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High protective, environmental friendly and short-time developed conversion coatings for aluminium alloys

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Abstract

There are a variety of procedures, described in the bibliography, for producing conversion coatings using salts of lanthanide elements, and the coatings obtained by means of some of these procedures show acceptable levels of protection. Nevertheless, the principal limitation usually presented by these procedures is the excessively prolonged treatment times required to achieve such levels of protection. This therefore limits the applicability of these treatments on an industrial scale.

Coatings on the alloy AA5083 obtained by using Ce(III) are characterised by having a mixed or heterogeneous nature, being composed of a layer of alumina covering the matrix, together with islands of cerium formed over the cathodic intermetallics that are present on the surface of the alloy. The results obtained indicate that, once these precipitates have been covered, the level of protection provided is conditional upon the thickness of the layer of alumina.

In this study, a procedure is proposed for obtaining conversion coatings on the alloy AA5083 based on immersion in solutions of Ce(III) at temperatures higher than ambient. By this means, coatings can be produced in only a few minutes, and of such quality that salt fog tests of 168 h duration are successfully passed. Furthermore, studies conducted employing electrochemical techniques of linear polarisation indicate that the degree of protection provided by these coatings is several orders of magnitude superior to that achieved with other treatments. © 2002 Published by Elsevier Science B.V.

Keywords: Corrosion protection; AA5083; NaCl; Conversion coatings; Cerium

1. Introduction

Three types of intermetallic compound, identified as Al(Mn, Fe, Cr), Al(Si, Mg) and a β -phase of Al–Mg, are present in the Al–Mg alloy AA5083 [1–3]. The corrosion behaviour of this alloy in aerated solutions of NaCl is conditioned by the presence and surface distribution of the first of the intermetallics

cited [1–8]. Thus, when a sample of alloy AA5083 is exposed to an aerated solution of NaCl at 3.5%, the main corrosion process that takes place on the surface of the alloy is localised alkaline corrosion (LAC) in the area immediately surrounding the Al(Mn, Fe, Cr) precipitates that act as permanent cathodes, without the rest of the precipitates being affected [1,4,9]. Taking place simultaneously with the LAC process is a second, consisting of the formation of a protective layer of oxide over the metal matrix, that increases in thickness with time of exposure [1,4].

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Accordingly, the design of an effective system of protection against the corrosion of alloy AA5083 in solutions of NaCl must be aimed at minimising the cathodic process that occurs around the Al(Mn, Fe, Cr) intermetallics. Therefore one way of approaching such a design could be based on the use of cathodic inhibitors. Lanthanide salts are known to be inhibitors of this type, and have proved successful in inhibiting corrosion of various metallic alloys in NaCl solutions. These salts have been applied in the development of conversion coatings for different metallic materials [10–16].

In previous studies [6,17–24], the efficacy of various lanthanide salts has been demonstrated in the protection of alloy AA5083 against corrosion in solutions of NaCl. The objective of these studies was not only the development of a system of protection based on a mechanism of cathodic inhibition, but also to provide, at the same time, a non-contaminating alternative to Cr(VI) compounds [25–27]. Further, the mechanism of inhibition of the Ln^{3+} cations was confirmed in these studies. Basically, the mechanism comprises two stages. In the first, a lanthanide compound is formed as a result of the reaction of the cation with the OH^- ions generated in the cathodic reaction that takes place over the precipitates of Al(Mn, Fe, Cr). This compound is highly insoluble, therefore in a second stage, it precipitates over the intermetallic compounds, blocking the reaction of cathodic reduction of oxygen and, consequently, preventing the LAC process.

2. Cerium conversion coatings on alloy AA5083: a survey

In the previous studies cited, different procedures have been used to obtain conversion coatings based on lanthanide elements on alloy AA5083. In the following, brief comments are made on the procedures employed up until now, and on the results obtained. These have been taken as the point of departure for the design of the protection systems presented in this study.

Articles referenced [24,28] analyse the protective behaviour of the coatings obtained by full immersion treatments of alloy AA5083 in aerated solutions of Ce(III) salts. According to the results obtained in these

studies, during the process of immersion a mixed coating is developed; this coating consists of dispersed islands of high cerium content located over and covering the cathodic intermetallics, together with a layer of aluminium oxide that covers the rest of the metallic matrix. Electrochemical data presented in these studies show that the thickness of the alumina layer formed during these treatments is less than that formed by the simple immersion of the samples in a solution of NaCl for the same period of time.

This difference in the thickness of the oxide layer obtained from treatments with cerium salt can be explained as the consequence of the precipitates of cerium deposited over the intermetallics of Al(Mn, Fe, Cr) blocking the cathodic reaction and, subsequently also blocking the associated anodic reaction that is responsible for the formation of the oxide layer covering the matrix. Despite this, the mixed coating produced in the immersion treatments in the salt of Ce(III) gives high protection because, following these treatments, the entire surface of the material is covered. The results presented in [24,28] allow to conclude that this mixed coating developed inhibits the activity of the system by a factor close to 25. The resistance of the mixed coating produced is 42 times greater than that corresponding to layer obtained in NaCl.

