Inhibition of the corrosion process of alloy AA5083 (Al-Mg) in seawater by cerium cations. An EIS study

Inhibierung des Korrosionsprozesses der Legierung AA5083 (Al-Mg) in Meerwasser durch Cer-Kationen. Eine EIS Untersuchung

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The principal corrosion process of the alloy AA5083 in aerated NaCl solutions mainly affects the zones occupied by Al(Mn,Fe,Cr) cathodic precipitates, over which the oxygen reduction reaction takes place. Thus, the design of an effective protection system could be based on the use of cathodic inhibitors. In previous papers, the inhibition efficiency of various lanthanide chlorides, particularly $CeCl_3$, has been proved. These compounds act as cathodic inhibitors, blocking these cathodic sites by means of the precipitation of a lanthanide oxide or hydroxide film. In this paper, EIS has been used to detect the blocking effect of the cathodic sites. This fact is reflected in the electrical response of the system through the minimisation of the values of those elements of the electrical loop that are related to the response of the cathodic intermetallics. In addition, the dielectric properties of the anodic film have been evaluated by measuring the value of the associated capacitance. From these values, it can be concluded that the thickness of the film produced over the matrix when the inhibitor is added is much lower than that produced in the bare solution. This finding is in good agreement with the results obtained with other techniques and may be related to the minimisation of the anodic reaction as a consequence of the decrease in the intensity of the cathodic process by the action of $CeCl_3$.

Der Korrosionsprozess der Legierung AA5083 in belüfteten NaCl-Lösungen betrifft im wesentlichen die Bereiche, die von den kathodischen Al(Mn, Fe, Cr)-Ausscheidungen, über die die Sauerstoffreduktionsreaktion stattfindet, eingenommen, wird. Daher könnte der Entwurf eines wirksamen Schutzsystems auf dem Einsatz kathodischer Inhibitoren basieren. In vorangegangenen Arbeiten wurde die Inhibierungswirksamkeit verschiedener Lanthanitchloride, im wesentlichen $CeCl_3$, nachgewiesen. Diese Verbindungen wirken als kathodische Inhibitoren, die die kathodischen Bereiche durch Ausscheidungen von Lanthanitoxiden oder Hydroxidfilmen blockieren. In der vorliegenden Arbeit wurde die Elektrochemische Impedanzspektroskopie (EIS) eingesetzt, um den Blockiereffekt der kathodischen Bereiche zu detektieren. In der elektrischen Antwort des Systems wird dies durch Minimierung der Werte derjenigen Elemente in dem elektrischen Schaltkreis reflektiert, die mit der Reaktion der kathodischen intermetallischen Verbindungen zusammenhängen. Zusätzlich sind die dielektrischen Eigenschaften des anodischen Films durch Messung der damit verbundenen Kapazität untersucht worden. Aus diesen Werten kann gefolgert werden, dass die Dicke des über der Matrix produzierten Films bei Zugabe des Inhibitors wesentlich geringer ist als in der inhibitorfreien Lösung. Dieser Befund steht in Übereinstimmung mit den Ergebnissen, die mit anderen Methoden beobachtet worden sind, und kann auf die Verringerung der anodischen Reaktion als Folge der Abnahme der Intensität des kathodischen Prozesses durch die Wirkung von $CeCl_3$ zurückgeführt werden.

1 Introduction

The microstructure of the alloy AA5083 (Al-Mg) is characterised by the presence of three types of intermetallic compounds, which have been identified as Al(Mn,Fe,Cr), Al (Si,Mg) and Al-Mg [1, 2]. The presence and distribution of Al(Mn,Fe,Cr) particles basically condition the corrosion behaviour of the alloy AA5083 in aerated NaCl solutions [1–6]. When a sample of the alloy AA5083 is immersed in a NaCl solution, the main corrosion process which takes place is localised alkaline corrosion in the metal matrix surrounding the Al(Mn,Fe,Cr) particles, which act as permanent cathodes [4–6]. The results reported in [1–6] show that the other two types of precipitates present do not have an immediate influence on the corrosion behaviour of the alloy. The cathodic behaviour of the Al(Mn,Fe,Cr) causes the reduction of oxygen to OH^- ions to take place immediately over the precipitates [7]. Consequently, there is a local pH increase in the zones closest to the precipitates [8]. All this gives rise to the dissolution of the oxide layer in the area of the metal matrix surrounding the precipitate and, subsequently, the local alkalisation causes an intense attack on the matrix. The evolution of this process over time can lead to the physical separation of the precipitate from the matrix, leading to the formation of hemispherical pits. Si-

