Combination of thermal activation and addition of H_2O_2 to improve cerium-based immersion treatment of alloy AA5083

Kombination von thermischer Aktivierung und Zugabe von H_2O_2 zur Verbesserung der auf Cer-basierten Tauchbehandlung der Legierung AA5083

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Intensive research has been undertaken in recent years aimed at finding non-contaminating alternatives to surface treatment processes based on the use of chromates. One of the alternatives proposed involves the use of lanthanide salts, and a variety of methods of protection have been described. In this study, the results of the treatment of samples of alloy AA5083 in a solution of Ce(III) at 323 K and incorporating small quantities of oxygenated water are presented. These results indicate that the application of this type of treatment gives a considerable reduction in the time required for this process and high levels of protection. This time reduction is associated with a combined effect caused, in part by the presence of oxygenated water, which facilitates the formation of islands of cerium, and in part by thermal activation, which facilitates a more rapid development of the alumina film over the metal matrix. Lastly, the results obtained indicate that these treatments provide increased resistance of the alloy against pitting corrosion.

In den letzten Jahren wurde intensive Forschung durchgeführt, um geeignete Alternativen für Oberflächenbehandlungsprozesse, die auf dem Einsatz auf Chromat basieren, zu finden. Eine der vorgeschlagenen Alternativen beinhaltet den Einsatz von Lanthanidsalzen. Hierzu sind eine Reihe von Schutzmethoden beschrieben worden. In der vorliegenden Arbeit werden die Ergebnisse der Behandlung von Proben der Legierung AA5083 in einer Ce(III)-Lösung und Zugabe geringer Mengen an H_2O_2 bei 323 K beschrieben. Die Ergebnisse zeigen, dass die Anwendung dieser Art der Behandlung zu einer beträchtlichen Reduzierung der erforderlichen Zeit für diesen Prozess führt und hohe Schutzeffekte liefert. Diese Zeitreduzierung ist verbunden mit einem kombinierten Effekt, der zum Teil durch die Anwesenheit des H_2O_2 verursacht ist, was die Bildung von Cerinseln erleichtert, um zum Teil durch thermische Aktivierung, was eine schnellere Entwicklung des Aluminiumoxidfilms über der Metallmatrix erleichtert. Außerdem zeigen die erzielten Ergebnisse, dass diese Behandlungen einen erhöhten Widerstand der Legierung gegenüber Lochkorrosion liefern.

1 Introduction

In recent years all sectors of industry have been obliged to re-orientate their operational philosophy towards the use of processes that are not aggressive to the natural environment [1]. One of the productive sectors most affected by new, stricter standards and regulations in respect of environmental protection is that of the surface treatment of metal alloys [2]. In this process area, there has for some years now been intensive research undertaken to find environmentally-friendly alternatives to surface treatment processes based on the use of chromates [3–5], since the high toxicity and contaminating power of chromates has now been convincingly demonstrated [3, 6–9].

For the protection of aluminium alloys in particular against corrosion, chromates have traditionally been employed as inhibitors, as pigments in formulation paints, as conversion coatings and as anodising or sealing baths [3, 7, 10, 11]. However, according to [4], the lack of basic knowledge about the mechanism of corrosion protection provided by chromates makes it difficult to develop new systems of protection for aluminium and its alloys on a firm theoretical basis. This situation is made even worse if no prior detailed study is made of the mechanism of corrosion of the alloy for which protection is required. In consequence, at the present time, the great majority of alternative systems proposed are only supported on essentially empirical bases.

This study presents a non-contaminating alternative for the application of anti-corrosive coatings based on the employment of lanthanide elements on the aluminium-magnesium alloy AA5083. To follow the approach already outlined, in the second section we present, briefly, the results previously obtained from a study of the corrosion behaviour of alloy

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AA5083 in solutions of NaCl at 3.5%. Then follows a description of some of the procedures previously tested for the application of conversion coatings on alloy AA5083 using treatment baths with lanthanide compounds. Finally, taking these antecedents into account, the results obtained in the characterization of coatings prepared from solutions containing cerium salts and hydrogen peroxide, when the treatments are performed with thermal activation, are presented and discussed.

