

Review

Review of coatings used for corrosion protection of aluminium alloys

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Dedicated to the memory of Prof. Dr. Boris Žemva

Abstract

Aluminium and aluminium alloys are major technological metals, offering desirable mechanical properties, low density, thermal and electrical conductivity. Importantly, they exhibit high recyclability. While these materials are relatively stable and corrosion-resistant in most environments, they are often subjected to corrosion and wear in harsh environments. Coatings are the most common method of corrosion protection of aluminium and its alloys. Coatings can improve not only corrosion resistance but also wear resistance, and can add functional properties to the surface. In the present review, the coatings are summarised in five groups: (1) barrier aluminium oxide coatings, including anodised coatings, plasma electrolytic oxidised coatings, coatings deposited by atomic layer deposition, and by hydrothermal treatment, (2) conversion coatings including zirconium, chromate, titanium, trivalent chromium, and phosphate (3) metallic coatings comprising clad and electroplated metal coatings, (4) organic coatings comprising powder and liquids organic coatings, and sol–gel coatings, and (5) inhibition and wettability control coatings, comprising coatings incorporating inhibitors or nanoparticles and superhydrophobic coatings. The review focuses on production methodologies and the physical-chemical characteristics of coatings. Advantages and potential shortcomings of individual coatings are discussed in terms of their use and corrosion protection.

Keywords: corrosion protection, coatings, aluminium and aluminium alloys, surface treatment.

1. Passivation and corrosion of aluminium metal and aluminium alloys

Aluminium alloys are today one of the major industrial metals. Alloying aluminium significantly increases strength, improves ductility and formability, and enhances thermal and electrical conductivity. Due to their excellent strength-to-weight ratio, high yield strength, light weight, low melting point, corrosion resistance, and conductivity, aluminium alloys are utilised in the automotive, aerospace, marine transportation, infrastructure (building materials), consumer goods, and food processing industries. In terms of costs, aluminium alloys are more affordable than, for example, copper alloys.¹ Their low density makes them suitable as lighting materials, particularly in transportation, where the vehicle's mass determines fuel consumption and, consequently, CO₂ emissions.

When exposed to air, aluminium metal self-passivates with a thin layer of aluminium oxide/hydroxide. Thanks to this, aluminium has excellent corrosion resistance and can be used without maintenance for many years. The passive layer has a bilayer structure, with an inner barrier Al₂O₃ layer, 3–5 nm thick, and an outer porous layer, 5–7 nm thick.² In aqueous solutions, the outer porous layer thickens and consists of bayerite / α-Al(OH)₃, gibbsite / γ-Al(OH)₃, hydralgite / Al(OH)₃·3H₂O or boehmite / γ-AlO(OH).² This layer protects the underlying metal when exposed to aqueous solutions that do not contain aggressive anions, such as chloride. It is thermodynamically stable at 4 ≤ pH ≤ 8.5.² Aluminium will corrode outside this pH range. Further, it will corrode even in this pH range if the passive film is locally damaged, for example, by the adsorption of chloride ions followed by the formation of soluble AlCl₄⁻ complexes, related to higher material loss due to dissolution, thereby exposing the underlying metal

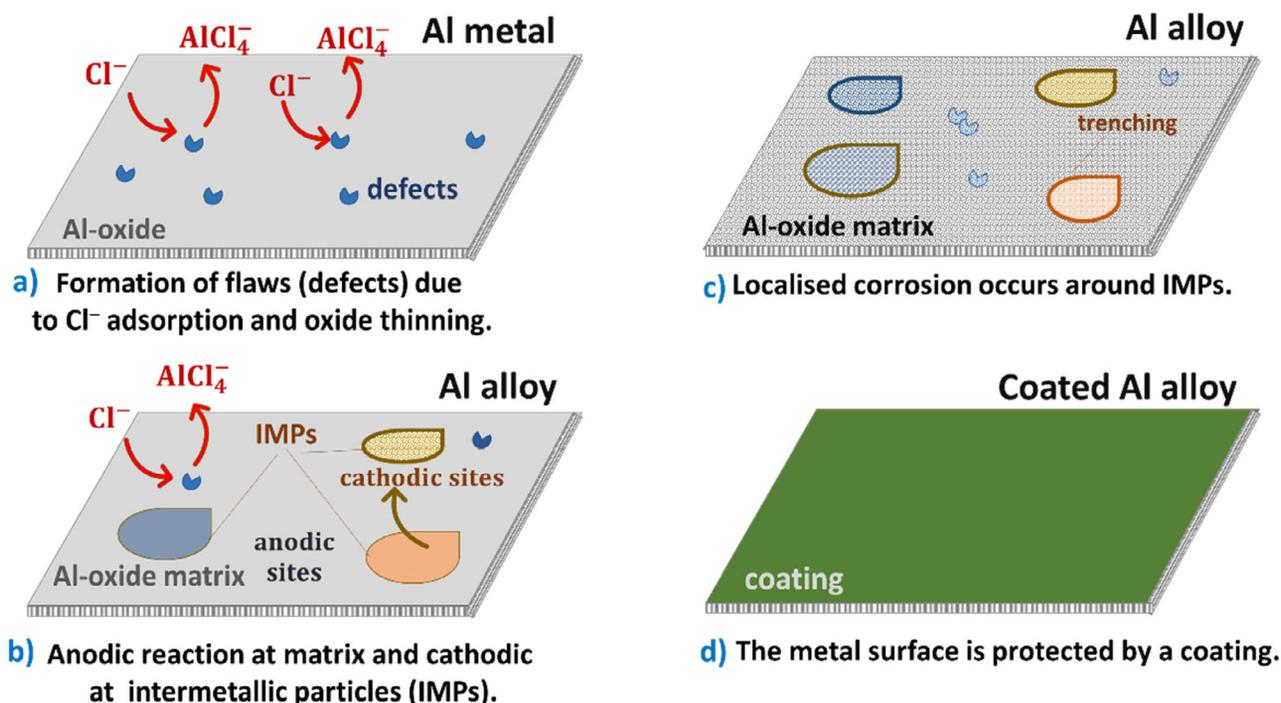


Figure 1. Schematic presentation of (a) corrosion of oxide layer on aluminium and (b, c) aluminium alloy due to adsorption of chlorides, and (d) coating on aluminium alloy. Intermetallic particles (IMPs) are inherent to each aluminium alloy series and vary in size and composition, as shown by spots of varying colours and sizes.

to the aggressive electrolyte and promoting metal dissolution (Figure 1a).

The situation is even more complicated for aluminium alloys (Figure 1b and c). Namely, alloying aluminium enhances its mechanical properties, but it also creates a heterogeneous microstructure with numerous intermetallic particles (IMPs). These IMPs are inherent to each aluminium alloy series and vary in size and composition,¹ as described in the following section. For example, the aluminium alloy 2024 of series 2xxx has round-shaped Al–Cu–Mg IMPs and larger, irregularly shaped Al–Cu–Mn–Fe IMPs. Aluminium alloy of series 5xxx, 5754, contains Mn–Fe–Al or Mn–Fe–Si–Al IMPs, whereas alloy 7075 of the series 7xxx contains MgZn_2 and Mg_2Si , and Al–Cu and Al–Cu–Fe IMPs. In the figure, these different IMPs are represented by spots of varying colours and sizes. Since IMPs are electrochemically more noble (i.e., their potential is more negative) relative to the surrounding aluminium matrix, they act as sites where the cathodic oxygen evolution reaction (1) occurs.



Depending on their composition, IMPs act as either stronger or weaker cathodic sites, thus governing the course of corrosion reactions. In contrast, the matrix is less noble (i.e., its potential is more positive) and thus acts as

an anodic site where the main reaction is the dissolution of Al (reaction 2).

The strong galvanic interaction between these IMPs and the aluminium matrix makes aluminium alloys vulnerable to localised attack when exposed to aqueous solutions containing chlorides or other aggressive ions that can damage the passive layer. The consequence is the susceptibility of Al alloys to localised corrosion, especially intergranular, galvanic, and pitting corrosion (Figure 1c).

Therefore, when subjected to harsher environments or wear and friction, aluminium alloys are susceptible to degradation without proper coating or surface modification.² The broad spectrum of applications of aluminium alloys exposes them to various chemical compositions of environments, pH values, and temperatures. Different types of coatings (Figure 1d) are used nowadays to offer improved corrosion resistance, enhanced wear resistance, and a more aesthetically pleasing appearance (with improved optical properties) compared to the base aluminium alloy. The type of corrosion protection depends on the base material and the environment it is exposed to.

Generally, the coating market represents the largest share of anticorrosion measures. Data on the size of the coating market may vary depending on the types of coatings and paints included. For example, the paints and coatings market size was estimated at approximately 212 billion USD in 2024 and is expected to reach around 280 billion USD by 2030, with a projected CAGR (compound annual growth rate) of 5%.³ Since the rise in aluminium alloy use

Table 1. Designation, major alloying elements and primary uses of wrought and cast aluminium alloys.

Wrought alloys			Cast alloys		
Designation	Major alloying element	Main use	Designation	Major alloying element	Main use
1xxx	unalloyed	electrical applications	1xx.x	unalloyed	rarely used, mainly for electrical applications
2xxx	Cu	aerospace industry	2xx.x	Cu	aerospace and marine industry
3xxx	Mn	cooking utensils	3xx.x	Si	engine blocks, wheels
4xxx	Si	welding wires	4xx.x	Si	
5xxx	Mg	bridges, transportation, marine applications, tanks	5xx.x	Mg	aerospace and marine industry, instruments, transportation, electronics
6xxx	Mg and Si	pipng, building project, consumer goods	6xx.x	not yet used	
7xxx	Zn	aerospace industry, mould-making	7xx.x	Zn	rocker arms, lightweight transportable bridges
8xxx	other elements	electrical wires and cables, packaging, automobile and aerospace applications	8xx.x	Sn	Al foil

over the last two decades coincided with the gradual phase-out of chromate coatings as a major corrosion-resistant coating, the development of alternative protection attracted significant attention in both academic and industrial communities. Several review papers have already summarised modifications to the surfaces of Al alloys and various coatings applied to them.^{4–16} The motivation for this review is to summarise various approaches and categorise them by coating type. Major coatings used for the corrosion protection and functionalisation of aluminium alloys are divided into five groups: barrier aluminium oxide coatings, conversion coatings, metallic coatings, paints, and inhibition and wettability control coatings, and are focused on their production methodologies and coating characteristics. Finally, various types of coatings are discussed, including their advantages and potential shortcomings.

