Glass-like Ce₉O₉₇ sol–gel coatings for corrosion protection of aluminium and magnesium alloys

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A R T I C L E   I N F O

Article history:
Received 21 October 2010
Accepted in revised form 1 July 2011
Available online 13 July 2011

Keywords:
Glass-like coating
Cerium
Corrosion
Self-healing protection

A B S T R A C T

This work reports the preparation of glass-like, environmentally-friendly, cerium-based coatings for active corrosion protection of aluminium and magnesium alloys. It describes the production of cerium sol–gel sols from cerium nitrate and their deposition by immersion and automatic spray onto aluminium and magnesium alloys to produce uniform coatings with amorphous (glass-like) structures (Ce₉O₉₇). The coatings have been characterised by profilometry, scanning electron microscopy (SEM), spectral ellipsometry and UV–visible, in order to analyse the structure and density of the glass-like cerium coatings as well as their redox ratio Ce⁴⁺/Ce³⁺ as a function of pH and sintering temperature. Finally, electrochemical measurements (EIS) and standard corrosion tests (neutral salt spray, filiform corrosion, immersion–emersion test and adhesion on embossing and T-bend test) have been performed to study the corrosion behaviour of the cerium glass-like coatings on aluminium and magnesium alloys. EIS measurements confirm the healing or blocking of the defects by the corrosion inhibiting species. Excellent corrosion protection is provided by cerium glass-like coatings, satisfying the most demanding industrial requirements.

1. Introduction

Through alloying and appropriate heat treatment, aluminium alloys of high strength to weight ratio and damage tolerance are available for widespread applications in aircraft and automobile designs. However, these alloys require appropriate corrosion control systems to reduce corrosion susceptibility. With increasing demand for light-weighting in order to reduce fuel consumption and emissions, magnesium alloys, with a density two-thirds that of aluminium [1], are now attractive for the transport sector [2]. Additionally, magnesium alloys benefit from high thermal conductivity, dimensional stability, electromagnetic shielding behaviour, and good machinability, together with easy recycling. However, the poor corrosion resistance severely limits their extensive applications in a variety of sectors.

A promising strategy to improve the corrosion resistance of aluminium and magnesium alloys is the application of conversion coatings with active corrosion inhibitors, usually obtained from corrosion inhibitor-containing baths. These treatments offer self-healing protection, defined as the ability of a material to recover/repair damage automatically, without external intervention. Chromate conversion coatings represent the benchmark for corrosion protection systems for industrial and aerospace applications [3,4] because of their high efficiency/cost ratio. Two types of chromate-based coatings have been widely used, namely chromate conversion coatings (CCC) of 300–500 nm thickness, and chromic acid anodizing (CAA) to generate porous anodic films of 2–3 μm thickness. The protection systems usually include chemical or electrochemical pre-treatment, followed by application of epoxy primers and polymeric top-coats [5,6]. In spite of their excellent corrosion protection behaviour, chromates are now declared environmentally hostile, since they are carcinogenic, produce DNA damage, skin allergy, asthmatic reactions, and ulcerations [7]. Consequently, the European Community has forbidden the use of chromate coatings in all industrial sectors, except aeronautics, from July 2007 [8]. Thus, replacing chromium-based coatings by environmentally-friendly systems has triggered the study and development of protective systems containing alternative corrosion inhibitors. In particular, cerium and other rare earth elements have shown promise as alternatives to chromium-based systems [9–11]. Hinton et al. [12,13] proposed cerium-based coatings as a potential alternative to chromate coatings, reporting that precipitation of cerium oxide, cerium hydroxides or cerium hydrates on cathodic sites improved the corrosion resistance. Although the protection mechanism is still subject of debate, the corrosion inhibiting role of cerium species has been confirmed by different electrochemical techniques, including EIS [14–16], split cell technique, and electrochemical noise analysis [17–20].