2 Antecedents

The principal corrosion process affecting alloy AA5083 in aerated solutions of NaCl at 3.5% is localized alkaline corrosion (LAC) taking place around certain intermetallic precipitates identified as Al(Mn,Fe,Cr), which act as permanent cathodes, but without the other types of precipitate present being affected [12–17]. Simultaneously with the LAC process, a second process takes place consisting of the formation of a protective layer of oxide over the metal matrix; the thickness of this layer increases with time of exposure [12, 14], Fig. 1. Given this, the design of an effective system of protection against the corrosion of alloy AA5083 in solutions of NaCl must be aimed at minimizing the cathodic process occurring around the Al(Mn,Fe,Cr) intermetallics. Therefore such a design should be based on the employment of cathodic corrosion inhibitors. Lanthanide salts are among the various types of such inhibitors. Their inhibitory capability has been sufficiently proven for a wide variety of metal alloys in solutions of NaCl [18–23], and they have been utilized in the application of conversion coatings on this type of alloy [24–29]. Further, the use of this class of substance does not represent any toxic or environmental risk [3].

In [30, 31], studies were performed of the protective effect obtained from treatments of alloy AA5083 immersed in aerated solutions of salts of Ce(III). According to the results obtained in these studies, during the process of immersion in the lanthanide salt, a mixed surface layer is produced, formed by dispersed islands with a high content of cerium, located over the cathodic intermetallics, and a layer of aluminium oxide that covers the rest of the matrix. The thickness of this oxide layer is less than that observed for untreated samples submerged in NaCl, because the precipitates of cerium deposited over the Al(Mn,Fe,Cr) intermetallics block the cathodic reaction and, as a result, the associated anodic reaction responsible for the formation of the oxide layer on the matrix, is inhibited. Despite this, the mixed layer produced in these immersion treatments gives a high degree of protection because, following the treatment, the entire surface of the material is left completely covered. From the results obtained in [31], it can be concluded that this layer reduces the activity of the system by a factor of close to 25; and its resistance, in relation to the layer formed in the NaCl solution, increases by a factor of around 40. However, the best results obtained in [31] require a minimum time of treatment of 2 days duration, which is not practical under industrial operating conditions. This duration is related to the time necessary for the alumina layer to form. Therefore, on the basis of these results, new treatments must be developed to enable at least the same levels of protection to be obtained in a much shorter period of time, to make them more useful to industry.

