Review

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Chromate-free chemical conversion coatings for aluminum alloys

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Abstract: Corrosion of metallic components represents a major issue in the aeronautical sector, giving rise to safety concerns and significant financial damages. Conversion coatings (CC) based on hexavalent chromium provide exceptional corrosion protection at relatively low cost. However, environmental issues and health concerns raised a growing interest in the development of alternative technologies. These must not only be cost effective and environmentally friendly but also provide corrosion resistance and adhesion performance comparable to Cr⁶⁺-based CCs. Simultaneously fulfilling all of these criteria is a difficult challenge, and an industrial application has so far only been achieved by a small number of systems. This review critically summarizes the recent scientific literature and patents for chromate-free CCs on aluminum alloys and tries to assess their potential regarding the highly demanding aerospace requirements. The bath composition and coating characteristics of the trivalent chromium process, rare earth chemical conversion coatings, transition metal oxyanion additives, Zr/Ti-based chemical conversion coatings, sol-gel coatings, and smart coatings providing stimulus-related inhibitor release are discussed. The advantages and disadvantages of the alternative technologies with regard to their practical implementation are debated, as the aeronautics industry is confronted with the necessity to move away from chromates in the near term.

Keywords: aluminum alloys; chemical conversion coating; chromate-free; corrosion protection; literature review.

1 Introduction

Wrought aluminum alloys (AA) are widely used in the aeronautical industry for airframe and structural materials due to their advantageous mechanical properties like, e.g. high strength at low density. Here, the AA2000 and AA7000 series are still the most widely used alloys for providing damage tolerance and stabilization in fuselage skin, frame and wing construction (Dursun & Soutis, 2014). However, the presence of copper (AA2000 series) or zinc (AA7000 series) in these alloys, although providing highly improved mechanical features, results in the formation of inhomogeneously distributed intermetallic particles (IMP) during their metallurgical treatment (Totten & MacKenzie, 2003). These IMPs can behave as electrochemical cathodes or anodes with respect to the Al matrix and produce erratic and weakened spots in the native oxide layer (Foley, 1986; Buchheit et al., 2001; Birbilis & Buchheit, 2005; Boag et al., 2011). The result is a significantly decreased resistance of these alloys to the occurrence of pitting, crevice corrosion, or galvanic corrosion in aggressive environments, and there will always be an engineering trade-off to their mechanical strength. For instance, AA2024 and AA7075 have been frequently used in aerospace applications and belong to the strongest alloys, but are very susceptible to localized corrosion (Guillaumin & Mankowski, 1999; Szklarska-Smialowska, 1999; Fonseca et al., 2002; Schuman, 2005). Consequently, there is an urgent need for the prevention of their environmental degradation, and this has been an important research area for a long time.

A widely adopted methodology for the corrosion protection of metallic substrates is the application of a multilayer coating system. This typically consists of different cleaning steps (alkaline and/or acid based), acid pickling stages, surface pre-treatments, and the deposition of an organic coating including primer and topcoat. Surface pre-treatments for AAs play a particular role in the aerospace industry for long-term durability and comprise anodizing and conversion coatings (CCs). Anodized AAs typically exhibit superior corrosion and wear resistance; however, CCs can be prepared more easily, much faster and at a lower cost (Sheasby & Pinner, 2001; Yoganandan

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et al., 2015). CCs can be applied by simple immersion of the metallic part into a chemical bath, by spraying at moderate temperatures, or by wipe application as a touch process. The latter two procedures render it possible to protect oversized aircraft components that may not be accessible to the anodizing lines or to protect cut edges and other local areas (Milošev & Frankel, 2018). Additionally, some CCs provide electrical conductivity, which may be beneficial for, e.g. space components or lightning protection purposes during the aircraft service life (Fletcher, 2008).

During the past decades, chromate conversion coatings (CCC) have been intensively applied in the aerospace industry due to their outstanding performance in corrosion resistance and paint adhesion for AAs. Thereby, a lot of knowledge about film formation mechanisms, growth dynamics, structure, and composition has been generated (Hawkins et al., 1987; Hughes et al., 1997; Xia & McCreery, 1998; Zhao et al., 1998; Brown & Kobayashi, 2001; Zhang et al., 2002; Kendig & Buchheit, 2003; Campestrini et al., 2004; Meng & Frankel, 2004; Liu et al., 2005; Kulinich et al., 2007c). The superior advantages of CCCs result from the “self-healing” ability provided by Cr^{6+} species, which may reform a protective layer after its mechanical or chemical damage. In detail, Cr^{6+} ions, which are stored in the coating, are highly mobile. In case of an exposure to an aqueous electrolyte, Cr^{6+} ions may diffuse to the defective area where they react with the bare aluminum to be electrochemically reduced to Cr^{3+} . A backbone of insoluble and hydrated Cr^{3+} oxide/hydroxides precipitates and prevents further pitting. Additionally, anodic inhibition restricts the rate of aluminum dissolution. The remarkable corrosion resistance of chromates is persistent over a wide range of pHs and electrolyte concentrations, which is only hardly matched by alternative compounds (Frankel & McCreery, 2001; Kendig & Buchheit, 2003; Fletcher, 2008). Nevertheless, despite their obvious advantages, CCCs pose severe health and environmental drawbacks due to the presence of hexavalent chromium, which is highly toxic and carcinogenic (O’Brien, 1995; Saha et al., 2011). Consequently, administrative legislations (e.g. the REACH EU Regulation EC No. 1907/2006 or OSHA final standard of 2006) specify a drastic reduction in human exposure to chromates during maintenance as well as manufacturing operations. It is of urgent need to find alternative technologies that are environmentally more friendly but provide a comparable corrosion protection and adhesion performance with the desire to develop an industrial “drop-in” replacement for the current procedures with hexavalent chromium.

In the past decades, numerous studies have been devoted for chromate substitution in CC formulation for AAs. However, until today, only a few systems have

achieved a maturity level that may seriously be considered by the industry for commercial application. Although the paint adhesion of alternative CC technologies frequently equals (or sometimes even outperforms) that of chromate-based systems, only a few seem to provide satisfactory overall corrosion resistance performance for the stringent requirements in the aerospace or defense sector. Therefore, hexavalent chromium replacement and the exemption of compliance for aeronautics still represents a major issue at international discussions (Lane et al., 2012; Fahrenholtz & O’Keefe, 2013; Robertson, 2013). This review focuses on important proceedings for chromium replacement and critically reviews alternative protective systems developed in the recent decades. Thereby, a comprehensive overview and the rudimentary chemical basics for the most relevant and promising technologies are given by considering published scientific results about the trivalent chromium process (TCP), rare earth chemical conversion coatings (RECC), transition metal oxyanion additives (TMOA), Zr/Ti-based conversion coatings (Zr/TiCC), sol-gel coatings, and smart coatings providing stimulus-related inhibitor release. In particular, the bath composition and coating characteristics are discussed with a focus on the corrosion protection performance and the resulting paint adhesion in comparison with chromate-based approaches. As the aeronautics industry is confronted with the necessity to move away from chromates in the near term, the advantages and disadvantages of alternative technologies with regard to their practical implementation are assessed.

