as a corrosion inhibitor of steels in a neutral medium. The importance of steel corrosion in neutral media is related to its industrial applications in heat exchangers and recirculating water systems.

Experimental

The steels selected for this study were stainless steels, types AISI 304, 316L, 430, and 409L.

The effect of samarium on the corrosion behavior of the steels was studied in 35g/L NaCl solutions, at pH = 6.4, with samarium present in various concentrations in the NaCl solution. Samarium was added as $Sm_2(SO_4)_3$ to give the desired Sm(III) concentration. After the addition of samarium, the pH was adjusted to 6.4 by adding NaOH solution. The solutions were prepared with deionized water and reagent grade chemicals without further purification.

The evaluation of the effect of samarium for corrosion inhibition was carried out from polarization measurements under potentiodynamic conditions. The curves obtained allow the measurement of the corrosion rates by the Tafel extrapolation technique. The potentiodynamic measurements were carried out at 25 °C in a glass cell (900 mL) according the ASTM G-5 specifications, with a Taccussel PJT 35-2 potentiostat.

The steel samples were mounted in epoxy resin, mechanically polished with emery paper, degreased in acetone, and rinsed with deionized water; the exposed area was 1 cm^2. The counter electrode was a platinum gauze, and the reference electrode was a saturated calomel electrode (SCE).

Since oxygen reduction is the major process controlling the corrosion process in neutral media, prior to the experiments the NaCl solutions were saturated with oxygen by passing pure oxygen for 3 h at a flow rate of 200 mL/min, to assure the reproducibility of the dissolved oxygen concentration.

Results and Discussion

Polarization curves

The effect of samarium on the corrosion behavior of steels was evaluated from the modifications observed at the cathodic and anodic sides of the polarization curves.

The general picture of the electrochemical behavior of the investigated stainless steels was obtained by potentiodynamic measurements with a slow sweep rate (0.2 mV/sec).

Polarization started at -1.1 V/SCE in the anodic direction until the electrode had been activated, and was then reversed with the same sweep rate. In all cases, two distinctive regions were observed:

- a limiting current, on the cathodic side, and
- a pitting region, on the anodic side

The relative position of those regions depends on the type of steel, the major differences being observed in the pitting region. The results obtained with different stainless steel samples are shown in Fig. 1.

Behavior in the limiting current region

This region is only observed in the presence of oxygen in solution, which indicates that this signal is associated with the oxygen reduction reaction. The value of the limiting current is not very dependent on the nature of the steel. On the contrary, this limiting current is strongly dependent on the samarium concentration in the NaCl solution, as shown in Fig. 2 for 430 stainless steel.

From Fig. 2 a reduction of the limiting current is observed when the samarium concentration is increased from samarium concentrations greater that 10^{-4} M. The reduction in the limiting current is observed with samarium concentrations on the order of 10^{-2} M. For samarium concentrations greater that 10^{-2} M, the limiting current is not dependent on the samarium concentration. In addition, a new signal at -0.81 V/SCE is observed when samarium is present in the solution. The signal is dependent on the samarium concentration. The nature of the electrochemical reaction associated with this signal is not clear because Sm(III) should not show electrochemical activity, considering the Pourbaix diagrams for samarium[9].

After the polarization measurements, the examination of the electrodes in an optical microscope shows the presence of an adherent thin film that can be dissolved in an acidic medium, but not in an alkaline medium. This fact shows the basic nature of this film. EDS analyses of the film show the presence of Sm, O, and Cl, evidencing the mixed anionic composition of the film.

The feasibility of the formation of the protective film depends on the initial potential of the polarization measurement, and the film is not observed when the potential sweep is started at more anodic potentials than that corresponding to the hydrogen evolution reaction.

These results suggest that the film is formed in the cathodic region at potentials where the reduction of water to hydrogen occurs; we assume that the film is formed with the OH^- ions generated from the reduction of water. Similar processes are involved in the formation of metallic hydroxide films[10-12], and explain the basic nature of the film. A model considering the possibility of a chemical reaction between the steel and samarium ions, similar to that involved in the formation of classical chromate conversion coatings[13-14], cannot be assumed because Sm(III) ions cannot be reduced or oxidized in aqueous solution under the conditions imposed by the chemical media studied (complexing power, pH).