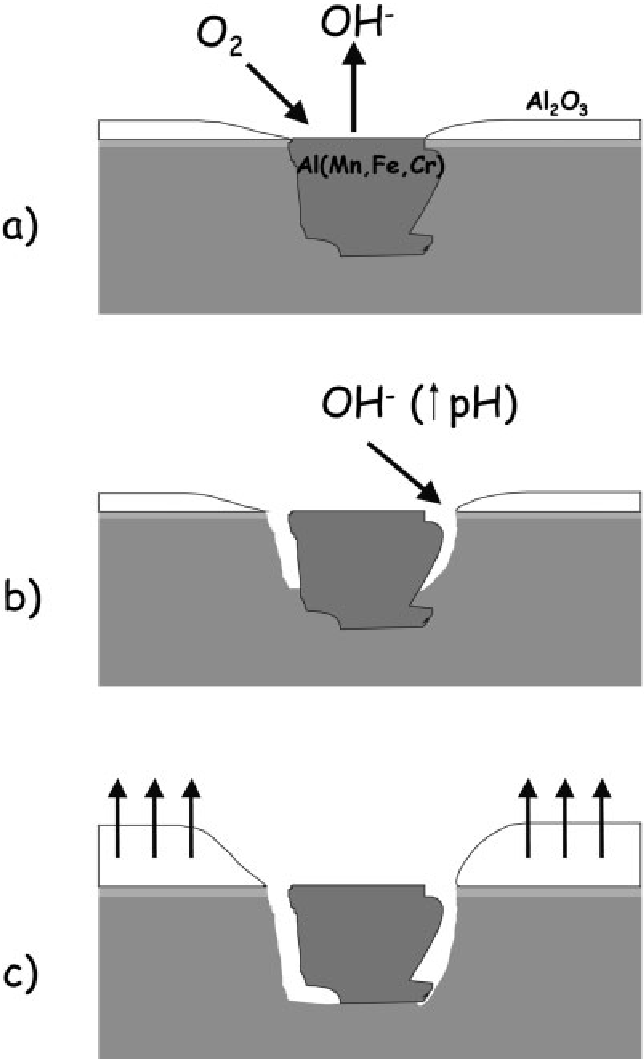

Fig. 1. Corrosion mechanism of AA5083 alloy in NaCl solutions. a) OH^- formation as a consequence of the cathodic reaction on the Al(Mn,Fe,Cr) intermetallic; b) local alkalinisation, aluminium oxide dissolution and local attack in the zone surrounding intermetallic; c) alumina film growth as a consequence of the anodic reaction

Abb. 1. Korrosionsmechanismus der Legierung AA5083 in NaCl-Lösungen. a) OH^--Bildung als Folge der kathodischen Reaktion an der intermetallischen Phase Al(Mn,Fe,Cr); b) lokale Alkalisierung, Aluminiumoxidauflösung und lokaler Angriff der die intermetallische Phase umgebenden Zone; c) Aluminiumoxidfilmwachstum als Folge der anodischen Reaktion

Further studies were performed in [32] of the protection provided by treatments derived from a modification of existing treatments of immersion in solutions of Ce(III); the modification involved the increase of the temperature of the solution during the treatment with the object of encouraging the growth of the alumina film. From the results obtained from this work, it was possible to reduce the time of treatment to only 5 minutes duration, yet achieving levels of protection superior to those given by immersion treatments at ambient temperature. However, a temperature of 363 K was required.

In the study presented here, the results are reported of applying a further modification to the previously described treatment involving thermal activation; this consists of incorporating small quantities of H_2O_2 to the solution of Ce(III), without the need to apply such a high temperature as that previously utilized in these earlier studies. The employment of H_2O_2 facilitates the formation of OH^- and, in consequence, the formation of the precipitates of cerium [33]. The addition of H_2O_2 to the solution of Ce(III) has already been tested by other authors, mainly in immersions treatments at ambient temperature and in electrochemical treatments; their results have demonstrated its efficacy for the protection of different metallic materials in solutions of NaCl [23]. Furthermore, as has already been commented, thermal activation allows a rapid formation of the layer of alumina over the matrix and has been successfully tested both in this alloy [32] and in other aluminium alloys [23]. But most of these require two stages in the treatment, whereas in the method of treatment described here, the effective conversion coating is produced in a single-stage process.

3 Experimental

The samples of alloy AA5083 used in this study were of 30 × 25 × 4 mm in size. The composition of this alloy in percentage mass is given in Table 1. Before being treated, the samples were polished with SiC paper to a finish of 500 grits. They were then degreased with ethanol and washed carefully with distilled water. The solutions employed for the treatments were aerated aqueous solutions of $Ce(NO_3)_3$ 0.005 M, at a temperature of 323 K, to which concentrations of 0.675, 1.250 and 2.500 ml/l of H_2O_2 were added. Treatments of 5, 15 and 30 minutes duration were tested.

The surface appearance of the layers produced were studied by Scanning Electron Microscopy (SEM) in a JEOL 820-SM microscope. The composition of the layer was analysed by Energy Dispersive Spectroscopy (EDS) in an AN-10000 LINK spectrometer connected to the microscope cited.

For the initial study of the corrosion behaviour of the samples treated, salt fog tests of 168 hours duration were carried out, in accordance with ASTM standard B-117 [34].

The protective effect of the treatments tested was evaluated in an aerated solution of NaCl at 3.5%, making use of the electrochemical techniques of Linear Polarization and Resistance of Polarization. These measurements were made using a K235 flat cell of Parc EG&G connected to a SI 1287 potentiostat of Solartron. An Ag/AgCl electrode of Crison (0.207 mV/SHE) was employed as reference electrode.

