Review Article

Review of rare-earth-based conversion coatings for magnesium and its alloys

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ABSTRACT

Rare-earth elements-based conversion coatings are actively researched as an environmentally benign alternative to conventionally used chromate-based conversion coatings for magnesium and its alloys. Here, we reviewed the topic comprehensively. The review starts with a short introduction on corrosion of magnesium alloys and chemical conversion treatments, and that is followed by a detailed description of cerium-based conversion coatings. Morphology, structure and composition of the cerium conversion coatings, their mechanism of formation and competence for corrosion control explained. Influence of various inorganic (hydrogen peroxide, phosphates, permanganates, vanadates, molybdates, etc.) and organic (silane, gelatin, phytic acid, etc.) co-additives discussed. Effect of various pre- and post-treatments described. Reported works on rare-earths other than cerium, viz. lanthanum, yttrium, samarium, neodymium, gadolinium and praseodymium are also reviewed. Future potentials of R & D presented.

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1. Introduction

Magnesium (Mg), the lightest structural metal has attracted significant research attention in recent years due to its striking characteristics such as high specific strength (density - 1740 kg m⁻³ and Young's modulus - 44 GPa), good thermal and electrical conductivity, vibration and shock absorption, castability, weldability, biodegradability, and biocompatibility [1–4]. Mg alloys are ideal materials for several applications ranging from automotive, aerospace, defence, electronics, construction and biomedical [5–8]. They are promising alternatives to
aluminium (Al) alloys in automobile/aerospace applications [5,6] and biodegradable polymers in implant applications [8,9].

The most critical shortcomings of Mg and its alloys that hamper its widespread usage are weak corrosion and wear resistance and poor mechanical properties other than the strength. Even though substantial advancements have been accomplished in developing cutting-edge Mg alloys and composites with improved mechanical properties, their poor aqueous and galvanic corrosion resistance remains a threat. Mg is highly prone to aqueous corrosion in neutral and acidic pH ranges (Fig. 1). The corrosion occurs rapidly when exposed to salt water, moisture, or acidic liquids with a strong inclination for the localized attack along with the production of hydrogen gas. In basic solutions, protective surface passivation is possible by the formed hydroxide layer (Fig. 1). The more negative standard reduction potential of Mg makes it prone to galvanic corrosion by external coupling with dissimilar metals or by internal coupling with secondary phases/impurities [4,10–13].

Mg dissolution in neutral and low pH environments occurs according to Eq. (1) with the corresponding electrochemical half-cell reactions (Eq. 2–4); accompanied by the hydrogen evolution.

$$\text{Mg}(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{Mg(OH)}_2(aq) + \text{H}_2(g)$$ (1)

$$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-; \quad E^o = -2.37 \text{V vs. SHE(anodic)}$$ (2)

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2; \quad E^o = 0 \text{V vs. SHE(cathodic, at acidic pH)}$$ (3)

$$3\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-; \quad E^o = -0.83 \text{V vs. SHE(cathodic, at neutral/alkaline pH)}$$ (4)

One of the well-identified problems in studying Mg corrosion is the negative difference effect (NDE), the abnormal hydrogen evolution (HE) behavior observed at more anodic potentials or current densities. More details on Mg corrosion can be found elsewhere [11–13,15–18].

A number of corrosion prevention strategies have been considered for Mg and its alloys that include intrinsic methods such as modification of alloy composition/microstructure, design considerations and extrinsic methods such as surface modifications (ion implantation, laser annealing etc.) and protective films and coatings (electroplating, chemical conversion coatings, electrochemical conversion coatings, vapor phase coatings, polymer coatings etc.) [6,7,17,19–24]. Mg alloys in practice require a proper surface treatment to combat the corrosion issues.

Among the different surface treatment approaches, chemical conversion coatings are particularly attractive due to the easiness, speed of action, and low operating and capital costs (low-temperature process, low energy consumption, short treatment time and high efficiency). The term conversion coating refers to a method of chemically converting the native surface oxides to new oxides/compounds with desired properties. The coating is expected to convert the metal substrate to a corrosion-resistant surface (film of metallic oxide/other compounds chemically bonded to the surface) that more easily bonds to a subsequent topcoat [25,26]. In general, a conversion coating works by stimulating the interfacial reactions with the subsequent precipitation/coating formation. The process is triggered by a decrease of the pH and an increase of the Mg$^{2+}$ concentration at the metal/solution interface. The chemical is having a slight dissolving action on the surface oxide/hydroxide layer and that facilitate further entry of the solution into the layer. A typical industrial conversion coatings process involves steps such as detergent clean, alkaline clean, acid etching, conversion coating, drying and rinsing [21,22,25–33]. Several factors determine the quality of a final conversion coating such as the alloy composition and phase structure, pre-treatment processes, composition and concentration of bath chemicals, bath temperature and pH, immersion time, degree of agitation and post-treatment conditions [34–37]. In general, various functional co-additives (to control bath pH, accelerate coating formation, etc.) are also used in the conversion bath. Composite conversion coatings including more than one conversion agents are widely investigated. More details on chemical conversion coatings can be found elsewhere [22,38–48].

The majorly used inorganic conversion coatings on Mg alloys are chromates [49,50], phosphates [51,52], perman- ganates [53], molybdates [54], and rare-earths (RE)-based systems [55] and their various multi-element/composite conversion coatings. In spite of the environmental regulations [56–58], hexavalent chromium remains the benchmark of conversion coatings in many industries, most importantly, aeronautics. Several efforts have been devoted in finding efficient alternatives for hexavalent chromium in the form of trivalent chromium [50,59], phosphates [51,52] and RE conversion coatings. Among them, RE conversion coatings (RECCs) are particularly attractive as an environmentally friendly approach that can provide excellent corrosion resistance to the underlying metallic substrate. In spite of the extensive information available on RECCs on Mg and its alloys, no
attempts have been made to comprehend the reported data in the form of a review article. Here, we comprehensively review and present the topic.

2. RE conversion coatings

The REs are a group of 17 elements that consists of the two transition metals (Sc and Y) and the fifteen lanthanides (La, Ce, Pr, Nd, Pm, Sa, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu). REs are vital to wide-ranging applications including automotive catalytic converters, petroleum refining catalysts, magnets, alloys, batteries, glass and ceramics, water purification chemicals, electronics, communication devices, defence technologies, electric power and corrosion control [60,61].

RE-based conversion coatings, mostly Ce-based conversion coatings (CeCCs), have been extensively investigated for Al [55,62-67] and Mg alloys [68-75]. Major advantages of RECCs are modest price, acceptable eco-friendliness, good corrosion resistance, and synergism and compatibility with inorganic and organic co-additives. REs are well known as environmentally acceptable aqueous corrosion inhibitors [76,77]. Most of the RE salts have high solubility in water. It is known that the majority of REs exist in solution as \(\text{RE} \cdot \text{H}_2\text{O}_n\) [24]. In addition to the \(\text{RE}^{3+}\) state, cerium is known to exist as \(\text{Ce}^{4+}\). Sm, Eu and Yb can have \(\text{RE}^{2+}\) ions in solution [25]. Studies showed that RE alloying elements have no antagonistic effect on the growth of living cells, but they can persuade inflammatory effects at high concentrations [78]. REs have proven anti-carcinogenic properties [79,80].

Table 1 summarizes the available reported information on RECCs for Mg and its alloys. A pie chart on the published data on various RECCs is provided in Fig. 2.

2.1. Cerium conversion coatings

Since the first reports on CeCCs for Al alloys by Hinton et al. [62], many works have been reported that showed the CeCCs could effectively inhibit the corrosion of Al alloys [55,66,67,81]. In the past two decades, they were also applied to Mg alloys [68,71,72,75,82]. It was Rudd et al. who extended RECCs to Mg and its alloys for the first time. The authors reported that the conversion coating productions by immersion in Ce, La or Pr solutions was beneficial in decreasing the Mg dissolution in a pH 8.5 buffer solution. Even though the coating performance worsened with continued immersion in the buffer solution, the polarisation resistance \(R_p\) of the coated alloy remained to be approximately three times higher than that of the uncoated alloy [68]. Dabalà et al. showed that the CeCC significantly amended the corrosion resistance of Mg alloy in aqueous chloride media [71].

Several parameters viz., the type and concentration of RE ions, pH, temperature, pre-treatments, time of coating and co-additives/co-conversion agents considerably affect the extent of coating formation. \(\text{H}_2\text{O}_2\) is a common coadditive (as an accelerator) in Ce conversion baths originally developed by Wilson and Hinton [62,83] for Al alloys (see section 2.1.4.1). Several co-conversion agents were also investigated in RECCs to enhance the corrosion resistance (see section 2.1.4). Table 1 classifies the reported works into three based on the co-conversion agents used, viz. (i) Ce alone (ii) Ce + inorganic conversion agents (section 2.1.4.1) and (iii) Ce + organic conversion agents (section 2.1.4.2). It can be seen that the majority of the works reported in the first and third categories employed \(\text{H}_2\text{O}_2\) to assist the coating process. For the second category, \(\text{H}_2\text{O}_2\) was rarely employed. Most of the works reported in the first category utilized room temperature deposition, whereas higher bath temperatures (40–70 °C) are preferred in the second and third categories. The time of deposition ranges from 30 to 1200s. Almost all these reports used an acidic bath with a pH at the range of 2-6. Ce nitrate is the most used salt, followed by Ce chloride and Ce sulphate. Specific details are provided in Table 1.

2.1.1. Morphology, structure and composition of CeCC

2.1.1.1. Coating morphology by electron microscopy. Typically, scanning electron microscopy (SEM) images of RECCs exhibit a cracked surface morphology, and that varies with the difference in the experimental conditions employed and the pre- and post-treatments followed. Lin et al. have shown that after a 0.5 min of immersion in Ce bath, the Mg surface was spotted with island-like particles (Fig. 3a). After 1 min, the coating covered the surface wholly, with the appearance of numerous surface micro-cracks. After 3 min of deposition, a thick coating with larger crack-widths developed and that completely masked the surface scratches (Fig. 3b). Numerous small micro-cracks were observed within each cracked region. More severe cracks were observed with a further increase of deposition time (Fig. 3c). Their optical microscopy images, however, do not reveal a cracked surface morphology, and that suggested that the cracks were not formed during the coating growth, but during the drying process [72]. In general, surface cracks in conversion coatings are attributed to the water evaporation, and the associated volume shrinkage and the stress developed. A thicker coating is expected to produce more severe cracking, and that can results in partial coating detachment from the surface. The cracked surface morphology is expected to decline the coating stability in the aggressive environments and hence the corrosion resistance. Typically, a higher coating temperature may favour the formation of larger micro-cracks. A close-up view of the coating formed after 20 min of deposition is also shown in Fig. 3. The image displayed interlaced nanoscale fibres [72]. Lei et al. have shown that spherical nanoparticles with diameters of 300 nm were discretely deposited on the alloy surface at the initial immersion times. However, after 5 min of immersion, porous nanoparticle aggregates with honeycomb-like morphology was formed. As the deposition time increased to 10 min, growth of new nanoparticle nodules and formation of a cauliflower-like surface morphology happened [84].

