

Chapter 14

Aluminum Coatings: Description and Testing

Overview

Pure aluminum, the 3xxx, 5xxx, and most 6xxx series alloys, are sufficiently resistant to be used in industrial atmospheres and waters without any protective coatings. Coatings are recommended for the higher strength 6xxx alloys, such as alloy 6013, and for all 2xxx and 7xxx alloys. The thickness of the natural oxide passive film can be increased by a factor of ~10 by prefilming in hot water and by a factor of 1000 or more by anodizing in sulfuric acid. Different options for mechanical and chemical surface preparation are available depending on choice of coating, appearance, and/or performance. Weak organic acids and their derivatives form insoluble salts and rely on the adsorption of the hydrophobic anions to provide a thin barrier layer. Chelating inhibitors create a thin tenacious passive layer (up to 20 nm). Aluminum alloys are protected by more active metals or by cathodic protection. Corrosion can be prevented or reduced by cladding. Some joint-sealing compounds that contain suitable soluble inhibitors are particularly recommended.

Aluminum can be protected by electroless or conventional plating. Aluminum and aluminum alloys in the active state act as a sacrificial anode in the form of plate or as a powder coating. Conversion layers can be created through physical vapor deposition, cathodic magnetron sputtering, high-energy ion beams, and laser ablation. Electrochemical anodization, plasma ablation, and chromate conversion coatings are frequently considered. There are thermoplastic coatings and converted coatings that are applied during or after processing and include principally three types of paints: epoxy, polyurethane, and moisture coatings. Corrosion monitoring is currently carried out by electrochemical impedance spectroscopy methods and electrochemical noise measurements.

General Considerations and Surface Preparation Pure aluminum and the 3xxx, 5xxx, and most 6xxx series alloys are sufficiently resistant to be used in industrial atmospheres and waters without any protective coatings. Examples of this are cookware, boats, and building products. Coatings are recommended for the higher strength 6xxx alloys, such as alloy 6013, and for all 2xxx and 7xxx alloys. One of the principal methods of protection is to enhance the thickness and quality of the natural oxide by prefilming in hot water, which can increase the thickness of the oxide passive film by about a factor of 10. The film can be thickened even more (to 1000 or more times the natural thickness) by

anodizing in sulfuric acid, for example. Chemical conversion treatments also provide protection, but to a much lesser degree, and are primarily used as a substrate for the subsequent application of organic films [1].

Conception, Alloy Selection, and Joint-Sealing Compounds During conception, the corrosion specialist should identify the different types of corrosion and prevention methods. Among the most common harmful effects are galvanic action, resulting from direct contact between aluminum and a dissimilar metal, such as copper, and indirect galvanic effects resulting from contact between aluminum and solutions containing reducible compounds of heavy metals. In some cases, design will prevent serious corrosion even though no other factors are altered. Similarly, since the various aluminum alloys differ widely in behavior, the selection of the most suitable alloy is important [2].

Aluminum-based alloys, such as 1100, 3300, 5052, 6053, Alclad 3300, Alclad 1017-T, and Alclad 2024-T, are highly resistant when freely exposed to most natural environments. They will all discolor or darken appreciably in most outdoor exposures, but will suffer no structurally appreciable changes in properties unless exposed in relatively thin sections below 0.076 mm (0.003 in.) thick [2].

Commercial aluminum alloys may contain other elements that provide special characteristics. Lead and bismuth are added to alloys 2011 and 6262 to improve chip breakage and other machining characteristics. Nickel is added to wrought alloys 2018, 2218, and 2618, which were developed for elevated-temperature service, and to certain 3xxx cast alloys used for pistons, cylinder blocks, and other engine parts subjected to high temperatures. Cast aluminum-bearing alloys may contain tin. In all cases, these alloying additions introduce microconstituent phases that are cathodic to the matrix and decrease resistance to corrosion in aqueous saline media. However, these alloys should be used in environments in which they are not subject to corrosion [2].