2 Trivalent chromium process (TCP)

Protective coatings prepared by the TCP, first patented by the US Navy’s Naval Air System Command (NAVAIR), consist of a mixture of amorphous oxides, hydroxides, and hydrated oxides based on Cr^{3+} species (Matzdorf et al., 2000). The latter is of relatively low toxicity compared to the Cr^{6+} ion (Saha et al., 2011). Typical conversion baths contain Cr^{3+} salts (e.g. the sulfate $\text{Cr}_2(\text{SO}_4)_3$), a fluorine compound (e.g. NaF , Na_2SiF_6 , or Na_2ZrF_6), and additions of NaOH or H_2SO_4 for the pH adjustment (Sheasby & Pinner, 2001). The fluoride is necessary in order to dissolve the alumina (Al_2O_3) of the native oxide layer and to inhibit the re-passivation of Al for accelerating the film formation reaction:

In situ measurements with a tungsten microelectrode confirmed that, due to the local pH increase at the

cathodic sites (i.e. IMPs), a Cr^{3+} -rich layer forms by alkaline precipitation (Li et al., 2013):

When hexafluorozirconate compounds are added as an activator, a mixed Zr/Cr film precipitates on the AA substrate with Zr and Cr constituting about 40 and 10 wt% of the coating, respectively (Guo & Frankel, 2012b). TCP films exhibit particles of several hundred nanometers in size distributed over the entire surface; however, the film thickness on the IMPs is usually thicker. The inner layer mainly comprises aluminum as oxides and/or fluorides, whereas the outer part is composed of the Cr- or Cr/Zr-rich phases (Qi et al., 2015, 2016a) (see Figure 1H). Indeed, the presence of a native-like Al_2O_3 interfacial layer after the conversion reaction was confirmed by EIS measurements (Boyer et al., 2018). Surface cracking was partly observed in scanning electron microscope (SEM) micrographs and ascribed to volume shrinkage due to dehydration processes in dry air or vacuum (Guo & Frankel, 2012b) (see Figure 1A).

TCP layers made up from $\text{Cr}^{3+}/\text{Zr}^{4+}$ provide significantly improved degradation resistance to AA2024 in aggressive environments during electrochemical measurements as well as in salt spray tests (SST) (see Figure 1B–G). This can be attributed to the suppression of both anodic dissolution and oxygen reduction reaction (ORR), whereby the ORR is inhibited more strongly due to blocking of O_2 chemisorption on IMPs (Guo & Frankel, 2012a, Cai et al., 2017, Shruti & Swain, 2018). However, as the coatings are considerably thinner than CCCs (approximately 40–120

vs. 500 nm, respectively), they demonstrate inferior corrosion protection in a SST with 5% NaCl (according to ASTM B117) (Pearlstein & Agarwala, 1994). Furthermore, some active protection on an artificial scratch seems to arise from mobile Cr^{6+} species that are formed locally by the oxidation of Cr^{3+} via H_2O_2 . The latter behaves as a strong oxidant that is produced by the reduction of O_2 at the IMPs, leading to the self-healing mechanism as mentioned above (Li et al., 2011a; Cai et al., 2017; Qi et al., 2017b). However, the level of Cr^{6+} is expected to be quite low and of a transient nature, and there is still debate about its presence in TCP coatings under aerated environments.

Commercial TCP solutions are available on the market, and their application has demonstrated promising corrosion resistance in relation to CCCs. A pre-screening study via SST was performed on eight different chromate-free protection systems in order to identify potential replacements for CCC, and the best candidates were further evaluated by electrochemical impedance spectroscopy (EIS) (Carreira et al., 2017). As a result, PreCoat A32 (AD International B.V., Heijningen, The Netherlands) was identified as superior TCP coating, which demonstrated high corrosion protection on both of the alloys, AA2024-T3 as well as AA2024-T81. EIS results during immersion in 0.5 M NaCl solution for up to 7 days even revealed slightly improved performance of PreCoat A32 compared to Alodine 1200 (Henkel Adhesives, Düsseldorf, Germany), and both SST military standards, MIL-DTL 5541 and 81706, were passed. Chromital (SurTec 650, Bensheim, Germany) showed promising degradation resistance for AA2024-T351 in EIS experiments, though its performance was slightly inferior compared to a CCC (Qi et al., 2016c; Mitton et al., 2017). However, a recent investigation stated a clear reduction of Cr^{6+} species in the TCP coating after adding Fe^{2+} into the conversion bath (Qi et al., 2018). It was assumed that the production of Cr^{6+} is suppressed due to the consumption of H_2O_2 by Fe^{2+} at the cathodic sites. The additive had a

Figure 1: (A) SEM micrograph of a TCP on AA2024-T3 after 10 min of immersion. Reprinted with permission from reference Guo & Frankel (2012b), Elsevier 2019. (B–G) Macro-morphologies of (B–D) uncoated and (E–G) coated samples after salt spray exposure: (B–D) correspond to uncoated samples after exposure for 6, 72, and 192 h, respectively; (E–G) correspond to coated samples after exposure for 6, 72, and 192 h, respectively. Reprinted with permission from reference Cai et al., (2017), John Wiley and Sons 2019. (H) Simplified scheme of a TCP coating structure.

minor influence on coating morphology, growth kinetics, and composition but slightly enhanced the corrosion resistance in EIS experiments in a 0.05 M NaCl solution (i.e. by a factor of ~ 1.4). The addition of CuSO_4 also suppressed the H_2O_2 formation at cathodic sites by promoting the four-electron ORR above Cu-rich deposits. However, no information on corrosion protection performance was given in the report (Qi et al., 2017c). A patent discloses a highly protective TCP coating when mixed with magnesium salts and aminoquinoline, which performed equal to a CCC (Huicheng et al., 2013).

Post-treatment strategies for TCP coatings on AA2024 have been employed in the last years and shown to enhance their corrosion resistance significantly. The most promising examples are bath immersions in warm water, treatment with H_2O_2 as well as lanthanum salts, and the aging in air at elevated temperatures (Li & Swain, 2013; Qi et al., 2016b,c, 2017a; Ely et al., 2017).

A valuable summary about the chemistry, film formation mechanism, and electrochemical behavior of the TCP processes was published by Mitton et al. (2017). Generally, TCP systems perform very well in combination with chromate-containing primers; however, the corrosion resistance is significantly lower when non-chromium organic coatings are applied. In addition, some suspicions arose regarding the carcinogenicity or genotoxicity risks for potential worker exposure (Gharbi et al., 2018). It is still difficult to give a final assessment about the reliable replacement of Cr^{6+} coatings by TCP. Although the corrosion resistance of the latter was occasionally outperformed, the TCP is highly sensitive to process parameters and pre-treatments. Consequently, a potential industrial success of this technology may rely on future research on understanding and optimizing the various process steps in order to exploit its full potential.