To determine the degree of protection provided by each treatment, two parameters have been employed. The activity in the NaCl solution of the samples treated in the solution of Ce(III) has been analysed from the value of the Resistance of Polarization, 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:

$$\Delta R_p = \frac{R_p}{R_p^0} \tag{1}$$

Table 1. Composition of the alloy AA5083 (% by mass)
Tabelle 1. Zusammensetzung der Legierung AA5083 (in Mas.-%)

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

Additionally, the value of the slope of the passivity section of the anodic branch of the curve of linear polarization, R_{cp}, has been used to evaluate the resistance of the mixed layer. According to [30–32], this parameter is a measure of the degree of covering achieved by this layer. From its value, the protection due to this layer can be evaluated in terms of its increase over the value corresponding to that obtained for the untreated samples, R_{cp}^0, in accordance with the expression:

$$\Delta R_{cp} = \frac{R_{cp}}{R_{cp}^0} \tag{2}$$

4 Results and discussion

Fig. 2(a,b) shows SEM images corresponding to samples of alloy AA5083 after 15 minutes of immersion in the solution of $Ce(NO_3)_3$ at 323 K with 1.25 ml/l of H_2O_2. The surface appearance of the samples after these treatments is very similar to that observed for the samples treated by immersion at ambient temperature in solutions of Ce(III) [31]. It can be seen that there is a layer that completely covers the surface of the alloy, in which a series of “islands” dispersed over the area of the surface are distinguishable. From the EDS analysis of the different zones comprising this layer, it can be confirmed that it is essentially heterogeneous. In effect, the mixed layer formed in these treatments also presents a similar composition to that generated by the immersion treatments at ambient temperature. The islands detected consist of a cerium compound, Fig. 2(c), that is deposited directly over the cathodic interme-

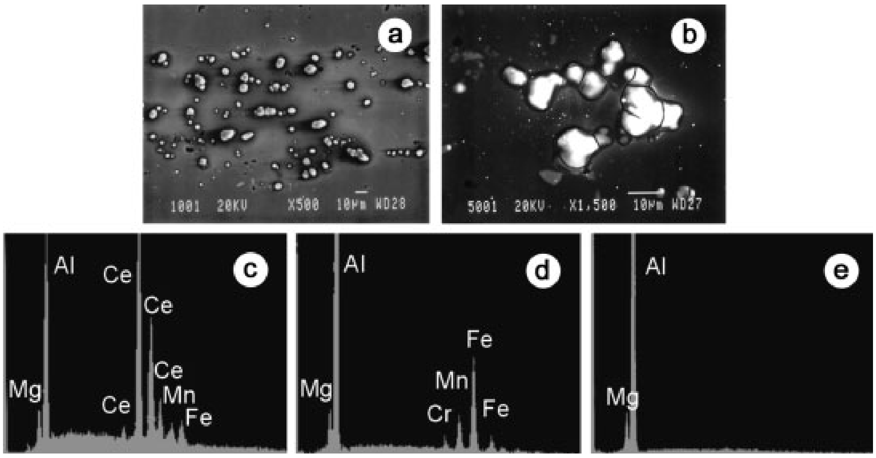

Fig. 2. (a,b) SEM images of AA5083 samples treated 15 minutes in the $Ce(NO_3)_3$ solution at 323 K with 1.25 ml/l of H_2O_2. EDS spectra acquired on (c) dispersed island, (d) substrate under these islands and (e) film covering the metallic matrix

Abb. 2. (a,b) REM-Abbildungen der AA5083-Proben, die 15 Minuten in der $Ce(NO_3)_3$-Lösung bei 323 K mit 1,25 ml/l H_2O_2 behandelt waren. EDS-Spektren auf den dispergierten Inseln (c), auf dem Substrat unter diesen Inseln (d) und auf dem Film, der die metallische Matrix bedeckt (e)