2. Classification, composition and applications of aluminium alloys

According to the fabrication process, there are two main alloy types: wrought and cast.¹ They are both heat-treatable and non-heat-treatable. Wrought alloys are mechanically worked by rolling, extrusion or forging and possess superior mechanical properties of high strength, stiffness and ductility. Wrought alloys account for approximately 85% of all aluminium alloys. The alloying elements, such as silicon, copper, zinc, and magnesium, contribute to the initial strength of a heat-treatable alloy. They can be strengthened further through heat treatment. Non-heat-treatable forms typically contain alloying elements such as silicon, manganese, and magnesium, which contribute to their initial strength. These alloys can be fur-

ther strengthened by strain hardening or cold working. Cast aluminium is produced by pouring molten metal into moulds, allowing for the creation of complex shapes. While this process typically yields lower strength and toughness compared to other wrought alloys, it remains an economical choice for producing intricate components, such as engine blocks and housings.

There are eight primary types of wrought aluminium alloys, each characterised by its main alloying element (Table 1). According to the Aluminum Association¹⁷ (AA) System, these alloys are classified into two categories: heat-treatable alloys (2xxx, 6xxx, and 7xxx) and non-heat-treatable alloys (1xxx, 3xxx, 4xxx, and 5xxx). The alloys are identified by a four-digit code (xxxx), where the first digit represents the major alloying element, the second digit (if not zero) indicates a modification of the alloy, and the third and fourth digits are arbitrary numbers used to distinguish specific alloys within the series. Standard temper designations for these alloys include: F (as-fabricated), O (annealed), H (strain-hardened), W (solution heat-treated), and T (thermally treated). There are other standard systems, for example, the European Norm (EN), the Unified Numbering System (UNS) and the International Organization for Standardization (ISO).

The cast aluminium alloy designation also follows a four- or five-digit system, where the first digit indicates the primary alloying element, the next two digits specify the particular alloy within that series, and the decimal part identifies the product form (0 for a casting, 1 or 2 for an ingot). A prefix letter like "A" denotes a specific modification of the alloy, and a temper designation (e.g., T6) may be added to specify heat treatment.

One of the main advantages of aluminium alloys is their high recyclability, making them an eco-friendly ma-

terial choice. In the European Union, over 90% of aluminium is recovered from construction and transport applications.¹⁸ Recycling reduces the energy needed for primary production by 95%, which is crucial for the sustainable use of aluminium alloys.

3. Coatings used for corrosion protection of aluminium alloys

Coating options for aluminium alloys are summarised in Figure 2. The following approach was adopted to present the various coating types.

Group 1: Barrier aluminium oxide coatings, which serve as a physical barrier between the substrate and the environment, are prepared by anodic oxidation, plasma electrolytic oxidation, atomic layer deposition, and hydrothermal treatment. Although the methodologies used to prepare these barrier coatings are versatile (i.e., electrolytic oxidation, thin-film deposition, and boiling in water), they all result in aluminium oxide coatings. Their thicknesses vary significantly, from nanometric to several hundred micrometres.

Group 2: Conversion coatings consist of inorganic (hydr)oxides of a metal other than aluminium. They are formed by precipitation and are nanometric in thickness.

These coatings provide primary corrosion protection and also serve as a basis for the adhesion of the organic topcoat.

Group 3: Metallic coatings include Alclad, thermally sprayed, and electroplated coatings. Their thickness is usually several tens of micrometres. Metallic coatings can be regarded as barrier coatings, although they also function as a wear protection.

Group 4: Organic coatings comprise paints, powder coatings and also hybrid (organic-inorganic) sol-gel coatings. These coatings typically serve as a topcoat, providing decorative appeal. They can also contain pigments, fillers, or nanoparticles to enhance their functional properties.

Group 5: This group comprises various coatings that exhibit self-sealing or self-healing properties, for example, layered double hydroxide with incorporated inhibitors, as well as superhydrophobic properties aimed at repelling electrolytes from the metal surface. With the incorporation of sealing or the addition of containing inhibitors, microcapsules, or nanoparticles, coatings from groups 1 and 4 are translated into those of group 5. With appropriate surface treatment to achieve a nanomicro rough surface and grafting a low surface energy organic coating, the organic coating acquires superhydrophobic properties.

Further, coatings can be broadly divided into two types: inorganic and organic coatings. Inorganic coatings

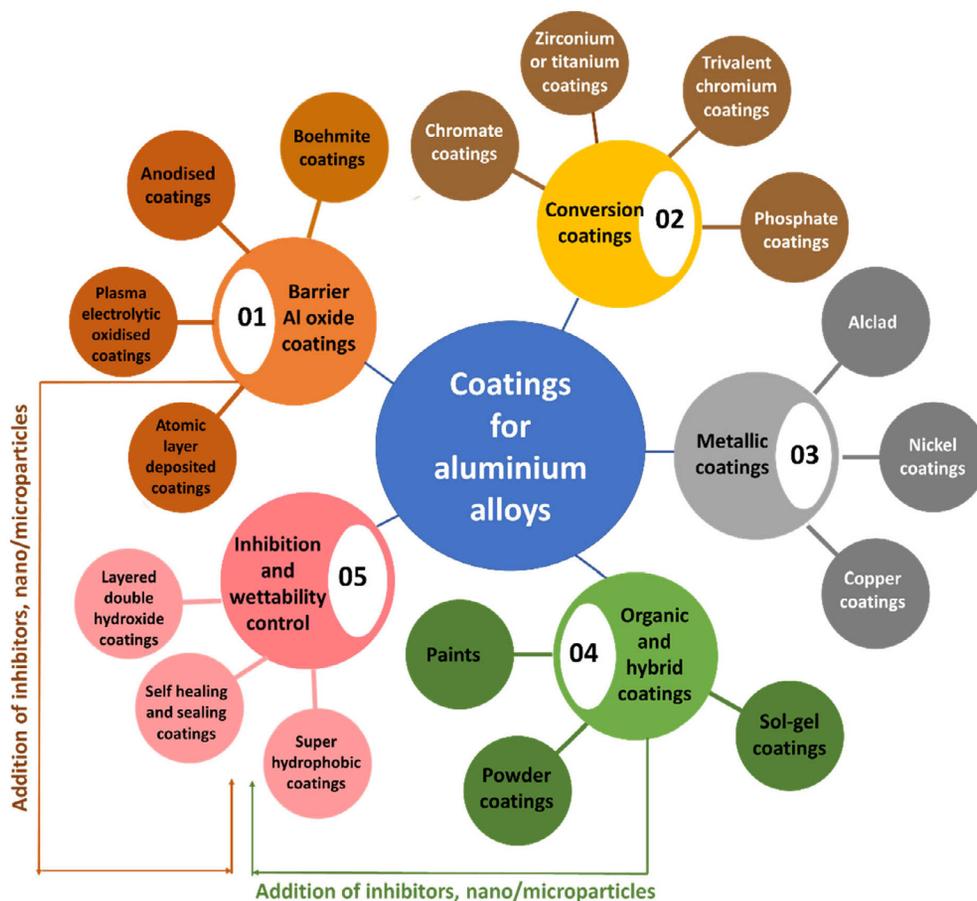


Figure 2. Schematic representation of different types of coatings used for corrosion protection of aluminium alloys grouped according to the coating type.

comprise barrier oxide, conversion, layered double hydroxide, and metallic coatings, while others belong to the organic coatings. Coatings differ relative to their thickness and span from nanometric (conversion and boehmite coatings) to several hundreds of micrometres (plasma electrolytic deposited coatings).

In this review, each coating group will be presented, with descriptions of their production methodologies and coating characteristics. Finally, all groups will be compared, including their advantages and potential shortcomings. Please note that corrosion inhibitors, as additives to solutions, were not considered herein; readers can further consult reviews published on organic inhibitors¹⁹, inorganic inhibitors²⁰, green inhibitors^{21–23} and lithium-based inhibitors.²⁴

3.1. Barrier Al oxide coatings

Barrier aluminium oxide coatings are produced by anodic oxidation, plasma electrolytic oxidation, atomic layer deposition and hydrothermal boehmite oxidation. In terms of coating thickness, the following order applies: atomic layer deposition (50–200 nm) < hydrothermal boehmite oxidation (100–500 nm) < anodic oxidation (50–100 μm) < plasma electrolytic oxidation (up to 200 μm).

3.1.1. Anodic oxidation

By submerging the base material into an acidic bath under an electric current, the surface reacts with the sur-

rounding media, forming an oxide layer. Anodisation (or anodic oxidation) is, therefore, an electrochemical process of controlled oxidation by which we modify the surface by forming an oxide layer that is thicker than a naturally formed one. The produced layer is durable, corrosion-resistant and suitable for colouring.

The anodisation process includes²⁵ several steps: (1) pretreatment, (2) anodising and (3) posttreatment. Pretreatment includes mechanical cleaning (abrasive polishing, sandblasting, or shot peening) and/or chemical cleaning, such as acid or alkaline etching and desmutting. This process is typically used to prepare the surface of aluminium alloys by removing the native oxide layer, eliminating impurities, and creating a hydrophilic surface.

The central step is the anodic oxidation (Figure 3). The sample to be oxidised is set in an electrochemical cell (or electrolytic bath) and connected to a direct current (DC) power supply, typically operating between 20 and 80 V and at low current density (1–10 A dm^{-2}) (Figure 3a). As the DC passes through the sample, the aluminium part becomes positively charged as electrons are drawn away from its surface.²⁶ The most critical role in the process is the high-field ionic conduction; oxide anions O^{2-} move inward to react with Al substrate and Al cations Al^{3+} move outward to react with water at the oxide/electrolyte interface and form an aluminium oxide (Al_2O_3) layer. At the cathode, electrons participate in the hydrogen reduction reaction, which produces hydrogen gas. The overall chemical reactions involved can be summarised as follows:

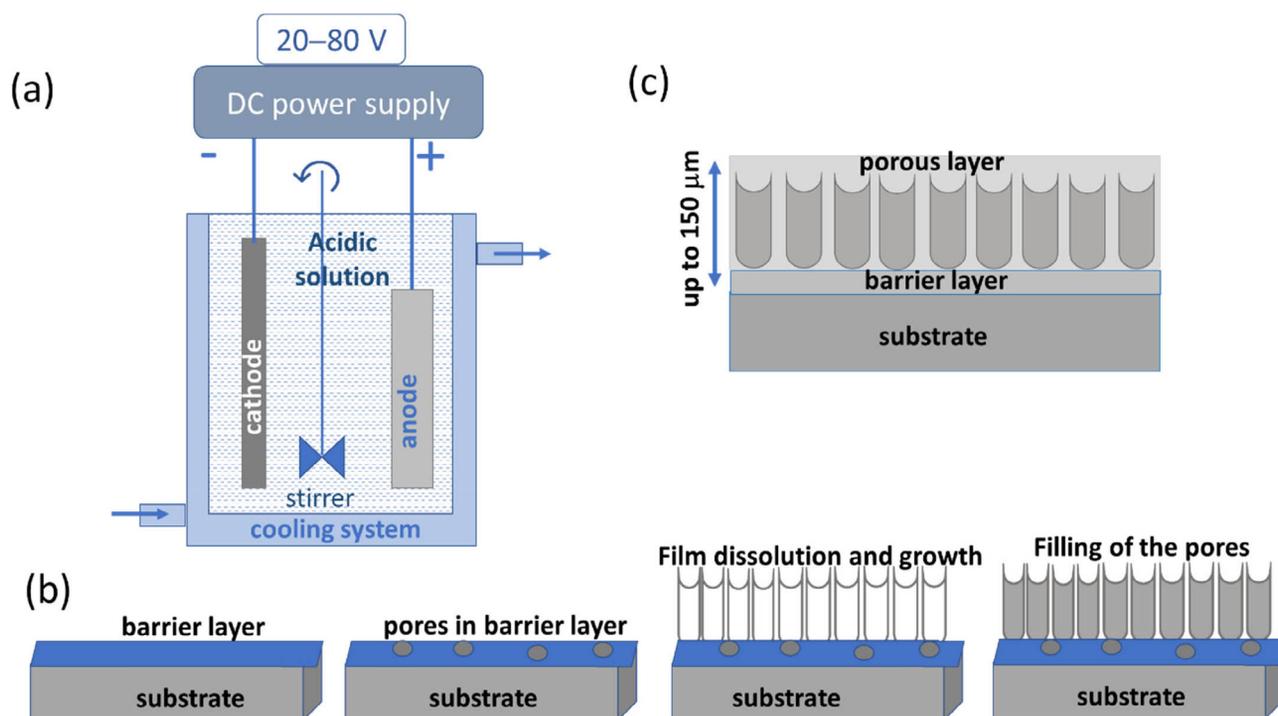
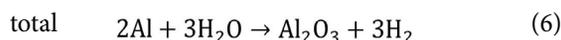
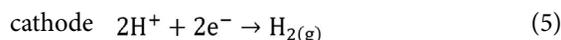
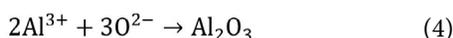
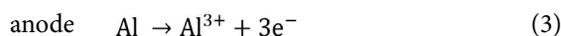


Figure 3. Schematic representation of (a) experimental set-up for anodic oxidation (AO), (b) consecutive steps in the formation of anodised layer, and (c) AO-coated substrate.



The bath composition is the primary determinant of whether the film will be barrier or porous.²⁶ Barrier oxide forms in near-neutral solutions, where aluminium oxide is hardly soluble, most commonly in ammonium borate, phosphate, or tartrate compositions. The majority of the oxide forms at the Al/oxide interface; however, oxide formation also occurs at the oxide/electrolyte interface.²⁷ For each bath composition and temperature, there is a maximum voltage that can be sustained before dielectric breakdown (localised sparking) occurs.²⁶ The typical thickness of the barrier layer is a few hundred nanometres.

Porous oxide²⁷ grows in acid electrolytes in which oxide can not only be formed but also dissolved; most commonly, dilute sulfuric acid is used. These porous layers are particularly relevant, for example, in aerospace applications. During anodisation, the anode reaction forms a barrier layer of aluminium oxide (Figure 3b). As the current passes through the aluminium, it tends to concentrate in weaker, more reactive areas of the surface, resulting in a highly porous or cellular structure. The aluminium oxides that form in these pores do not react with oxygen anions but, instead, are dissolved in the acidic bath.²⁸ The explanation lies in the field-assisted dissolution or field-assisted direct anion injection.²⁷ The thickness of the porous layer can reach a few hundred micrometres and is directly related to the duration of electrolysis and the applied voltage; longer electrolysis times and higher voltages produce thicker films with more pronounced column-like structures. Additionally, the pore dimensions are influenced by the bath's voltage, temperature, and acid concentration.^{29–31}

Commonly used acidic electrolytes are chromic and sulfuric acids. The most widely used specifications are Type I (chromic acid (H_2CrO_4) anodising) and Types II and III (sulfuric acid (H_2SO_4) anodising). Type I produces 0.5–18 μm thick coatings, i.e. thinner than those produced by the Type II process. The oxide layer produced is typically transparent, undyed, and exhibits good corrosion resistance, thus making it suitable for precision applications and metals with seams.

Type II produces thicker (1.8–25 μm) and more porous layers, thus allowing it to be dyed with a wide variety of colours and used in light-wear and decorative applications where good corrosion resistance is required (consumer goods, medical devices, some automobile parts). Type III process, also called hard anodising, produces darker, thicker layers (13–150 μm), which are suitable for more extreme environments, requiring superior wear re-

sistance, such as aerospace, automobile and industrial components. Type III process takes place at low temperature, usually below 0 °C and 5 °C, which is critical for slowing down the chemical dissolution of the growing layer.

In addition to classifications Types I–III, other specifications are used for anodisation. U.S. Military specifications refer to the term MIL-A-8625, AMS (Aerospace Material Specifications) standards are e.g., AMS2469 and AMS2471, BS EN ISO (British Standard identical to a European standard (EN) and an International Organization for Standardization (ISO) refers to BS EN ISO 7599 and BS ISO 10074, and ASTM (American Standard for Testing and Materials, e.g. ASTM B580.³²

The trend of replacing chromic acid due to the carcinogenicity of Cr(VI) has dictated the use of other, more environmentally friendly acids. In addition to pure sulfuric acid, the bath can be mixed with organic acid electrolytes such as tartaric, oxalic, malic, malonic and citric acids.²⁷ The other group includes phosphoric acid anodisation (PAA, also known as the Boeing Process).³³ It produces a thin, approximately 400 nm-thick, microporous layer that does not require hydration or sealing.

The third step of the process is the posttreatment.²⁸ It includes colouring and sealing. After rinsing, the anodised part can be colour-treated. Various methods are commonly used. In electrolytic two-step anodising, the component is immersed in a bath containing metallic salts (commonly nickel, cobalt, tin, or copper). Upon electrolysis, the metal salt is deposited within pores. The colour depends on the type of salt used. In interference colouring, the pores within the oxide layer are expanded, and a metal salt is then deposited to produce various interference colours. In integral colouring, oxide film is dyed during anodisation by a combination of sulfuric and organic acids. In dip colouring, the component is submerged in a dye-containing step.

Due to their porous nature, layers produced by anodic oxidation are sealed.³⁴ The purpose of sealing is to enhance corrosion resistance by filling the pores of the oxide layer and also to maintain the aesthetic appearance (Figure 3b, c). Most popular sealing is conducted in deionised water at temperatures close to boiling to form a crystalline hydrate phase (boehmite), which fills the pores and flattens the surface.



Other popular types of sealants include fluoride sealants, acetate-based solutions, silicate- or sulphate-based solutions, layer double hydroxide sealants, sol-gel sealants, or aluminate sealants. The advantage of these sealants is that they operate at lower temperatures than hot-water sealing. Furthermore, they present an environmentally friendly alternative to toxic chromate sealing, which remains essential in the aerospace industry.

The unique microstructure of the anodised layer and favourable application procedures make this type of sur-

face treatment particularly interesting for the aerospace, gas and oil, textile, and other related sectors, especially for parts subjected to high mechanical loads (such as gear wheels, rotors, and sealing rings). It can also be used as a pretreatment before organic coating application, performing a function similar to that of conversion coatings by increasing adhesion.^{29,30,35} Among aluminium alloys³⁶ suitable for anodising are those from series 5xxx, 6xxx and 7xxx. Series 1xxx lacks the mechanical properties required for specific applications. Series 2xxx contains copper, which is unsuitable for anodisation because it alters the colour of the oxide layer and decreases corrosion resistance. Anodisation of series 3xxx and 4xxx provides good corrosion resistance, but the manganese in series 3xxx causes the colour to turn brown; anodisation of series 4xxx results in a dark grey colour. Therefore, alloys of series 5xxx, 6xxx and 7xxx are most suitable for anodising, resulting in transparent oxide layers with good mechanical and corrosion-resistant properties.

3.1.2. Plasma electrolytic oxidation

Plasma Electrolytic Oxidation (PEO)—also known as micro-arc oxidation, plasma chemical oxidation, or

anodic oxidation by spark discharge—was developed to address some limitations of conventional anodisation, particularly in enhancing corrosion resistance and mechanical properties.³⁷ Unlike anodisation, PEO operates at much higher voltages (typically 400–700 V), exceeding the dielectric breakdown threshold (Figure 4). Power sources for the process may include DC, AC, or pulsed currents (unipolar or bipolar).

For aluminium, PEO is typically performed in alkaline electrolytes (pH 7–12), commonly containing silicates, phosphates, aluminates, or fluorides. The process begins with the formation of a thin anodic barrier layer, followed by dielectric breakdown. This breakdown leads to oxide ionisation and gas evolution, resulting in a distinctive three-layer coating structure: an inner barrier layer, a dense intermediate (working) layer, and a porous outer layer (often referred to as the technological layer) (Figure 4b). The resulting oxide coatings, composed of a mix of amorphous and crystalline aluminium oxide phases, can reach thicknesses of up to 200 μm . These coatings exhibit high hardness and excellent adhesion to the substrate. However, typical PEO coatings often contain pores and cracks, and the process is energy-intensive, with treatment times up to 1 hour.

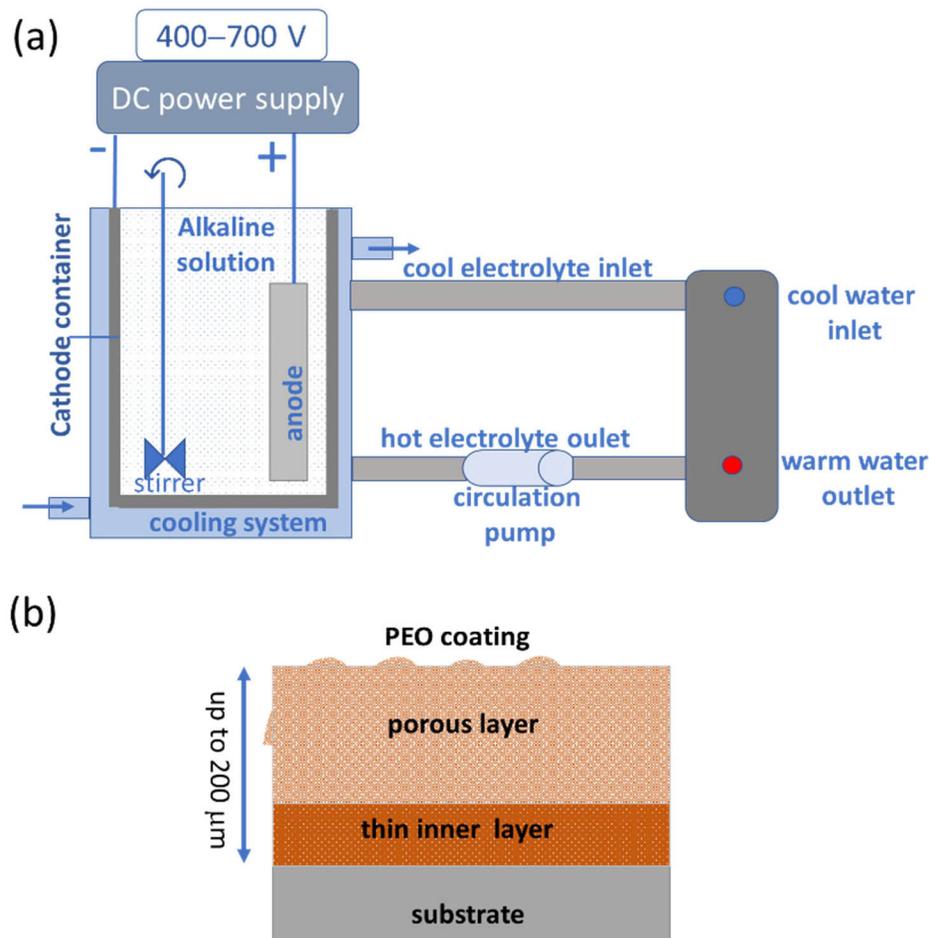


Figure 4. Schematic representation of (a) experimental set-up for plasma electrolytic oxidation (PEO), and (b) PEO-coated substrate.