Behavior in the pitting region

In this region a change from cathodic to anodic current without the activation-passivation transition is observed. This behavior is due to the oxide layer formed when the electrode is in contact with moist air. After this zone, the increase in the current starts at the breakdown potential, E_b, continuing even after the potential scan reversal. From the anodic behavior observed, it is possible to determine the pit nucleation potential E_n (the potential below which no pitting occurs, and above which pit nucleation starts) from the

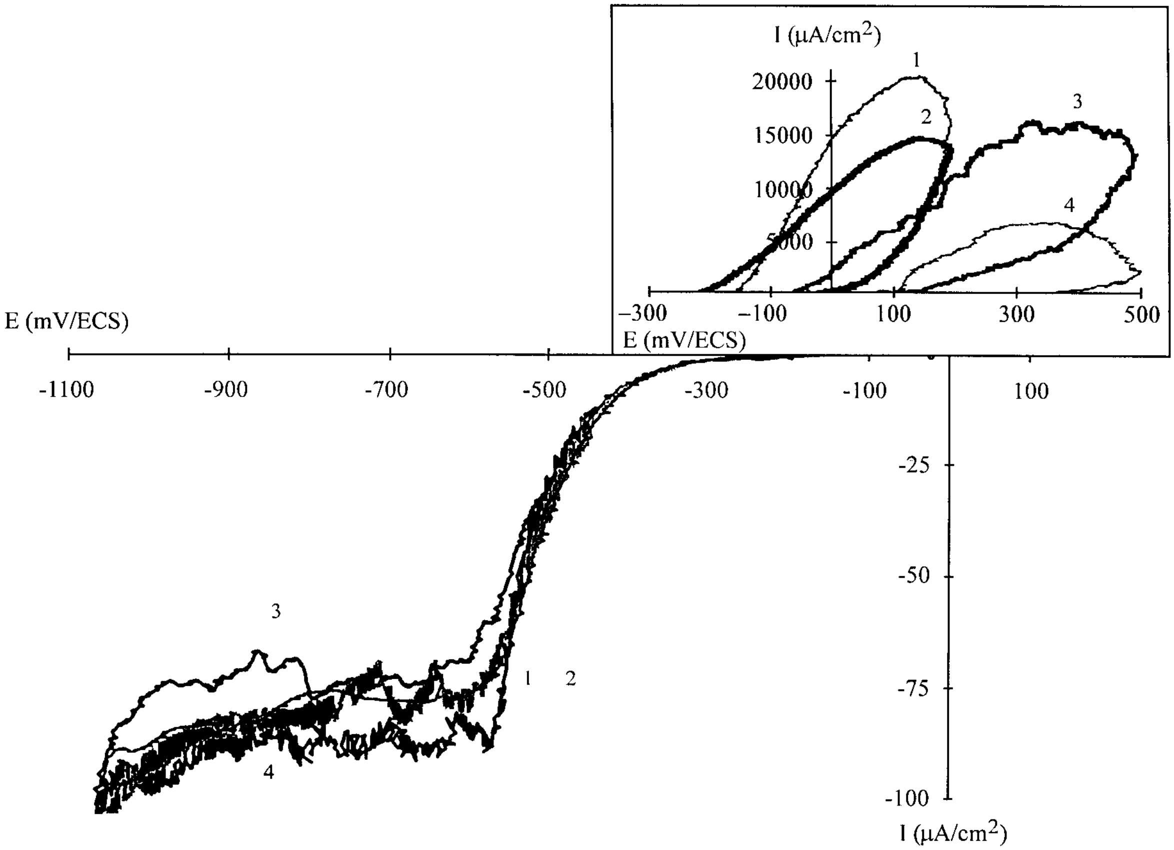

Figure 1. Polarization curves obtained on different steels in NaCl 35 g/L, satured with O_2. 1) Stainless steel type 430; 2) Stainless steel type 409L; 3) Stainless steel type 304; 4) Stainless steel type 316L.