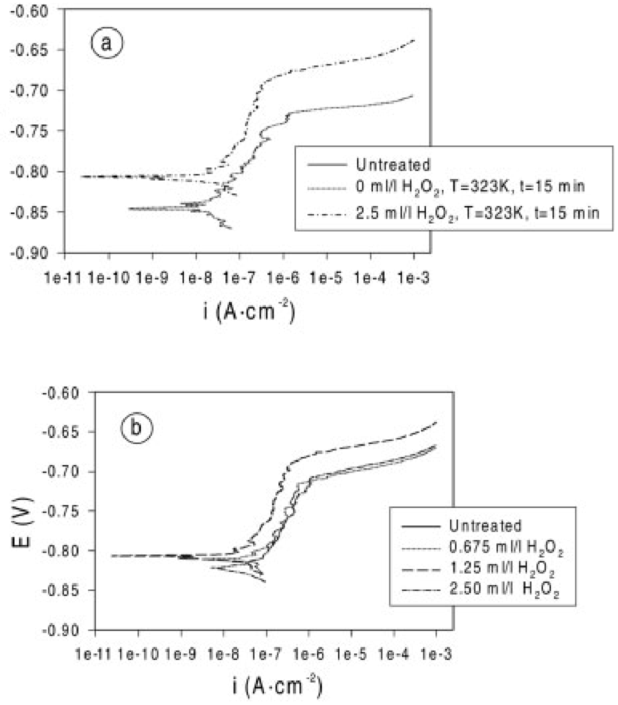

Fig. 3. Different linear polarisation curves acquired on treated samples in the indicated conditions. Aggressive medium: NaCl at 3.5% solution

Abb. 3. Unterschiedliche lineare Polarisationskurven verschieden behandelter Proben. Aggressives Medium: 3.5%ige NaCl-Lösung

tallics found scattered over the surface of the alloy, Fig. 2(d), while the rest of the surface of the metal matrix is covered by a film of aluminium oxide, Fig. 2(e).

In accordance with these observations, it would be expected that the mixed layer formed by thermal activation in the solution of Ce(III) with H_2O_2 should also have a protective character.

In order to evaluate the degree of protection provided by the layers formed, the treated samples were submitted to tests of Linear Polarization (LP) in a solution of NaCl at 3.5%. Fig. 3 shows several of the LP curves obtained in the solution of NaCl, for samples treated at different temperatures and times of immersion in the solutions of $Ce(NO_3)_3$, with the various concentrations of H_2O_2 employed. As a reference, the curve corresponding to an untreated sample is also included in this figure.

As can be observed, the treated samples present a similar behaviour in all the cases. First, a decrease is seen of the corrosion potential, E_{corr}, in comparison with that measured for the untreated samples. This finding is related to the cathodic character of the type of protection provided [18, 19, 22, 23]. Another notable feature of these curves is the increase of the pitting nucleation potential, E_{pit}, of the treated samples, in comparison with the untreated samples. This finding may be related to the quality of the layer formed which, under the test conditions, impede the formation of crystallographic pits at the nucleation potential corresponding to the untreated alloy [35, 36]. This observation is considered reinforced by the fact that the passivity section of the LP curve, measured as $\Delta E = E_{pit}\text{-}E_{corr}$, increases considerably for the treated samples. This effect has not been observed in the treatments previously applied to this alloy either by immersion at ambient temperature or by thermal activation [30–32]. For this reason, everything seems to indicate that this effect must be related to the addition of the oxygenated water. According to [33], the presence of H_2O_2 in the treatment baths gives rise to the oxidation of the Ce(III) to Ce(IV). Visual inspection of the treated samples reveals the presence of a yellowish-coloured film, characteristic of the presence of Ce(IV) in its composition. This finding was not detected in the samples treated without the presence of oxygenated water. In consequence, the evidence indicates that the presence of Ce(IV) in the conversion coatings is the factor responsible for the increase of the pitting nucleation potential. However, in the study of the behaviour of alloy AA5083 in solutions of NaCl, no crystallographic pits were detected [12, 14]. This suggests that the search for an effective protection for this alloy should not be focused on coatings that increase its E_{pit}. Rather, as previously commented, the principal corrosion problem affecting AA5083 in solutions of NaCl is localised alkaline corrosion (LAC) and therefore the objective should be to minimise this particular process.

