On the mixed nature of cerium conversion coatings

Über die Eigenschaften von Cer-Umwandlungsschichten

A. Aballe, M. Bethencourt, F. J. Botana*, M. J. Cano and M. Marcos

Alternative pretreatments are currently under development in order to avoid the environmental impact produced by using surface finishing processes based on chromates. Some of the environmentally friendly alternatives proposed involve the use of lanthanide based compounds.

In this study, conversion coatings on AA5083 (Al-Mg) samples developed using full immersion pretreatments in 500 ppm $CeCl_3$ aqueous solutions have been investigated. Their microscopic and compositional features have been analyzed using SEM images and EDS spectra. From this analysis it has been determined that this layer over the surface of the samples is of a heterogeneous composition. This coating is formed by an alumina coating covering the aluminum matrix and dispersed cerium-rich islands deposited over the cathodic sites of the alloy. A characterization methodology is proposed based on the utilization of different electrochemical techniques, such as Open Circuit Potential monitoring (OCP), Linear Polarization (LP) and Electrochemical Impedance Spectroscopy (EIS).

Zur Zeit sind alternative Vorbehandlungen in der Entwicklung, um die Umweltbelastungen, die durch Chromat-basierende Oberflächenbehandlungsverfahren verursacht werden, zu vermeiden. Einige der vorgeschlagenen umweltfreundlichen Alternativen enthalten auf Lanthaniden basierende Verbindungen.

In der vorliegenden Studie wurden Umwandlungsschichten, die sich durch Vorbehandlungstauchen in 500 ppm wässrigen $CeCl_3$-Lösungen entwickelten, auf AA5083(Al-Mg)-Proben untersucht. Ihre mikroskopischen Eigenschaften sowie ihre Zusammensetzung wurden mittels REM-Aufnahmen und EDS-Spektren analysiert. Aus dieser Analyse geht hervor, dass die Schicht auf der Oberfläche der Proben eine heterogene Zusammensetzung besitzt. Die Beschichtung wird durch eine Aluminiumoxidschicht, die die Aluminiummatrix bedeckt, und dispergierte Cer-reiche Inseln, die über den kathodischen Bereichen der Legierung abgeschieden sind, gebildet. Basierend auf dem Einsatz verschiedener elektrochemischer Techniken, wie Monitoring des Potentials bei offenem Stromkreis (OCP), lineare Polarisation (LP) und elektrochemische Impedanzspektroskopie (EIS), wird eine Charakterisierungsmethodik vorgeschlagen.

1 Introduction

Competitive advantages in markets today are increasingly derived from the employment of technologies and processes that are not aggressive towards the natural environment. Recent and proposed legislation on environmental subjects and the adoption of industrial standards related to environmental protection (ISO 14000) are forcing industrial companies to make far-reaching changes in their production systems and in their working philosophy [1].

Hence today, the viability of any industrial initiative necessarily includes the assessment of the impact on the natural environment. One of the production sectors that is being most seriously affected by environmental restrictions is that working on the surface treatment of aluminum alloys [2]. In this area of activity, in the immediate future, companies must progressively abandon those processes that involve the use of compounds, which have been reasonably proven to be toxic and aggressive towards the natural environment [3].

In this context of technological renewal, in recent years there has been intense research activity aimed at finding non-contaminating alternatives to surface treatment processes based on the use of chromates. At the present time, many lines of research are open in which a wide range of organic and inorganic compounds is being tested to this end. For several years, in our laboratories, non-contaminating anticorrosive pretreatments have been studied as alternatives to classic treatments based on chromates. These studies have been directed towards the use of lanthanide elements in systems of anticorrosion protection of aluminum alloys [4–22].

As confirmed by the results obtained in these studies, the mechanism of inhibition of these elements is based on blocking the cathodic reaction by the formation of an insoluble compound of the lanthanide element that precipitates on to the cathodic zones of the material. In turn, the metallic matrix formed by the alloy is then protected by the deposition of an anodic covering of alumina formed as a result of the exposure to an aqueous medium.

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

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

This paper presents a study undertaken of the protective coatings developed from immersion treatments of an aluminum-magnesium alloy in solutions containing $CeCl_3$. This type of treatment has already been studied by other authors for different alloys [8, 23, 24]. However, in the bibliography, no studies have been found in which either the mechanisms of formation of these coatings or their electrochemical properties have been researched in depth. In fact, in most of the cases, published studies have mainly been focused on evaluating the protection provided by these coatings. This has led as a consequence to the present situation in which methods for producing this type of coating are continuing to be developed based only on empirical considerations. For this reason, one of the fundamental objectives of this study is to gain a deeper understanding of the mechanisms of coating formation and corresponding electrochemical properties in order that future work to prepare conversion coatings rich in cerium should be more solidly based.

2 Experimental

To conduct the tests rectangular samples of 30 × 25 × 5 mm of the alloy AA5083 (Al-Mg) were used. The composition of this alloy is given in Table 1. The test pieces were sanded with SiC paper of 220 and 500 grits, and cooled under running water. Then they were rinsed with distilled water and dried in a current of air. An aerated solution NaCl at 3.5% by weight was employed as the aggressive medium.

The conversion coatings were prepared by immersion of the samples in aerated aqueous solutions of 500 ppm of $CeCl_3$ for periods of time ranging from 1 to 5 days.

The surface aspect of the layers thus formed was studied by Scanning Electron Microscopy (SEM) using a JEOL 820-SM microscope. Its composition was analyzed by Energy Dispersive Spectroscopy (EDS) in an AN-10000 LINK spectrometer connected to the microscope cited.

To assess the degree of protection provided by the layers formed, electrochemical techniques of linear polarization (LP) and monitoring of open circuit potential (OCP) were applied. For this, a SI 1287 potentiostat from Solartron, connected to a K235 flat cell from Parc EG&G, was used. As reference electrode, an Ag/AgCl electrode from Crison (− 0.207 mV/SHE) was used. In addition, Electrochemical Impedance Spectroscopy (EIS) was applied to analyze discriminately the electrochemical response of the layers formed. The EIS measurements were performed using the Solartron model 1287 potentiostat coupled to a Frequency Response Analyzer (FRA) from Solartron, model SI 1255.