Joints, depressions, and other areas where moisture and dirt accumulate are more susceptible to corrosion than regions exposed to the atmosphere. Most plastic or semisolid joint-sealing compounds that conform and firmly adhere to adjacent metal surfaces are highly effective in preventing special attack in these regions. Some of these joint-sealing compounds that contain soluble inhibitors are particularly suitable [2].

In some cases, other mechanical factors, such as formability or hardness, may be of great importance in selecting an appropriate alloy for a specific application. Aluminum alloys such as 1100, 3300, or 5052, in the softer tempers, are readily formable and are also highly resistant to corrosion. If greater strength is required, alloy 6061 should be considered. This alloy combines good formability (in the W temper) with relatively high strength and good resistance to corrosion [2].

Surface Preparation by Plasma Ablation Surface preparation that includes cleaning first is well established for the currently used methods of aluminum finishing and coating for appearance and performance. Different mechanical and chemical options are available. Mechanical surface preparation includes abrasive blast cleaning, barrel finishing, polishing and buffing, and satin finishing [3]. Plasma ablation takes place by one of two methods—*sputtering* or *chemical etching*. Sputtering is used to remove organic contaminants and oxides from the metal surface. The surface is cleaned by bombarding it with inert gas plasma. Argon and hydrogen are used extensively for this procedure. Chemical etching involves chemical reaction between the impinging ion and the dislodged atoms. Oxygen is used with chemical etching to ‘clean’ the surface of a metal as well as deposit a synthetic oxide layer. The energy and quantity of oxygen control the properties of the oxide layer [4].

14.1. INHIBITORS

Most organic inhibitors come in the form of weak acids and their derivatives that form insoluble salts at the metal surface. There have been some reports on chelating inhibitors that formed an intimate bond between the organic complex and the metal surface or its oxide. The result was the creation of a thin (up to 20 nm) but tenacious passive layer. Organic salts rely on the adsorption of the hydrophobic anions to provide a thin barrier layer [4]. Solutions of sodium sebacate ($\text{NaOOC}(\text{CH}_2)_8\text{COONa}$), potassium hydrogen phthalate ($\text{C}_8\text{H}_5\text{O}_4\text{K}$), and sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$) were added to a solution of AlCl_3 to test their effectiveness within a simulated aluminum pit. The sodium sebacate solution (0.1 M) immediately formed a thick white precipitate, while the other two inhibitors did not. Electrochemical evaluation of the sodium sebacate solution on fresh and already corroded aluminum found that it functions as an inhibitor to both pit nucleation and pit growth as long as the chloride concentration remained below 0.3 M.

Inhibitors and Control of the Environment Current knowledge makes possible the inhibition of aluminum in a wide range of both acidic and alkaline environments. Single materials and combinations have been identified that can be used with considerable confidence, frequently, however, within a narrow range of conditions. Inhibitors may be classified by surface reactivity as adsorptive or surface-reactive (where a precipitated film is formed to provide a barrier between the corrosive agent and the aluminum surface). Chromates, silicates, polyphosphates, soluble oils, and other inhibitors are commonly used to protect aluminum. Aluminum is concentration-sensitive to chromate solutions as well as to other anodic inhibitors. Combinations of polyphosphates, nitrites, nitrates, borates, silicates, and mercaptobenzothiazole are used in systems that include aluminum and other metals [2].

Composition differences among aluminum alloys often determine whether or not an alloy can be inhibited in a given environment, and so an understanding of the metallurgical variables is important. Investigations into the fundamental reactions at the aluminum–environment interface have added significant new understanding that now permits the selection of inhibitors to be made with greater precision and their application to proceed with fewer trial-and-error adjustments [2].

In a limited number of cases, removing some minor constituent from the contacting liquid or gas can prevent corrosion. For instance, copper compounds, which may make water corrosive to aluminum, can be removed by passing the water through a tower packed with aluminum chips. Finally, the use of periodic cleaning procedures may be highly beneficial in specific cases [2].