Non-chromate conversion coatings (NCCC) may be obtained from aqueous solutions of rare earths with or without the presence of activator agents [21]. Other coatings include phosphate conversion coatings or coatings obtained by deposition of conducting polymers. Films produced from fluorotitanic or fluorozirconic acids, cobalt salts,
and phosphate permanganate coatings are available, but they are less effective than the traditional chromate treatments [22–25].

Sol–gel technology is an alternative approach for coating generation, being environmentally-compliant and compatible with organic paints. A key advantage of sol–gel films resides in their covalent bonding and strong adhesion to the substrate, as well as the barrier effect, limiting the access of the environment to the alloy surface [26–29]. Inorganic sol–gel coatings offer excellent barrier properties [30–32], but the high temperatures required for coating densification are usually incompatible with the preservation of the light alloy microstructure and properties [33]. In order to remedy the previous, organic and hybrid coatings containing cerium, vanadium, molybdenum, lanthanides or organic inhibitors have been developed [34–39]. These coatings can be densified at relatively low temperature (≤300 °C) to obtain glass-like structures without any crystallisation, and little change of the microstructure of aluminium and magnesium alloys.

Alkylalkoxides with methacrylate or epoxy-functionalised groups have been used as a base to form barrier-type coatings. The addition of selected inhibitors to the base formulation has also provided self-healing ability [35–37,40–42]. However, the addition of active corrosion inhibitors to the precursor sols frequently results in degradation of the barrier properties of the coatings and deactivation of the inhibiting properties [34,43,44].

For active inhibition, pure cerium oxide coatings have been prepared from sol–gel sols with sintering at relatively high temperatures of 350–800 °C, resulting in CeO2 nano-crystalline films [45,46]. CeO2 crystalline coatings have been also prepared from aqueous sol–gel suspensions containing CeO2 nano-particles after sintering at high temperatures [47–51].

The aim of this work was to establish a new procedure for producing glass-like, environmentally-friendly, cerium-based coatings for corrosion protection of aluminium and magnesium alloys. The coatings, generated from alcoholic sol–gel sols, are densified at reduced sintering temperatures, i.e. below 250 °C. This method [52] produces uniform coatings with amorphous structures and excellent adhesion to the metallic substrates and to various organic primers. The process involves the stabilisation of Ce3+ ions in a glass-like structure, a primary route to facilitate their diffusion or migration to damaged regions to inhibit localised corrosion. Further, the CeO2 glass-like coatings can be used in conjunction with paint systems, primers and/or topcoats, to provide further corrosion resistance. Aluminium and magnesium alloys treated with the cerium-based coatings successfully passed various, commonly accepted, accelerated corrosion tests. Thus, the treated substrates surpass the most demanding requirements of the aircraft, automobile and building industries, thereby providing an alternative to chromium-based coatings.

2. Experimental

2.1. Preparation and characterisation of cerium sol–gel sols

Cerium sol–gel sols were prepared with pH = 2 (labelled as Ce–Al sol) and pH = 6 (labelled as Ce–Mg sol) employing cerium nitrate Ce(NO3)3·6H2O as the precursor. For both sols, the preparation involved two steps. In the common first step, a cerium nitrate solution was prepared by dissolving 39.1 g of cerium nitrate in 142 g of ethanol and 13.8 g of acetic acid. In the second step of the Ce–Al sol, 8.5 g of citric acid and 6.5 g of butanediol were added to the cerium nitrate solution resulting in a final pH close to 2. In the case of the Ce–Mg sol, 2.85 g of diethanolamine and 3 g of glycidyl-methacrylate were dissolved in the initial cerium nitrate sol leading to a pH sol close to 6. Both sols were stored at 5 °C, their stability was evaluated by following the change of viscosity with time using a rheometer (Haake RS50, Germany). The synthesis of both sols was scaled-up to pilot plant scale, 5 L, for deposition with industrial spraying robots.

