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LANTHANIDE COMPOUNDS AS ENVIRONMENTALLY-FRIENDLY CORROSION INHIBITORS OF ALUMINIUM ALLOYS: A REVIEW

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Abstract—Currently, chromates are among the most common substances used as inhibitors or incorporated in anticorrosive pretreatments of aluminium alloys. However, these compounds are highly toxic and their use produces serious environmental hazards. Consequently, an intense research effort is being undertaken to replace chromates by more ecological compounds. In recent years, several authors have begun studies of the behaviour of lanthanide compounds in the corrosion protection of metallic alloys.

After a brief overview of the use of chromates and their ecological alternatives in corrosion protection systems, the paper reviews progress from the literature published to date concerning the application of lanthanide compounds as corrosion inhibitors of aluminium alloys in aqueous solution. Aspects of the mechanism involved in the cathodic inhibition process by lanthanides are also dealt with. In addition, these compounds have been used to prepare chromate-free conversion coatings by full-immersion and electrochemical activation methods. Treatments proposed for these conversion coatings are discussed in detail.

From the comprehensive review presented in this article, it is concluded that lanthanide compounds fulfil the basic requirements for consideration as components of more environmentally-friendly formulations: low toxicity and acceptable protective capacity. However, methods proposed up to now present various limitations that restrict their application in practice. Further research efforts are necessary to develop feasible treatments for industry.
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CORROSION INHIBITION BY CHROMATES

Cr(VI) compounds, mainly chromates, are widely applied as corrosion inhibitors in aqueous media. A wide range of metals and alloys, such as iron, steels, aluminium alloys, zinc, copper, lead and others,[1–6] can be protected using chromates. Their high efficiency/cost ratio has made them standard corrosion inhibitors.[7] Nevertheless, due to their oxidising nature, chromate concentration in the medium must be periodically checked, in order to avoid undesirable corrosion results, since concentrations lower than a critical value can promote a pitting process.[8–11] Even if the chromate content is at an optimum, the presence

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of reducing agents in solution can cause their concentration to fall below the critical range.[12] Moreover, an upper concentration limit must not be exceeded either, in order to maintain their inhibiting properties, for example, when chromates are used as pigment of primers.[13]

In the anticorrosive pretreatments of metallic alloys, they are in common use across a range of different industries, from aerospace to the automotive and naval sectors. In this application, chromium is incorporated into protective coatings applied to metallic surfaces. These coatings provide effective corrosion protection and, in addition, they facilitate the application of further finishing treatments, in particular, painting. In the specific case of surface finishing procedures for aluminium alloys, chromates have been applied in three different ways: incorporated into conversion coatings, as an additive in anodising baths and as pigment in painting primers.[14–17]

By their general working mechanism, chromates can be considered as anodic oxidising inhibitors.[18,19] There are several models related to the growth of protective chromium-rich films.[20,21] However, in spite of their extensive use, the full details of precisely how they work are still not known. At the present time, it is accepted that better knowledge of the inhibition mechanism of chromates is required, and attempts to provide this are continuously being published.[22]

In spite of their high efficiency and established industrial application, process plants using chromates will have to be shut down progressively over the next few years. Recently-enacted environmental laws in many countries have imposed severe restrictions on chromate use due to its high toxicity[12,23] and consequent environmental hazards.[24]

Ecological alternatives to chromates

Regarding the protection of aluminium alloys, in recent years more ecological alternatives have been investigated to replace chromates in their different fields of application. Thus, efforts towards this have been focused on the search for new corrosion inhibitors and new formulations of both anodising baths and conversion coatings.[25] In agreement with Cohen,[25] the development of viable alternatives to chromates is still in its infancy. Many of the new systems are only in the experimental phase and a wide variety of approaches is being investigated.

A variety of passivating inhibitors have been tested. Ions such as MoO_4^{2-}, MnO_4^{2-}, SiO_4^{2-} and WO_4^{2-} have shown efficiencies similar to that of chromate in protecting aluminium alloys.[26–29] Other anions, like benzoate or nitrite, have been shown to give a high degree of protection to stainless steels exposed to solutions containing chlorides.[26,30,31]

In relation to replacements for chromic acid anodization on aluminium, different attempts have been reported.[32–34] The most promising candidate in this field seems to be thin-film H_2SO_4 anodization.[33] The advantage claimed for this treatment is that it avoids the fatigue performance limitations resulting from conventional H_2SO_4 anodising.

Regarding chromate-free conversion coatings, various different processes have been proposed based on phosphate and sulphate solutions, also incorporating nitrite or borate respectively.[35–37] Also, in relation to chromate-free primers for aluminium alloys, passivating inhibitors such as vanadate, molybdate or phosphate have been successfully tested.[38–40]

A different approach, studied for the replacement of chromates as corrosion inhibitors, involves using cathodic or mixed inhibitors. The behaviour of various salts containing zinc, calcium, barium or manganese has also been studied.[41–43] In this respect, lanthanide compounds are among the substances that have been investigated as an alternative to chromates, both as cathodic inhibitors and in the development of conversion coatings. In the following section, a review of the information available on this topic is presented.

LANTHANIDE SALTS AS CORROSION INHIBITORS

It is well known that lanthanide ions form insoluble hydroxides[44] which enable them to be used as cathodic inhibitors. Lanthanides have a low toxicity and their ingestion or inhalation has not been considered harmful to health[45] whilst the toxic effects of their oxides are similar to those produced by sodium chloride.[46] Furthermore, lanthanides can be considered as economically competitive products[47] because, as elements, some of them are relatively abundant in nature;[48] cerium, for instance, is as plentiful as copper.[49] Production of lanthanides has shown a continuous increase in recent years.[50] Taking all these facts into account, it is reasonable to consider the development of corrosion protection methods using this family of compounds.