However, the best results obtained in [24,28] require a minimum treatment time of 2 days duration, which makes them unviable on an industrial scale. With the objective of reducing working times, in [24] procedures are proposed based on the electrochemical activation of the system by means of the application of cathodic currents for periods of time not exceeding 90 s in solutions of CeCl_3 . By means of such treatments, a reduction of the activity of the system by a factor of nearly 3 and an increase of the resistance of the coating by a factor of more than 4 were achieved. These levels of protection may be considered acceptable, given the short duration of the treatments. Nevertheless, the analysis of the samples treated demonstrated that this type of process inhibits the growth of the film of alumina, hence it can only be considered an intermediate stage within a wider process for producing protective coatings based on cerium.

To summarise, the results presented in [28] show that using electrochemical activation treatments it is

possible to reduce working times involved. But due to the insufficient thickness of the alumina film produced, the level of protection does not increase, and actually decreases if it is compared with the obtained by full immersion treatments.

Thermal activation has been applied by other authors in order to accelerate the development process of lanthanide conversion coatings [26,29–31]. However, neither data nor studies about the mixed nature of the coatings have been found in literature. Even more, some authors consider the cerium conversion coating only as the cerium island deposited over the cathodic intermetallics [15].

The present study describes the results obtained from characterising coatings obtained by treatments of immersion in solutions of Ce(III) at temperatures exceeding ambient. On the one hand, by means of these treatments the LAC process can be blocked by the immediate formation of Ce(III) precipitates over the intermetallics present in the alloy, and on the other, the rate of growth of the oxide layer over the metal matrix can be increased by means of thermal activation with the objective of achieving high levels of protection with treatments of reduced time duration.

3. Experimental

To conduct this study samples of $30 \times 25 \times 4 \text{ mm}^3$ size of alloy AA5083 were employed. The composition of this alloy in percentage mass terms is given in Table 1. Before being treated, the samples were polished using SiC paper to a finish of 500 grits. Then they were degreased with ethanol and cleaned carefully with distilled water. Aqueous aerated solutions of $\text{Ce}(\text{NO}_3)_3$ and CeCl_3 0.005 M, at temperatures ranging from 298 to 363 K, were used for the immersion treatments. The pH value of both solutions was adjusted around 5.5.

The surface aspect of the layers produced was studied by scanning electron microscopy using a JEOL 820-SM instrument. Their composition was

Table 1
Composition of the alloy AA5083 (% by mass)

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

analysed by energy dispersive spectroscopy (EDS) in an AN-10000 LINK spectrometer connected to the microscope used.

The corrosion resistance of the samples treated was evaluated by means of electrochemical techniques of linear polarisation and polarisation resistance, in an aerated solution of NaCl at 3.5%. Measurements were made in a K235 flat cell of Parc EG&G, using an SI 1287 potentiostat of Solartron. The reference electrode used was a Ag/AgCl electrode of Crison (0.207 mV/SHE). Two parameters have been used to determine the degree of protection provided by each treatment.

First, the activity of the samples treated by immersion in the solution of Ce(III), in the solution of NaCl has been analysed from the value of the polarisation resistance, R_p . In this case, the degree of protection has been evaluated by comparing the value of this resistance with that corresponding to an untreated sample, R_p^0 , from the parameter:

$$\Delta R_p = \frac{R_p}{R_p^0} \quad (1)$$

Second, as described in [28], the value of the slope, R_{cp} , of the passivity section of the anodic branch of the linear polarisation curve is proposed as a measure of the degree of coverage of the mixed layer. From this value, the protection provided by this layer can be evaluated in terms of its increase in comparison with the value corresponding to that obtained for the untreated samples, R_{cp}^0 , in accordance with the expression:

$$\Delta R_{cp} = \frac{R_{cp}}{R_{cp}^0} \quad (2)$$

Lastly, the validity of this type of treatment on an industrial scale has been confirmed by its behaviour under salt fog tests [32]. In this standard, it is considered that a protective treatment is acceptable if it exceeds 168 h of exposure to the saline atmosphere. For this reason, the samples treated in this study were subjected to salt fog tests of 168 h duration, in accordance with the ASTM standard B-117 [32].

4. Results and discussion

Fig. 1 shows the SEM image obtained of a sample of alloy AA5083 after 2 days of immersion in a solution