3 Rare earth conversion coating (RECC)

Among the rare earth elements, lanthanide salts demonstrated to be effective retardants for corrosive attack of metallic substrates, and initial investigations were reported by Hinton et al. (1984) and Hinton (1992). Since then, a large number of academic research papers as well as patents have been published; however, only those that displayed promising corrosion resistance for AAs are further evaluated (Wang et al., 2012; Tianquan et al., 2014). In particular, the trivalent cerium ion (Ce^{3+}) is a powerful cathodic inhibitor for IMPs on various AAs, and

the most studied element in the field of RECC (Muster et al., 2010, 2012). The latter can be surely ascribed to the fact that, while Ce is of relatively low toxicity (compared to Cr^{6+}) and occurs abundantly in nature as, e.g. CeCl_3 and $\text{Ce}(\text{NO}_3)_3$, corrosion inhibition ability close to CCC was frequently achieved (Muecke & Möller, 1988; Mansfeld et al., 1991; Bethencourt et al., 1997; Aballe et al., 2001; Mishra & Balasubramaniam, 2007; Allachi et al., 2010). The following section puts its main focus on these Ce-based protection systems as the auspicious paradigm, but conclusions should be transferable to other lanthanide members due to their similar electrochemical behavior.

The immersion of an AA substrate into a Ce-based conversion bath leads to the buildup of a mixed oxide/hydroxide composite with Al and Ce species. Al-rich phases (i.e. mainly Al_2O_3) evolve primarily over the alloy matrix areas, whereas Ce compounds (oxides/hydroxides) precipitate over the IMPs due to the increase in the pH during the chemical reactions [see Eqs. (2) and (3)] (Kolics et al., 2003; Bethencourt et al., 2008; Paussa et al., 2012; Sánchez-Amaya et al., 2012; Matter et al., 2013; Venkatasubramanian et al., 2014; Li et al., 2015). Indeed, Palomino et al. showed that a Cu-rich smut leads to the homogeneous precipitation of a Ce-based CC (Palomino et al., 2006). The detailed mechanism of inhibition depends on the counter anion of the salt (e.g. chloride, acetate, nitrate, malate, etc.), but ultimately a mixture of $\text{Ce}^{3+}/\text{Ce}^{4+}$ oxides and hydroxides deposits over the surface by a successive oxidation of $\text{Ce}(\text{OH})_3$ to $\text{Ce}(\text{OH})_4$ (Decroly & Petitjean, 2005; Yasakau et al., 2006; Catubig et al., 2015; Rodič & Milošev, 2016; Hu et al., 2019). CeCl_3 and $\text{Ce}(\text{NO}_3)_3$ were frequently applied on AAs, whereby CeCl_3 led to a higher precipitation with the formation of a thicker coating. However, $\text{Ce}(\text{NO}_3)_3$ or mixtures of $\text{CeCl}_3/\text{Ce}(\text{NO}_3)_3$ resulted in a more homogeneous film with improved corrosion resistance (Dabalà et al., 2004; Brunelli et al., 2012). Earliest attempts demonstrated the need for extended immersion times of the substrate (~ 100 h) in order to cover the entire surface (Hinton et al., 1986). However, newer types of Ce-based CCs involve higher temperatures and H_2O_2 as additive, which significantly increase the deposition rate of the coating from several days to a few minutes (Bethencourt et al., 2002, 2003; Dabalà et al., 2004; Rivera et al., 2004; Scholes et al., 2006; Zhao et al., 2010; Brunelli et al., 2012; Kozhukharov et al., 2014; Valdez et al., 2014; Chen et al., 2015). Polarization measurements displayed a broadening of the passive range and confirmed that the CeCC effectively protects the matrix against localized corrosion and acts as a diffusion barrier for the active zones (see Figure 2G). There exists a large amount of scientific reports about the application of inorganic and organic Ce-based compounds as pigments

Figure 2: Photographs of as-prepared (A–C) and 168 h SST (D–F) ZrCC, ZrCeCC, and chromate-based CC specimens. Reprinted with permission from reference Yoganandan et al., (2015), Elsevier 2019. (G) Potentiodynamic polarization measurements for AA2024-T3 in 0.1 M NaCl without or with addition of 3 mM Ce(III) and Ce(IV) salts as corrosion inhibitors. Free via Creative Commons from reference Rodič & Milošev (2016).

for AA protection; however, only key findings in terms of corrosion resistance are mentioned here.

$\text{Ce}(\text{NO}_3)_3$ was added to a mixed solution of $\text{ZrO}(\text{NO}_3)_2$ (zirconyl nitrate) and H_2O_2 and significantly improved the electrochemical corrosion protection of AA2024 compared to the Zr-only treatment or the bare metal (Yoganandan et al., 2015). With progressing immersion time in an aggressive 0.6 M NaCl solution, the inhibiting activity seemed to increase by displaying enhanced EIS responses, while after 168 h of neutral SST (NSST) the ZrCeCC performed nearly equivalent to a conventional CCC, displaying very little pitting (see Figure 2A–F). Damage tolerance and scratch cell tests confirmed a self-healing ability of the Ce-doped coating by displaying an increase in the charge transfer resistance (R_{ct}) and a concomitant visual repair of the defect.

Improved corrosion resistance can also be achieved via cerium addition as an organic salt. Cerium tartrate, when added as a saturated pigment into a 0.05 M NaCl solution, effectively avoided pitting of AA2024-T3 specimens by acting as both cathodic and anodic inhibitor (Hu et al., 2015). The carboxylic groups of the tartrate anion bond to the Al matrix obstructing corrosive attack, while cerium oxides and/or hydroxides precipitate at the cathodic IMPs. The small particle size and low solubility render cerium tartrate an attractive inhibitor pigment. Cerium cinnamate and dibutylphosphate (dbp) showed a similar behavior by acting as cathodic and anodic inhibitor, whereby the organic sublayer offers additional barrier protection to Cl^- ions (Ho et al., 2006; Shi et al., 2011; Garcia et al., 2013).

Cerium compounds can be successfully incorporated as inhibiting additives into other types of corrosion protective systems. For instance, inorganic sol-gel coatings provide barrier properties for oxygen and water diffusion. However, due to the lack of a self-healing ability like in CCCs, the ingress of corrosive species via micropores or cracks after mechanical damage cannot be avoided. Sugama doped an aminopropylsilane triol solution with cerium acetate (up to 10 wt%) and observed an *in situ* conversion to $\text{Ce}(\text{OH})_3$ followed by a subsequent transformation to Ce_2O_3 during the heat treatment (Sugama, 2005). With an optimized value of 3 wt% for cerium acetate, the ORR at the cathodic sites could be significantly suppressed, and even a nanoscale coating (i.e. with a thickness of less than 5 nm) lowered the corrosion rate by 2 orders of magnitude. The SST resistance could be enhanced from ~40 h to more than 1440 h. Similarly, Tiringer et al. and Bahrami et al. introduced cerium nitrate into a hybrid sol-gel coating based on tetraethoxysilane (TEOS) and 3-glycidoxypentyl-trimethoxysilane (GPTMS) for AA7075 and AA6061, respectively, in order to obtain an active corrosion protection (Bahrami et al., 2015, 2017; Tiringer et al., 2018). The electrochemical responses during exposure to a NaCl solution were clearly enhanced in both cases. Additional studies on cerium-organic acid compounds confirmed their beneficial effects on sol-gel coatings (Yu et al., 2015).