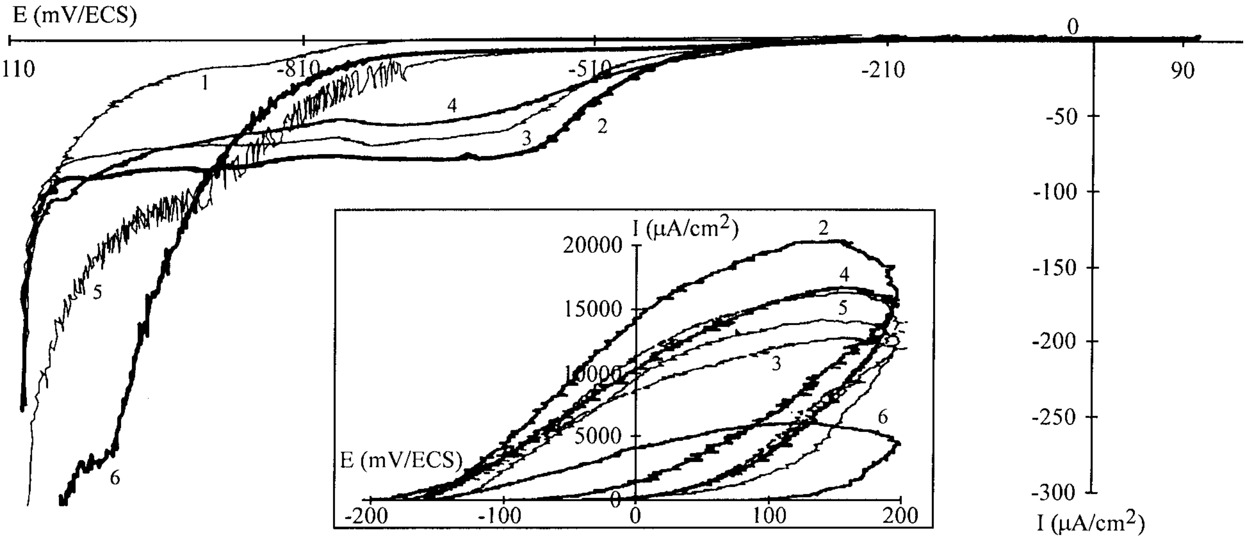

Figure 2. Polarization curves obtained on 430 stainless steel in NaCl 35 g/L at various sumarium concentrations: 1) N_2, Sm 10^{-3} M; 2) O_2 saturated solution without Sm (III); 3) O_2 saturated solutions, Sm (III) 10^{-4} M; 4) O_2 saturated solution, Sm (III) 10^{-3} M; 5) O_2 saturated solution, Sm (III)5 x 10^{-3} M; 6) O_2 saturated solution, Sm (III) 10^{-2} M.

hysteresis loop observed. The values of the E_b and E_n potentials appear to depend on the nature of the steel and on the samarium pretreatment, as shown in Table 1.

From the results in Table 1, more anodic values for E_b and E_n in the presence of samarium are observed, indicating a more energetic corrosion process. Modifications of the anodic behavior due to the presence of samarium is not clear, but may be explained by the surface modification produced by the film formed at more cathodic potentials.

Corrosion rate measurements

The corrosion rates were evaluated using the Tafel extrapolation technique with the data obtained from the potentiodynamic measurements. The values obtained with a samarium concentration of 10^{-3} M in the NaCl solution are shown in Table 2.

These results show a reduction in the corrosion rate in the presence of samarium, indicate that samarium in solution produces a diminishment of the corrosion rate: the inhibitory effect of samarium is evidenced by the modifications in the polarization curves.

Table 1. Values of breakdown potentials (E_b) and pit nucleation potentials (E_n) for different steels in NaCl solutions (35 g/L) without and with Sm. $[Sm^{3+}] = 10^{-3}$ M.

	without Sm (mV/SCE)		with Sm (mV/SCE)	
Steel	E_b	E_n	E_b	E_n
409 L	-105	- 290	- 50	- 260
304	95	- 170	93	- 140
430	- 60	- 233	- 51	- 216
316 L	130	- 55	177	- 185

Table 2. Corrosion rates for different steels in NaCl solution (35g/L) without and with Sm. $[Sm^{3+}] = 10^{-3}$ M

Steel	Corrosion rate (mm/year)	
	without Sm	with Sm
409 L	0.0056	0.0002
304	0.0015	0.0009
430	0.001	0.001
316 L	0.009	0.006

Conclusions

Samarium in NaCl solutions inhibits it steel corrosion: shifts the breakdown potentials, E_b, and the nucleation potentials, E_n, towards more anodic values. In addition, the presence of samarium reduces the limiting current value for the oxygen reduction reaction directly involved in the corrosion process in NaCl solutions. The behavior observed appears to be dependent on the nature of the steel and on the samarium concentration, and was associated with the hydroxide conversion coating formed on the surface.

Since samarium effects are observed at low concentrations, their use in industrial applications as a corrosion inhibitor is conceivable.

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