Continuing with the analysis of the linear polarization curves obtained for the treated samples, Fig. 3, the displacement of the current density can be observed, towards lower values in comparison with the curve obtained for the untreated samples. This result is indicative of a decrease in the electrochemical activity of the system, which can be measured by means of the value of R_p. Table 2 gives the values of R_p obtained from the LP curves for each of the treatments applied. From these values, by applying the expression (1), the value of ΔR_p has been determined for each of the treatment conditions tested, Table 2. This value is indicative of the degree of protection provided to the alloy by the mixed layer and represents the reduction of the activity of the system [14, 31]. In Fig. 4 the values of ΔR_p are compared for each of the treatments tested. As can be observed, the best results are obtained for treatments of 15 minutes employing a concentration of H_2O_2 of 1.25 ml/l. In this case, the factor of reduction achieved in the activity of the system is nearly 14. These results are of the same order as those obtained in [31] for immersion treatments at ambient temperature without the addi-

Table 2. Electrochemical parameters obtained from linear polarization curves of samples treated by full immersion at 323 K in an aqueous solution of 0.005 M of $Ce(NO_3)_3$ with the indicated H_2O_2 concentrations. Medium: solution of 3.5% NaCl

Tabelle 2. Aus den linearen Polarisationskurven der bei 323 K in einer wässrigen Lösung von 0,005 M $Ce(NO_3)_3$ mit den angegebenen H_2O_2-Konzentrationen behandelten Proben ermittelten elektrochemischen Parameter. Medium: 3,5%ige NaCl-Lösung

$[H_2O_2]$ (ml/l)	t (min)	R_p (kΩ)	ΔR_p	R_{cp} (kΩ)	ΔR_{cp}
Untreated		27.72	1	16.13	1
	5	132.22	4.77	96.36	5.93
0.675	15	167.86	6.06	136.50	8.46
	30	159.40	5.75	140.50	8.71
	5	142.87	5.15	122.70	7.61
1.250	15	380.40	13.72	282.10	17.49
	30	149.50	5.39	245.01	15.19
	5	100.68	3.63	87.23	5.41
2.500	15	134.70	4.86	136.80	8.48
	30	195.50	7.05	145.70	9.03