14.2. METALLIC COATINGS

Aluminum can be protected by electroless or by conventional plating. Aluminum and aluminum alloys act as a sacrificial anode in the form of plate (Alclad) or as an applied coat, or for long-duration sacrificial anodes on condition that they do not passivate in the specific medium. Aluminum alloys are protected by more active metals or by cathodic protection of Al alloys. Aluminum is used for metallic powder application as a protective coat. Also, magnesium can be used as a pigment in primers for a paint coating system (see Section 14.5).

14.2.1. Conventional Plating and Electroless Plating of Aluminum

Electroplating of aluminum and its alloys is occasionally used to provide resistance to corrosion since other anodic treatments of surface conversion are currently used and give efficient corrosion prevention. However, electrolytic metallic coatings are used to obtain a certain metallic appearance, increased electrical conductivity, improved solderability, or improved frictional properties. Aluminum-based alloys are more difficult to electroplate because of the highly passive aluminum oxide formed on the surface. Also, most metals are more noble than the alloy and any void, discontinuity, or scratch can lead to severe localized corrosion [5].

Electroless plating with nickel and copper seems to be the most established plating method and is currently used in aircraft/aerospace industry and electronics industry applications. Nickel is chemically plated on aluminum parts with complex shapes, such as that of integrated electronic circuits. A number of different reducing agents have been used in preparing electroless nickel baths such as sodium hypophosphite, amino boranes, sodium borohydride, and hydrazine. Sodium hypophosphite baths are currently used. Their principal advantages are lower cost, greater ease of control, and better corrosion resistance of the deposit [5].

Plating of aluminum becomes possible by the use of a zincate pretreatment to remove the aluminum oxide film. By the use of a double zincate treatment, the homogeneity of the zincate film can be increased. This consists of stripping the first deposited layer and performing the second treatment for the homogeneity of the zincate film. A commercial hypophosphite-based nickel electroless layer can be used for bumping. The pH value is 4.5 and the bath is operated at 90 °C. A plating rate of 25 $\mu\text{m}/\text{h}$ is obtained. The deposits from this electrolyte contain 10% phosphorus [6].

Electroless Nickel Deposition on Al Integrated Circuits Electroless plating is an electrocatalytic process corresponding to the chemical reduction of metal ions on a base substrate in aqueous solution. Deposition progresses essentially linearly with time and quite heavy deposits can be produced analogous to those produced by conventional plating. However, electroless plating can produce very uniform thicknesses and layers since the nonuniform current distribution in the plating cell is avoided [6].

14.2.2. Surface Preparation for Thermal Spraying

Substrate surface preparation prior to thermal spraying is a key step to ensure good adhesion of the resulting coating. The most common approach consists of two successive stages:

1. Surface degreasing by solvent application to remove organic contaminants.
2. Surface roughening by grit blasting to ensure mechanical anchoring between the coating and the substrate.

This approach faces limitations and drawbacks for certain applications. One drawback is related to the use of solvents that are controlled by legislation protect peoples' health and for environmental considerations. Another issue is that grit blasting gives rise to residues that can be trapped in the material. These residues create some interface defects that either weaken the coating adhesion or create a severe indentation on the substrate [7].

Aluminum coatings can provide galvanic cathodic protection for several metals and alloys. In order to be a suitable protective solution on structural components, the mechanical integrity must be preserved. In particular, the fatigue properties are a challenge for thermal spray protective coatings on mechanical structures. To address the issue of the fatigue integrity of the aluminum alloy 7075 with an arc-sprayed protective coating, different surface preparations prior to arc spraying were considered. A feasibility study was performed using laser ablation as a surface preparation technique before or during arc spraying of coatings. Both fatigue and adhesive properties of aluminum coatings were evaluated in relation to substrate surface preparation techniques including laser ablation (PROTAL process), grit blasting, and shot peening [7].