3 Results and discussion

In previous studies made of this alloy, three types of intermetallic compounds were observed on its surface [9, 14]. These precipitates have been identified as Al(Mn,Fe,Cr), Al(Si,Mg) and a β phase of Al-Mg. According to the findings presented in these studies, when alloy AA5083 corrodes freely in aerated solutions of NaCl, a process of localized alkaline corrosion is confirmed around cathodic precipitates of Al(Mn,Fe,Cr) and, in parallel, the oxide layer over the rest of the matrix increases in thickness [14–16, 25]. According to [26], the presence of the other two types of precipitate does not significantly affect the behavior of the alloy in this medium.

This behavior is reflected in the electrochemical response of the system. Fig. 1 shows the evolution over time of the OCP of a sample of alloy AA5083 in an aerated solution of NaCl at 3.5% [15, 22]. It can be observed in this figure how the value of the corrosion potential of the sample is of the order of − 0.850 V (Ag/AgCl) in the first moments of exposure. In the first two hours of immersion, the potential evolves to reach a value of between − 0.740 and − 0.760 V; it then stays within this range for periods of up to 30 days of exposure to the medium. The value of the corrosion potential is, at all times, less than that of the pitting nucleation potential, E_{pit}, which for this alloy is − 0.720 V [5]. For this reason, in these previous studies cited, crystallographic pitting characteristic of these alloys has not been detected.

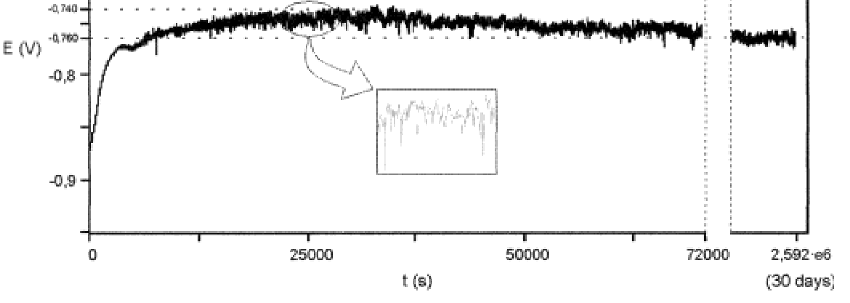

Fig. 1. E_{corr}-t diagram corresponding to AA5083 sample in 3.5% NaCl solution

Abb. 1. E_{corr}-t-Diagramm einer AA5083-Probe in 3,5% NaCl-Lösung

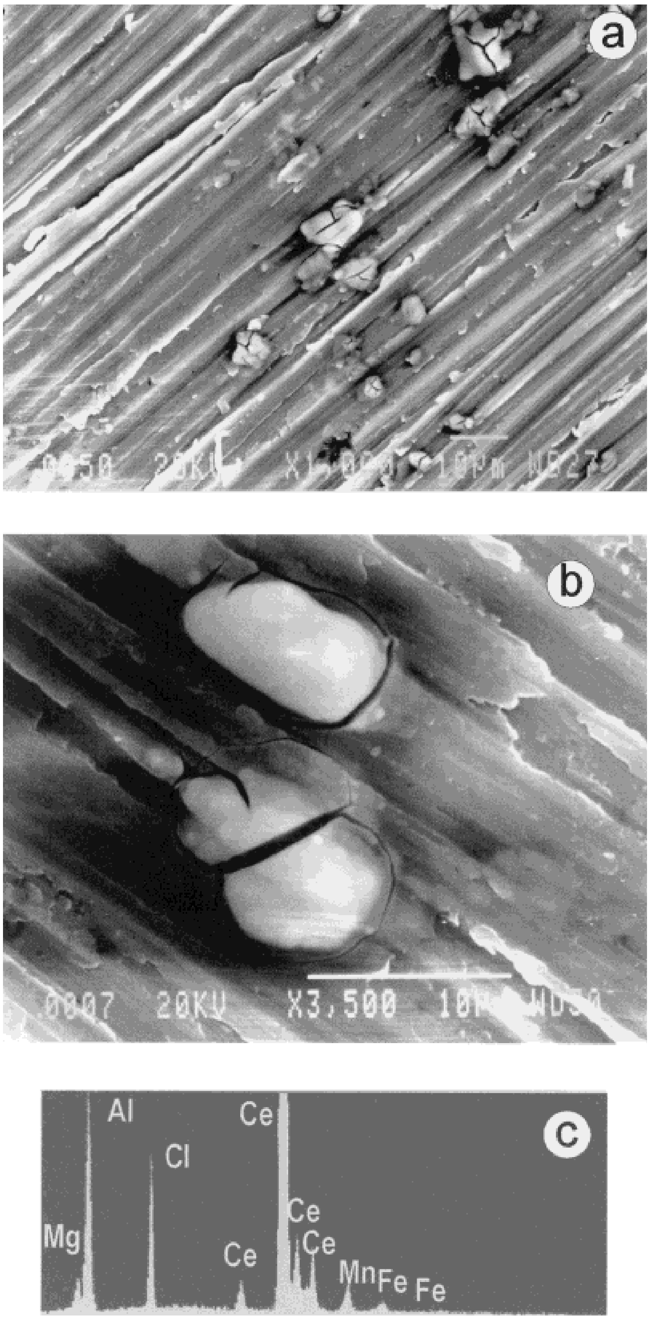

Fig. 2. (a) SEM image of a sample of AA5083 alloy after two hours of immersion in a 3.5% NaCl solution doped with 500 pmm of $CeCl_3$. (b) Enlarged SEM image showing cerium-containing islands. (c) EDS spectrum acquired on a cerium island

Abb. 2. (a) REM-Aufnahme der Probe der Legierung AA5083 nach zwei Stunden Tauchen in einer 3,5% NaCl-Lösung, die mit 500 ppm $CeCl_3$ dotiert war. (b) Vergrößerte REM-Abbildung, die Cer-enthaltene Inseln zeigt. (c) EDS-Spektrum an einer Cer-Insel

In this type of system, one of the factors determining the value of the initial corrosion potential is the ohmic fall caused by the natural film of oxide formed during the manipulation of the sample [27]. If this film is not sufficiently thick for the alloy to reach the passive state, the metal will oxidize until this situation is produced [28]. For this, the system should be polarized anodically, increasing the value of the corrosion potential, until a stationary state marked by a potential E_{st} is reached. The stationary state potential does not remain really constant (see Fig. 1), but rather continuous oscillations around this value are observed. In accordance with [29], the falls in potential observed in these oscillations are produced by the increase in the anodic area as a consequence of the localized alkaline corrosion The repassivation of these zones would cause the ennobling of the potential.