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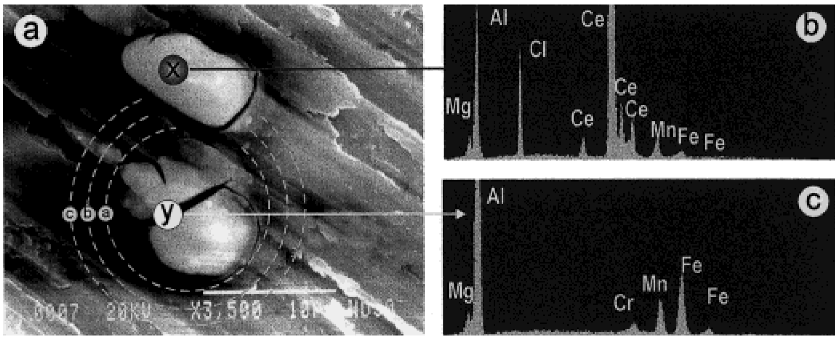

Fig. 1. (a) SEM image of a sample of AA5083 alloy after two hours of immersion in a 3.5% NaCl solution doped with 500 pmm of $CeCl_3$. (b) EDS spectrum acquired on the cerium island. (c) EDS spectrum acquired on the substrate in a cerium island

Abb. 1. REM-Abbildung einer Probe der Legierung AA5083 nach 2-stündigem Tauchen in eine mit 500 ppm $CeCl_3$ dotierte 3,5% NaCl-Lösung. (b) Auf den Cerinseln erfasstes EDS-Spektrum. (c) Auf dem Substrat in einer Cerinsel erfasstes EDS-Spektrum

multaneously to the process of localised alkaline corrosion, a second process takes place. This process is related to the formation of an oxide film covering those zones of the matrix that are free of cathodic intermetallic particles. The thickness of this oxide film increases with the time of exposure.

The consequence of the preceding comments is that the protection against corrosion of the AA5083 alloy in NaCl solutions must be focused on minimising the effects of the presence of the cathodic compounds. To achieve this, the protection system must be designed around the use of cathodic inhibitors, which act directly on the cathodic reaction by blocking the cathodic sites present in the material [9].

In the last decade, various different protection systems have been developed in order to inhibit the corrosion process of different aluminium alloys in NaCl solutions [10, 11]. Most of these systems were developed as environmentally-friendly alternatives to the use of Cr (VI) compounds, and lanthanide compounds are among the substances that have been investigated as an alternative to chromates as cathodic inhibitors and in the development of conversion coatings [11–18].

In relation to the corrosion process of the AA5083 alloy in aerated NaCl solutions, the efficiency of different lanthanide chlorides, $LnCl_3$, as inhibitors has been proved in previous studies [19–24]. In these papers, the cathodic mechanism of the inhibition process has been confirmed. Basically, this mechanism operates in two steps. In the first step, an oxide or hydroxide of the lanthanide cation is formed as a consequence of the reaction of this cation with the OH- ions formed in the cathodic reaction occurring over the Al(Mn,Fe,Cr) cathodic precipitates. Since the lanthanide compound formed is highly insoluble, in a second step, this compound is precipitated over the intermetallic particles, blocking the cathodic reaction and, therefore, the corrosion process, Fig. 1. The results obtained in [19–24] have shown that the greatest degree of inhibition is obtained when a concentration of 500 ppm of $CeCl_3$ is attained in the bare solution. These results have been quantified mainly by weight loss and DC electrochemical tests. Both techniques provide information about the overall behaviour of the alloy. However, from this kind of study, it is not possible to analyse and evaluate how the inhibition process affects each of the sub-processes taking place in the system.

In this paper, Electrochemical Impedance Spectroscopy (EIS) has been applied to the study of the process whereby cerium chloride ($CeCl_3$) inhibits corrosion of the alloy AA5083 in aerated NaCl solutions. It is well known that this technique yields information related to the different processes that can take place almost simultaneously in complex systems. Thus, applying EIS to this corrosion system, it is possible to evaluate the influence of the addition of $CeCl_3$ to the medium, on the electrochemical response of each sub-process that occurs when alloy AA5083 is corroding.