At first, the lanthanide elements, principally cerium, were used in protection against corrosion at high temperatures. Using several incorporation methods, cerium and, to a lesser extent, other Rare Earth (RE) elements have been used to improve the adherence of oxide films developed during the oxidation processes of different metallic alloys.[51–58] In this particular application, special attention has been paid to ionic implantation as the lanthanide incorporation method.[59–65]

Surface films generated on RE-doped alloys have improved behaviour against both high temperature oxidation and aqueous corrosion. Thus, Lu and Ives[65] showed that implantation of cerium on AISI 316 stainless steel decreases its corrosion rate in NaCl solution by two orders of magnitude. These authors suggest that the growth of a CeO_2 surface film blocks both anodic and cathodic active surface areas, thus leading to the above-mentioned decrease in corrosion rate.

The earliest applications of lanthanides as corrosion inhibitors were stimulated by the need to replace chromates imposed by new international environmental standards. There are several papers in the literature dealing with the use of lanthanides as corrosion inhibitors for several metals and alloys such as zinc,[66–69], bronze,[70,71], nickel,[72] mild steels[73–75] or stainless steels.[76–89] Since chromates are in most extensive use in the pre-treatment of aluminium alloys, most of the research to date has been focused on the application of RE salts to the anticorrosive protection of these alloys.

LANTHANIDES AS CORROSION INHIBITORS OF ALUMINIUM ALLOYS

The pioneering studies concerning the application of lanthanides for the corrosion protection of aluminium alloys are those by Hinton, Arnott and Ryan.[90–95] These authors study the effect of increasing the concentration of $CeCl_3$, on both uniform and pitting corrosion of AA7075 (Al–Zn) alloy. The degree of protection provided by the addition of cerium, in concentrations ranging from 0 to 1000 ppm, to NaCl solution was evaluated by weight loss and linear polarisation measurements. Corrosion rate values calculated from data included in[90] allow study of the evolution of this parameter as a function of inhibitor

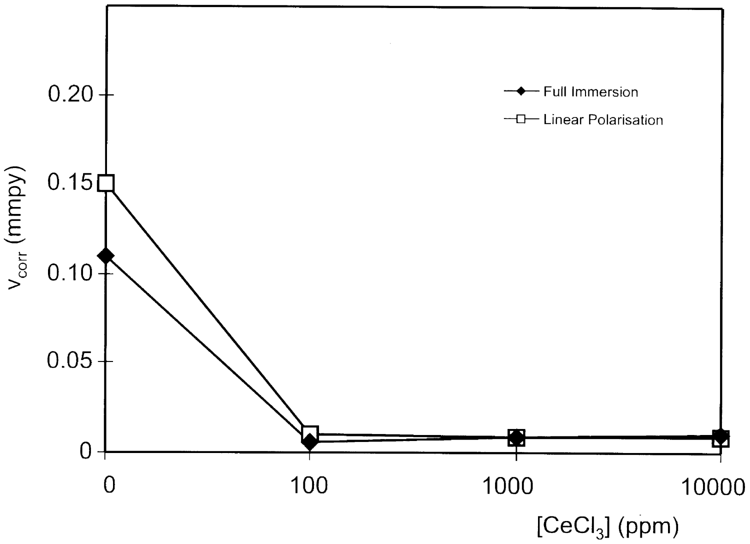

Fig. 1. Evolution of corrosion rate of alloy AA7075 in NaCl solutions as a function of $CeCl_3$ concentration. Data adapted from reference 90.

concentration, Fig. 1. This figure shows that the uniform corrosion rate decreases steeply up to 100 ppm of $CeCl_3$. Higher concentrations of $CeCl_3$ only produce a stabilisation in the rate of corrosion. The optimum inhibitor concentration was found to correspond to a concentration of 100 ppm of $CeCl_3$ in the solution. Moreover, good agreement between the results obtained from both experimental techniques can be observed in this figure.

Regarding pitting corrosion, some conclusions can be obtained from the polarisation curves included in Ref. 90. Pitting generation resistance, R, can be evaluated as the difference between the pitting nucleation potential, E_{pit}, and the corrosion potential, E_{corr}. The linear polarisation curve, carried out in bare solution, shows a nearly horizontal anodic branch in which pitting nucleation potential is very close to E_{corr}, indicating an almost zero R value. Figure 2 plots the evolution of R parameter as a function of $CeCl_3$ concentration. According to this figure, resistance to pitting corrosion increases slowly from 0 to 100 ppm and shows the steepest increase in the range between 100 and 1000 ppm, whilst a steady value of R is obtained for higher concentrations up to 10000 ppm of $CeCl_3$.

Similarly, the inhibition behaviour of other lanthanide salts such as YCl_3, $LaCl_3$, $PrCl_3$ and $NdCl_3$, has been investigated by the same authors.[67,68,91–95] A trend in the evolution of corrosion rates with lanthanide salt concentrations similar to that depicted in Fig. 1 is observed. The protective power of RE trichloride has also been compared with other salts such as $FeCl_2$, $CoCl_2$ and $NiCl_2$. Figure 3 plots the values for degree of protection provided by the above mentioned salts. In these experiments, the corrosion rates of aluminium alloy AA7075, in NaCl 3.5% plus 1000 ppm of inhibitor, have been measured. According to data included in Fig. 3, the best degree of inhibition is achieved with Ce^{3+} cations. It is significant that the degree of inhibition provided by the optimum concentration of $CeCl_3$ is similar to that obtained with chromate, showing that lanthanide salts can be considered both as efficient and as ecological alternatives to chromate.

