



Review paper

Progress in eco-friendly aerospace coatings: the future beyond chromates

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Abstract

Aluminium alloys have a good strength-to-weight ratio and low density, but they are not impervious to corrosion. Therefore, it is necessary to evaluate their corrosion performance in the atmospheric environment. Paints are typically used to prevent corrosion on aluminium alloys. A conversion or anodized layer, an inhibitor/metal-doped primer, and a polyurethane topcoat are used as 3-layer coatings for aluminium alloy corrosion protection in the aerospace industry. However, major modifications have been made to the protection of aluminium alloys against corrosion as a result of environmental issues. REACH, a European regulation, has significantly altered some finishing procedures for aluminium alloys by prohibiting or restricting the use of Cr(VI)-based compounds, such as chromate conversion, chromic acid anodizing, and chromate sealing. Searching for alternatives to Cr has yielded intriguing results. For many years, sol-gel-based hybrid coatings have been a promising alternative to pretreatment and primer layers, with promising results. This review discusses the current development and advancement in chrome-free corrosion-resistant layer coating systems for aluminium alloys.

Keywords

Aluminium alloys, surface pre-treatment, corrosion protection, aerospace applications

Introduction

The aviation industry has made great progress in reducing aircraft weight and, consequently, fuel consumption during the past several decades. Another important requirement in this industry is a reduction in cost, which may be accomplished by reducing functional/overhaul expenses, increasing the frequency of periodic assessments, and enhancing the serviceable life [1]. Based on most design trials, the most effective way to improve structural efficiency is a reduction in density [2-4],

maintaining a high strength-to-weight ratio with some other required properties such as lightweight, thermal stability, corrosion resistance and creep resistance.

The selection of materials for aerospace applications is driven by the need for high strength-to-weight ratios, fatigue resistance, and durability under harsh environmental conditions. Among the various materials considered, aluminium alloys (Al alloys), titanium alloys (Ti alloys), magnesium alloys (Mg alloys), and advanced composites have emerged as the primary choices for aircraft structural components [5].

Aluminium alloys provide various benefits for aircraft applications, including low density and high specific mechanical characteristics, which can be achieved by element alloying and heat treatment methods [6]. In addition, the cost parameter must be evaluated without compensating for the quality of the materials used. From 1995 to 2015, aluminium production worldwide surged by nearly 300 %, with the aerospace sector playing a key role in this rapid growth. Aluminium is not only valued for its exceptional strength-to-weight ratio but also for being lightweight and recyclable, qualities that make it a preferred choice in modern aircraft design. Despite their inherent tendency to form a protective oxide film, aluminium alloys are still susceptible to localized forms of corrosion. The addition of alloying elements and the formation of intermetallic phases can result in localized electrochemical potential differences, act as anodic or cathodic sites, creating localized galvanic cells on the alloy surface. Moreover, factors such as mechanical stress, surface imperfections, and environmental conditions, including humidity, temperature changes, and airborne contaminants, can weaken or damage the protective oxide layer, thereby speeding up the corrosion process. These vulnerabilities are particularly critical under the harsh operational conditions of aerospace environments, thereby justifying the need for advanced protective coatings. Oxide layers formed on aluminium are susceptible to dissolution in both acidic and alkaline environments [7,8]. These native oxides are also unstable in chloride-rich environments, which are prevalent in aerospace and industrial operating conditions. Furthermore, in highly alloyed aluminium grades, the presence of intermetallic compounds introduces heterogeneities in electrochemical potential, thereby compromising the integrity of the oxide layer and promoting localized galvanic corrosion. Therefore, the aim of the present extended review is to summarize recent trends in replacing the now-banned Cr(VI) compounds with ecological alternatives for the corrosion protection of industrial aluminium alloys. Additionally, the review highlights key technological parameters involved in the deposition of reliable and durable coating systems.

Brief overview of conventional aircraft alloys

Aluminium alloys are widely used because of their low density, favourable mechanical properties, and cost-effectiveness. Titanium alloys provide superior strength and fatigue resistance, but are limited to critical load-bearing components due to their high density and cost. Magnesium alloys, though lighter, are restricted to less demanding applications owing to lower strength and corrosion resistance. Composites offer a balance of low density and tailored mechanical performance, making them suitable for modern lightweight airframe designs. A comparison of these materials and their key aerospace-relevant properties is presented in Table 1

Table 1. Evaluation of the structural materials for aerospace applications [9-13].

Material	Density, kg m ⁻³	Fatigue resistance, MPa, at 10 ⁷ cycles)	Yield strength, MPa
Al alloys	2720	68.2 to 169	109 to 439
Ti alloys	4610	351 to 633	470 to 1090
Mg alloys	1810	75 to 140	109 to 216
Composites	1550 to 1860	55 to 300	145 to 760

Aluminium alloys

Aluminium alloys (AA) have long been used as primary structural materials in aircraft due to their proven performance, well-established design methodologies, production, and reliable inspection procedures [14]. Aluminium and its alloys offer several advantages that make them dominant in the aerospace sector, including low density, high specific strength, and good corrosion resistance, except under highly acidic or alkaline conditions where protection is required. Alloying elements are introduced to enhance the strength of the aluminium matrix by forming secondary-phase microstructures with electrochemical potentials different from that of the matrix, leading to micro-galvanic coupling and the formation of localized anodic and cathodic sites in the presence of electrolytes [15-18]. AA are broadly classified as cast or wrought; however, cast and non-age-hardenable wrought alloys generally exhibit inadequate mechanical properties for aerospace use. Consequently, load-bearing aircraft components primarily employ wrought, heat-treatable alloys [19]. Common aerospace aluminium alloys include the 2xxx, 6xxx, 7xxx, and 8xxx series (Table 2), among which the 2xxx and 7xxx series provide superior specific mechanical properties but are more susceptible to corrosion [20,21].

Table 2. Various aluminium alloys depicting their alloying elements and their properties for aerospace applications [22-31]

AA series	2xxx	6xxx	7xxx	8xxx
Material	2024, 2017, 2004	6013, 6050, 6061	7055	8090
Major alloying elements	Copper/magnesium	Magnesium/silicon	Zinc/magnesium/copper	Lithium/copper/magnesium
Properties	Good machinability, high strength/fatigue corrosion resistance	Good formability and weldability, high strength, corrosion resistance	Highest strength/toughness good machinability	Low density, excellent fatigue and toughness, crack growth resistance

The 2xxx series, mainly alloyed with copper, can be heat-treated to achieve steel-like strength through the formation and precipitation of Al_2Cu and Al_2CuMg phases, offering enhanced damage tolerance and fatigue resistance; AA 2024 is extensively used in aircraft wings, fuselage, internal structures, and non-structural components [32-35]. The 7xxx series, primarily alloyed with zinc, achieves the highest strength levels, as increased Zn content and the addition of Mg and Cu promote the formation of strengthening phases such as $MgZn_2$, Al_2CuMg , and $AlCuMgZn$ [36-38].