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

2 Experimental

Samples of alloy AA5083 of 30 × 25 × 4 mm were used. The composition of this alloy is given in Table 1. Before testing, the samples were wet-polished with SiC paper of up to 500 grits, de-greased with ethanol and rinsed carefully in distilled water.

The corrosion tests were performed in distilled water containing NaCl at 3.5 %. In order to inhibit the corrosion process of the alloy, $CeCl_3$ was added to obtain a 500 ppm solution.

The impedance spectra were acquired using a SI 1287 potentiostat coupled to a SI 1255 FRA. An Ag/AgCl electrode was used as reference electrode. A PC running the Corrware and ZPlot programs of Scribner controlled both devices. In general, the amplitude of the AC signal applied was 5 mV. The FT-ENGINE routine of the Equivalent Circuit option of the ZView application of Scribner was used to construct the equivalent circuit model.

3 Results and discussion

An EIS study of the behaviour of the AA5083 alloy against corrosion was presented in [25]. In this study, three time constants were identified in the recorded impedance spectra. The time constant appearing at highest frequencies was related to the reactions taking place in those areas occupied by the cathodic intermetallic compounds. The second time constant, located in the intermediate range of frequencies, was associated with the formation of the oxide film over the metallic matrix surface. Lastly, the time constant observed at lowest frequencies was associated with the charge transport phenomena present in the system. From these considerations, an equivalent circuit model was proposed, Fig. 2(a). Data included in [25] show that this model reproduces the electrochemical response of the system. Moreover, the analy-

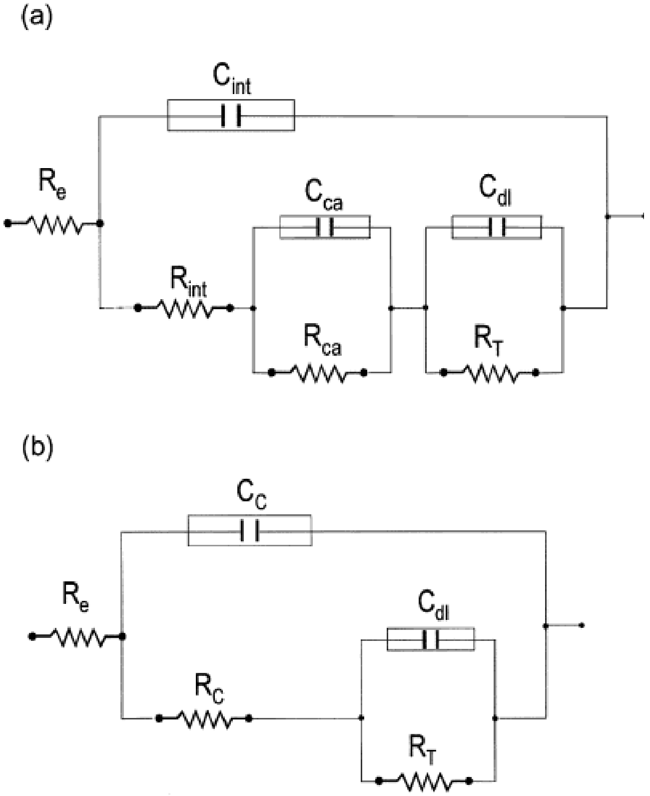

Fig. 2. Equivalents circuit for reproducing the electrochemical response of the system. (a) Three-loop circuit proposed for simulating the electrochemical behaviour of the AA5083 alloy in aerated NaCl solution at 3.5%. (b) Two-loop circuit proposed for simulating the electrochemical behaviour when the inhibitor is added