Synergistic effects on the corrosion protection of AAs were studied by the combination of cerium salts with organic as well as inorganic compounds, and these demonstrated to be more effective than the effects from single additions. The inhibitive performances during

electrochemical measurements in corrosive electrolytes were typically enhanced accompanied by occasional self-healing of artificial scribes. Additionally, anodic suppressions were frequently observed. Noticeable reports were published with cerium nitrate and dodecylbenzenesulfonate (DBS) on AA5052 (Liu et al., 2016a), cerium chloride and DBS on AA2024 (Zuo et al., 2017), cerium nitrate and glutamic acid on AA5052 (Zhu et al., 2018), cerium chloride and benzotriazole (BTA) on AA2024 (Coelho et al., 2018), cerium acetate and sodium sulfate (Na_2SO_4) on AA7075 (Rodič & Milošev, 2019), and cerium diphenylphosphate (dpp) and praseodymium dpp on AA2024 (Markley et al., 2007). Mixing of different lanthanide salts also showed promise to enhance the corrosion protection of AAs (Milošev & Volarič, 2017). Cerium dpp provides a complex that showed excellent corrosion inhibition for AA2024 similar to a CCC. Furthermore, filiform corrosion under harsh environmental conditions was efficiently suppressed when added as a pigment to an epoxy coating (Forsyth et al., 2008). The adhesion performance was slightly improved over the chromate control (Sastri, 2011). Promising corrosion inhibition with cerium dpp was also reported for the AA7000 series (Hill et al., 2011). Wittmar et al. reported a very effective corrosion resistance in SST for a hybrid silica-based sol-gel coating that was doped with a mixture of cerium, praseodymium, and phosphates. The bulk of an AA2024 was not affected for more than 1500 h (Wittmar et al., 2012). Chambers and Taylor reported a method for the rapid assessment of corrosion protection performance by fluorometric probes at different pH values as well as immersion times in 0.6 M NaCl (Chambers & Taylor, 2007). They observed that the synergistic behavior of mixed inhibitive pigments is strongly dependent on the solution concentrations and pH. Mixtures of cerium chloride or lanthanum chloride with sodium molybdate demonstrated excellent inhibition comparable to dichromate-based solutions.

However, a potential drawback that was reported for rare earth coatings on AA2024 specimen is the inferior stability of the precipitated oxides in acidic environments. Compared to, e.g. a Cr_2O_3 layer, the improvement in corrosion current and pitting potential is moderate (Kolics et al., 2003; Wang et al., 2004).

4 Transition metal oxyanions (TMOA)

Common TMOA coatings include transition metal cations in their highest oxidation state, which may form stable oxyanions in aqueous solution. As these metal ions can be

electrochemically reduced and subsequently form insoluble oxides, a similar chemical behavior to chromates was observed. The most promising candidates in terms of future industrial implementation are permanganates (MnO_4^-), molybdates (MoO_4^{2-}), and vanadates (VO_4^{3-}). It is expected that the main inhibition mechanism follows a competitive adsorption of these anions with corrosive species like chlorides or sulfates (Cicek, 2014).

Manganese-based conversion treatments were suspected to provide some self-healing ability to AAs due to their high equilibrium potential that leads to the reduction of Mn^{7+} species to Mn^{4+} at flawed or chemically damaged regions. Typical MnO_4^- conversion baths produce a coating that is a mixture of hydrated MnO_2 , Mn_3O_4 , Mn_2O_3 , and Al_2O_3 . The inner layer is mainly comprised of Mn and Al oxides, whereas the outer part is enriched by Mn oxides. The films exhibit a yellowish appearance with a thickness in the range of 50–100 nm, and the electrochemical growth process seems to follow that for CCCs (Bibber, 2001; Hughes et al., 2006; Yoganandan et al., 2012; Madden & Scully, 2014; Oki & Adediran, 2018; Shamsi et al., 2018). Multi-element composite coatings in combination with rare earths were patented and displayed promising corrosion inhibition efficiency as well as good wear resistance (Du Jun et al., 2013). Although permanganates possess some environmental and health concerns, their toxicity in comparison with hexavalent chromium is considerably less. Paint adhesion and atmospheric corrosion protection were stated to be comparable to CCCs; however, the susceptibility to pitting for a lacquer-coated specimen in an aggressive NaCl solution was inferior (Oki et al., 2018). Furthermore, MnO_4^- -based coatings seem to perform worse on AA2000 and AA7000 series, which are the most relevant substrates for aerospace applications. An irregular film growth on the IMPs leads to a different failure mechanism in corrosion protection, and cracks start to appear due to thickness variations. The small amounts of MnO_4^- species on the top surface further indicate a limited self-healing potential (Kulinich et al., 2007a,b).

Scientific reports or patents on AA protection by permanganates are quite scarce in the literature, which can be mainly ascribed to the disparagement of its general protective features. However, a conference report was published indicating the encouraging performance and the potential to replace chromate-based systems on aircraft-relevant AAs (Bibber, 1999). Synergistic treatments with KMnO_4 and $\text{Al}_2(\text{SO}_4)_3$ or $\text{Al}(\text{NO}_3)_3$ showed improved corrosion protection for AA3003 specimens by reducing both the cathodic current and pitting initiation (Danilidis et al., 2007). Additionally, the presence of Zn^{2+} enhanced the inhibition efficiency in electrochemical experiments

for a permanganate coating on pure aluminum via accelerated mass transport (Agnesia Kanimozhi & Rajendran, 2010). A spin-coated no-rinse permanganate film successfully inhibited pitting corrosion on AA3003 by driving the corrosion potential to more positive values. The inhibition was mainly an anodic one. Exposure to a 0.5% NaCl solution demonstrated a similar polarization resistance compared to a CCC system (Danilidis et al., 1999).

Similar to the behavior of permanganates, CCs based on MoO_4^{2-} demonstrated to provide corrosion inhibition for AAs due to the reduction of Mo^{6+} species to Mo^{5+} and/or Mo^{4+} . The latter are able to precipitate as insoluble oxides (e.g. as MoO_2 or Mo_2O_3) (Rodriguez & Chidambaram, 2013). Molybdenum is not fully harmless, but has a very low toxicity during human exposure. The potential to effectively protect aluminum and replace highly toxic chromates led to an extensive exploration in the scientific literature, and relevant findings are discussed in this section.