In the aerospace sector, service conditions are highly demanding. Corrosion protection systems must withstand temperatures ranging from -55 to 80 °C (and higher in engine-adjacent regions) and resist aggressive media such as water, fuel, de-icing fluids, chloride solutions, hydraulic fluids, and occasional microbiological attack [39]. Additionally, the system should act as an effective barrier to prevent galvanic corrosion between dissimilar materials. To ensure long-term durability, corrosion protection must remain effective for at least three decades. Consequently, corrosion control must be integrated into the design stage, considering factors such as appropriate material selection, avoidance of crevices, and adequate drainage [40]. Along with optimized design, the protection system should provide sustained passive or active corrosion resistance throughout service life.

Corrosion protection coatings

Recently, significant attention has been directed toward developing new technologies for the formulation and application of conversion coatings/pre-treatments and primer layers. Traditionally, these layers have relied on hexavalent chromium, which remains one of the most effective corrosion inhibitors for aluminium alloys [41]. In aircraft applications, aluminium alloys are commonly protected using a three-layer coating system comprising a pre-treatment layer at the aluminium-primer interface, a primer, and a topcoat, as illustrated in Figure 1.

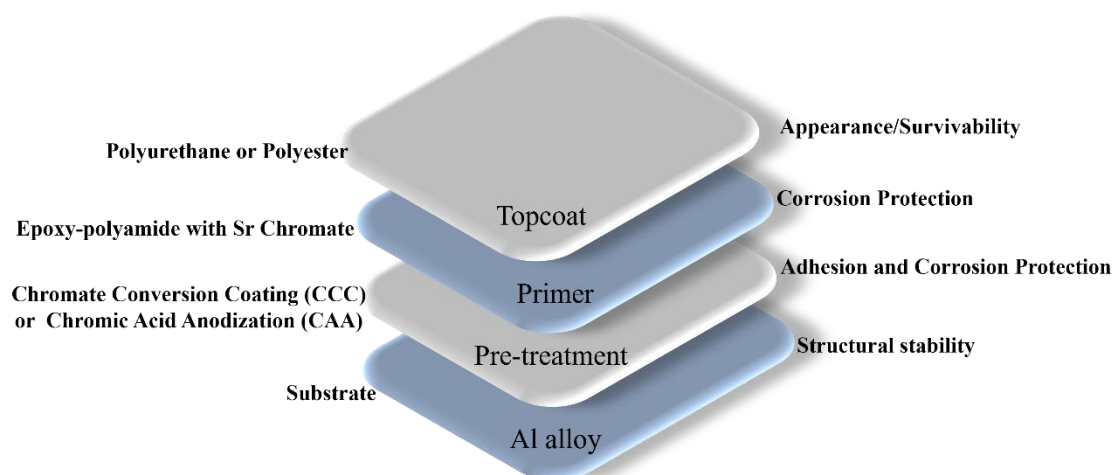


Figure 1. Schematic representation of a three-layered corrosion protection coating used in Al-based aircraft structures

The first pre-treatment layer is typically a chromate conversion coating (CCC) or chromic acid anodization (CAA) with a thickness of approximately 5 μm . This layer provides corrosion protection for damaged areas and facilitates primer adhesion. Chrome(VI) coating also plays a key role in improving the adhesion of primer coating to the metal substrate [42]. In the CCC layer, hexavalent chromate exhibits low solubility and self-healing properties. Cr(VI) in the coating is reduced to Cr(III), which is insoluble and offers self-healing, *i.e.*, it only leaches out on demand when the base metal has been damaged/scratched. Over this layer, the epoxy-polyamide with strontium chromate primer is present, which is much thicker than the CCC layer. This layer exhibits excellent anticorrosive properties due to the presence of hexavalent chromium pigments, specifically strontium chromate. Primers are also important for maintaining the integrity of the airframe and for ensuring adhesion to the substrate. The topcoat, polyurethane or polyester, maintains decorative and survivability. In aerospace coating, the topcoat as well as the complete coating system must withstand temperatures from -65 to 150 $^{\circ}\text{C}$ and also protect against hydraulic fluid [43]. However, due to their carcinogenic nature, the usage of chromates, as well as other chromium-containing compounds, has been reduced since 1982 [44]. Still, chromium(VI) maintains the benchmark against corrosion protection during a wide range of pH and different concentrations of electrolyte [45].

Despite this, chromium(VI) remains a benchmark for corrosion protection across a wide range of pH values and electrolyte concentrations. Hexavalent chromium has been by far the most effective on aluminium and is commonly considered a "yardstick" against other conversion coatings. Because chromates behave as both anodic and cathodic inhibitors, they prevent metal dissolution and also limit the rate of the reduction process [46]. To achieve excellent corrosion protection, these three-layer coating systems must function effectively. Therefore, researchers worldwide are seeking chrome-free green alternatives for aircraft coating systems, as shown in Figure 2.

Therefore, a detailed description of the three-layer coating system used in the corrosion protection of aircraft structures is presented in the following section.

In general, cladded AA with a pure aluminium sheet of about 60 to 80 μm improves corrosion protection. The thickness of AA 2024 will not be uniform all over the surface due to exposure or mechanical disruption [47]. Furthermore, the inherent oxide of alclad aluminium alloys rarely provides significant corrosion protection in various environments, requiring the use of a protective coating.

The formation of non-uniform oxide on AA and galvanic couples (intermetallic particles - aluminium matrix) may contribute to corrosion attack [48,49].

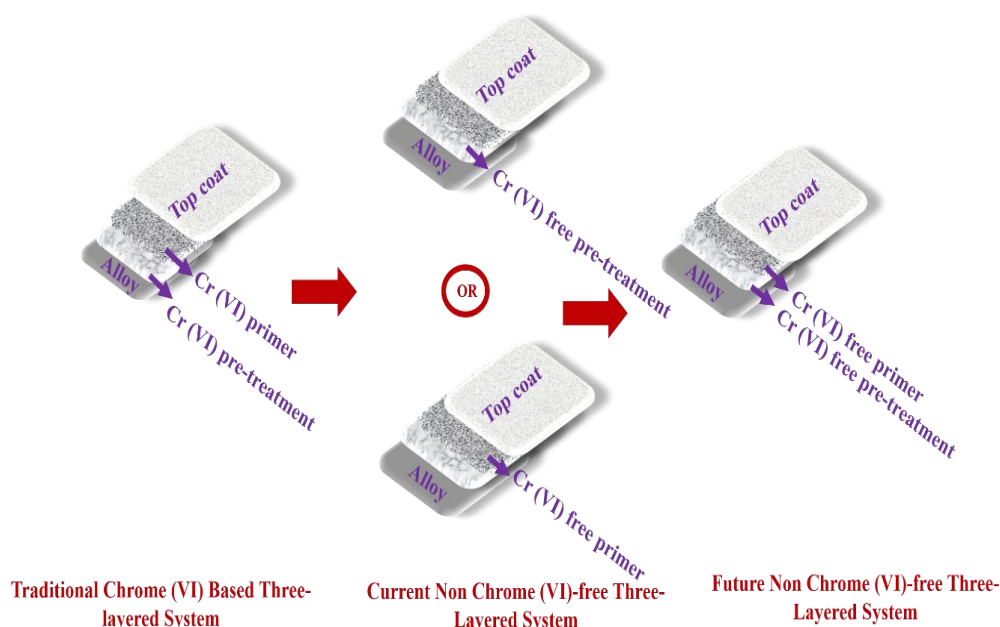


Figure 2. Schematic representation of chrome-free three-layer coating system for aircraft

Figure 3 represents pitting corrosion in AA. Specifically, the presence of halides (Cl^- , F^- , Br^-) in the environment causes corrosion on the surface of aluminium owing to the formation of soluble salts [50].