Castano et al. described the microstructural evolution of CeCC on AZ31 Mg alloy after different processing steps: viz. a uniform layer (50 nm thick) formed after the grinding step (layer I), the surface after an acid pre-treatment (layer II, 90 nm thick), a porous layer formed on II after an alkaline treatment (layer III), surface formed after CeCC (layer IV) and surface after a phosphate post-treatment (layer V) (Fig. 4); where the layer IV exhibited a cracked morphology with tiny Ce-rich nodules characteristics of RECCs. Cross-sectional micrographs showed the existence of two layers, an interior layer, which had an
<table>
<thead>
<tr>
<th>Type</th>
<th>Alloy used</th>
<th>Conversion coating bath parameters</th>
</tr>
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<tbody>
<tr>
<td>REs</td>
<td>Mg, WE43</td>
<td>50 × 10⁻³ mol/dm² Ce(NO₃)₂/La(NO₃)₃/Pr(NO₃)₃; Room Temp.; pH 3.6; Time 5 min.</td>
</tr>
<tr>
<td>Ce [68]</td>
<td>AZ63</td>
<td>10 mg/L CeCl₃ + 50 mg/L H₂O₂; Room temp.; Time 30–180 s.</td>
</tr>
<tr>
<td>Ce [71]</td>
<td>AZ31B</td>
<td>0.05 M Ce(NO₃)₃; Temp. 30 °C; pH 5.2; Time 0.5–20 min.</td>
</tr>
<tr>
<td>La, Ce [73]</td>
<td>AZ31</td>
<td>1.0 × 10⁻³ M Ce(NO₃)₃/La(NO₃)₃; Temp. 22 °C; pH 6; Time 1–60 min.</td>
</tr>
<tr>
<td>Ce [75]</td>
<td>AZ91D</td>
<td>0.05 mol/L Ce(NO₃)₃; Room temp.; pH 3.5; Time 15 min.</td>
</tr>
<tr>
<td>Ce [84]</td>
<td>AZ31</td>
<td>0.1 M CeCl₃ + 5 mL/L H₂O₂; Room temp.; pH 6; Time 1–10 min.</td>
</tr>
<tr>
<td>Ce [86]</td>
<td>AZ31</td>
<td>0.05 mol/L Ce(NO₃)₃; Temp. 25 °C; pH 3.6; Time 60 min.</td>
</tr>
<tr>
<td>Ce [87]</td>
<td>AZ31B</td>
<td>0.05 kmol/m³ Ce(NO₃)₃ + 0.25 kmol/m³ H₂O₂; Temp. 30 °C; pH 2.7–5.2; Time 10 min.</td>
</tr>
<tr>
<td>Ce [94]</td>
<td>AZ31</td>
<td>1.0 × 10⁻³ M Ce(NO₃)₃/CeCl₃/Co₃(SO₄)₃/CePO₄; Temp. 22 °C; pH 6; Time 10, 600, 3600 s.</td>
</tr>
<tr>
<td>Ce [97]</td>
<td></td>
<td>Mg coated mild steel; Room temp.; Time 2 min.</td>
</tr>
<tr>
<td>Ce [99]</td>
<td>AZ31</td>
<td>10 g/L Ce(NO₃)₃ + 20 mL/L H₂O₂; Temp. 60 °C; Time 5 min.</td>
</tr>
<tr>
<td>Ce, La, Sm [108]</td>
<td>AZ31</td>
<td>0.05 mol/dm³ Ce(NO₃)₃/La(NO₃)₃/Sm(NO₃)₃; Temp. 25 °C; pH 4.5–5.5; Time 8 min.</td>
</tr>
<tr>
<td>Ce [114]</td>
<td>AZ91D</td>
<td>0.03 mol/L Ce(NO₃)₃ + 0.025 mol/L KMnO₄; Temp. 35 °C; pH 2; Time 20 min.</td>
</tr>
<tr>
<td>Ce [120]</td>
<td>AZ31</td>
<td>0.05 M Ce(NO₃)₃ + 0.254 M H₂O₂; Room temp.; pH 2.9; Time 180 s.</td>
</tr>
<tr>
<td>Ce [134]</td>
<td>AZ91D</td>
<td>0.05 M Ce(NO₃)₃ + 0.254 M H₂O₂; Room temp.; pH 2.9; Time 2–20 s.</td>
</tr>
<tr>
<td>Ce [145]</td>
<td>Mg, AZ91, AM50</td>
<td>0.05 M CeCl₃ + 25 mL/L H₂O₂; Room temp.; Time 30–180 s.</td>
</tr>
<tr>
<td>Ce [149]</td>
<td>AZ91D</td>
<td>0.05 M Ce(NO₃)₃ + 0.254 M H₂O₂; Room temp.; Time 30–180 s.</td>
</tr>
<tr>
<td>Ce [148]</td>
<td>AZ91D</td>
<td>0.03 mol/L Ce(NO₃)₃ + 0.025 mol/L KMnO₄; Temp. 35 °C; pH 2; Time 20 min.</td>
</tr>
<tr>
<td>La [156]</td>
<td>Mg-Li</td>
<td>5 g/L La(NO₃)₃; Temp. 25 °C; pH 5; Time 20 min. (Post-treatment – Hot air dry).</td>
</tr>
<tr>
<td>La [161]</td>
<td>Mg-Li</td>
<td>0.05 mol/L La(NO₃)₃; Microwave synthesis (0–300 W); Temp. 40 °C; Time 10 min.</td>
</tr>
<tr>
<td>La [166]</td>
<td>AZ91</td>
<td>12 g/L La(NO₃)₃; pH 4; Temp. 30–50 °C; Time 10–30 min.</td>
</tr>
<tr>
<td>Gd [182]</td>
<td>AZ91</td>
<td>5 g/L Gd(NO₃)₃ + 20 mL/L H₂O₂; Temp. 50 °C; Time 20 min.</td>
</tr>
<tr>
<td>Nd [173]</td>
<td>AZ91</td>
<td>5 g/L Nd(NO₃)₃; Temp. 50 °C; Time 20 min.</td>
</tr>
<tr>
<td>Nd [175]</td>
<td>AZ31</td>
<td>5 g/L Nd(NO₃)₃ + 5 mL/L H₂O₂; Temp. 40 °C; pH 6.5; Time 7 min.</td>
</tr>
<tr>
<td>Nd [172]</td>
<td>AZ91</td>
<td>5 g/L Nd(NO₃)₃ + 20 mL/L H₂O₂; Temp. 50 °C; Time 20 min.</td>
</tr>
<tr>
<td>Pr [183, 184]</td>
<td>AZNd</td>
<td>0.2 M Pr(NO₃)₃; Time 30 s. (Post-treatment – in 0.2 M NaOH solution for 2 min).</td>
</tr>
<tr>
<td>Sm [177]</td>
<td>AZ91</td>
<td>Nd(NO₃)₃ / Sm(NO₃)₃ + H₂O₂; 50–20 min.</td>
</tr>
<tr>
<td>Y [168]</td>
<td>AZ91D</td>
<td>10 g/L Y(NO₃)₃; Temp. 30°; (Post-treatment - in 30% mass fraction of silica sol solution, air dried for 24 h, heating at 250 °C for 2 h).</td>
</tr>
<tr>
<td>Y [167]</td>
<td>AZ91D</td>
<td>10 g/L Y(NO₃)₃; Temp. 30°; Time 50 min.</td>
</tr>
<tr>
<td>PEO + Ce [153]</td>
<td>AZ31</td>
<td>0.03 M CeCl₃ + 0.5 M H₂O₂; Temp. 70 °C; pH 3–10; Time 0.5–1 h.</td>
</tr>
<tr>
<td>PEO + Ce [91, 124]</td>
<td>AZ31</td>
<td>0.03–0.1 mol/L Ce(NO₃)₃ + 0.03–0.1 mol/L ZrO(NO₃)₂ + 0.02–0.05 Nb₂O₅F₃; Room temp., 40 °C; Time 3 min, 24 h.</td>
</tr>
<tr>
<td>La + Mg [162]</td>
<td>AZ31, AZ61, AZ91, AM60</td>
<td>La(NO₃)₃ + Mg(NO₃)₃; Room temp. (Pre-treatment – Alkaline degrease in NaOH and H₂PO₄; Acid pickling in H₂PO₄, and/or surface activation in NaF solution).</td>
</tr>
<tr>
<td>RE + Mg [165]</td>
<td>Mg-RE</td>
<td>10⁻¹⁰ mol/dmm² Mg(NO₃)₂ + 10⁻¹⁰ mol/dmm² RE nitrate; Time 1 day; Room temp. (Post-treatment – Dried under air flow for 1 day at 90 °C).</td>
</tr>
<tr>
<td>Type [Ref.]</td>
<td>Alloy used</td>
<td>Conversion coating bath parameters (Pre-/Post-treatments)</td>
</tr>
<tr>
<td>-------------</td>
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<td>-------------------------------------------------------------</td>
</tr>
<tr>
<td>Zn + Ca + Ce + P [127]</td>
<td>AZ31</td>
<td>10 g/L Na2HPO4 + 4 g/L NaNO3 + 6 g/L Zn(NO3)2 + 2 g/L Ca(NO3)2 + 2 g/L NaF + 1 g/L Ce(NO3)3; Temp. 50 °C; pH 2.5; Time 20 min.</td>
</tr>
<tr>
<td>Zn + Ce [128]</td>
<td>–</td>
<td>10-30 g/L Na2HPO4 + 4-6 g/L Zn(NO3)2 + 2-4 g/L NaNO3 + 0.5-2 g NaF + 0.5-2 g Ca(NO3)2 + 0.5-2 g Ce(NO3)3; Temp. 40-70 °C; pH 2-3.</td>
</tr>
<tr>
<td>Ce + Al [92]</td>
<td>AZ31</td>
<td>5 mM Ce(NO3)3 + Al(NO3)3 + Ca(OH)2; pH 4.7; Time 15 min.</td>
</tr>
<tr>
<td>Ce + Al [115]</td>
<td>AZ81</td>
<td>3-15 g/L Ce(NO3)3 + 5 mL/L H2O2 + 5 g/L Al(NO3)3; Room temp.; pH 2; Time 10 min.</td>
</tr>
<tr>
<td>Ce + Al [136]</td>
<td>AZ91D</td>
<td>0.05 mol/L Al(NO3)3 + 0.001-0.05 mol/L Ce(NO3)3; Time 2 min; Temp. 15-20 °C. (Post-treatment – Hot air drying)</td>
</tr>
<tr>
<td>Ce + Mo [113]</td>
<td>AZ91</td>
<td>Ce(NO3)3 + 3-4 g/L Na2MoO4; Temp. 25 °C; pH 2.3-2.5; Time 2-15 min. (Pre-treatment – Soaking in alkaline solution for 2 min)</td>
</tr>
<tr>
<td>Ce + Mo [135]</td>
<td>–</td>
<td>2-15 g/L Na2MoO4 + 4-20 g/L Ce(NO3)3 + 0.1-2.5 g/L Citric acid/Tetaboric acid + 0.1-2 g/L disodium ethylene diamine tetraacetate + HNO3; pH 2-3. (Pre-treatment – Hot air dry).</td>
</tr>
<tr>
<td>La + Mo [164]</td>
<td>AZ31</td>
<td>6 g/L La(NO3)3 + 3 g/L Na2MoO4; Time 20 min; pH 4, 25 °C. (Post-treatment – Soaking in alkaline solution)</td>
</tr>
<tr>
<td>Ce + V [132]</td>
<td>AZ31</td>
<td>4.0 g/L Ce(NO3)3 + 2.4 g/L Na2O3; Temp. 50 °C; pH 2.5; Time 20 min. (Pre-treatment – 0.8 vol.% HNO3 for 10-20 s; dipped in 16 vol.% HF for 5 min.)</td>
</tr>
<tr>
<td>Ce + V [133]</td>
<td>AZ31</td>
<td>0.92-46.1 mM Ce(NO3)3 + 19.7 mM NaNO3; Temp. 50 °C; pH 2.5; Time 20 min. (Pre-treatment – 0.8 vol.% HNO3 for 10-20 s; dipped in 16 vol.% HF for 5 min.)</td>
</tr>
<tr>
<td>Ce + Mn [124]</td>
<td>AZ31</td>
<td>0.0011 mol/L Ce(NO3)3 + 5.0 mL/L H2O2 + 0.04 mol/L NaF + 0.0099 mol/L Mn(NO3)2; 4H2O + 0.0023 mol/L PVA; Temp. 25 °C; pH 3-5; Time 5 min.</td>
</tr>
<tr>
<td>Ce + Mn [125]</td>
<td>AZ91</td>
<td>15 g/dm3 Ce(NO3)3 + 30 g/dm3 KMnO4 + 15 g/dm3 Mg(NO3)2; Temp. 333 K; Time 2-5 min. (Pre-treatment – (i) Alkaline cleaning in 10 dm3 NaOH + 15 dm3 Na2CO3 + 10 dm3 Na2SiO3 + 5 g/dm3 Triethanolamine; Temp. 60 °C; Time: 3-10 min. (ii) Acid pickling in 20-50 dm3 HNO3 + 100-2000 dm3 Mg(NO3)2; 200-400 dm3/dm3 Ethanol; Temp. 293 K; Time: 10-20 s. (Post-treatment - Hot air dry).)</td>
</tr>
<tr>
<td>Ce + La + Mn [74]</td>
<td>Mg-8.5Li</td>
<td>2 g/L Ce(NO3)3 + 2 g/L La(NO3)3 + 2 g/L KMnO4; Temp. 40 °C; pH 4; Time 5 min. (Post-treatment – Hot air dry)</td>
</tr>
<tr>
<td>Ce + La + Mn [137]</td>
<td>AZ61</td>
<td>0.001 M Ce(NO3)3 + 0.001 M La(NO3)3 + 0.0158 M KMnO4; Room temp.; Time 30-120 min.</td>
</tr>
<tr>
<td>Ce + La + Mn [163]</td>
<td>AZ31</td>
<td>0.4 g/L La(NO3)3 + 0.4 g/L Ce(NO3)3 + 25 g/L KMnO4; Room temp.; Time 30 min. (Pre-treatment – (i) 10 g/L Na2PO4 + 40 g/L NaOH for 15 min at 60 °C. (ii) in 63 wt.%, 100 mL/L HNO3 and 125 g/L CrO3 for 30 s.)</td>
</tr>
<tr>
<td>Ce + P [126]</td>
<td>AZ91D</td>
<td>2 g/L ZnO + 12 g/L H3PO4 + 1 g/L NaF + 4 g/L C6H12O6Na2 + 6 g/L NaNO3 + 0.5 g/L Na2P2O7 + 0-4 g/L nano-CeO2; Temp. 60 °C; Time 60 min.</td>
</tr>
<tr>
<td>Y + Mn + P + Ca [171]</td>
<td>–</td>
<td>KMnO4 + Na2PO4 + Ca(NO3)3 + Y(NO3)3</td>
</tr>
<tr>
<td>Y + Mg [169]</td>
<td>–</td>
<td>1-20 mM Mg(NO3)2 + 1-20 mM Y(NO3)3; Room temp.; Time 5 h. (Pre-treatment – (i) Alkaline degrease in 37 g/dm3 NaOH and 10 dm3 NaH2PO4; 90 °C, 6 min. (ii) Acid pickling in 85 g/L H2PO4; Room temp.; 30 s. (iii) Surface activation in 10-40 g/dm3 NaF; 70 °C; 10 min.)</td>
</tr>
</tbody>
</table>