In general, MoO_4^{2-} are classified as both anodic and cathodic inhibitors, which increase the pitting potential to more noble values with respect to the open circuit potential (OCP) (Shaw et al., 1990; Breslin et al., 1994; Emregül & Aksüt, 2003; Silva et al., 2005; Li et al., 2011b; Rodriguez et al., 2013; Kwolek et al., 2016). However, it was observed that the corrosion potential and, in turn, the extent of inhibition are dependent on the concentration of MoO_4^{2-} anions in the conversion bath (Jakab et al., 2005, 2006; Li et al., 2011b). Diluted solutions typically perform better than concentrated ones, and the surface morphology resembles that of other CCs by displaying a mud-cracked appearance (Naimi et al., 2012; Liang et al., 2014). A study on the corrosion protection of AA2024 indicated a two-step process with intermediate $\text{MoO}(\text{OH})_2$ species that are formed over the IMPs and a subsequent oxidation to molybdenum oxide in the presence of oxygen. A threshold concentration of $\sim 0.1 \text{ M}$ of Na_2MoO_4 led to an increase in the pitting potential as well as to a reduced corrosion current (i_{corr}), and the total impedance in EIS measurements was increased by a factor of ~ 40 (see Figure 3) (Lopez-Garrity & Frankel, 2014). The general protection mechanism of molybdates was suggested to be due to a closure of cavities inside the boehmite film (i.e. $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) on the surface of the AA substrate. It was stated that the surface pre-treatment via NaOH etching is an essential step allowing the efficient reduction of Mo^{6+} to Mo^{4+} (Bairamov & Verdiev, 1992). When the conversion bath becomes too acidic, larger polymeric molybdate species (e.g. $\text{Mo}_8\text{O}_{26}^{4-}$, $\text{Mo}_7\text{O}_{24}^{6-}$, $\text{Mo}_6\text{O}_{21}^{6-}$, or $\text{Mo}_3\text{O}_{11}^{4-}$) may form from the orthomolybdate. These are not able to penetrate into the flawed areas of the passive film and provide active inhibition. As a consequence, the corrosion protection in aggressive

chloride solutions was found to be not as good as for CCCs (Breslin et al., 1994; Krishnan et al., 2007). Furthermore, a direct comparison of electrochemical measurements displayed an inferior corrosion protection of molybdates compared to chromates or dichromates on a Cu-rich AA (Ghassem Mahjani et al., 2008).

The necessity to apply high molybdate contents to solutions containing chlorides spurred the investigation of synergistic effects with inorganic chemicals (Moshier & Davis, 1990; Emregül & Aksüt, 2003). For instance, a synergistic effect between molybdates and rare earth elements (i.e. Ce and La) yielded corrosion inhibitor performances similar to Na_2CrO_4 in high-throughput fluorescent experiments (Chambers et al., 2005; Chambers & Taylor, 2007; Taylor & Chambers, 2008). Cerium molybdate nanowires on AA2024 demonstrated corrosion inhibition ability in highly concentrated NaCl solutions (Yasakau et al., 2013). The effect was ascribed to a structural transformation from a mixed amorphous phase into crystalline $(\text{NaCe})_{0.5}\text{MoO}_4$, which enables the release of Ce^{3+} species. Organic additions (i.e. ethylenediaminetetraacetate and triethanolamine) to the MoO_4^{2-} conversion bath significantly enhanced the corrosion resistance as well as surface morphology of the CC on AA6063 (Mu et al., 2016). A considerable film thickness of up to $30 \mu\text{m}$ was achieved. Recent patents indicate good adhesion properties and high corrosion resistance when molybdate species are mixed with fluorozirconates or trivalent chromium salts (Xiaoling et al., 2016; Raoling, 2018). Generally, the availability of scientific reports on the corrosion inhibition of AAs is encouraging; however, concrete relation to the performance of state-of-the-art CCCs for the aerospace sector is substantially lacking.

Vanadates are the salts of the naturally unstable vanadium acid. Compounds that contain vanadium were generally thought to be of low toxicity compared to chromates; acute or subchronic toxicity to human exposure was not reported (Cicek, 2014). However, recent evidence on the potential carcinogenicity and mutagenicity for animals raised some concerns about the long-term viability of vanadium and its compounds, and future research direction should be reconceived (Ress et al., 2003; Hosseini et al., 2013; Imura et al., 2013; Gharbi et al., 2018). Despite their incipient health concerns, the corrosion-inhibition features are discussed here for the sake of completeness.

Similar to other oxyanions, vanadates exhibit protective functions by acting as a competitive adsorptive species for, e.g. Cl^- and by the formation of insoluble $\text{V}^{5+}/\text{V}^{4+}$ oxides on the IMPs (Guan & Buchheit, 2004; Iannuzzi et al., 2006; Iannuzzi & Frankel, 2007; Kharitonov et al., 2017; Kharitonov et al., 2018a,b). Iannuzzi and

Figure 3: (A) Naturally aerated polarization curves for AA2024-T3 in 0.1 M NaCl solution at varying Na₂MoO₄ concentrations. (B) Bode magnitude and phase-angle plot after immersion in 0.1 M NaCl with and without 125 mM Na₂MoO₄ in aerated solution. (C) SEM micrograph of the surface after 2 h exposure to 0.1 M NaCl + 125 mM Na₂MoO₄ solution at 1100 mV SCE fixed potential. (D) Optical micrographs after 1-day exposure to (left) NaCl-only solution and (right) 0.1 M NaCl + 125 mM Na₂MoO₄ solution at the OCP. Free via Creative Commons from reference Lopez-Garrity & Frankel (2014).

Frankel as well as Ralston et al. observed that only the tetrahedrally coordinated metavanadate and pyrovanadate forms inhibit the ORR on AA2024 to a comparable extent like chromate. The octahedrally coordinated decavanadate does not (Iannuzzi et al., 2006, 2007; Iannuzzi & Frankel, 2007; Ralston et al., 2008). As the latter forms only by polymerization under acidic conditions, this should not be an issue due to aircraft-exposed electrolytes being typically neutral or slightly basic. The mitigation of anodic metal dissolution during the initial stages of exposure to NaCl solution was also recognized (Kharitonov et al., 2017, 2018b). However, it was reported that the decrease in the overall corrosion rate is strongest on the Cu-rich aeronautical AAs 2024 and 7075, displaying a significant increase in the passivity range in potentiodynamic polarization curves (see Figure 4) (Ralston & Buchheit, 2013). For Cu-less AAs like, e.g. 6061, the inhibition becomes increasingly anodic in nature. Reduction reactions to, e.g. V⁴⁺ species occur quite slowly and were

not ascribed to provide a similar inhibition mechanism like Cr⁶⁺ coatings. Vanadates suppressed the formation of large pits during an SST according to ASTM B117 for more than 168 h (Guan & Buchheit, 2004). During the electrochemical investigation of 27 compounds for the corrosion inhibition of AA2024 specimens, sodium metavanadate performed best and demonstrated a possible replacement for sodium chromate (Cook & Taylor, 2000). The corrosion resistance values (R_{corr}) during a 10-day EIS measurement in a 0.6 M NaCl solution were constantly on a high level, and the resulting pit depths were excellent. Shrestha et al. reported the use of multiple-beam interferometry with a surface forces apparatus in order to directly visualize the crevice corrosion process with Ångstrom resolution. They observed an efficient corrosion inhibition of aluminum for 25 h in a 5 mM NaCl solution by adding 2.5 mM sodium metavanadate (Shrestha et al., 2015).

Oxyanions of transition metals may behave as electrochemical analogs to chromates; however, as Cr⁶⁺ is a

Figure 4: (A) Qualitative corrosion morphology after 24 h of exposure in 0.1 M NaCl of AA7075-T6 without (left) and with (right) 0.0025 M NaVO₃. (B) Sample potentiodynamic polarization curves for AA2024-T3, AA7075-T6, and AA6061-T6 obtained in 0.1 M NaCl with and without 0.0025 M NaVO₃ after both “short” and “long” OCP stabilizations. Reprinted with permission from reference Ralston & Buchheit (2013), Electrochemical Society 2019.

stronger oxidant, they will only give a comparable stability to Cr-based oxides when deposited as polyoxometallates. Nevertheless, synergistic effects of vanadates with organic and inorganic compounds were reported. Especially in combination with Zr/Ti species, the protective coatings demonstrated superior performances in the corrosion resistance of AAs (Zhong et al., 2013, 2015). The corresponding details will be discussed later in the section Zr/TiCC.