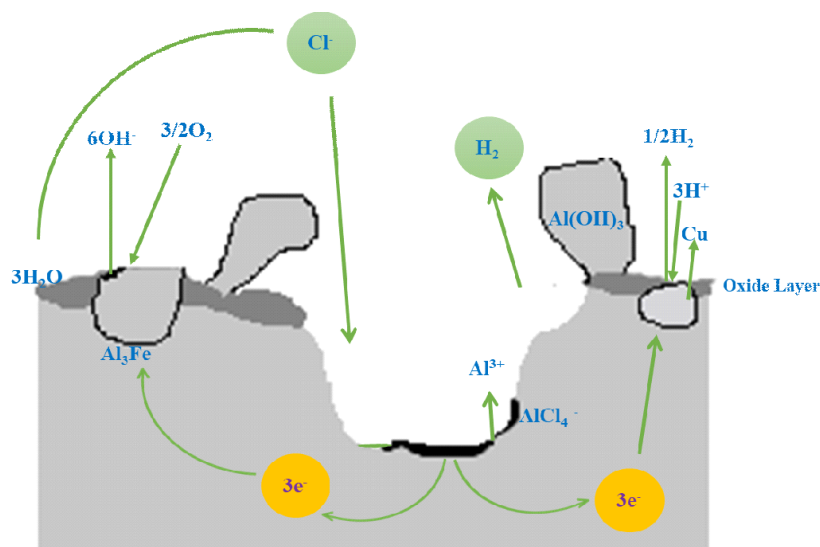


Figure 3. Schematic representation of pitting corrosion of AA

Surface pre-treatment methods

To prevent failure and ensure stability in bonded metal-metal assemblies, appropriate surface pre-treatment is essential. The conventional pre-treatment process currently employed in the aerospace sector is shown in Figure 4 and includes degreasing, etching, anodizing, and primer application, all of which traditionally involve Cr(VI)-based chemicals [51-54]. Initially, the aluminium alloy is degreased to remove oils, grease, and contaminants acquired during manufacturing. This is followed by etching, where the surface is treated with acidic or alkaline solutions, typically a mixture of sulphuric and chromic acids, to remove the surface layer. Subsequently, anodization is performed via an electrochemical process in which aluminium is oxidized to form an oxide layer consisting of a thin non-porous barrier layer and a thicker porous layer [55]. In addition to pre-treatment and anodization, chromates are widely used as pigments in primer coatings, where chromated primers provide corrosion protection through passivation via controlled pigment dissolution

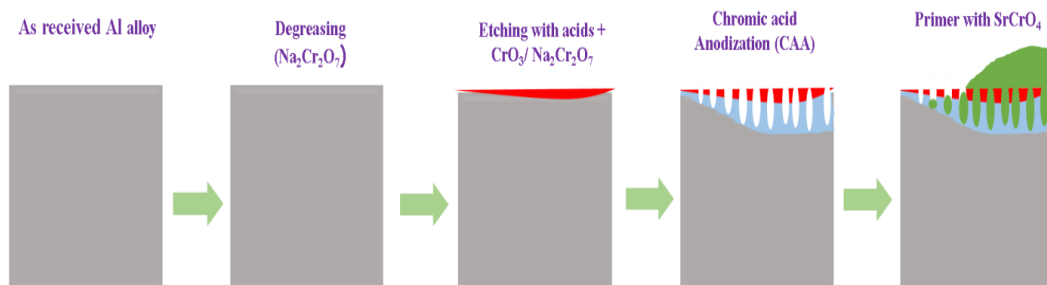


Figure 4. Schematic representation of pre-treatment process presently used in aerospace application

Anodization as a preliminary surface treatment

Chromic acid anodization

Chromic acid anodization (CAA) is another way to improve the corrosion protection of AA by forming an artificial thick oxide layer (anodization) on the metal surface. Generally, the naturally present oxide layer on AA is insufficiently resistant to the harsh medium. Anodization is an electrochemical surface treatment in which the thickness of oxide can be tuned by different operating conditions, such as electrolyte chemical composition, pH, and temperature of electrolyte/ electrode. The current density plays an essential role in the morphology and properties of the obtained oxide layer [56-58]. The anodic oxide layers formed in chromic acid exhibit favourable morphological and chemical properties, ensuring effective corrosion protection, enhanced fatigue resistance, and improved adhesion.

Alternatives to chromic acid anodization

A lot of efforts have been made over the last two decades to develop alternatives to CAA, such as sulphuric, tartaric-sulphuric acid, boric-sulphuric anodization, etc. [59-64] as shown in Table 3. It describes the existing alternatives to CAA. These alternatives, although they have effectively replaced Cr-based approaches for some components, fall short of CAA in numerous aspects and may not be utilised as general solutions for the Cr(VI) surface treatment system. The following section discusses the currently available alternatives to CAA.

Table 3. Different procedures and compositions for Cr(VI)-free anodization process

Procedure	Chemical composition	Thickness, μm
Sulphuric acid anodization (SAA)	H_2SO_4	5-20
Tartaric sulphuric acid anodization (TSA)	$\text{H}_2\text{SO}_4 : \text{C}_4\text{H}_6\text{O}_6$	3-5
Boric sulphuric acid anodization (BSA)	$\text{H}_2\text{SO}_4 : \text{H}_3\text{BO}_3$	~3
Phosphoric sulphuric acid anodization (PSA)	$\text{H}_2\text{SO}_4 : \text{H}_3\text{PO}_4$	1-5

Cr(VI)-free anodization

The best electrolytes studied as alternatives to chromic acid can generally be divided into two categories. The first category includes phosphoric acid-based and alkaline electrolytes, which are known to provide better adhesion of subsequent coatings due to the porous nature of the anodic oxide structure. However, their corrosion protection performance is relatively poor, mainly because of the open morphology of the anodic oxide layer and the presence of phosphate species, which inhibit the precipitation of aluminium hydroxide during the sealing stage [65]. The second category comprises sulphuric acid-based electrolytes, which yield anodic films with strong corrosion protection. Nevertheless, these coatings typically exhibit poor adhesion due to their thick, porous oxide morphology [66]. Thus, while sulphuric and phosphoric acid systems remain the most promising electrolytes, the trade-off between adhesion and corrosion resistance underscores the

need for process optimization, hybrid electrolyte formulations, or post-anodization treatments to achieve balanced performance in aerospace-grade applications. The suitability of different acids for anodizing AA 2024 alloys varies significantly. Sulfuric and phosphoric acids facilitate the formation of stable anodic oxide films, while hydrochloric and nitric acids tend to cause severe surface dissolution and damage. These findings highlight that electrolyte selection is crucial for achieving successful Cr(VI)-free anodizing [67].

