

Review

Review of Cr-Free Coatings for the Corrosion Protection of Aluminum Aerospace Alloys

Fabienne Peltier ^{1,*}  and Dominique Thierry ² 

¹ French Corrosion Institute, 29200 Brest, France

² Rise Kimab, 16440 Kista, Sweden; dominique.thierry@ri.se

* Correspondence: fabienne.peltier@institut-corrosion.fr

Abstract: Aluminum alloys are known to have many advantages (e.g., light weight and low cost) but they are not immune to corrosion. So, it is important to assess their corrosion behavior, in particular under atmospheric conditions. To protect aluminum alloys against corrosion, paints are generally applied onto the materials. Corrosion protection in the aerospace industry consists of a conversion or anodized coating, an inhibited primer, and a top-coat. Chromate conversion coating (CCC) and primers containing chromate pigments have been widely used in the aerospace industry over the last decades. However, new environmental regulations have led to major changes for aluminum corrosion protection. By limiting or prohibiting some chemicals, for instance Cr(VI), the European regulation REACH (Regulation on Registration Evaluation, Authorization and Restriction of Chemicals) has induced major changes to some of the finishing processes of aluminum alloys (e.g., chromate conversion, chromic acid anodizing, and chromate sealing). Interesting results have been obtained while seeking replacements for Cr(VI), for example, with the incorporation of cerium, lithium salt, or nanocontainers loaded with corrosion inhibitors in organic coatings. For several years, hybrid sol-gel coatings able to replace the pre-treatment and primer steps have been under development, showing interesting results. New prospects for the future involve the use of photopolymerization to reduce the energy-intensive heat treatment needed in sol-gel technology. It will also be necessary to test these new technologies in service conditions or in accelerated corrosion tests before being able to conclude on the real effectiveness of these coatings. This review summarizes the recent developments in Cr-free coatings for aluminum alloys. Their advantages and drawbacks are also discussed.

Keywords: chromate replacement; Cr-free; coatings; corrosion; aluminum



Citation: Peltier, F.; Thierry, D. Review of Cr-Free Coatings for the Corrosion Protection of Aluminum Aerospace Alloys. *Coatings* **2022**, *12*, 518. <https://doi.org/10.3390/coatings12040518>

Academic Editor: Alexander D. Modestov

Received: 15 March 2022

Accepted: 8 April 2022

Published: 11 April 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

In recent years, much research has been completed on the development of hybrid and organic coatings loaded with corrosion inhibitors (e.g., pigments and additives). Under specific stimulus (pH, mechanical rupture, etc.), coatings can provide the protection of a substrate. In recent years, the use of environmentally friendly compounds in coating formulations has become the most important aspect of coating design [1]. For example, sol-gel coatings are constituted by a silica-rich layer which, in addition to being thin, has very good mechanical properties. This type of coating can be used as a pre-treatment or primer on different alloys, and their protection performances are dependent on their thicknesses and final barrier properties. Another alternative to Cr(VI) could be the encapsulation of nanocontainers or inhibitor reservoirs dispersed in the coating matrices. Unfortunately, the developed systems have mostly been applied to steel substrate, and results on aluminum alloys are still limited [2,3]. As an environmentally friendly replacement for chromate conversion coating, the trivalent chromium process (TCP) has been developed as a treatment, showing an effective barrier to protect aluminum against corrosion attacks [4]. The use of Vanadate, cerium or lithium salt as inhibitors has also presented interesting results [5–7].

The aim of this review was to discuss the conventional paint systems used for 2xxx and 7xxx aluminum alloy protection based on Cr(VI) technology and the alternatives developed to replace them in recent decades. Their advantages and drawbacks will be also presented.

2. Generalities on Corrosion Mechanisms in Aluminum Alloys

Corrosion corresponds to the degradation of a material due to reactions with aggressive species (such as chloride and pollutants) [1]. Many studies have been performed on aluminum and its alloys [8,9], showing that the type of corrosion of a material depends on the chemical composition and the microstructure of the alloy, the chemical composition of the environment, some physical parameters (temperature, irradiation, etc.), and mechanical solicitations (stress, friction, etc.). Hence, different forms of corrosion may occur. The following paragraphs describe the type of corrosion detected on 2xxx and 7xxx aluminum alloy series which are mostly used in aerospace industry. The aluminum–copper (2xxx series) alloys are the primary alloys used in airframe structural applications where the main design criterion is damage tolerance. The aluminum–zinc (7xxx series) alloys show higher strength compared to other alloys, and are selected in the fabrication of upper wing skins, stringers, and horizontal vertical stabilizers. Uniform corrosion is mostly encountered on aluminum alloys, and it is defined as the least dangerous form of corrosion because the entire surface of the material is attacked at the same corrosion rate. Localized corrosion is the second type of corrosion observed on aluminum alloys, with different morphologies as described in the following sections.

→ Pitting corrosion

According to Landolt and Huisert, pitting corrosion occurs on a metal with passive oxide layers under the action of chloride or other aggressive ions [8,10]. It induces some cavities of few tens of micrometers in diameter, as shown in Figure 1. The occurrence of a pit is linked with the presence of heterogeneities at the surface, which determine the formation of anodic sites. The danger of this type of corrosion lies in the fact that propagation in the depth of the corrosion pit can lead to metal perforation. The presence of corrosion products in the orifice of the pit and the high oxygen concentration at the metal surface can promote pitting corrosion.



Figure 1. Pitting corrosion observed on AA 2050 T8.

→ Intergranular corrosion

Intergranular corrosion is a localized attack along the grain boundaries stemming from the microstructure of metals and alloys, or the intermediate vicinity of polycrystalline metal (Figure 2). The electrochemical potential difference between the bulk of the grain and the grain boundaries, coming from the precipitation of intermetallic phases, is the principal cause of intergranular corrosion.

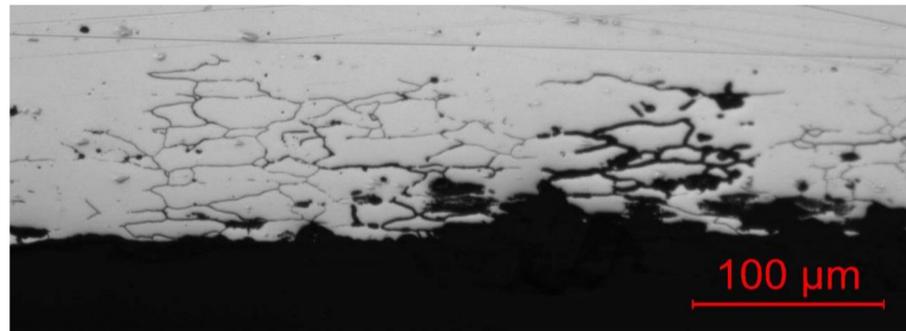


Figure 2. Intergranular corrosion observed on AA 2024 T351.

Although intergranular corrosion is clearly linked with the initiation of pitting corrosion, there is no link between the penetration depth and the diameter of the pit [9]. In the case of intergranular corrosion, the metal loss is insignificant, but the properties of the materials are completely affected and lead to the rupture of the components. This type of corrosion is often connected to chemical segregation effects (impurities tend to be enriched at grain boundaries) or specific phases precipitated at the grain boundaries.

→ Exfoliation corrosion

Exfoliation corrosion is another form of intergranular corrosion associated with high strength aluminum alloys. It is a type of selective corrosion that propagates along many planes, running parallel to the rolling direction (Figure 3) [9].

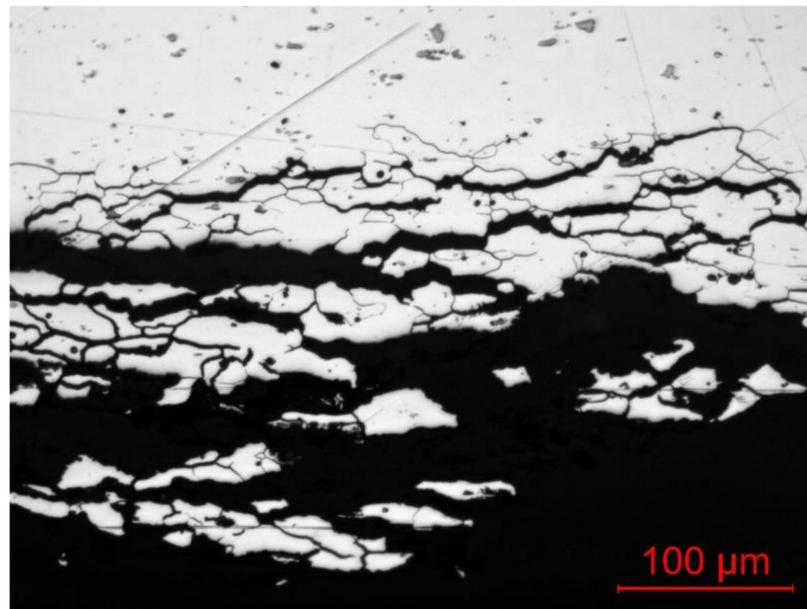


Figure 3. Exfoliation corrosion on AA 2024 T351.

→ Galvanic corrosion

Galvanic corrosion is induced when two (or more) dissimilar materials are coupled in a corrosive electrolyte or under atmospheric conditions. When a galvanic couple forms, one of the metals in the couple becomes the anode and corrodes faster than it would by itself, while the other becomes the cathode and will thus remain immune. Aluminum is very electronegative compared to steel or stainless steel, meaning that many aluminum assemblies are found to be in contact with other metals.

To protect aluminum alloys against corrosion, different types of paint can be applied. Depending on the pieces to be protected and their stresses, different approaches can be followed, e.g., passive protection or barrier effects, active protection, inhibitive effects, etc.

3. Mode of Corrosion Protection: Cr(VI) as a Reference

The corrosion protection system in the aerospace industry consists of a conversion or anodised coating, an inhibited primer, and a topcoat, as depicted in Figure 4.

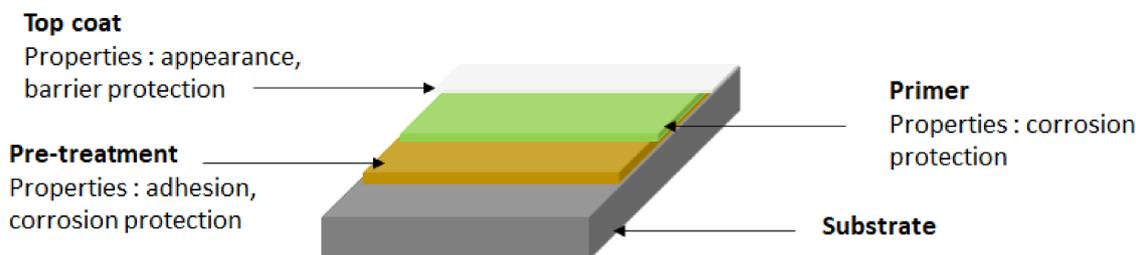


Figure 4. Schematic illustration of a coating system for corrosion protection in aircraft structures.

Often, the first layer is a chromate conversion coating (CCC). As described by Twite et al. and Martinez-Viademonte et al. in their respective review, the layer is very thin (<10–60 nm), provides corrosion protection, and improves adhesion between the substrate and the primer [5,11]. The primer provides similar functions to the first layer, but it is constituted of a pigmented (Cr(VI)) organic resin matrix. The application thickness of the primer can vary from 5 to 200 μm . According to Twite et al., typical formulations consist of both chromated (such as BaCrO_4 or SrCrO_4) and non-chromated pigments enveloped in an epoxy polyamide matrix together with other compounds such as fillers, UV absorbers, and coloring agents [5]. Finally, a topcoat is applied to act as a barrier against environmental degradations such as extreme climates and ultra-violet rays. The protection system therefore provides a barrier to the ingress of moisture and corrosive agents, but also contains an inhibitive reservoir that is available to heal defects in the coating by releasing inhibitors and forming a protective layer in the defect, as presented in Figure 5 [12].

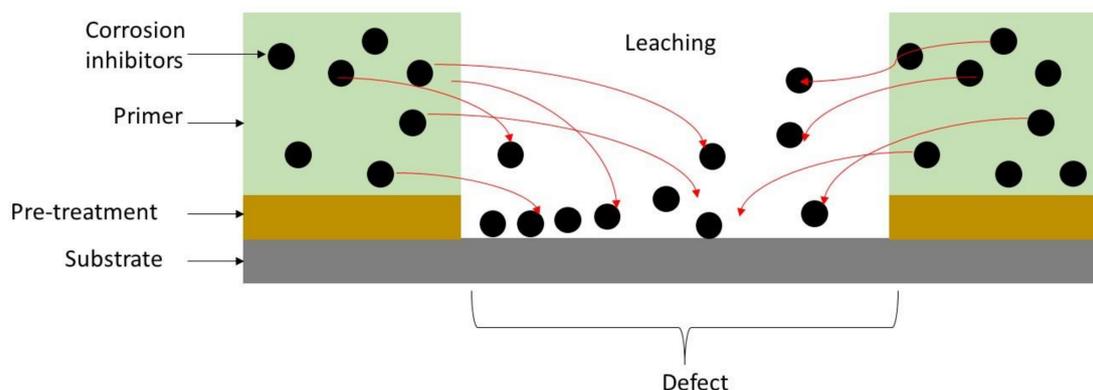


Figure 5. Schematic representation of the corrosion inhibitors leaching from the primer.

As mentioned previously, chromate inhibitive pigments were mostly used in the past. As reported by Snihirova et al., these pigments are very efficient against corrosion because they can inhibit corrosion in active areas [1]. Indeed, without chromate inhibitive pigments, the oxygen reaction reduction (ORR) quickly triggers coarse intermetallic particles (Al_2Cu , Al_2CuMg) leading to the attack of the intermetallic layer due to alkalization in extreme conditions (see Figure 6a). However, in the presence of chromate, the cathodic inhibition involves the reduction of Cr(VI) to Cr(III), which adsorbs on the Cu-rich particles and suppresses the oxygen reduction reaction (see Figure 6b).