The behavior described in the foregoing will be taken as a reference when the mechanism of protection of the systems designed is analyzed. In accordance with this behavior, the principal corrosion process of the alloy AA5083 in solutions of NaCl is due to the cathodic reaction that takes place in the zones occupied by the precipitates of Al(Mn,Fe,Cr). This finding suggests that in the design of a system of protection, the aim should be to minimize the intensity of the cathodic process.

Lanthanide salts customarily behave as cathodic inhibitors [8, 30–35]. In respect specifically of alloy AA5083 in solutions of NaCl, in [5, 6, 21, 22], the inhibitory effectiveness of various lanthanide compounds of the $LnCl_3$ type is proven and the cathodic mechanism of inhibition of these compounds is confirmed. Basically, this mechanism consists of two stages. First, an oxide or hydroxide of the lanthanide element is formed as a consequence of the reaction of the cation Ln^{+3} with the OH^- ions generated during the cathodic reaction over the precipitates of Al(Mn,Fe,Cr). The lanthanide compound formed is highly insoluble [36]. Therefore, in a second stage, this compound precipitates over the intermetallic particles, blocking the cathodic reaction and, consequently, the associated anodic reaction. This mechanism causes the formation of dispersed islands with a high content of the lanthanide element, situated over the intermetallic compounds of cathodic character, Fig. 2.

The results presented in [5, 6, 18–21] demonstrate that the greatest degree of inhibition is obtained when $CeCl_3$ is added to the solution NaCl, to give a concentration of up to 500 ppm. For this reason, of the various lanthanide elements tested in [5, 6, 18–21], cerium has been selected for the design of the systems of protection studied in the present paper.

3.1 Immersion treatments

To obtain the conversion coatings the samples of alloy AA5083 were treated by immersion in an aerated aqueous solution of 500 ppm of $CeCl_3$ for periods of 1, 2 and 5 days. In Fig. 3 are shown the SEM images corresponding to each of these samples. It can be seen from these images that there exist dispersed islands that cover certain zones of the surface, leaving the rest of the surface by a more homogeneous layer. Also included in Fig. 3 are the EDS spectra obtained for the matrix (1), for these dispersed islands (2) and for the substratum of these islands (3). An initial finding to be noted is that the islands observed present a high content in cerium. Further, the analysis by EDS of the substratum in the zones covered by these islands, reveals that the cerium precipitates preferentially over the intermetallics of Al(Mn,Fe,Cr). It is significant to note from the SEM/EDS analysis that no deposition of cerium over the aluminum matrix can be detected, even after 5 days of immersion. Thereby, only the characteristic peaks of Al and Mg can be seen in the EDS spectrum recorded for the aluminum matrix.

Fig. 4 shows the evolution of the corrosion potential, E_{corr}, with time of exposure to the solution of NaCl, for samples treated with $CeCl_3$ for various numbers of days. As reference,

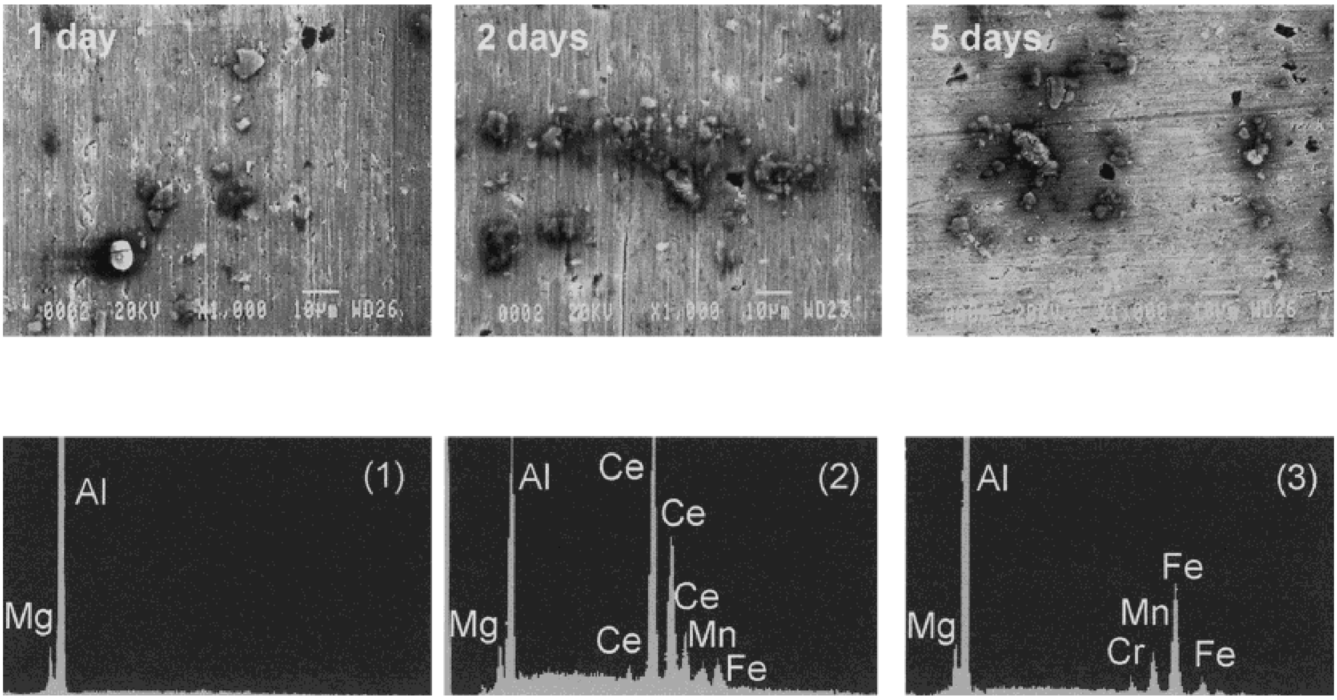

Fig. 3. SEM images of AA5083 samples after 1, 2, and 5 days of immersion in a 500 pmm of $CeCl_3$ solution. EDS spectra acquired on: (1) matrix; (2) cerium island; (3) intermetallic under cerium island