To address these drawbacks, flash-PEO techniques have been developed. These produce much thinner coatings (1–5 μm) within a few minutes, significantly reducing energy consumption. To further enhance the corrosion resistance of flash-PEO coatings, particularly in aggressive environments, corrosion inhibitors can be incorporated into the treatment process. For further reading, please consult the following references.³⁷

3.1.3. Atomic layer deposition

Atomic Layer Deposition (ALD), developed in the 1960s and 1970s, is a specialised form of chemical vapour deposition (CVD) widely used for creating thin films. Originally commercialised for microelectronics, ALD gained attention for its ability to produce ultra-thin, nanometer-scale films with exceptional thickness uniformity and conformity—even on highly complex or nanostructured surfaces, including within nanoporous materials. This capability is particularly valuable for applications in biomedical engineering and biotechnology. Additionally, ALD enables the formation of defect- and im-

purity-free films through precise gas-to-solid chemical reactions, making it especially effective for corrosion protection.

Figure 5 schematically illustrates the ALD process using alumina as an example. The process consists of four sequential steps.³⁸ A gaseous precursor—aluminium(III) chloride (AlCl_3) or trimethylaluminum ($\text{Al}(\text{CH}_3)_3$ or TMA)—is introduced into the reaction chamber, where it reacts with the substrate surface to form a chemisorbed monolayer. This reaction produces hydrogen chloride (HCl) or methane (CH_4) as a by-product, depending on the conditions.

An inert gas, such as nitrogen or argon, is used to purge the chamber. This removes any excess precursor and volatile by-products, ensuring a clean surface for the following reaction step. A second gaseous precursor, typically an oxidising agent—water (H_2O) in this case—is introduced. It reacts with the adsorbed AlCl_3 layer through a surface-limited reaction, further building the film. The chamber is finally purged again with inert gas to eliminate any unreacted water and reaction by-products (mainly HCl). This results in the formation of a uniform, solid-state

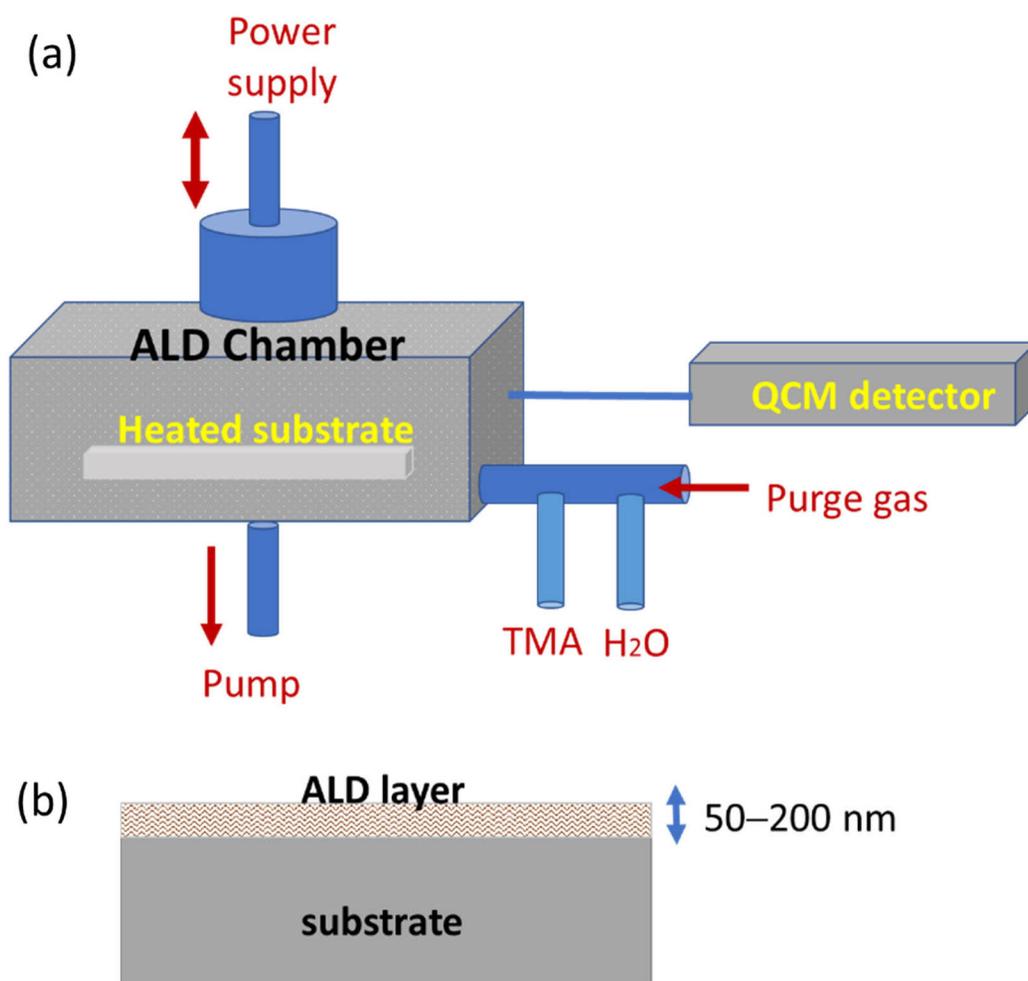
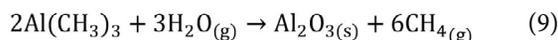


Figure 5. Schematic representation of (a) experimental set-up for atomic layer deposition (ALD), and (b) ALD layer-coated substrate.

monolayer of Al_2O_3 on the substrate, which can be expressed as:



This cycle can be repeated as needed to achieve the desired film thickness with atomic-level precision (Figure 5b). ALD enables the growth of highly uniform, conformal, and hole-free coatings, even on complex or large-area substrates. Typical values of pressure and temperature during the ALD process are between 1 and 10 mbar, and from 100 °C to 500 °C, respectively. The system can be equipped with a quartz crystal microbalance (QCM) to monitor the thickness of the deposited layer in real time.

This self-controlled process delivers excellent adhesion and a dense film, both of which are crucial for efficient corrosion protection. Despite a slow deposition rate (100–300 nm/h), ALD compensates with high production and processing capability. Due to its high film density, it provides adequate protection with thinner layers than CVD-produced films. In case of aluminium, which naturally forms a protective oxide film, ALD-deposited Al_2O_3 coatings at thicknesses of 10–50 nm significantly enhance corrosion resistance, reducing corrosion currents and increasing pitting potential.^{39–42} Due to its ultra-thin, barrier properties, ALD may be a viable alternative to replace the synthetic resin coatings used in aluminium cans in the food industry.⁴³

3.1.4. Boehmite coatings

A typical surface product formed during the interaction of aluminium with water is boehmite (AlOOH), a hydrated aluminium oxide widely utilised for corrosion pro-

tection and to enhance adhesion properties. Boehmite coatings are usually formed when the native aluminium oxide layer reacts with water at elevated temperatures, typically 60–70 °C (Figure 6). Under these conditions, a surface-mediated reaction occurs between aluminium and water vapour, forming a uniform boehmite layer. In aqueous environments, layer thicknesses reaching several hundred nanometers can be achieved within a few hours.⁴⁴

Boehmite is a naturally occurring, thermodynamically stable form of hydrated alumina. Its formation on metallic aluminium proceeds via electrochemical mechanisms, involving both anodic and cathodic half-reactions:

Anodic reaction:

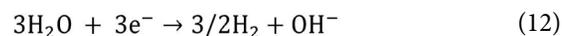


or



depending on whether the surface is bare or covered with a native oxide layer.

Cathodic reaction:



While the anodic process occurs almost uniformly across the exposed aluminium surface, the cathodic reaction is localised primarily at grain boundaries, accompanied by the evolution of hydrogen gas. Anodic dissolution leads to the formation of hydrous oxides, which subsequently precipitate and transform into pseudo-boehmite, thereby contributing to layer growth. After heating at temperatures from 200 °C to 300 °C, boehmite with a reduced hydroxyl content is formed. Above 350 °C, boehmite transforms into Al oxide:



Boehmite layers can be deposited by several methods. The first set of methods includes preparing boehmite coatings by immersing the substrate in boiling water un-

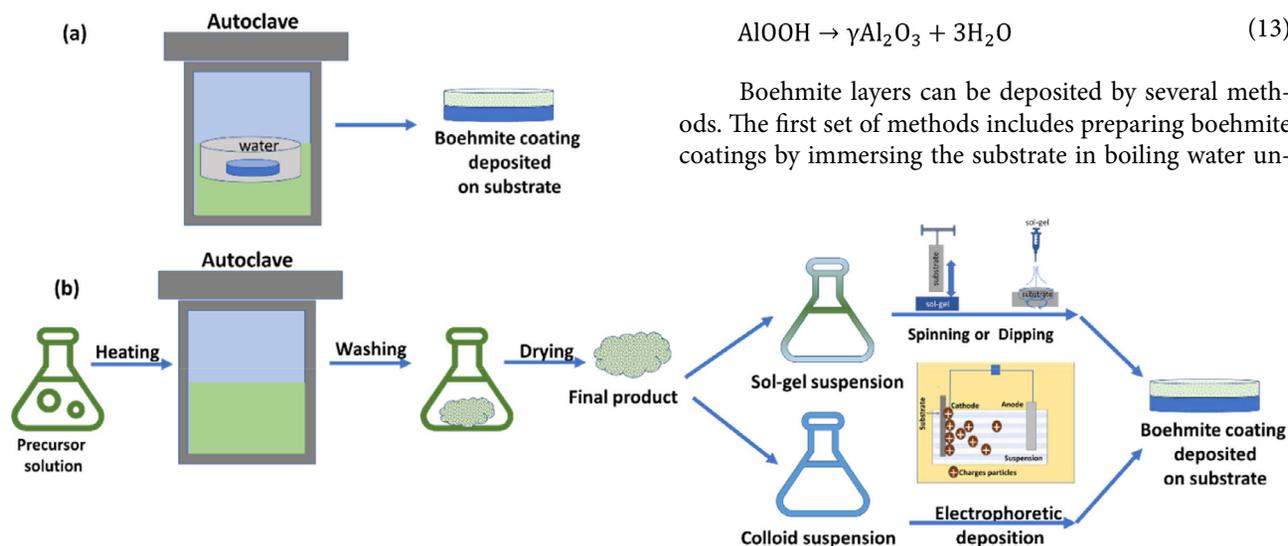


Figure 6. Schematic representation of the procedure for preparing boehmite coatings: (a) direct deposition on the substrate in an autoclave, and (b) preparation of boehmite powder followed by the sol-gel deposition from suspension or electrophoretic deposition from colloidal suspension.

der atmospheric pressure (hydrothermal method) (Figure 6a) or by exposing it to pressurised steam at approximately 120 °C.⁴⁵ The visual appearance of the resulting coating—ranging from milky white (typically formed in neutral or alkaline boiling water) to grey (observed on copper-containing aluminium alloys)—is influenced by both the chemical composition of the alloy and the formation environment. Nevertheless, studies have shown that the overall thickness and morphology of boehmite layers are largely consistent across different aluminium alloy families, indicating that alloy composition and temper are not the primary factors controlling layer development. Instead, the chemistry of the aqueous medium plays a critical role.⁴⁶

Originally, boehmite films were prepared using ultra-pure water, but subsequent research showed that the presence of alkaline additives significantly enhances layer formation. These additives include inorganic bases (e.g., ammonia) and organic compounds, particularly amino alcohols such as diethanolamine (DEA) and triethanolamine (TEA).