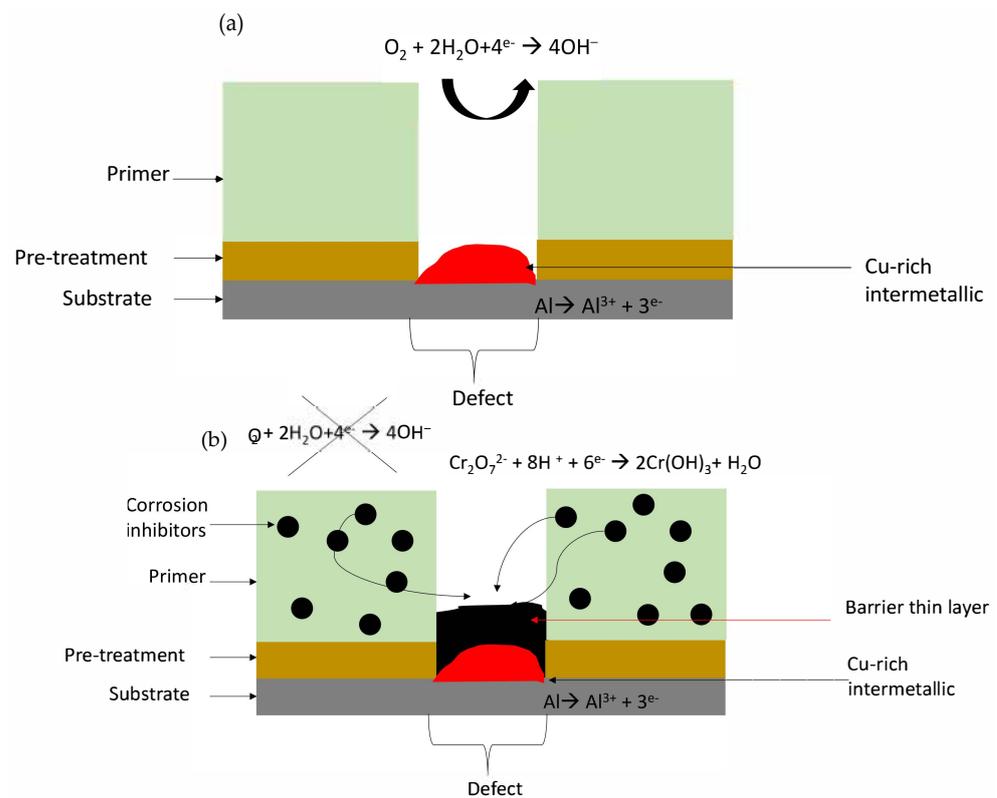


Figure 6. Scheme representing the mechanisms of corrosion (a) and protection by Cr(VI) (b) of aluminum alloys.

According to Kendig et al., the effectiveness of this coating is due to its oxidant power, water solubility, and the passive nature of its reduction products [13].

It was also reported by Vanderkloet et al. that the corrosion protection by CCC film could be attributed to several factors including the inhibition of oxygen reduction kinetics, an increase in film resistance, and the presence of residual unreacted Cr(VI) in the protective film [14,15]. This film can act as a reservoir in which the unreacted Cr(VI) pigments can be reduced when the aluminum surface is exposed via film cracks or defects, thereby regenerating the protective oxide film. This phenomenon was demonstrated by Scholes, Furman and Lee, who studied the kinetics of release of chromate ($SrCrO_4$) from polyester primer immersed in 5% (*w/v*) NaCl at different times [16–19]. They reported an increase in chromate conversion with the time of immersion, and highlighted the inhibiting effect on corrosion when the chromate was released from the coating of a defect. However, they also showed that once the corrosion was initiated, the presence of chromates had no influence on the corrosion, but corrosion did not occur if the chromates were initially present in the solution.

However, due to environmental regulations, an effort to minimize Cr(VI) release into the environment has been made. Thus, several types of coating formulations loaded with pigments, nanocontainers, or corrosion inhibitors (e.g., salt) are in or under development.

4. Development of Cr-Free Coatings and Treatment as Alternative to Chromates

Thanks to the application of coatings, corrosion can be limited and controlled by different mechanisms.

According to Nazeer et al., different mechanisms hinder the corrosion of aluminum alloys: (1) cathodic protection, (2) anodic passivation, (3) electrolytic inhibition, and (4) active corrosion protection [20]. Cathodic protection is accomplished by a coating with a highly electro-positive metal that polarizes the substrate and behaves as an approximate anode. The anodic passivation consists of the formation of a passivating layer on

the metal surface that inhibits the redox reduction by generating an ion-selective barrier. Electrolytic inhibition prevents corrosion by hindering the ion migration between the anode and cathode using a matrix with low conductivity and diffusion barriers.

On the other hand, active corrosion inhibition involves components that are released selectively after damage to the coating to reconstruct a protective barrier at the metal–environment interface. This type of coating is considered a smart coating. These materials can adapt their properties dynamically to an external stimulus. These coatings can heal or repair damages automatically and independently, without any external intervention. For these materials, two strategies have been pursued: (1) the mending of defects formed in the polymeric coating matrix via the addition of polymerizable agents; (2) the inhibition of corroding areas due to the presence of corrosion inhibitors [20]. In the following section of this review, the different types of pre-treatment and primer presenting interesting results as alternatives to Cr(VI) are presented.

4.1. Conversion Coatings or Anodizing

As mentioned previously, the first layer of a painted system is often a chromate conversion coating, or involves electrochemical anodizing. This first layer must promote adhesion and improve corrosion resistance of the coating. According to Martinez-Viademonte et al., anodizing is an electrolytic process that replaces a few nanometers of the native aluminum oxide with an oxide layer up to 20 μm . [11]. An inconvenience of the anodizing step/process is the detrimental effect on the fatigue properties of the alloy, which decrease with the increase in oxide film thickness. The chromic acid anodizing process (CAA) is very interesting considering the balance between corrosion protection, adhesion, and fatigue properties. However, due to REACH (Regulation on Registration Evaluation, Authorization and Restriction of Chemicals) legislation, an alternative had to be developed [21].

Two classes of electrolyte were reported by Martinez-Viademonte et al. to replace CAA:

- Phosphoric acid-based and alkaline electrolytes;
- Sulfuric acid-based [11].

The first class show good adhesion properties but poor corrosion protection performance, while the second class of electrolyte have the opposite behavior, due to the morphology (dense and porous) of the oxide.

According to the authors, different forms anodizing have emerged, such as phosphoric acid anodizing (PAA), phosphoric-sulfuric acid anodizing (PSA), sulfuric acid anodizing (SAA), and tartaric-sulfuric acid anodizing (TSA). Unfortunately, one type of process is not enough to be used across the entire range of necessary applications. For example, the phosphoric acid-based process (PSA, PAA) will be used for structural bonding applications, while tartaric-sulfuric acid anodizing (TSA) will be employed for corrosion protection applications.

Concerning the replacement of chromate conversion coating, several studies conducted by Khramov et al. [22–24] and Voevodin et al. [25] have shown the advantages of nanostructured inorganic/organic hybrid conversion coatings for the long-term protection of aluminum alloys against atmospheric corrosion. This approach, known as the self-assembled nanophase particle (SNAP) process, consisting of two steps, is based on a combination of the sol–gel processing of organo-functional silanes, and a conventional coating formation process, as presented in Figure 7. The formation of organosilica nanoparticles with the peripheral epoxy functional group represents the first step of synthesis of SNAP coatings. The second step consists of a reaction between amino and epoxy functionalities, allowing the nanoparticles to crosslink together. The coating formation at the surface of the substrate is the product of the evaporation of the solvent, the crosslinking, and the assembly of the nanoparticles.

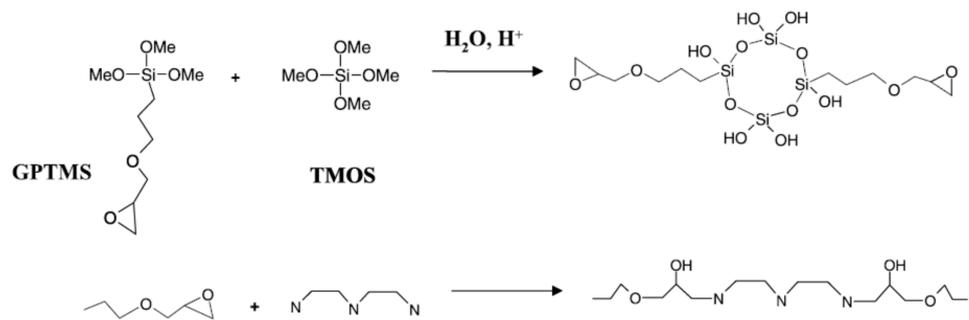


Figure 7. Schematic diagram of the SNAP coating process. Reprinted with permission from Ref. [24]. Copyright 2003, Elsevier.

The advantages of SNAP coatings are their excellent adhesion and barrier properties for high-strength aluminum alloys. However, their main drawback is their limited corrosion protection performance when the coating is damaged [23]. To overcome this problem, different methods can be followed. First, the addition of amino-silanes as a crosslinking agent was tested to obtain coatings with higher crosslinking to allow the formation of a very stable, continuous, and highly adherent protective film on the metal surface [24]. Different coatings with several crosslinking agents (Mono-, di- and tri-functional amino silanes) were studied. By the potentiodynamic scans of 0.35 wt% $(\text{NH}_4)_2\text{SO}_4$ and 0.05 wt% NaCl, presented in Figure 8, Khramov et al. showed that all coated samples reduced corrosion currents compared to that of the aluminum alloys. The same conclusion was obtained by scanning vibrating electrode technique (SVET) measurements, which indicated good protection properties of the coating [24].

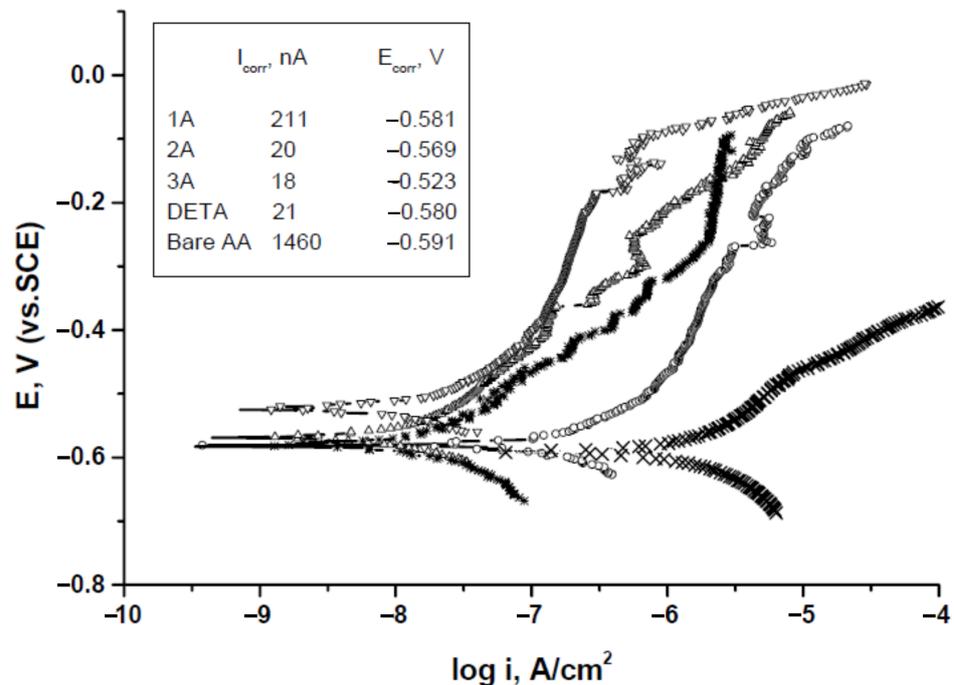


Figure 8. Potentiodynamic scans of 2024 T3 aluminum alloys where SNAP coatings were applied and prepared with several crosslinking agents (1A: 3-aminopropyltrimethoxysilane (\circ), 2A: 3-(2-aminoethyl)aminopropyltrimethoxysilane (Δ), 3A: 3-(trimethoxysilyl) propyldiethylenetriamine (∇), DETA: diethylenetriamine ($*$) and bare AA 2024 T3 (\times). Reprinted with permission from Ref. [24]. Copyright 2003, Elsevier.

Another way to improve the protection performance of this type of coating is by incorporating corrosion inhibitor into the coating. However, Khramov et al. highlighted the difficulty in controlling the release of the entrapped inhibitors from the coating film [23]. If this is too fast, the protection will be limited after long-term exposure. If it is too slow, a competition will emerge between the release, the transport of the inhibitors, and the initiation of the corrosion in the defect. The authors showed that the solution could be the incorporation of corrosion inhibitors into the coating material as inclusion complexes with cyclodextrin [22,23]. In this method, the inclusion complexes would be bulkier and more easily trapped within the cross-linked nanoporous coating, making it more difficult for the inhibitor leach out, and thus prolonging the inhibition effect of the doping agent. The release of inhibitors and the restoring of a defect in a coating over a long period can also be ensured by the slow delivery of an inhibitor from the molecular cavity of β -cyclodextrin. In their work, Khramov et al. studied the behavior of SNAP coating with the encapsulation of mercaptobenzothiazole (MBT) and mercaptobenzimidazole (MBI) as corrosion inhibitors, in both the presence and absence of β -cyclodextrin [23]. By SVET measurements, they observed the improvement of the corrosion protection with these two corrosion inhibitors in presence or absence of β -cyclodextrin, but formulations containing β -cyclodextrin demonstrated superior corrosion protection properties. This result was explained by the slow delivery of the corrosion inhibitor from the cyclodextrin/inhibitor inclusion complexes, followed by the restoring of the defects in the coatings.