Abb. 3. REM-Aufnahmen der AA5083-Proben nach 1, 2 und 5 Tagen Tauchen in einer 500 ppm $CeCl_3$-Lösung. EDS-Spektren von: (1) Matrix; (2) Cer-Inseln; (3) Intermetallische Phase unter den Cer-Inseln

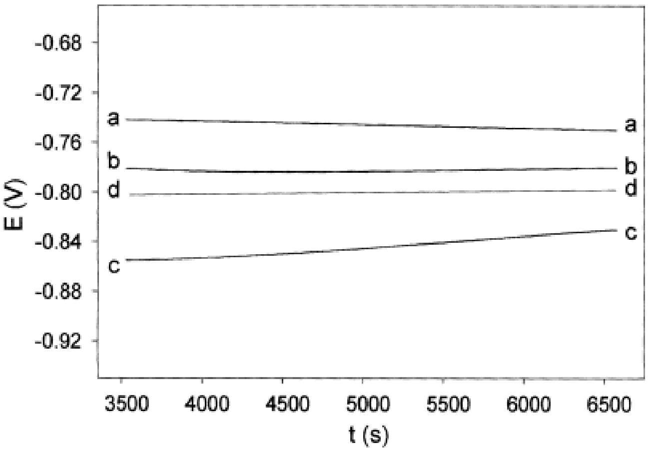

Fig. 4. $<E_{corr}>$-t diagrams corresponding to AA5083 sample treated in the following conditions: (a) Bare sample; (b) 1 day of full immersion in a 500 pmm of $CeCl_3$ solution; (c) 2 days of full immersion in a 500 pmm of $CeCl_3$ solution; (d) 5 days of full immersion in a 500 pmm of $CeCl_3$ solution. Samples tested in 3.5% NaCl solution

Abb. 4. $<E_{corr}>$-t-Diagramme von AA5083-Proben die unter nachfolgenden Bedingungen behandelt wurde: (a) Blanke Probe; (b) 1 Tag Tauchen in einer 500 ppm $CeCl_3$-Lösung; (c) 2 Tage Tauchen in einer 500 ppm $CeCl_3$-Lösung; (d) 5 Tage Tauchen in einer 500 ppm $CeCl_3$-Lösung. Die Proben wurden in 3,5% NaCl-Lösung geprüft

the curve corresponding to an untreated sample has been included. The evolution experienced by the treated samples when they are immersed in NaCl will depend on the level of protection provided. The first finding to be noted in these diagrams is that all the treatments applied produce a reduction in the values of the corrosion potential. In agreement with the analysis conducted by SEM and EDS, this finding could be associated with a blocking of the cathodic zones being produced in the treated samples; this then causes a reduction in the effective cathodic area and, in consequence, a decrease in the cathodic current of the system. In this way, when the samples are immersed in NaCl, the blocking of the cathodic zones is translated into a decrease in the rate of growth of the oxide film that forms over the matrix. In the E_{corr}-t diagrams, this behavior is reflected in the slopes of E(t) during the first hours of exposure. As can be observed, the treated samples present a branch with a steeper slope than that obtained for the untreated samples, which means that in these samples the layer of oxide has not reached the thickness necessary for the stabilization potential to be reached [15, 22, 25]. These results show that, during the treatment in the $CeCl_3$ solution, due to the low activity of the system, the anodic layer does not grow sufficiently. For this reason, when the samples are immersed in NaCl, this layer may continue growing. However, the rate of growth is low due to the blocking of the cathodic zones.

From a comparison between the samples treated for various periods in $CeCl_3$, it can be seen that the sample presenting the lowest value of E_{corr} is that subjected to a treatment of two days, while the sample immersed for just 24 hours presents a behavior most similar to that of the untreated sample. This latter finding could be explained by the cerium coating not having had sufficient time to cover all the cathodic precipitates of the alloy in 24 hours, leaving some cathodic zones still active. Also, the higher potential observed for the samples treated for five days, in comparison with that immersed for two days, could be explained by the formation of a thicker layer of oxide during the five days of treatment.

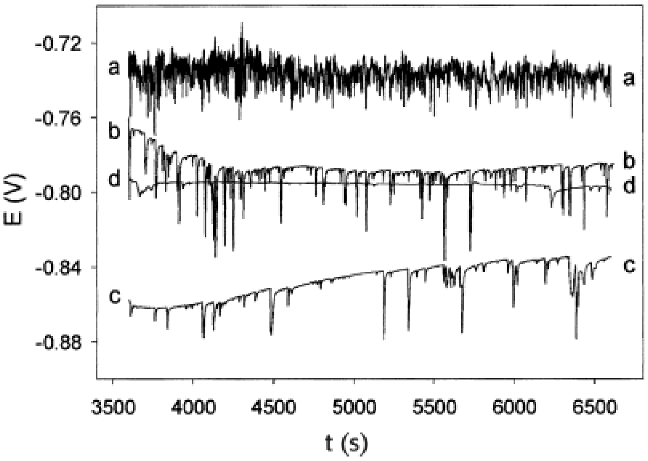

Fig. 5. E_{corr}-t diagrams corresponding to AA5083 sample treated in the following conditions: (a) Bare sample; (b) 1 day of full immersion in a 500 pmm of $CeCl_3$ solution; (c) 2 days of full immersion in a 500 pmm of $CeCl_3$ solution; (d) 5 days of full immersion in a 500 pmm of $CeCl_3$ solution. Samples tested in 3.5% NaCl solution