Sulphuric acid anodization

The most widely used and traditional approach for anodizing AA is sulphuric acid anodization (SAA). It is useful in applications that require hardness and abrasion resistance. SAA forms a thick, sulphate-containing, porous oxide layer, resulting in poor primer adhesion. SAA often has a thicker layer than CAA, resulting in a reduction in fatigue strength. SAA could be enhanced by considering the influence of key parameters, such as process duration, on the characteristics of anodic aluminium oxide (AAO) layers [68]. Nonetheless, SAA has proven to be effective against corrosion in both untreated and painted environments. CAA was replaced by SAA in several corrosion-sensitive applications [69,70], but it cannot be used as a CAA substitute in painting/bonding applications for aerospace. These limitations, however, can be addressed by introducing weak organic acids. When organic acids are used alone as anodizing electrolytes, barrier oxide layers are formed; however, when combined with sulphuric acid, porous anodic oxide layers are formed. Organic acids have been introduced to sulphuric acid electrolytes for a variety of purposes [71]. The effects of adding various carboxylic acids to sulphuric acid on the morphology/composition and corrosion behaviour of anodic oxide coatings on AA2024 alloy were investigated [72]. They were compared to the CAA oxide layer in terms of performance. They studied the effects of adding carboxylic acid (oxalic, malonic, citric and tartaric acids) to a sulphuric acid electrolyte [73-76], and observed that the addition of tartaric (TSA) and malic (MSA) acids to sulphuric acid retarded stable pit formation compared to only uses of sulphuric acid. The improved corrosion protection behaviour in TSA and MSA electrolytes may be attributed to reduced dissolution of copper-rich precipitates, resulting in fewer voids and irregularities in the oxide layer. Tartaric-sulphuric acid anodizing has been widely discussed in the literature as an alternative to CAA for corrosion-prevention applications among organic sulphuric-acid-based electrolytes. Significant improvements in barrier thickness and corrosion resistance can be achieved through tartaric-sulphuric acid anodizing [77].

Boric sulphuric acid anodization

Boric sulphuric acid anodization (BSA), patented by Boeing, is used as an alternative to CAA and it is commonly proposed for non-fatigue sensitive applications in aircraft. The BSA-formed anodized oxide structure resembles SAA, whereas CAA shows smaller pores and a more regular hexagonal arrangement, providing more favourable results. According to Zhang *et al.* [78], the introduction of phosphoric acid into the anodizing electrolyte increased the bond strength and longevity of the BSA anodization process. This process creates the bigger pores, which increase the primer penetration and oxide endurance. The anodic layer may be due to larger ordered pores, which improve primer penetration, adhesion, and oxide stability [79]. However, both anions, sulphate and borate, are ineffective inhibitors of aluminium corrosion - the resultant coatings have poorer fatigue and corrosion resistance compared to CAA. Furthermore, as boric acid is harmful, it is not advised as a replacement.

Phosphoric sulphuric acid anodization

Phosphoric sulphuric acid anodization (PSA) has a comparable pore size and thickness to CAA [80]. On the other hand, PSA has a lower corrosion resistance than CAA and is only suitable for structural bonding-based applications. Only a few applications meet these criteria, and they are typically used in combination with Cr-based systems. However, it does not meet military criteria (MIL-A-8625). PSA is an efficient technique that requires extensive research for more understanding and clarity.

Conventional anodization with cations/anions

From the 1990s, various salts containing rare earth elements were added to SAA/TSA electrolytes to investigate the anodization of aluminium [81]. It is required that the corrosion-resistant pre-treatment layer must follow MIL specifications (MIL- DTL- 5541F) for aluminium alloys. In recent years, MnO_4^- , VO_4^{3-} and other oxyanion salts have received some attention. These multiple oxidations are preferred for active corrosion protection.

Sealing approaches for the anodic layer

Post-treatment of anodic layer (sealing)

Post-treatment refers to the steps performed after anodization, including sealing. They are discussed in more details in the following sections.

Cr-based sealing

Cr based sealing is performed using Alodine® 1200, SurTec 650™, SOCOSURF TCS™ in the aircraft industries [82,83]. Cr sealing creates a thin protective layer of Cr hydroxide over the oxide layer and its pores. By this process oxide layer gets closed and later it becomes hydrated in nature. In the micro-pores of the oxide layer, depending on the pH, this sealing forms aluminium oxochromate or aluminium dioxychromate [84].

Finally, the formation of hydrated- Al_2O_3 , *i.e.* boehmite, exhibits a larger volume compared to Al_2O_3 and the pores get interlocked [85]. Cr based sealing provides adequate corrosion and wear resistance. The presence of chromate remnants facilitates self-healing and re-passivation.

Cr(VI) free alternatives for sealing of oxide layer

Hot water sealing

Hot water sealing (HWS) is employed to seal oxide pores by forming boehmite (aluminium oxide hydroxide) upon immersion in hot water [86]. HWS is a cost-effective and acceptable approach for anodizing operations with no rigorous surface protection requirements. However, Al-Cu alloys and Cu-rich compounds may precipitate at grain boundaries during this process, which decreases hardness and abrasion properties. Further, adhesion, fatigue properties, and corrosion resistance performance are frequently unsatisfactory. To address this problem, nickel acetate is employed as an additive. Compared with HWS, Ni with oxide pores provides good corrosion protection and adhesion. In this regard, Fedel *et al.* [87] investigated the influence of coating thickness and sealing treatments on the corrosion resistance of anodic oxide coatings on AA, demonstrating that both parameters significantly affect the long-term protective performance of anodized layers. Regrettably, this development does not yet apply to aircraft.

Nickel fluoride sealing

Anodized pore sealing may be done at low temperatures (30 °C) using NiF (nickel fluoride). Due to low temperature, the produced seals are shallower compared to hydrothermal [88]. Because of

the use of hazardous compounds, this approach is not employed in the aviation industry and does not comply with aircraft regulations.

Some of the most prominent alternative process has been developed for the replacement of CAA in AA and their details are given in Table 4.