The alloys studied by Hinton *et al.* are mainly used in the aerospace industry. Never-

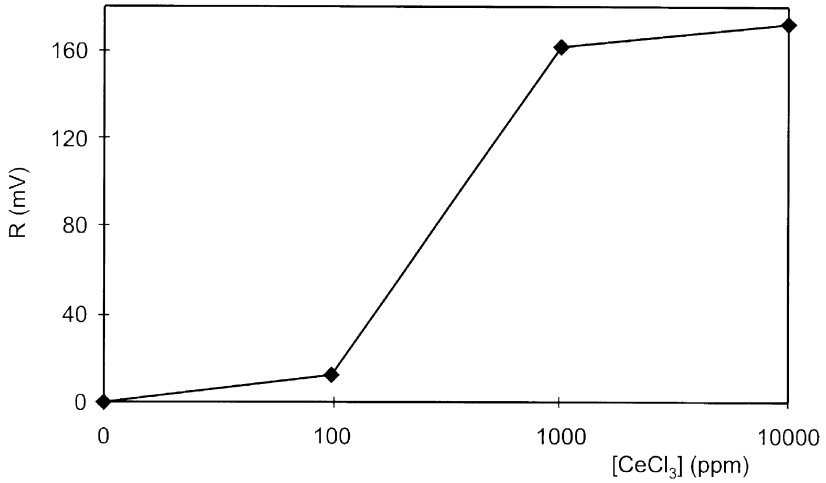

Fig. 2. Evolution of pitting resistance as a function of $CeCl_3$ concentration for alloy AA7075 in NaCl solutions. Data computed from reference 90.

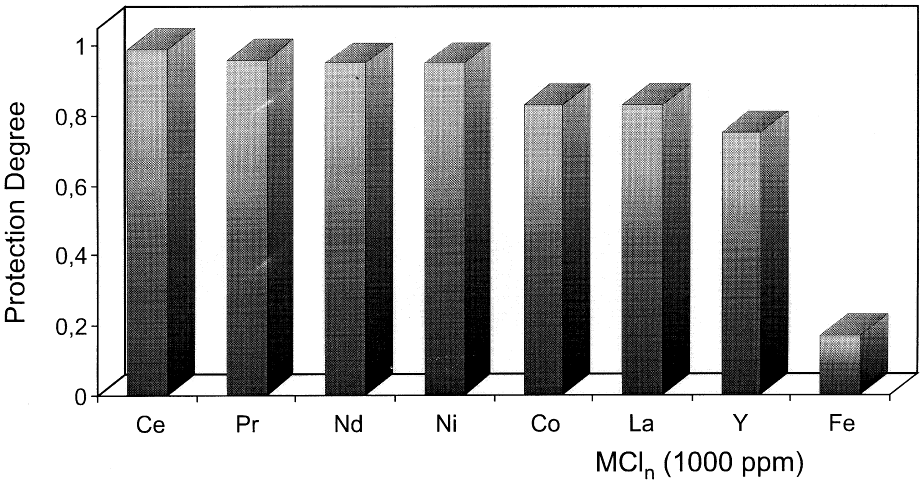

Fig. 3. Degree of protection against uniform corrosion of alloy AA7075 in NaCl solutions provided by additions of 1000 ppm of different metallic chlorides. Data adapted from Refs. 90–95.

theless, other studies following Hinton have been carried out on alloy Al–Mg 5083, developed for specific applications in marine environments. The protection of this alloy against uniform and pitting corrosion by lanthanide salts in seawater has been studied in Refs. 96–100 In,[97] the effect of $CeCl_3$ concentrations from 0 to 1000 ppm in 3.5% NaCl aerated aqueous solutions is considered. Figure 4, taken from this reference, shows that the evolution of the corrosion rates with increasing inhibitor concentration is similar to that observed for the AA7075 alloy in Fig. 1. For the Al–Mg alloy, a steep decrease of corrosion rate due to the addition of inhibitor is evident up to 100 ppm concentration whilst an almost

