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Advanced generation of green conversion coatings for aluminium alloys

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Abstract

Anticorrosive cerium based treatments have been proved as efficient green alternatives to those based on environmentally undesirable Cr(VI) compounds. Thus, full immersion in cerium salt solutions allows reaching similar protection level against aluminium alloys corrosion that chromates treatments. However, treatment time is too high for being considered in industrial applications.

In this work, accelerated methods for obtaining cerium-rich conversion coatings on aluminium–magnesium alloys are proposed. The films developed have been characterised by SEM and EDS. These studies have revealed that the coatings have a mixed or heterogeneous nature, being composed of a layer of alumina covering the matrix, together with islands of cerium formed over the cathodic intermetallics that are present on the surface of the alloy. Furthermore, studies conducted employing electrochemical techniques indicate that the degree of protection provided by these coatings is several orders of magnitude superior to that achieved with other treatments.

Keywords: Corrosion; Aluminium alloys; Conversion coatings; Cerium; Green treatments

1. Introduction

AA5083 (Al–Mg) alloy is commonly used in naval industry. Therefore, the corrosion and protection of this alloy in chloride media need to be studied.

The main corrosion process that is developed on the surface of alloy AA5083 alloy in aerated NaCl solutions is the localised alkaline corrosion (LAC) in the aluminium matrix surrounding Al(Mn,Fe,Cr) cathodic intermetallics [1]. In parallel, as a consequence of the anodic reaction, an aluminium oxide film covering the metallic matrix is developed [1]. This film grows with the exposure time. Thus, in order to protect the alloy, it is needed to design a process which blocks the cathodic reaction over the cathodic precipitates and allows forming the aluminium oxide film onto the metallic matrix.

In previous papers, the behaviour of cerium as blocker of the cathodic reaction in the corrosion process of AA5083 alloy has been demonstrated [2,3]. Additionally, cerium salts employed are non-

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contaminating and can be considered as ecological alternatives to chromates [4,5]. Starting from all this, cerium based treatments have been designed. The easiest of them consists in the full immersion of the alloy in Ce(III) salts aerated solutions. Results obtained by this procedure showed that after immersion in the Ce(III) salt, the alloy is covered by a mixed film formed by cerium islands placed onto the cathodic particles and an aluminium oxide film extended onto the aluminium matrix [6]. Cerium island avoids the cathodic reaction over the Al(Mn,Fe,Cr) precipitates and aluminium film protects the matrix. The best protection level, comparable with that obtained with chromate based treatments, is reached after 2 days of exposure to the inhibitive solution. This excessively prolonged treatment time required to achieve such level of protection limits the industrial application of the treatment. The excessive duration of the treatment is associated to the time necessary for developing the aluminium oxide film which grows more slowly because the cathodic reaction is minimised.

This work reports on the results obtained when accelerated treatments for obtaining cerium-rich conversion coatings on aluminium–magnesium alloys are applied. These treatments are based in the activation of the system by three methods: electrical activation at different cathodic currents, thermal activation at 363 K and thermal activation at 323 K with the addition to the treatment bath of small amounts of H_2O_2.

2. Experimental

30 mm × 25 mm × 4 mm AA5083 (Al–4.5Mg–0.5Mn–0.3Fe–0.1Cr) samples have been used in this study. The solutions employed in the thermally acti-