2.2. Metal substrate preparation

Aluminium alloy AA2024 was given to a three-step cleaning procedure, with surface preparation including alkaline cleaning (Metaclean T2001 — Chemie Vertrieb Hannover GmbH & Co KG), alkaline etching (Turco Liquid Aluminetch Nr.2 — Turco Chemie GmbH) and a final step of acid desmutting (Turco Liquid Smutgo NC — Turco Chemie GmbH). The aluminium alloy AA3105 was cleaned using alkaline etching (Gardoclean S 5080 — Chemetall) and acid desmutting (Gardoclean 450 — Chemetall) at 45 °C.

Magnesium alloy AZ-31 was pre-treated by mechanical polishing to #2000 emery paper finish and then cleaned with nitric acid (0.01 N), for 30 s. The AZ91 alloy was exposed to two-step cleaning procedure, first with 2.5 N NaOH for 5 min and subsequently with 10 vol% HF for 10 min.

2.3. Deposition methods and treatments of cerium coatings

The Ce–Al sol–gel sol was applied to the AA2024 and AA3105 substrates using automatic spray. The coatings were densified for 12 h at 120 °C in air. A complete protection system was obtained on AA2024 by automatic spraying at Fraunhofer Institut Produktionstechnik und Automatisierung (IPA, Germany) to provide a 15–25 μm epoxy primer and a Mankiewicz 20–30 μm top-coat deposited on the Ce–Al glass-like coatings (labelled as AA2024–complete Ce-Al system). In the case of the AA3105 alloy, the Ce–Al glass-like coatings were covered by a polyester based paint (primer CP22-0422 White Basf, and the top-coat CI24-0095 P S White) applied by coil coating at PLALAM (labelled as AA3105-complete Ce–Al system).

The Ce–Mg sol–gel sol was deposited on AZ91 and AZ-31 substrates by dip-coating at a withdrawal rate of 30 cm/min and densified for 10 min at 250 °C in air. A primer coat of 15–20 μm thickness was further applied using an automatic spray over the Ce–Mg glass-like coating on the AZ-91 alloy to generate a complete protection system (AZ91–complete Ce–Mg system).

2.4. Physical and electrochemical characterisation of coatings

The coating thickness was measured by profilometry (Talystep-Taylor Hobson, UK) and scanning electron microscopy (SEM) (ZIESS EVO 50). A spectroscopic ellipsometer (Woollam M2000U, USA) was utilised to determine the coating thickness and the refractive index, and their change with room humidity. Coatings produced from both sols were analysed by transmission electron microscope (TEM), X-Ray diffraction was employed to follow the possible crystallisation of CeO2 in the films. TEM samples were obtained by scratching the films and placing the fragments onto carbon-coated copper grids.

Ultraviolet-visible spectra (Perkin Elmer, Lambda 950) were recorded in transmission mode for coatings deposited on SiO2 substrates. The Ce4+/Ce3+ ratio was determined for both Ce–Al and Ce–Mg films after deconvolution of absorption curves using Origin 8.

Electrochemical impedance spectroscopy was performed on AZ-31, bare and protected with the Ce–Mg glass-like coating as a function of the immersion time in 0.35 gl−1 NaCl solution. EIS measurements were performed using a Solartron Modulab potentiostat at open circuit potential with an AC voltage amplitude of 10 mV, in the frequency range from 10 mHz to 40 kHz. The area exposed (working electrode area) to the electrolyte was 7.5 cm2 and platinum sheet was used as the counter electrode.

2.5. Standard corrosion tests

The AA2024-complete Ce–Al system was scribed and exposed to neutral salt spray test (SST) following ASTM B-117. For inspection, samples were washed with deionised water, dried and examined at intermediate times during the 1000 h test. Filiform corrosion testing
(EN 3665) and immersion–emersion testing were also performed on this system according to U-type scratch and DIN-EN-3212, respectively. After initiation with concentrated hydrochloric acid, the specimens were placed in the test chamber at an angle of 6° from the vertical, and evaluated by visual inspection at 168, 500 and 960 h. Immersion–emersion testing was also applied to this system (DIN-EN-3212).