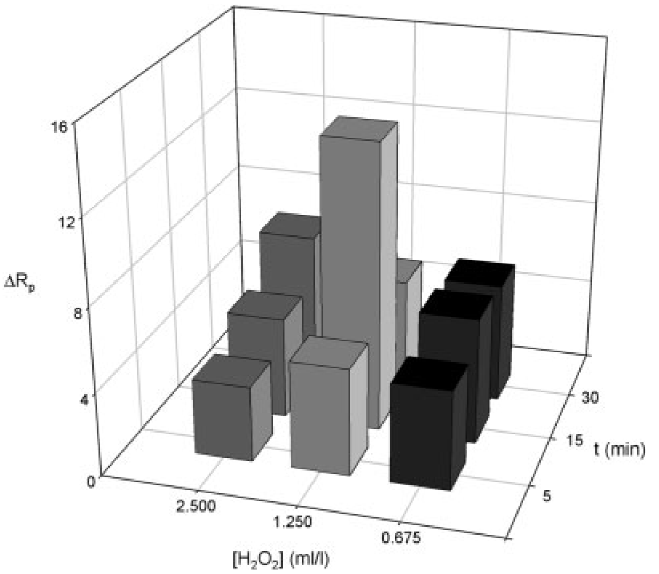

Fig. 4. Comparison of the values of ΔR_p for each of the treatments tested

Abb. 4. Vergleich der Werte für ΔR_p für jede der untersuchten Behandlungen

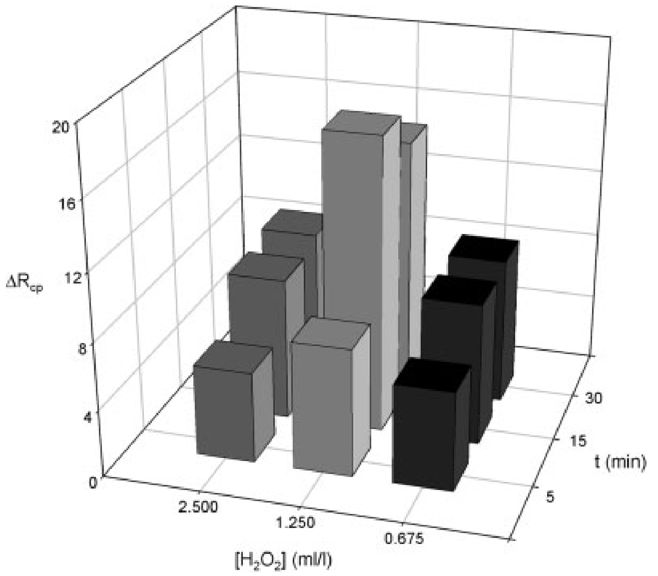

Fig. 5. Comparison of the values of ΔR_{cp} for each of the treatments tested

Abb. 5. Vergleich der Werte für ΔR_{cp} für jede der untersuchten Behandlungen

tion of H_2O_2. However, the key difference is in the reduction of the optimum time duration of the treatment to only 15 minutes, as against the two days required for immersion treatments at ambient temperature without the presence of H_2O_2. This represents a time saving of approximately 20,000%, which should increase the appeal of this type of treatment to industry. In summary, the combination of an increase in the temperature of the solution of Ce(III) with the addition of H_2O_2 facilitates a much faster formation of the mixed layer, while providing protective properties similar to those obtained by immersion at ambient temperature.

According to [31] this advantage is due to two factors. The first is that thermal activation allows a more rapid growth of the film of alumina over the metal matrix. The second is that, as confirmed in [26–28], the islands of cerium are formed during the initial moments of immersion in the solution containing Ce(III) and H_2O_2.

As previously commented, in [31] R_{cp} is proposed as a measure of the degree of covering provided by the mixed layers formed by immersion. In the treatments tested in the present study, conversion coatings with a similar morphology are produced. For this reason, the parameter R_{cp} has been employed for the evaluation of the resistance of these coatings. The values of this parameter are given in Table 2. From these, making use of the expression (2), the value of ΔR_{cp} has been determined for each case, Table 2 this in effect determines the degree of protection due to the increase of the resistance of the coating. In Fig. 5 the values of ΔR_{cp} obtained for each of the treatments studied are compared. As can be appreciated, a good correlation exists between these values and those corresponding to ΔR_p, to the same extent as those observed in [31] for immersion treatments at ambient temperature.

Thus the best results are obtained for treatments of 15 minutes duration at 323 K, employing a concentration of 1.25 ml/l of H_2O_2. Under these conditions an increase is achieved of the resistance of the mixed layer by a factor of the order of 20, similar to that obtained in [31] for treatments by immersion.

Finally, with the object of verifying the protective character of the treatments tested, the samples treated were submitted to 168 hours salt fog tests, in accordance with the standard described in [34]. In Fig. 6 are shown macrographs corresponding to different samples following these tests. As a reference, the images corresponding to an untreated sample before and after being submitted to this type of trial are included. As can be appreciated, no signs of corrosion are detected in the treated samples.

5 Conclusions

The treatment of samples of the alloy AA5083 by immersion in solutions of Ce(III) lead to the formation of a mixed layer consisting of islands of cerium situated over the cathodic intermetallic compounds present on the surface, and a film of alumina that covers the rest of the metal matrix. When these treatments are applied at ambient temperature, the optimum time of treatment is conditioned by the slow rate at which the oxide film over the matrix is produced, and requires two days of treatment to obtain an acceptable degree of protection.

With the aim of accelerating the formation of the protective layer or coating, tests have been conducted of immersion treatments of alloy AA5083 in solutions of $Ce(NO_3)_3$ at 323 K to which different concentrations of H_2O_2 have been added.

The thermal activation at 323 K of the solution of Ce(III) causes a more rapid growth of the layer of oxide that covers the matrix of aluminium. At the same time, the addition of small quantities of H_2O_2 to the treatment baths accelerates the formation of the islands of cerium that block the cathodic activity in the immediate surroundings of the Al(Mn,Fe,Cr) intermetallics.