The second set of methods includes first the preparation of boehmite powder from a precursor solution, typically aluminium hydroxide or soluble aluminium salts, such as chloride, sulphate or nitrate, in an autoclave, followed by washing and drying (Figure 6b). The powder is then used to prepare either a sol–gel suspension^a and deposit on the substrate by spinning or dipping,⁴⁷ or a colloidal suspension^a and deposit on the substrate using electro-

a A suspension is a heterogeneous mixture of particles with diameters of about 1 μm that are distributed throughout a second phase. Common suspensions include paint, blood, and hot chocolate, which are solid particles in a liquid, and aerosol sprays, which are liquid particles in a gas. If the suspension is allowed to stand, the two phases will separate, which is why paints must be thoroughly stirred or shaken before use. A colloid is also a heterogeneous mixture, but the particles of a colloid are typically smaller than those of a suspension, generally in the range of 2 to about 500 nm in diameter. Colloids include fog (liquid particles in a gas), milk (solid particles in a liquid), and butter (solid particles in a solid). Unlike in a suspension, the particles in a colloid do not separate into two phases on standing. Ref. <https://chem.libretexts.org/>

phoretic deposition (EPD).^{48,49} prepared on aluminum alloy (AA The EPD includes the generation of positive or negative charge on the suspension of colloidal particles, the movement of the charged particles under the applied current to the oppositely charged electrode and finally the deposition of the charged particles due to coagulation.⁵⁰

Beyond surface protection, boehmite has important applications in industrial catalysis, where it serves as a porous support material for the dispersion of active catalytic phases due to its large surface area and stability. Upon calcination, boehmite undergoes a thermal transformation to γ-alumina, reaction (13), thereby further extending its functionality in high-temperature catalytic systems.⁵¹

3.2. Conversion coatings

Conversion coatings (CCs) are chemically or electrochemically applied layers used as surface pretreatments for organic coatings to increase adhesion to the metal substrate or as stand-alone surface corrosion protection. These protective layers form when the alloy is immersed in a chemical bath, which initiates surface reactions between metal (or other) ions in solution and the metallic surface. The result of such treatment is a thin, chemically deposited layer that (partially) replaces the naturally formed oxide layer. While conversion coatings can be used as a stand-alone top layer, they are more often a part of the complex multilayer coating system, as will be presented below.^{12,52}

The most important conversion coatings used for corrosion protection and adhesion are chromate conversion coatings (CCCs) and phosphate coatings. CCCs, produced in a conversion bath containing sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) and some sulphuric acid (H_2SO_4), are highly corrosion-protective. They consist of a backbone of chromium oxide/hydroxide with Cr predominantly in the 3+ oxidation state, but also contain some regions where Cr is in the 6+ oxidation state.^{53,54} After local damage to the oxide layer, CCCs can self-heal by the reduction of remaining Cr(VI) in the coating to an insoluble Cr(III) compound.

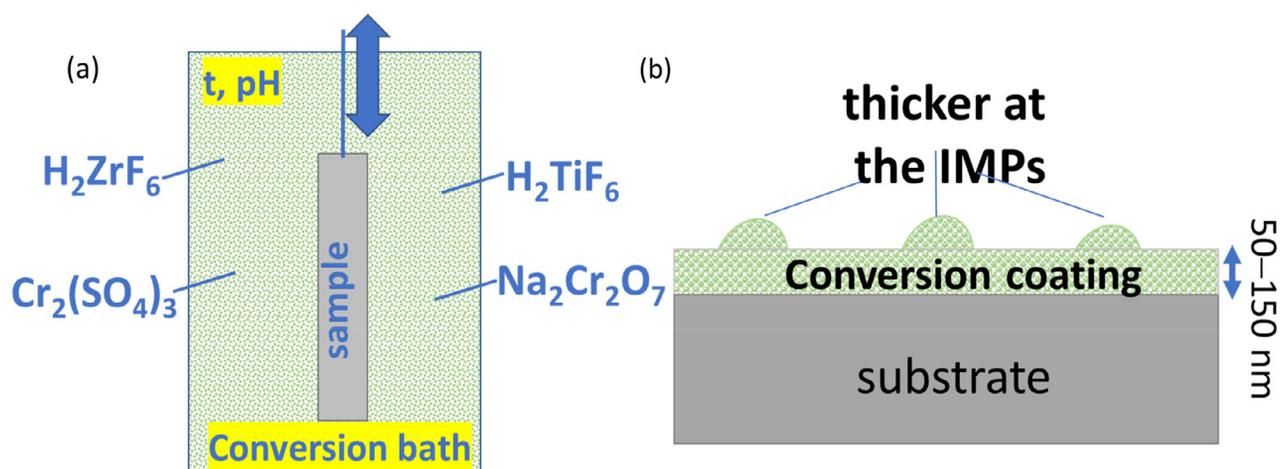
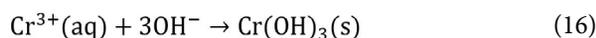
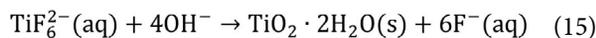
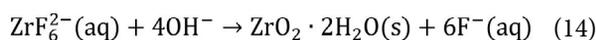


Figure 7. Schematic representation of (a) experimental set-up for conversion coating (CC) deposition, and (b) CC-coated substrate.

Phosphate coatings are hard, continuous, insoluble, electrically non-conducting, and used in numerous applications in the automotive, agricultural, and appliance industries. Both CCCs and phosphating have some health, environmental and energy drawbacks. The use of hexavalent chromium is restricted in the European Union and the USA. Most legislation worldwide today limits the production of chromate coatings.^{12,35,54–56} Phosphate coatings pose different problems; discharge from concentrated phosphate baths can have a detrimental effect on groundwater sources due to eutrophication in freshwater lakes and reservoirs.

Due to these restrictions and the fact that conversion coatings are low-cost, easy to prepare, there has been significant interest in developing green conversion coatings based on other metals, including zirconium, cerium, and titanium.^{12,54,57–61} Currently, the commercial CCs based on non-toxic elements are zirconium (ZrCCs),⁶² often combined with trivalent chromium (Zr-CrCCs), and titanium conversion coatings.

The surface must be degreased and chemically cleaned (alkaline or acid-based¹²) before submersion in a chemical bath to achieve a uniform layer. ZrCCs are usually applied by immersing the metallic substrate (Figure 7a) in hexafluorozirconic acid (H_2ZrF_6), hexafluorotitanic acid (H_2TiF_6) or chromium(III) sulphate ($\text{Cr}_2(\text{SO}_4)_3$) conversion bath, which initiates the following reaction:^{54,63,64}



The conversion process is pH-driven because it proceeds at the pH at which precipitation from solution onto the metal surface is thermodynamically feasible. This occurs due to specific parameters of the conversion bath, namely the concentration of the inorganic compound, temperature, conversion time, and pH. The conversion is not a simple process but involves several steps, including partial dissolution of the native oxide layer at the surface of the Al alloy, precipitation of hexafluoro complexes and trivalent chromium as hydroxides, and layer growth.

In a trivalent chromium (Cr(III)) conversion bath, chromium sulfate ($\text{Cr}_2(\text{SO}_4)_3$) provides the Cr^{3+} ions. The “chromium sulfate to hydroxide” part is not a direct transformation within the solution but rather the precipitation of Cr(III) from its complexed sulfate form into insoluble chromium hydroxide on the metal surface due to localised pH changes during the electrochemical process.⁵⁴

Inorganic Zr, Ti and Cr(III) conversion coatings comprise hydrated inorganic hydroxide with some oxyfluoride. These coatings are approximately 50–150 nm thick on average, classifying them as nanocoatings (Figure 7b).⁶² Most ZrCCs have been applied to wrought Al alloys and much less to cast alloys.^{54,61}

3.3. Metallic coatings

3.3.1. Cladding

Alclad layers are used to improve the corrosion resistance of Al alloys by coating bare aluminium while preserving the alloy's beneficial mechanical properties. Cladding represents the bonding of dissimilar metals. Generally, the cladding layers (Alclad) are selected to be anodic to the core alloy, typically AA2024, thereby providing corrosion protection (Figure 8a). Among popular clads, those AA1230 consisting of ≥ 99.3 wt.% Al, ≥ 0.70 wt.% Si+Fe, ≥ 0.10 wt.% Zn, ≥ 0.10 wt.% Cu, and other elements, with the minimum average clad thickness of 4%, are the most common. The clad thickness is ca. 20 μm . Alloys containing Alclad sheet are widely used in applications that require a combination of good mechanical properties and excellent corrosion resistance, such as in the manufacture of commercial aircraft. The protective layer can be clad by roll bonding (Figure 8a), in which two or more layers of different metals are passed through a pair of rollers under sufficient pressure to bond them. When the metal is rolled above its crystallisation temperature, the process is called hot rolling. Another possibility for forming a clad is extrusion of two metals through a die (Figure 8b). Here, a metal billet is forced under high pressure through an opening (die) to create longer, uniform products. As a rolling process, it can be done as a cold or hot

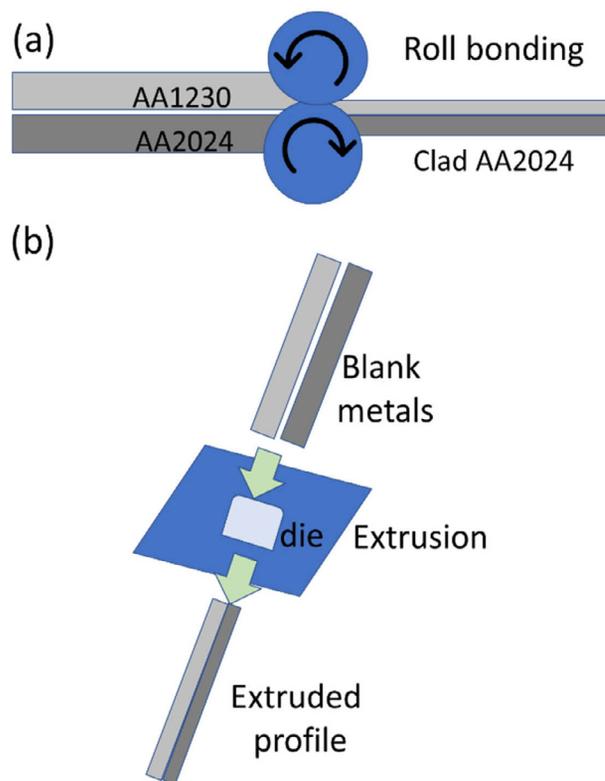


Figure 8. Schematic representation of experimental set-up for the preparation of clad layer by (a) roll-bonding and (b) extrusion through a die.

process. Both procedures, rolling and extrusion, create a metallurgical bond (Figure 8).