Experimentation has shown that it is possible to thermally spray a metallic aluminum coating on to Al alloy 7075 without reducing the fatigue properties. Nitrogen as the atomizing gas for the arc spraying process provides significant improvement for the microstructural density of the aluminum coating. Moreover, laser ablation allows the deposition of aluminum coating on Al alloy 7075 using nitrogen as the atomizing gas with a clean interface and adequate adhesion. The combination of these two parameters on a shot-peened substrate allows for a significant improvement in fatigue properties to the level of an uncoated substrate and consequently maintains the material integrity and fatigue properties for structural applications [7].

It is feasible to use the PROTAL process with the arc spraying process in spite of the large plume and the significant overspray of the arc spray process. A similar bond strength to grit blasting can be achieved with the appropriate laser energy density for scouring and deoxidation modes. Finally, laser ablation allows a one-step process for both surface preparation and arc spraying on a robotic station [7].

14.2.3. Sacrificial Protection by Aluminum Alloys

Alclad Alloys These are duplex wrought products, supplied in the form of sheet, tubing, and wire, which have a core of one aluminum alloy and a coating on one or both sides of aluminum or another aluminum alloy. The cladding on each side is 2–5% of the total thickness. The coating is metallurgically bonded to the core over the entire area of contact. The coating is usually selected to be anodic to the core alloy in most natural environments and will galvanically protect the core where it is exposed at cut edges, rivet holes, or scratches. Such Alclad alloys are usually more resistant to penetration by neutral solutions than are any of the other aluminum-based alloys. Corrosion can be prevented or reduced by cladding with a more corrosion-resistant alloy, such as high-purity aluminum, a low magnesium–silicon alloy, or an alloy of 1% zinc. All of these cladding materials are frequently employed to give added corrosion protection to the 2000 and 7000 series alloys [8].

Sacrificial Aluminum Anodes Sacrificial aluminum anodes are used for cathodic protection of steel in seawater. Most aluminum sacrificial anodes are cast Al–Zn–Sn, Al–Zn–In, or Al–Zn–Hg alloys containing about 94–95% Al and 3.5–5% Zn. An addition of gallium (0.01–0.1%) or mercury (~0.05%) has been used in sacrificial anodes to avoid passivation. Al–Zn alloys with as little as 0.01% Sn in commercial-grade aluminum will cause surface darkening on annealing and increase susceptibility to corrosion, which appears to be due to migration of Sn to the surface. This effect may be reduced by small additions of copper (0.2%). These alloys are used in environments where aluminum remains active [8, 9].

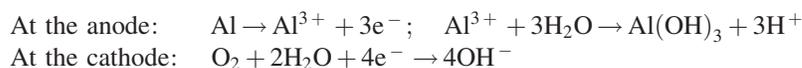
Atmospheric corrosion and salt spray tests (ASTM Specification for Salt Spray Fog Testing B117-73) of aluminum–zinc alloy-coated steel showed that 55 w% aluminum–zinc is two to four times as corrosion resistant as a galvanized coating of similar thickness. Furthermore, for the galvanic protection of cut edges of sheet in some environments, this coating proved to be superior to aluminum coating [8].

Aluminum as Sacrificial Anode to Steel Structural aluminum displays potentials for the unalloyed metal (~99.5% pure) in the range of 0.6–0.8 and varies with the environment, while aluminum alloys exhibit a variety of potentials—some of them sufficiently active to be used as cladding materials for the more noble alloys. Copper has a dramatic effect on the anode alloy and it is suggested that a minimum of 0.025 of mercury is necessary for reasonable anode activity. With low iron and copper levels, consistently good performance can be achieved with 0.4% zinc and 0.04% mercury. A higher level of zinc is beneficial in anaerobic mud. Another developed group of alloys are all of a generic strain, which uses indium (~0.005–0.03 wt %) as the principal alloying metal. Usually, with high-purity aluminum and some zinc, the capacity of the anode is high and it operates close to 90% efficiency; it can exhibit higher driving force than the mercury anodes, usually at -1.10 V to the Ag,AgCl/KCl electrode or 0.3 V to the protected steel [10].