The corrosion resistance of scribed SNAP coating was also demonstrated by Voevodin et al., using salt spray according to ASTM B117 for 2000 h [25]. Corrosion products were visible in the scribe but no underpaint corrosion was noted, thus attesting to the resistance of this type of technology.

Another alternative to chromate conversion coatings (CCCs) is the trivalent chromium process (TCP) treatment [4]. This type of conversion coating was found to form a dense layer of particles of hundreds of nm on the coating surface, similar to CCCs. TCP is considered to be an environmentally friendly replacement for chromate conversion coatings because the TCP bath and the resulting film contain no Cr(VI) species and only Cr(III). Indeed, as explained by J-T Qi et al., a trivalent chromate conversion coating bath contains ZrF_6^{2-} , Cr^{3+} and SO_4^{2-} [26]. However, the question of the possible re-oxidation of Cr(III) to Cr(VI) has arisen. Indeed, recent research has reported that Cr(VI) species are present in coatings after ageing in air, or following a corrosion test in sodium chloride solution [26–29]. Another work considered the possibility of the oxidation of Cr(III) species by hydrogen peroxide generated by the reduction of oxygen in copper-rich particles in an AA2024 alloy in a sodium chloride solution [29].

The coatings obtained with TCP have a two-layered structure with zirconium-chromium mixed oxide in the outer layer and aluminum oxide or oxyfluoride at the metal–coating interface.

An increase in the breakdown potential on AA2024-T3 coated with a trivalent chromium process coating was shown by Guo and Frankel [4]. This can be explained by the formation of chromium oxide or oxyhydroxide layers at the surface of the AA2024-T3, which act as an effective barrier to protect the matrix against corrosion attacks by suppressing the oxygen reduction reaction.

Yu et al. [30] noted the same results on AA 6063 aluminum alloys coated with a trivalent-chrome coating ($KCr(SO_4)_2$) in 3.5 wt% NaCl. They showed that the deposition of Cr^{3+} on the aluminum alloys decreased the corrosion current density and shifted the corrosion potential towards the more positive region, as shown in Figure 9.

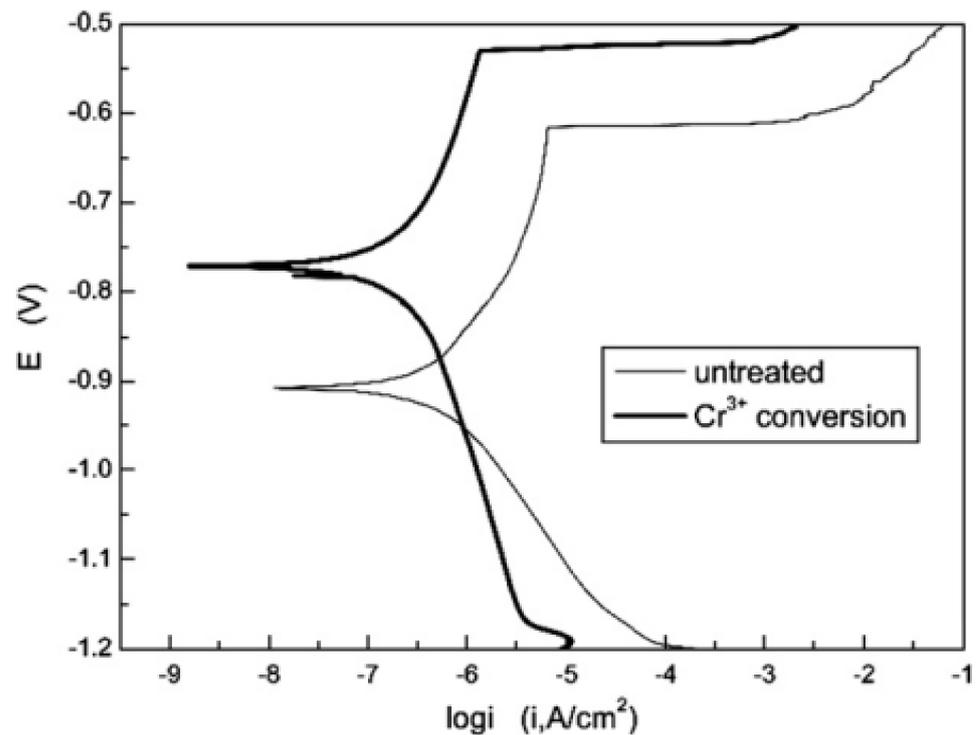


Figure 9. Polarization curves of the 6063 Al alloy without and with Cr^{3+} surface treatment in 3.5% NaCl solution at room temperature. Reprinted with permission from Ref. [30]. Copyright 2008, Elsevier.

To replace CCC, Buchheit et al. studied the corrosion resistance of the conversion coating formed on aluminum alloys (6061-T6, 7075-T6) after pre-exposure to CeCl_3 [31].

The conversion coating consisted primarily of hydrated Al_2O_3 with Ce deposited on intermetallic particles as $\text{Al}_7\text{Cu}_2\text{Fe}$ in AA2024. The corrosion protection mechanism consisted of the release of Ce from the coating to the defect sites to inhibit corrosion (behavior analogous to chromate). Similar results were described by Lakshmi et al. [32] who showed the corrosion performance of silica–alumina-based sol–gel coating containing cerium oxide nanofibers. By electrochemical impedance spectroscopy, after 336 h of the neutral salt spray test (NSST), they observed a good resistance to corrosion due to the high concentration of active Ce^{3+} on the nanofiber surface, which efficiently blocked the corrosive sites with insoluble precipitations. After 336 h of the NSST, no blistering or peeling off was seen on the painted coupons.

4.2. Coatings as Pre-Treatment or Primer—The Choice of Corrosion Inhibitors

Different mechanisms of inhibitor corrosion protection have been listed in the literature [7,20,33–36]. Three main mechanisms can be mentioned:

- (1) The inhibitor is absorbed at the metal surface and forms a thin protective layer directly due to the effect of the inhibitor or by a reaction of the ions from the inhibitor and the metal surface;
- (2) The inhibitor reinforces a pre-existing barrier; the oxide layer or hydroxide naturally form in the medium or in the alkaline environment. These inhibitors are known as passivating inhibitors;
- (3) The inhibitor reacts with a corrosive medium species and forms a protective complex which acts as a protective barrier.

These corrosion inhibitors can be classified in different ways, according to their electrochemical mechanisms or their nature (organic or inorganic).

Several inhibitors have been tested as an alternative to chromate in pre-treatments and primers. This part of the paper describes the different types of systems studied.

4.2.1. Inorganic Corrosion Inhibitor

In their review, Kendig et al. classified inorganic corrosion inhibitors into three categories [13].

(1) Reducible hypervalent transition metals (Mo, Vn, Mn, Tc). Some studies have been performed on permanganate, but with the difference of Cr this element is thermodynamically unstable except in alkaline solutions where it is inert [13].

By the formation of a stable oxide layer, technetates (Tc) behave like chromate and inhibit corrosion on ferrous materials [13]. Vanadate and molybdate also hinder corrosion when they are combined with tungstate or permanganate.

Kharitonov et al. investigated the corrosion properties of AA6063-T5 in molybdate-containing NaCl (0.05 M) [37]. By spectroscopic measurements, they observed the formation of a layer consisting of mixed Mo (VI, V, IV) species. This layer was able to provide inhibition with an efficiency of 90% after 4 h of immersion in molybdate-containing NaCl solution, which decreased to 70% after one week of immersion. The mechanism of corrosion inhibition highlighted by the authors was the formation of a mixed-valence Mo(V) and Mo(VI) compound by the reduction of Mo(VI) to Mo(IV) on intermetallic particles, following by oxidation. The effectiveness of molybdate and permanganate was also studied by Moutarlier et al. [38]. By polarization measurements in 5% NaCl and GDOES (glow discharge optical emission spectroscopy), they showed that molybdate and permanganate decreased the sol-gel network stability and were too soluble, resulting in the rapid leaching from the sol-gel films in an aggressive medium. However, due to the sol-gel stability and the low solubility of Cr(III), the corrosion protection was enhanced.

The performance of the inhibitors is also dependent on the application and the matrix used. Indeed, Yoganandan et al. noticed that the use of Mn-Mo oxyanions (PMMO) as sealing agents in sulfuric acid anodization showed comparable corrosion performance in neutral salt spray (1000 h) compared to the chromic acid-anodized (CAA) specimen with no corrosion products on PMMO surface [39].

(2) Difficult-to-reduce transition metal oxides (Zr, Hf, Ta, Ti, Y) and covalent oxides (oxides and mixed oxides of Si, Ge, P, Te). In their highest oxidation state, Nb, Hf, Ti, Zr and Ta elements form very stable oxides. However, the precursors of these oxides are difficult to stabilize in aqueous solution. Peroxo complexes and acid fluorides of Nb, Hf, Ti, and Zr exist at a low pH. They form the basis of several patents. Thin Zr coatings rapidly form a very thin self-limiting layer. Alkoxides of these species can also be used to form stable dispersions (sols), leading to sol-gel routes for coating formation [13].

Santa Coloma et al. studied the corrosion resistance of AA2024 T3 and 7075 T6 coated with a conversion coating based on Zr/Ti/Mn/Mo compounds [40]. By potentiodynamic measurements, they showed a decrease in the current density indicating an obvious improvement in the corrosion resistance, also confirmed by a neutral salt spray test of 168 h. They noted that better results were observed with formulation containing only Zr, Mn and Mo (without Ti). According to the authors, even if the Cr-free conversion coatings did not fully meet the aircraft industry specifications, they could still offer a direction of research.

On the same type of technology, Bouali et al. reported a good corrosion resistance and remarkable adhesion performance to the metallic substrate from zirconium and/or titanium-based conversion (Zr/TiCC) coatings [41]. Mainly used in the automotive industry on 5xxx and 6xxx series, this type of conversion can also be used on aluminum alloys as AA 2024 in the aerospace industry. The use of Zr/TiCCs is energy and cost effective as the formation process requires less time and lower temperatures in comparison to other conversion coatings. Only defined as barrier protective and not as self-healing, the use of this type of conversion coating is limited but can be improved by the addition of corrosion inhibitive agents such as vanadate, cerium, and trivalent chromate into the Zr/Ti formation bath for the corrosion protection of aluminum alloys.

(3) Precipitated coatings (boehmite, hydrotalcite coatings) and rare-earth metal coatings. Markley et al. studied the resistance of epoxy coatings loaded with Cerium diphenyl phosphate ($\text{Ce}(\text{dpp})_3$) and mischmetal diphenyl phosphate ($\text{Mm}(\text{dpp})_3$) to under-paint corrosion [34]. The two coatings were scribed (10 mm in length) and then exposed to HCl vapor as per standard DIN65472, with the initiation time reduced to 15 min (instead of 1 h). After this initiation step, the samples were exposed during 1000 h at 80%RH and 40 °C. In this way, optical microscopy showed the reduction in the number of filaments and the decrease in the maximum length of filaments. By calculating the growth rate (average filament length divided by the duration of the test), they demonstrated the decrease in this parameter in the presence of inhibitors, compared to the coating without the inhibitors. Based only on the growth rate, they showed a better inhibitive effect of $\text{Ce}(\text{dpp})_3$ compared to $\text{Mn}(\text{dpp})_3$.

However, using Fourier Transform Infrared (FTIR) measurements, they showed that the $\text{Mm}(\text{dpp})_3$ compound interacted chemically with the epoxy/solvent combination used which resulted in some degree of crosslinking, allowing sufficient inhibition from leaching to the damaged area of the coating. Thanks to water uptake, they also noticed a greater water absorption for the epoxy containing $\text{Ce}(\text{dpp})_3$, and consequently a greater inhibitor compound solubility.

Epoxy silicate sol-gels containing different percentages of cerium salts (cerium (III) chloride, cerium (III) nitrate hexahydrate, and ammonium cerium (IV) nitrate) were investigated by Kasten et al. as coatings for the aluminum alloy AA 2024 T3 [42]. By X-ray Photoelectron Spectroscopy (XPS) and Electrochemical Impedance Spectroscopy (EIS), they noted that the addition of Cerium, whose oxidation state remains stable in sol-gel coatings, improved the corrosion protection of 2024-T3 aluminum alloys.

Similar results on the corrosion protection provided by the cerium-containing coatings were presented by Terada et al. [43]. The mechanism of protection was obtained by the suppression of the cathodic oxygen reduction reaction due to the formation of cerium oxide/hydroxide film at the surface of the alloy. As observed in the electrochemical impedance spectroscopy by Buchheit et al., better results were obtained with Ce-modified hydrotalcite conversion coatings [31]. The corrosion resistance in a simulated scratch cell was obtained as a function of exposure time in the 0.05 M NaCl solution for the AA 2024 alloy, Ce-HT-coated AA 2024 T3, and Ce conversion-coated AA 2024 T3. The authors showed that the surface exposed in the simulated scratch cell with the Ce-HT exhibited R_c values nearly an order of magnitude greater than that of a surface exposed only to another bare surface. According to the authors, the release of Ce from the Ce-HT coating allowed the protection of the unpainted surface in the simulated scratch cell.

Metallic magnesium can be also used as a corrosion inhibitor. When two different metals are in contact with an aggressive media, the most active metal will be preferentially corroded; thus, ensuring a sacrificial protection of the most noble metal. This concept is widely used for the protection of steel by primers rich in Zn. Based on this principle, Nanna et al. [33] studied the behavior of primer coatings using particulate Mg-rich pigmentation. To ensure an effectiveness protection, the Mg particles must be in electrical contact with each other and with the substrate. Thus, the coating should be formulated at a concentration near or above the critical pigment volume concentration (CPVC). As shown in Figure 10, Mg-rich primer consists of magnesium particles, and the distance between particles is less than 1 μm covered by a thin layer of binder.

Exposure testing was also performed by Nanna et al. using ASTM D5894-96 on Mg-rich primer hybrid N3300 at 50% CPVC with ELTTM topcoat and compared to the same type of system with a non-Mg-pigmented primer [33]. They noticed that the Mg-pigmented primer gave better performance than the standard chromate-based system with similar topcoat, with signs of failure after 5000 h, while corrosion was observed on the non-pigmented primer after 1800 h.