AA3105 alloy, protected with the AA3105 complete Ce–Al system, was adhesion tested by embossing and T-bend testing according with ISO 6272–2:2002 and ECCA T7–1996, respectively. The embossing test is a method for studying the deformation produced by the impact of a spherical indenter of diameter 12.7 mm or 15.9 mm, onto a coated substrate, that evaluates the effect of such deformation on the coating adhesion.

AZ91-complete Ce–Mg system was tested by cross-cut scribing (adhesion test) and scratching combined with neutral salt spray testing for up to 312 h following ASTM-117 and adhesion complemented with SST.

3. Results and discussion

3.1. Characterisation of the sols and deposition of the coatings

Cerium sol–gel sols with acid (Ce–Al sol) and neutral (Ce–Mg sol) pH were prepared following the processes previously described. The final pH of the sol is a key parameter to prevent the degradation of the substrates and the associated loss of chemical and mechanical properties, and corrosion resistance. It is necessary to combine the substrate stability during coating deposition (some seconds for both dipping and spraying) with the suitable rheology of the sol. In the case of aluminium alloys the substrates are not affected by Ce–Al sol with pH ~2, but magnesium alloys dissolve throughout deposition in these pH conditions [53]. Thus, Ce–Mg sol was modified by addition of diethanolamine up to pH ~6, the higher pH compatible with rheological stability of the sol.

The presence of one or more organic solvents, ethanol and/or butanediol, decreases the surface tension, improving the wettability of the sols and consequently the adherence to the substrate as well as aiding dissolution of the salts and complexing agents. Both sols show Newtonian behaviour with a viscosity around 2.5 mPa.s. The stability of Ce–Al and Ce–Mg sols was improved by storing at − 5 °C, maintaining the properties for more than 90 days. Prior to deposition of the Ce–Al and Ce–Mg sols, the alloy substrates were subjected to surface pre-treatments and/or cleaning process. Ce–Al sol was used for coating AA2024 and AA3105 substrates, employing an automatic robot spray, whereas the AZ91 and AZ31 alloys were coated by immersion in the Ce-Mg sol.

Transparent and uniform glass like CeOx coatings were obtained after drying and thermal treatment. The coatings were highly adherent and transparent with a light yellow-colour after the thermal treatment. The thickness, measured by ellipsometry and profilometry, was around 600 nm; the results from both techniques coinciding with an error below 2%.

The amorphous structure and absence of crystallisation or precipitated phases were confirmed by TEM with X-ray diffraction analysis. Fig. 1 shows the X-Ray diffraction patterns of the glass-like Ce–Mg coating deposited on MgAZ31.

Scanning electron microscopy (SEM) revealed that the coatings covered the alloy surface; although the films are cracked, neither peeling nor flaking of the coatings was evident (Fig. 2). Since the main function of the coatings is to provide active corrosion protection, the barrier against the environmental access is offered by the subsequently applied paint system on the CeOx glass-like coatings.

3.2. Optical characterisation of the coatings

There is abundant literature on crystalline CeO2 coatings, due to their interesting properties of high refractive index, high transparency in the visible, near and middle-IR, strong adhesion, and high stability against mechanical abrasion, chemical attack and high temperature [54,55].

The structure and density of the coatings depend largely on the deposition technique. Oxide films deposited by vacuum evaporation generally display a columnar structure with many pores that are readily filled by moisture under ambient conditions [56]. UV–visible spectroscopy, probing the absorption band around 2.97 μm, can be used for determining the water content. The transmittance spectra of Ce–Al coatings displayed a pronounced dependence on humidity, with a wide and increasing band around 3 μm indicating high open porosity. A similar, but less pronounced behaviour was observed for the Ce–Mg coatings that again suggested porous morphologies (not shown). Spectral ellipsometry was used to measure the refractive index and thickness of the coatings following exposure to ambient humidity. Thus, the relative film density of both coatings was calculated using relatively dense (3.93 g/cm3) CeO2 [57] as a reference. Ce–Al films present a pore volume of 43%, while Ce–Mg coatings, in agreement with the increased sintering temperature, show a reduced total pore volume of 34%; both values are in good agreement with the literature [56,58].