Abb. 2. Äquivalenzschaltkreis zur Reproduzierung der elektrochemischen Antwort des Systems. (a) Zur Simulation des elektrochemischen Verhaltens der Legierung A5083 in belüfteter 3,5% NaCl-Lösung vorgeschlagener dreischleifiger Schaltkreis. (b) Zur Simulation des elektrochemischen Verhaltens nach Inhibitorzugabe vorgeschlagener zweischleifiger Schaltkreis

sis of the time evolution of the impedance spectra enabled the study of the evolution corresponding to each of those sub-processes. Furthermore, in the study described in [25], the information obtained from the analysis using the equivalent circuit of Fig. 2(a) was compared with that constructed using a classical two-loop circuit, such as that represented in Fig. 2(b) [26]. To a first approximation, both circuits are mathematically equivalent through the relationships

$$C_C = C_{ca} + C_{int} \tag{1}$$

and

$$R_C = R_{int} + R_{ca} \tag{2}$$

However, the analysis of the values of the circuit of Fig. 2(b) showed discrepancies with those obtained by fitting the experimental results with the circuit plotted in Fig. 2(a). The divergences were mainly because the first loop of the circuit plotted in Fig. 2(b) provides overall information on the responses associated with the film and with the cathodic compounds.

To sum up, and in accordance with the preceding comments, the electrochemical response of the alloy AA5083 in the NaCl solution would be simulated by using the equivalent circuits plotted in Fig. 2. In the same way, both circuits can be used to compare this response with the one obtained when the solution contains $CeCl_3$ at 500 ppm.

Fig. 3 plots experimental Nyquist (a) and Bode (b) diagrams recorded for samples immersed in a NaCl solution with 500 ppm of $CeCl_3$. In this figure, the spectra fitted by using the circuits of Fig. 2 are also included. It must be noticed that, with both circuits, the simulated spectra show fits to the experimental data that are as good as when no inhibitor was used [25]. According to the data obtained by SEM and EDS, when the cerium salt is added to the medium, the cathodic zones are blocked, Fig. 1, producing a decrease in the activity over them [19–24]. As a result, the localised corrosion process taking place in these zones is minimised. In agreement with these results, when the three-loop circuit is used to simulate the experimental data obtained in the inhibited solution, very low values of R_{int} and C_{int} must be obtained. In effect, when the experimental data are fitted employing the circuit of Fig. 2(a), the estimated values of R_{int} are around 1 $\mu\Omega \cdot cm^2$, while the calculated values of C_{int} are around 10^{-6} $\mu F \cdot cm^{-2}$.

In other words, using EIS, it is possible to detect the blocking of the cathodic sites on the metallic surface as a consequence of the inhibition process. This inhibition effect is reflected in the electrical model through the minimisation of the element values of the electrical loop related to the response of the cathodic intermetallics. Thus, in order to study the time evolution of the system, the obtained values of C_{int} and R_{int} lead to the conclusion that when the inhibitor is used, the RC loop associated with the electrical response of cathodic intermetallics can be obviated. Therefore, the two-loop circuit, Fig. 2(b), can model the electrochemical behaviour of the system when $CeCl_3$ is added to the medium.

3.1 Inhibition by $CeCl_3$

Fig. 4 shows the EIS spectra recorded for samples treated for different times of exposure in NaCl solutions, with a concentration of 500 ppm of $CeCl_3$ and in its absence. In this figure, it can be appreciated that, when the lanthanide salt is added to the bare solution, an increase in the impedance of the system occurs, particularly in the range of low frequencies. When the experimental data are fitted to the two-loop model, it can be observed that the increase of the |Z| values is strongly conditioned by the value of R_T, Fig. 5. According to [25], the value of R_T is related to the insulating properties of the aluminium oxide film protecting the material. As already mentioned, this film does not completely cover the surface of the alloy when it is exposed to the NaCl solution without inhibitor. Therefore, the increase observed in the values of R_T when the cerium salt is added to the bare solution might be related to the formation of a more compact film, as a consequence of the precipitation of cerium in the cathodic zones. Hence, the zones where the charge transference was higher disappear and the difference between the values of R_T calculated with and without inhibitor in the solution increases with the exposure time, Fig. 5. Thus, after 24 h, the value of R_T in the inhibited system is almost 3 times higher than in the system where no inhibitor is added. This value can be taken as a reference of the power of inhibition shown by the lanthanide salt.