Abb. 5. E_{corr}-t-Diagrame von AA5083-Proben, die unter nachfolgenden Bedingungen behandelt wurde: (a) Blanke Probe; (b) 1 Tag Tauchen in einer 500 ppm $CeCl_3$-Lösung; (c) 2 Tage Tauchen in einer 500 ppm $CeCl_3$-Lösung; (d) 5 Tage Tauchen in einer 500 ppm $CeCl_3$-Lösung. Die Proben wurden in 3,5% NaCl-Lösung geprüft

On the other hand, in accordance with the analyses made in [14, 15, 22], the reduction in the effective cathodic area should bring with it a decrease of the oscillations in the pseudo-stationary branch of the E_{corr}-t diagram. Fig. 5 shows sections of one hour of this diagram, obtained in the solution of NaCl for the samples subjected to pretreatment for different lengths of time. As can be observed, as the time of treatment in $CeCl_3$ increases, there is a decrease in the level of the oscillations in the E_{corr}-t diagrams, which, in principle, demonstrates the reduction of the effective cathodic area already referred to. However some authors have related these oscillations with the existence of phenomena in the layer/electrolyte interface, associated with the possible adsorption of Cl^- ions in the passive layer, as the origin of the process of solution of this layer and the nucleation of pits in the matrix [37]. With the aim of analyzing the influence of the presence of chlorine in the pretreatments, an EDS analysis was performed on this layer. The spectra obtained presented an aspect like that shown in Fig. 3(1), with the incorporation of Cl into the passive film that forms on the matrix not being detected.

To summarize, the treatment by immersion in the solution of $CeCl_3$ leads to the formation of a mixed coating consisting both of islands of a compound of cerium situated over the cathodic precipitates of the alloy, and of a film of alumina that covers the metallic matrix, which is free of Ce and Cl. The thickness of this coating determines the evolution over time of the E_{corr} of the samples, when these are immersed in NaCl solutions.

3.2 Assessment of the effectiveness of the protection

To assess the degree of protection provided by the treatments with $CeCl_3$, two electrochemical methods were employed: Linear Polarization (LP) and Electrochemical Impedance Spectroscopy (EIS).

In Fig. 6 are shown the LP diagrams recorded for samples treated with $CeCl_3$ and immersed for two hours in NaCl. As a reference, the curve corresponding to an untreated sample is included in this figure. It can be observed in these diagrams that, as was found from the open circuit analysis, the corrosion potential is decreased compared with the untreated alloy. This finding is repeated for each of the treatment times studied, Table 2. Similarly, it can be appreciated from this figure that the current density drops to lower values. Both findings are characteristics of cathodic protection systems [5, 6, 18, 23, 31–35]. In addition, it can be seen that the pitting nucleation potential E_{pit}, is not affected by the pretreatment. This all goes to demonstrate that the immersion in cerium does not directly affect the properties of the matrix and only acts on the cathodic zones of the alloy AA5083.

Taking an interval of polarization of ± 25 mV around the corrosion potential, the value of R_p was determined in each case studied, Table 2. The level of protection provided by the pretreatment has been assessed in terms of the increase of R_p recorded. This has been represented by ΔR_p,

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

with R_p^0 being the value of R_p for the untreated alloy. In accordance with all the data included in Table 2, the maximum level of protection is achieved by treatment in a solution of $CeCl_3$ for a period of two days duration. The values obtained indicate that an increase in the polarization resistance by a factor of almost 25 was achieved, in other words, by treating the alloy AA5083 by immersion in the solution of $CeCl_3$, it has been possible to reduce the activity of the system by more than 2300%.

Another notable finding from the Linear Polarization curves included in Fig. 6 is the relative position of the anodic branches. As can be seen in this figure, the density of the passivation current decreases considerably in the samples pretreated in $CeCl_3$. The largest decrease is observed for the sample treated for two days. In line with the comments already made, even though the surface of the samples treated in $CeCl_3$ presents only a thin film of oxide, this is enough to cover the matrix. This enables the combined result, which could be termed the mixed coating layer, to present a greater degree of protection, as reflected in the values of the density of passivation current. In contrast, in the untreated samples, despite the oxide layer having grown more, the existence of exposed cathodic precipitates leaves the system less protected, and therefore its passivation current is higher. Further, it can be observed in this figure how the slopes of the anodic branches, in the zone of passivity, are also altered by the effect of the pretreatment. Hence the slope of these branches of the curve

Table 2. Electrochemical parameters obtained from LP curves plotted in Fig. 6

Tabelle 2. Aus den in Abb. 6 dargestellten LP-Kurven ermittelte elektrochemische Parameter

t (days)	Rp (kΩ · cm²)	Ecorr (V)	ΔRp
0	34.1	– 0.761	1
1	360.6	– 0.804	10.57
2	829.9	– 0.850	24.34
5	317.4	– 0.805	9.31

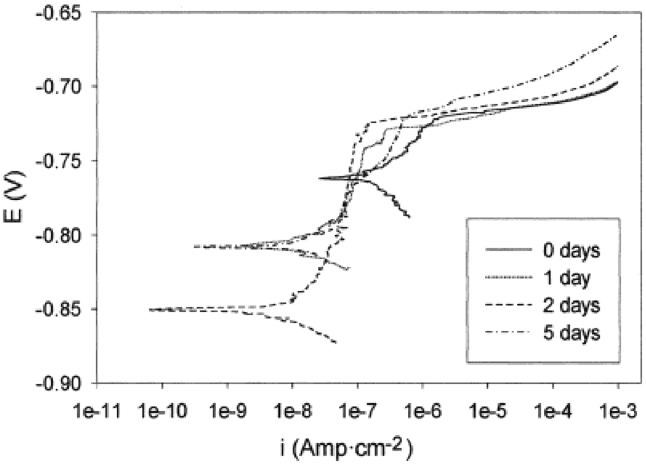

Fig. 6. Linear Polarisation curves corresponding to AA5083 sample treated by full immersion in a 500 pmm of $CeCl_3$ solution during the indicated periods. Samples tested in 3.5% NaCl solution

Abb. 7. Lineare Polarisationskurven von AA5083-Proben, die entsprechend den angegebenen Zeiten durch Tauchen in einer 500 ppm $CeCl_3$-Lösung behandelt waren. Die Proben wurden in 3,5% NaCl-Lösung geprüft

could serve as an indirect measure of the activity taking place in the immediate surroundings of the cathodic precipitates. Thus, the value of the slope will be related to the degree of covering of the surface of the samples. In this way, in the untreated samples, curves are obtained with a flatter slope whereas the slope is steeper in the samples treated with $CeCl_3$.