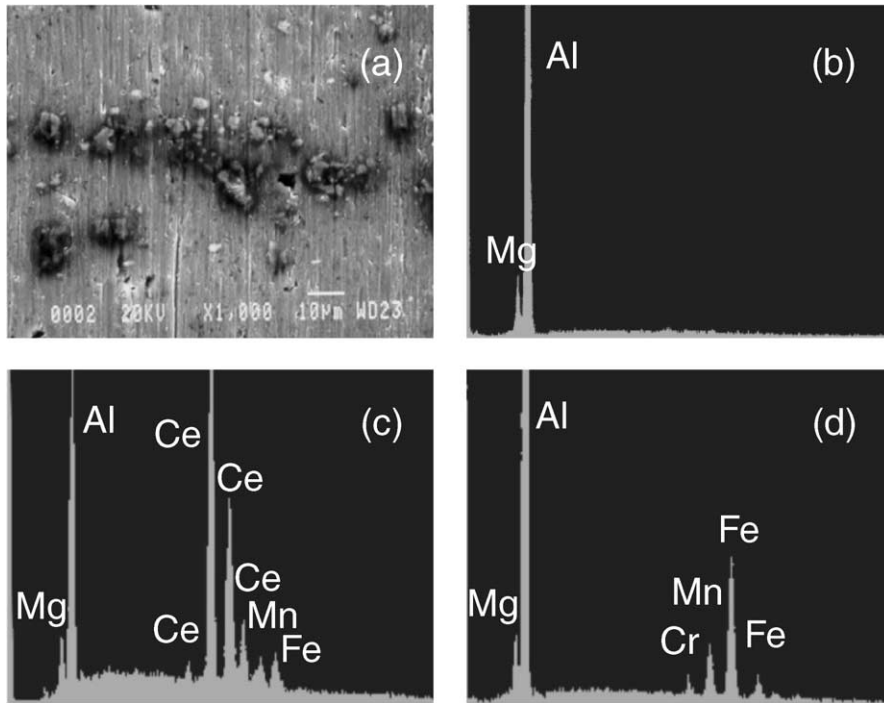


Fig. 1. (a) SEM image of a sample of AA5083 alloy after 2 days of immersion in a 500 ppm of CeCl_3 solution at 298 K; (b) EDS spectrum acquired on metallic matrix; (c) EDS spectrum acquired on a Ce island; and (d) EDS spectrum acquired on an intermetallic particle under a cerium island.

of 500 ppm of CeCl_3 . As can be appreciated, the immersion treatment gives rise to the formation of a mixed coating consisting of dispersed islands rich in cerium, situated over the cathodic precipitates of $\text{Al}(\text{Mn}, \text{Fe}, \text{Cr})$, and a film of aluminium oxide covering the metal matrix. In agreement with the results obtained in [28], this coating confers on the alloy a high degree of protection against corrosion in solutions of NaCl at 3.5%. However, as previously commented, the long duration of these treatments make them unviable industrially. Therefore, with the aim of reducing the treatment times, and on the basis of the mechanism of protection analysed in [28], in this study the design of these treatments has been modified by varying the temperature of the system. Thus samples of the alloy AA5083 have been treated by immersion in separate solutions of CeCl_3 and $\text{Ce}(\text{NO}_3)_3$ at different temperatures ranging from 298 to 363 K.

Fig. 2 includes SEM images corresponding to samples of alloy AA5083 after 5 min of immersion in a solution of $\text{Ce}(\text{NO}_3)_3$ at 363 K. As can be appreciated

in this figure, the surface appearance of the samples after this treatment is similar to that observed in the case of immersion treatments at room temperature. The EDS analysis of the various different zones making up the total surface provide confirmation that the mixed coating produced in these treatments also presents a composition similar to that generated by the full immersion treatments at room temperature (Fig. 2).

In order to assess the degree of protection afforded by the coatings produced, the treated samples were subjected to linear polarisation tests in a solution of NaCl at 3.5%. Figs. 3 and 4 present the linear polarisation curves obtained in the NaCl solution for samples treated at various temperatures and for various times of immersion in the solutions of CeCl_3 and $\text{Ce}(\text{NO}_3)_3$, respectively. As a first reference, included in each figure are the curves corresponding to an untreated sample, and samples treated in the same conditions in NaCl and NaNO_3 . As it can be observed, sample treatments in the later solutions have not

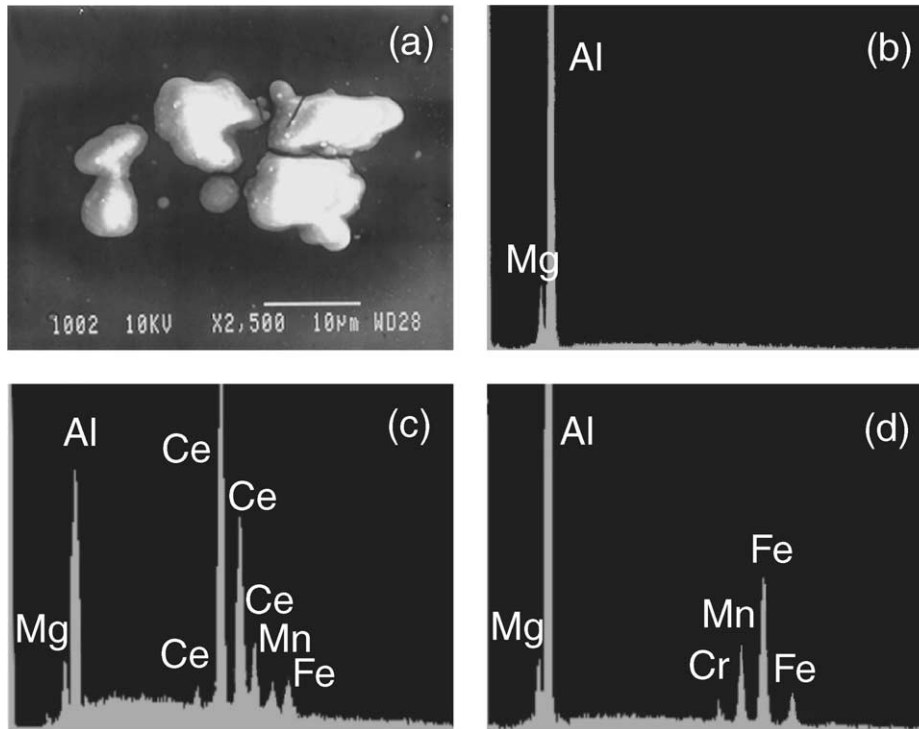


Fig. 2. (a) SEM image of a sample of AA5083 alloy after 5 min of immersion in a 0.005 M of $\text{Ce}(\text{NO}_3)_3$ solution at 363 K; (b) EDS spectrum acquired on metallic matrix; (c) EDS spectrum acquired on a Ce island; (d) EDS spectrum acquired on an intermetallic particle under a cerium island.