UV–visible spectra were acquired between 190 and 1000 nm on Ce–Al and Ce–Mg coatings, deposited on SiO2 substrates and treated under similar conditions to the studied alloys, to determine the redox ratio Ce4+/Ce3+. Fig. 3A. Two main bands appear in both absorption spectra; one band is centred at 200 nm and assigned to Ce4+ charge
from the absorption coefficient $\alpha$, (Eq. (1)) and the extinction coefficient $k$, (Eq. (2)) using the expressions:

$$\alpha = 4nk/\lambda$$

(1)

$$\varepsilon = 4nk/\lambda C$$

(2)

where $\lambda$ is the wavelength of the incident light and $C$ is the ion concentration.

Ce$^{4+}$ is a 4f$^0$ system, with no f→f transitions; the colour of Ce$^{4+}$ salts arises from the tail of a strong charge transfer band in the UV, around 200 nm that is independent of the environment from glass matrices to pure CeO$_2$ films. Although the wavelength of this electronic transition is nearly constant, the molar absorptivity changes significantly, depending on the nature of the complex and the electronegativity of the ligands [59], varying from 3800 L mol$^{-1}$ cm$^{-1}$ in silicate glasses up to 4000–7000 L mol$^{-1}$ cm$^{-1}$ in crystalline CeO$_2$ films deposited by different techniques and with different nanostructures [54].

Ce$^{3+}$ has a 4f$^1$ ground electronic configuration with two free ion states separated by about 2000 cm$^{-1}$. The first excited configuration is 5d and the optical spectra of Ce$^{3+}$ therefore consist of one f→f transition in the near infra-red that is Laporte forbidden with very low molar absorptivity, and two Laporte allowed f→d transitions ($^2F_{5/2} \rightarrow ^2D_{3/2, 5/2}$) and nf→n-1d transitions in the UV [60]. The band maxima corresponding to these transitions depend mainly on the neighbouring ligands, being situated at 262, 298 and 328 nm in ethanol solvent. Since cerium glass-like coatings are prepared from alcohol sols, and the UV-visible absorption bands appear at similar wavelengths (267 and 310 nm), it is reasonable to assign the molar absorptivities corresponding to these bands, of 480 and 150 L mol$^{-1}$ cm$^{-1}$ for a semi-quantitative calculation of the Ce$^{3+}$ concentrations. The band at 328 nm is not visible because $\varepsilon$ is very low.

From these data, calculated redox ratios Ce$^{4+}$/Ce$^{3+}$ for both glass-like cerium coatings are 0.55/0.45 for Ce–Al, and 0.05/0.95 for Ce–Mg, in good agreement with the increased sintering temperature of the Ce–Mg films that shifts the redox ratio to reducing conditions.

3.3. Electrochemical and standard corrosion tests

Various experimental techniques have been used to study the anticorrosion performance of the coatings. Accelerated corrosion tests, especially salt spray tests (SST), are valuable for validation and comparison of the performance of different coatings. However, it is generally recognised that such tests provide little information on the interaction between the inhibitors and the alloys, or the mechanism of protection.

Conversely, electrochemical impedance spectroscopy (EIS) is widely used to characterise the corrosion behaviour of coating systems, allowing not only comparison of different systems but also providing information on coating degradation and the corrosion mechanism [43,61]. Both EIS and SST were used to assess the performance of the CeO$_2$ glass-like coatings on the aluminium and magnesium alloys.