Sacrificial Aluminum Coat Spraying Aluminum spraying is a current practice to coat less-resistant alloys. For some composites, the corrosion behavior is governed by galvanic action between the aluminum matrix and the reinforcing material. Aluminum thermal spraying has been reported as a successful protection method for discontinuous silicon carbide–aluminum composites; for continuous graphite–aluminum or silicon carbide–aluminum composites, sulfuric acid (H_2SO_4) anodizing has provided protection, as have organic coatings or iron vapor deposited aluminum [2].

More recent work on corrosion prevention of aluminum alloys used for aerospace applications by sprayed sacrificial coatings has been reported. This can be applied in situ for maintenance. In one study, a coating 125 μm thick was sufficient since only 12.5 μm was consumed during 1000 hours of immersion of the coated alloy in agitated and aerated 3.5% sodium chloride solution at 25 °C. The Al–5Mg sprayed alloy offers similar protection as other sacrificial coatings based on Al, Zn, Al–Zn or Zn–15 Mg, although it gives the least sacrificial current. This coating can give better performance in alkaline environments since magnesium offers better resistance than aluminum for cathodic corrosion. This coating can prevent stress corrosion cracking; however, for pitting corrosion it is not so efficient since pitting potential is lower than the mixed potential of the coating and the substrate. Pitting, although retarded, can lead to transgranular ruptures and corrosion fatigue ruptures. It has also been shown that the corrosive medium can infiltrate through the pores of the coating to the alloy–coating interface similar to that observed with clad alloys [8, 11].

Stable Aluminum Anodes for Impressed Cathodic Protection Systems Most domestic water installations are protected using impressed cathodic current systems. A typical system uses aluminum anodes to protect the interior surface of the steel reservoir and the pipes. The principal reactions are



The anodic reaction produces aluminum hydroxide in a colloidal form while the cathodic one consumes oxygen. The formed aluminum hydroxide, on the order of 0.1–0.2 mm thick, acts as a protective layer for the interior cathodic surface of the reservoir that can be made of steel, galvanized steel, or copper. The pH of water should be controlled between 6 and 8.5, which is the zone of passivation of the aluminum anode.

Steel or aluminum can be used as consumable anodes in seawater for cathodic protection impressed current systems. Both operate at higher efficiencies than in fresh water, steel being about 90–100% efficient while aluminum is about 50–90%. However, permanent anodes made from lead alloys or platinum film electrodes are the two most suitable ones [10].

14.2.4. Aluminum Powder as a Coating

Cementation or diffusion of aluminum is used currently as a coating to protect metallic objects. A mixture of aluminum and appropriate flux are placed on the metallic surface at a high temperature in order to allow the diffusion of the coating material into the basic substrate. Zinc and chrome powders are used for the same purpose.

Electrophoretic Powder Deposits Electrophoretic powder deposits are obtained in galvanic baths, for example, alcohol, microadditives of $\text{Mg}(\text{NO}_3)_2$ or $\text{Al}(\text{NO}_3)_3$, and aluminum powder. A voltage of 100–120 V and a current density of 50–150 A/m^2 are recommended to deposit aluminum powder on steel substrate using the electrophoresis method. The electrostatic method permits one to deposit larger particles than the electrophoresis method [12]. The advantages of the hydroimpulse coating are its small grains, the possibility of applying the coating on parts of various shapes and configurations, and the fact that its adhesion to steel substrate is ~ 100 MPa.

The coating is composed mainly of pure aluminum and some microalloying elements such as Mg, Na, and other trace elements. Hydroexplosive aluminum coating on steel substrate is comprised of three zones: an outwardly textured zone with grain sizes from 1 to 5 μm , the 10 μm thick inwardly (inner) ultrafine grain zone with grain diameters from 0.1 to 1 μm , and the 2–3 μm thick transition zone.