Following on from the observations made in the preceding paragraph, this study proposes to use the value of the slope of the Linear Polarization curves, specifically the slope in the passivity zone, in order to measure the resistance of this heterogeneous coating layer, R_{cp}. With the objective of being able to associate physical units of resistance ($\Omega \cdot cm^2$) with this layer, the value of the slope will be calculated from the linear scale representation of the LP curves. Thus, for the section of curve considered:

$$R_{cp} = \frac{\Delta E_{pas}}{\Delta i_{pas}} \qquad (2)$$

In the above equation, ΔE_{pas} is the variation of potential (V) in the interval of passivity, whereas Δi_{pas} is the variation of the density of current ($A \cdot cm^{-2}$) in this interval. Table 3 gives the values of R_{cp} obtained from the Linear Polarization curves. The parameter ΔR_{cp} has been established as the measure of the increase of resistance of the layer, from the expression

$$\Delta R_{cp} = \frac{R_{cp}}{R^0_{cp}} \qquad (3)$$

in which R^o_{cp} is the resistance of the passive layer for untreated samples. The values of ΔR_{cp} are also included in Table 3. As can be appreciated, by treating the samples in $CeCl_3$, the resistance of the heterogeneous layer has been increased by factor of up to 42. This result is consistent with the observation previously made in this paper. In effect, although the growth of the layer of alumina has been impeded by the treatment with Ce, the heterogeneous coating formed gives a better coverage of all the surface of the alloy, protecting it from the action of the medium.

With the objective of analyzing individually the contribution of each of the interfaces present in the system, measurements have been made by EIS in a solution of NaCl at 3.5%, of the samples treated in $CeCl_3$. In previous studies [22], it has been demonstrated that the electrochemical response of alloy AA5083 in a solution of NaCl can be reproduced by making use of an equivalent circuit, such as that shown in Fig. 7(a). In this circuit, R_e is the resistance of the electrolyte, R_{int}-C_{int} is the loop associated with the reactions taking place around the intermetallics, R_{ca}-C_{ca} represents the response of the layer, R_T is the resistance of load transfer, and C_{dl} is the capacity of the double layer.

Alternatively, in accordance with [25], in the presence of cerium, the process of localized alkaline corrosion is minimized. Thus, the response corresponding to the intermetallics is also minimized, with the loop R_{int}-C_{int} disappearing. In this case, the electrochemical response of the system is modeled by means of a circuit such as that in Fig. 7(b). In line with the comments previously made, this circuit can be employed to simulate the electrochemical response in a solution of NaCl, of the samples treated by immersion in the solution of $CeCl_3$. In this circuit, the loop R_C-C_C would represent the response of the heterogeneous layer formed on the surface of the alloy during the treatment. In accordance with [22, 25] this response is demonstrated in the zones of the spectrum corresponding to the highest frequencies. For this reason, in order to perform the electrochemical characterization of the mixed layer, only the zone of the spectrum between 10 kHz and 1 Hz needs to be analyzed [22, 25].

In Fig. 8 are shown the electrochemical impedance spectra acquired in NaCl on the samples treated in the solution of $CeCl_3$. For reference, the spectra corresponding to an untreated sample are included.

In accordance with [22], the arc that appears in the Nyquist diagram for the untreated samples corresponds to the superposition of the responses due to the intermetallics and to the layer formed over the metallic matrix, Fig. 8(a). In the case of the treated samples, this arch represents the response of the heterogeneous layer formed [25]. As can be appreciated, this arc presents, for each treated sample, a larger diameter compared with the untreated sample, which implies a greater degree of protection, due basically to the blocking of the cathodic zones. This is evident in the higher values of |Z|

Table 3. R_{cp} parameter obtained from LP curves plotted in Fig. 6. ΔR_{cp} calculated from Eq. (3) is also included

Tabelle 3. Aus den in Abb. 6 dargestellten LP-Kurven ermittelte R_{cp}-Parameter. Die mit Gl. (3) berechneten ΔR_{cp}-Werte sind ebenfalls aufgeführt

Time in immersion	0 days	1 day	2 days	5 days
R_{cp} ($\Omega \cdot cm^2$)	$3.035 \cdot 10^4$	$2.519 \cdot 10^5$	$12.854 \cdot 10^5$	$1.014 \cdot 10^5$
ΔR_{cp}	1	8.3	42.3	3.34

