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Lanthanide salts as alternative corrosion inhibitors

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Abstract

Lanthanum and samarium nitrates and chlorides have been investigated as corrosion inhibitors of AISI 434 SS in sodium chloride solutions, at room temperature. Electrochemical techniques allowed to evaluate the degree of protection and the cathodic nature of the inhibitors. Scanning electron microscopy and energy dispersive spectrometry were used to analyze the composition of the protective films formed after full-immersion tests.

Keywords: Corrosion; Inhibitors; Lanthanides; Stainless steel

Introduction

At present a variety of inorganic salts including chromates are being used as effective inhibitors of the metal corrosion in aqueous environments [1]. In the last few years a good deal of research efforts have being devoted to developing new corrosion inhibitors with lower environmental impact than the conventional ones [2]. In this sense, the rare earth ions constitute interesting alternative corrosion inhibitors [3]. Thus, lanthanide ions have proved to be efficient as corrosion inhibitors, in chloride solutions, of aluminum alloys [4–8], zinc and zinc coated steel [9,10]. The mechanism of operation of these inhibitors seems to be related with kinetic modifications of the cathodic reduction of oxygen [6]. In Ref. [11] based in scanning vibrating probe (SVP) experiments, an anodic mechanism is considered to be responsible for the protective action of $CeCl_3$ against C1020 steel in NaCl solution. This proposal contrasts with the cathodic character reported for other alloys [6–10]. The rare earth elements have also been used as inhibitor of the high temperature corrosion of stainless steel [12–14].

This work reports on the behaviour of different lanthanide salts as inhibitors of uniform corrosion processes on AISI 434 SS in NaCl solutions.

Experimental

The materials used in this study were 30×25×1.5 mm sheets of AISI 434 stainless steel. The chemical composition of such an alloy, expressed in wt.% is: 16.28Cr–0.95Mo–0.39Si–0.33Mn–0.16Ni–0.10Cu–0.053C–0.023P–0.010Sn–0.002S, Fe remainder.

Before the metallographic study, the sample was polished and further immersed during two minutes in Vilella etchant. The micrographs revealed the presence of ferritic equiaxed grains. Randomly dispersed chromium carbide particles were also observed in the alloy. The grain size of this sample corresponds with number nine of the ASTM-E-112 standard.

Prior to carrying out the corrosion tests, the alloy surfaces were wet polished with silicon carbide to 600 grit, carefully degreased with benzene and finally rinsed with distilled water.

The corrosion essays were performed in distilled water containing 3.5% NaCl. Lanthanide salts were added to each solution in concentration ranging from 100–1000 ppm in Ln^{3+}. Nitrogen or synthetic air was bubbled in the solution to get deaerated or oxygen saturated solutions.

Linear polarization data at 298 K were obtained in an EG&G Flat Cell attachment connected to a Versastat model EG&G potentiostat. The range of operating voltage was selected to avoid pitting or crevice corrosion phenomena during linear polarization.

Full immersion tests were carried out at different exposure times ranging from 1–60 days and the surfaces of the samples were further observed in a JEOL 820-SC scanning microscope equipped with an AN-10000 LINK EDS spectrometer.

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Results and discussion

It is well established that polarization diagrams can help to understand how an inhibitor works [1]. Inhibitors can modify the anodic process, the cathodic process or both, leading in any of these ways to a decreased rate of the global corrosion process. The changes observed in polarization curves give a clear indication of the role played by the inhibitor, see Fig. 1. Cathodic inhibitors reduce the corrosion current, shifting negatively the corrosion potential, while this value is shifted positively due to the action of anodic inhibitors. This shifting in the corrosion potentials can be used as a criterion to classify inhibitors as anodic or cathodic. Mixed inhibitors modify both processes, the sign and magnitude of the net shift being determinated by the relative intensity of the anodic and cathodic inhibition.

Our results show that rare earth nitrates act as mixed inhibitors, the shift in the corrosion potential depending on the salt concentration, Figs. 1(a)–1(c). The nitrate ion is considered to be an anodic inhibitor; accordingly, the cathodic contribution we have observed must be assigned to the presence of lanthanide ions in solutions. This behaviour of the lanthanide ion is reinforced when the experiments are run in aerated solutions, Fig. 1(d). This figure shows polarization curves corresponding to solutions doped with 1000 ppm of $La(NO_3)_3$ under both aerated and deaerated conditions. In effect, it can be deduced from Fig. 1(d) that the corrosion potential due to the cathodic polarization process shifts towards more negative values as the oxygen concentration increases. In Refs. [4,5] it is proposed a mechanism to explain the cathodic behaviour of lanthanides salts on aluminum alloys. According to such a mechanism, the lanthanide ions block the cathodic sites by forming a film-like precipitate with the hydroxide groups generated in the oxygen reduction reaction. Our results suggest that, in the inhibition process of the AISI 430 SS, a similar mechanism can be operating. Furthermore, this mechanism would explain the stronger cathodic behaviour observed in aerated conditions.