### REs + Organic co-additives

| Ce [90] | AZ91D | 5-10 g/L Ce(NO3)3 + 5-12 mL/L H2O2 + 3-5 g/L Ni(NO3)2 + 0.1-0.3 g/L sodium dodecyl benzene sulfonate. (Pre-treatment – Alkaline deoxidization, Acid polishing) |
| Ce + Gelatin [85] | AZ31B | 4 wt.% CeCl3 + 6.7 wt.% H2O2 + 0.25 wt.% Gelatin; Time 120 s. (Pre-treatment – in 1 wt.% HNO3, 30 s, Room temp., followed by treatment in 5 wt.% Na2SiO3, 5 min, Room temp.) |
| Ce + Gelatin [88] | AZ31B | 4 wt.% CeCl3 + 6.7 wt.% H2O2 + 0.25 wt.% Gelatin; Room temp.; Time 5-180 s. (Pre-treatment – (i) in 1 wt.% HNO3, 30 s followed by (ii) alkaline cleaning in 5 wt.% of Na2SiO3; 5 min.) |
| Ce + Gelatin [111] | AZ91D, AZ31B | 4 wt.% CeCl3 + 6.7 wt.% H2O2 + 0.25 wt.% Gelatin; Room temp.; Time 2 min. (Pre-treatment – in (i) 0.5 wt.% HF, 30 s, Room temp., followed by (ii) Alkaline treatment in 5 wt.% NaOH, 30 s, Room temp.). (Post-treatment – in 2.5 wt.% NaH2PO4, 5 min, 85 °C.) |
| Ce + Gelatin [116] | AZ31 | 0.005 M Ce(NO3)3 + 5 mL/L H2O2 + 0-5 g/L Gelatin; Temp 30 °C; pH 3.8; Time 300-1200s. |
| Ce + Gelatin [123] | AZ91D | 205 g Ce stock solution + 0.8 g Gelatin + 0-12 vol.% H2O2; Time 6 s spray. (Pre-treatment – in 0.5 wt.% HF, 20 s; Room temp.; followed by treatment in 10 wt.% NaOH, 1 min, 65 °C. (Post-treatment – in phosphate solution, 5 min, 85 °C.) |
| Ce + Silane [139,140] | AZ31 | 5 vol.% BTESP in 90 vol.% Ethanol and 5 vol.% H2O + 0.1 M CeCl3 + 5 mL/L 30 wt.% H2O2; Time 5 min. (Pre-treatment – 4 g/L NaOH solution; Room temp.; 5 min.). (Post-treatment – Oven-dried at 110 °C.) |
| Ce + SAM [92] | AZ3 | 0.05 M Ce(NO3)3; Room temp.; pH 5; Time 900 s. (Post-treatment – Organic SAM formation. |
| La + Gelatin + Chitosan [142] | AZ91D | 40 g/L La(NO3)3 / Ce(NO3)3 + 25 g/L Gelatin + 25 g/L Chitosan. A 25 g/L Ce(NO3)3 was prepared as the passivation solution and 10 mL/L H2O2 was used as the accelerator. |
Fig. 2 – Pie chart on reported RE-based conversion coatings for Mg and its alloys (Source: SciFinder - CAS).

analogous appearance to layer II and an exterior layer (layer IV, 400 nm thick) (more descriptions on Fig. 4 are provided in section 2.1.5.2) [85]. Li et al. also showed that the CeCC on AZ31 alloy had a two-layered structure (surface layer and interior layer) as revealed by SEM and atomic force microscopy (AFM) images. The adhesion between the surface layer and the interior layer was found to be much feebler than that between the interior layer and the metallic surface. The interior layer has consisted of uneven particles with sizes at the range of 10–100 nm whereas the surface layer has some nanoscale poultry-claw shaped tubes [86].

In contrast, TEM cross-sectional images revealed the existence of a three-layered structure. Lin et al. showed that a three-layered structure comprising porous Mg/Al hydroxide/oxide layer (under layer), a compact middle layer, and a major fibrous overlay sequentially formed on AZ31 alloy [72]. The authors observed that the major fibrous overlay transformed into a compact layer as H₂O₂ was added to the Ce bath [72,87]. The bonding between the compact and the fibrous layers was the weakest. The surface oxide layer (before immersion) of 50 nm was wholly substituted by the CeCC after 0.5 min of immersion in the conversion solution. The Ce composition in both the compact and the fibrous layers was identical. It was also observed that the fibrous layer contributed to the greatest coating thickness, though the layer was discontinuous. Nevertheless, the fibrous layer exhibited poor adhesion to the compact layer. Selective area diffraction (SAD) patterns revealed the existence of nano-sized crystals in both the compact and fibrous layers. However, the SAD pattern corresponding to the porous layer showed diffused halos indicative of amorphous structure. The layer thickness vs. immersion time (Fig. 3) plot showed that all the layers displayed an increase in thickness with immersion time. The order of growth rate was: compact < porous < fibrous [72]. Castaño et al. showed that the as-formed coating had a three-layered structure: (i) a nanocrystalline MgO transition layer over Mg substrate, (ii) an interior nanocrystalline CeCC layer, and (iii) an exterior amorphous CeCC layer. The thickness of the nanocrystalline CeCC layer varies as a function of the immersion time and that ranged from a minimum of 100 nm.
(immersion time of 5 s) to a maximum of 400 nm (immersion time of 120 s) [88].

These reports support the fact RECCs do have a typical cracked surface morphology of chemical conversion coatings, and that is mostly associated with the dehydration process. The multilayered structure, as revealed by electron microscopy studies, suggests that with suitable experimental conditions, a compact CeCC with optimized interior nanocrystalline layer can be realized.

2.1.1.2. Structure and composition. X-ray diffraction (XRD) studies conducted by most of the reports demonstrated that the as-formed CeCCs are typically amorphous [89,90]. The SAD patterns also suggested that the film is mostly amorphous; however, the presence of nanocrystalline domains was also detected as the pattern contained continuous rings corresponding to CeO₂ [88]. Hariprasad et al. reported that XRD plots of the CeCCs showed the presence of CeO₂ and Ce₂O₃ phases along with the Mg substrate peak [91]. Salman et al. also showed that after a conversion treatment in 5 mM Ce nitrate solution (pH 4.5), XRD peaks corresponding to Mg, Mg(OH)₂, Ce₂O₃, and Ce(OH)₃ were appeared [92,93]. HRTEM images by Castano et al. revealed a nanocrystalline structure for the CeCC (layer IV) that was characterized by nodular nanocrystals entrenched within an amorphous matrix. The lattice spacing of layer IV was 0.32 nm, and that was in agreement with the (111) planes of the cubic structure of CeO₂ [85].

The CeCC is found to be comprised of Ce hydroxides/oxides, in which Ce(III) and Ce(IV) species co-exist [73,85,86,94–96]. Various theories/mechanisms have been proposed to explain their co-existence (see section 2.1.2.). X-ray photoelectron spectroscopy (XPS) studies by Li et al. showed that CeCC on AZ31 alloy has a time-dependent composition. The Ce3d and O1s peak intensities augmented with an increase in the immersion time, whereas Mg1s and Mg2p peaks diminished progressively. At the initial deposition period (time >1 min), only the peaks corresponding to Mg oxide and hydroxide were detected. After 5 min of deposition, Ce−O, Mg−O, Ce−OH, and Mg−OH were detected at 529.2, 531.0, 531.6, and 532.4 eV, respectively. The presence of oxides and hydroxides of Ce suggested the formation of Ce(OH)₃, Ce(OH)₄, and CeO₂. At this period of immersion, the coating was mostly composed of oxides and hydroxides of Mg and Ce, with Ce hydroxide in dominant. With extended deposition, the film lost adhesion with the substrate and part of the film get detached. Interestingly, the percentage of Ce(IV) showed a regular increment with the deposition time. The at.% of Ce(IV) detected after 1, 5 and 10 min of deposition were 83.9, 87.3 and 92.7, respectively [84]. XPS analysis by Castano et al. displayed that the layer IV (CeCC) was mostly comprised of Ce and O with minor amounts of Mg, Al, and C. Fitting the HRXPS peaks (Fig. 4) showed co-existence of Ce(III) and Ce(IV) species on layer IV with Ce(IV) predominant (63%). The high-resolution TEM images displayed that Ce(IV) (CeO₂ nanocrystals) were entrenched in an amorphous network and that suggested that the amorphous region was mostly Ce(III) species such as Ce(III) hydroxides [85]. In contrary, Hassen et al. revealed that the relative abundance of Ce(III) and Ce(IV) in the CeCC was around 90 and 10%, respectively. Ce in the bulk conversion layer was mainly in the Ce(III) state and corresponded to the presence of Ce(OH)₃ [97]. The presence of Ce(IV) was mainly correlated to the CeO₂ formation [73,94,97] (see next section). Ardelean et al. showed that CeCC formed from a bath containing Nb and Zr salts was composed of CeO₂, Ce₂O₃, ZrO₂, Nb₂O₆, MgO, and MgF₂ as main constituents. The coating mainly consisted of 36% of Ce oxide, 20% of Zr oxide, 15% of Nb oxide, 12% of Mg oxide, 13% of Mg fluoride, and 2% of Mg carbonate. The left-over 2% corresponded to metallic Mg [82]. Chen et al. showed that a Ce-La composite conversion coating mainly composed of Ce(OH)₃, CeO₂, and La(OH)₃ [98]. Cui et al. displayed that the chemical composition of the CeCC formed on AZ31 alloy was CeO₂, CeO, Ce₂O₃, MgO, Mg(OH)₂, and Al₂O₃ [99]. The available reports on phase structure analysis of CeCCs suggested a mixed amorphous-crystalline nature with the
predominant existence of amorphous phases. There are conflicting reports with the relative existence of Ce$^{3+}$ and Ce$^{4+}$ in the coating. The relative presence of these phases in solution is critical in determining the deposition mechanism (see next section).

