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$CeCl_3$ and $LaCl_3$ binary solutions as environment-friendly corrosion inhibitors of AA5083 Al–Mg alloy in NaCl solutions

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Abstract

Lanthanum and cerium chloride and their binary mixtures have been investigated as corrosion inhibitors of AA5083 Al–Mg alloy in aerated 3.5% NaCl aqueous solution. Their inhibitor power was evaluated by using electrochemical techniques together with full immersion tests. The highest protection degree was found for the binary solution doped with 250 ppm $CeCl_3$ and 250 ppm $LaCl_3$. Scanning electron microscopy and energy dispersive spectroscopy enabled us to confirm the cathodic nature of the inhibition process and to establish some features of the inhibition process. © 2001 Published by Elsevier Science B.V.

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1. Introduction

Currently, chromates are widely used in anticorrosive pre-treatments of aluminium alloys [1,2]. Because of their high toxicity and environmental impact, an intense research effort is being undertaken to look for the replacement of chromates by more environment-friendly compounds. In this sense, lanthanide compounds have been tested as corrosion inhibitors for different metallic alloys [1,3]. In our laboratories, lanthanide compounds, such a $LnCl_3$, have been used as corrosion inhibitors and in the development of conversion coatings for AA5083 aluminium alloy [4]. In these studies the best performance has been obtained using $CeCl_3$.

In a variety of practical applications where lanthanide compounds are used, it has been shown that the performance of pure compounds can be enhanced using mixtures of rare earth elements [5]. In spite of this, no data are presently available regarding the use of mixtures of rare earth ions as corrosion inhibitors.

The present work reports on first results obtained in the study of $LaCl_3$, $CeCl_3$ and mixed solutions of the latter ones in the corrosion protection of AA5083 (Al–Mg) alloy in NaCl solutions.

2. Experimental

Test specimens were 30×24×4-mm sheets prepared from AA5083 (Al–Mg) wrought alloy in O-temper (without thermal treatment). The composition of the alloy was determined by acid digestion using an ICP-AES equipment (Table 1). The exposed surfaces were wet-polished with silicon carbide paper from 220 to 500 grits. The specimens were then degreased with acetone and rinsed in distilled water. In the cases where it was necessary, the corrosion products were eliminated by immersion of the samples in HNO_3 at 70% for 2 min before the microscopic examinations.

Full immersion treatments were achieved in aerated 3.5% NaCl aqueous solutions at pH 5.5, containing $CeCl_3$ or $LaCl_3$ at concentrations between 0 and 1250 ppm. In addition, other solutions contained 500 ppm of mixtures of $CeCl_3$ and $LaCl_3$ with ratios of 1:4 or 1:1. Tests were performed in accordance with the ASTM-G31 standard, for 1–30 days. Corrosion rates were determined through weight loss of the tested specimens. Afterwards, micro-

Table 1
Composition (wt%) of AA5083 alloy

Mg	Mn	Fe	Si	Ti	Cu	Cr	Al
4.9	0.5	0.3	0.13	0.03	0.08	0.13	rest

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structural features of the samples were analysed in a Jeol 820 SM scanning microscope equipped with an AN-10000 Link EDS spectrometer.

Electrochemical measurements were carried out within a K-352 Flat Cell of Parc EG&G, connected to a 1287 Solartron potentiostat controlled through a PC. A Crison model 42–40 Ag/AgCl electrode was used as reference electrode, which has a potential of -0.207 V against NHE.

3. Results and discussion

The corrosion inhibiting behaviour of lanthanide salts for AA5083 alloy has been previously established in Ref. [6]. According to data reported in this paper and those by Hinton et al. [1,2] corrosion inhibition by lanthanide salts is associated with the formation and precipitation of lanthanide oxides or hydroxides over cathodic precipitates, 100 μm^2 inclusions rich in Fe, Mn and Cr, on the metals surface. These precipitates give rise to a blocking effect and reduce the rate of the corrosion reactions.

In this paper, the nature of the inhibition process has been studied by linear polarisation measurements. Fig. 1 contains linear polarisation curves corresponding to AA5083 samples in bare NaCl solution and with 500 ppm of $CeCl_3$, 500 ppm of $LaCl_3$ and 250 ppm of $CeCl_3$+250 ppm of $LaCl_3$. In all cases the typical behaviour of the cathodic inhibitors was observed [7]. Thus, addition of $LnCl_3$ to the NaCl solution causes a negative shift of the corrosion potential (E_{corr}) as well as a displacement of the cathodic branch of the curves toward lower current densities. The maximum displacement has been observed after an addition of 250 ppm of $CeCl_3$+250 ppm of $LaCl_3$.