By combining these two effects, conversion coatings on alloy AA5083 have been obtained, with a morphology similar to those obtained by means of immersion treatments at ambient

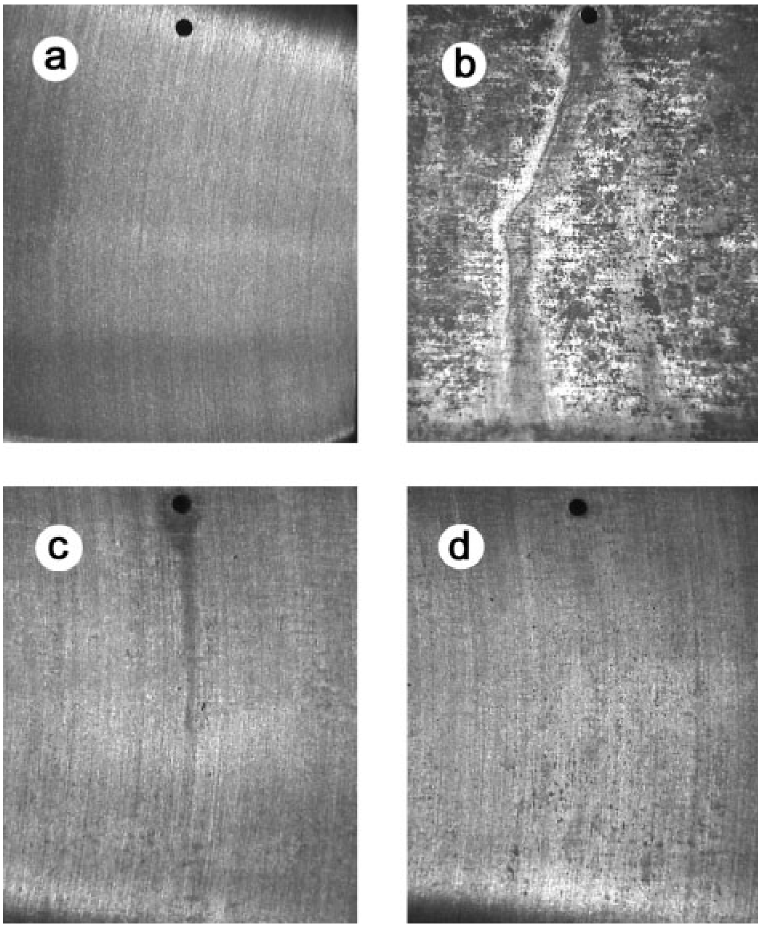

Fig. 6. (a) Macrograph corresponding to an untreated AA5083 sample. Macrographs corresponding to AA5083 samples salt fog tested during 168 hours pretreated in the following conditions: (b) untreated; full immersion treated in 0.005 M $Ce(NO_3)_3$ solution at 323 K with 2.5 ml/l of H_2O_2 during (c) 15 and (d) 30 minutes

Abb. 6. (a) Makrographische Aufnahme entsprechend einer unbehandelten AA5083-Probe. Makrographische Aufnahmen von AA5083-Proben nach 168 Stunden Prüfung im Salzsprühnebel mit folgenden Vorbehandlungsbedingungen: (b) unbehandelt; Tauchbehandlung in 0,005 $Ce(NO_3)_3$-Lösung bei 323 K mit 2,5 ml H_2O_2 während (c) 15 und (d) 30 Minuten

temperature. Additionally, the protective effect of these coatings remains at a similar level to that obtained for samples of this alloy treated by immersion at ambient temperature. Most significantly, the length of time required for the treatment is reduced by a factor of around 200, which should considerably increase the appeal of this treatment method to industry.

Furthermore, the addition of H_2O_2 to the treatment baths causes the increase of the pitting nucleation potential, E_{pit}. This effect leads to a reduction of the metal's susceptibility to corrosion by crystallographic pitting. Although this type of corrosion has been observed in previous studies conducted on alloy AA5083, the conversion coatings developed have the potential to be applied for the protection of alloys that present crytallographic pitting corrosion.

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