3.3.2. Electroplated coatings

Electroplating is an electrodeposition process by which a metal layer is deposited onto the substrate. Electroplated metal layers are commonly over five μm thick, which is difficult to achieve with evaporation or sputtering at the micrometre scale. Electroplating can be performed at room temperature or lower, with minimal thermal stress on the metallic substrate, by submerging the substrate (the cathode) in an aqueous solution of a metal salt. Because of the difference in potential (natural or induced by an outside source) between two metals (anode and cathode), metal can be deposited onto the cathode, as shown in Figure 9. Electrochemical reaction on the metallic surface (M) can be represented as a sum of the following reactions:^{65–69}



By electroplating aluminium, we can increase its corrosion resistance and surface durability. A thin layer of nickel is often used to improve wear resistance, enhance appearance, and provide a base for other coatings, especially in decorative, automotive, and aerospace applications. Another metal commonly used when electroplating aluminium is copper. Unlike nickel, copper is mainly used as a surface pretreatment for electroplating nickel or chrome to improve adhesion.^{65–69}

Aluminium poses challenges in electroplating due to its natural tendency to form a tough oxide layer upon exposure to air. This oxide layer must be removed by pre-cleaning, etching, desmutting, and, often, zincating. The surface preparation process allows for proper adhesion of electroplated coatings. Zincate or copper pretreatment is

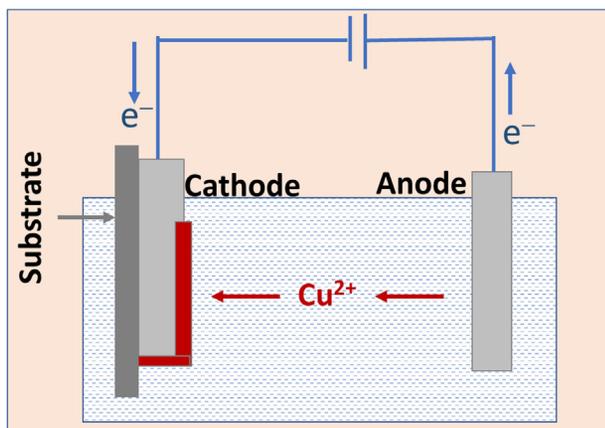


Figure 9. Schematic presentation of electroplating copper onto a metal substrate.

commonly used to achieve better adhesion between aluminium and the plated metal. The metallic coating can be applied directly to aluminium (or an aluminium alloy) or to a metallic base layer. Depending on the top metallic coating, a base metallic coating is required before the top-coat is applied. When electroplating chromium, a layer of copper or nickel is necessary to mitigate the risk of accelerated corrosion if chromium is applied directly. Research indicates that nickel-phosphorus coatings and zincate treatments improve adhesion and corrosion resistance.^{65,66,69–71}

Several studies have shown the effectiveness of electroless nickel coatings for enhancing the durability and fatigue strength of plated aluminium alloys.^{66,69–71} Coatings must be deposited by fast nucleation and slow growth. However, improper pretreatment of aluminium can still result in defects like blisters, delamination, and detached coatings. By controlling the size of microstructural elements, we can avoid preferential corrosion at grain boundaries within the alloys – grain boundaries can become anodic or cathodic relative to the grain interior. This type of corrosion is widespread in aluminium-copper alloys, where copper precipitates at grain boundaries, creating a potential difference.^{66,69–71}

3.4. Organic and hybrid coatings

Organic and hybrid coatings are effective and widely used for protecting a range of materials. They are readily applicable and highly effective at creating a robust barrier between the substrate and its environment.

3.4.1. Powder and liquid organic coatings and paints

The most common used organic materials are polymers, such as polyester, polyurethane, polyacrylic, acrylic and vinyl. There are several methods of organic coating application, most commonly starting with a liquid material. Liquid paint consists of a mixture of non-volatile components (binder, additive, pigments, fillers) and a volatile component (solvent) (Figure 10a). Liquid paints can be applied with a brush, roller, spray, dip, or other methods, such as flow coatings, roll coating, electrodeposition and curtain coatings. After application, the coating is cured. During curing, the solvent evaporates, leaving the other components to form a dry coating. Curing of liquid paint can be in the oven-dried or air-dried.

Traditional organic coatings provide very high protection, but many may contain toxic components, such as volatile organic compounds (VOCs) used as solvents in liquid paints (also referred to as “solvent-borne” paints). VOCs have high vapour pressure and low water solubility, and are usually human-made chemicals used in the manufacture of paints, pharmaceuticals, and refrigerants. In recent years, sustainability issues have emphasised the im-

portance of using non-VOC-containing paints. In that context, low-toxicity water-based⁷² and water-borne paints are being developed to reduce harmful effects on human health and the environment. Often, the terms water-based and water-borne paints are used interchangeably, although they differ in composition and application. “Water-based” paints are water-soluble and are commonly used for painting walls and crafts. “Water-borne” paints use water-reducible technology, in which the mixture contains a binder, pigments, solvent and additives dissolved in water. In water-borne paints, water is the carrier. Both technologies, water-based and water-borne, aim to reduce VOCs. In the latter, alkyd or acrylic resins are typically used as binders and glycol ether or glycol is typically used as a solvent. After application, for example in the automotive industry, the water and then the solvent evaporate, and the particles fuse into a single layer. These paints are characterised by fast drying and weather resistance. While these paints are sufficient for a broad spectrum of uses, adhesion between polymeric coating and metal may be severely weakened or completely lost in the presence of water.^{73–75} Water-borne paints may be susceptible to flash rusting.⁷⁶

In addition to liquid coatings, another technology of great interest is powder coating technology.⁷⁷ It is more environmentally friendly than liquid-based technology because it contains no VOCs and generates less waste and hazardous chemicals.

The powder coating is a dry, solvent-free process in which polymer powder is electrostatically sprayed onto an aluminium alloy substrate, then heat-cured in an oven or under UV light to produce a thick, tough metal finish (Figure 10b). The typical temperatures are between 160 and 200 °C, which is suitable for Al-based substrates. Higher temperatures may affect the mechanical properties of aluminium alloys by reducing the material’s strength and increasing brittleness.¹ The five principal components of powder coatings include polymer resins, fillers, curing

agents (also called hardeners or cross-linkers), pigments, and additives.⁷⁸ Depending on the curing method, powder coatings are classified as thermoset, thermoplastic, or UV-curable.

Therefore, the primary difference between the powder and liquid methodologies is the use of a solvent. The advantage of powder coatings is excellent scratch and impact resistance. Possible disadvantages may include adhesion issues and the risk of thermal degradation. The benefits of liquid coatings include a broader range of substrates, a smoother finish, and a wide colour selection.

3.4.2. Sol-gel hybrid coatings

Since traditional conversion coatings are a vital surface pretreatment step, but also toxic, there is a lot of research focused not only on the development of green conversion coatings but also on alternative coatings, such as sol-gel coatings. Inorganic sol-gel coatings, made from metal alkoxides, metal acetates (also metal nitrates or metal oxides) and reactive solvents (alkyl-alcohols, ether-alcohols, poly-alcohols or methanol/acetic acid), have high cracking potential. To counter this undesired effect, an organic component can be introduced to form a hybrid sol-gel system. This type of coating has better mechanical properties, lower cracking potential and porosity. Because of their dual nature, hybrid sol-gel coatings can accommodate both organic and inorganic coating properties. With controlled synthesis conditions, we can create coatings with specific properties tailored to different applications. These coatings can be much thinner than commonly used organic coatings and can still provide a durable barrier and corrosion protection.

According to the standard definition, a sol-gel process is any synthesis route that begins with a solution of precursors and proceeds through the formation of a *sol* and then a *gel*. A *sol* is a stable suspension of colloidal particles in a liquid, while a *gel* is a rigid, interconnected three-dimensional network.⁷⁹

The precursors used in sol-gel chemistry may be inorganic or organic. Modern approaches often employ hybrid sol-gel systems, which combine both types. Inorganic precursors are typically metal alkoxides, $M(OR)_4$, whereas organic precursors are organic alkoxides of the form $(R-O)_{4-n}MR_n$, where:

- **M** is a network-forming element such as Si, Ti, Zr, or Al
- **R** is an alkyl group (C_xH_{2x+1})
- **R'** is an organic chain containing a functional group (e.g., epoxy, amino)

The transformation from precursors to a gel occurs through chemical reactions. First, hydrolysis replaces the alkoxy ($-OR$) groups with hydroxyl ($-OH$) groups in the presence of water and an acid or base catalyst (reaction 17). Next, polycondensation of hydroxyl groups forms an extended network, ultimately producing the gel structure.

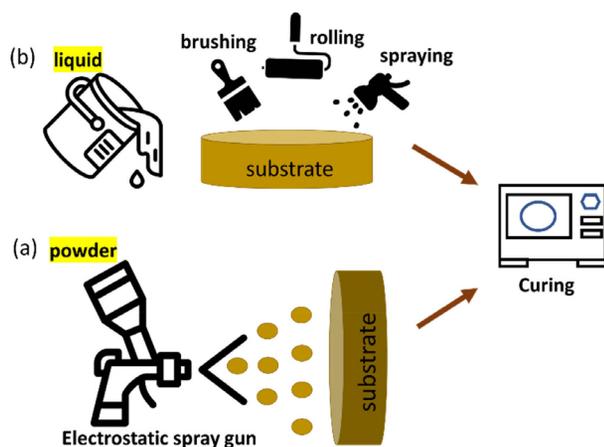
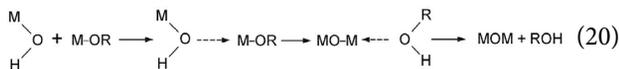
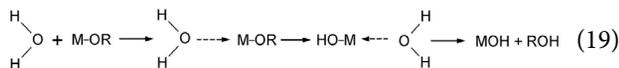


Figure 10. Schematic representation of typical experimental set-up for (a) liquid organic coatings and (b) powder organic coatings.