Table 2
E^{o}_{corr} (mV), R_p (KΩ) and %PI obtained from linear polarisation curves of the AA5083 alloy in 3.5% NaCl solution containing different quantities of $LnCl_3$

$LnCl_3$	ppm	E^{o}_{corr} (mV)	R_p (KΩ)	%PI
None	0	−760	20.88	0
$CeCl_3$	500	−988	82.90	297
$LaCl_3$	500	−981	44.56	113
$CeCl_3/LaCl_3$	250/250	−1032	119.67	856

The curves included in Fig. 1 allow to evaluate other parameters related to the behaviour of the treated samples. Thus, Table 2 contains the characteristic values of the best treatments: E^{o}_{corr} (mV), R_p (KΩ) and the inhibition protection, PI (%), calculated as:

$$\%PI = \frac{(R_p - 20.88) \times 100}{20.88}$$

were 20.88 is the R_p value of the linear polarisation without inhibitor. The maximum displacement of the E^{o}_{corr} and the highest values of R_p and PI (Fig. 2) have been observed for the $CeCl_3/LaCl_3$ binary solution. On the other hand, the value of the pitting corrosion potential (E_{pit}) seems not to be affected, showing that addition of $LnCl_3$ does not influence crystallographic pitting.

Similar results have been obtained in full immersion treatments. Fig. 3 plots weight loss versus time curves of samples immersed in aerated 3.5% NaCl solutions with or without addition of lanthanide salts. Important differences can be observed between samples exposed to NaCl solution and those immersed in solutions containing also $LnCl_3$. Solutions with $CeCl_3$ and $LaCl_3$ show quite similar plots for the whole exposure time, while the average slope of $CeCl_3/LaCl_3$ binary solution shows the lowest value. The addition of lanthanide salts results, in all cases, in a significant decrease in weight loss.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) techniques were employed in

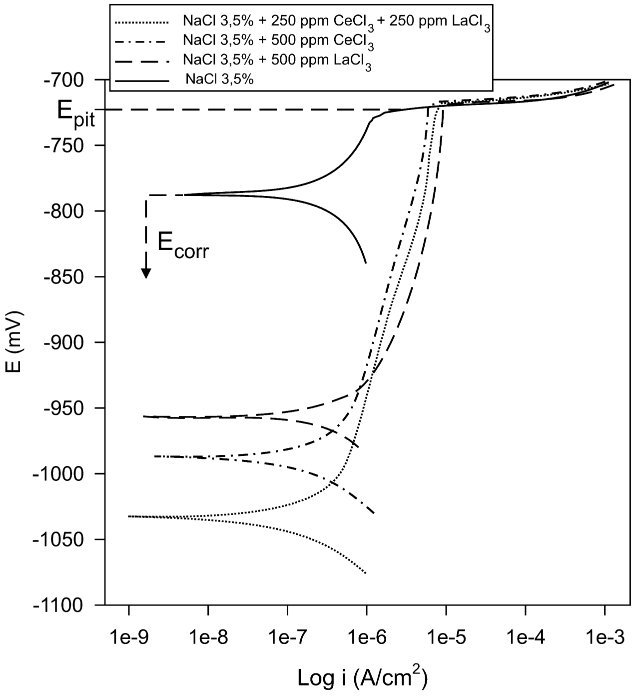

Fig. 1. Linear polarisation curves for AA5083 in bare NaCl solution and with different additions of $LnCl_3$.

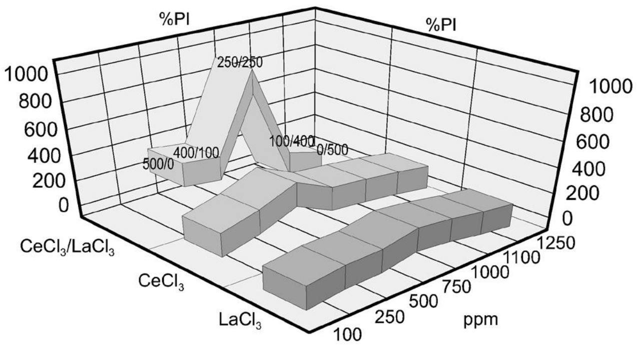

Fig. 2. %PI observed for three different treatments with $LnCl_3$.