EIS was used to investigate the corrosion behaviour of Ce–Mg glass-like coatings on AZ31 in 0.35 wt.% NaCl electrolyte under naturally aerated conditions at room temperature for immersion times up to 196 h (Fig. 4). For comparison, EIS spectra were acquired also for the bare AZ31 but the acquisition of EIS spectra was interrupted earlier (10 h) as the corrosion of the uncoated specimens was severe. During the early stages of immersion, significant differences appear evident between the EIS spectra of the coated and uncoated specimens; both the low frequency impedance modulus (at 0.01 Hz) and the high frequency impedance modulus (above 100 Hz) of the cerium glass-like coated AZ31 were significantly higher compared to that of the bare alloy. The higher impedance observed at high frequencies for the cerium coated specimens is associated to the barrier effect (high resistance, low

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Fig. 3. (A) Absorption UV–vis spectra of Ce–Al and Ce–Mg glass-like coatings deposited on SiO$_2$ substrates. (B) Deconvolution of Ce–Mg glass-like spectra (C) Deconvolution of Ce–Al glass-like spectra to determine the redox Ce$^{4+}$/Ce$^{3+}$ ratio.

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Transfer, with a further, wider band around 265 nm in Ce–Al films and shifted to near 310 nm in Ce–Mg coats, both associated with Ce$^{3+}$. Deconvolution of the Ce–Al spectra confirmed the qualitative analysis, with two bands centred at 201 nm and 267 nm (Fig. 3C). Conversely, deconvolution of the Ce–Mg spectra resulted in three bands at 198, 265 and 310 nm (Fig. 3B). Calculation of the redox ratio, Ce$^{4+}$/Ce$^{3+}$, requires knowledge of the molar absorptivity ($\varepsilon$) corresponding to the different transitions observed. $\varepsilon$ can be derived...
The cerium sol–gel coatings have a glass-like structure, meaning a more open structure and higher enthalpy compared with crystalline CeO₂ films. The porous structure with high specific surface area of these coatings further facilitates the lixiviation of cerium ions and their mobility and diffusion to corrosion sites. After sufficient immersion time, the corrosion initiates on the magnesium surface, producing an increase of the local pH that triggers the inhibition process. In this process the mobile cerium ions diffuse towards the corrosion sites, precipitating as oxides, hydroxides or even hydrates (see Pourbaix diagrams) depending on pH, onto magnesium corrosion products already formed.

It is clear that the recovery of the impedance at low frequency (Fig. 4A) and the absence of significant corrosion processes are related to the presence of the CeO₂ glass-like coating acting as an inhibition agent. The glass-like, porous structure of Ce–Mg coatings, with more than 95% of cerium ions present as Ce³⁺, allows fast diffusion of Ce³⁺ to the electrolyte and the subsequent precipitation on the corrosion sites as cerium oxides, hydroxides and even hydrates as a result of local pH change. Although the composition of the precipitates on the defects was not identified, EIS spectra confirm the healing or blocking of the defects by the corrosion inhibition species. The electrochemical behaviour is thus a clear indication of active self-healing corrosion protection provided by the CeO₂ glass-like coatings.

Standard corrosion tests that are usually employed in the aeronautical, automotive and other metallurgical industries were also performed to assess the anticorrosion performance of CeO₂ glass-like coatings on the different substrates. SST was performed on the AA2024-complete Ce–Al system according to the ASTM B117 standard. The substrates, provided by EADS, were sections cut from large demonstrator panels. The main focus of the corrosion tests was the investigation of the stringer areas, where the coating thickness was lower due to limited accessibility of the spraying process. The deposition of Ce–Al coatings from a scaled-up Ce–Al sol and further protection with primer and top-coat was performed at IPA (Stuttgart) and tested by EADS. The panels were scribed and exposed to a neutral salt spray for times up to 1000 h. The panels were removed at intermediate times, with visual inspection showing no defects on the scratched region. (Fig. 5A). Only minor corrosion occurred in the scribed region, indicating active protection of the coating system. However, some evidence of creepage was evident at the end of the scratch. Fig. 5B shows AA2024 coated with the same primer and top-coat; after 168 h under SST, the sample appears totally corroded while the alloy protected by glass-like cerium coating surpass 1000 h of SST without evidence of generalised corrosion.