Table 4. *Electrolytes and sealing agents used for anodization of AA 2024 [89-92]*

Electrolyte for anodization	Sealing agents and observations
10 vol.% H ₂ SO ₄	KMnO ₄ , Na ₂ MoO ₄ - Enhances corrosion protection
20 wt.% H ₂ SO ₄	Hot Ni(CH ₃ CO ₂) ₂ , cold Ni(CH ₃ CO ₂) ₂ Cold saturated Ni(CH ₃ CO ₂) ₂ , hot water sealing - All sealing decreases the pore size - Hot Ni(CH ₃ CO ₂) ₂
0.41 M H ₂ SO ₄ + 0.53 M C ₄ H ₆ O ₆	Hot water sealing - Oxide layer exhibits low porosity which contributes to improved corrosion protection
0.46 M H ₂ SO ₄ + 0.53 M C ₄ H ₆ O ₆	LDH-NO ₃ , LDH-VO _x , Hot water sealing - LDH sealing's helps in active corrosion protection and maintains the stability
0.46 M H ₂ SO ₄ + 0.53 M C ₄ H ₆ O ₆ with and without Na ₂ MoO ₄ ×2H ₂ O	No sealing - Presences of Na ₂ MoO ₄ ×2H ₂ O to anodization bath enhances corrosion inhibition.
40 g L ⁻¹ H ₂ SO ₄ + 80 g L ⁻¹ C ₄ H ₆ O ₆	Hot water sealing, Hybrid sol gel (TEOS + GPTMS) - Improves the corrosion resistance of oxide layer
55 g L ⁻¹ H ₂ SO ₄ + 88 g L ⁻¹ C ₄ H ₆ O ₆	Hot water, NiF ₂ followed by hot water sealing Hot K ₂ Cr ₂ O ₇ , KMnO ₄ + Na ₂ MoO ₄ + LiNO ₃ Excellent corrosion resistance shown by sealed oxide layer

Conversion coatings

A conversion coating (CC) is an electrochemical/chemical treatment that forms a protective layer over a metal substrate. Conversion coatings provide good corrosion protection and provide a good foundation for paint adherence. Conventional methods (*viz.*, dip, spray, and immersion) can be used to apply conventional coatings on metal substrates [93,94]. Immersion in an inorganic salt-containing solution is the most common method used in industry. In the section below, we will discuss different types of conversion coatings.

Chromate conversion coatings

Chromate conversion coatings (CCC) have been widely employed in the aircraft industry in recent decades due to their higher corrosion resistance and improved paint adhesion on aluminium alloys. A chromate conversion coating is a chemically produced oxide layer that acts as an active barrier layer and slows down the cathodic oxygen reaction rate.

To decrease the oxide coating and to activate the surface, acidic deoxidizers are utilised and many factors, such as chromate concentration, temperature, time and pH, are employed to tune the coating's characteristics.

In this process, when an oxidizer is present, Al is oxidized and Cr(VI) is reduced to Cr(III). During this process, formation of coatings occurred by hydrolysis and condensation reaction to form Cr³⁺ monomer, dimer, trimer and tetramer, followed by Cr(III) condensation driven by a rise in pH at the surface of the aluminium alloy. The mechanism of CCC formation is indicated in Figure 5.

Cr-free conversion coatings

Chromium-free conversion coatings represent a crucial advancement in corrosion-protection solutions for lightweight structural metals.

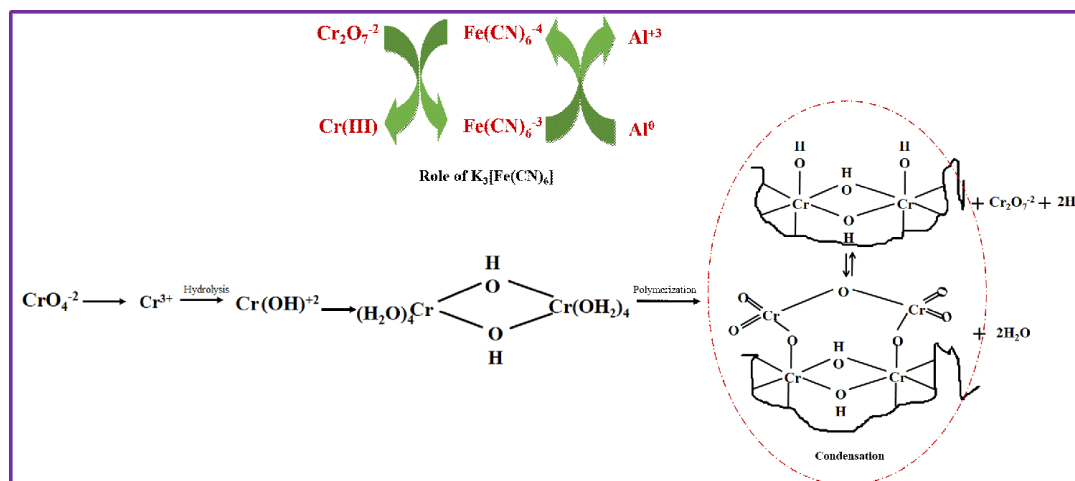


Figure 5. Mechanism of formation of chromate conversion coating over Al alloy

Types of Cr-free conversion coatings [95-101] and their key chemical systems are listed in Table 5. Phosphate-based conversion coatings, such as iron, zinc, and other heavy-metal phosphates, form a protective phosphate network on the metal surface, improve the coating adhesion and exhibit moderate corrosion resistance. Rare-earth conversion coatings, which are most commonly composed of cerium, yttrium, lanthanum, neodymium, samarium, and praseodymium, have gained prominence due to their ability to deposit insoluble hydroxides/oxides at the cathodic sites of the substrate. These precipitated phases inhibit localized electrochemical activity and can impart limited self-repair capability when defects arise. In addition, other conversion coatings have been developed as viable Cr-free strategies. Systems based on molybdates, permanganates, vanadates, and tungstates function by redox-driven formation of passivating oxide layers, suppressing anodic dissolution. Fluozirconate and fluotitanate conversions, alongside trivalent chromium (Cr(III)) pretreatments, have also achieved industrial relevance, offering robust film adhesion and compatibility with aerospace coating systems while meeting stringent environmental and occupational-safety requirements.

Table 5. Types of Cr-free conversion coatings for AA

Conversion coatings	Examples
Phosphate conversion coatings	Iron phosphates, zinc phosphates, heavy phosphates.
Lanthanide-based (rare-earth) conversion coatings	Cerium (Ce), yttrium (Y), lanthanum (La), neodymium (Nd), samarium (Sm), and praseodymium (Pr)
Miscellaneous-based coatings	Molybdates (Mo), permanganates (Mn), vanadates (V) and tungstate (W), fluotitanate and fluozirconate conversion coatings and trivalent Cr(III) conversion pretreatment (TCP) coatings

Phosphate conversion coatings

The phosphating method uses a solution of dilute phosphoric acid. To obtain a phosphate coating, phosphate ions must precipitate on a divalent metal surface [102-104]. This procedure forms an insoluble phosphate layer that is hard and electrically nonconductive. The obtained phosphate coating is insoluble, continuous, and strongly adheres to the metal surface, thereby offering excellent corrosion resistance [105]. Phosphate conversion coatings are categorized into iron, zinc and heavy phosphates. Phosphate conversion coatings can be applied to metals and alloys by spraying or immersion methods. When applied efficiently, phosphate conversion coatings can provide effective barrier protection for metals. When integrated with a paint topcoat, a thicker phosphate conversion coating can provide greater barrier properties. Although phosphate coatings provide high adhesion and some barrier protection, they also lose their self-healing potential due to their limited phosphate solubility. It also exhibits pH instability in a variety of applications, such as chromate coatings, making

it unsuitable as a substitute for Cr(VI) in conversion or priming coatings [106]. In phosphate coatings, self-healing can occur when soluble phosphates leach from the coating and form precipitates at damaged sites. Compared with conventional zinc phosphate, zinc aluminium polyphosphate provides superior corrosion protection, attributed to its enhanced solubility. Strontium aluminium polyphosphates exhibit greater solubility, providing better substrate corrosion protection.