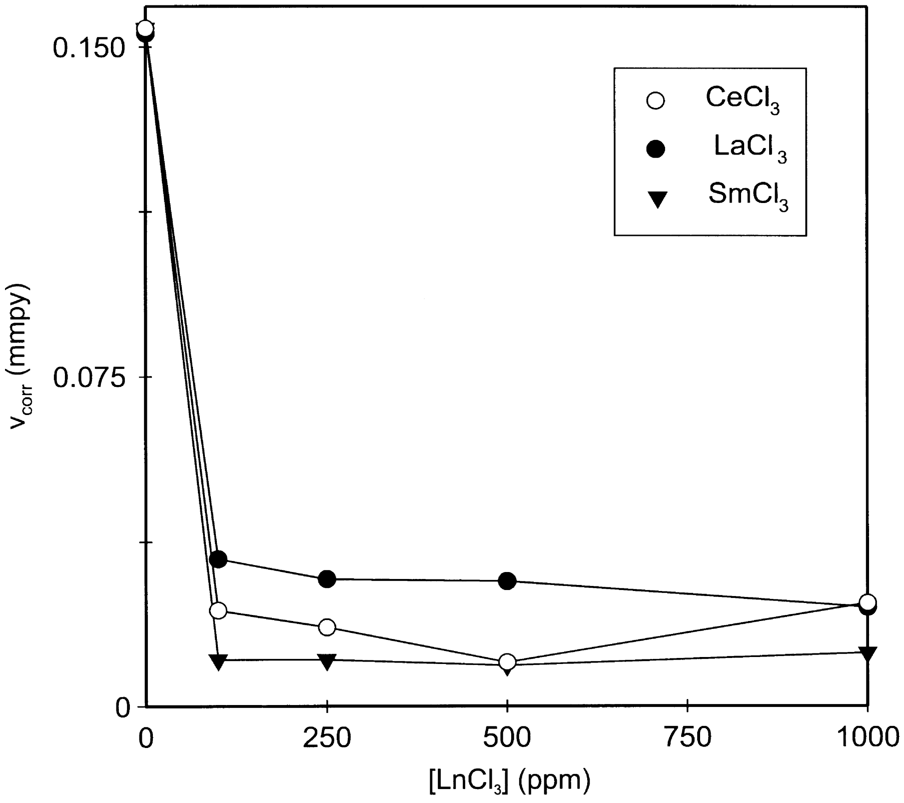

Fig. 4. Evolution of corrosion rate of alloy AA5083 in NaCl solutions as a function of LnCl$_3$ concentration. Data adapted from reference 97.

stable value for the degree of protection is observed for higher inhibitor concentration. It is also notable that there are no substantial differences between the different lanthanide salts tested in this study.

The highest degree of inhibition against uniform corrosion is observed for a 500 ppm concentration of cerium chloride in the basic NaCl solution. For this inhibitor concentration, the uniform corrosion rate is reduced by more than 90%, a value similar to both that obtained with sodium chromate and the rate measured by Hinton *et al.* for AA7075 alloy.

In Refs. 97 and 100 the increase of pitting nucleation resistance due to the presence of cerium chloride in NaCl solutions is analysed from cyclic polarisation curves, Fig. 5. In this figure, E_{pit} corresponding to AA5083 alloy in NaCl solution can be measured, in contrast to AA7075. From this value, the pitting nucleation resistance, $R^0(E^0_{corr} - E^0_{pit})$, in this solution can be determined. Figure 5 also includes the cyclic polarisation curve recorded with the addition of CeCl$_3$. The value of E_{pit} remains close to E^0_{pit}, while the value corresponding to E_{corr} is lower than that obtained in the bare solution. These modifications finally lead to an increase of the pitting nucleation resistance, R. From calculated values of R and R^0, the pitting nucleation protection percentage, P_{pit}, can be evaluated for different concentrations of Ce, La and Sm trichlorides (Figure 6). An increase of the pitting

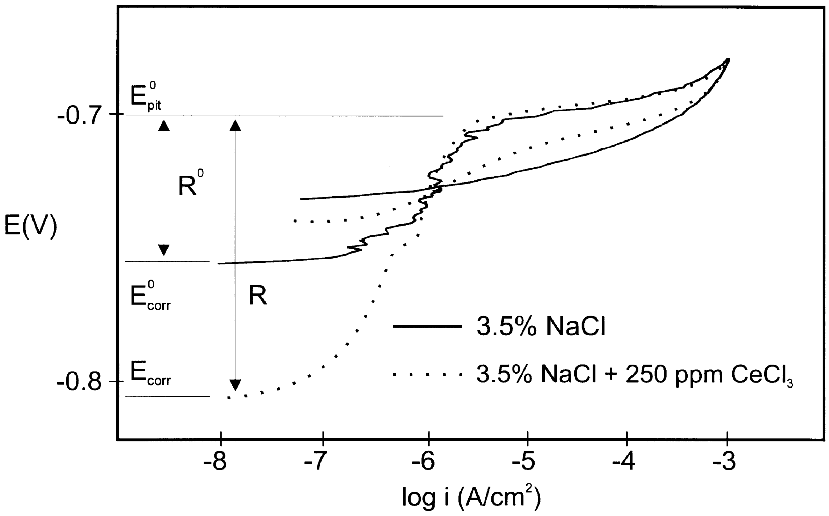

Fig. 5. Cyclic Polarisation diagrams for AA5083 in bare NaCl solution and with 250 ppm addition of CeCl$_3$. The "0" superscript values in the figure are those corresponding to the absence of inhibitor.

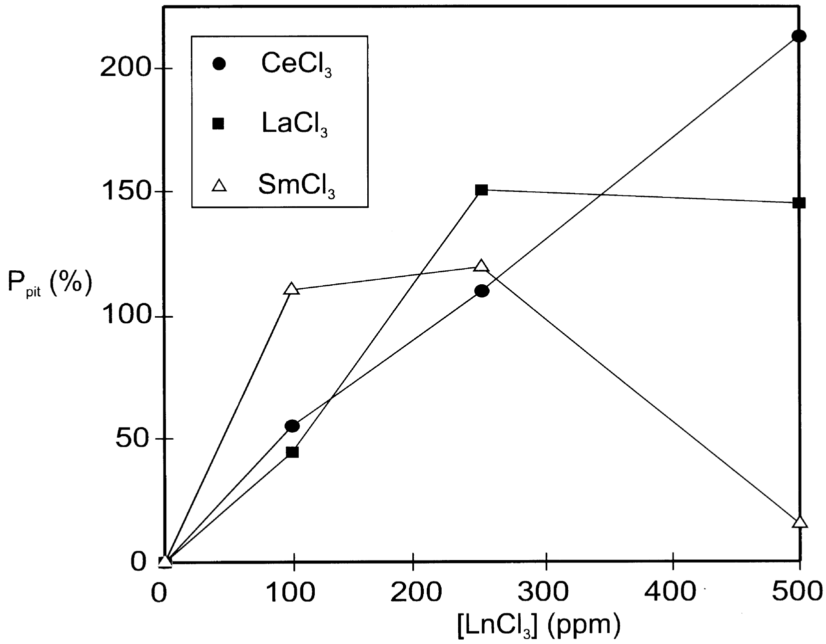

Fig. 6. Estimated values of the degree of protection against pit nucleation as a function of Ln^{3+} concentration, for alloy AA5083 in NaCl solutions.