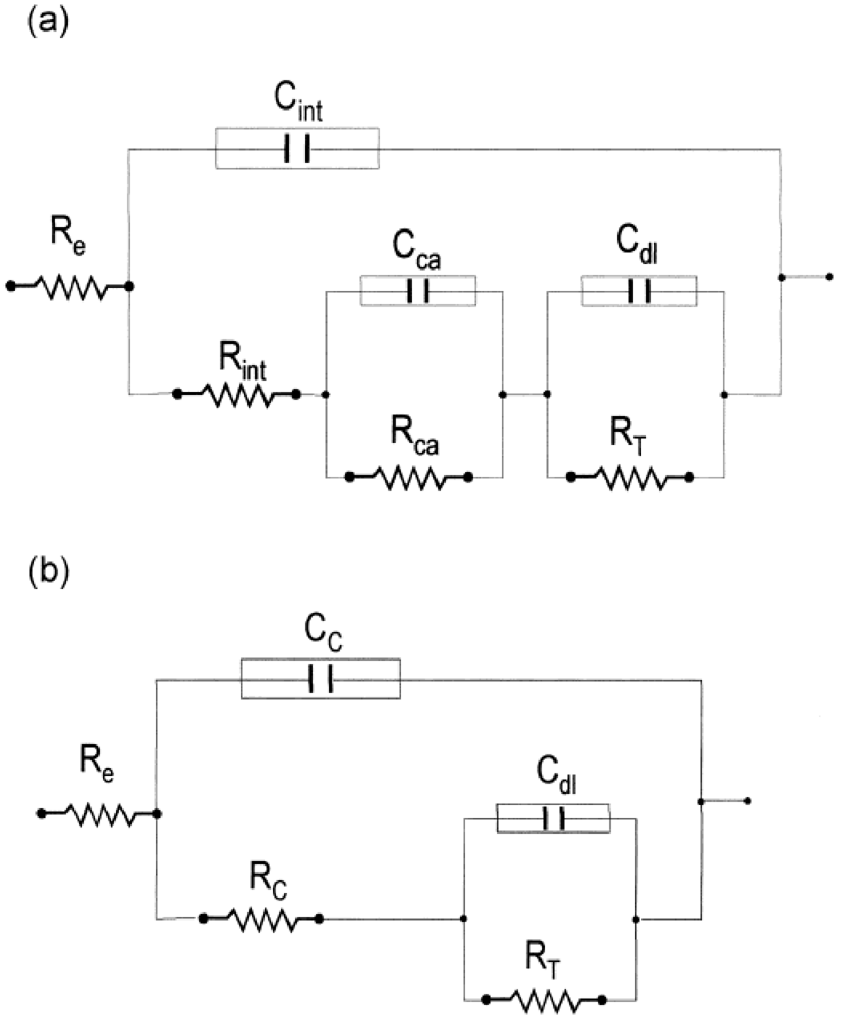

Fig. 7. Equivalent circuit for reproducing the electrochemical response of the system. (a) Three-loop circuit proposed for simulating the electrochemical behaviour of the AA5083 alloy in aerated NaCl solution at 3.5%. (b) Two-loop circuit proposed for simulating the electrochemical behaviour of the treated samples

Abb. 7. Analogieschaltkreis zur Wiedergabe der elektrochemischen Antwort des Systems. (a) Drei-Schleifen-Schaltkreis zur Simulation des elektrochemischen Verhaltens der AA5083-Legierung in belüfteter 3,5% NaCl-Lösung. (b) Vorgeschlagener Zwei-Schleifen-Schaltkreis zur Simulation des elektrochemischen Verhaltens der behandelten Proben

of the Bode diagrams in Fig. 8(b). In its turn, the greater degree of coverage of the surface of the pretreated samples can be seen reflected in the Bode diagram for the phase. In effect, as can be seen in this figure, in the spectra corresponding to the treated samples, the maximum value is conserved in a wider range of frequencies.

Further, from a comparison between the diagrams corresponding to the treated samples, it can be observed that the greatest degree of protection is achieved by the immersion pretreatments of two days' duration. This is in good agreement with the results obtained by the stationary state techniques.

The findings described in the preceding paragraphs should be reflected in the values of the elements that form the equivalent circuit of the system. It must be taken into account that, in the case of the samples treated with cerium, the reactions in the intermetallics have been minimized, with only the response associated with the mixed layer previously described being produced. In Table 4 are included the values obtained for the elements of the circuit shown in Fig. 7(b) on fitting the experimental data of Fig. 8. As can be appreciated, the optimum values are obtained for an immersion treatment of two days' duration, which is in good agreement with the comments previously made.

On comparing the values of the capacity C_C corresponding to the treated samples, with the value of C_{ca} obtained for the untreated sample, it can be observed how this latter value is noticeably lower than the former. Assuming an expression for the capacity as follows

$$C = \varepsilon_0 \varepsilon \, \frac{S}{d} \tag{4}$$

In this expression, ε_0 is the vacuum permitivity, ε is the dielectric constant of the film, S is the sample surface and d is the thickness of the film. The application of Equation (4) to the values of C_C and C_{ca} indicates that the thickness of the film formed on the surface of the matrix in the untreated samples is much greater than that corresponding to the heterogeneous layer on the treated samples. These results confirm the finding previously noted that the pretreatment with cerium inhibits the growth of the oxide layer.

The protective effect has been assessed in terms of the resistance of the layer, using for this a comparison of the values of R_C corresponding to the treated samples, with the value of R_{ca} corresponding to the untreated sample. Thus Table 4 gives the values of the increase in the resistance of the layer, calculated using the expression:

$$\Delta R_{ca} = \frac{R_C}{R_{ca}} \tag{5}$$

Table 4. Values of the elements of the first loop of the equivalent circuit for the alloy AA5083 in NaCl, after having been treated by immersion in $CeCl_3$

Tabelle 4. Werte für die Elemente der ersten Schleife des Analogieschaltkreises für die Legierung AA5083 in NaCl; nach der Behandlung durch Tauchen in $CeCl_3$

Days	R_e ($\Omega \cdot cm^2$)	C_c ($\mu F \cdot cm^{-3}$)	φ	R_c ($\Omega \cdot cm^2$)	ΔR_{ca}
0		8.70	0.926	32759 (R_{ca})	1
1	15.94	7.37	0.942	285010	8.7
2	17.89	6.85	0.939	1057700	32.3
5	15.93	10.52	0.915	119450	3.6

As can be observed in this table, by treating the samples by immersion in $CeCl_3$, the resistance of the layer increases by a factor of up to 32, for the sample treated for two days.