The cerium diphenyl phosphate has been shown to be effective as a corrosion inhibitor in NaCl solution when used in an epoxy primer system [107].

Rare earth conversion coatings

Potential corrosion-inhibiting properties of rare earth (lanthanide) elements have long attracted researchers' interest. Examples of rare earth elements include Ce, Y, La, Nd, and Sm. Early studies demonstrated that rare-earth metal salts could protect aluminium and its alloys against corrosive ions, prompting several subsequent patents and academic studies. Among these, the cerium ion (Ce^{3+}) acts as a strong cathodic inhibitor for aluminium alloy intermetallics [108,109]. Importantly, Ce^{3+} is considerably less hazardous than Cr^{6+} and is typically available as CeCl_3 and $\text{Ce}(\text{NO}_3)_3$, both of which exhibit corrosion inhibition performance comparable to chromate conversion coatings [110-113]. Cerium-based conversion coatings can be prepared either by long-term immersion of the metal/alloy substrate in a neutral cerium salt solution or more rapidly through the addition of H_2O_2 to an acidified cerium salt solution, enabling coating formation within minutes. Studies have shown that Ce-based conversion coatings provide corrosion protection across various metals, with protection ranging from minimal to moderate, though in some cases, limited by poor adhesion [114]. In addition to their role as cathodic inhibitors, cerium compounds have also been employed in versatile ways, such as in spontaneous and electrochemical cerium oxide primer layers (CeOPL), incorporation into anodized films to form Ce-O-Al protective layers, encapsulation in nanoparticles for self-healing coatings, and reinforcement phases in composites [114]. These multiple approaches highlight the adaptability of cerium compounds in environmentally compliant corrosion protection systems for aluminium and its alloys.

It is well established that Ce^{3+} ions provide significantly better corrosion inhibition than Ce^{4+} , especially for aluminium alloys like AA2024. This improved performance stems from Ce^{3+} 's ability to form stable cerium hydroxide and oxide layers at cathodic sites, effectively blocking the oxygen reduction reaction and slowing localized corrosion. In a detailed comparison, Matter *et al.* (2012) found that Ce^{3+} ammonium nitrates outperformed their Ce^{4+} counterparts under low-chloride conditions, highlighting the superior protective behaviour of Ce^{3+} [115]. Their complementary study further revealed that Ce^{3+} ions offer more consistent passivation, whereas Ce^{4+} can trigger undesirable oxidative interactions, ultimately reducing coating stability [116].

Equally important is the role of the anionic component in cerium salts. Machkova *et al.* [117] showed that different Ce(III) salts have varying inhibition efficiencies depending on their anion. Their results ranked the performance as $\text{Ce}(\text{NO}_3)_3 > (\text{NH}_4)_2\text{Ce}(\text{NO}_3)_5 > \text{Ce}_2(\text{SO}_4)_3 > \text{CeCl}_3$, suggesting that nitrate-based salts are particularly effective at forming adherent, uniform protective films [117]. This finding reinforces the idea that both the cationic and anionic parts of the inhibitor must be carefully considered for optimal protection.

The discussion has also been extended to incorporate recent progress in hybrid surface treatment methodologies. An emerging and effective approach involves combining anodization with cerium-based conversion coatings. Based on the investigation by Kozhukharov and Girginov, anodizing the aluminium surface before applying the cerium coating improves adhesion, enhances barrier properties, and provides longer-lasting protection [118]. Electrochemical tests and salt spray

experiments confirmed that this dual-layer strategy offers significantly better performance than cerium coatings alone

Together, these studies support the preference for Ce^{3+} ions in environmentally friendly corrosion protection systems. They also highlight the importance of not only the oxidation state of cerium but also the choice of accompanying anions and pre-treatment methods in designing effective, sustainable coatings for aluminium alloys.

Transition metal oxyanion-based conversion coatings

When transition metal cations in their highest oxidation state can form extremely stable oxyanions in solution, these oxyanions are employed as transition metal oxyanion (TMOA) coatings. These metal ions exhibit behaviour similar to that of chromates: they can be reduced electrochemically and subsequently form insoluble oxides. Examples include permanganates (MnO), vanadates (VO_3) and molybdates (MoO_2). The main inhibitory mechanism is believed to be the preferential adsorption of anions by aggressive ions, such as chlorides or sulphates. Conversion coatings based on manganese are expected to exhibit self-healing potential with AAs because of their significant equilibrium potentials, which drive the reduction of Mn^{7+} to Mn^{4+} at degraded regions.

Molybdates have been extensively used as chromate replacements owing to their oxidizing nature and the stability of their reduction products. Mo is used as an additive in conversion coating and primer systems. Breslin *et al.* [119] mentioned the influence of Mo oxide with different oxidation states. The inhibition efficiency of Mo was determined by the solubility and size of the Mo oxide (MoO_2). Further study reveals that the pitting potential of the Mo inhibitor was more dependent on Cl^- concentration than on solution pH. A low Mo concentration provides greater corrosion protection than a higher concentration by forming a passivation layer. The coating produced by typical MnO conversion consists of hydrated MnO_2 , MnO_4 , Mn_2O_3 , and Al_2O_3 . The inside layer is mostly made up of oxides of Al and Mn, while the outer layer is mostly made up of oxides of Mn. The obtained coating shows 52-100 nm in thickness, and the electrochemical growth mechanism is similar to that of chromate conversion coatings. The use of composite coatings incorporating rare-earth elements was recognized, and these coatings showed promise in corrosion protection by forming a protective oxide layer at cathodic sites in an alkaline solution.

Although permanganates have some environmental concerns, their hazard is much lower than that of Cr(VI). It was observed that paint adhesion and corrosion protection were comparable to those of CCCs and a lacquer-coated substrate, which was more prone to pitting in an aggressive anion environment. The formation of an irregular layer on the intermetallic surface impairs corrosion protection, and cracks develop due to thickness variations.

Trivalent chromium process conversion coatings

Many researchers have carried out research on the usage of Cr(III) after Cr(VI) was banned and it is called the "second best" alternative. Treatments with trivalent chromium are commonly referred to as trivalent chromium-based conversion coatings (TCC). Trivalent chromium has been used in aluminium alloys to form corrosion-resistant coatings. Trivalent chromium coatings offer barrier properties but considerably lower self-healing properties than Cr(VI).