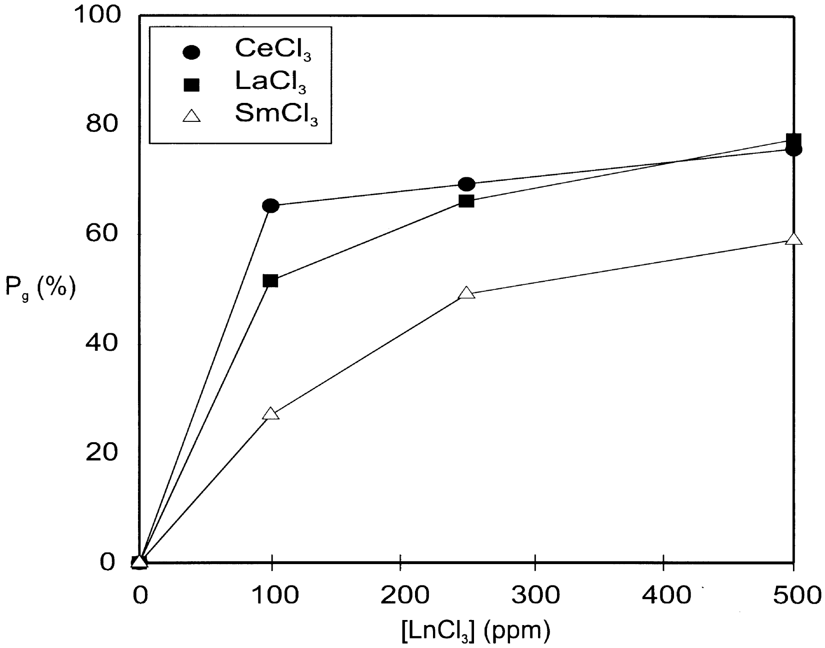

Fig. 7. Evolution of the degree of protection against pit growth as a function of inhibitor concentration, for alloy AA5083 in NaCl solutions.

nucleation resistance is observed in the presence of $LnCl_3$. It is significant that, with a 500 ppm concentration of $CeCl_3$, the degree of protection is greater than 200%, corresponding to a R value greater than the maximum obtained by Hinton and co-workers for AA7075.

In Refs. 99 and 100, the protection against pitting growth, P_g, is also evaluated in terms of the percentage of area lost in the anodic hysteresis loop of the cyclic polarisation diagram, plotted in E–i style. Fig. 7 shows that $LnCl_3$ addition leads to an increase of the pitting growth resistance. From data included in Figs. 6 and 7, it can be concluded that the addition of 500 ppm of $CeCl_3$ provides the best improvement in the behaviour of the alloy AA5083 against both pitting nucleation and pitting growth processes.

Other studies of corrosion inhibition by $CeCl_3$ for different aluminium alloys can be found in the literature. For instance, Liu studies the protection against corrosion of Al–Zn–Mg alloys in solutions containing NaCl as a function of $CeCl_3$ concentration and pH.[101] Similar studies have been done using $Ce(NO_3)_3$ and $Ce_2(SO_4)_3$, although the inhibitor effect of cerium is masked in these cases by the presence of the corresponding oxidising anions such as nitrates and sulphates.[102] In Ref. 103, a pitting nucleation delay of two days is reported for AA6061 alloy and AA6061–SiC composites in the presence of Ce in 3.5% NaCl aqueous solutions.

In summary, lanthanide salts, particularly cerium trichlorides, have been shown to be promising cathodic inhibitors against uniform and localised corrosion of a large variety of aluminium alloys. It may reasonably be expected that future developments in this field will provide efficient alternative inhibitors to the classic, but highly toxic, chromates.

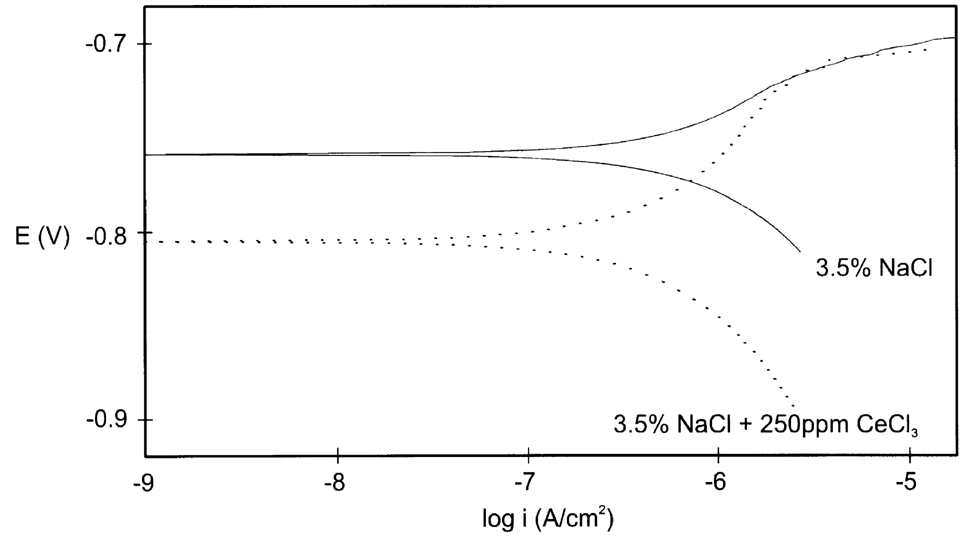

Fig. 8. Linear Polarisation diagrams for alloy AA5083 in bare NaCl solution (solid line) and with 250 ppm addition (dotted lines) of $CeCl_3$.