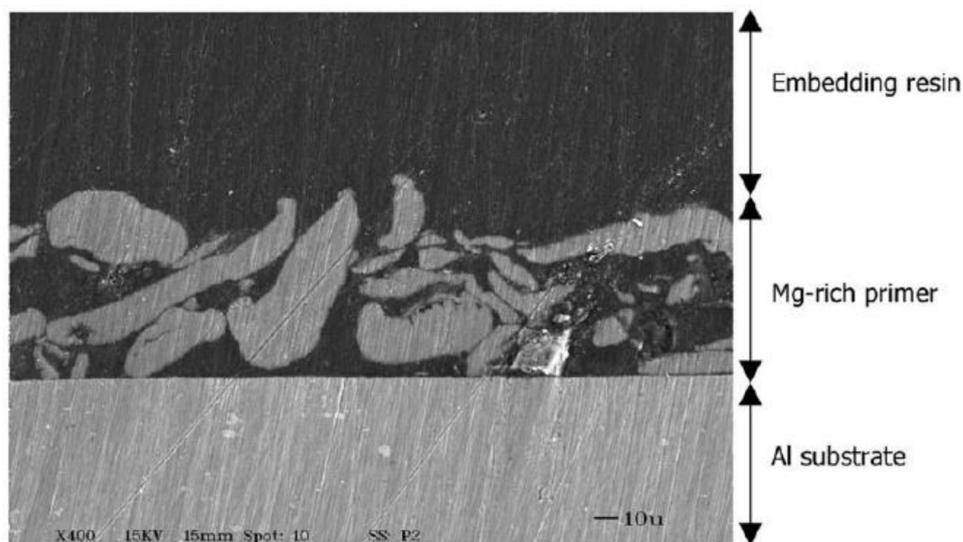


Figure 10. Cross-section micrograph of Mg-rich primer on aluminum alloy. Reprinted with permission from Ref. [44]. Copyright 2006, Elsevier.

The corrosion protection of the AA2024-T3 aluminum alloy with a Mg-rich primer can be extended by adding organic corrosion inhibitors. According to Lin et al., the addition of sodium benzoate (SB), sodium dodecylbenzenesulfonate (SDBS) or 8-hydroxyquinoline (8-HQ) extended the cathodic protection over time while increasing the barrier properties of Mg-rich primers [45]. The addition of these organic inhibitors reduces the rate of consumption of particulate magnesium. However, it appears that the inhibitors not only act on the Mg pigments, but have also an effect on the aluminum substrate.

The drawback of these metallic particles when used as corrosion inhibitors is their coating density, which is incompatible with the lightening of structures required in the aeronautical industry.

4.2.2. Organic Corrosion Inhibitor

(a) Nanocontainers or Reservoir Species

Some inhibitors must be incorporated into coatings at very low concentration to reduce the formation of defects in the matrix. To minimize this risk, the use of reservoirs or nanocontainers can be a good alternative. Indeed, the progressive release of corrosion inhibitors contained in reservoirs compensates for the defects while adding excellent self-healing properties [46].

In their review, Fu et al. reported the use of various containers to encapsulate anticorrosion agents, such as polymeric microcapsules, hollow fibers, layered double hydroxides (LDHs), halloysite nanotubes, and mesoporous SiO_2 , into coating systems [47].

Ideal nanocontainers are characterized by a high loading capacity and the ability to quickly release corrosion inhibitors under stimuli (e.g., defects in the coating, pH, etc.) [48].

The solubility of corrosion inhibitors is an important parameter to consider in order to effectively protect the alloy. Indeed, if the solubility is too low, the concentration of inhibitors in the defect will not provide protection of the substrate and conversely a too high solubility will protect the substrate, but only for a very short time. A high solubility, which is linked to the osmotic pressure, also promotes the appearance of blisters, delamination, and causes the destruction of the passive matrix [46].

The application of nanocontainers can be used for mechanical, pH, or redox responsive intelligent anticorrosion coatings.

I. Stimuli Response for Triggering mechanical rupture

Smart coatings have been developed to protect a substrate when a mechanical stress occurs (e.g., impact scratching, cutting, and pressing), as modeled by Javierre et al. [49].

As shown in Figure 11, Javierre et al. proposed a diffusion model adapted to the mechanisms involved during the activation of a microcapsule. After dissolving, this will release inhibitory species that can be transported to the external surface, constituting the wall of a scratch in contact with an electrolyte. This work is therefore based on the formulation of laws for each step that occurs inside the polymer matrix loaded with microcapsules that can release an inhibitor by dissolution of the encapsulated pigment. The author built his model by successively defining the relative laws:

1. At the water absorption stage of the polymer matrix, assuming a diffusion process, it is possible to define a diffusion front which will interact with the distance “ d_i ”;
2. Then, there is a rupture phase of the capsule which is characterized by a process of dissolution coupled with the diffusion of water in the thickness of the capsule;
3. Finally, the transport of the inhibitor ion results in dissolution in a gradient concentration set by an ion diffusion regime in the polymer.

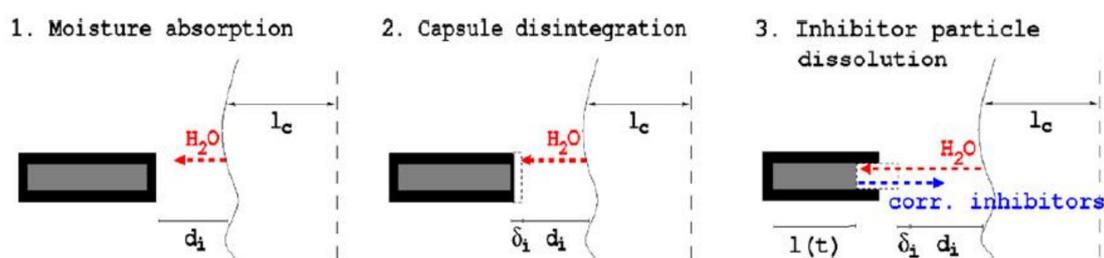


Figure 11. Modelling of the different steps of the nanocontainers' release. Reprinted with permission from Ref. [49]. Copyright 2012, Elsevier.

According to Fu et al., a drawback of this type of nanocontainer can be the large cavity volume of microcapsules, which can compromise the structural stability of the coating matrix, and cause corrosion species permeation from the application environment [47].

Shchukin et al. classified nanocontainers as self-assembled nanocontainers or layer-by-layer-assembled containers (LbL) [46]. Self-assembled nanocontainers are self-organizing block copolymers and liquid nanocontainers which can entrap hydrophobic active materials within their core, while the outer shell confers water solubility. The ratio between the blocks and the concentration of the polymer influences the aggregation of block copolymers into vesicles, spheres, lamellae, rods, and other related structures.

The procedure of LbL nanocontainer construction consists of the templating of LbL-assembled films on the surface of micrometer and submicrometric-sized colloidal particles. The adsorption on the surface of the template particle of polyelectrolytes or other charged species allows it to recharge [46]. According to Zheludkevich et al., the nanocontainers coated with polyelectrolyte shells by the LbL technique are interesting systems due to the pH-triggered mechanism for the release of inhibitors, but their scale up is limited due to the methodology of LbL [50].

Noiville et al. studied the release of Ce(III) corrosion inhibitors from silica and boehmite nanocontainers [51]. The authors demonstrated that a concentration of cerium between 0.2 and 0.6 wt% was optimum, because a higher concentration led to defects in the coating. By the introduction of corrosion inhibitors trapped in reservoirs in the hybrid coatings, this detrimental effect was minimized. By EIS measurements, the authors showed that the chemical nature and the morphology of the nanocontainers had an important effect on the release of inhibitors. The best results were obtained with boehmite nanocontainers loaded with a strong concentration of cerium nitrate (10^{-2} mol/L). In this way, the release of the inhibitors was ensured up to 336 h of immersion in a 0.045 Mol/L NaCl solution. The effect of cerium was also studied by Kartsonakis et al. [52]. By the application of a sol-gel coating synthesized with nanocontainers of cerium and molybdenum oxides, loaded with the anodic corrosion inhibitor 2-mercaptobenzothiazole (2-MBT), they showed the improvement of the corrosion protection of AA2024 T3. The anti-corrosion performance

was attributed to the simultaneous inhibitory action of cerium and molybdate ions with 2-MBT. These reservoirs also have a positive mechanical influence on the coating, since they result in an increase in wear resistance and a decrease in the coefficient of friction.

Sol-gel coatings are interesting due to their compatibility with nanocontainers. Indeed, D. J. Carbone et al. studied the local activity of an AA2024-T3 coated with sol-gel by scanning electrochemical microscopy (SECM) [53]. Corrosion inhibitors were added to the sol-gel, either as soluble chemical species, namely 1,2,3-benzotriazole, Na-(diethyl(dithiocarbamate)), and piperazine, or using Ce(III)-montmorillonite containers. By using nanocontainers filled with Ce(III), the authors showed an enhancement in both the barrier characteristics of the silane layer and the insulating properties towards electron transfer in SECM. They also showed good results with the piperazine. M.L. Zheludkevich et al. and Wang et al. showed similar results with Ce compounds [54,55].

Nanostructured hybrid sol-gel coatings doped with cerium ion were investigated as pre-treatment for the AA 2024-T3 alloy by Zheludkevich et al. [54]. The sol-gel films were synthesized from the tetraethylorthosilicate (TEOS) and 3-glycidoxypropyltrimethoxysilane (GPTMS). Additionally, the hybrid sol was doped with zirconia nanoparticles. The authors showed that the direct addition of cerium nitrate as inhibitors in the coatings or in the nanoparticles led to an increase in the corrosion protection of the AA 2024 T3. Indeed, as presented in Figure 12, the reference coating E, prepared using only the hybrid organosiloxane sol without the addition of ZrO_2 nanoparticles and cerium-based inhibitors, showed a very fast decrease in the resistance of the intermediate oxide layer (R_{oxide}), while the coating D doped with ZrO_2 nanoparticles presented the maximum initial resistance. However, the resistance dropped relatively quickly.

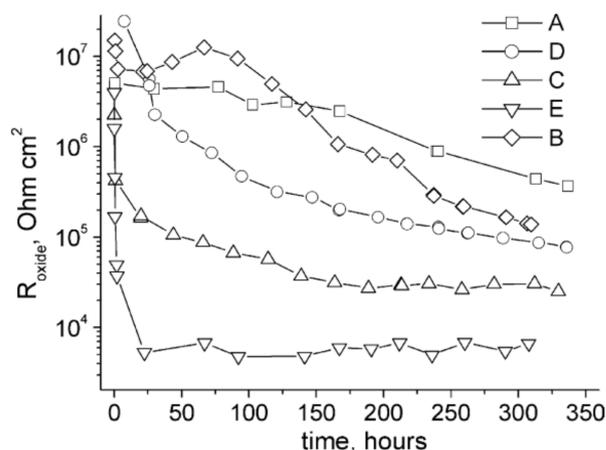


Figure 12. Evolution of the resistance of the intermediate oxide layer for the different coatings during immersion. (A— ZrO_2 nanoparticles + cerium in nanoparticles 0.5%wt, B— ZrO_2 nanoparticles + Cerium in the hybrid matrix, C— ZrO_2 nanoparticles + cerium in nanoparticles 1%wt, D— ZrO_2 nanoparticles, E-reference). Reproduced with permission from Zheludkevich et al., *Electrochimica Acta*; published by Elsevier, 2005 [54].

After 300 h of immersion, the resistance of the oxide for the coating B was of the same order of magnitude than the undoped D coating.

The resistance for coating A (with cerium-doped nanoparticles) decreased throughout the immersion but finally reached a value five times greater than the other coatings.

The long-term delivery of the cerium ions from the zirconia nanoparticles explained the good results of coating A compared to the other coatings and consequently conferred a better protection.

The detrimental effect of the addition of highly soluble inhibitors was reported by Yasakau et al. who studied the behavior of amorphous cerium molybdate nanowires (CMN) in hybrid sol-gel coatings on AA 2024 T3 [56]. Indeed, the addition of inhibitors can destroy the coating matrix by forming crystalline aggregates after curing or causing

blistering. Consequently, to control the inhibitor release, the inhibiting compound can be immobilized on a carrier such as oxide nanoparticles or zeolite fillers or nanowires. By EIS and SVET measurements, they noted that sol–gel containing CMN showed higher mixed oxide layer resistance and polarization resistance, demonstrating an improvement in active corrosion protection during immersion in 0.5 M NaCl solution. A suppression of the local corrosion activity in artificial defects was also visible in SVET measurements.

II. Stimuli Response for Triggering pH Gradient

Many local pH changes are observed during the corrosion of aluminum alloys. A local alkalization can be observed when the oxygen reduction reaction (ORR) occurs, and acidification can be detected during the hydrolysis of dissolved aluminum. Some nanocontainers or reservoirs can be sensitive to pH and release corrosion inhibitors in response to pH changes [1].

Good results were obtained by Zheludkevich et al. from a system composed of hybrid sol–gel films (silica–zirconia-based hybrid film) loaded with nanocontainers that delivered benzotriazole in response to pH variations encountered during the corrosion of aluminum alloys [57].

Snihirova et al. studied the protective ability of water-based epoxy loaded with pH-sensitive particles and micron-sized calcium carbonate beads modified with different inhibitors (cerium nitrate, salicylaldehyde and 2,5-dimercapto-1, 3, 4-thiadiazolate) [58]. These particles were sensitive to acidic pH, and released the inhibitors which then prevented the corrosion of the aluminum alloys. By EIS and LEIS (low-energy ion scattering) measurements, the authors reported the most important inhibition effects from CaCO₃ microbeads modified with cerium ions.