The trivalent chromium process (TCP) uses a combination of oxides (amorphous oxides, hydrated oxides, and hydroxides) that are primarily based on Cr^{3+} to create protective coatings, which the US Navy has initially patented [120]. Compared with Cr^{6+} , Cr^{3+} has shown lower toxicity. Cr^{3+} salts with sulphate, a fluorine compound, and an adjusted pH are common requirements for conversion baths [121]. Fluoride is required to etch the native alumina layer and prevent Al from re-passivating,

thereby accelerating the film-forming reaction. An addition of hexafluorozirconate compound used as an activator, which leads to Zr/Cr film formation on the AA substrate [122].

Particles as small as a few hundred nanometres are scattered across the whole surface of TCP films; however, the thickness of the film is much thicker on intermetallic particles (IMPs). The inner layer is primarily made up of aluminium oxides, and the outer layer is made up of Cr- or Cr/Zr-rich based phases [123]. EIS measurements confirmed the presence of a native Al₂O₃ interfacial film following the conversion treatment.

Cr₃/Zr₄ TCP layers provide significantly greater corrosion resistance for AA 2024 under harsh conditions during electrochemical measurements and salt spray tests (SST). This is owing to anodic dissolution and oxygen reduction reaction inhibition, with oxygen reduction reaction being more restricted due to O₂ chemisorption blocking on intermetallic particle sites [124]. However, because the coatings are significantly thinner than CCCs, they provide poor corrosion protection in 5 % NaCl [125]. Additionally, mobile Cr⁶⁺ species produced locally by Cr oxidation via H₂O₂ appear to provide some active protection. The latter acts as a powerful oxidant that is created when O₂ is reduced at the IMPs, resulting in the self-healing system described above [126]. Though Cr⁶⁺ levels are intended to be lower and temporary, and the existence of Cr⁶⁺ in TCP coatings in aerated conditions is still a point of contention. TCP solutions are commercially available, and their corrosion resistance has proven quite promising compared to CCCs.

Zirconium/titanium conversion coatings

Zr/Ti conversion coatings have attracted interest since their emergence as a potential replacement for chromates. This technology has advanced significantly and is now available in numerous commercial products.

Zirconium/titanium conversion coatings (Zr/TiCCs) were developed for 2xxx AA and 6xxx AA for automotive body applications. Various studies have examined the formation mechanism of Zr/TiCCs and its impact on the composition of aluminium alloys. Peltier and Thierry [127] recently published a review that classifies the development of Zr/TiCC on AA into two steps. In the first step, dissolutions of Al occur in which the inherent oxide layer is triggered by aggressive hexafluoro-metallate complexes in a bath with a low pH between 2.8 and 4, and hexafluoroaluminate compounds are formed. The second step involves the precipitation of metal oxide layers (Zr/Ti) upon raising the pH on the cathode side to 8.5. The usage of Zr/TiCCs is advantageous due to their high corrosion resistance and excellent adhesion to metallic substrates.

Compared with other conversion coating processes, the forming process requires less time and lower temperatures, thereby saving money and energy.

Furthermore, the preparation bath generates minimal sludge, and the resulting compounds are non-carcinogenic and non-eutrophic. Despite the many advantages of Zr/Ti conversion coatings (Zr/Ti-CCs), further development is required, as these coatings lack self-healing capability, function primarily as barrier layers, and are often non-homogeneous. One effective approach to enhance Zr/Ti-CC performance is the incorporation of organic or inorganic corrosion-inhibiting pigments. Studies have shown that the addition of inhibitors such as cerium and molybdate to Zr/Ti systems significantly improves the corrosion resistance of aluminium alloys [128]. Moreover, the use of mixed additives can promote more homogeneous Zr/Ti-CC formation, highlighting the strong potential of inhibitor- and additive-modified Zr/Ti coatings for improved corrosion protection. Table 6 summarises the composition and performance characteristics of conversion coatings used for aluminium alloys.

Table 6. Composition and performance characteristics of chromate-free conversion coatings [129-135]

Composition of conversion coatings	Significant results
Phosphates conversion coatings: Zn^{2+} , H_3PO_4	- Effective corrosion protection - Good adhesion
Cerium conversion coatings: $CeCl_3$, $Ce(NO_3)_3$	- Good corrosion resistant and efficient paint adhesion - Expensive
Manganese conversion coatings: $KMnO_4$	- Layer thickness and adhesion results are comparable to Cr(VI) conversion coatings - Corrosion resistant - Low wet adhesion performance.
Oxyanions (Mo, V) based conversion coatings: Na_2MoO_4 $NaVO_3$	- Corrosion resistant. - Expensive.
Zirconium/titanium based conversion coatings: K_2ZrF_6 and /or K_2TiF_6 with their respective acids	- Good adhesion with paints - Effective corrosion resistance - Costly
Lithium conversion coatings: $LiCO_3$ and/or $LiOH$	- Low wet adhesion performance - Eco-friendly

Sol-gel and hybrid sol-gel coatings

Over the past two decades, significant research has focused on sol-gel-based coatings for corrosion protection of various metals, driven by the need for eco-friendly and non-toxic alternatives to chromate conversion coatings (CCCs). Sol-gel technology is simple, cost-effective, and widely used for corrosion protection as well as for improving adhesion between metal alloys and primer coatings, attracting considerable attention.

The sol-gel technique is a chemical synthesis process involving the controlled condensation of liquid precursors to form an alkoxide network. Initially developed for inorganic materials, the process also enables the fabrication of hybrid coatings. It is regarded as a green technology due to its use of environmentally benign chemicals, minimal waste generation, absence of washing steps, and low processing temperatures, often near room temperature.

Furthermore, this approach may readily produce materials with high specific porosity and a defined surface area, thereby enabling the incorporation of chemical substances, such as inhibitors. The thermal volatilization and degradation of the entrapped species are minimized because the synthesis temperatures are low. In addition to the organic component, various additives can be readily incorporated into the sol-gel system, thereby enhancing the corrosion resistance of metals and their alloys. Nonetheless, sacrificial metal pigments, such as zinc, magnesium, and their alloys, can be incorporated into the sol-gel coating formulation to protect various metal surfaces from corrosion.

To carry out a synthesis using the sol-gel technique, the chemical components, *i.e.* precursors, are required. Since chemical precursors are mostly liquid, they may be cast into complex shapes and thin films without the need for machining or melting.

Sol-gel coatings can be prepared using two methods: a hydrolytic process in aqueous media or a non-hydrolytic process in organic media. Using any of these processes, a variety of sol-gel coatings with diverse characteristics can be produced. These characteristics may be modified by altering the composition of reactive species, the functional groups present, time, pH, and temperature, which affect their corrosion-prevention performance. Sol-gel coatings have been intensively investigated as a potentially environmentally benign alternative to Cr(VI)-based surface treatments for aluminium alloys. Early sol-gel coatings employed inorganic silane precursors, which have high mechanical properties and promote better adhesion to the metal substrate, thereby limiting oxygen diffusion [136]. Sol-gel coating systems are inherently porous, and densification at higher curing temperatures can lead to sensitization and deterioration of the AA's mechanical properties. As a result, they are unsuitable for protecting these metals against corrosion.