The dielectric properties of the film can be evaluated through the value of the associated capacitance. This value can be estimated by fitting the experimental EIS data using

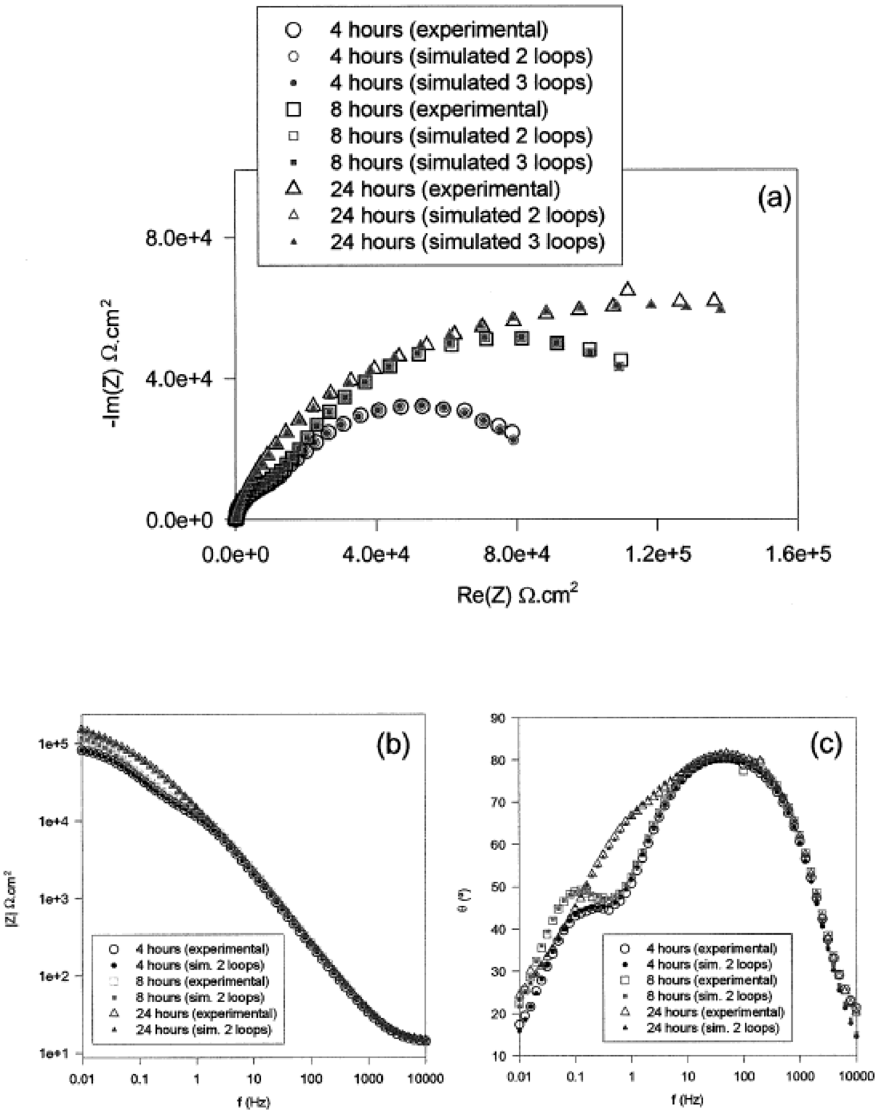

Fig. 3. EIS spectra recorded on AA5083 samples in 3.5% NaCl solutions doped with 500 ppm of $CeCl_3$ at different times. Simulated spectra are also included

Abb. 3. An AA5083 Proben in 3,5% NaCl-Lösungen, die mit 500 ppm $CeCl_3$ dotiert waren, zu verschiedenen Zeiten aufgenommene EIS-Spektren. Simulierte Spektren sind ebenfalls enthalten

the electrical models included in Fig. 2. According to [25], the value of C_C, obtained by using the two-loop circuit, only provides overall information of the dielectric properties of the film. This is due to the fact that this parameter jointly evaluates the electrical capacitances of the passive film over the matrix and over the intermetallic compounds. Thus, the overall evaluation on the sample surface produces a value of C_C notably higher than that corresponding to the film developed on the matrix, C_{ca}, which can be evaluated through the three-loop model. Therefore, the average thickness determined through C_C would be lower than that of the film actually developed on the matrix, which is calculated through C_{ca}.

On the other hand, according to the aforementioned, when the inhibitor is used, the value of the capacitance associated with the film can be calculated by using the two-loop circuit, Fig. 2(b), due to the fact that, in this case, the film completely covers the sample surface.