THE MECHANISM OF INHIBITION

Based on linear polarisation curves similar to those shown in Fig. 8 for AA5083 alloy,[99] lanthanide chlorides have been classified as cathodic inhibitors. This assumption was made in the earliest research by Hinton with AA7075, taking into account the relative position of cathodic branches in the polarisation diagrams from tests with and without inhibitors.

Recently, Isaacs has confirmed the cathodic nature of lanthanide inhibitors.[104] In Ref. 104 a simple method is proposed to discover the inhibition mechanism of cerium salts on AA2024 aluminium–copper alloy in NaCl-containing solutions. In the tests proposed by Isaacs, an aluminium–copper galvanic couple is formed. This couple would mimic the electrochemical behaviour of the cathodic copper-containing intermetallic precipitates within the alloy. The results obtained from these tests showed that the corrosion inhibition process was related to the development of a cerium-rich film over the cathodic copper surface. Results reported in Ref. 105 reveal further details regarding the origin of the protective effect observed in AA5083 samples treated with cerium-containing solutions. According to Ref. 105 samples treated for 48 hours in a 500 ppm $CeCl_3$ solution develop a surface coating in which the major component is Al, whereas cerium accumulates in dispersed islands [Fig. 9(a)]. An enlargement of the island marked with an arrow in Fig. 9(a) can be observed in Fig. 9(b). The EDS spectrum included in Fig. 9(c), shows that this island contains mainly cerium. The presence of cracks, observed in Fig. 9(b), allows us to analyse the actual nature of the metallic substrate underlying these cerium islands. The EDS spectrum recorded on this area [Fig. 9(d)] indicates that the cerium islands have formed over the $Al_6(MnFe)$ precipitates. If we recall that these precipitates are the most cathodic ones in the alloy, a feasible mechanism for the inhibition process can be envisaged. Thus, during the first stages of the corrosion process, OH^- groups would be generated over the cathodic intermetallic precipitates. This proposal has been supported by the results of

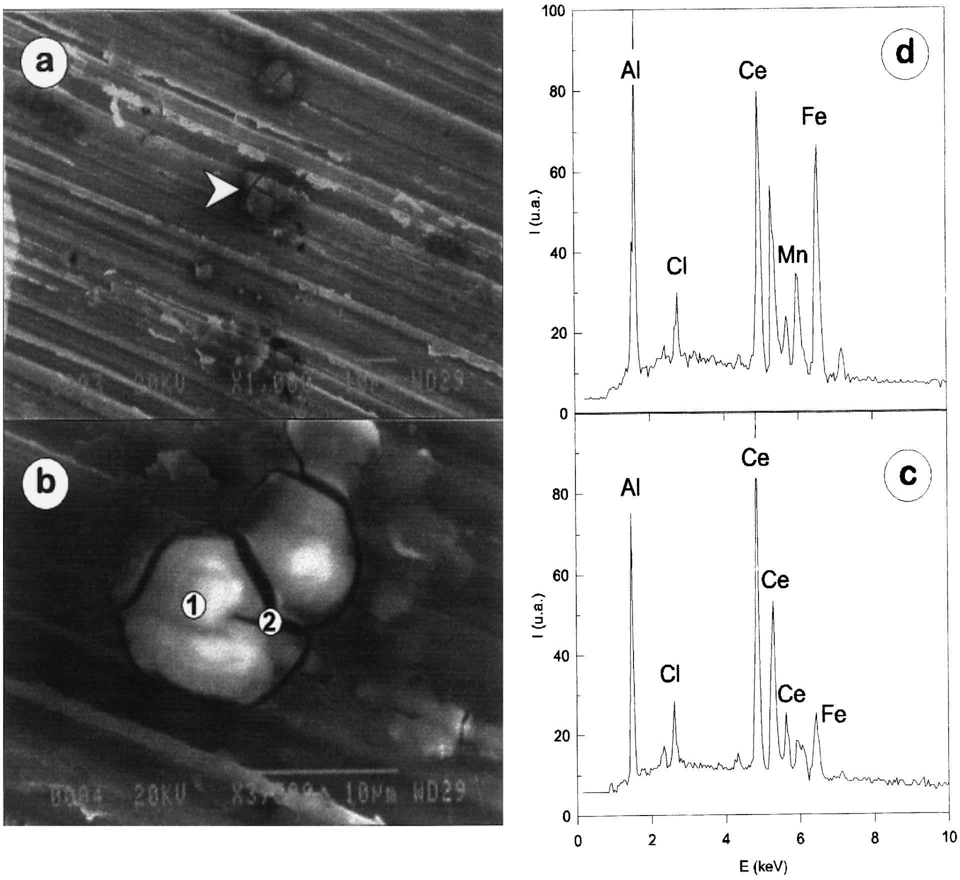

Fig. 9. (a) SEM image recorded on a sample of alloy AA5083 after a 48 hours of inmersion in 500 ppm $CeCl_3$ solution; (b) high magnification view of one of the islands observed in (a); (c) EDS spectrum recorded in (1); (d) EDS spectrum recorded in (2). Data taken from reference.[105]

Davenport, Isaacs and co-workers, who detected local increases of pH at the cathodic sites on alloy AA2024 due to the oxygen reduction.[106–110]

The hydroxyl groups formed over the cathodic sites would react with the cerium ions present in the solution. This reaction gives rise to the formation of cerium islands observed in Fig. 9(a,b). The blockage of the cathodic sites by these islands decreases the available cathodic current and, therefore, reduces the overall corrosion rate.