In hybrid sol-gel coatings, this process leads to the formation of $M-O-M$ bonds (reaction 18), which create the inorganic backbone of the hybrid material (Figure 11).



This route describes the most common route of the sol-gel process, the so-called polymeric route. Another possibility, which has received less attention, is the colloidal route.⁸⁰ In the polymeric route, a slow, controlled hydrolysis in a non-aqueous solvent leads to partial hydrolysis of the metal precursors, allowing their condensation and polymerisation to form a 3D network. The catalyst in this route facilitates hydrolysis. In the case of the colloidal route, the hydrolysis of the metal precursor in aqueous media is fast and uncontrolled, taking place in seconds and generating large precipitates that are subsequently broken into aggregates of nanoparticles thanks to the charge generated by the catalyst on the particles' surface. The latter process is called peptisation. Several ceramic materials, such as TiO_2 , Al_2O_3 , Nb_2O_5 , can be synthesised using the colloidal sol-gel route.⁸⁰

Coating can be applied to the base metal using several methods, including spin and dip coating (Figure 11).^{81,82} After deposition, the coated substrates are cured.

In recent years, organic–inorganic hybrid sol-gel coatings have been recognised as possible substitutes for chromate-based conversion coatings. Currently, they are mainly used as surface pretreatments for multilayer coat-

ing systems rather than as stand-alone coatings. The production process of these coatings also allows the incorporation of inorganic particles, which can be loaded with an inhibitor to serve as inhibitor nanoreservoirs, thus creating a “self-repairing” coating with controlled release properties. In addition to excellent adhesion to various aluminium substrates with surface Al-OH groups, they are non-toxic and have a low production cost.^{61,81,82} For further reading, please consult the following review papers.^{83–88}

3.5. Inhibition and wettability control coatings

Two types of coatings are presented: layer double hydroxides, which can incorporate corrosion inhibitors and thus act as smart coatings, and (super)hydrophobic coatings, which, by tuning surface wettability, prevent electrolyte access to the metal surface.

3.5.1. Layered double hydroxides

Layered double hydroxides (LDHs) are recognised as lamellar inorganic materials with a brucite-like structure similar to hydrotalcite. They comprise consecutive layers of divalent and trivalent metal hydroxides, coordinated to hydroxide groups and held together by van der Waals forces. Partial substitution of divalent cation fraction by triva-

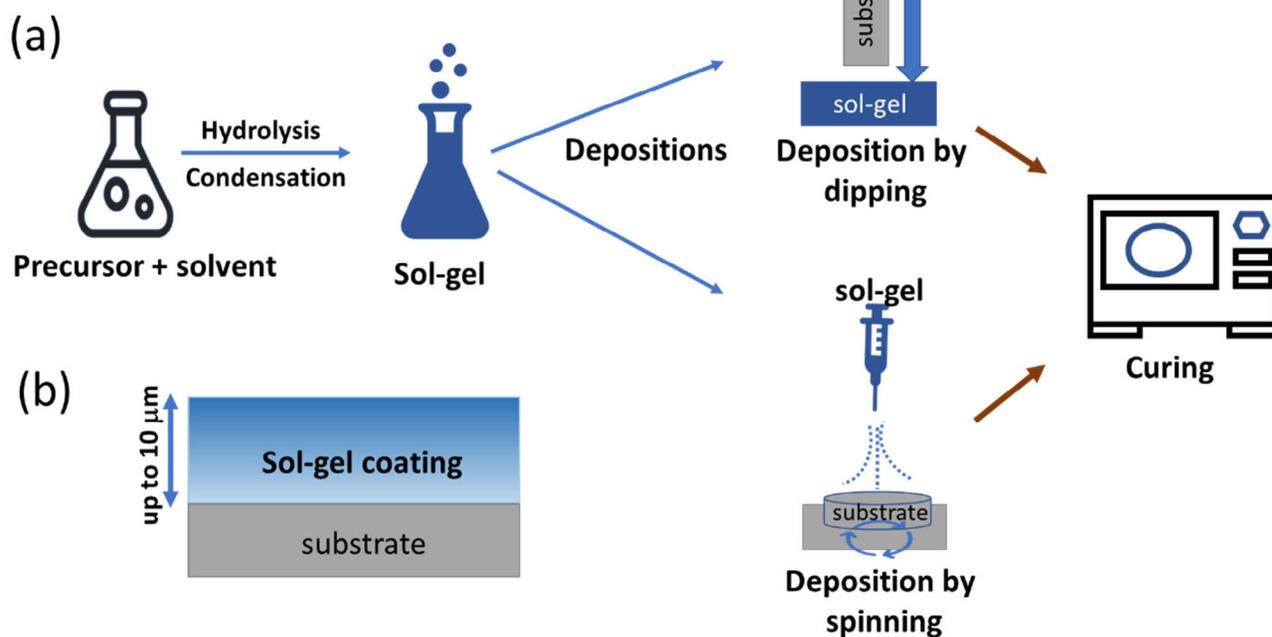
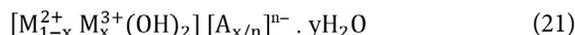


Figure 11. Schematic representation of (a) experimental procedure for the synthesis and deposition of sol-gel coatings, and (b) sol-gel coated substrate.

lent cations results in a positive sheet charge, compensated by anions in the interlayer galleries. They can also be described as anionic clays with a lamellar inorganic structure or positively charged host layers with exchangeable anions (interlayer regions contain exchangeable anions and water molecules). The general formula describes these materials:



where M^{2+} and M^{3+} are divalent and trivalent metal cations (e. g. Mg^{2+} , Ca^{2+} , Zn^{2+} , Al^{3+} , Cr^{3+} , Fe^{3+} , etc.), respectively, A is an interlayer anion (NO_3^- , Cl^- , CO_3^{2-} , PO_4^{3-}) with charge n^- and x is the molar ratio $[M^{3+}/M^{2+}+M^{3+}]$ (Figure 12a). Due to their ion-exchange capacity, LDHs offer great potential for encapsulating corrosion inhibitors, such as phosphates, organic molecules, molybdates, vanadates) and releasing them, when necessary, either by dissolution of the LDH framework at extreme pH values or by anion exchange within the LDH. The corrosion process can alter pH, so this principle is used in so-called smart coatings for active corrosion protection.⁸⁹

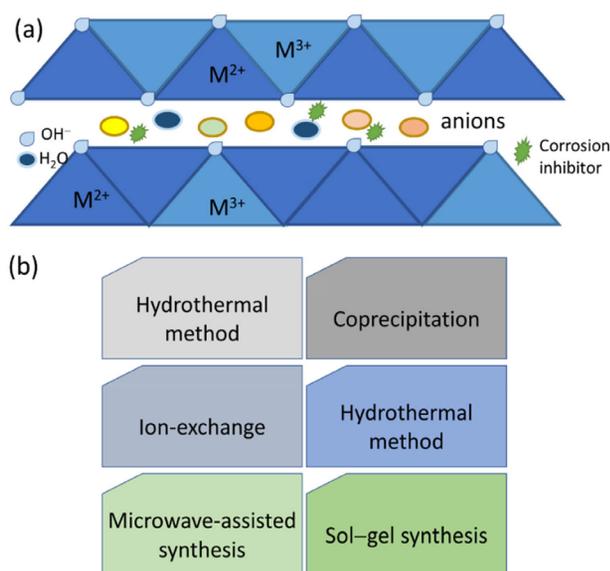


Figure 12. Schematic representation of (a) layer double hydroxide (LDHs) structure, and (b) methods for preparation of LDHs.

Because of their layered, interlayer-anion structure, they offer tunable structural features, such as compositional flexibility, interlayer-anion adjustment, exfoliation, and topological transformation. These properties make LDHs highly applicable in heterogeneous catalysis as catalysts, supports, or precursors. The performance of LDH-based catalysts can be enhanced by modulating surface defects, controlling active-site geometry, tuning acid-base concentrations, and leveraging the confinement effects of 2D materials. Through structural transformations, LDHs enable the creation of advanced catalysts, including single-metal and bimetallic systems with tailored properties. Their ad-

aptability makes them ideal for a wide range of applications, including CO_2 adsorption, catalysis, drug delivery, fire retardancy, cement additives, and polymer nanocomposites.^{89,90}

LDHs are particularly valuable for surface protection because they can encapsulate and release inhibitors upon surface damage. Because their dissolution behaviour is pH-dependent, the inhibitor is released only once the top layer has been breached. Methods for synthesising LDHs, such as co-precipitation and advanced techniques, including reverse microemulsion systems, allow precise control over particle size and morphology. Exfoliation techniques (for reducing layer thickness), including “top-down” delamination and “bottom-up” direct synthesis, have unlocked new possibilities for ultrathin nanosheets with high anisotropy, large surface areas, and strong interlayer forces. However, challenges such as strong electrostatic interactions and hydrogen bonding necessitate innovative exfoliation strategies, including the use of alcohol-based solvents and surfactant intercalation. The exfoliation of LDHs into nanosheets has also opened new frontiers in multifunctional material design, including applications in oxygen evolution reactions, light-emitting devices, supercapacitors, flame-retardant nanocomposites and catalytic materials. Despite challenges in scalability and precise active site modulation, LDHs remain a research hotspot with immense potential in creating nanocomposites and advanced functional materials.^{89,91,92}

LDHs are synthesised using various methods⁹³ (Figure 12b), primarily co-precipitation (mixing metal salts and slowly adding base to control pH), which is simple and common but can yield less crystalline products. Other key techniques include hydrothermal synthesis (ageing in hot water to form better crystals), sol-gel (mixing of precursors in a solution, forming a gel that converts to LDH), ion exchange (interlayer anions of a pre-existing LDH are exchanged with desired anions), and newer green methods such as mechanochemistry (ball milling) and microwave-assisted synthesis, which offer faster, solvent-free, or more controlled processes. For further reading, please consult the following review papers.^{94–96}

3.5.2. (Super)hydrophobic coatings

One of the basic conditions for corrosion progression is the presence of an electrolyte, which enables ion diffusion. While most coatings aim to create a physical barrier between the metallic surface and the environment, hydrophobic and superhydrophobic coatings create a surface with an unfavourable water contact angle, resulting in water repulsion. In the absence of water (an electrolyte), corrosion cannot proceed, and the material is protected. Superhydrophobic surfaces are characterised by high water contact angle (θ) above ($\theta > 150^\circ$), low contact angle hysteresis ($< 10^\circ$) and low sliding angle ($\alpha < 5^\circ$), as shown in Figure 13a.^{97–99}

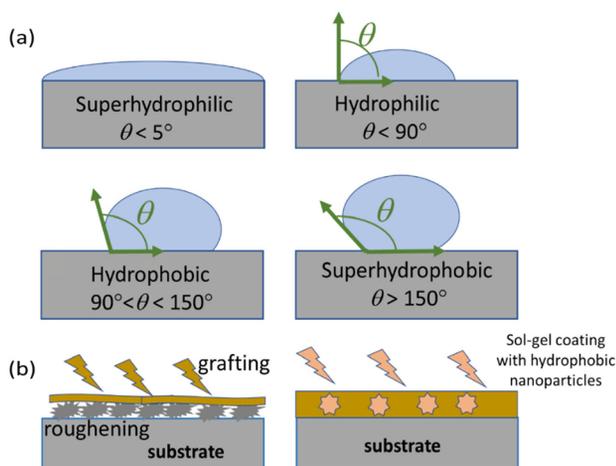


Figure 13. Schematic presentation of (a) surfaces of different wettability, and (b) methodologies of preparation of superhydrophobic surfaces. θ is the contact angle of a water drop.