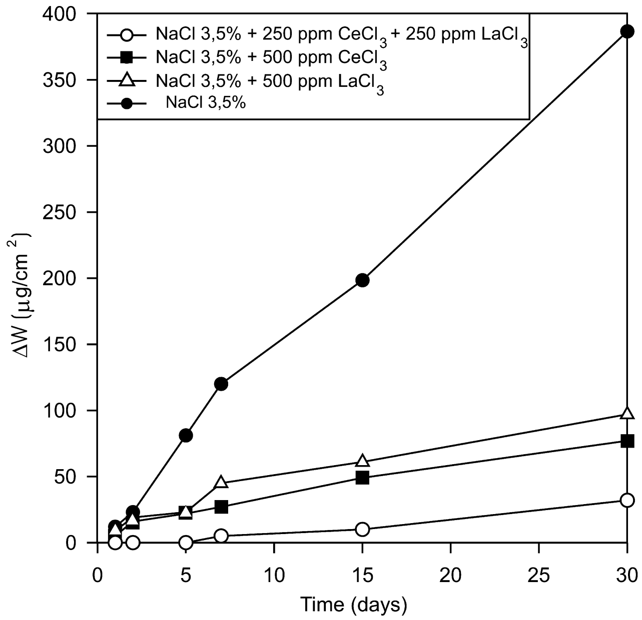

Fig. 3. Weight loss–time curves of full immersed samples of AA5083 in 3.5% NaCl aerated solutions. The highest decrease in weight loss is observed for the $CeCl_3/LaCl_3$ mixture.

order to get additional information on the inhibition mechanism. The results obtained from these technique showed that the corrosion inhibition process was related to the development of a lanthanide-rich film over the cathodic intermetallic. Results reported in Refs. [4,6,8] reveal further details regarding the origin of the protective effect observed in AA5083 samples treated with cerium-containing solutions. In fact, Fig. 4 shows samples treated for 2 h in a 250 ppm $CeCl_3$ + 250 ppm $LaCl_3$ solution. These samples develop a surface coating in which the major component is Al, whereas a mixture of cerium–lanthanum accumulates in dispersed nodules (Fig. 4a). An enlargement of the nodule marked with an arrow in Fig. 4a can be observed in Fig. 4b. The EDS spectrum in Fig. 4c, shows that this nodule contains mainly cerium and a smaller quantity of lanthanum. The presence of cracks, observed in Fig. 4b, enables us to analyse the actual nature of the intermetallic substrate underlying these lanthanide nodule. The EDS spectrum recorded on this area (Fig. 4d) indicates that cerium has been formed over the Al(Mn,Fe,Cr) precipitates. Previous studies of this alloy have revealed that the presence and distribution of this intermetallic conditions the general behaviour of the AA5083 alloy in NaCl 3.5% solution [9]. In this sense, those results are in agreement with the cathodic nature of the precipitates. Accordingly, the cathodic character of Al(Mn,Fe,Cr) precipitates causes the reaction of oxygen reduction to occur on them. Thus, during the first stages of the corrosion process, OH^- ions would be generated over the cathodic intermetallic precipitates.

The OH^- groups formed over the cathodic sites are expected to react with the lanthanide ions present in the solution. The reaction gives rise to the precipitation of lanthanide oxides or hydroxides over cathodic sites and the nodule formation observed in Fig. 4a,b. Blocking of the cathodic sites by these nodule decreases the available cathodic current and, therefore, reduces the principal corrosion process of this alloy, the alkaline localised pitting. This explanation is supported by the results of several authors [10–12].

Nevertheless, these results are similar to those obtained with $CeCl_3$ or $LaCl_3$ treatments, and SEM/EDS techniques are not sufficient to determine the origin of the synergy between cerium and lanthanum in binary solutions.