LANTHANIDE-CONTAINING CONVERSION COATINGS ON ALUMINIUM ALLOYS

Based on the previously mentioned film forming properties of lanthanide salts and the protective behaviour of such films, different treatments have been proposed in order to develop alternative conversion coatings to those based on chromates. In general terms, two different methods have been used to grow lanthanide films on aluminium alloys: full immersion and electrochemical activation.

As in the case of their use as inhibitor, the earliest attempts to obtain lanthanide-containing conversion coatings by full immersion were made by Hinton *et al.*[92] In this research, coatings were formed on AA7075 using 1000 ppm $CeCl_3$ solutions and a minimum corrosion rate value was observed after 90 hours of immersion.[90] Scanning Electron Microscopy (S.E.M.) studies, included in Refs. 90 and 93 confirm this time period as the optimum for the formation of a cerium-containing film that covers the whole exposed surface. Nevertheless, according to the authors, after an immersion period of about 20 hours, a significant protection level is reached. Unfortunately, such long time periods make these immersion treatments commercially unattractive.

The influence of lanthanide salts in the protection against corrosion of aluminium–lithium alloys AA2090 and AA8090 has been studied in aerated 0.5 M $Na_2(SO_4)$ and 3.5% NaCl solutions and deaerated 3.5% NaCl solutions.[111] In this research, an effective protection against pitting corrosion provided by pretreatments of full immersion in cerium-containing solutions is concluded. However, it is also observed that the protective effect of this coating is limited to a very short period of time.

In a similar fashion, Mansfeld *et al.* have proposed a full immersion method to develop cerium protective films on alloys AA2091 and AA6061, and on metal matrix composites such as AA6061–SiC and AA6061–Graphite.[112] Previously, the behaviour of cerium salts as inhibitors of these materials had been studied in 0.5 N NaCl aqueous solutions at room temperature, using Electrochemical Impedance Spectroscopy (EIS).[112–116]

The treatment tested by Mansfeld consists of exposing the material to a solution containing 1000 ppm of $CeCl_3$ open to the air and at room temperature for a period of seven days. The films obtained were tested by EIS techniques after immersion in NaCl containing solutions after different time intervals.

These cerium conversion coatings not only show a good performance against corrosion but they also improve the adherence of epoxy layers deposited onto the metallic surfaces. The degradation behaviour of such epoxy-coated samples was studied by EIS after drilling a 0.6 mm hole into the coated material. After 5 days of exposure to the NaCl solution, the surface of the coated AA6061 alloy showed filiform corrosion starting from the edge of the hole. However, Al/Gr and Al/SiC metal matrix composites did not show any kind of corrosion phenomena even after three months of exposure to the aggressive medium. By increasing the test aggressiveness, only a soft delamination was observed on the Al/SiC after 83 days, whilst the other composites remained unaltered.

A new and rapid film deposition method, named “Cerating”, has been developed and patented by Hinton and Wilson.[117] In this process, the metallic alloy is immersed in an aqueous cerium salt solution containing both oxidising agents and organic additives. The Cerating method has been successfully applied not only to aluminium alloys but also to a wide range of other metallic alloys, such as zinc, galvanised steels, stainless steels, cadmium and magnesium. However, according to the authors, the corrosion performance of these coatings in the salt spray test was not satisfactory.

Recently, further improvements of this method have led to a new patented treatment named “Cerate Coating”.[118] Basically, the Cerate coating is obtained by full immersion of the metallic alloy for 10 minutes in an aqueous solution of cerium chloride with a 0.3% by-volume hydrogen peroxide content, at 316 K and pH 1.9.[119] A prior surface cleaning and deoxidising treatment is applied. A silicate solution is used as a post-treatment stage in order to seal the coatings obtained. This process has been successfully applied to AA2024 aluminium–copper alloy. The linear polarisation data for bare and "Cerate Coated" AA2024 alloy in sodium chloride-containing solutions show a decrease in the corrosion rate of about 95%. The corrosion potential is decreased by almost 200 mV, whilst the pitting nucleation potential remains at a stable value. Because of this, a high pitting nucleation resistance can be achieved with this coating. The sealed Cerate coating survived 336 hours in the salt spray test before corrosion was apparent. The aircraft industry requires chromate conversion coatings to protect aluminium substrates for at least 168 hours in this test. The level of protection provided by the coating depends heavily on the pre-treatment prior to coating and the sealing stage after coating.

Sol–gel routes have also been researched in the deposition of CeO_2 films[120] and commercial organometallic precursors are available. However, high temperature conditions are required to generate an oxide from the initially-deposited gel film. These preparation conditions limit the use of sol–gel procedures to generate films on aluminium alloys.

In relation to alloys used in marine applications, in Ref. 121 AA5083 samples have been treated by full immersion in $CeCl_3$ solutions. The electrochemical characterisation data reported in this study indicate a significant improvement in the behaviour of the alloy against both uniform and pitting corrosion. EIS data suggest that this improvement is related mainly to the resistance of the coating formed by this treatment.