### 2.1.2. Mechanism of formation

Conversion coating treatment is accomplished by a series of dissolution, oxidation, reduction and precipitation reactions. It is known that corrosion inhibition by Ce salts is associated with the precipitation of Ce oxides or hydroxides over cathodic sites and that in turn, give rise to a blocking effect diminishing the reduction reactions [100,101]. The formation of RECCs has been explained by the cathodic mechanism. According to this, the increase of the local surface pH resulting from the cathodic reactions induces the localized precipitation of RE hydroxides (Eq. 5), ultimately forming a conversion coating. The extent of RE precipitation varies with the interface pH variations and the solubility of the formed hydroxide layer. Along with the dissolution process (dissolution of pre-formed native oxide/hydroxide film and dissolution of Mg), the cathodic reactions occur, accompanying the hydrogen gas evolution and pH increase at the interface and the coating formation. In reality, and in the presence of co-additives such as H$_2$O$_2$, the process is expected to be accompanied by various hydrolysis and condensation reactions [25,26,73,102–107].

$$\text{RE}^{n+} + n\text{OH}^- \rightarrow \text{RE(OH)}_{2n+1}(5)$$

As mentioned earlier Ce can exist in solution as either Ce(III) or Ce(IV) species. Aldykiewicz et al. [95] reported that the oxidation of Ce(III) to Ce(IV) happens in solution with the subsequent precipitation of insoluble CeO$_2$. During the formation of the solution species Ce(OH)$_2$$^{2+}$, oxidation of Ce(III) occurs (Eq. 6). The solution species can eventually get precipitated as hydrated Ce oxide (Eq. 7) [25,95].

$$4\text{Ce}^{3+} + 2\text{O}_2 + 4\text{OH}^- \rightarrow 4\text{Ce(OH)}_{2}^{2+} (6)$$

$$\text{Ce(OH)}_{2}^{2+} + 2\text{OH}^- \rightarrow 2\text{CeO}_2 + 2\text{H}_2\text{O}(7)$$

At lower pH values, Ce(III) is the more stable form, whereas, at higher pH ranges, Ce(IV) becomes more stable. Ce(III) oxidation is spontaneous in alkaline pH [109]. At a suitable pH, H$_2$O$_2$ or other oxidizing agents in the bath can enhance the conversion rate of Ce(III) to Ce(IV) [96]. Chen et al. suggested that some of the Ce(III) oxidized to Ce(IV) during open-air exposure [98].

Li et al. [108] through in situ ellipsometric studies (the conversion bath contained only RE salt) showed that once the interfacial pH was high enough, Ce(III) underwent hydrolysis and precipitated as solid ternary Ce/hydroxides (Eq. 8) and subsequently oxidized to hydrated CeO$_2$ (Eq. 9):

$$\text{Ce}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Ce(OH)}_{3}^{+} + 3\text{H}^+ (8)$$

$$\text{Ce(OH)}_{3}^{-} + \text{H}_2\text{O} \rightarrow \text{CeO}_2 + \text{H}^+ + \text{e}^- (9)$$

Calculations revealed that a solid phase transformation from Ce(IV) hydroxide to oxide (Eq. 10) is favoured [96].

$$\text{Ce(OH)}_{4} \rightarrow \text{CeO}_2 + 2\text{H}_2\text{O}(10)$$

Montemor et al. showed that the film developed at the initial immersion periods have primarily consisted of Ce(III) hydroxides. As the immersion time increased, Ce(IV) species become dominant [73]. In effect, the growth process consists of precipitation of hydroxides of Ce(III) and Ce(IV) (Eqs. 11 and 12) along with the precipitation of Mg hydroxides and that is followed by the conversion of Ce(OH)$_3$ into CeO$_2$ (Eq. 10), forming a Ce(IV)-rich external layer [94].

$$\text{Ce}^{3+} + 3\text{OH}^- = \text{Ce(OH)}_{3}^{+}(11)$$

$$\text{Ce}^{4+} + 4\text{OH}^- = \text{Ce(OH)}_{4}(12)$$

Yu et al. reported that the local pH enhancement led to the conversion of Ce(III) to Ce(IV) and that occurred inside the coating, and subsequently, the Ce(IV) cations get precipitated as CeO$_2$ [110]. Lin and Fang [72] proposed that after immersion in Ce salt solution, the surface-Mg oxide film promptly dissolved and the Ce(III) precipitates on the Mg/Al hydroxide, developing a compact layer followed by the deposition of a fibrous external layer. Their XRD pattern identified Ce oxides, and that suggested that Ce hydroxides could be oxidized to Ce oxides during the air drying. EDS results indicated that both the fibrous and the compact layers were composed of Ce and Mg hydroxides or oxides [72]. Ce(III) can be oxidized to Ce(IV) via Ce$_2$O$_3$ formation (Eqs. 13 and 14) [93].

$$2\text{Ce(OH)}_{3} = \text{Ce}_2\text{O}_3 + 3\text{H}_2\text{O}(13)$$

$$\text{Ce}_2\text{O}_3 + \text{O}_2 = 2\text{CeO}_2(14)$$

All these studies suggest that Ce exists predominantly as Ce$^{4+}$ in the coating. The conversion of Ce$^{3+}$ to Ce$^{4+}$ happens either in solution or in coating.

The coating formation mechanism strongly depends on the alloy microstructure [111]. Alloys like AZ91D reveals a two-phase structure, Mg-rich α and Al-rich β phases. The difference in the reduction potentials of α (−1.71 V) and β (−1.0 V vs. SHE) phases in effect can lead to galvanic corrosion between the phases accompanied by the selective phase dissolution and the coating formation [33,85,111–113]. Castanoa et al. have shown that the CeCC on AZ91D alloy presented a better salt spray performance than an analogous coating on AZ31B alloy. The coated AZ31B alloy had several pits and significant salting after 216 h of salt spray whereas negligible salt tainting was observed for the coated AZ91D alloy. The superior performance of the later alloy was attributed to the higher Al content in the alloy [111].

Motemor et al. have shown that the mechanism of conversion coating depends on the anions present in the Ce salt (Ce chloride, Ce nitrate, Ce sulphate and Ce phosphate). The study showed that the conversion layers formed in Ce chloride were the thickest and the most corrosion-resistant. Their XPS studies showed that after a 10s of immersion, the relative Ce3d peak intensities were in the order: phosphate < nitrate < sulphate < chloride. The O1s peak for the coupon treated in the cerium sulphate bath showed the presence of hydroxides, suggesting that the development of the Ce oxide was hindered in the presence of sulphate ions. No traces of nitrate or chloride detected in the film whereas small contributions of phosphate were detected after a deposition time.
of 10 s. Auger depth profiling showed that the exterior layers of films formed in Ce chloride and Ce nitrate were composed of Ce and O. Perversely, the films developed in Ce phosphate and Ce sulphate revealed the presence of Mg in the exterior layers, and that suggested a lesser extent of film formation or film formation with defects. The film formed in Ce chloride was nearly two and four times thicker than the corresponding films formed in Ce nitrate and Ce phosphate solutions [94].

2.1.3. Variation of coating thickness and corrosion resistance with time
Potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS) were mainly utilized to investigate the corrosion resistance of the coated alloys. As shown in Table 1, the experimental parameters such as bath composition, temperature, pH, immersion (deposition) time, nature of co-additives (see section 2.1.4), and kind of pre- and post-treatment (see section 2.1.5) determine the final quality of the prepared coating.

Dabalâ et al. have shown the existence of a negative hysteresis in cyclic potentiodynamic polarization plot of both the bare and the coated alloys where the corrosion potential ($E_{corr}$) was nobler than the repassivation potential, and that suggested a reasonable risk for localized corrosion even after the conversion coating. Even though the CeCC produced a higher corrosion-resistant surface, the pitting formation probability was elevated as the reverse scans of the coated and uncoated samples overlapped. Nevertheless, the conversion coating increased the pitting potential of the alloy considerably. The thickness of the CeCC rapidly grew up to 167 nm (in 30 s of immersion) and remained approximately constant afterwards. The thickness after 180 s of deposition was 200 nm [71]. Comparison of Tafel plots of two differently coated samples: one achieved by a single immersion (180 s) and the other by repeated immersions (six repetitions with 30 s each), displayed that the repeatedly coated sample possessed better corrosion resistance. The authors attributed the enhanced corrosion resistance to the possible denser and less porous layer formed by the repeated immersion coating. The passive layer formed with each step of the six repetitions is expected to be more compact during the drying step, and that can be helpful to make the subsequent deposition more efficient. However, when ten repeated immersions were employed, the corrosion resistance showed a decline, and that was associated with the possible partial dissolution of the coating happened with the extended immersion time [71]. Time-dependent EIS studies of the coated alloys in 3.5 wt.% NaCl revealed that during the first 24 h of immersion, the impedance magnitude does not show a notable decline, which suggested that the CeCC significantly reduced the surface reactivity of the Mg alloy, and effectively prevented the chloride ion penetration. However, a half order of magnitude of impedance decreased during the next 48 h of immersion due to the localized corrosion resulted from the electrolyte penetration through the cracks. The impedance continued to be decreased with the further increase of immersion time [114].

Lin and Fan showed that at the initial deposition periods, both the weight gain and the coating thickness quickly increased with the time of deposition. As the immersion time increased, the weight gain increased at a constant rate, and saturated coating thickness (3–4 μm) was achieved after 10 min and, that was attributed to the formation of a more compact film [72]. Yu et al. have shown that after the conversion coating, the corrosion current ($i_{corr}$) goes down and, that was independent of the immersion time. At initial deposition periods (1–2 min of immersion in Ce salt solution), the $E_{corr}$ of the coated Mg alloy (during the corrosion experiment in 3.5% NaCl solution) moved towards the negative direction. After 4 min of deposition, the anti-corrosion property significantly improved, and the $E_{corr}$ shifted to positive directions. However, After an 8 min of deposition, there was a substantial increase in the $i_{corr}$ [115]. EIS results by Hassen et al. showed that impedance of the Ce-coated samples augmented for shorter immersion times and got deteriorated with longer time due to the coating breakdown [97]. Arthanari et al. showed that shorter deposition time and lower deposition temperature provided better corrosion resistance. Lengthy deposition created merely a loosely bound coating and that in effect, reduced the corrosion resistance [116]. Optical images of the phosphate post-treated CeCC after 5 days of salt spray test displayed that a 5 s coated sample had superior corrosion resistance whereas a 180 s coated alloy revealed numerous pits and salt tails. The presence of fewer and smaller surface cracks in the 5 s immersion panels was suggested to be the reason for the enhancement [88].

Conversely, Salman et al. noticed that increasing the immersion time enhanced the anticorrosion property, and the best corrosion resistance was achieved after a 15 min of deposition. After 5 min of deposition, the sample surface was partially covered by particles aligned in rows along the scratch marks induced during the polishing process, indicative of a thin film formation. After 10 min of immersion, a thicker coating resulted that covered the surface completely. Several cracks were observed after 15 min of immersion. At the initial immersion periods from 2–10 min, the mass gain was significant and, during 10–15 min, the mass gain increased at a constant low rate [92]. Electrochemical measurements by Ardelean et al. showed that a 24 h coated Mg alloy in a Ce–Zr–Nb solution exhibited reduced $i_{corr}$, and increased $R_p$ than a 3 h coated sample. For shorter deposition time (from 0.5 to 3 h), no ennoblement of $E_{corr}$ was observed, $i_{corr}$ was moderately low, and $R_p$ was slightly higher than the bare alloy. By increasing the deposition time from 3 to 5 h, the $E_{corr}$ and $R_p$ increased, and the $i_{corr}$ decreased considerably. Between 5 and 24 h of deposition, the upsurge of $R_p$, and the decline of $i_{corr}$ were remarkable. $i_{corr}$ of bare, 1, 5 and 24 h treated samples were 626, 139, 55 and 13 μA cm$^{-2}$ respectively. Accelerated atmospheric corrosion tests in humid (85% relative humidity) SO$_2$ (0.5 ppm) environment for 15 and 30 days showed excellent corrosion resistance for the Ce–Zr–Nb coated alloy [82].

In situ spectroscopic ellipsometry was used to investigate the initial regime of RECC formation on AZ31 Mg alloy by Li et al. Deconvoluted ellipsometric data displayed a 15.80 nm thick native oxide/hydroxide film on the as-polished alloy. The formation kinetics of the three RECCs (Ce, La and Sm) showed different exponential functions, and that indicated that their properties and anti-corrosion performance are different. The optical properties of the surface film principally correlate with their density and porosity. The different optical properties of the investigated RECCs reveal that their density
and porosity are different. The study showed that La coating had the highest density and hence can provide the most consistent protection to the substrate, whereas the anti-corrosion performance of the Sm coating was speculated to be poor. The results confirmed that the proton reduction leads to interfacial pH upsurge and that cause the precipitation of RE hydroxide gel [108].