Hybrid sol-gel coatings (HSG) were introduced in the early 1980s and comprise both inorganic and organic precursors, with the organic component enabling low-temperature drying and enhancing mechanical properties, thereby increasing their ability to fulfil aircraft industry requirements.

HSG coatings protect aluminium alloys from corrosion by acting as a barrier, but they do not provide any effective protection against corrosion when damage occurs. Corrosion inhibitors and nanoparticles might be incorporated to improve the active corrosion protection characteristics of HSG.

Different types of organically modified sol-gel coating alloys have been investigated for corrosion protection of aluminium [137]. The majority of them are made from organo-alkoxysilane-based precursors with organo-functional groups, such as epoxy [138] methacrylic, which can be polymerized to increase the density of the coating and therefore improve its barrier effect [139]. Hence, this hybrid sol-gel coating exhibits superior anticorrosive properties compared with non-functional organosilanes. Other functional groups, such as phenyl groups, are used to enhance the coating's hydrophobicity, whereas phosphonate groups strengthen the bond to the substrate. As a result, various organic groups are employed to modify the properties of sol-gel coatings to achieve compliance with paint systems. Amino groups react with epoxy resins, thereby making paint systems compatible. Therefore, the synthesis of epoxy-silica-based hybrid sol-gel coatings, amine-based cross-linkers are used for the formation of organic networks at low temperatures.

Furthermore, the process is mainly water-based, making it ecologically beneficial. However, due to low hydrolytic stability, the amino-cured hybrid coatings formed at ambient temperature exhibit decreasing water-barrier properties over time.

Vreugdenhil *et al.* [140] and Davis *et al.* [141] used diethylenetriamine (DETA) to investigate the corrosion inhibition behaviour of an amine-cured epoxy-silane coating. DETA is a typical epoxy cross-linker that forms a thick protective layer that resists corrosion. In addition, Donley *et al.* [142] also investigated epoxy-silane coatings crosslinked with amino-silanes and identified a considerable increase in corrosion performance when compared to coatings crosslinked with DETA

Amino-silanes have the added benefit of assisting in the development of inorganic networks. In comparison with amino-silane, other amines, which include di-amines with extended carbon chains [143] or branched amines [144-146] have been investigated as alternatives to DETA, showing enhanced corrosion protection compared with DETA-containing compositions. When organic molecules are incorporated into sol-gel films, they yield denser, crack-free coatings with improved corrosion resistance. Several strategies have been investigated to overcome this problem. However, they lose mechanical characteristics and wear resistance, rendering them more susceptible to physical destruction.

Later, N. N. Voevodin *et al.* [147] used the self-assembled nanophase particle technique with tetramethoxysilane (TMOS) and GPTMS. Figueira and Silva described the utilisation of ZrTPO and methacrylic acid (MAA) in different molar concentrations that have been combined with a sol made from TEOS and 3-methacryloxypropyl trimethoxysilane [148]. The coatings exhibited good corrosion protection to AA under simulated aircraft conditions.

The incorporation of corrosion inhibitors has been widely investigated to enhance the corrosion-inhibiting performance of hybrid sol-gel networks. Both inorganic inhibitors (phosphates, V-, Ce-, and Mo-based compounds) and organic inhibitors (mercaptobenzothiazole, phenylphosphonic acid, benzotriazole, and 8-hydroxyquinoline) have been extensively explored.

Significant improvements in hybrid sol-gel coatings have been achieved by incorporating porous ceramic nanoparticles, such as Al₂O₃, which act as nanocontainers for cerium chloride (CeCl₃). These nanocontainers enable controlled, localized release of inhibitors at corrosion-prone sites, imparting

a self-healing effect and markedly enhancing the long-term corrosion resistance of aluminium substrates, particularly aerospace-grade AA2024 alloys.

Kozhukharov *et al.* [149] embedded CeCl_3 -loaded Al_2O_3 nanoparticles into an oxysilane sol-gel matrix, which leads to a significant improvement in the durability of coatings applied to AA2024-T3 AA. Controlled and sustained release of cerium ions from within the nanoporous carriers enabled these coatings to maintain high barrier properties and resist corrosion for extended periods, up to 3000 hours in a NaCl solution.

Introduction of CeCl_3 into the sol-gel matrix negatively impacted the coating's structure, mainly due to rapid leaching and subsequent destabilization. Encapsulating the inhibitor within Al_2O_3 nanocontainers helped avoid these issues, highlighting the significance of nanoparticle-based delivery systems in sustaining and enhancing coating performance. Further evidence is provided by Tsaneva *et al.* [150], who showed that such functional nanocomposite coatings not only enhance corrosion protection but also integrate well within the multilayer coating architectures typically used in industrial applications. This emphasizes the synergistic effect between sol-gel layers and functional nanoparticle additives, improving both barrier performance and the system's ability to self-repair through localized inhibitor release.

These studies highlight the potential of nanoparticle-loaded hybrid sol-gel coatings as eco-friendly replacements for Cr(VI)-based systems.

The study demonstrates that spontaneous and low-current cathodic deposition are the most effective regimes for producing uniform, adherent, and corrosion-resistant CeCC layers on anodized AA2024-T3, while explicitly highlighting the limitations of anodic, AC, and high-current cathodic approaches. This depth of analysis, coupled with the practical guidance it offers, directly supports the optimization of electrochemical deposition strategies in aerospace corrosion protection [151]. The systematic linkage of deposition parameters with coating microstructure, chemical composition, and corrosion performance, established through electrochemical studies and advanced surface characterization, offers strong, well-substantiated support for the authors' conclusions. The identification of spontaneous and low-current cathodic deposition as optimal not only guides industrial-scale adoption but also delivers fundamental insights into the interfacial mechanisms governing CeCC formation on anodized substrates [152]. Together, these contributions make the work highly relevant to both academic research and aerospace manufacturing practices, particularly in advancing durability and sustainability objectives.

Conclusion

The increasing demand for environmentally sustainable materials and the enforcement of regulations such as REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals), have accelerated the shift away from Cr(VI)-based corrosion protection systems for aluminium alloys. In response, significant research efforts have focused on developing alternative solutions that ensure high corrosion resistance while eliminating hazardous substances. Among these alternatives, sol-gel-based hybrid coatings have emerged as highly promising candidates, demonstrating excellent performance as substitutes for conventional pretreatment and primer layers. These innovations not only meet stringent environmental standards but also preserve the mechanical integrity and longevity required for aerospace applications. Continued advancements in chrome-free three-layer coating systems are crucial to support the aerospace industry's transition toward safer, more sustainable corrosion protection technologies.

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