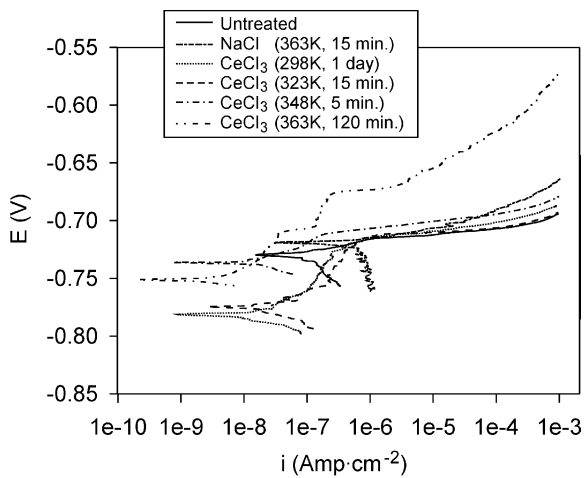


Fig. 3. Linear polarisation curves corresponding to AA5083 samples treated by full immersion in a 0.005 M of CeCl_3 solution at the indicated temperatures and time periods. Samples tested in 3.5% NaCl solution.

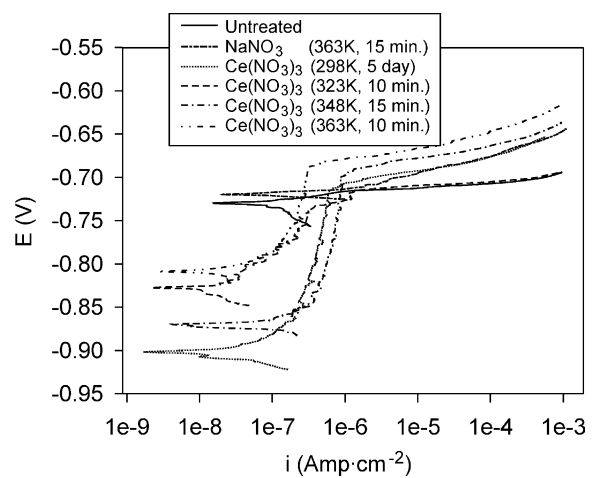


Fig. 4. Linear polarisation curves corresponding to AA5083 samples treated by full immersion in a 0.005 M of $\text{Ce}(\text{NO}_3)_3$ solution at the indicated temperatures and time periods. Samples tested in 3.5% NaCl solution.

Table 2

Electrochemical parameters obtained from LP curves acquired in NaCl on AA5083 samples treated in CeCl_3 at the indicated temperatures and time periods

Treatment	T (K)	t (h)	R_p (k Ω)	ΔR_p	R_{cp} (k Ω)	ΔR_{cp}
–	298	0	27.72	1	16.131	1
CeCl_3	298	24	258.9	9.34	173.940	10.78
		48	326.5	11.78	478.710	29.68
		120	455.9	16.45	626.060	38.81
	323	0.08	63.647	2.30	18.341	1.14
		0.17	144.87	5.23	93.381	5.79
		0.25	153.31	5.64	105.320	6.53
		0.50	105.94	3.82	68.505	4.25
		1.00	90.38	3.26	78.256	4.85
		2.00	51.26	1.85	30.228	1.87
	348	0.08	144.12	5.20	107.810	6.68
		0.17	66.71	2.41	142.370	8.85
		0.25	90.123	3.25	71.638	4.44
		0.50	67.92	2.45	65.223	4.04
		1.00	65.74	2.37	60.352	3.74
		2.00	3667.8	132.32	4483.120	277.92
	363	0.08	88.17	3.18	123.160	7.64
		0.17	103.35	3.73	282.530	17.51
0.25		47.26	1.70	75.882	4.70	
0.50		33.70	1.22	40.580	2.52	
1.00		193.66	6.99	23.777	1.47	
2.00		980.01	35.35	2340.600	145.10	
NaCl	323	0.25	12.314	0.444	–	–
	348	0.25	11.496	0.414	–	–
	363	0.25	5.257	0.190	–	–

protective effects. Even more, a decrease of R_p values was observed (Tables 2 and 3), leading to ΔR_p values lower than 1, determined through Eq. (1). On the other hand, their anodic curves do not show a passivity region. Thereby, R_{cp} cannot be measured. The negative effect of this type of treatment can be better understood by analysing the corresponding SEM images (Fig. 5). Images include in this figure correspond to the above-mentioned samples after descaling. Samples treated in both NaCl and NaNO_3 solutions show evidence of localised alkaline corrosion (Fig. 5(a) and (b)). Summarising, thermal activate treatments in NaCl or NaNO_3 cannot be used as reference because they active the production of damage in the samples.