The coating does not have open porosity and the closed porosity is only 2–3%. However, there is a lack of structure in the brittle intermetallics. This coating is not prone to SCC in wet sulfide media, but coated steel is prone to SCC in wet sulfide solutions containing NaCl additives. The coating is anodic in NaCl solutions while it is cathodic in hydrogen sulfide solutions. In NaCl and in wet sulfide solutions, corrosion rates are lower than that of pure aluminum. The coating is more resistant to pitting corrosion than pure Al [12, 13].

14.2.5. Cathodic Protection of Aluminum Alloys

Godard cited an early example of aluminum protection using sacrificial zinc anodes and Hatch mentioned the use of impressed current protection systems to protect painted aluminum ship hulls. Cathodic protection requires careful control to ensure that adequate protection is maintained without overprotection, which can lead to alkali attack (cathodic corrosion). Alclad alloys (layered aluminum products with one aluminum alloy integrally bonded to a more noble aluminum alloy core) may be viewed as having a self-contained cathodic protection system [2].

Buried aluminum pipelines are usually protected by sacrificial anodes: zinc for coated lines and magnesium for uncoated lines. Impressed current (rectifiers) systems are not used to protect aluminum pipes [8, 14]. In some applications, aluminum alloy parts, assemblies, structures, and pipelines are cathodically protected. The suggested practice is to shift the potential at least to -0.15 V but not beyond the value of -1.20 V versus a saturated Cu/CuSO_4 reference electrode. High cathodic currents can make the solution sufficiently alkaline to cause significant cathodic corrosion. In some soils, potentials as low as -1.4 V have been encountered without appreciable cathodic corrosion.

14.3. CONVERSION COATING

Conversion coatings are the most widely used prepaint treatment processes for metal substrates. Processes specifically designed for aluminum are of recent origin. Historically, however, phosphoric acid cleaners, wash primers, and iron and zinc phosphates and chromate-oxide coatings have all been utilized with satisfactory results. Accelerated chromate phosphates, chromate oxides, and anodizing and nonchromate formulations have recently been developed [15]. Conversion layers provide the ability to modify the aluminum surface to give better adhesion, a surface free of contaminants, or a coating layer that contains active corrosion inhibitors. Conversion coating can be selected based on corrosion protection functions and/or paint pretreatments. Corrosion prevention, at least partially, can be achieved through passivation of the metallic base of aluminum, by a barrier against moisture, by oxygen and other aggressive agents, by electrochemical insulation, and by protection against mechanical erosion. For paint pretreatments, an effective and continuous bonding, chemical stability, insolubility, imperviousness, and flexibility are essential properties, in addition to providing a wettable substrate for paint application and maintaining adhesive integrity between the metal and the paint film [15].

The U.S. aerospace industry places a high demand on coatings used to paint or repaint existing aircraft fleets. A typical coating system (pretreatment/primer/topcoat) is comprised of three individual coating layers. The first layer, a conversion coating, is the product of substrate pretreatment. The conversion coat is usually a very thin (10–60 nm) inorganic layer that provides corrosion protection and improved adhesion between the substrate and the primer, which is the second layer of the coating system. The primer provides similar functions to the conversion coat, but is comprised of a pigmented organic resin matrix. The application thickness of the primer can vary from 5 to 200 μm although a thickness of 25 μm (1 mil) is typically desired due to weight constraints on the aircraft. The primer is the principal provider of corrosion protection. Typical formulations consist of both chromated and nonchromated pigments enveloped in an epoxy resin. Finally, a top coat is applied that serves as the main barrier against environmental influences such as extreme climates and ultraviolet rays and it provides the aircraft with decoration and camouflage [4].

Conversion layers can be created through a variety of techniques, which include physical vapor deposition, cathodic magnetron sputtering, high-energy ion beams, and laser ablation. The most common conversion layers are from electrochemical anodization, plasma ablation, and chromate conversion coatings and modifications thereof [4].