Lei et al. showed that the $E_{\text{corr}}$ of the bare, 1 min coated, and 5 min coated AZ31 alloys were $-1.55$, $-1.51$, and $-1.49$ V, respectively. The $E_{\text{corr}}$ shifted to more negative directions for 5 and 10 min coated samples. Despite the different $E_{\text{corr}}$, the shape of the cathodic curves remained the same, showing that the deposition time had a meager effect on the cathodic reaction. The best anti-corrosion properties were obtained for the 5 min-coated sample that unveiled the most negative oxidation current density, and that was one magnitude lower than the corresponding value recorded for the bare alloy. The EIS plot recorded for the bare alloy and the 1 min coated alloy showed two capacitive loops at high and middle-frequency ranges, followed by the presence of an inductive arc. However, the 5 and 10 min coated samples exhibited only the capacitive loops, and no inductive arc was appeared [84]. Chen et al. showed that with an increase of immersion time, the $i_{\text{corr}}$ rises firstly and then falls, as in the acidic deposition bath (pH 5), the Mg surface oxide film dissolves off along with the RE film formation. With the extension of deposition time, the native oxide film is progressively substituted by the Ce and La oxide/hydroxide [98].

These studies showed that an optimum deposition time is essential for achieving the best corrosion resistance properties, and that varies with case to case. With low deposition time, thin films with less surface cracks forms. As the deposition time exceeds a threshold limit, formation of thicker coating with apparent higher surface cracks results. The coating adherence also decreases with longer immersion due to the continuous interface reactions causing substrate/coating dissolution in the acidic environment. RECCs fabricated at optimized experimental conditions can provide excellent short-term corrosion resistance for Mg alloys in aggressive electrolytes.

2.1.4. Co-additives to Ce bath

The RECCs suffers from disadvantages such as poor adhesion, lack of self-healing ability, and inability to provide long-term corrosion protection, and hence, further modifications are desired. Different co-additives (accelerator, pH adjuster) and co-conversion agents (organic and inorganic) are investigated in this direction (Table 1).

2.1.4.1. Inorganic additives.

a) $\text{H}_2\text{O}_2$

One primary concern with the RECC was the slow reaction rate [65,117,118] and that can be overcome by adding an appropriate amount of $\text{H}_2\text{O}_2$ into the deposition bath [83]. The accelerating effect of $\text{H}_2\text{O}_2$ to the coating formation was associated with its rapid reduction at cathodic sites generating $\text{OH}^-$ ions [55,71,121]. $\text{H}_2\text{O}_2$ addition causes oxidation of $\text{Ce(III)}$ to $\text{Ce(IV)}$. $\text{H}_2\text{O}_2$ can readily substitute one or more of water of hydration forming $\text{Ce}$ peroxo species. It also enhances the oxidation and dissolution of $\text{Mg}$ substrate [25,72,75,82,87,119,120]. Studies showed that the presence of $\text{H}_2\text{O}_2$ increased the coating deposition rate, and inhibited the formation of dehydration cracks; however, induced blister formation [87,122]. Presence of excess of $\text{H}_2\text{O}_2$ is detrimental to the corrosion resistance [71].

The presence of $\text{H}_2\text{O}_2$ distinctly affects the morphology and crack density of the coating [87,123]. Maddela et al. have shown that Ce coated AZ91D alloy without $\text{H}_2\text{O}_2$ (Fig. 5a) had wide, continuous surface cracks when compared to the corresponding coating in the presence of $\text{H}_2\text{O}_2$ (Fig. 5b-d). The crack density and crack size decreased with increasing $\text{H}_2\text{O}_2$ concentration, and that was attributed to a uniform distribution of the nanocrystalline Ce oxide particles in the coating. The study suggested that in the absence of $\text{H}_2\text{O}_2$, Ce solution reacted with the Mg surface resulting in building up of an Mg oxide layer more than the Ce oxide/hydroxide precipitation. The inset figure clearly shows that $\text{H}_2\text{O}_2$, in effect enhanced the coating formation (Fig. 5). Mg alloy panels coated with 4 and 8 vol.% of $\text{H}_2\text{O}_2$ performed the best in the salt spray test. Samples coated with 4 vol.% $\text{H}_2\text{O}_2$ had the highest impedance ($\sim 12,000 \, \Omega \cdot \text{cm}^2$), whereas the impedance of 0 vol.% $\text{H}_2\text{O}_2$ was $\sim 3000 \, \Omega \cdot \text{cm}^2$ only [123]. Lin et al. reported that upon addition of $\text{H}_2\text{O}_2$ to the conversion solution, a compact layer was formed instead of the fibrous major overlay. After 1 min of CeCC (without $\text{H}_2\text{O}_2$ addition), the sample surface presented a light grey color and, that progressively changed to dark grey; while, a sample treated in $\text{H}_2\text{O}_2$ containing bath revealed a pale yellow color during the early period of immersion and that gets intensified with continued immersion. The major overlay of the coating formed in the Ce only solution was fibrous $\text{Ce(III)}$ hydroxide/oxide, whereas that developed in the solution comprising $\text{H}_2\text{O}_2$ was compact $\text{Ce(IV)}$ hydroxide/oxide. The coating formed with $\text{H}_2\text{O}_2$ added Ce bath provided better corrosion resistance to the underlying Mg alloy [87].

- Phosphates and Permanganates

Some reports are available where phosphates and permanganates were used as co-conversion agents in RE conversion bath. Rocca et al. employed a Ce-phosphate-permanganate conversion treatment on AZ91 alloy as a green alternative to traditional chromating. Electrochemical measurements showed mixed-type protection due to the inhibition of both cathodic and anodic reactions, persuading a negative $E_{\text{corr}}$ shift with the appearance of an effective anodic passivation region. Their non-electrochemical tests (by weight loss methods) viz. climatic chamber (for 28 days), immersion test (for 10 days) and salt spray (for 96 h) respectively revealed corrosion rates of 0.0037, 0.067, and 0.76 mmpy for the Ce-coated alloy. The corresponding values of Ce-phosphate-permanganate coated alloy were 0.0029, 0.055, and 0.19 mmpy. The corrosion rates calculated for the bare alloy under the same experimental conditions were 0.0066, 0.083, and 1.01 mmpy, respectively [75].

Saeia et al. reported a series of CeCCs comprising $\text{Mn(NO}_3)_2\cdot 4\text{H}_2\text{O}$, $\text{Co(NO}_3)_2\cdot 6\text{H}_2\text{O}$, and polyvinyl alcohol (PVA). The results showed that a thicker film with low crack density
formed in the Ce-Mn-PVA solution. The film displayed a mixed type of corrosion inhibition by affecting both hydrogen evolution and anodic dissolution reactions. Studies on several binary compositions showed that the Mn\(^{2+}\) cations enhanced the corrosion protection, whereas the Co\(^{2+}\) adversely affected the Ce film formation. EIS studies showed that the low-frequency impedance of the coated alloy was significantly improved. An inductive behaviour indicative of localized attack was presented in the Nyquist plot of the uncoated alloy whereas the Ce-Mn-PVA coated alloy did not show an inductive behaviour even after 1 h of immersion in 3.5 wt.% NaCl. EDS results showed that Mn\(^{2+}\) addition to the Ce bath was beneficial to enrich the Ce content in the film (Ce content increased from 0.8 to 1.4 wt.%). The Mn content was 39 wt.%. When PVA was used alone, the Ce precipitation rate declined, whereas the synergistic mixture of Mn\(^{2+}\) and PVA significantly increased the Ce content in the film (4.9 wt.%). Presence of PVA also augmented the Mn\(^{2+}\) content to 61.4 wt.%. XPS analysis indicated that the Ce-Mn-PVA coating was comprised of CeO\(_2\) and Ce\(_2\)O\(_3\). The co-additives significantly affected the film wetting behavior; the order of contact angle obtained for the samples was Ce < Ce-PVA < Ce-Mn-PVA < Ce-Mn [124]. Zheng and Liang showed that an amorphous red-brown conversion coating completely covered the sample surface after 3 min of immersion in a permanganate-RE bath. XPS analysis suggested that the main coating components were CeO\(_2\), MnO, MnO\(_2\), MgO, Mg(OH)\(_2\), and MgAl\(_2\)O\(_4\). Potentiodynamic polarization studies showed improved corrosion resistance for the composite coated alloy, and that was even better than an analogous chromate conversion coating. The open circuit potential (OCP) of the uncoated, chromate coated and permanganate-RE coated samples were −1.58, −1.34 and −1.28 V vs. SCE, respectively [125].

Zhou et al. reported a nano-CeO\(_2\)/phosphate composite conversion coating. The resultant coating had fewer mud-cracks and pores and was comprised of Zn\(_2\)(PO\(_4\))\(_2\)-4H\(_2\)O, Zn\(_2\)Mg(PO\(_4\))\(_2\) and CeO\(_2\). The Ce content in the composite coating fabricated from 1 and 2 g L\(^{-1}\) nano-CeO\(_2\) containing bath were 0.58 and 0.83 wt.%, respectively. The adhesive force and micro-hardness of Ce-P coating were higher than those of single phosphate (P) coating. The coating resistance (R\(_c\)) of the composite coating as derived from EIS plots were at the range of 745 to 2430 kΩ cm\(^2\), whereas the corresponding value of the P coating was 561.74 kΩ cm\(^2\). The coated sample treated in 2 g L\(^{-1}\) nano-CeO\(_2\) bath presented the lowermost i\(_{corr}\) value of 0.41 μA cm\(^{-2}\) (i\(_{corr}\) of the bare sample was 8.38 μA cm\(^{-2}\)). STM topographies revealed that the maximum height of P and Ce/P coatings were 72.80 and 33.41 nm respectively, and that indicated a smoother surface with the later (Fig. 6). The improved corrosion resistance was attributed to the synergistic effect of nano-CeO\(_2\) particles on the grain refinement, dispersion strengthening and defect blocking [126].

Zinc calcium phosphate (Zn-Ca-P) and Ce-doped zinc calcium phosphate (Zn-Ca-Ce-P) coatings were prepared on AZ31 Mg alloy by Zheng et al. The results indicated that both the coatings primarily contained crystalline Zn\(_3\)(PO\(_4\))\(_2\)-4H\(_2\)O, Mg\(_3\)(PO\(_4\))\(_2\) and Ca\(_3\)(PO\(_4\))\(_2\), and traces of non-crystalline MgF\(_2\) and CaF\(_2\). The Zn-Ca-Ce-P coating was more compact than the Zn-Ca-P coating attributed to the formation of CePO\(_4\). The quaternary coating displayed improved corrosion resistance than the ternary coating. Here, CePO\(_4\) precipitate formation is preferred as its solubility product constant (K\(_{sp}\) = 2 × 10\(^{-48}\)) is inferior to that of Ca\(_3\)(PO\(_4\))\(_2\) (K\(_{sp}\) = 2 × 10\(^{-29}\)). No thorough cracks were found on the quaternary coating, suggesting that the incorporation of Ce\(^{3+}\) ions promoted the film homogeneity. Hydrogen evolution studies showed that the corrosion initiation of the quaternary-coated alloy was significantly delayed [127]. Zeng et al. patented a phosphating solution comprising of disodium hydrogen phosphate 10–30 g, zinc nitrate 4–6 g, sodium nitrite 2–4 g, sodium fluoride 0.5–2 g, calcium nitrate 0.5–2 g, and cerium nitrate 0.5–2 g (solution pH 2–3) [128].

- Molybdates, Vanadates

Hamdy et al. recognized that vanadium (V) conversion coatings have a definite self-healing capability, although its barrier protection was poor [129–131]. A few works reported Ce-V conversion coatings for Mg alloys [132,133].

Fig. 5 – SEM micrographs of Ce-coated AZ91D alloy with different concentrations of H\(_2\)O\(_2\): (a) 0, (b) 2, (c) 4, and (d) 8 vol.%. EIS spectra of Ce-coated alloys in 1.6 wt.% NaCl with different concentrations of H\(_2\)O\(_2\). The optical images corresponding to the SEM images are also provided in the inset [123].
Fig. 6 – EIS and polarisation plots of single-phosphated (P) and composite-coated (Ce-P) samples in borate buffer solution. SEM images of (a) P and, (b–d) Ce-P coatings formed in (b) 1, (c) 2, and (d) 4 g·L⁻¹ nano-CeO₂ bath. STM topographies of (a) P and (b) Ce-P coatings formed in 2 g·L⁻¹ nano-CeO₂ bath [126].