As can be appreciated in Figs. 3 and 4, the treated samples in CeCl_3 and $\text{Ce}(\text{NO}_3)_3$ present a similar behaviour in both cases. On the one hand, a reduction of the corrosion potential, E_{corr} , is observed, compared with that measured for the untreated samples. Equally,

in the linear polarisation curves obtained for the treated samples, a displacement can be observed of the current density towards lower values, relative to the curve obtained for the untreated samples. This finding is indicative of a decrease in the electrochemical activity of the system.

The values of R_p obtained from the linear polarisation curves for each of the treatments applied are shown in Tables 2 and 3. The value of ΔR_p has been determined from the R_p values by applying the expression (1), for each of the treatment conditions applied. This value is indicative of the degree of protection provided to the alloy by the mixed coating, and represents the reduction of the activity of the system [1,28]. Fig. 6 gives a comparison of the values of ΔR_p for each of the treatments tested. As it can be observed, for the employment of either CeCl_3 or $\text{Ce}(\text{NO}_3)_3$, the best results are obtained for treatments of 120 min duration, at 348 K. When CeCl_3 is employed, an increase of the resistance of polarisation by a factor

Table 3

Electrochemical parameters obtained from LP curves acquired in NaCl on AA5082 samples treated in $\text{Ce}(\text{NO}_3)_3$ at the indicated temperatures and time periods

Treatment	T (K)	t (h)	R_p (k Ω)	ΔR_p	R_{cp} (k Ω)	ΔR_{cp}
–	298	0	27.72	1	16.131	1
$\text{Ce}(\text{NO}_3)_3$	298	24	179.24	6.47	71.990	4.46
		48	401.91	14.83	413.700	25.64
		120	270.71	9.77	287.980	17.85
	323	0.08	174.33	6.29	43.660	2.71
		0.17	315.54	11.38	115.780	7.18
		0.25	170.56	6.15	90.020	5.58
		0.50	154.65	5.58	31.530	1.95
		1.00	185.20	6.68	78.090	4.84
		2.00	248.89	8.98	68.230	4.23
	348	0.08	181.2	6.54	344.410	21.35
		0.17	143.8	5.19	172.330	10.68
		0.25	136.8	4.94	261.600	16.22
		0.50	173.9	6.27	252.120	15.63
		1.00	135015	4870.68	138563.0	8589.86
		2.00	343104	12377.5	180755.0	11205.4
	363	0.08	66.00	2.38	36.085	2.24
		0.17	269.4	9.72	477.070	29.57
		0.21	23557.9	849.85	23693.0	1468.79
0.25		173961	6275.65	192462.0	11931.2	
0.50		48223.7	1739.67	135421.0	8395.08	
1.00		34785.0	1254.87	95402.0	5914.20	
2.00		98223.4	3543.41	84401.01	5232.22	
NaNO_3	323	0.25	10.286	0.371	–	–
	348	0.25	6.354	0.229	–	–
	363	0.25	4.334	0.156	–	–

of 135 is achieved. Even more notable are the results obtained for the samples treated in $\text{Ce}(\text{NO}_3)_3$, for which an increase in the resistance of the system by a factor higher than 12 000 is achieved. These results are extraordinarily superior to those obtained in [24,28] for full immersion treatments applied at room temperature. Thus, an increase in efficacy by a factor of 5 is achieved in the thermally activated immersion treatments in CeCl_3 , and by a factor of 500 in those employing $\text{Ce}(\text{NO}_3)_3$. This contrasts with the optimum results of full immersion treatments at room temperature, that were obtained for a treatment time of 2 days [24,28]. Consequently, the thermal activation of the immersion treatments not only produces coatings with far superior protection properties but also achieves these optimum values of protection with treatment times that are 20 times shorter.

However, this time is 120 min, and this, together with the cost of the thermal energy required for the process, makes it industrially unattractive. But if the values given in Table 3 are analysed, it can be observed that, even for shorter duration times, immersion treatments at 363 K using $\text{Ce}(\text{NO}_3)_3$ offer a considerable improvement in the behaviour of the system in comparison with immersion treatments at room temperature.

In fact, as can be observed, from treatment times of 10 min, levels of protection are achieved that are more than 100 times superior to those obtained for samples treated by full immersion at room temperature. With the objective of “fine-tuning” for the optimum treatment time, tests have been conducted in $\text{Ce}(\text{NO}_3)_3$ at 363 K for 12.5 min duration. The samples treated for this time presented a value for ΔR_p close to 850, which means an improvement by a factor of close to 40