All the comments made above must be taken into account when comparing the values of the capacitances associated with the film developed with and without inhibitor. Thus, the values of C_C obtained in the bare solution are higher than those obtained for the samples treated with $CeCl_3$, when the two-loop circuit is used to fit the experimental data, Fig. 6(a). From these results, a greater thickness of film should be expected to be produced over the surface of samples immersed in the solution containing cerium. However, as has been commented, it is necessary to take into account that, when no inhibitor is added, the value of C_C averages the contributions of the films over both the matrix and the intermetallic compounds.

Therefore, in order to compare the thickness of the films over the matrix, it would seem more appropriate to use the C_{ca} value, calculated from the three-loop model, for the case of samples exposed to the bare solution [25]. Fig. 6(b) plots the evolution with the exposure time of both the values of C_C, for samples treated with $CeCl_3$, and C_{ca}, for samples not treated with the lanthanide salt. This figure indicates that the value of C_{ca} is lower than that of C_C for the first four hours of treatment. This difference can be explained in terms of the thickness of the film, which covers the metallic matrix. Thus, from these data, the thickness developed over the matrix when the inhibitor is added is much lower than that developed in the bare solution. On the other hand, from the evolution over time of these values, it can be concluded that the thickness of the film produced increases continuously in the samples immersed in the $CeCl_3$ containing solution. However, this

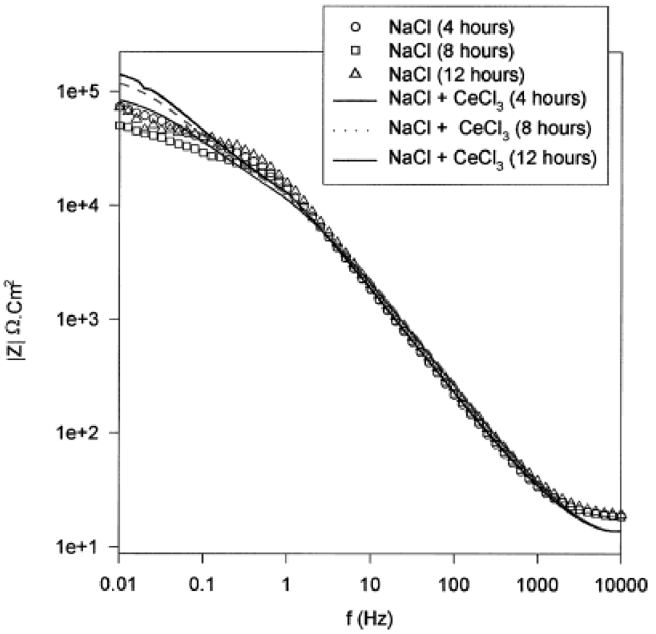

Fig. 4. Bode plots recorded at different times on AA5083 samples in 3.5% NaCl solution doped with 500 ppm of $CeCl_3$ and in its absence

Abb. 4. Zu verschiedenen Zeiten an AA5083 Proben in 3,5% NaCl-Lösungen, ohne und mit Zugabe von 500 ppm $CeCl_3$, aufgenommene Bode-Darstellungen

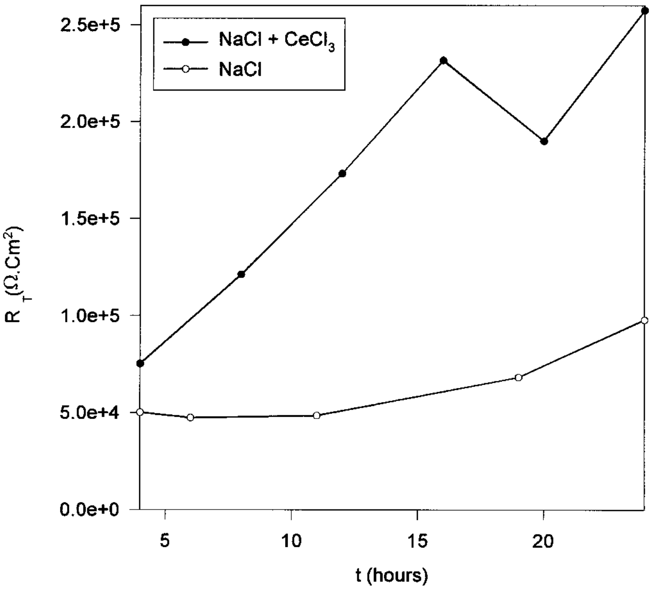

Fig. 5. Time evolution of R_T estimated on AA5083 samples in 3.5% NaCl solution doped with 500 ppm of $CeCl_3$ and in its absence

Abb. 5. Von AA5083 Proben in 3,5% NaCl-Lösungen, ohne und mit Zugabe von 500 ppm $CeCl_3$, abgeschätzte zeitliche Entwicklung von R_T

parameter remains approximately constant in the case of samples immersed in the bare solution.