The complete Ce–Al system was also subjected to filiform attack, by scratching according to U-type and maintained the test in the chamber up to 960 h. Visual observation at 168, 500 and 960 h (Fig. 6) showed excellent protection against filiform corrosion. The scratch appeared unchanged, even on stringers or on the welding seam, indicating a high resistance of the coatings to the propagation of defects.

Alternate immersion–emersion test was also carried out on this system according to DIN EN 3212, revealing protection in the scratched area, and confirming the active protection process (Fig. 7). The yellow colour developed in the scratch indicates the participation of cerium species in the protection process.

AA3105 complete Ce–Al system was also tested by evaluating adhesion on a T-bend and adhesion after embossing. These tests enable evaluation of the flexibility and adhesion of coatings by observing the presence of cracks or loss of adhesion in the regions where the coated substrate is bent or deformed. Fig. 8 shows the AA3105–complete Ce–Al system (glass-like Ce–Al coating deposited at IPA and painted at PLALAM by coil coating with polyester based primer and top-coat) a) after adhesion on embossing and b) after T-bend adhesion tests.
The macroscopic image from the embossing test shows that the complete system is capable of resisting impact without peeling or cracking. Similar behaviour was observed in the case of the T-bend test. The system was bent through 2° without flaking or peeling, thereby being evaluated as T1 (very good). Adhesion tests reveal the excellent resistance to impact and cracking of the AA3105-complete Ce–Al system. Corrosion penetration and adhesion after 1000 h of neutral salt spray (SST) also showed outstanding results satisfying the most demanding industrial requirements (not shown).

AZ91-complete Ce–Mg system was also exposed to neutral salt spray (SST) and adhesion tests. Fig. 9A and B, displays the appearance of AZ91 coated only by the primer and Fig. 9C and 9D shows the samples protected with the complete-Ce-Mg system after 24 and 312 h in SST respectively, enabling comparison of the corrosion behaviour of the substrate with and without the cerium glass-like coating. Visual inspection of the scribed region after removal from the SST chamber shows minor deterioration of the complete protection system, indicating good adhesion and active protection. The samples without the cerium coating are largely destroyed after 312 h in SST.

The outcome of the adhesion test for AZ91 protected with complete Ce–Mg coats is presented in Fig. 10A and B. Visual observation shows that the scratched regions are well adhered and no peeling or material loss is revealed. Some delamination or chipping was detected at the edges of the samples, where, by problems related to sample geometry provokes a thinner or lacking of Ce–Mg coating. This behaviour confirms that the presence of Ce–Mg glass-like coating reduces significantly the metal susceptibility to corrosion of the metal.
Adhesion cross cut test on Complete-Ce

Fig. 10. Adhesion cross cut test on Complete-Ce-Mg system deposited on MgAZ91 (A) as prepared and (B) after 312 h in SST.

4. Conclusions

Uniform CeO$_2$ glass-like coatings can be produced by immersion and automatic spraying with subsequent sintering temperatures from 120 °C up to 250 °C that are sufficiently low to avoid deterioration of the alloys microstructure and mechanical performance. Electrochemical and standard corrosion tests demonstrate that cerium glass-like coatings display outstanding anticorrosion properties on various substrates. The experimental results confirm that active corrosion protection is provided by cerium coatings through the blocking or healing of defects, confirming the inhibition capability of cerium products. The SST and adhesion tests results show that cerium-based systems are a promising alternative to chromium-based systems.

Acknowledgements

The authors acknowledge the funding provided by the European Community, MULTIPROTECT project: “Advanced environmentally friendly multifunctional corrosion protection by nanotechnology”, Contract No NMP3-CT-2005-011783 and especially to EADS Innovation Works, PLALAM.SpA and INASMET-TECNALIA. The EPSRC LATEST2 programme grant is also acknowledged for the financial support of MC.

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