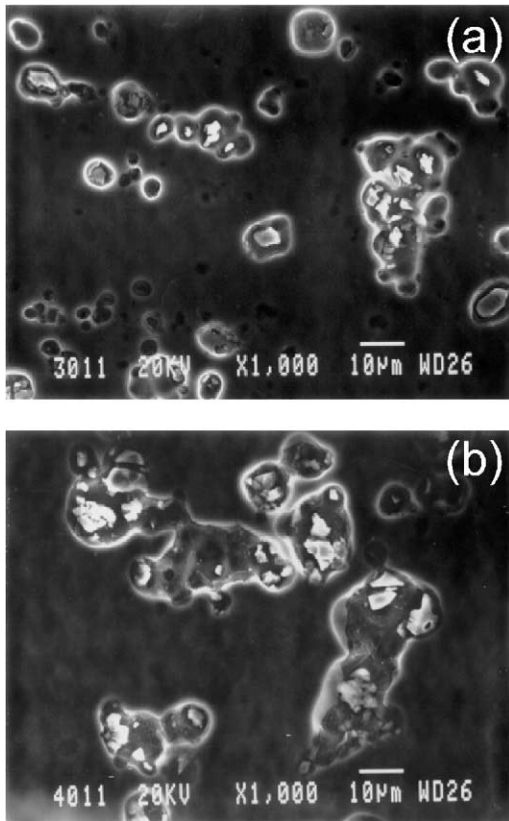


Fig. 5. SEM images of descaled samples of AA5083 alloy after 5 min of immersion at 363 K in: (a) 0.005 M of CeCl_3 solution and (b) 0.005 M of $\text{Ce}(\text{NO}_3)_3$ solution.

relative to immersion treatments at room temperature, but in a period of time 200 times shorter. This considerably increases the attraction of the treatment for industrial purposes.

According to the results obtained in [24,28], the long time duration of the immersion tests at room temperature is basically due to the slow rate of formation of the layer of alumina covering the matrix. In contrast, as demonstrated in [6,17,18,21], the islands of cerium are formed in the first instants of immersion in the solution containing Ce(III). Consequently, the results obtained for the samples treated by immersion with thermal activation indicate that by increasing the temperature, the formation of the layer of aluminium oxide on the metal matrix is encouraged.

As previously commented, in [28] R_{cp} is proposed as a measure of the degree of coverage of the mixed

coating provided by the immersion treatments performed at room temperature. Given the conversion coatings with a similar morphology are produced using the treatments studied in these tests, this parameter has been employed for the evaluation of the resistance of the mixed coatings deposited using immersion treatments with thermal activation. The values of R_{cp} are given in Tables 2 and 3. From these values, using the expression (2), the value of ΔR_{cp} has been determined for each case (Tables 2 and 3); this value indicates the degree of protection provided as a result of the increase of the resistance of the coating. In Fig. 7, the values for ΔR_{cp} obtained for each of the treatments studied are compared. As can be appreciated, there exists a good correlation between these values and those corresponding to ΔR_{p} , to the same extent as was observed in [28] for the immersion treatments. Thus, whether employing CeCl_3 or $\text{Ce}(\text{NO}_3)_3$, the best results are obtained for treatments of 120 min at 348 K. In the case of CeCl_3 , an increase of the resistance of the mixed coating by a factor of about 275 is achieved, whereas employing $\text{Ce}(\text{NO}_3)_3$, the increase of this resistance achieved is by a factor in excess of 11 000. As commented before, the length of treatment time is almost certainly excessive for the industrial application of these treatments. Thus, it would seem more practical to consider treatments of immersion in $\text{Ce}(\text{NO}_3)_3$ at 363 K of shorter duration time, in accordance with the results given in Table 3. By applying treatments of 15 min, an improvement in the resistance of the coating by a factor of 300 is achieved, compared with room temperature treatment. Similarly, samples treated for 12.5 min in $\text{Ce}(\text{NO}_3)_3$ at 363 K showed an improvement in the resistance of the coating by a factor of about 30; this is some 1500 times better than the untreated samples.

Finally, with the objective of verifying the protective character of the coatings produced by the selected immersion treatments with thermal activation, the samples treated by immersion in the solution of $\text{Ce}(\text{NO}_3)_3$ at 363 K were subjected to salt fog tests of 168 h. Fig. 8 shows the macrographs corresponding to these samples after conducting these salt mist tests. As a reference, also shown is the macrograph corresponding to an untreated sample before and after being subjected to this type of test. As can be appreciated, no signs of corrosion are evident in the treated samples.