Hydrophobic coatings, or rather hydrophobic surface modifications, are achieved by combining a certain level of surface roughness with low surface energy (which can be imparted by a coating or surface modification) (Figure 13b). The term surface modification might be more appropriate, since the substrate surface is either etched using alkaline or acidic solutions or metal chlorides, or microfabricated, for example, by laser structuring.^{100–102} Roughening is followed by grafting of a low-surface-energy layer, for example, perfluorinated compounds or long-chain carboxylic acids. Another possibility is to avoid the surface roughening by depositing a sol-gel coating containing superhydrophobic nanoparticles. The hierarchical structure and low-surface-energy film trap air on the surface. This significantly decreases the contact area between the liquid and the substrate, creating a hydropho-

bic surface, also known as the lotus effect. The lotus effect refers to the super-hydrophobic nature of certain surfaces (like the lotus leaf) where water droplets form near-spherical shapes and roll off rather than slide. On a lotus leaf, this phenomenon occurs due to weak water-surface interactions and a combination of surface features, including a waxy coating and rough, nanoscale protrusions. These features, much like artificial surface modifications, cause water droplets to trap air beneath them, allowing them to roll off and collect dirt and debris as they roll away. The higher the contact angle, the better its self-cleaning ability, with the lotus leaf being a prime example of this highly efficient mechanism. For further reading, please consult the following review papers.^{104–107}

4. Multilayer coating systems

In the present review, the coatings are summarised in five groups: (1) barrier aluminium oxide coatings, (2) conversion coatings, (3) metallic coatings, (4) organic coatings and (5) inhibition and wettability control coatings, as summarised in Figure 14. Thicknesses and coating structures are also noted. To provide a better overview of coating properties, similarities, and differences, all key components are presented in Table 2.

In industrial practice, technological aluminium alloys are coated with a multi-coating system to achieve optimal performance (Figure 15). First, alloys are subjected to a surface pretreatment, which may include pretreatment comprising mechanical grinding and/or chemical cleaning (alkaline or acidic etching or degreasing), followed by intermediate coating (primer) coating, which role is to increase the adhesion of the metal substrate with the top organic layer, reduce the risk of delamination and to serve as a first-aid corrosion protection. These may be anodised,

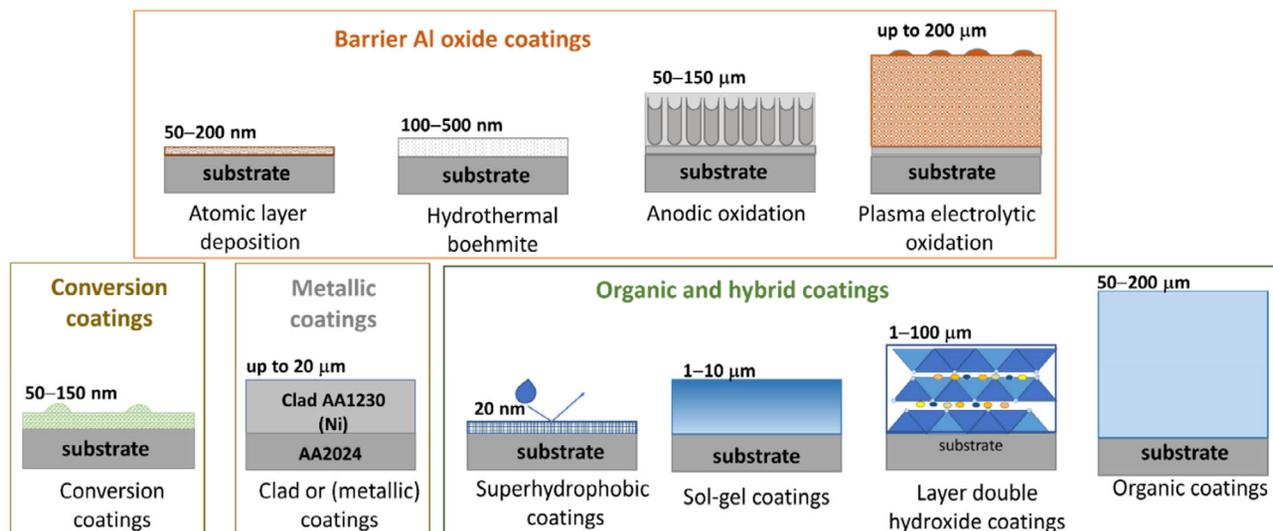
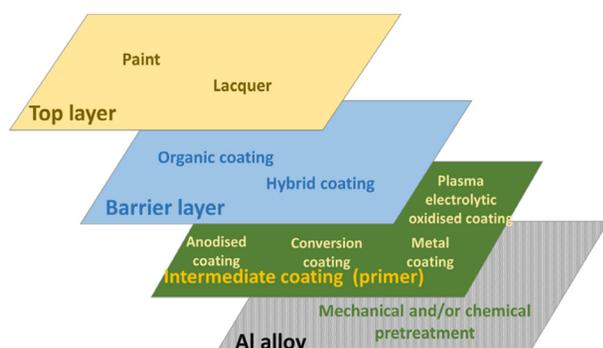


Figure 14. Schematic representation of coatings used for corrosion protection of aluminium alloys presented in terms of thickness and structure.

Table 2. Overview of key characteristics for different types of coatings.

Coating type	Corrosion resistance	Wear resistance	Environmental impact
Anodised and PEO coatings	high, strong barrier	high	moderate (non-toxic)
Atomic layer deposition	high	low	low
Boehmite coatings	moderate, improvement of base corrosion resistance	low	low
Conversion coatings	moderate to high, depending on the type	low to moderate	high for chromate (toxic), lower for phosphate and green alternatives
Electroplated coatings	moderate to high; varies by type of metal	moderate to high (depending on the metal)	moderate, depends on metals and the pretreatment process
Layer double hydroxides	good, especially when combined with inhibitors	high (depends on the LDH type)	low
Organic coatings	high, very effective barrier	moderate (can vary by composition)	low for water-based, moderate to high for solvent-based coatings
Sol-gel coatings	high, effective barrier and corrosion resistance	moderate to high, depending on the composition	low (green alternative to chromate-based coatings)
Hydrophobic coatings	moderate, water repulsion prevents corrosion	low	low-to moderate (depends on the surface layer)

PEO or conversion coatings. All three coatings can be used individually, with the former two sealed by a suitable sealant. Another option is to use metal coatings such as cladding and electroplated metal coatings. The next layer comprises an organic layer, typically a powder coating or a liquid paint. It is noteworthy that the typical temperatures to be used for coating processing and curing should not exceed 160–200 °C to avoid affecting the mechanical properties of aluminium alloys. An additional top layer of the multilayer system provides aesthetic appeal, ensures sealing, and adds to durability and environmental protection.

**Figure 15.** Schematic representation of multilayer coating systems used in industrial applications.

5. Conclusions

Aluminium and its alloys are widely used in various industries due to their excellent strength-to-weight ratio, corrosion resistance, and conductivity. However, in specific environments, additional protection or surface modifi-

cation is necessary to enhance these properties. Each type of coating is specifically tailored to accommodate the substrate material, environment and mechanical properties of a given application. In the present review, the coatings are summarised in five groups: (1) barrier aluminium oxide coatings, (2) conversion coatings, (3) metallic coatings, (4) organic coatings and (5) inhibition and wettability control coatings. The review focused on production methodologies and the physical-chemical characteristics of coatings. Advantages and potential shortcomings of individual coatings are discussed in terms of their use and corrosion protection. There is no universally best coating; each coating system should be aligned with the substrate type and the environmental conditions of a specific application. In academic research, numerous options beyond those reviewed here are being explored, aiming to further improve coating performance, prolong the coating's lifetime and reduce its potential environmental impact.

Conflict of interest

The authors report no conflict of interest.

Authors contributions

I. M. conceptualisation, writing, creating figures and supervising. A.K. writing, editing.

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Dedication

This article is dedicated to the memory of Prof. Boris Žemva, an exceptional scientist in the field of fluorine

chemistry, whose knowledge and influence reached far beyond national borders. For several decades, Prof. Žemva served as Head of the Department of Inorganic Chemistry and Technology and as a member of the Scientific Council of the Jožef Stefan Institute. He was not only a highly respected scientist but also a dear colleague and mentor. His thoughtful advice, generous support, and insightful suggestions will be remembered with deep gratitude and respect.

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Povzetek

Aluminij in aluminijeve zlitine so pomembne tehnološke kovine, ki ponujajo zaželeno mehanske lastnosti, nizko gostoto, toplotno in električno prevodnost ter izkazujejo visoko stopnjo recikliranja. Čeprav so ti materiali večinoma relativno stabilni, so v zahtevnih okoljih izpostavljeni koroziji in obrabi. Prevlake so najpogostejša metoda zaščite aluminijevih zlitin pred korozijo. Prevlake lahko izboljšajo tudi odpornost proti obrabi in površini dodajo funkcionalne lastnosti. V tem preglednem članku so prevleke za aluminijeve zlitine povzete v pet skupin: (1) barijerne prevleke iz aluminijevega oksida, pripravljene z anodno oksidacijo, plazemsko-elektrolitsko oksidacijo, nanašanjem atomskih plasti in s hidrotermalno obdelavo, (2) konverzijske prevleke na preveleke na osnovi kromata, cirkonija, titana, trivalentnega kroma ali fosfata, (3) kovinske prevleke, (4) organske in hibridne sol-gel prevleke, in (5) prevleke, ki vsebujejo dodatke, ki zavirajo korozijo ali povečujejo omočljivost površine. Pregled se osredotoča na proizvodne metodologije in fizikalno-kemijske lastnosti prevlek. Obravnavane so prednosti in morebitne pomanjkljivosti posameznih prevlek z vidika njihove uporabe in zaščite pred korozijo.



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