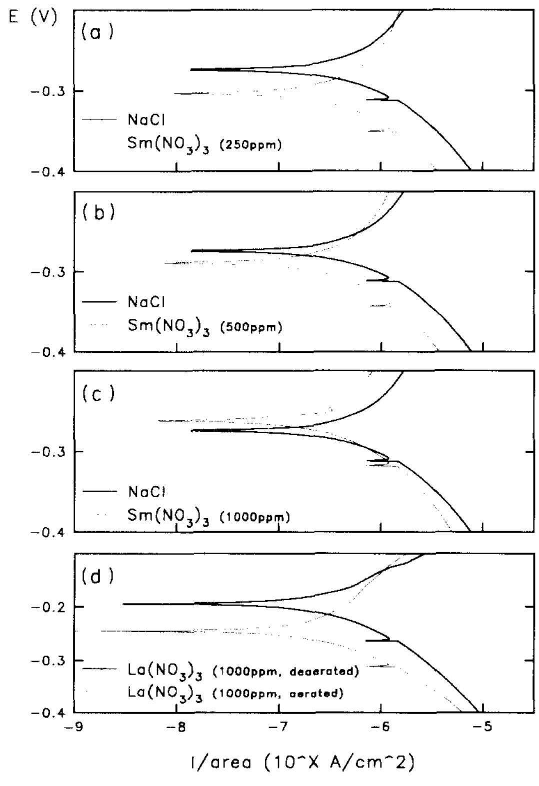

Fig. 1. Linear polarization curves both with and without inhibitor for (a) 250 ppm $Sm(NO_3)_3$, (b) 500 ppm $Sm(NO_3)_3$, (c) 1000 ppm $Sm(NO_3)_3$. (d) Linear polarization curves for 1000 ppm $La(NO_3)_3$ in aerated and deaerated solutions.

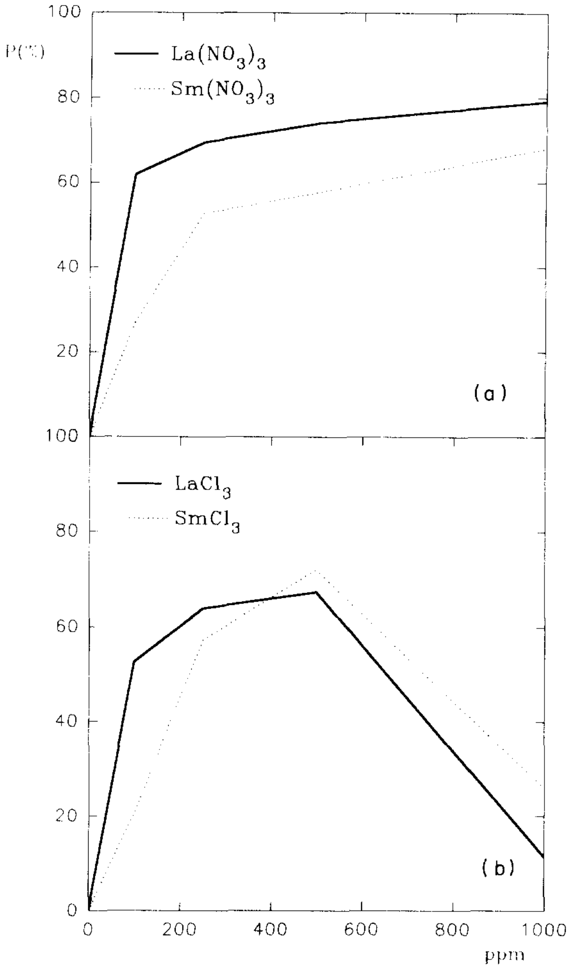

Fig. 2. Protection percentage versus inhibitor concentration plots for (a) $La(NO_3)_3$ and $Sm(NO_3)_3$, and (b) $LaCl_3$ and $SmCl_3$.

The Stern–Geary method has been used to determine the corrosion rates from the corresponding Evans diagrams. From them, the protection degree, P, could be estimated as the percentage of decrease of the corrosion rate with respect to that observed in 3.5% NaCl aerated solution without inhibitor. Fig. 2 shows the evolution of P vs. the lanthanum and samarium nitrate (a) or