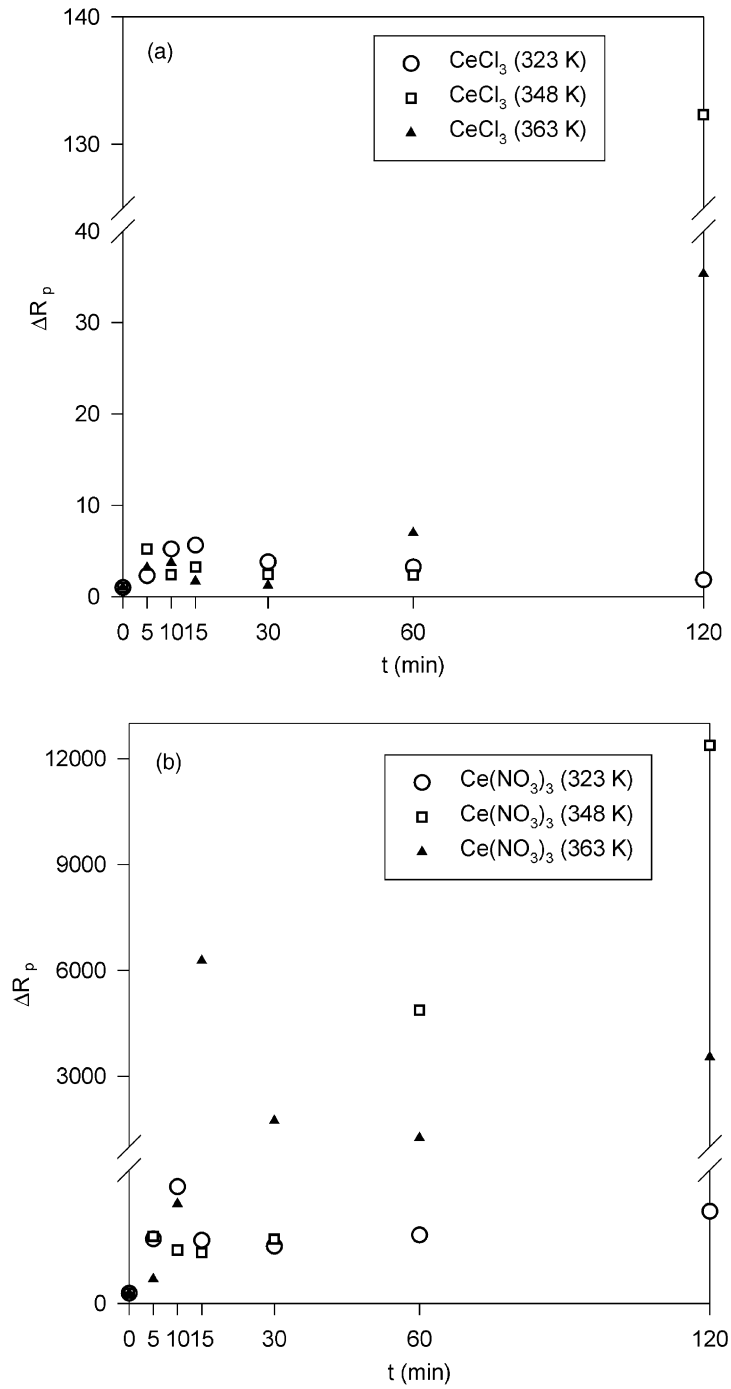


Fig. 6. Evolution of ΔR_p parameter with the time of treatment, at the indicated temperatures, in: (a) 0.005 M of CeCl_3 solution and (b) 0.005 M of $\text{Ce}(\text{NO}_3)_3$ solution.

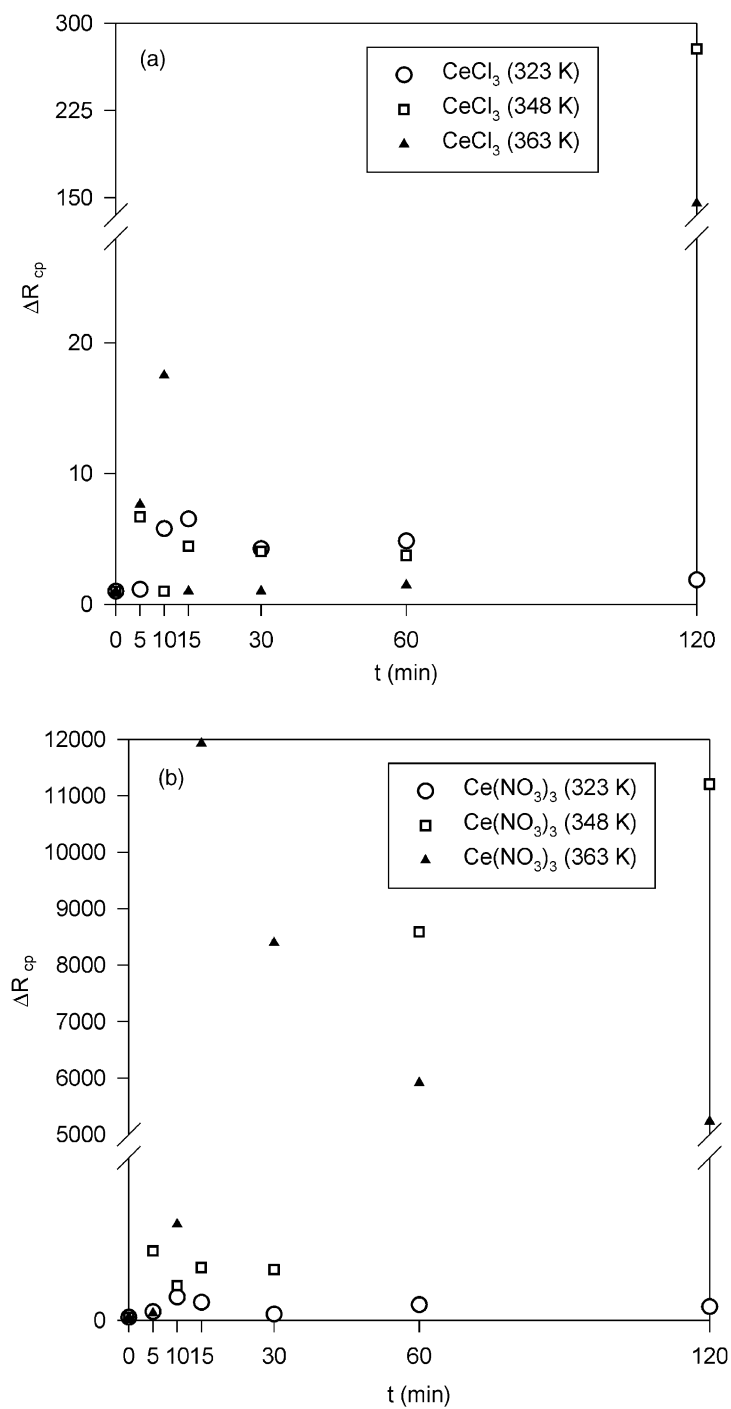


Fig. 7. Evolution of ΔR_{cp} parameter with the time of treatment, at the indicated temperatures, in: (a) 0.005 M of $CeCl_3$ solution and (b) 0.005 M of $Ce(NO_3)_3$ solution.