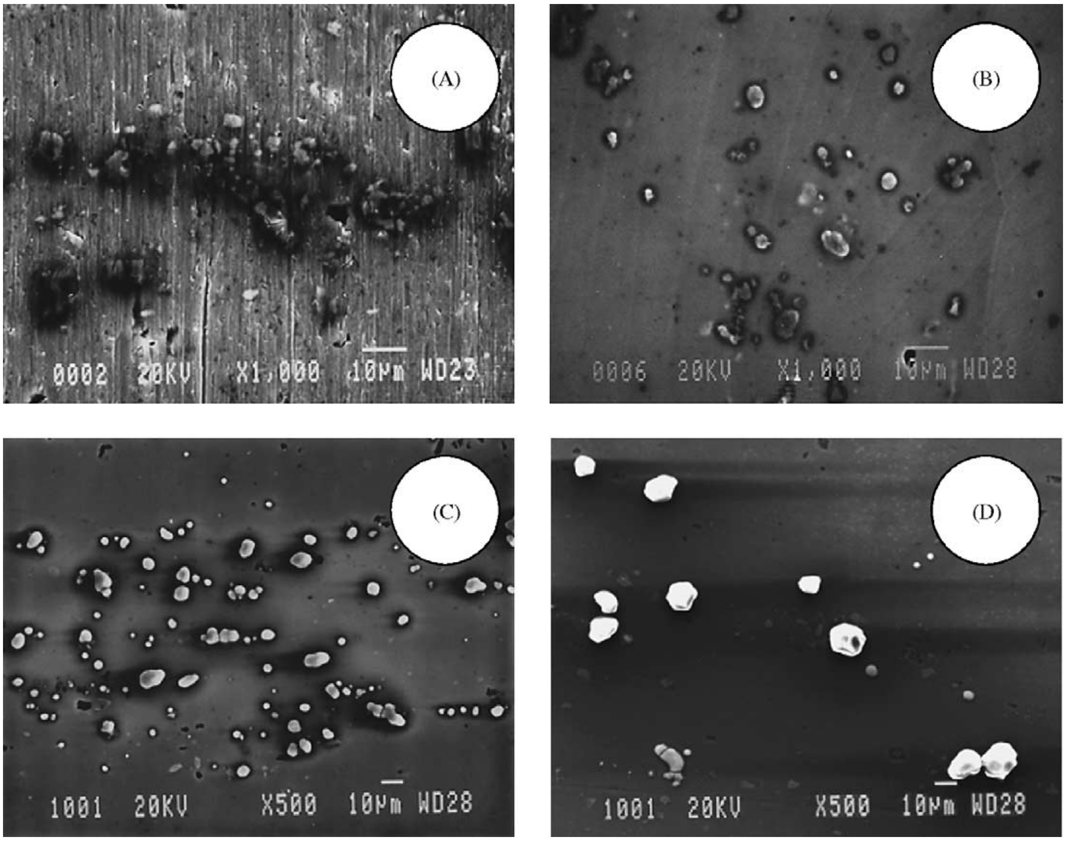

Fig. 1. SEM images of alloy AA5083 samples after treating in Ce(III) aerated aqueous solutions by: (A) full immersion at room temperature; (B) electrochemical activation at -0.01 mA/cm^2; (C) thermal activation at 363 K; (D) thermal activation at 323 K with addition of H_2O_2.

vated (TA) treatments were aerated aqueous solutions of $CeCl_3$ 0.005 M at 363 K. Same solution without additives at 298 K was used for electrically activated treatments. In this type of treatments cathodic currents of 0.01 and 0.10 mA/cm^2 are imposed to the systems during short time periods. When the TA treatment was applied with H_2O_2, aerated aqueous solutions of $Ce(NO_3)_3$ 0.005 M at 323 K were used adding to it 1.250 ml/l of H_2O_2.

The protective effect of the treatments was evaluated in NaCl at 3.5% aerated solution using electrochemical techniques as linear polarisation and polarisation resistance. The surface appearance of the coatings developed was studied by scanning electron microscopy (SEM) and their composition was analysed by energy dispersive spectroscopy (EDS).

3. Results and discussion

Fig. 1 shows SEM images corresponding to the different treatment applied. As a reference a full immersion treated sample at room temperature is included. As can be appreciated in this figure, the surface appearance of each sample is similar. Thus, two zones can be distinguished clearly. A first region consisting of dispersed islands and a second area where a lower thickness film is covering a wide zone of the alloy.

EDS allows determining the compositional characteristics of both zones. Fig. 2 is representative of the EDS spectra acquired (A) on the film, (B) on the dispersed islands and (C) on the substrate under these island. As it can be observed, the islands are mainly formed by cerium and they are placed onto the Al(Mn,Fe,Cr) cathodic particles. On the other hand, Fig. 2(A) an oxide film is developed over the aluminium matrix. Therefore, according to [6] all the treatments give rise to a mixed film formed by cerium rich islands deposited over the cathodic sites of the alloy and an aluminium oxide coating covering the metallic matrix. It can be expected that, as in the full immersion treatments, this mixed film protects to the alloy.

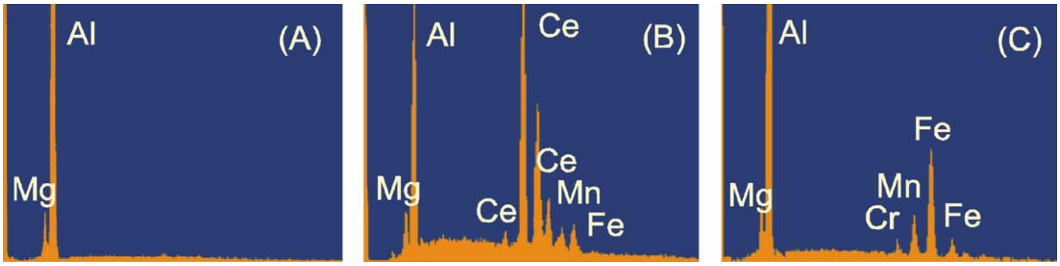

Fig. 2. Representative EDS spectra acquired on alloy AA5083 samples after treating in Ce(III) aerated aqueous solutions: (A) oxide film over the aluminium matrix; (B) cerium rich islands; (C) substrate under the cerium islands.