Fig. 7 – Surface morphology of the conversion coatings obtained in the vanadate solution (19.7 mM) with addition of (a) 0, (b) 4.61 and, (c) 23 mM Ce solution. Nyquist plots of (left) uncoated AZ31 alloy and (right) Ce–V conversion coated alloy in 3.5 wt.% NaCl [133].
Jiang et al. assessed the self-healing behaviour of the Ce–V coating on AZ31 alloy, and revealed that Ce addition was beneficial to prevent the reduction of V⁵⁺ to V⁴⁺ during the deposition process. Ce salt addition to vanadate solution led to a thicker and compact CeVO₄ coating formation with fewer surface cracks (Fig. 7). The release and migration of V ions provided a certain extent of self-healing effect. When the Ce concentration in the bath varied from 0 to 23 mM, two capacitive loops (at high and medium frequencies) were observed in the EIS plots of the coated alloy. At still higher Ce concentrations (46.1 mM), the Nyquist plots showed an additional inductive loop at low frequencies. The diameter of the high-frequency arc showed a regular increase with the increase of Ce concentration from 0 to 9.21 mM, and thereafter a decline from 9.21 to 46.1 mM (Fig. 7). Conversely, Nyquist plot of bare alloy showed one capacitive loop with the typical inductive behavior (Fig. 7) attributed to the severe localized corrosion and the relaxation of adsorbed species. The best conversion coating (with yellow metallic luster) was obtained with the sample treated in 9.21 mM Ce bath [134]. In a related publication, the authors showed that the Ce–V conversion coating principally consisted of Ce₂O₃/Ce(OH)₄, CeO₂/ Ce(OH)₄, and V₂O₅/V(OH)₅. The composite coating displayed better corrosion resistance properties than an equivalent chromate conversion coating. The \( \Delta E_{corr} \) values calculated for the composite and chromate-coated alloys were 1.245 and 6.13 μA cm⁻², respectively. It is suggested that V hydroxides form at the beginning as soon as the interfacial pH changed with the subsequent precipitation of Ce hydroxides. Thus, the coating was an inner layer made of V oxides/hydroxides and an exterior layer composed of V and Ce oxides/hydroxides [132]. Lee et al. compared CeCC with an alkaline stannate conversion coating [134].

An effective Mo–Ce conversion coating was fabricated on AZ91 Mg alloy by Mu et al. The conversion coating was mostly amorphous and comprised of MoO₃, MoO₂, CeO₂, Ce₂O₃, MgO and Mg(OH)₂. The bare alloy showed no passivation region in the polarisation plots and got dissolved with a current density of 10 μA cm⁻² at −1.4 V vs. SCE. A distinct passivation plateau was observed for the coated alloys; notably, a 10 min-coated sample exhibited an extended passive region from −1.35 to −0.85 V, with a smaller current density. The OCP of the bare alloy decreased from −1.604 to −1.692 V at the initial periods and stabilized at −1.526 V whereas the OCP of the coated alloy quickly shifted from −1.604 V to a stable value of −1.402 V [113]. Du et al. patented a treatment liquid for preparing a Mo–Ce composite conversion coating that consisted of molybdate (sodium molybdate/ammonium molybdate) 2–15, RE salt (Ce nitrate/ammonium ceric nitrate) 4–20, organic acid (citric acid/tetraboric acid) 0.1–2.5, activator (disodium ethylene diamine tetraacetate) 0.1–2 g L⁻¹ and a pH regulator (nitric acid to adjust bath pH to 2–3). The method includes the alkali pre-treatment for 2–6 min and then soaking in the conversion liquid at 20–35 °C for 3–20 min. The alkali solution contained sodium hydroxide 10–15, sodium phosphate 35–45, sodium silicate 13–18, and sodium carbonate 10–15 g L⁻¹ [135].

- Others

Studies showed that adding aluminium nitrate to RE conversion bath enhances the surface passivity of Mg alloys and help to form a stable film with amplified adhesion intensity [115]. Wang et al. have investigated the effect of Ce concentration on the surface morphology and corrosion resistance of Al-based conversion coatings. A film formed with 0.005 mol L⁻¹ Ce was dense with narrow micro-cracks. The coating was consisted of Al(OH)₃, Al₂O₃, Mg(OH)₂, MgO, CeO₂ and Ce₂O₃. However, with higher Ce concentrations (0.02 and 0.05 mol L⁻¹), the conversion coatings appeared to peel off, and wide micro-cracks appeared [136]. Salam et al. showed that addition of Ca(OH)₂ and Al(NO₃)₃ to Ce-bath enhanced the anticrosion property of the coated alloys significantly [92].

Ardelean et al. suggested that the addition of Zr and Nb compounds to Ce-bath is essential to further improve the corrosion resistance of Mg alloys [82]. Seizadíeh et al. reported that the best antircorrosion performance was obtained after a 60 min of deposition in a Ce–La–permanganate solution at room temperature [137]. Chen et al. showed that dual RE conversion film treated in the solution containing Ce and La salts was denser and more uniform than the corresponding film formed in individual solutions [98]. A Ce-La conversion coating reported by Yang et al. on Mg-8.5Li alloy was comprised of La₂O₃, Ce₂O₃, Mn₃O₇ and MnO₂ [74]. A black conversion coating containing trivalent chromium and >0.0010 g m⁻² RE metals was patented by Hidekazu et al. [138].

2.1.4.2. Organic co-additives. Conversion coatings based on organic compounds are an attractive approach for Mg alloys [22]. REs can form a number of chemical compounds with various organic ligands [25]. The following section describes organic co-additives investigated in CeCCs.

- Silanes

Some works employed organic silanes to improve the properties of CeCCs [139,140]. The cross-linking property of silane molecules can considerably diminish the coating porosity and improves the coating adhesion, and hence, the modified surface can act as an effective barrier layer to aggressive species [141].

Lei et al. showed that addition of bis-[triethoxysilylpropyl] tetrasulphide (BTESPT) to the Ce conversion bath was effective in fabricating a more compact and homogenous barrier film. The non-modified film displayed numerous surface cracks (average crack width 0.1–0.5 μm) with the typical dry-mud morphology. A large number of white globular Ce-enriched particles were also seen. A high magnification image (Fig. 8a) revealed a loosen and porous coating, with a honeycomb-like morphology. The silane-modified coating reduced the extent of surface cracking (Fig. 8b) and crack widths (>0.1 μm) considerably. Higher magnification images (not shown) displayed a pretty homogeneous and dense surface with much-reduced particles. The Si–OH groups can establish hydrogen bonds with Ce–OH or Mg–OH (on the native metallic surface) groups, forming Si–O–Mg bonds. The cross-linked structure formed by Si–O–Si bonds can further help in the orderly deposition of Ce nodules, and that can improve the coating morphology. The water contact angle of the Ce-coated and the silane-modified coatings were estimated to be 55 and 115°, respectively, demonstrating the formation of a superhydrophobic surface. Fig. 8 also shows the results of the standard
cross-cut tape test where the silane-modified coating displayed excellent adhesion with no squares being peeled away. The surface cracks on CeCC severely affected its adherence. The study suggested that the generation of Si-O-Mg covalent bonds, in fact, occurred at the metal/solution interface. The $E_{corr}$ of the CeCC and the silane-modified coatings were $-1.487$ and $-1.352\ V$, respectively, while the corresponding $i_{corr}$ value were $6.966 \times 10^{-8}$ and $1.476 \times 10^{-6}\ \text{A}\cdot\text{cm}^{-2}$. The silane-modified coating exhibited a greater capacitive arc in Nyquist plot indicative of higher corrosion resistance [139]. Authors in a subsequent work showed that the modified coating retained higher $R_p$ values even after immersion for 72 h in 0.05 M NaCl solution [140].

- **Gelatin**

This natural polymer is a desired co-additive, mainly to improve the coating adhesion. Arthanari et al. investigated the effect of gelatin addition on the CeCC. An apparent make-over in the surface morphology and crack density were noticed with varying gelatin content in the conversion bath. At low gelatin concentration (1 g L$^{-1}$), the coating was comprised of particulate morphologies with numerous crisscrossed cracks. The crack density significantly decreased when the gelatin content increased to 3 or 5 g L$^{-1}$. XRD and Raman spectroscopy results showed that the coating mostly comprised of nano-crystalline CeO$_2$. The corrosion resistance of the coated alloy showed a regular increment with the increase of gel content. However, prolonging the coating duration had a negative impact. The composite coated alloy exhibited 5 times enhancement in the $R_p$ when compared to the uncoated alloy [116].

Song et al. prepared gelatin-chitosan microcapsules by complex coacervation method using glutaraldehyde as a cross-linking agent. The microcapsules solutions were prepared by mixing of 40 g L$^{-1}$ La(NO$_3$)$_3$ or Ce(NO$_3$)$_3$, 25 g L$^{-1}$ gelatin and 25 g L$^{-1}$ chitosan (at 50°C, pH 4). The obtained solution was mixed for 2–4 h with a magnetic stirrer. A 25 g L$^{-1}$ Ce(NO$_3$)$_3$ was prepared as the passivation solution and 10 mL L$^{-1}$ of H$_2$O$_2$ was used as the accelerant. The microcapsules containing La or Ce salt-coated alloys showed excellent corrosion resistance with improved self-healing ability during a 4 h of immersion in 3.5% NaCl. The self-healing action of the conversion coating was suggested to be similar to the on-demand release smart coatings. The coating impedance obtained for the Ce and La microcapsules-incorporated coating were 1.3 and 2.0 kΩ cm$^{-2}$, respectively, while the corresponding value of the CeCC without microcapsules was 0.8 kΩ cm$^{-2}$. The $i_{corr}$ and $E_{corr}$ values of the conversion coating without microcapsules were $1.094 \times 10^{-4}\ \text{A}\cdot\text{cm}^{-2}$ and $-1.484\ V$, respectively, while the corresponding values of Ce microcapsules-coated (3.466 $\times 10^{-6}\ \text{A}\cdot\text{cm}^{-2}$ and $-1.348\ V$) and La microcapsules-coated (8.813 $\times 10^{-9}\ \text{A}\cdot\text{cm}^{-2}$ and $-1.249\ V$) samples were much nobler [142].

- **Phytic acid**

The peculiar structure of phytic acid (C$_{20}$H$_{12}$O$_{14}$P$_6$) with twenty four O atoms, twelve $\text{–OH}$ groups and six phosphate carboxyl groups gives it a potent chelating ability with many metal ions [22,143]. Gao et al. reported an innovative eco-friendly Ce-phytic acid (Ce-PA) coating on AZ31B Mg alloy. Firstly, the PA conversion coating was fabricated and that was followed by the CeCC. The processing parameters for the
CeCC were optimized to be: 0.06 mol·L⁻¹ Ce nitrate, 30 min and 50 °C. XPS analysis suggested the existence of P–OH, HPO₄²⁻, PO₄³⁻, Ce₂ and a little Ce(OH)₂ in the composite coating. The Ce-PA-coated sample had the best corrosion resistance, and that was higher than that of an analogous chromate conversion-coated sample. The measured i_corr of the PA-coated (in 4 g L⁻¹ PA; pH 2; 40 °C; 40 min) and chromate-coated (in 200 g L⁻¹ K₂Cr₂O₇ + 180 mL L⁻¹ HNO₃; 28.5 °C, 10 min.) samples were 3.60 and 6.13 μA·cm⁻², respectively. The total volume of hydrogen evolved (after 12 h) for the bare, chromate-coated, PA-coated and Ce-PA-coated samples were 22, 310, 5821, 5470 and 3120 mL·m⁻², in that order [144].

- Others

It has been shown that the addition of surfactants such as sodium dodecyl benzene sulfonate resulted in a notable enhancement in the coating compactness, and that was helpful to reduce the time of deposition. The additive enhanced the Ce content in the film from 18.92 to 25.08 wt.% The i_corr of the bare alloy, and the coated alloys in Ce(SO₄)₂ + H₂O₂, Ce(SO₄)₂ + H₂O₂ + Ni(NO₃)₂, and Ce(SO₄)₂ + H₂O₂ + sodium dodecyl benzene sulfonate were 56.2 × 10⁻⁵, 7.41 × 10⁻⁵, 4.05 × 10⁻⁵ and 2.20 × 10⁻⁵ A·cm⁻², respectively [90]. The additive enhanced the deposition and the growth of Ce hydroxides particles resulting in a smooth and compact film [98]. More details are provided in Table 1.