Maia et al. reported the self-healing effect at long immersion times of functional nanoreservoirs based on silica nanocapsules (SiNC) loaded with 2-Mercaptobenzotriazole (MBT) [59]. From their results, the authors demonstrated that MBT is sensitive to alkaline and acidic conditions, where the release of inhibitors was more prominent than in neutral conditions. This behavior is linked to the solubility of MBT in different pH ranges.

Ferrer et al. studied the corrosion protection performance of double-doped zeolites (NaY) for aluminum alloys (NaY-Ce or NaY-Ce-DEDTC (diethylditiocarbonate)) [60]. The concept of double doping and release comprises the incorporation of two different inhibitors in the carrier (zeolite). When the carrier was exposed to certain corrosive media, one inhibitor was first released for quick protection of the exposed metal through complexation. The second inhibitor remained in the host zeolite structure for slower release, and was triggered by ion exchange when the corrosion process advanced. By electrochemical measurements, they reported that the most significant and encouraging results were observed with NaY-Ce-DEDTC.

The inhibition corrosion performance of hollow mesoporous silica nanoparticles (HMSs) as smart nanocontainers implanted into SNAP coating was also reported by Fu et al. [48]. They used the polyelectrolyte layer-by-layer assembly technique to synthesize shells of nanocontainers sensitive to pH and to control the delivery of the trapped corrosion inhibitors. The mode of action of polyelectrolyte multilayers (PEMs) comprises three actions: (1) the pH buffering activity of polyelectrolyte which fixes the pH solution; (2) the release of self-healing agents to prevent corrosion propagation due to pH changes; (3) the elimination of cracks by transferable polyelectrolytes [47].

The use of microcapsules which are sensitive to pH is interesting, since the delivery of inhibitors is dependent on the pH variations occurring during the corrosion process. However, Fu et al. noted that, although the fluctuation of pH due to corrosion activities is an easily available condition for stimuli-responsive smart coatings, pH changes are often uncertain and significant differences depend on the metal and the environment [47]. In addition, pH changes may often occur at the microscale resulting in questions concerning the availability of microcapsules at these particular locations. Consequently, the use of redox response intelligent anticorrosion coating is interesting because the corrosion potential is linked with corrosion activities.

III. Stimuli Responsible for Triggering Redox Response

Conductive polymers (polyaniline, polypyrrole, polythiophene) can be used to trap corrosion inhibitors which will be delivered when the corrosion potential decreases. The use of CPs has several drawbacks: (1) only anionic inhibitor can be encapsulated; (2) the unwanted release of inhibitors due to the incorporation of cations; (3) reactions with some non-noble metals can lead to the loss of their ability to perceive corrosion potential changes.

Sun et al. [61] studied the redox response performance of hollow mesoporous silica spheres (HMSS) for the encapsulation and controlled release of corrosion inhibitors. The authors synthesized HMSS loaded with corrosion inhibitor MBT and encapsulated with a redox-responsive supramolecular nanovalve and ZnO quantum dots. By measuring the redox-responsive release of MBT, they showed that these nanoparticles offer a great promise for the development of a nano delivery system for corrosion protection accompanying redox environment change. Fu et al. [48] noted the same results with nanovalves loaded with cucurbit [7] and uril (CB7).

Chunling et al., reported the use of hollow mesoporous organosilica nanoparticles (HMON) encapsulated with MBT as a pH and redox double-stimuli-responsive nanocontainer in the controlled release of corrosion inhibitor molecules [62]. By EIS measurements, the authors demonstrated the favorable corrosion inhibition performance of the alloy with the addition of 1.6 g/L of MBT/HMON. However, a too-low or a too-high concentration of MBT/HMON in the corrosion media is averse to the formation of corrosion inhibitor film and could accelerate the corrosion of aluminum alloy.

The behavior of silica nanoparticles, in terms of storing a payload of small molecules and releasing them following an activation process, was investigated by Khashab et al. [63]. The storage and release of the payload is controlled by the host-guest interaction between the ferrocene moiety (guest) and the ring moiety (CB7 and β -cyclodextrin (β -CD)). The authors demonstrated that Ferrocene-based mechanized nanoparticles (FMNPs) operated successfully under redox control in the presence of β -CD and under pH control (deprotonation of ferrocenedicarboxylic acid pH > 4) in the presence of CB7.

(b) Exchange Ions Pigments

Ion exchange pigments are inorganic oxides charged with ionic corrosion initiators by the exchange of ions with hydroxyl groups on the surface of the inorganic particle. The oxides are chosen for their acidic or basic nature to exchange cations or anions. Thus, silica is used as a cation carrier and alumina for anion exchange. The pigments used in the anti-corrosion coatings can be calcium exchange silicas, hydrotalcites (double-lamellar hydroxides) based on zinc, aluminum or vanadate, or cation exchange pigments, e.g., bentonite loaded with Ca^{2+} and Ce^{3+} , which is a clay consisting of aluminum phyllosilicates. These pigments are used as containers to trap inhibitors and can be incorporated into coatings to provide self-healing properties. The presence of aggressive ions (as chloride) activates an exchange process between these aggressive agents and the inhibitors [1]. Dias et al. studied zeolites as ion exchange pigments. Zeolite microparticles were doped with Ce^{3+} and their delivery occurred in the presence of ionic species (Cu^{2+}) implied in the corrosion of AA2024. As represented in Figure 13, copper ions resulting from the dissolution of the intermetallic particles and Cl^- ions from the electrolyte were absorbed in zeolite [64].

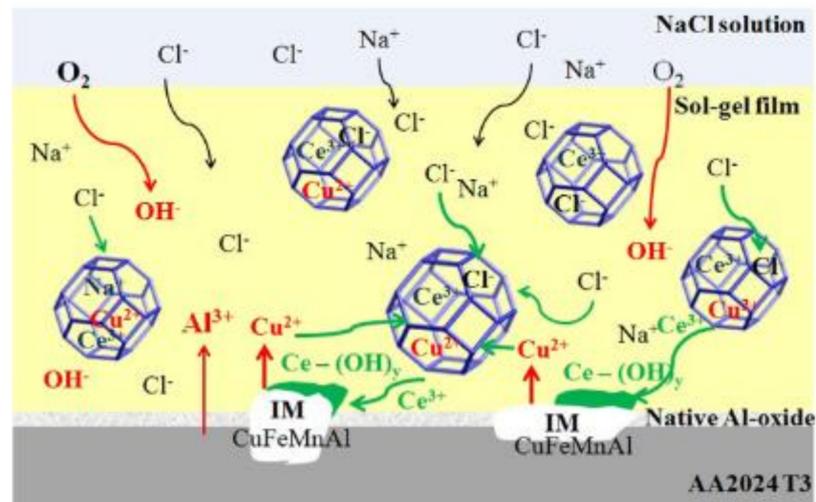


Figure 13. Representation of the mechanism of inhibitor release in the ion exchange process. Reprinted with permission from Ref. [64]. Copyright 2013, Elsevier.

Chico et al. studied the behavior of alkyd paint coatings formulated with anionic vanadate hydrotalcite (HT/V) and cationic calcium/silica pigments [65]. After 1 year of atmospheric exposures, different accelerated corrosion tests (NSST-ISO 9227, humidity (ISO 6270-1), etc.), and electrochemical measurements (potentiodynamic curves, EIS), they showed that HT/V behaves well in chloride environments (e.g., salt spray and NaCl solutions), while Ca/Si performed well in the humidity condensation and SO₂ tests. However, the authors also noted that these ion-exchangeable pigments did not equal the anticorrosive behavior of the zinc chromate in the different tests. Indeed, the corrosion potential of steel was more noble (from -922 mV/ECS to -637 mV/ECS) for the ZnCrO₄ pigment, while this potential was weaker with the ion exchange pigments Ca/Si and HT/V, as illustrated by polarization curves in Figure 14.

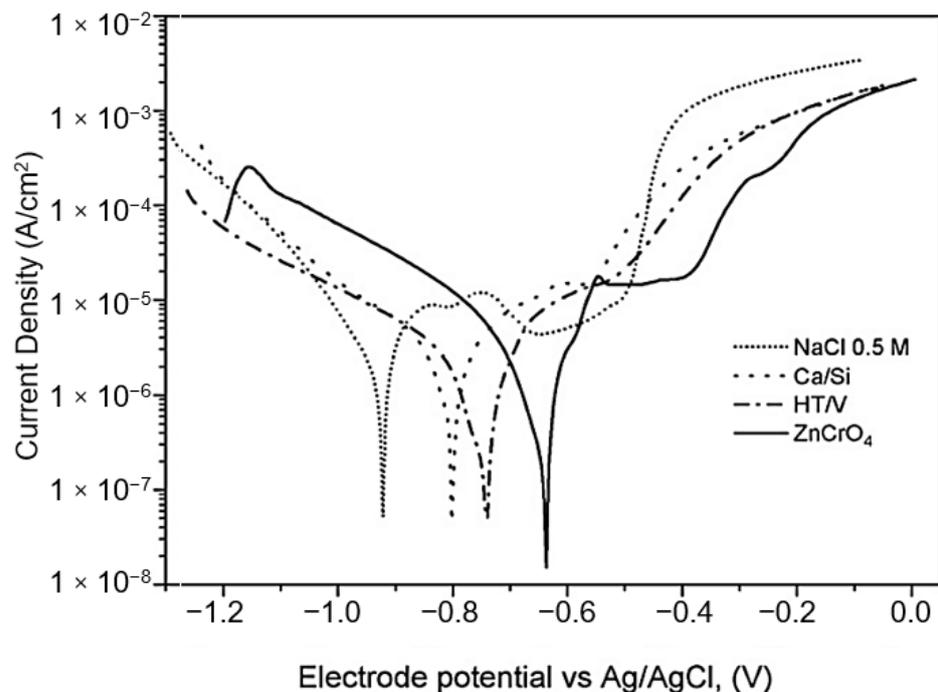


Figure 14. Polarization curves for steel in contact with different anticorrosive pigments in 0.5 M NaCl. Reproduced with permission from Chico et al., *Progress in Organic Coatings*; published by Elsevier, 2008 [65].

Buchheit et al., meanwhile, studied the inhibiting effects of decavanadate trapped in crystalline Al-Zn-hydroxide-based hydrotalcite particles [6]. After 240 h exposure in neutral salt spray and EIS measurements, they also showed that anionic vanadate hydrotalcite (HT-V) is a good corrosion inhibitor. By EIS measurements, an increase in the coating resistance linked with the delivery of Zn^{2+} ions by the pigment was observed. Polarization curves reported the inhibition of the anodic reactions in the presence of vanadate. All these results, and the consequent corrosion protection of the materials, originate from the leaching of vanadate (cathodic inhibitors) and Zn^{2+} (cathodic inhibitors) [6].

Zeolites are also used as ion exchange pigments, as demonstrated by Dias et al. [64,66,67]. Indeed, an interesting role of the corrosion protection of Ce(III)-enriched zeolite microparticles for silica-zirconia sol-gel films was highlighted by the authors [64,67]. After 2 weeks of immersion in 0.0035 M NaCl, the integrity of the sol-gel films remained unchanged. In response to the adsorption of ionic species implied in the corrosion of AA2024, microparticles (Ce(III)-loaded zeolite) were released, therefore enhancing the protective effect of the coating. In their work, Dias et al. showed the decrease in chloride concentration as a function of the time of immersion in NaCl, highlighting the exchange of species, as demonstrated in Figure 15 [64]. They explained this phenomenon by two hypotheses: (1) the chloride ions are ionically bonded to the Ce atoms; or (2) they are “trapped” inside the zeolite voids with Brønsted acid properties.

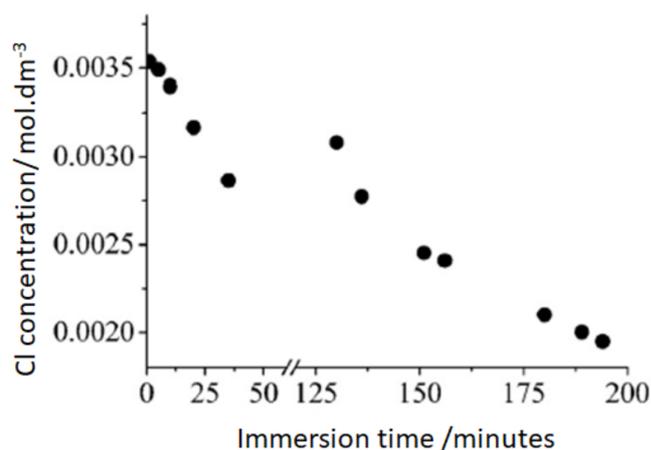


Figure 15. Evolution of chloride concentration in NaCl solution during 200 min of immersion of microparticles, with V/P ratio = 40. Reprinted with permission from Ref. [64]. Copyright 2013, Elsevier.

Dias et al. also showed the ability of protection of La- and Mo-enriched zeolites in sol-gel coatings [66]. By EIS and LEIS (local electrochemical impedance spectroscopy), they noted the synergistic effect of La and Mo. The mechanism of protection of these pigments was characterized by the release of molybdate and lanthanum ions from the loaded zeolite followed by the formation of molybdenum oxide/hydroxide and a Mo-Na-La compound from the intermetallic particles.

A drawback of ion exchange pigment is that the release mechanism can be activated by any metallic cations present in corrosion-active areas. Indeed, the presence of these cations may not be uniquely linked to the corrosion process, but may result in an unexpected release of inhibitors, resulting in a loss of inhibitors and therefore a loss of protection.

Anion exchange pigments can also play a double role because they can absorb corrosion-inducing chlorides, delivering the inhibiting ions in return. The rate of corrosion is then reduced by the absorption of chloride ions (electrolyte) around the defect, decreasing the aggressiveness of the corrosion medium. Only the “trap” function was found provide the additional anticorrosion effect in filiform corrosion tests when non-inhibited pigments with carbonates and sulfates were used in organic coatings [68]. In their work, Tedim et al. studied the inhibitive effect of Zn-Al-layered double hydroxides (LDHs) intercalated with nitrate ions, such as chloride nanotraps for organic polymeric

coatings [69]. LDHs are anionic clays or hydrotalcite (HT)-like compounds, and are defined by anion exchange. They are composed of stacks of positively charged mixed-metal hydroxide layers, between which anionic species and solvent molecules are intercalated [68].