A second group of treatments, based on electrolytic activation methods have also been proposed in the literature. Thus, Hinton and co-workers propose a method based on galvanostatic treatment with cathodic currents from 0 to 0.2 mA cm^{-2} in solutions containing $CeCl_3$.[92] The best results are obtained for 0.1 mA cm^{-2} currents and an exposure time of 30 minutes in a 1000 ppm $CeCl_3$ solution. Samples coated by this method show a reduced corrosion rate in NaCl solution of one order of magnitude. However, the improvement in pitting corrosion resistance is not as high as that observed when applying the full immersion method or when the lanthanide salts act directly as inhibitors in the aggressive medium. Although the electrolytically-deposited coating reduces the required treatment time by comparison with the full immersion procedure, the degree of corrosion protection is also reduced. The presence of small holes in the coating due to hydrogen evolution has been suggested as the cause of the loss of protective properties of the film.

A better performance was observed by these authors for coatings developed in $Ce(NO_3)_3$ solutions applying a cathodic potential of 90 V for 150 seconds on AA7075 aluminium alloy.[92] In these samples, the corrosion rate is reduced by one order of magnitude and pitting nucleation resistance is higher than 300 mV. Based on Auger spectroscopy data, these authors suggest that the improvement of the protective properties of the film seems to be related to an enrichment in Ce^{+3}. Given that high DC potentials in conjunction with highly volatile organic solvents are required with this technique, large scale depositions could present practical difficulties.

Mansfeld has also proposed a two step, electrolytically activated pre-treatment based on cerium salts for the AA6061 alloy, self-named "stainless aluminium".[122] At first, the alloy is immersed for two hours in dilute hot $Ce(NO_3)_3$ and $CeCl_3$ solutions. After this pre-treatment, the alloy is anodically polarised to 0.5 V *vs.* SCE in 0.1 M $Na_2(MO_4)$. A highly stable oxide layer is obtained on the metal surface which inhibits the oxygen reduction reaction. This process has been also successfully tested for aerospace aluminium alloys such as AA7075 and AA2024.[123]

The inhibitor effect derived from the joint action of cerium and molybdate had previously been studied by Baldwin and co-workers for several alloys employed in the aerospace industry.[124] One of the most effective systems found by Baldwin consists of the application of organic epoxy films pigmented with $Ce_2(MO_4)_3$.

Regarding the cerium–molybdate treatment, Kendig and Thomas[125] have investigated the contribution of each of the two components, Ce and Mo, to the overall protective effect. In order to study the role of Ce^{+3} ions, AA6061 samples were treated in boiling Ce^{3+} solutions, as described by Mansfeld.[122] Afterwards, an anodic polarisation at 0.5 V *vs.* SCE in buffered borate (pH 9.6) was applied for two hours. To investigate the role of Mo, the cerium pre-treatment was replaced by four hours of immersion in a boiling 0.030 M $NaNO_3$ solution. The polarisation step was carried out, in this case, in the sodium molybdate solution. Finally, a treatment that eliminates the contribution of the two heavy metals from the "stainless aluminium" processes was considered by combining the two mentioned treatments, i.e., boiling in $NaNO_3$ solution and anodic polarisation in borate buffer. The samples pre-treated by the three methods were tested by EIS in 0.5 M NaCl aerated aqueous solutions. EIS spectra included in Refs. 122 and 125 suggest that Ce and Mo act synergistically in the protection against the corrosion process.

To summarize, in general, the different treatments commented on above enhance the behaviour against corrosion of several aluminium alloys. However, data reported to date suggest that conversion coatings based on lanthanide compounds present various handicaps that limit their application on an industrial scale.

CONCLUSIONS

Environmental regulations in industrialized countries are increasing the pressure to eliminate, in the short term, a number of compounds widely used in industrial coatings to prevent corrosion. Hexavalent chromium-based processes are one of the most affected by these regulations. A number of "green" alternatives to chromates are currently emerging, oriented primarily towards minimizing environmental impact and, secondarily, towards providing effective corrosion inhibition.

From the comprehensive review of the literature presented in this article, lanthanide-based compounds seem to fulfil the basic requirements to be considered as a component of more environmentally-friendly formulations: low toxicity and acceptable inhibition power.

In relation to the corrosion protection of aluminium alloys by lanthanide compounds, most of the recently published studies have focused on the study of their behaviour as inhibitors in aqueous solutions. Several attempts have been made to incorporate lanthanide into non-chromate conversion coatings. There is a lack of research into lanthanides as alternatives to chromic anodizing. Regarding the metallic materials studied, lanthanides have been tested as corrosion inhibitors of aerospace aluminium alloys and, to a lesser extent, of those alloys commonly used in marine environments.

In respect of the first approach cited above, various authors have shown that lanthanide salts are effective inhibitors against uniform and pitting corrosion in aqueous environments from tests with several aluminium alloys. These compounds show an efficiency similar to that obtained using classical Cr(VI) based inhibitors. Cerium salts have proven to be the most efficient lanthanide corrosion inhibitors. The optimum inhibitor concentration varies considerably according to the specific alloy to be protected.

Dealing with the inhibition mechanism, results obtained in the study of different systems suggest that lanthanide salts behave as cathodic inhibitors. They act by blocking the cathodic sites in the metallic alloys. During the inhibition process, protective surface films incorporating the lanthanide element, are formed. This property has been used by several authors to design various methods of producing lanthanide-based conversion coatings.

The applications of rare earths in the anticorrosive pretreatments of aluminium alloys have been carried out either by immersion or by electrolytic activation methods. Reasonable protection levels have been demonstrated for lanthanide-containing conversion coatings prepared by some of these treatments. However, the methods proposed up to now have different limitations that restrict their application in practice. Further research efforts are necessary to develop industrially feasible treatments.

Taking all the above observations into account, there is reasonable justification for basing future research and development of new high-performance and environmentally-friendly anti-corrosion coatings for aluminium alloys on lanthanide compounds.

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