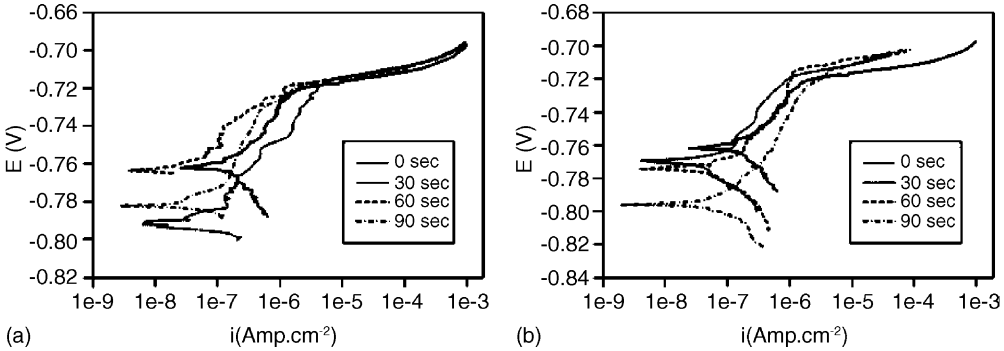

Fig. 3. Linear polarisation curves acquired on alloy AA5083 samples EA treated in Ce(III) aerated aqueous solutions. Medium: NaCl at 3.5% aerated aqueous solution.

Table 1
ΔR_p and ΔR_{cp} values obtained from linear polarisation curves

Treatment	ΔR_p	ΔR_{cp}
Untreated	1	1
EA (−0.01 mA/cm^2) 60 s	2.7	4.4
EA (−0.1 mA/cm^2) 30 s	2.7	3.4
TA (363 K) 5 min	3.2	7.7
TA (363 K) 10 min	3.8	17.5
TA (323 K) + H_2O_2 5 min	5.2	7.7
TA (323 K) + H_2O_2 15 min	13.8	17.5

The protection degree has been evaluated through linear polarisation (LP) techniques. Fig. 3 plots LP curves acquired on the EA samples, as a representation of all the treatments. As a reference, the curve corresponding to the untreated sample has been included. In all the cases, a displacement of corrosion potential, E_{corr}, toward more active values can be observed. This is characteristic of the cathodic inhibition. The activity of the system has been evaluated in terms of the polarisation resistance R_p. The change (%) of R_p with respect to the value obtained for the untreated sample, ΔR_p, has been taken as a measure of the protection degree in terms of the decrease of the system activity.

On the other hand an increase of the sweep of the anodic branches of the LP curves, R_{cp}, can be observed in Fig. 3. This increase can be associated to the average thickness and efficiency of the mixed film. The change (%) of this parameter with respect to the value obtained for the untreated sample, ΔR_{cp}, indicates the increase of the barrier properties of the mixed film.

Table 1 contains the values of ΔR_p and ΔR_{cp} for the different treatments applied. Notice that all the treatment supply protection levels higher than 300%, reaching in any cases values close to 2000%. On the other hand the treatment duration is highly reduced with respect to the necessary in the full immersion treatments at room temperature (2 days) [5].

As it can be observed, the best results are obtained when 5 and 15 min of TA + H_2O_2 treatments are applied. These protection levels are similar to those obtained for full immersion at room temperature, but reducing the time of treatment in a factor close to 200.

4. Conclusions

When samples of AA5083 alloy are full immersed in Ce(III) solutions a protective mixed film is developed. This film consists of Ce islands deposited over the Al(Mn,Fe,Cr) cathodic particles and an aluminium oxide layer which covers the rest of the alloy. The best protection level is obtained after 2 days of immersion. In order to accelerate the treatment three ways have been tested: cathodic electrical activation for accelerating the Ce deposition, thermal activation for accelerating the oxide film formation and a combination of thermal activation and H_2O_2 addition in order to accelerate the two steps.

The best results have been obtained in this last case. A protection level close to 800% and an increase of the resistance of the mixed film close to 1800% have been obtained. Additionally, treatment time is reduced in a factor close to 200. Thus, this treatment can be considered industrially acceptable.

Acknowledgements

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References

[1] A. Aballe, M. Bethencourt, F.J. Botana, M.J. Cano, M. Marcos, Corros. Sci. 43 (2001) 1657.
[2] A. Aballe, M. Bethencourt, F.J. Botana, M. Marcos, J. Alloys Comp. 323/324 (2001) 855.
[3] M. Bethencourt, F.J. Botana, J.J. Calvino, M. Marcos, M.A. Rodriguez-Chacon, Corros. Sci. 11 (1998) 1803.
[4] A. Bahadur, Corros. Rev. 10 (1992) 155.
[5] S.M. Cohen, Corrosion 51 (1995) 71.
[6] A. Aballe, M. Bethencourt, F.J. Botana, M.J. Cano, M. Marcos, Mater. Corros. 53 (2002) 176.