5 Zirconium/titanium conversion coating (Zr/TiCC)

Protective coatings based on Zr and/or Ti belong to the most important alternative systems that have achieved a maturity level for commercial utilization. The fast processing times, thin-film properties, and small amounts of phosphates or heavy metal eutrophication during waste disposal render them attractive for large-scale application. Consequently, a variety of scientific papers and patents have been published in the recent years providing

information on coating properties and pre-treatment conditions. Typical conversion baths contain hexafluorometallate complexes (e.g. H₂ZrF₆, Na₂ZrF₆, H₂TiF₆, etc.), inorganic acids for the pH adjustment, and additives in order to modify the film formation kinetics or adhesion properties (Niknahad et al., 2010; Khun et al., 2013; Zhong et al., 2013; Ruiguang et al., 2014; Santa Coloma et al., 2015; Yi et al., 2015; Zuo et al., 2015; Liu et al., 2016c; Li et al., 2016; Zhu et al., 2017). The hexafluoro ions simultaneously act as surface activators. Slightly acid conditions (i.e. a pH of ~4) and immersion times between 2 and 5 min may produce well-performing layers at mild conditions near room temperature. Thereby, the nucleation and film growth starts mainly from the IMPs (i.e. precipitation of hydrated metal oxides, mainly ZrO₂, due to the local pH increase) followed by the deposition on the Al matrix. The cross-sectional dimensions of the coatings range between 50 and 100 nm, depending on the processing parameters. Although most of the research on Zr/TiCCs was conducted with stagnant immersion tanks, stirring was observed to aid a faster film formation due to the accelerated mass transport of activating species and CC components

(Cerezo et al., 2016). In general, Zr- or mixed Zr/Ti-based systems performed superior on AAs compared to pure Ti-based coatings.

Organic and inorganic additives were found to play a major role for the inhibitive properties and adhesion performance of Zr/TiCCs. The homogeneity of the CC, interaction with the substrate, and adhesion to organic topcoats are typically modified by polymer additives, whereas inorganic compounds affect the kinetics of deposition and provide self-healing abilities. The adhesion to organic topcoats is generally improved due to the rough surface morphology of Zr/Ti layers (Khun et al., 2013; Liu et al., 2016c; Zhu et al., 2016; Milošev & Frankel, 2018). A patent on a polyhydroxy-esterified Zr/TiCC demonstrates high corrosion protection performance for AAs capable of substituting chromate treatments (Liu et al., 2012). Combined

additions of polyacrylic acid (PAA) and polyacrylic amide (PAM) to a ZrCC demonstrated promise in the corrosion protection of AA1050 by displaying a similar visual appearance after 1000 h of SST compared to a mixed chromate/phosphate coating (Niknahad et al., 2010). The adhesion strength to an epoxy topcoat was slightly inferior to the former in dry as well as in wet conditions (see Figure 5A, B). Tannic acid (TA) and NaVO_3 were simultaneously incorporated into a mixed Zr/TiCC and showed excellent corrosion protection on AA6063 in SST as well as in electrochemical measurements (Zhu et al., 2017). The integrity of the coating after 168 h exposure to NSST was comparable to a CCC (i.e. DCHZ-405) and even slightly superior in polarization experiments. Pull-off adhesion showed a similar strength to the epoxy coating in wet or dry conditions (see Figure 5C, D), which was ascribed to the high

Figure 5: (A) CPCC: chromate/phosphate and No. 10: Zr/PAA/PAM CC on AA1050 after 1000 h SST. (B) Pull-off adhesion strength of various pretreated epoxy coats on AA1050 and percentage of adhesive remaining after humidity test according to ASTM D 3359. Reprinted with permission from reference Niknahad et al., (2010), Elsevier 2019. (C) Tafel polarization curves of Zr/TiCC + TA + NaVO_3 (TZVCC) on AA6063, CCC on AA6063 and AA6063 after 30 min immersion in 3.5 wt% NaCl solution at $25 \pm 2^\circ\text{C}$. (D) Epoxy-coated AA6063, epoxy-coated TZVCC/AA6063, and CCC/AA6063 samples after pull-off tests. Reprinted with permission from reference Zhu et al., (2017), Elsevier 2019.

roughness, wettability, and OH^- content. Similarly, Zuo et al. reported the preparation of a smooth, compact, and pin-hole free Zr/TiCC due to the addition of TA (Zuo et al., 2015). The metavanadate species significantly decreased the film formation period, and the final coatings provided improved electrochemical corrosion resistance compared to an unaltered Zr/TiCC. A purely Zr-based CC with additions of phosphoric acid (H_3PO_4) and NaF demonstrated an outstanding corrosion protection on AA5083 that was better than from a chromium-free CC (i.e. Alodine 5200) and nearly comparable to a commercial CCC (i.e. Alodine 1200S) (Liu et al., 2016c). The multilayer system comprised various phases like Na_3AlF_6 , AlPO_4 , ZrO_2 , and $\text{Zr}(\text{HPO}_4) \cdot \text{H}_2\text{O}$ and provided a similar pull-off adhesion strength to an epoxy resin comparable to the CCC.

Various mixtures of Zr/TiCCs with heavy elements or rare earths were reported to achieve significantly improved corrosion resistance on AAs compared to the undoped coating systems. Mo, Mn, Cu, or Zn additions successfully shifted the pitting potential toward more noble values and decreased the corrosion currents by some orders of magnitude (Sarfraz et al., 2014; Santa Coloma et al., 2015; Yi et al., 2015; Li et al., 2016). Vanadium, trivalent chromium, and cerium behave similar to Cr^{6+} species and provide a self-healing ability to the coating with greatly improved corrosion protection (Zhong et al., 2013; Yoganandan et al., 2015; Cai et al., 2017). In summary, Zr/TiCC systems showed to provide remarkable performance in corrosion protection and epoxy adhesion on AAs when combined with organic and/or inorganic additives. However, further improvements are still necessary as SST frequently yields inferior performance compared to CCCs. A valuable report about Zr- and Ti-based systems on different metallic substrates was recently published by Milošev and Frankel (2018). They reviewed the large number of scientific papers with an emphasis on corrosion protection and topcoat adhesion.