2.1.5. Pre- and post-treatment

2.1.5.1. Pre-treatments. Studies revealed that the best conversion coatings resulted when Mg samples were subjected to polishing/grinding, acid cleaning, and alkaline cleaning processes [34,71,112,145]. These pre-treatements are useful to reduce the number of active cathodic sites and promote the formation of a more protective surface film [85].

The corrosion resistance enhancement through polishing/grinding is mainly associated with the reduction in the surface contaminants and hence the active cathodic sites. The potential formation of a homogeneous and thin surface oxide layer after the grinding also contributes to the improvement [85,111,146]. Acid cleaning has been used conventionally as a surface activation method that removes contaminants and the natural oxide layer. In the case of Mg-Al alloys, the acid treatment can produce an Al-rich oxide/hydroxide surface layer [85,147]. The enhancement in corrosion resistance due to the acid pre-treatment is primarily attributed to the development of a thicker, more homogeneous, and adherent surface film [85,120]. Most of the reported studies employed an alkaline treatment after acid treatment. Alkaline treatment is used to remove the residual impurities and to dissolve the second phases of Al, and can produce a hydroxide rich, porous surface layer. This passive layer is protective and can enhance adhesion of a subsequent conversion coating. The increase in surface area due to the alkaline treatment is also beneficial for better adhesion and corrosion resistance [85,148].

Brunelli et al. showed that the acid pre-treatment was helpful to produce a thicker (with higher amounts of Ce) and more homogeneous CeCC. SEM images revealed homogeneous surface dissemination of the Ce oxide agglomerates with dry-mud morphology (Fig. 9b). The amount of Ce in the acid pre-treated-Ce coated sample was almost two-fold when compared to the Ce-coated sample without pre-treatment. Interestingly, a passivation behavior was observed in the anodic branches of the polarisation curves of the acid pre-treated-Ce-coated sample (Fig. 9). The improved corrosion resistance was also ascribed to the occurrence of Al oxides/hydroxides in the film.

Fig. 9 – Microstructure of AZ91 alloy after (a) HCl pre-treatment, and (b) HCl pre-treatment followed by CeCC. (c, d) SEM images of the conversion coated alloy after five days of immersion in chloride media (c) without acid pre-treatment and, (d) with acid pre-treatment. Nyquist and polarisation plots of differently coated alloys are also provided [145].
The Nyquist plots exhibited two capacitive loops typical to the coated alloys indicating good corrosion resistance properties for the pre-treated alloy (Fig. 9). Surface images after five days of immersion in chloride solution showed distinct differences. The uncoated sample showed apparent localized corrosion with pits with diameters of 3 mm while the acid pre-treated-Ce-coated sample appeared unaffected (Fig. 9c,d). A Ce-coated sample without acid pre-treatment showed partial coating dissolution [145].

Lee et al. showed that for the AZ91D pre-treated in 0.5 wt.% HF solution, the β phases were preferentially attacked whereas, for an HCl-pre-treated alloy, the dissolution happened mainly at the α grains. When a vanadate solution was used for the pre-treatment, the dissolution initiated at the center of primary α grains. The results of the study showed that the pre-treatment significantly affected the coating morphology. The CeCC on the as-polished alloy displayed a high population density of blisters with deficient adhesion and inadequate corrosion protection. On the other hand, the 0.5 wt.% HF-pre-treated-Ce-coated alloy showed only a lesser extent of blistering even though the cracking was still predominant. The blisters were not seen on a 11 wt.% HF-pre-treated-Ce-coated alloy. In the case of HCl-pre-treated alloy, the Ce precipitation happened mostly at the α grains. A nearly complete Ce layer sprinkled with fine particles with very less extent of blister formation was formed on the vanadate pre-treated-Ce-coated alloy. The pretreatment, however, not affected the bilayered coating structure as revealed by TEM images [149]. Su et al. showed that a short (20 s) HF or HCl pre-treatment boosted the adhesion and the corrosion resistance of CeCC on AZ31 alloy and that was mainly ascribed to the reduced alloy dissolution via the corrosion film formed during the acid pre-treatment. The acid treatment markedly reduced the average size and population density of blisters, signifying an elevation in the breakdown potential. The corrosion film formed on HF-treated alloy was thinner than that formed on HCl-treated alloy. The CeCC on the HCl-pickled alloy comprised of two layers, i.e., an interior porous layer (0.4 μm thick, mainly composed of Mg/Al oxides/hydroxides) and a compact outer Ce oxide layer whereas a three-layered structure was observed for the Ce coating on the HF-pickled alloy (an inner fluoride layer, F-containing oxide/hydroxide middle layer, and a thin Ce oxide exterior layer) [120].

2.1.5.2. Post-treatments. A suitable post-treatment can significantly augment the surface morphology and corrosion resistance of CeCCs. Post-treatments are generally employed as a sealing step to improve corrosion resistance. Most frequently employed sealing steps include phosphate-based and silicate-based. Table 1 listed the different post-treatments strategies reported. Many works employed a post-heat treatment.

Phosphate post-treatment has been employed commonly [25,33,150,151]. The treatment is expected to produce insoluble CePO₄ on the surface, and that can deliver added corrosion protection. Wang et al. employed a post-treatment in 3 wt.% Na₃PO₄ solution. XPS analysis revealed that the post-treated CeCC has consisted of CeO₂, Ce₂O₃, CePO₄, Al₂O₃, Mg₃(PO₄)₂ and MgO. The average weight loss (after 7 days in 3.5 wt.% NaCl) obtained for the uncoated, Ce-coated and Ce-coated-phosphate post-treated AZ91D alloys were 0.60, 0.42 and 0.30 mg cm⁻² d⁻¹, respectively [33]. Castano et al. have shown that a phosphate post-treatment, a dense and homogenous coating with fewer surface cracks with a nodular morphology resulted (Fig. 4b). The post-treatment augmented the Ce(III) content in the film from 37 to 47 at.%(Fig. 4) whereas the Ce(IV) content reduced to 53 from 63 at.%(Fig. 4). The post-treated sample was mainly composed of CeO₂/CePO₄·H₂O nanocrystals embedded in an amorphous matrix. Fig. 4 also shows the Nyquist plots of Mg alloy after grinding (step I), CeCC (step IV), and phosphate post-treatment (step V) in 0.05 M NaCl and the results indicated a four-fold enhancement in corrosion resistance for the post-treated alloy. At low frequencies, Ce-coated alloy exhibited a small inductive loop indicative of diffusion of aggressive species through coating defects, and that was absent in the post-treated alloy [85].

Salman et al. fabricated a silane self-assembled monolayer (SAM) on the surface of CeCC by using (tridecafluoro-1, 1, 2, 2-tetrahydrooctyl) trimethoxysilane and tetrakis (trimethyl-siloxy) titanium (catalyst) by a vapor phase method. Contact angle measurements displayed that the hydrophilicity of Mg alloy (contact angle - 49°) increased after CeCC (contact angle - 13°). However, after SAM formation, the wettability was remarkably reduced with a relative contact angle of 169° generating a superhydrophobic surface. Theoretical and electrochemical studies showed that the corrosion resistance of the Ce-coated alloy significantly improved after SAM formation [93].

Han et al. patented a post-sealing method that comprises immersing the conversion-coated sample in an oxidized graphene suspension solution for 20–30 min and drying at 30–60 °C for 1–3 h. The post-treatment enhanced the compactness and surface coverage of the RECC and considerably improved the corrosion resistance [152]. Chen et al. investigated an eco-friendly sol-gel CeO₂ coating on CeCC [114].

A few studies employed CeCC as a post-modification strategy on plasma electrolytic oxidation (PEO) coating [91,153]. Lim et al. showed that the surface of an as-formed porous PEO coating on AZ31 Mg alloy was transformed into a non-porous compact coating by a post-CeCC. It was presumed that dissolution of PEO coating happened during the conversion process with subsequent precipitation of Ce oxides/hydroxides on the surface of the remaining PEO coating. The pores and defects of PEO coating were efficiently wrapped by the CeCC, and the resultant composite coating acted as an excellent barrier layer [153]. Hariprasad et al. employed two types of duplex coatings on pre-treated biodegradable AZ31 Mg alloy; namely, CeCC followed by PEO coating (CPE) and PEO followed by CeCC (PEC). The surface morphology of PEO and CPE samples unveiled pores typical of PEO coatings. The CPE sample always showed a more uniform surface with smaller and fewer pores. PEC sample displayed the typical morphology of CeCCs. The thickness of the samples was found to be 1.5, 30, 35, and 30.6 μm for CeCC, PEO, CPE and PEC samples, respectively. The CPE coating showed the best corrosion and scratch resistance, and that was credited to its higher coating thickness and less surface porosity. The icorr of CeCC, PEO, CPE and PEC coatings were 83, 0.34, 0.18 and 0.0012 μA·cm⁻², respectively. The measured contact angles for bare, CeCC, PEO, CPE and PEC samples were 54, 110, 9, 7 and 120° in that order [91].
2.2. Lanthanum conversion coatings

La is the second largest compound investigated for RECCs [68,154,155]. LaCC mainly consists of La(OH)3 with small amounts of Mg hydroxides [73]. The film growth follows a similar mechanism to that of Ce.

Rudd et al. showed that treatment of pure Mg or Mg alloys in La-containing solutions has led to a significant upsurge in the corrosion resistance. The La-coated sample exhibited a three-time higher Rp after a 10 h of immersion in pH 8.5 buffer solution; even though the coating failed to provide long-term corrosion protection [68]. Montemor et al. showed that a Ce-coated sample displayed only a marginally nobler potential than a corresponding La-coated sample. For the former, the OCP rose from −1.70 V vs. SCE and steadied at −1.35 V after 4000 s of immersion in 0.005 M NaCl whereas for the latter, the corresponding values were −1.60 and −1.30 V. Scanning vibrating electrode technique (SVET) maps showed practically null activity for a 60 min La-coated sample [73]. Yang et al. showed that the corrosion resistance of Mg-6Li alloy could be upgraded through LaCC. Ecorr of the La-coated sample displayed 0.28 V positive shift to that of the bare alloy. The La-coated sample displayed wide passivation region with a significantly reduced lcorr [156].

In recent times, microwave (MW) synthesis strategies have attracted much research attention due to its key advantages such as fast heating rate, reduced processing time, energy saving, and eco-friendliness [157,158]. This technique is helpful to synthesize highly pure nanoscale particles with homogeneous distribution [159]. A few reports employed MW strategy for LaCC [160,161]. In a typical method, the Mg samples were placed in a glass vessel to which La salt solution (10 mL) slowly added. The reaction vessel was located in an atmospheric pressure MW synthesis system. Song et al. showed that LaCC with MW heating resulted in the formation of a greater extent of intermetallic compounds of La (Al2La9.15Mg8.85, La9Al24O39.6, and LiLaO2) on Mg-Li alloy. MW heating was beneficial for the crystallization of the constituents, and that in turn increased the corrosion resistance. Cross-cut tape tests showed that the coating deposited by the MW-assisted approach was more compact and uniform than that achieved at room temperature. The lcorr (Ecorr) of bare, room temperature La-coated, and MW-assisted La-coated alloys were 1.87 × 10−4 (−1.57), 3.58 × 10−6 (−1.56) and 1.95 × 10−6 A·cm−2 (−1.54 Vs), respectively. The corresponding Rp values were 143, 1570, and 6830 Ω·cm2. An inductive loop was not presented in the MW treated sample [161].

A few studies investigated composite conversion coatings based on La such as Mg-La [162], Mn-La [137,163] and Mo-La [164]. Takenake et al. showed that the corrosion resistance of Mg alloys improved considerably when the conversion bath contained both Mg and La salts [162,165]. An island-like structure was observed by SEM. XPS detected Mg, Al, O and La in the film. XRD does not show any crystalline peaks corresponding to Mg or La oxides. The uncoated alloy suffered severe corrosion after a 10 h of immersion in 5% NaCl, whereas the surface of the coated alloy exhibited a lower extent of corrosion [162]. Seifzadeh and Farhoudi replaced traditional HF pretreatment (before Co-P electroless coating) with a Ce-La-permanganate conversion coating, and a 60 min coated alloy showed enhanced corrosion resistance [137,163]. Yang et al. reported a Mo-La-based composite conversion coating comprised of globular nodules [164]. The Ecors of the coated alloy shifted positively by 0.50 V, and the lcorr decreased by two orders of magnitude when compared to bare alloy [164].