In order to evaluate the efficiency of the inhibition

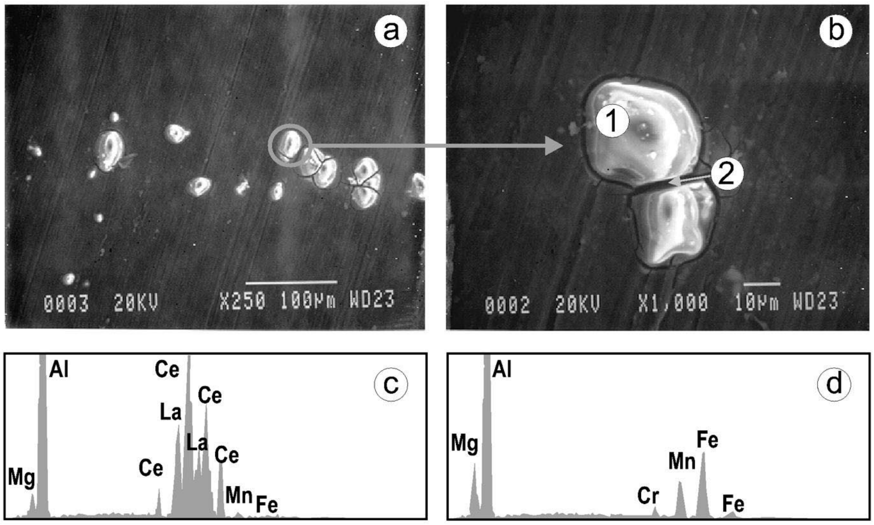

Fig. 4. (a) SEM image recorded on a sample of the AA5083 alloy after 2 h of immersion in 250 ppm $CeCl_3$ + 250 ppm $LaCl_3$; (b) high magnification view of one of the nodules observed in (a); (c) EDS spectrum recorded in (1); (d) EDS spectrum recorded in (2).

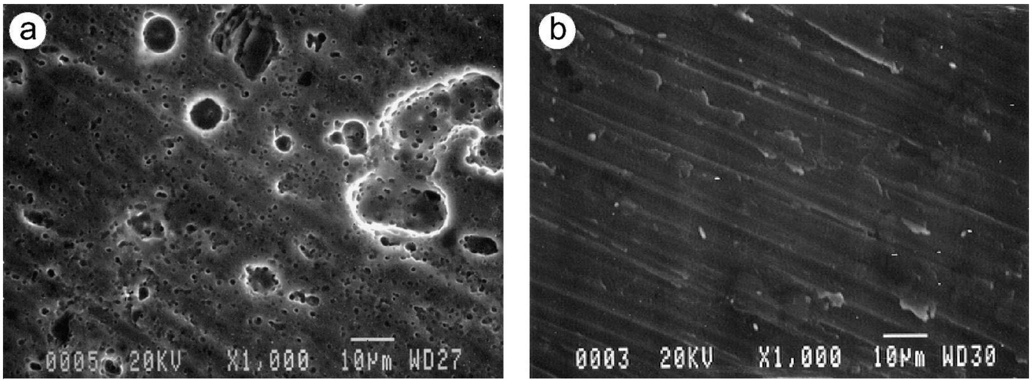

Fig. 5. SEM micrographs, of cleaned AA5083 samples after 30-day full immersion tests in (a) bare NaCl 3.5% solution and (b) doped with 250 ppm $CeCl_3 + 250$ ppm $LaCl_3$.

process, samples coming from long-time full immersion test were examined by SEM. Fig. 5a shows the SEM micrograph presenting the appearance of a sample tested in aerated 3.5% NaCl solution after 30 days of exposure and after a chemical cleaning of the corrosion products. A high density of alkaline pits can be observed. In contrast, no pits are observed in SEM images of samples tested, under the same experimental conditions, in $LnCl_3$ containing solutions (Fig. 5b). This result is in agreement with the result suggested by the weight loss.

4. Conclusions

Full immersion test and electrochemical techniques have been applied in order to evaluate the anticorrosive effects of lanthanide inhibitors. From the whole set of data obtained in this study, it can be concluded that Ce/La binary solutions show a better performance than those containing solely $LaCl_3$ or $CeCl_3$.

The protection factors against corrosion obtained from linear polarisation data in doped solutions with cerium or lanthanum are of the same order as those found with classical Cr(VI)-based compounds, being much higher when using a mixture of 250 ppm $CeCl_3$ and 250 ppm $LaCl_3$.

As a consequence, a synergistic effect seems to exist when cerium and lanthanum ions act simultaneously as inhibitors. SEM and EDS techniques were used to get further microstructural and analytical information about the inhibition process.

However, further studies are necessary to gain complete understanding of the origin and mechanism of this synergism.

Acknowledgements

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