Figure 16 shows the protection process that takes place when LDH are inserted into coatings. First, a coating with the mixed LDH is applied onto the substrate (AA 2024). The LDH release is activated by the exposure to a corrosive medium, humidity, and Cl^- ions (corrosive species). Then, the structure captures the corrosive species (Cl^-) and releases the corrosion inhibitor anions that form a protective layer on the substrate. The protection provided by Mg-Al-LDH stops when the anion exchange is over (step 2). By exposing the structure to radiation by UV light or daylight, it is possible to improve the corrosion protection with the degradation of the hydroxide layer structure and the release of Ce^{3+} cations (step 3) [70].

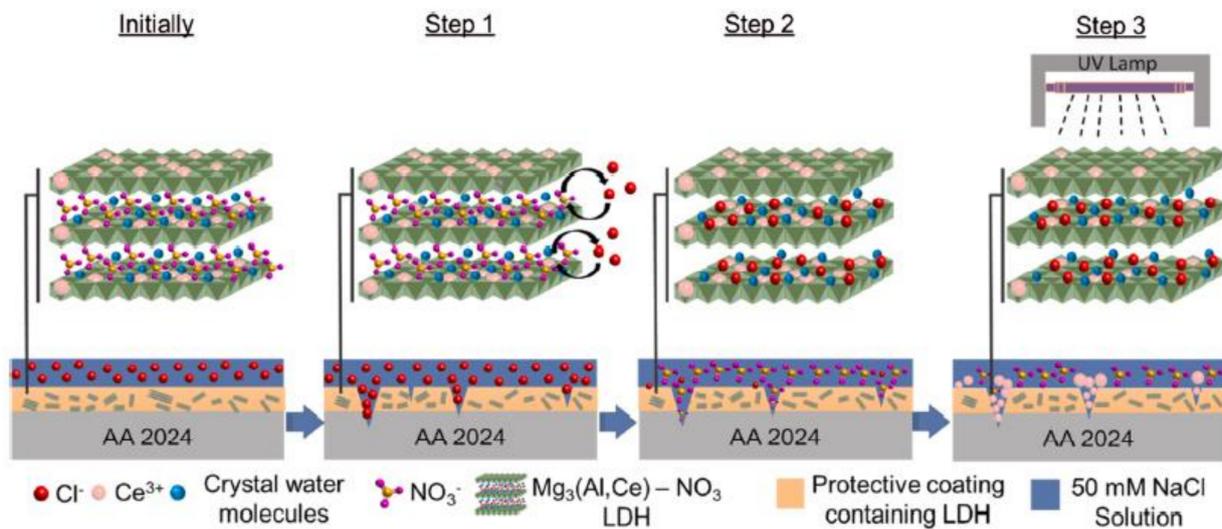


Figure 16. Schematic presentation of LDH structure. Reprinted with permission from Ref. [70]. Copyright 2022, Elsevier.

According to Bouali et al., using LDH for pigment in paints or as a direct pre-treatment for the conversion layer makes their implementation even more convenient [41]. In a solution of 0.5 M NaCl, Tedim et al. showed that Zn(2)-Al-NO₃ LDHs are responsive to the concentration of chlorides, and the release of nitrates is accompanied by the entrapment of chloride, with the process governed by the ion exchange equilibrium [69]. Zn(2)-Al-NO₃ LDH exhibited significantly lower permeability to chlorides when compared to both unmodified and LDH-Cl-containing coatings, which proves the applicability of LDHs in delaying coating degradation and corrosion initiation. By using a two-compartment cell, a potentiostat, and a three-electrode arrangement, the permeability of the coatings to chloride ions was determined. Thanks to the diffusion of chloride anion from solution 1 (0.5 M NaCl) through the coating layer, it was possible to measure the chloride concentration in the second solution (0.5 M Na(OOCCH₃)) during the 30 days of immersion.

Using permeability measurements (Figure 17), they observed—in the presence of Zn(2)-Al-NO₃ LDHs—a decrease in the permeability of chloride through the coating by 20 times. This phenomenon is linked to the entrapment of chloride in LDH-NO₃ which defers the diffusion of chloride ions, proving the entrapment effect.

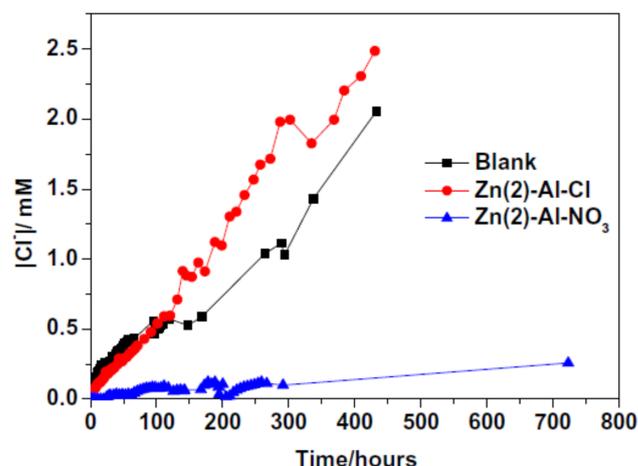


Figure 17. Permeability measurements of Cl^- through the coating as a function of time. Reproduced with permission from Tedim et al., *Corrosion Science*; published by Elsevier, 2012 [69].

Similar results were reported by Zheludkevich et al. on nanostructured double-layered Mg/Al and Zn/Al hydroxides with divanadate anions located in the interlayer regions [68]. By measurements of the coating resistance, the authors showed the self-healing effect of coating doped with Zn/Al LDH nanocontainers and their superior corrosion protection properties compared to environmentally unfriendly chromate-based systems.

Accelerated corrosion tests were also performed to validate the results with aeronautical requirements. After 2000 h in NSST, Zn/Al LDH containers showed good results and passed the aeronautical requirements (max length 2.2 mm after 960 h).

However, blistering corrosion was also tested on these coatings. After 1000 h of the QCT (condensation test), the coatings with nanocontainers presented single blisters all over the surface. This effect, resulting from the local alkalinization of the metal substrate in the presence of LDHs, can be countered with the acidification of the corrosive medium [68].

(c) Pigments

Sinko demonstrated that an effective inhibitor must be able to inhibit the ORR and to stop the anodic dissolution of intermetallic particles [71].

Molybdates, for example, are an interesting alternative to chromates thanks to their oxidizing power and the stability of their corrosion products, which form a passive layer. If the protection involves the formation of species based on Mo, Mo^{3+} and MoO_3 , then molybdenum oxides are created. The size and solubility of MoO_3 oxides determine the anti-corrosion efficiency.

Organic coatings loaded with corrosion inhibitors are widely used for the protection of aluminum alloys. The corrosion protection of this type of coating is based on the leaching of corrosion inhibitors when a defect or crack appears on the surface of the coating. In their work, P. Visser et al. explained that benzotriazole (BTA) and 2-mercaptobenzothiazole (2-MBT) are considered as copper inhibitors which cover copper-rich intermetallic particles [7]. Indeed, Harvey et al. reported that both inhibitors were able to inhibit the corrosion of AA2024-T3 and AA7075-T6 aluminum alloys with inhibitor efficiencies higher than 90% [72]. The ORR can be suppressed by the two different inhibitors by the formation of an insoluble complex or polymeric film. Although they are efficient as corrosion inhibitors, they can lose their inhibiting properties due to their sensitivity to photodegradation (by solar irradiation) [1]. Recently, research has been completed on lithium salt as an alternative to chromate in organic coatings [7,36]. Indeed, the authors demonstrated that lithium salts can be transported to a defect and form a protective layer on it, and therefore hinder the corrosion.

In view of these results, Visser et al. decided to compare the active properties of Li_2CO_3 and the organic inhibitors BTA and 2-MBT [35]. They noted a non-permanent adsorption of BTA and 2-MBT on the copper-rich intermetallic and aluminum alloy, and the desorption

of the physically adsorbed inhibitor molecules when the inhibitor concentration decreased. On the contrary, Li_2CO_3 retains its protective properties when the concentration of the corrosion inhibitors decreases. The irreversibility behavior of lithium salt as a corrosion inhibitor is essential for long-term corrosion protection [35]. All these observations were performed thanks to immersion and electrochemical measurements (EISs), but when these three inhibitors were incorporated in an organic coating, it was observed that only the Li_2CO_3 -loaded coating showed conclusive results after 7 days of the neutral salt spray test.

4.2.3. Sol–Gel/Polymer Coatings

The principle of the sol–gel process is based on the simple polymerization of precursors in solution at moderate temperature. The precursors used can be inorganic salts ($\text{Al}(\text{NO}_3)_3$, for example), but they are most often transition metals or silicon alkoxides of the general formula $\text{M}(\text{OR})_4$ with $\text{M} = \text{Si}, \text{Ti}, \text{Zr}$, etc., of the OR alkoxide group. The most popular and widely used alkoxides are silicon based. These alkoxides react by hydrolysis then by condensation to create a molecular network.

In the literature, several advantages to sol–gel processes were reported [54–56,73–75]. The main advantages are given below:

- (1) Low synthesis temperature limits the degradation of the corrosion inhibitors;
- (2) The formation of thin films without the need for machining or melting;
- (3) “Green” coating technologies: this method is waste-free and excludes the stage of washing [55].

The protection of aluminum by sol–gel coatings has been demonstrated by their barrier properties. Yang et al. [76] studied the behavior of a sol–gel conversion layer on aluminum alloy AA 2024 T3 when immersed in dilute Harrison’s solution (3.5 g/L $(\text{NH}_4)_2\text{SO}_4$, 0.5 g/L NaCl). Although pitting corrosion and degradation products appeared on the surface of the sol–gel coating after two days of immersion, the corrosion did not extend further. In addition, the modulus of impedance increased during the first four weeks of immersion. The sol–gel coating, therefore, appears to stabilize the protective layer on the substrate after the initiation of corrosion. Hamdy et al. described a silica-based sol–gel treatment providing corrosion protection to the alloy AA6061-T6 [77].

They explained the protection of the alloy by the formation of protective oxides acting as a barrier to the diffusion of oxygen towards the metal surface.

Due to a strong tendency to cracking, inorganic sol–gel coatings cannot offer an efficient protection against corrosion. To avoid this, the introduction of organic composites in the inorganic sol–gel coating led to the formation of a functionalized, thinner, and more flexible coating. Hybrid sol–gel/polymer coatings have thus demonstrated interesting properties for corrosion protection thanks to their good barrier properties. As reported by Olmo et al., hybrid sol–gel coatings (HSG) were developed in the early nineteenth century as promising alternatives to chromates [73]. They can be used as both pretreatments and primers and have intermediate properties between minerals and polymers. The inorganic part improves the mechanical properties of the coating thanks to a barrier effect due to the high density of the network, while the organic part improves flexibility and compatibility with organic paint systems. In addition, since the viscosity of the solution is often increased compared to conventional sol–gel solutions, the deposition can be carried out at a thickness comparable to the primers used in aeronautics (15–25 μm).

An advantage of this type of coating is the possibility of obtaining thicker coats without cracks due to the organofunctional silanes which act as coupling agents or adhesion promoters and enhance flexibility, reduce defects, and provide hydrophobicity. The main drawback of this technology is its delamination. To limit the corrosion process, inhibitors can be incorporated into the sol–gel film and may interact chemically or through bonding with the organic or inorganic part of the sol–gel network. Organic precursors, as nitrogen-rich compounds, allow the improvement of corrosion protection while bonding with chloride, and have a strong affinity to copper (the preferential site of the initiation of corrosion). The efficacy of inhibition depends on the solubility of the compounds in the

sol-gel. Cerium, vanadate, molybdates, permanganate or phosphate can act as inorganic precursors, although they do not all show the same efficiency [78,79]. Indeed, at high concentrations, the formation of defects in the sol-gel film due to particle aggregation was reported [78].

Collazo et al. studied the effect of EDTA disodium salt and monosodium citrate on anodized aluminum alloys coated with sol-gel [78]. They showed that adding an inhibitor to sol-gel increases its barrier properties by modifying the cross-linked network during the condensation of sol-gel. By EIS measurements, they also detected an improvement in resistance during the initial time of immersion, indicating network densification and pore blockage when the modified sol-gel coated samples were exposed to the aqueous environment.

HSG coatings act as physical barriers against aggressive species, but their protection is limited in the presence of a defect. The addition of corrosion inhibitors (as Ce salts) into a coating can improve the protection of the substrate [73].

By studying the corrosion resistance performance of silica-based hybrid sol-gel coatings doped with LiNO_3 and $\text{Ce}(\text{NO}_3)_3$ as corrosion inhibitors, Olmo et al. showed that—by EIS measurements and immersion tests in 0.5 mol/L NaCl—the in situ incorporation of Ce and Li into the formulation improved the coating stability and resulted in less degradation of the coatings, compared to that of the sol-gel without an inhibitor [73].

Similar results were noted by Pirhady Tavandashti et al. on silica-based organic-inorganic hybrid nanocomposite films on the alloy AA 2024 T3 [80].

Similar results were observed by Wang et al. on the corrosion performance of a hybrid epoxy-silica-alumina coating also doped with cerium nitrate [55]. From the EIS measurements, they noted that the corrosion protection mechanism of the sol-gel coating could be attributed to a combination of the sol-gel barrier properties and an “intermediate layer” at the sol-gel substrate interface. They also demonstrated by an exfoliation test (immersion in a solution of 4 M NaCl, 0.5 M KNO_3 and 0.1 M HNO_3), that the hybrid sol-gel coating had good resistance to corrosion.

Sol-gel materials require energy-intensive heat treatment to densify their network.