6 Sol-gel coatings

Corrosion protection of metallic substrates by sol-gel coatings is a fiercely debated issue in the scientific community, and several valuable reviews have been published in the recent time concerning the basic chemistry and corrosion inhibition mechanisms (Figueira et al., 2015, 2016; Barton et al., 2017; Gonzales et al., 2018; Pehkonen & Yuan, 2018). In a typical sol-gel process, progressive condensation reactions of alkoxide-based molecular precursors contained in a liquid medium result in the buildup of a 3-D oxide network. The metals/metalloids can be different elements

such as Si, Zr, Ti, Al, Fe, etc., whereby the most frequently applied alkoxides are based on silicon due to its low cost and ease of exploitation. Strong chemical bonds to the aluminum substrate are created via oxygen bridges, and the inclusion of organic compounds enables the efficient interaction with an organic topcoat. Purely inorganic films can be prepared from, e.g., tetraethylorthosilicates (i.e. tetraethoxysilanes, TEOSs) or tetramethoxysilanes (TMOSs), but these are only limited applicable for AAs due to need for high curing temperatures ($>300^\circ\text{C}$) and the concomitant metallurgical changes (Brinker et al., 1990; Conde et al., 2003). However, a sol-gel coating based on zirconium tetrapropoxide (ZrTPO) was successfully cured at temperatures below 100°C with additions of the surfactant Triton X-100 during the alkaline cleaning step (Sepúlveda et al., 2007). Hybrid sol-gel systems can be prepared by augmenting the inorganic coatings with functional or non-functional organic groups. These demonstrated enhanced flexibility as well as density and enabled significantly lower curing temperatures (i.e. $<150^\circ\text{C}$). Phenyl trimethoxysilane, for instance, provides superior electrochemical corrosion protection compared to coatings from inorganic TEOS, which is ascribed to the increased hydrophobicity of the resulting coating (Sheffer et al., 2003). Even more promising is the modification with functional organic groups like, e.g. epoxy or methacrylic. The first reports indicated promising short-term corrosion protection, which partially outperformed chromate-containing Alodine 1200 (Parkhill et al., 2001; Voevodin et al., 2001). However, an amine-based cross-linking agent was usually necessary to aid the epoxy-ring opening reaction. From this point on, several coating systems encompassing polymerizable organo-functional groups were studied for the corrosion inhibition of aeronautical AAs. The results in electrochemical investigations and salt spray testing are promising (Metroke et al., 2002, 2004; Voevodin et al., 2006; Rosero-Navarro et al., 2009; Álvarez et al., 2010b; Andreatta et al., 2011; Kozhukharov et al., 2012; Rodič et al., 2014, 2016; Bera et al., 2015).

Favorable corrosion protection for AAs was also demonstrated by mixtures of silanes with one component being a bisfunctional silane like, e.g. bis-sulfur silane, bis-(trimethoxysilylpropyl)amine, or bis-aminosilane-vinyltriacetoxysilane. In painted conditions, these systems performed similarly compared to a CCC in polarization experiments as well as in SST (see Figure 6) (Zhu & van Ooij, 2004a,b). The hydrophobic character of the coatings provides a barrier for the diffusion of water and corrosive ingredients like Cl^- or O_2 .

Sol-gel coatings typically exhibit a moderate wear resistance and poor mechanical properties. However, the incorporation of inorganic nanoparticles into the

Figure 6: (A) Structures of (1) bis-(trimethoxysilylpropyl)amine and (2) vinyltriacetoxysilane (VTAS). (B) Cathodic polarization curves of AA 2024-T3 treated with and without silane mixture. (C) Polyurethane-powder-painted AA 2024-T3 panels after 1008 h of SST: (1) untreated, (2) chromated (CHEM CODE 105®) and (3) silane treated. (D) Polyester-powder-painted AA 2024-T3 panels after 1008 h of SST: (1) untreated, (2) chromated (CHEM CODE 105®), and (3) silane-treated. Reprinted with permission from reference Zhu & van Ooij (2004a), Elsevier 2019.

conversion bath may hurdle this issue. ZrTPO and methacrylic acid (MAA) improved the hydrophobic properties as well as the electrochemical corrosion resistance of a TEOS sol-gel film under simulated aerospace conditions (Rodič et al., 2016). Good anticorrosive properties and excellent adhesion for an upper topcoat on an AA2024 specimen were also found for a hybrid titania-silica film. However, the SST performance was slightly inferior compared to a CCC (Poznyak et al., 2008).

The lack of an active protection of sol-gel coatings motivated the incorporation of corrosion inhibitors to the bath formulations. Thereby, cerium showed great promise to enhance the electrochemical properties as well as abrasion resistance of AAs (Sugama, 2005; Bahrami et al., 2015, 2017; Yu et al., 2015; Hu et al., 2018; Tiringier et al., 2018). Typically, $\text{Ce}(\text{OH})_3$ precipitates at the cathodic sites and partially transforms to CeO_2 during the sol-gel curing step at temperatures of $\sim 100^\circ\text{C}$. Both species can be released from the matrix and provide pitting inhibition, as shown in exposure tests in 0.1 M NaCl and in polarization experiments (see Figure 7) (Shi et al., 2010).

Polyaniline demonstrated a self-healing ability on AA2024 in combination with a silica-based sol-gel coating due to its ability to undergo oxidation-reduction reactions.

Immersion into acidic and neutral 3.5% NaCl solutions revealed a protective performance up to 24 months, and 500 h of SST were passed without signs of corrosion or undercutting (Akid et al., 2011).

Hybrid sol-gel coatings were evaluated in a large diversity with enhanced physico-chemical and morphological properties. They are becoming a serious candidate for “smart” protection systems due to combining good barrier properties and effective self-healing (Khobaib et al., 2001; Figueira et al., 2015; Gonzales et al., 2018). Nevertheless, despite their worthy performance in the corrosion protection of AAs, this technology has to be examined more intensively in combination with sustainable aerospace paint systems, as research was frequently conducted with chromate-based primers and/or topcoats (Osborne et al., 2001; Voevodin et al., 2003).

7 Coatings with stimulus-related inhibitor release

Nanostructured components can also be used to incorporate corrosion inhibitors into hybrid sol-gel systems and

Figure 7: (A) Images of AA7075-T6 substrate uncoated and coated by hybrid silica (GTS-D-R) and by silica-Ce (GTS-Ce-D-R) coatings during an immersion test for 50 days in 0.1 M NaCl at room temperature. Images were taken after different times of immersion. (B) Potentiodynamic polarization curves recorded in 0.1 M NaCl, after 1 h of stabilization, with a scan rate of 1 mV/s, for AA7075-T6 both uncoated and coated by hybrid GTS and for silica-Ce coatings GTS-Ce subjected to curing with (GTS-D-R and GTS-Ce-D-R) and without ramp (GTS-D and GTS-Ce-D). Reprinted with permission from reference Tiringier et al., (2018), Springer Nature 2019.

to confer it with a self-healing ability. Thereby, the use of “smart” micro- or nanocontainers intends to negotiate the drawbacks associated with free inhibitor occlusion and stability decrease due to interactions with the polymer matrix (Garcia-Heras et al., 2004; Zheludkevich et al., 2012; Figueira et al., 2016). The triggering mechanisms for inhibitor release comprise mechanical damage, ionic interaction, light irradiation, or pH change, and the types of containers can be categorized into container layer, inorganic nanocontainers, organic nanocontainers, and layer-by-layer assemblies (Yasakau et al., 2017). A cost-effective layer-by-layer deposition of silica nanoparticles loaded with the inhibitor benzotriazole in combination with polyelectrolyte molecules significantly improved the long-term corrosion resistance of AA2024 specimens and provided effective inhibitor storage together with a pH-stimulated release “on demand” (Shchukin et al., 2006). A similar behavior was observed for SiO₂ containers loaded with 2-(benzothiazol-2-ylsulfanyl)-succinic acid (Skorb et al., 2009).