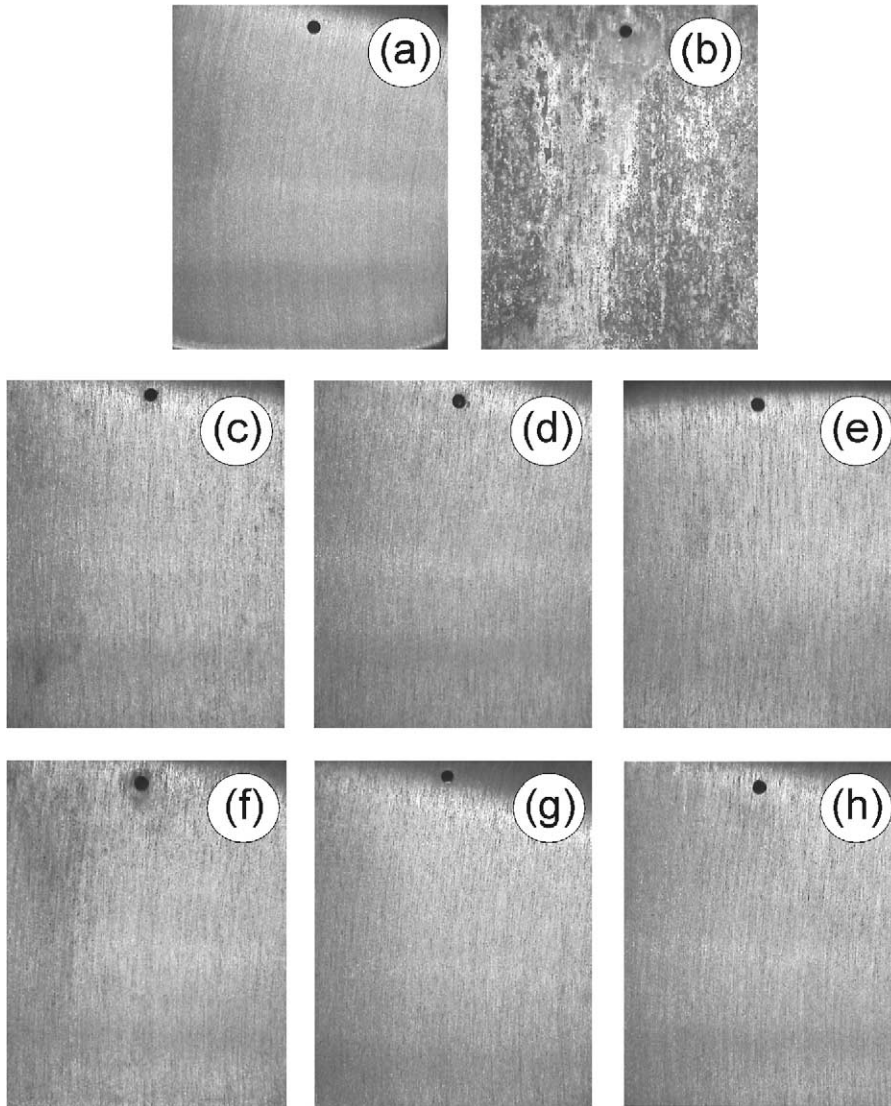


Fig. 8. (a) Macrograph corresponding to an untreated AA5083 sample. Macrographs corresponding to AA5083 samples tested during 168 h in salt fog chamber pretreated in the following conditions: (b) untreated; full immersion treated in 0.005 M $\text{Ce}(\text{NO}_3)_3$ solution during (c) 5 min, (d) 10 min, (e) 15 min, (f) 30 min (g) 60 min and (h) 120 min.

5. Conclusions

The treatment of samples of alloy AA5083 by immersion in solutions of Ce(III) lead to the formation of a mixed coating consisting of islands of cerium situated over the intermetallic compounds of cathodic character, and a film of alumina that covers the metal matrix. When these treatments are

applied at room temperature, the optimum time of treatment is conditioned by the relatively slow rate of formation of the oxide film over the matrix. This requires 2 days of treatment to obtain acceptable levels of protection.

The thermal activation of the solution of Ce(III) produces a much faster rate of growth of the oxide film and a higher degree of coverage of the mixed coating,

thus providing a greater level of protection than treatments applied at room temperature.

When the treatments are applied at 363 K for 12.5 min in a solution of $\text{Ce}(\text{NO}_3)_3$, a decrease in the activity of the system by a factor of nearly 850 and an increase in the resistance of the mixed coating by a factor close to 1500, are achieved. These results are notably better than those obtained at room temperature, and more significantly are achieved with a reduction in the treatment time by a factor of 200.

Lastly, the samples treated under these conditions have passed the salt fog tests. This proof of efficacy, considered with the very short treatment time required, makes such treatments much more attractive and potentially viable on an industrial scale.

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