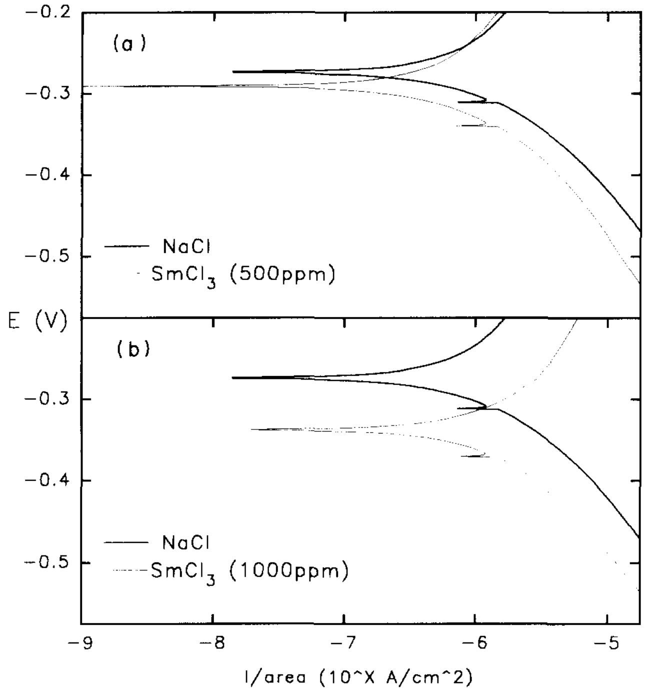

Fig. 3. Linear polarization curves both with and without inhibitor for (a) 500 ppm $SmCl_3$ and (b) 1000 ppm $SmCl_3$.

chloride (b) contents. It can be concluded that when used nitrate solutions, the combined effect of both the anion and the lanthanide ions leads to a more effective protection. Also worth of noting in Fig. 2(a), the highest value of P (around 70%) corresponds to the highest inhibitor concentration evaluated.

In the case of chloride solutions, the corrosion protection is only due to the operation of the cathodic inhibition mechanism induced by the lanthanide ions, Fig. 3(a). The highest P value for chlorides is only slightly lower than that for nitrates, thus showing the strong role played by lanthanide ions in both cases. Compared to La^{3+}, Sm^{3+} is a more oxidizing ion; however, no large differences of corrosion inhibition capability are observed, at least under the experimental conditions investigated here.

The main difference we can note between nitrates and chlorides is the decrease of percentage of protection observed in the high concentration range for chlorides: 500–1000 ppm. This negative effect is interpreted as due to the increase of chloride ion concentration, inherent to which a shift of the anodic branch of the polarization curve, Fig. 3(b), is observed. This would increase the corrosion rate.

Scanning electron microscopy images and EDX measurements helped us to confirm the cathodic nature of the inhibition effect of lanthanide salts on AISI 434 in chloride solutions. Fig. 4(a) shows a SEM image corresponding to an AISI 434 sample that was fully immersed in a 100 ppm $LaCl_3$, 3.5% NaCl during 6 days at room temperature. A surface film can be observed in this figure, similar to the one detected on AA 7075 by Hinton [7]. The EDX spectrum included in the Fig. 4(b) reveal the presence of lanthanum in this protective film.

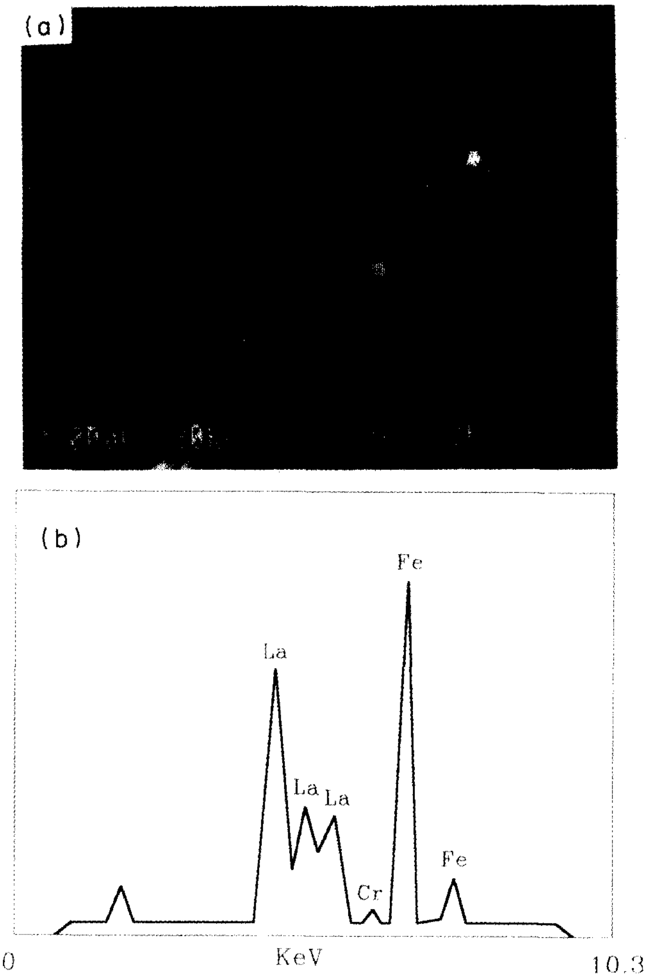

Fig. 4. (a) Scanning Electron Microscopy micrograph of an AISI 434 SS sample fully immersed in 3.5% NaCl with 100 ppm of $LaCl_3$ during six days. (b) EDX spectrum corresponding to the region marked with a circle in (a).

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