14.3.1. Phosphates and/or Chromates

Corrosion coatings (chromates or phosphates) are recommended for the preparation of aluminum alloys. For milder environments, paint may be applied on the conversion coating, but a chromated primer should be applied for more aggressive media. Almost any type of paint (acrylic, alkyl, polyester, vinyl, etc.) is suitable. One or two coats of the finish paint should follow the primer. In general, a coating contains micropores, areas of low cross-link density or high pigment volume concentration (PVC), that provide a path for diffusion of corrosive agents such as water, oxygen, and chloride ions to the coating–metal interface. Therefore it is most often necessary to incorporate inorganic or organic inhibitors into a paint system for corrosion protection [4].

The chemical treatment of aluminum by immersion in acid chromate solutions is often employed to produce protective coatings on the metal surface. The coatings, known as chemical conversion coatings, increase the corrosion resistance of the metal and also serve as adhesive bases for organic finishes such as paints. The most effective corrosion inhibitor in use is hexavalent chromium (Cr^{6+}). A chromate conversion coating is a chemically grown oxide layer on the alloy substrate that provides an active barrier layer that reduces the rate of the cathodic oxygen reaction. The final result is a 10–60 nm thick film consisting of $\text{Cr}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ [4].

Brown et al. [16] examined the morphology and structure of the chemical conversion coating developed on annealed high-purity aluminum in an acid chromate–fluoride solution by transmission electron microscopy of stripped films and ultramicrotomed sections. A mechanism for conversion coating has been suggested. Deposition of hydrated chromium oxide at the cathodic sites takes place on the aluminum surface at preexisting metal ridges. Such material develops extensively over the ridged structure with time of immersion. The anodic sites exist between the preexisting metal ridges. At such regions, the fluoride-containing acid solution chemically thins the original air-formed film, resulting in a dynamic equilibrium between alumina film growth and its dissolution. The consequential loss of Al^{3+} ions to the solution results in local scalloping at the metal–conversion coating interface.

Growth of chemical conversion coatings on aluminum is strongly dependent on the purity of the metal. For specimens up to 99.99% purity, the aluminum surface is not homogeneous. Flaws are always present in the thin oxide layer covering the aluminum surface; such flaws are situated above the grain boundaries and cellular boundaries associated with impurity segregation in the aluminum substrate. These flaws are of the residual type and provide easy paths for electronic conduction in an otherwise insulating oxide layer. Consequently, coating growth (i.e., the reduction of the dichromate species to hydrated chromium oxide) occurs preferentially along the grain boundaries or cellular boundaries of the aluminum substrate [17].

However, for aluminum specimens of 99.9996% purity or higher, where the cellular structure is absent, the population density of the residual-type flaws in the oxide layer is considerably reduced. It is suggested then that coating growth proceeds by the tunneling of electrons through the thin, insulating, passive oxide layer to produce a coating of more uniform appearance than associated with substrates of reduced purity [17].

Growth of chemical conversion coatings on aluminum is also closely related to the heterogeneity of the aluminum surface. Even minor heterogeneities, such as grain boundaries or cellular boundaries, play an important role in the coating growth process. In practical situations, where various alloying additions are present within the metal, the coating growth process is expected to be considerably more complex than described

here, due to the presence of precipitates and intermetallic particles of varying sizes and electrochemical behavior [17].

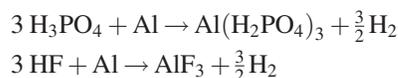
Zinc Phosphate Treatment Properly applied, this group of phosphates is good for corrosion protection and finds widespread use in mixed steel and aluminum product lines. The process of phosphating is used frequently before cold deformation of aluminum alloys for corrosion protection. The aluminum and its alloys can be deformed rapidly with appropriate lubricant and without the application of surface conversion treatment. In difficult situations of deformation of aluminum alloys, the use of crystalline zinc sulfate is indispensable after the application of a specific lubricant, as in the case of extrusion or dishing of a very thick plate of metal. An important preparation of the surface before phosphating is necessary to eliminate any leached metallic component of the alloy, such as copper or silicon [18].