All these results are in agreement with the conclusions that can be drawn from the analysis of the time evolution of the open circuit potential [27]. Fig. 7 shows the E_{corr}-t diagrams corresponding to samples exposed to the NaCl solution with and without $CeCl_3$ at 500 ppm. As can be observed in this figure, both diagrams present two clearly defined zones: a transient zone, where E_{corr} evolves from an initial potential to a steady-state potential, which defines the second zone. The initial value of the E_{corr} and the transition time are strongly dependent on the density of intermetallics present in the metallic surface [4, 20, 27]. During the transition time, the alloy is polarised due to the development of a film as a consequence of the anodic reaction. The intensity of this reaction is conditioned by the intensity of the cathodic process, which depends on the number of permanent cathodic sites on the sample surface. Thus, when the number of cathodic inclusions is high, the intensity of the cathodic process is also high and, consequently, the film develops quickly. However, when the lantha-

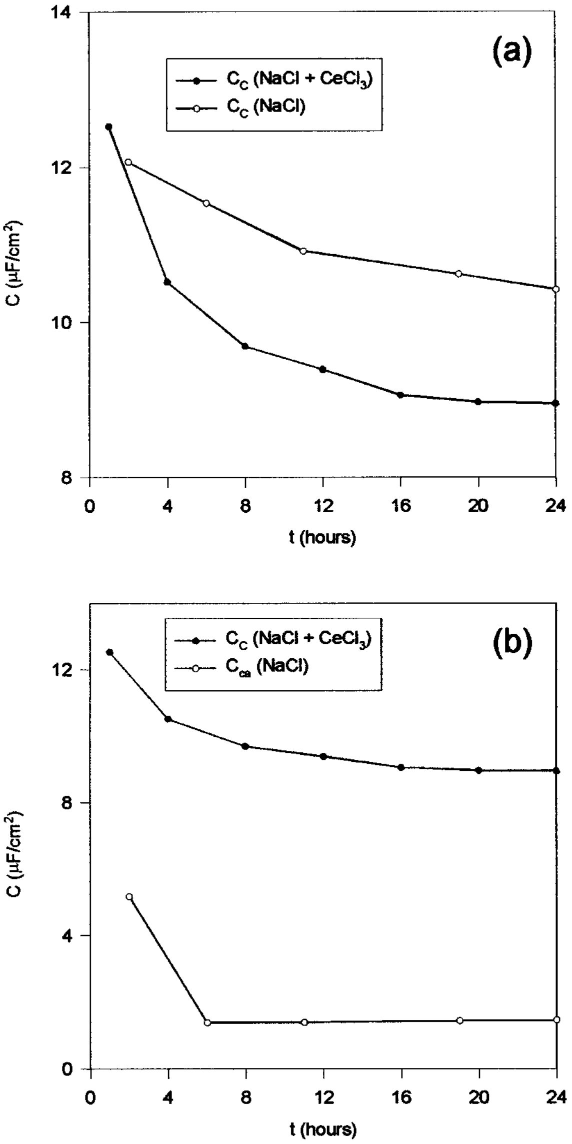

Fig. 6. Time evolution of the capacitances associated with the film for AA5083 samples in 3.5% NaCl solution doped with 500 ppm of $CeCl_3$ ((a) and (b) C_C) and in its absence ((a) C_C and (b) C_{ca})

Abb. 6. Zeitliche Entwicklung der mit dem Film verbundenen Kapazitäten für AA5083 Proben in 3,5% NaCl-Lösung, die mit 500 ppm $CeCl_3$, dotiert war ((a) und (b) C_C) und bei Abwesenheit von Cer ((a) C_C und (b) C_{ca})