Layered double hydroxides (LDH) represent another type of corrosion inhibitor reservoirs and consist of stacks of positively charged metal hydroxides (brucite type) and stabilizing anions and/or solvent molecules, which are electrostatically bound between these layers. The release of inhibitor follows an anion-exchange mechanism and can be triggered by the pH change during the corrosion process. Additionally, LDHs may entrap aggressive anionic species such as chlorides (see Figure 8G), while markedly enhancing the corrosion resistance of AA2024 specimens when dispersed in a mixed Zr/Si sol-gel coating or as a stand-alone addition (Poznyak et al., 2009;

Álvarez et al., 2010a; Yasakau et al., 2014, 2018). Patents demonstrating the ease of application with promising results in the corrosion protection of AAs are available (Lida et al., 2013). LDHs doped with, e.g. cerium or vanadate species were also investigated as stand-alone coatings or as nanocontainers for hybrid sol-gel systems. The corrosion resistance in electrochemical measurements on AAs during immersion in aggressive electrolytes were significantly improved, as shown by simple exposure tests and EIS results (see Figure 8A–F, H, and I) (Buchheit et al., 2002; Zheludkevich et al., 2010; Tedim et al., 2011, 2014; 2016; Liu et al., 2015; Wu et al., 2017; Zhang et al., 2017). However, the hydrothermal conditions during the immersion procedure can be a determining factor regarding industrial applications.

The establishment of active corrosion protection for aeronautical AAs by the modification with encapsulated corrosion inhibitors was mainly investigated for hybrid sol-gel coatings and revealed great promise in terms of efficient container storage. Various reports have appeared in the recent years, which address the modification of sol-gel systems with porous nanocontainers or LDHs (Zheludkevich et al., 2005; Lamaka et al., 2006, 2007; Tedim et al., 2010). The latter are relatively easy to synthesize and provide the opportunities for a large range of potential inorganic and organic inhibitors due to their anionic exchange ability. Nevertheless, according to a valuable issue summary, which was recently published by Yasakau et al., some important points must be tackled in the near future in order to allow an industrial uptake (Yasakau et al., 2017). The load capacity of the containers should be increased, the efficiencies of the

Figure 8: (A) Optical photos of the AA2024 surface after 15 days of immersion in (A) 0.05 M NaCl, and 0.05 M NaCl doped with (B) LDH- H_xPO_4 , (C) LDH-MBT, (D) LDH- VO_x , (E) LDH- H_xPO_4 /LDH- VO_x , and (F) LDH-MBT/LDH- VO_x . (G) Schematic view of the LDH action in corrosion protection: the release of inhibitors (Inh^-) is triggered by the presence of anions in solution (Cl^-). (II) LDHs play a double role, providing inhibitors to protect the metallic substrates and entrapping aggressive species from the environment. Reprinted with permission from reference Tedim et al., (2010), ACS 2019. (H) SEM images of the bare substrate (left) and Zn-Al LDH intercalated with $\text{V}_2\text{O}_7^{2-}$ (right). (I) EIS spectra of AA2024 plates immersed in 0.05 M NaCl for 1 month. Reprinted with permission from reference Tedim et al., (2011), RSC 2019.

current inhibitors are amendable and should be further improved, the compatibility of the container to the hybrid matrix should be optimized, and their shelf life must be enhanced. Furthermore, the ease and speed of immersion and/or spray application regarding oversized aerospace components, which is provided by alternative CC methods described above, is still not met by nanocontainer-modified systems.

8 Conclusions

Trivalent chromium became a standard alternative for chromate-based coatings and is increasingly envisaged by the aerospace industry due to its promising corrosion protection for AAs. However, the transient presence of

hexavalent chromium could be inconsistent with legislative restrictions, as it is highly toxic and carcinogenic. Future research should be related to the ultimate appearance of Cr^{6+} depending on the preparation conditions.

Cerium salts were extensively studied as direct additives as well as main components in the field of RECC and frequently showed similar corrosion protection to CCCs. The deposition mechanism is somewhat dependent on the surface chemistry and nature of the counter ion. Generally, cathodic inhibition is expected to be the predominant mechanism, but anodic or mixed protection was also observed. The application of synergistic inhibitor combinations is a strategy that provides even higher corrosion protection and allows the use of smaller pigment amounts, which may render them very attractive for industrial implementation. Furthermore, while most reports are based on dual combinations, mixtures that are

more complex can be prepared aiming at increasing the inhibitive efficiencies.

Zr/TiCCs achieved good results on AAs considering corrosion protection as well as paint adhesion and seem to fulfill many criteria for an environmentally friendly pre-treatment. Additionally, the low concentration of ionic species in the conversion baths may prevent issues in terms of sludge waste formation. The corrosion inhibition of Zr/TiCCs is mainly associated with the barrier properties of the coating; however, additive incorporation can upgrade the functionality by providing self-healing mechanisms. However, further understanding of the interactions that take place between the CC and an organic topcoat is required in order to improve the general adhesion and cathodic delamination processes. Thereby, the assessment of a pre-treatment layer alone does not provide sufficient information about the performance of a full coating system.

Hybrid sol-gel coatings for the protection of AAs have become a very complex and fast-growing issue with an exponential increase in the number of scientific reports over the last decades. A large variety of compositions is already available including optimized physico-chemical, morphological, as well as mechanical properties. The wide range of organic monomers and inorganic nanoparticles makes it worthwhile to explore possible hybrid combinations with tailored properties in the near future. Moreover, the possibility of forming barrier layers with intelligent self-healing characteristics (i.e. with inhibitor encapsulation) render them a serious “green” candidate for the replacement of chromates. However, technically more integrated solutions are necessary as the developments of less complex formulations and preparation conditions for industrial implementation are still at an early stage. Furthermore, compatibility testing with industrial paints is still insufficient for assessing their aerospace relevance.

In the last decade, several reports appeared concerning the potential of lithium-containing coatings for the protection of AAs. This technology will probably become an interesting alternative for chromates due to their concomitant features of barrier properties and leaching-assisted self-healing (Visser et al., 2015, 2016; Liu et al., 2016b; Gharbi et al., 2018; Marcoen et al., 2018). These novel protection systems provide active inhibition and comprise a three-layered structure with a dense inner layer, a porous middle layer, and a flake-like upper layer. Electrochemical measurements confirmed promising corrosion protection of these layers with some long-term potential. However, this technology is still at an early stage of research in the field of CCs and far from industrialization.

Today, the vast majority of explored alternative technologies for CCCs show great promise in terms of corrosion inhibition performance for AAs. However, scale up and cost considerations for their industrial application are still in the early stages of development. Furthermore, experimental results about long-term exposition to aggressive environments and adhesion performance with organic topcoats are rarely reported in the literature and should be addressed more intensively. At the same time, the development of new CC designs and experimental methodologies allows a progressive understanding of the fundamental chemical mechanisms and factors that trigger the corrosion processes on AAs.

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