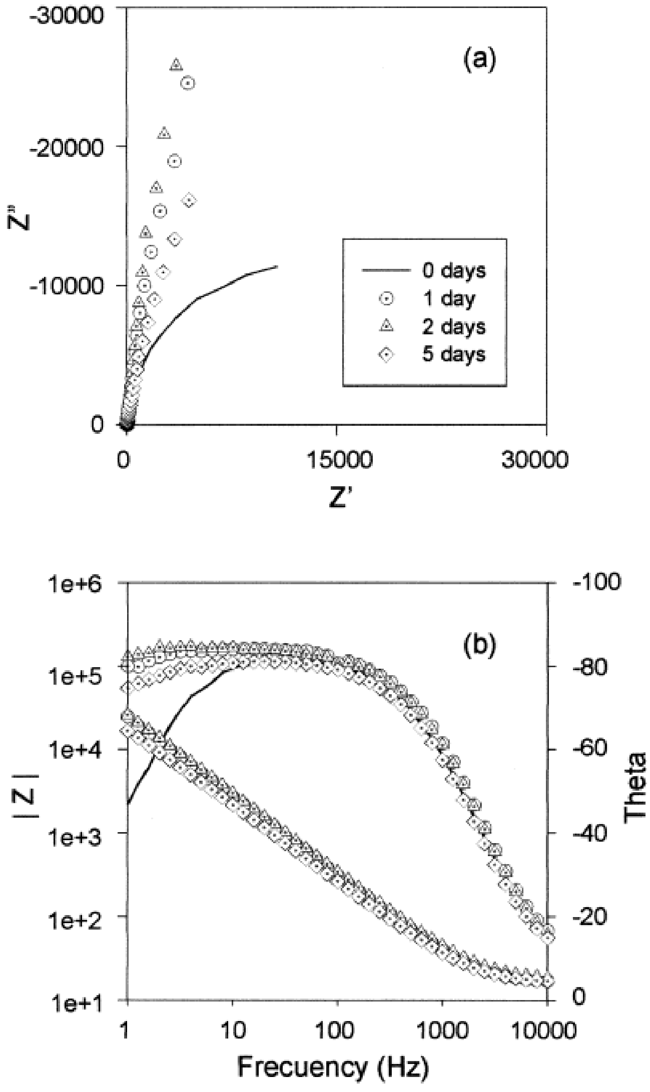

Fig. 8. (a) Nyquist and (b) Bode diagrams corresponding to AA5083 sample treated by full immersion in a 500 pmm of $CeCl_3$ solution during the indicated periods. Samples tested in 3.5% NaCl solution

Abb. 8. (a) Nyquist- und (b) Bode-Diagramme von AA5083-Proben, die entsprechend den angegebenen Zeiten durch Tauchen in einer 500 ppm $CeCl_3$-Lösung behandelt waren. Die Proben wurden in 3,5% NaCl-Lösung geprüft

On the other hand, the parameter R_{cp} was defined from the slope of the LP curves in the passive zone. This parameter was used as an averaged measure of the resistance of the heterogeneous layer. The validity of this parameter can be confirmed by comparing the evolution over the time of treatment of the values of ΔR_{cp}, with those obtained by means of EIS for ΔR_{ca}, Fig. 9. In this figure it can be observed how both parameters, calculated by different techniques, show very similar values and the same evolution. Therefore, it can safely be concluded that the parameter R_{cp} can be employed as a measure of the resistance of the mixed layer and as an indicator of the degree of coverage of the surface.

4 Conclusions

The results presented in this paper demonstrate that treatment by immersion in solutions of $CeCl_3$ applied to samples of alloy AA5083 (Al-Mg) leads to the formation of a mixed layer that completely covers the surface of the samples. This layer consists of islands of an insoluble compound of cerium that are deposited over the cathodic precipitates in the alloy, and by a film of oxide that is generated covering the aluminum matrix. The analyses performed by SEM and EDS have confirmed that, during the treatment times studied, neither the cerium nor the chloride have been incorporated into the layer formed over the matrix.

The studies carried out by electrochemical techniques have enabled the assessment of the protection provided by the pre-

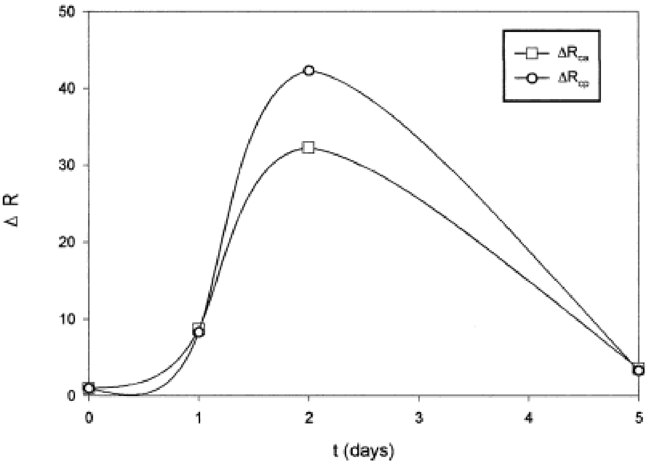

Fig. 9. Evolution of ΔR_{ca} and ΔR_{cp} parameters with the time of treatment in 500 pmm of $CeCl_3$ solution

Abb. 9. Entwicklung der Parameter ΔR_{ca} und ΔR_{cp} mit der Behandlungszeit in 500 ppm $CeCl_3$-Lösung treatments. Thus from the values of polarization resistance obtained by Linear Polarization, it has been proved that a reduction in the activity of the system by a factor of close to 25 is achieved. Equally, it has been proposed that the slope of the anodic branch of the linear polarization curves may be used as a parameter to assess the average resistance of the heterogeneous layer formed. From the values obtained for this parameter, it is possible to achieve an increase in the resistance of this layer by a factor close to 42. The validity of this parameter has been confirmed from study of the resistance associated with this layer, assessed using the EIS diagrams. The results obtained for the capacity of the layer also indicate that the thickness of the film formed over the matrix is less than that obtained using untreated samples. However, in the samples treated by immersion in $CeCl_3$ the cathodic precipitates are left sufficiently covered that, despite the layer over the matrix being less thick, the heterogeneous layer provides a greater degree of protection. This is reflected in the results obtained by using electrochemical techniques.

In accordance with these results, the optimum degree of protection is achieved with pretreatments by immersion for a period of two days duration. But regardless of the high degree of protection given by the proposed treatments, this relatively long duration of the process makes it very unlikely that this type of treatment would be practical on an industrial scale. However, in the present paper a model of the layer and a methodology for characterizing its electrochemical properties are proposed, and this may constitute a basis for improving the design of processes that are more viable industrially.

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