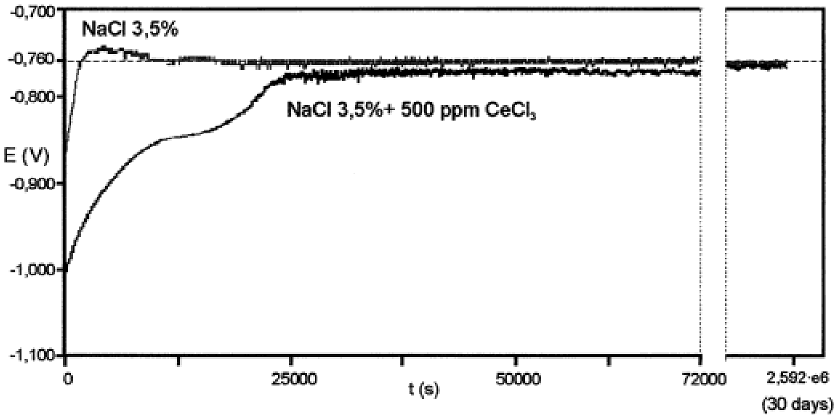

Fig. 7. E_{corr}-t diagrams corresponding to AA5083 samples in 3.5% NaCl solution doped with 500 ppm of $CeCl_3$ and in its absence

Abb. 7. E_{corr}-t-Diagramme für AA5083 Proben in 3,5% NaCl-Lösung ohne mit 500 ppm $CeCl_3$

nide salt is added to the aggressive medium, the cathodic sites are blocked, producing a decrease in the intensity of the cathodic process. This process involves a decrease in the intensity of the anodic process and, as a result, the film develops more slowly.

According to these considerations, the production of the oxide film over the matrix surface is faster when the samples are exposed to the bare solution. In this case, the steady-state potential is reached sooner. When this situation is reached, the increase in the thickness of the film is halted. This explains the evolution observed for C_{ca}, Fig. 6(b). On the other hand, when the samples are exposed to the $CeCl_3$ containing solution, the value of C_C decreases continuously. This may be due to the fact that the steady-state potential has not been reached in the time of exposure studied and the film is still increasing.

4 Conclusions

A previous study [4] indicated that the main corrosion process of the AA5083 (Al-Mg) alloy in NaCl solutions is the localised alkaline corrosion in the metal matrix surrounding the Al(Mn,Fe,Cr) cathodic precipitates. Simultaneously, the anodic reaction provokes the formation of an oxide film covering the zones of the matrix free of those cathodic particles. In accordance with [25], a three-loop circuit can model the electrochemical response of the alloy, Fig. 2(a), where each loop is associated with one of the sub-processes which takes place in the alloy.

In this paper Electrochemical Impedance Spectroscopy has been applied to evaluate the influence of the addition of $CeCl_3$ to the NaCl solution, on the electrochemical response of each sub-process that takes place when alloy AA5083 is corroding. This compound acts as a cathodic inhibitor, blocking the zones occupied by the cathodic intermetallics through the precipitation of a cerium oxide or hydroxide. Thus, using EIS, it is possible to detect this blocking of the cathodic sites. The inhibition effect is reflected in the electrical response of the system by the minimisation of the values of those elements of the electrical loop related to the response of the cathodic intermetallics. Therefore, a two-loop circuit, Fig. 2(b), must be constructed to model the electrochemical behaviour of the system when $CeCl_3$ is added to the medium.

In addition, by using EIS it has been established that the film produced over the metal surface can be characterised by the values of R and C in each loop. Thus, the increase observed in the values of R_T when the cerium salt is added to the bare solution could be related to the formation of a more compact film, as a consequence of the precipitation of cerium in the cathodic zones. The dielectric properties of the film have also been evaluated by the value of the associated capacitance. From these values, it can be concluded that the thickness of the film formed over the matrix when the inhibitor is added is much lower than that formed in the bare solution. Moreover, our results show that the thickness of the film produced increases continuously in the samples immersed in the $CeCl_3$-containing solution. However, this parameter remains approximately constant in the case of samples immersed in the bare solution. This finding is in good agreement with the results obtained with other techniques and may be related to the minimisation of the anodic reaction as a consequence of the decrease in the intensity of the cathodic process by the action of $CeCl_3$.

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