An alternative is the use of photopolymerization which induces the formation of a polymer network by the rapid transformation of a liquid monomer (or mixtures of monomers) into a solid film with selected physicochemical and mechanical properties.

According to Amerio et al., the UV-induced crosslinking reaction might be followed by a hydrolysis condensation (sol-gel process) of tetraalkoxysilane, and condensation with the alkoxy groups of the coupling agent; this leads to a silica phase strictly interconnected with the polymer matrix [81]. This process has many advantages of conventional thermal crosslinking. Indeed, the densification is rapid and robotization is possible, making it possible to reduce the production cycle time and therefore the manufacturing costs. On the other hand, room temperature crosslinking is considered environmentally friendly since energy consumption is reduced, and it does not use a solvent. This alternative crosslinking uses the energy of photons from radiation sources in the short wavelength of the electromagnetic spectrum (between 100 and 400 nm) to create reactive species that trigger a crosslinking reaction in fast growing chains. According to Senani et al., UV-curable hybrid materials may provide new opportunities to replace both conversion coatings and primers [82]. The authors showed that only the coatings photopolymerized or followed by thermal curing were equivalent to that of the thermal-cured coatings. Moreover, the presence of photo-initiators in the sol-gel formulation decreased the adhesion properties of the resulting coatings.

Few studies have been completed on the photopolymerization of sol-gel coatings; therefore, future studies should look to improve the corrosion resistance of sol-gel coatings. This review also found that the existing knowledge on some corrosion inhibitors needs to be improved, such as Zr/Ti/Mn/Mo compounds, which currently do not meet aeronautical specifications. The use of Mg-rich primer also shows good prospects for the future, but it will be necessary to resolve the problem of density, which is incompatible with the

requirements of the aeronautical industry. Validation of these different coatings and inhibitors, for example by accelerated corrosion tests, will be also important to replace Cr(VI) on future aircraft.

5. Conclusions

To limit the corrosion on aluminum alloys, different types of paint are applied. Depending on the pieces to be protected and their stresses, different approaches can be followed. Currently, protection is provided by multilayer systems containing Cr(VI)-based compounds, providing increased corrosion protection for aluminum alloys.

However, these compounds are toxic and will soon be banned from use by the REACH regulation. To minimize Cr(VI) release into the environment, several types of coating formulations loaded with pigments, corrosion inhibitors, or nanocontainers are under development as alternatives to Cr(VI). Table 1 summarizes the alternatives that have developed to replace Cr(VI). The advantages and the drawbacks of these technologies are also given.

Table 1. Advantages and drawbacks of the different alternatives to Cr(VI) cited in this review.

	Name	Advantages	Drawbacks
Anodizing	Phosphoric acid anodizing (PAA)	Good adhesion on substrate	Poor corrosion protection
	Phosphoric sulfuric acid anodizing (PSA)		
	Sulfuric acid anodizing (SAA)	Good corrosion protection	Poor adhesion on substrate
	Tartaric-sulfuric acid anodizing (TSAA)		
Conversion coatings	Self-assembled nanophase particle (SNAP)	Excellent adhesion and barrier properties	Limited corrosion protection performance when the coating is damaged—solved by the incorporation of corrosion inhibitors
	Trivalent chromium process (TCP)	Environmentally friendly Effective barrier	Possible re-oxidation of Cr(III) to Cr(VI)
Inorganic corrosion inhibitors	Reducible hypervalent transition metals Mo, Vn, Mn Tc	Inhibiting effect	Mo and Mn too soluble
	Difficult to reduce transition metal oxides Zr, Hf, Ta, Ti, Y	Very stable oxides in their highest oxidation state	Soluble and mobile precursors of these oxides are unstable
	Boehmite, hydrotalcite coatings, rare-earth (Ce)	Corrosion protection of aluminum	
	Metallic magnesium	Corrosion protection of the substrate	Coating density, incompatible with the lightening of structures (aeronautic)
Organic corrosion inhibitors	Nanocontainers or reservoir species	Self-healing properties	Limited according to the solubility of inhibitors
	Exchange ion pigments	Corrosion protection of aluminum	Can be activated by any metallic cations present in solution—non-expected release

Table 1. Cont.

	Name	Advantages	Drawbacks
Pigments	BTA, 2-MBT, Lithium salt	Effective corrosion protection	Non-permanent adsorption of BTA and 2-MBT
Sol-gel coatings		Green coating technologies Corrosion protection performance when loaded with corrosion inhibitors	Energy intensive heat treatment to densify the network-solved using photopolymerization

As demonstrated in this review, different technologies have been developed as an alternative to Cr(VI), but very little data are available on these coatings, either in service conditions or in accelerated corrosion tests. It is in the long term that we will see the real effectiveness of these technologies.

Author Contributions: Writing—review and editing, F.P. and D.T.; supervision, D.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Snihirova, D.; Lamaka, S.V.; Montemor, M.F. Smart composite coatings for corrosion protection of aluminium alloys in aerospace applications. In *Smart Composite Coatings and Membranes: Transport, Structural, Environmental and Energy Applications*; Elsevier Inc.: Amsterdam, The Netherlands, 2016; pp. 85–121. [\[CrossRef\]](#)
2. Van Benthem, R.A.T.M.; Ming, W.; De With, G. Self Healing Polymer Coatings. In *Self Healing Materials: An Alternative Approach to 20 Centuries of Materials Science*; (Springer Series in Materials Science); Springer: New York, NY, USA, 2007; Volume 100, pp. 139–159. [\[CrossRef\]](#)
3. Mookhoek, S.D.; Blaiszik, B.J.; Fischer, H.R.; Sottos, N.R.; White, S.R.; van der Zwaag, S. Peripherally decorated binary microcapsules containing two liquids. *J. Mater. Chem.* **2008**, *18*, 5390–5394. [\[CrossRef\]](#)
4. Guo, Y.; Frankel, G. Characterization of trivalent chromium process coating on AA2024-T3. *Surf. Coat. Technol.* **2012**, *206*, 3895–3902. [\[CrossRef\]](#)
5. Twite, R.; Bierwagen, G. Review of alternatives to chromate for corrosion protection of aluminum aerospace alloys. *Prog. Org. Coat.* **1998**, *33*, 91–100. [\[CrossRef\]](#)
6. Buchheit, R.G.; Guan, H.; Mahajanam, S.; Wong, F. Active corrosion protection and corrosion sensing in chromate-free organic coatings. *Prog. Org. Coat.* **2003**, *47*, 174–182. [\[CrossRef\]](#)
7. Visser, P.; Liu, Y.; Terry, H.; Mol, J.M.C. Lithium salts as leachable corrosion inhibitors and potential replacement for hexavalent chromium in organic coatings for the protection of aluminum alloys. *J. Coat. Technol. Res.* **2016**, *13*, 557–566. [\[CrossRef\]](#)
8. Landolt, D. *Corrosion et Chimie de Surfaces des Matériaux*; EPFL Presse: Lausanne, Switzerland, 2003.
9. Vargel, C. *Corrosion of Aluminium*; Elsevier Inc.: Amsterdam, The Netherlands, 2004.
10. Huisert, H. Electrochemical Characterization of Filiform Corrosion on Aluminium Rolled Products. Ph.D. Thesis, Technical University of Delft, Delft, The Netherlands, 2001.
11. Martínez-Viademonte, M.P.; Abrahami, S.T.; Hack, T.; Burchardt, M.; Terry, H. A Review on Anodizing of Aerospace Aluminum Alloys for Corrosion Protection. *Coatings* **2020**, *10*, 1106. [\[CrossRef\]](#)
12. Zhao, J.; Frankel, G.; McCreery, R. Corrosion Protection of Untreated AA-2024-T3 in Chloride Solution by a Chromate Conversion Coating Monitored with Raman Spectroscopy. *J. Electrochem. Soc.* **1998**, *145*, 2258–2264. [\[CrossRef\]](#)
13. Kendig, M.W.; Buchheit, R.G. Corrosion Inhibition of Aluminum and Aluminum Alloys by Soluble Chromates, Chromate Coatings, and Chromate-Free Coatings. *Corrosion* **2003**, *59*, 379–400. [\[CrossRef\]](#)
14. Kloet, J.; Schmidt, W.; Hassel, A.; Stratmann, M. The role of chromate in filiform corrosion inhibition. *Electrochim. Acta* **2004**, *49*, 1675–1685. [\[CrossRef\]](#)
15. Kendig, M.; Jeanjaquet, S.; Addison, R.; Waldrop, J. Role of hexavalent chromium in the inhibition of corrosion of aluminum alloys. *Surf. Coat. Technol.* **2001**, *140*, 58–66. [\[CrossRef\]](#)

16. Furman, S.; Scholes, F.; Hughes, A.; Jamieson, D.; MacRae, C.; Glenn, A. Corrosion in artificial defects. II. Chromate reactions. *Corros. Sci.* **2006**, *48*, 1827–1847. [CrossRef]
17. Scholes, F.; Furman, S.; Hughes, A.; Nikpour, T.; Wright, N.; Curtis, P.; Macrae, C.; Intem, S.; Hill, A. Chromate leaching from inhibited primers. *Prog. Org. Coat.* **2006**, *56*, 23–32. [CrossRef]
18. Scholes, F.; Furman, S.; Hughes, A.; Markley, T. Corrosion in artificial defects. I: Development of corrosion. *Corros. Sci.* **2006**, *48*, 1812–1826. [CrossRef]
19. Dorman, S.E.G.; Lee, Y. Effect of chromate primer on corrosion fatigue in aluminum alloy 7075. *Procedia Eng.* **2011**, *10*, 1220–1225. [CrossRef]
20. Nazeer, A.A.; Madkour, M. Potential use of smart coatings for corrosion protection of metals and alloys: A review. *J. Mol. Liq.* **2018**, *253*, 11–22. [CrossRef]
21. U.R. European Chemicals Agency. Available online: <https://echa.europa.eu/regulations/reach/understanding-reach> (accessed on 1 June 2007).
22. Khramov, A.; Voevodin, N.; Balbyshev, V.; Mantz, R. Sol-gel-derived corrosion-protective coatings with controllable release of incorporated organic corrosion inhibitors. *Thin Solid Film.* **2005**, *483*, 191–196. [CrossRef]
23. Khramov, A.; Voevodin, N.; Balbyshev, V.; Donley, M. Hybrid organo-ceramic corrosion protection coatings with encapsulated organic corrosion inhibitors. *Thin Solid Film.* **2004**, *447–448*, 549–557. [CrossRef]
24. Khramov, A.; Balbyshev, V.; Voevodin, N.; Donley, M. Nanostructured sol-gel derived conversion coatings based on epoxy- and amino-silanes. *Prog. Org. Coat.* **2003**, *47*, 207–213. [CrossRef]
25. Voevodin, N.; Balbyshev, V.; Khobaib, M.; Donley, M. Nanostructured coatings approach for corrosion protection. *Prog. Org. Coat.* **2003**, *47*, 416–423. [CrossRef]
26. Qi, J.-T.; Hashimoto, T.; Walton, J.; Zhou, X.; Skeldon, P.; Thompson, G. Trivalent chromium conversion coating formation on aluminium. *Surf. Coat. Technol.* **2015**, *280*, 317–329. [CrossRef]
27. Pearlstein, F.; Agarwala, V.S. Trivalent chromium solutions for applying chemical conversion coatings to aluminium alloys or for sealing anodized aluminium. *Plat. Surf. Finish.* **1994**, *81*, 50–55.
28. Li, L.; Swain, G.P.; Howell, A.; Woodbury, D.; Swain, G.M. The formation, structure, electrochemical properties and stability of trivalent chrome process (TCP) coating on AA 2024. *J. Electrochem. Soc.* **2011**, *158*, C274–C283. [CrossRef]
29. Li, L.; Kim, D.Y.; Swain, G. Transient Formation of Chromate in Trivalent Chromium Process (TCP) Coatings on AA2024 as Probed by Raman Spectroscopy. *J. Electrochem. Soc.* **2012**, *159*, C326–C333. [CrossRef]
30. Yu, H.-C.; Chen, B.-Z.; Shi, X.; Sun, X.; Li, B. Investigation of the trivalent-chrome coating on 6063 aluminum alloy. *Mater. Lett.* **2008**, *62*, 2828–2831. [CrossRef]
31. Buchheit, R.G.; Mamidipally, S.B.; Schmutz, P.; Guan, H. Active Corrosion Protection in Ce-Modified Hydrotalcite Conversion Coatings. *Corrosion* **2002**, *58*, 3–14. [CrossRef]
32. Lakshmi, R.; Sampath, S.; Aruna, S. Silica-alumina based sol-gel coating containing cerium oxide nanofibers as a potent alternative to conversion coating for AA2024 alloy. *Surf. Coat. Technol.* **2021**, *411*, 127007. [CrossRef]
33. MNanna, M.E.; Bierwagen, G.P. Mg-Rich Coatings: A New Paradigm for Cr-Free Corrosion Protection of Al Aerospace Alloys. *JCT Res.* **2004**, *1*, 69–80.
34. Markley, T.A.; Mardel, J.I.; Hughes, A.E.; Hinton, B.R.W.; Glenn, A.M.; Forsyth, M. Chromate replacement in coatings for corrosion protection of aerospace aluminium alloys. *Mater. Corros.* **2010**, *62*, 836–840. [CrossRef]
35. Visser, P.; Terryn, H.; Mol, A. On the importance of irreversibility of corrosion inhibitors for active coating protection of AA2024-T3. *Corros. Sci.* **2018**, *140*, 272–285. [CrossRef]
36. Visser, P.; Liu, Y.; Zhou, X.; Hashimoto, T.; Thompson, G.E.; Lyon, S.B.; van der Ven, L.G.J.; Mol, A.J.M.C.; Terryn, H.A. The corrosion protection of AA2024-T3 aluminium alloy by leaching of lithium-containing salts from organic coatings. *Faraday Discuss.* **2015**, *180*, 511–526. [CrossRef]
37. Kharitonov, D.S.; Dobryden, I.; Sefer, B.; Ryl, J.; Wrzesińska, A.; Makarova, I.V.; Bobowska, I.; Kurilo, I.I.; Claesson, P.M. Surface and corrosion properties of AA6063-T5 aluminum alloy in molybdate-containing sodium chloride solutions. *Corros. Sci.* **2020**, *171*, 108658. [CrossRef]
38. Moutarlier, V.; Neveu, B.; Gigandet, M. Evolution of corrosion protection for sol-gel coatings doped with inorganic inhibitors. *Surf. Coat. Technol.* **2008**, *202*, 2052–2058. [CrossRef]
39. Yoganandan, G.; Balaraju, J.; Low, C.H.; Qi, G.; Chen, Z. Electrochemical and long term corrosion behavior of Mn and Mo oxyanions sealed anodic oxide surface developed on aerospace aluminum alloy (AA2024). *Surf. Coat. Technol.* **2016**, *288*, 115–125. [CrossRef]
40. Coloma, P.S.; Izagirre, U.; Belaustegi, Y.; Jorcin, J.; Cano, F.; Lapeña, N. Chromium-free conversion coatings based on inorganic salts (Zr/Ti/Mn/Mo) for aluminum alloys used in aircraft applications. *Appl. Surf. Sci.* **2015**, *345*, 24–35. [CrossRef]
41. Bouali, A.; Serdechnova, M.; Blawert, C.; Tedim, J.; Ferreira, M.; Zheludkevich, M. Layered double hydroxides (LDHs) as functional materials for the corrosion protection of aluminum alloys: A review. *Appl. Mater. Today* **2020**, *21*, 100857. [CrossRef]
42. Kasten, L.; Grant, J.; Grebasch, N.; Voevodin, N.; Arnold, F.; Donley, M. An XPS study of cerium dopants in sol-gel coatings for aluminum 2024-T3. *Surf. Coat. Technol.* **2001**, *140*, 11–15. [CrossRef]