La solutions were used for post-treatment of PEO-coated AZ91 alloy. The sealing treatment was performed in 12 g·L−1 of La salt solution at pH 4. The study optimized 50°C and 30 min as the best bath parameters. The better corrosion resistance of the post-treated PEO samples was accredited to the realization of a homogeneous sealing layer, composed of La(OH)3. The lcorr of the bare, PEO and the sealed PEO coatings were 2.0 × 10−6, 1.5 × 10−6 and 2.8 × 10−7 A·cm−2, respectively [166].

2.3. Yttrium conversion coatings

A few works employed Y-based conversion coatings (YCC) for Mg alloys [167–169]. The mechanism of YCC was similar to that of other RECCs. Han et al. presented that Y deposition initiated (within 10–30 s) at the sites of eroding pits. As the immersion time increased to 5 min, spherical particles were deposited, and as the time prolonged to 20 min, a uniform conversion coating resulted. The coating was predominantly made of Y2O3, YO2, Al2O3 and MgO. A simple SiO2 sol-gel overcoating was carried to heal the surface cracks and coating defects. Electrochemical studies showed that the Ecors of the Y-coated alloy shifted positively about 0.23 V, and the lcorr diminished by two orders of magnitude. The Ecors of the bare, Y-coated, and SiO2−treated-Y-coated alloys were −1.60, −1.46 and −1.37 V, respectively. The corresponding lcorr values were 7.02 × 10−6, 5.88 × 10−6 and 5.82 × 10−7 A·cm−2 [168].

The authors in an earlier work showed that a phosphate post-treatment could reduce the number and size of the cracks in the YCC. The phosphate-treated-Y-coating was mainly composed of Y2O3, YO2, Mg3(PO4)2, AlPO4 and YPO4. The hydrogen evolution kinetics of Y-coated samples decreased significantly after the phosphate treatment [167]. A few patents are available where Y was used as a component in conversion baths [170,171].

2.4. Neodymium conversion coatings

Nd has been widely used as an alloying element for Mg alloys [165]. A few works are available on Nd-based conversion coatings (NCC) [165,172–176]. Jin et al. showed that NCC is made of Nd oxides and has a crack-mud structure. The at.% of Nd in the coating was 23.6. The coating was bilayered with a total thickness of 4–5 μm. The total impedance of the coated and the uncoated alloys as revealed by EIS were 4500, and 1300 Ω·cm2, respectively [172].

At initial deposition periods, a competition between the matrix dissolution process and the Nd/Mg oxide deposition happened and with the further increase of time, the Nd oxides deposition dominated. With prolonged time, a thick coating formed and that easily peels off from the matrix, leading to coating weight reduction. A fresh coating formed instantaneously on the exposed surface, accompanied by a weight gain [173,176].

Cui et al. showed that after a 20 min of deposition, a compact coating comprised of Nd oxides with a lesser amount
of Mg oxides/hydroxides formed on a Mg-Al alloy. The alloy exhibited an \( \alpha + \beta \) two-phase structure (Fig. 10a). The figure also shows the systematic variation of the crack-mud structure of the NCC as a function of the immersion time. After 2 s of conversion treatment, local areas of the sample surface found covered with a loose and uneven coating. With longer immersion time, thick coating with numerous surface cracks formed. EDS results have shown that at the initial stages (after 2 s), Mg (51.69 at.%) dominated in the coating with remaining Al (1.46%), O (39.83%) and Nd (7.02%). As the coating deposition time increased from 30 s to 5 min, the amount of Mg decreased gradually from 55.44 to 31.96 at.%, meanwhile, the content of O and Nd increased to 55.21 and 11.77 at.%, correspondingly. The at.% of Al reduced gradually from 9.11 to 1.06. After 10 min of deposition, the content of O and Nd increased rapidly, whereas %Mg showed a sharp decrease to 11.85. Here, a complete surface coverage happened, and hence, the elements in the matrix were not detectable. After that, the film composition remained almost the same (O 72.84, Mg 8.77 and Nd 18.73 at.%) (Fig. 10) [173]. The authors also investigated a PA post-treatment on NCC. The magnified image of the post-treated sample showed that there were many granulated particles deposited on the innermost compact coating layer and that filled the surface cracks and improved the corrosion resistance significantly (Fig. 10) [173]. Zhao et al. studied the role of an alumina-based sol-gel post-treatment on NCC [176].

Cui et al. reported a carboxylic acid-Nd anhydrous conversion film by using ethyl alcohol as the solvent and four types of carboxylic acids (citric acid, oxalic acid, tartaric acid and, PA) as activators. The conversion bath was composed of the carboxylic acid, Nd nitrate and \( \text{H}_2\text{O}_2 \). The results revealed the presence of \( \text{Nd}_2\text{O}_3 \), MgO, \( \text{Mg(OH)}_2 \), and the carboxylate of Nd in the film. Comparison of surface morphology showed that films formed in oxalic acid and PA were similar. Fewer cracks were presented on the film made in citric acid. The morphology of the film developed in solution added with tartaric acid was identical to that obtained for a pure NCC. Among all the cases studied, the one formed in PA showed the best corrosion resistance properties. The \( R_p \) of the bare, NCC, oxalic acid, tartaric acid, citric acid and PA added NCCs were 680, 2771, 3195, 2900, 4435 and 8480 \( \Omega \cdot \text{cm}^2 \), respectively [175].

2.5. Samarium conversion coatings

A few works on Sa-based conversion coatings are available [152,169,177]. Hou et al. reported that Sa conversion coating (SCC) had a crack-mud structure with small and thick cracks dispersed in the compact coating. The as-formed film was amorphous and comprised of \( \text{Sm}_2\text{O}_3 \), \( \text{Sm}_2(\text{C}_2\text{O}_4)_3 \), \( \text{Mg(OH)}_2 \) and \( \text{Al}_2\text{O}_3 \). An EDS spectrum revealed the presence of O (32.24), Mg (55.31), Al (3.09) and Sm (9.36 at.%) in the film. The coating thickness was 2–3 µm. EIS results showed that the total impedance of the coated and uncoated alloys were 2500 and 1300 \( \Omega \cdot \text{cm}^2 \), respectively [177].

Han et al. reported a sealing method by immersing SCC in an oxidized graphene suspension for 20–30 min [152].

2.6. Gadolinium conversion coatings

Gadolinium (Gd) and its oxides have many applications in MW technology, atomic energy industry, and in advanced alloys [178–182].

A report by Cui et al. is available on Gd conversion coating (GCC) for Mg alloys [182]. Their AEM images showed that the conversion coating was compact, except for some homogeneous fine cracks and some randomly distributed elliptical white tesserae. The coating thickness was 4–5 µm. XPS analysis showed the presence of \( \text{Gd}_2\text{O}_3 \), MgO, \( \text{Mg(OH)}_2 \) and \( \text{Al}_2\text{O}_3 \).
in the film. The GCC decreased the $i_{corr}$ by almost two orders of magnitude. The total impedance of the coated and the uncoated alloys were 8370, and 1300 $\Omega$ cm$^2$ respectively. The mechanism of deposition was shown to be similar to that of Ce and La [182].

The authors patented a method of GCC that includes the steps (a) grinding, (b) ultrasonic cleaning, (c) cold wind drying, (d) conversion coating (in RE salt + H$_2$O$_2$), (e) water washing, blow drying, (f) post-treating in phytic acid, and (g) water washing, blow drying [170].

2.7. Praseodymium conversion coatings

A few works are reported on Pr-based conversion coating (PCC) for Mg alloys [183,184]. Research has shown that Pr compounds are useful as co-additives in corrosion inhibitors for epoxy polyamide primers [185].

Jamali et al. fabricated a PrO$_x$ film with 0.7–1 $\mu$m thickness on AZNd alloy for biomedical applications. A novel electrochemical approach using scanning electrochemical microscopy (SECM) was used to evaluate the accompanying H$_2$ evolution. The study showed that low concentrations of Pr salt be likely to deposit a discontinuous PrO$_x$ film whereas high concentrations (>0.5 M Pr salt in the bath) or lengthy deposition time tend to attack the substrate harshly. The study also showed that an alkaline pre-treatment in 0.2 M NaOH for 2 min was helpful to produce a uniform PCC as the pre-treatment reduced Mg corrosion during the conversion coating process. Comparison of local impedance and H$_2$ evolution maps for coated and non-coated alloys in simulated body fluid revealed a more insulating surface on the coated alloy attributed to the formation of the PrO$_x$ layer. The study also showed that some insulating domains of the PrO$_x$ film broke down after 2 h of immersion with an associated enhanced H$_2$ evolution. SECM results of the coated alloy displayed a significant decline in H$_2$ evolution [183]. The authors in a subsequent report on AZ80X Mg alloy showed that Pr$^{3+}$ functions as an active corrosion inhibitor for Mg with self-healing features resulting in a dynamic deposition of Pr oxide/hydroxide species at highly alkaline domains [184].

3. Future potentials

Conversion coating deposition is a complex process and depends on several parameters. Hence, optimization of experimental conditions is requisite for commercialization of a particular conversion coating. More studies in this direction need to be explored with RECCs so that standards and specifications can be developed for a specific application. REs including erbium, europium, holmium, lutetium, scandium, thulium, ytterbium and dysprosium have not been studied as a conversion agent.

RECC requires suitable pre-treatment and post-treatment strategies to enhance its adhesion and corrosion resistance. Modified pre-treatments such as silicate treatment can yield fruitful results with Mg alloys. Zhang et al. recently showed that a more uniform and compact LaCC could be developed on a silicate pre-treated hot-dip galvanized steel [186]. Novel post-treatment approaches to seal the coating defects can be explored. Studies showed that zinc phosphate post-treatment considerably increased the corrosion resistance of Ce-coated steel [187]. Green inhibitor-based post-treatment baths can be utilized. Recently, Mahidashitia et al. showed that Urtica leaf extract could be used to modify CeCC on steel [188]. Similar studies reported with other metals and alloys could be extended for Mg alloys. More studies on post-treatments based on different organic conversion agents such as tannic and gallic acids need to be explored [22,189].

RE-based composite conversion coatings with novel inorganic and organic co-conversion agents can be studied. Low Cr containing synergistic combinations providing self-healing effect will be fruitful for aerospace applications. Role of novel additives as fillers analogous to the reported works on chrome, phosphate and molybdate conversion coatings can be investigated. For example, SiO$_2$ or Al$_2$O$_3$ nanoparticles containing RECCs can be studied for Mg alloys [190,191]. Further studies on RECCs along with electrochemical conversion coatings are desirable. Advanced studies in theoretical and computer-modelling on the mechanism of crack formation will be beneficial to fabricate crack-free RECCs.

4. Conclusions and outlook

A significant number of works were reported on RECCs for Mg and its alloys. Published information is available on Ce, La, Nd, Y, Sm, Pr and Gd-based RECCs. Most of the reported works are based on Ce; La follows that. The present work provides a comprehensive review of the topic for the first time.

Electron microscopy studies showed that RECCs typically have a crack-mud surface morphology with a bi/tri-layered structure having an inner compact crystalline layer. Phase analysis suggested a mixed amorphous-crystalline nature with predominant amorphous phases. The coating is found to be mainly composed of oxides and hydroxides of REs along with Mg oxides/hydroxides. With optimization of experimental conditions, RECCs with compact interior nanocrystalline layer could be fabricated. The mechanism of protection has been intensively investigated. The relative presence of Ce$^{3+}$ and Ce$^{4+}$ phases determines the deposition mechanism.

Literature analysis recommended that a combined acid and alkaline-based pre-treatment strategy is the preferred one. Most of the corrosion studies suggested that RECCs can provide excellent corrosion resistance to the underlying substrate in aggressive electrolytes, especially for shorter durations. For long-term performance, a subsequent post-treatment or topcoat is essential. A commonly employed post-treatment is phosphate-based. It is apparent that REs are best suited as a component in multi-element baths, along with other desired organic and inorganic conversion agents. Organic co-additives such as silanes and gelatins can significantly improve the coating adhesion and the corrosion resistance.

The collective information provided in this review will be helpful to researchers to explore novel advanced conversion coating solutions for Mg and its alloys.
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