43. Terada, M.; Queiroz, F.; Aguiar, D.; Ayusso, V.; Costenaro, H.; Olivier, M.-G.; de Melo, H.; Costa, I. Corrosion resistance of tartaric-sulfuric acid anodized AA2024-T3 sealed with Ce and protected with hybrid sol-gel coating. *Surf. Coat. Technol.* **2019**, *372*, 422–426. [[CrossRef](#)]
44. Battocchi, D.; Simoes, A.; Tallman, D.; Bierwagen, G. Electrochemical behaviour of a Mg-rich primer in the protection of Al alloys. *Corros. Sci.* **2006**, *48*, 1292–1306. [[CrossRef](#)]
45. Lin, J.; Battocchi, D.; Bierwagen, G.P. Inhibitors for prolonging corrosion protection of Mg-rich primer on Al alloy 2024-T3. *J. Coat. Technol. Res.* **2017**, *14*, 497–504. [[CrossRef](#)]
46. Shchukin, D.G.; Möhwald, H. Self-Repairing Coatings Containing Active Nanoreservoirs. *Small* **2007**, *3*, 926–943. [[CrossRef](#)]
47. Fu, X.; Tian, L.; Fan, Y.; Ye, W.; Qiao, Z.-A.; Zhao, J.; Ren, L.; Ming, W. Stimuli-responsive self-healing anticorrosion coatings: From single triggering behavior to synergetic multiple protections. *Mater. Today Chem.* **2021**, *22*, 100575. [[CrossRef](#)]
48. Fu, J.; Chen, T.; Wang, M.; Yang, N.; Li, S.; Wang, Y.; Liu, X. Acid and Alkaline Dual Stimuli-Responsive Mechanized Hollow Mesoporous Silica Nanoparticles as Smart Nanocontainers for Intelligent Anticorrosion Coatings. *ACS Nano* **2013**, *7*, 11397–11408. [[CrossRef](#)] [[PubMed](#)]
49. Javierre, E.; García, S.; Mol, J.; Vermolen, F.; Vuik, C.; van der Zwaag, S. Tailoring the release of encapsulated corrosion from damaged coatings: Controlled release kinetics by overlapping diffusion fronts. *Prog. Org. Coat.* **2012**, *75*, 20–27. [[CrossRef](#)]
50. Zheludkevich, M.; Tedim, J.; Ferreira, M. “Smart” coatings for active corrosion protection based on multi-functional micro and nanocontainers. *Electrochim. Acta* **2012**, *82*, 314–323. [[CrossRef](#)]
51. Noiville, R.; Jaubert, O.; Gressier, M.; Bonino, J.-P.; Taberna, P.-L.; Fori, B.; Menu, M.-J. Ce(III) corrosion inhibitor release from silica and boehmite nanocontainers. *Mater. Sci. Eng. B* **2018**, *229*, 144–154. [[CrossRef](#)]
52. Kartsonakis, I.A.; Koumoulos, E.P.; Charitidis, C.A. Advancement in corrosion resistance of AA 2024-T3 through sol-gel coatings including nanocontainers. *Manuf. Rev.* **2017**, *4*, 2. [[CrossRef](#)]
53. Carbonell, D.J.; García-Casas, A.; Izquierdo, J.; Souto, R.M.; Galván, J.C.; Jiménez-Morales, A. Scanning electrochemical microscopy characterization of sol-gel coatings applied on AA2024-T3 substrate for corrosion protection. *Corros. Sci.* **2016**, *111*, 625–636. [[CrossRef](#)]
54. Zheludkevich, M.; Serra, R.; Montemor, F.; Yasakau, K.; Salvado, I.; Ferreira, M. Nanostructured sol-gel coatings doped with cerium nitrate as pre-treatments for AA2024-T3. *Electrochim. Acta* **2005**, *51*, 208–217. [[CrossRef](#)]
55. Wang, D.; Bierwagen, G.P. Sol-gel coatings on metals for corrosion protection. *Prog. Org. Coat.* **2009**, *64*, 327–338. [[CrossRef](#)]
56. Yasakau, K.; Kallip, S.; Zheludkevich, M.; Ferreira, M. Active corrosion protection of AA2024 by sol-gel coatings with cerium molybdate nanowires. *Electrochim. Acta* **2013**, *112*, 236–246. [[CrossRef](#)]
57. Zheludkevich, M.L.; Shchukin, D.G.; Yasakau, K.A.; Möhwald, H.; Ferreira, M.G.S. Anticorrosion Coatings with Self-Healing Effect Based on Nanocontainers Impregnated with Corrosion Inhibitor. *Chem. Mater.* **2007**, *19*, 402–411. [[CrossRef](#)]
58. Snihirova, D.; Lamaka, S.; Montemor, F. “SMART” protective ability of water based epoxy coatings loaded with CaCO₃ microbeads impregnated with corrosion inhibitors applied on AA2024 substrates. *Electrochim. Acta* **2012**, *83*, 439–447. [[CrossRef](#)]
59. Maia, F.; Tedim, J.; Lisenkov, A.D.; Salak, A.N.; Zheludkevich, M.L.; Ferreira, M.G.S. Silica nanocontainers for active corrosion protection. *Nanoscale* **2012**, *4*, 1287–1298. [[CrossRef](#)] [[PubMed](#)]
60. Ferrer, E.; Rollon, A.; Mendoza, H.D.; Lafont, U.; Garcia, S. Double-doped zeolites for corrosion protection of aluminium alloys. *Microporous Mesoporous Mater.* **2014**, *188*, 8–15. [[CrossRef](#)]
61. Sun, S.; Zhao, X.; Cheng, M.; Wang, Y.; Li, C.; Hu, S. Facile preparation of redox-responsive hollow mesoporous silica spheres for the encapsulation and controlled release of corrosion inhibitors. *Prog. Org. Coat.* **2019**, *136*, 105302. [[CrossRef](#)]
62. Li, C.; Zhao, X.; Meng, C.; Zhang, T.; Sun, S.; Hu, S. Application of hollow mesoporous organosilica nanoparticles as pH and redox double stimuli-responsive nanocontainer in the controlled release of corrosion inhibitor molecules. *Prog. Org. Coat.* **2021**, *159*, 106437. [[CrossRef](#)]
63. Khashab, N.M.; Trabolsi, A.; Lau, Y.A.; Ambrogio, M.W.; Friedman, D.C.; Khatib, H.A.; Zink, J.I.; Stoddart, J.F. Redox- and pH-Controlled Mechanized Nanoparticles. *Eur. J. Org. Chem.* **2009**, *2009*, 1669–1673. [[CrossRef](#)]
64. Dias, S.; Marques, A.; Lamaka, S.; Simoes, A.; Diamantino, T.C.; Ferreira, M. The role of Ce(III)-enriched zeolites on the corrosion protection of AA2024-T3. *Electrochim. Acta* **2013**, *112*, 549–556. [[CrossRef](#)]
65. Chico, B.; Simancas, J.; Vega, J.; Granizo, N.; Díaz, I.; de la Fuente, D.; Morcillo, M. Anticorrosive behaviour of alkyd paints formulated with ion-exchange pigments. *Prog. Org. Coat.* **2008**, *61*, 283–290. [[CrossRef](#)]
66. Dias, S.A.S.; Lamaka, S.; Diamantino, T.C.; Ferreira, M. Synergistic Protection against Corrosion of AA2024-T3 by Sol-Gel Coating Modified with La and Mo-Enriched Zeolites. *J. Electrochem. Soc.* **2014**, *161*, C215–C222. [[CrossRef](#)]
67. Dias, S.; Lamaka, S.; Nogueira, C.; Diamantino, T.C.; Ferreira, M. Sol-gel coatings modified with zeolite fillers for active corrosion protection of AA2024. *Corros. Sci.* **2012**, *62*, 153–162. [[CrossRef](#)]
68. Zheludkevich, M.; Poznyak, S.; Rodrigues, L.; Raps, D.; Hack, T.; Dick, L.F.P.; Nunes, T.; Ferreira, M.G.S. Active protection coatings with layered double hydroxide nanocontainers of corrosion inhibitor. *Corros. Sci.* **2010**, *52*, 602–611. [[CrossRef](#)]
69. Tedim, J.; Kuznetsova, A.; Salak, A.N.; Montemor, F.; Snihirova, D.; Pilz, M.; Zheludkevich, M.L.; Ferreira, M.G.S. Zn–Al layered double hydroxides as chloride nanotraps in active protective coatings. *Corros. Sci.* **2012**, *55*, 1–4. [[CrossRef](#)]
70. Vieira, D.E.; Salak, A.N.; Ferreira, M.G.; Vieira, J.M.; Brett, C.M. Ce-substituted Mg–Al layered double hydroxides to prolong the corrosion protection lifetime of aluminium alloys. *Appl. Surf. Sci.* **2021**, *573*, 151527. [[CrossRef](#)]
71. Sinko, J. Challenges of chromate inhibitor pigments replacement in organic coatings. *Prog. Org. Coat.* **2001**, *42*, 267–282. [[CrossRef](#)]

72. Harvey, T.; Hardin, S.; Hughes, A.; Muster, T.; White, P.; Markley, T.; Corrigan, P.; Mardel, J.; Garcia, S.; Mol, J.; et al. The effect of inhibitor structure on the corrosion of AA2024 and AA7075. *Corros. Sci.* **2011**, *53*, 2184–2190. [[CrossRef](#)]
73. Del Olmo, R.; Tiringier, U.; Milošev, I.; Visser, P.; Arrabal, R.; Matykina, E.; Mol, J. Hybrid sol-gel coatings applied on anodized AA2024-T3 for active corrosion protection. *Surf. Coat. Technol.* **2021**, *419*, 127251. [[CrossRef](#)]
74. Voevodin, N.; Jeffcoate, C.; Simon, L.; Khobaib, M.; Donley, M. Characterization of pitting corrosion in bare and sol-gel coated aluminum 2024-T3 alloy. *Surf. Coat. Technol.* **2001**, *140*, 29–34. [[CrossRef](#)]
75. Wang, H.; Akid, R. A room temperature cured sol-gel anticorrosion pre-treatment for Al 2024-T3 alloys. *Corros. Sci.* **2007**, *49*, 4491–4503. [[CrossRef](#)]
76. Yang, X.; Tallman, D.; Gelling, V.; Bierwagen, G.; Kasten, L.; Berg, J. Use of a sol-gel conversion coating for aluminum corrosion protection. *Surf. Coat. Technol.* **2001**, *140*, 44–50. [[CrossRef](#)]
77. Hamdy, A.S.; Butt, D. Environmentally compliant silica conversion coatings prepared by sol-gel method for aluminum alloys. *Surf. Coat. Technol.* **2006**, *201*, 401–407. [[CrossRef](#)]
78. Collazo, A.; Ezpeleta, I.; Figueroa, R.; Nóvoa, X.; Pérez, C. Corrosion protection properties of anodized AA2024T3 alloy sealing with organic-based species. *Prog. Org. Coat.* **2020**, *147*, 105779. [[CrossRef](#)]
79. Figueira, R.B.; da Silva, C.J.R.; Pereira, E.V. Organic-inorganic hybrid sol-gel coatings for metal corrosion protection: A review of recent progress. *J. Coat. Technol. Res.* **2015**, *12*, 1–35. [[CrossRef](#)]
80. Tavandashti, N.P.; Sanjabi, S.; Shahrabi, T. Corrosion protection evaluation of silica/epoxy hybrid nanocomposite coatings to AA2024. *Prog. Org. Coat.* **2009**, *65*, 182–186. [[CrossRef](#)]
81. Amerio, E.; Sangermano, M.; Malucelli, G.; Priola, A.; Voit, B. Preparation and characterization of hybrid nanocomposite coatings by photopolymerization and sol-gel process. *Polymer* **2005**, *46*, 11241–11246. [[CrossRef](#)]
82. Senani, S.; Campazzi, E.; Villatte, M.; Druetz, C. Potentiality of UV-cured hybrid sol-gel coatings for aeronautical metallic substrate protection. *Surf. Coat. Technol.* **2013**, *227*, 32–37. [[CrossRef](#)]