Phosphate conversion coatings are popular because of low operational cost and low environmental toxicity [15]. Zinc phosphates were the initial replacement pigments for zinc chromates. They display no toxic effects and provide some corrosion protection to aluminum alloys by forming a $Zn_3(PO_4)_2 \cdot 4H_2O$ film. Bath composition typically consists of phosphoric acid, zinc dihydrogen phosphate, fluoride, and an oxidation accelerator such as NO_2 at pH 2–4 [4].

The zinc phosphate bath should have a balanced composition of salts and free acid. Its established total acid value should be maintained as well as the free-acid value for satisfactory performance. Accelerators such as sodium nitrite are used in some zinc phosphate solutions [3]. The metal phosphates are soluble in strong acids but crystallize out when the acidity is reduced. This mechanism occurs as the acid ions react with the aluminum surface, become neutralized, and produce an integral crystal growth on the metal surface. The aluminum surface is therefore converted to a finely crystalline phosphate film with acceptable texture for paint bonding. Crystalline phosphate films may be iridescent to gray and coating weights can be 0.108–0.538 g/m^2 (10–50 mg/ft^2) for iron phosphates, and 1.08–3.24 g/m^2 (100–300 mg/ft^2) for zinc phosphates [15].

Phosphating is an electrochemical and chemical reaction and gives rise to several passivating phenomena, namely, a precipitation to the amorphous state, crystallization and growth, and crystalline reorganization. The mechanism of iron and steel phosphating in zinc phosphate bath accelerated with nitric acid has been frequently examined. Effectively, the crystalline phosphate layers on steel are composed of metal oxide, iron phosphate, phosphophillite ($Zn_2Fe(PO_4)_2 \cdot 4H_2O$), and hopeite ($Zn_3PO_4 \cdot 4H_2O$). This can be extrapolated to another metal such as aluminum, except that the highly passive nature of aluminum oxide and the presence of fluoride in the bath as etcher and complexing agent of aluminum ions necessitate a fundamental explanation of the mechanism of aluminum phosphating that can lead to better understanding of the process [19].

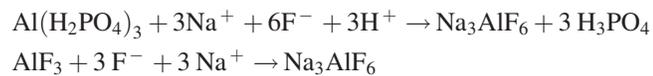
The polarization curve of electrochemical reduction of hydrogen ions on the pure aluminum surface is situated at very low negative or active potentials. The phosphating solution contains phosphoric acid, zinc phosphates, nitrates, and fluorides or free hydrofluoric acid. As in chromate–phosphate treatments (see Section 14.3.2), the HF initiates a rapid homogeneous attack of the aluminum surface [18]:



The kinetics of the attack increases with fluoride ions and the oxygen saturation of the solution. The principal reaction of formation of insoluble tertiary phosphates of zinc (hopeite) starts at slightly higher pH due to the initial attack of the metal, since the acid bath contains the soluble zinc monophosphates:



The formation of fluoride aluminum complexes, such as AlF_6^{3-} , occurs and these are critical for the support of the acid attack of the aluminum surface and can give rise to the precipitation of fluoride aluminum compounds [18]. This can lead gradually to the accumulation of fluorides, aluminates, and phosphates of aluminum in the bath. Sodium or potassium salts are then present to prevent the buildup of soluble aluminum in the bath, which inhibits coating formation. In the presence of sodium, aluminum, and fluoride ions, the following reactions are possible:



Layer Composition Simple analysis of the phosphate layers gives 34–37 wt% PO_4 , 35–38 wt% Zn, 3–5 wt% Al, 4–6 wt% F, and water of crystallization [18]. It has been found that the phosphate layer is composed essentially of tertiary zinc phosphate (hopeite), with a thickness of 1–5 μm giving film weights of 2–6 g/m^2 . In these phosphating solutions an underlayer of Al_2O_3 is formed. The addition of a ferrous salt can help the formation of the underlayer and this was found to consist of $\gamma\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$. It has been suggested that the identical structure of the two oxides can lead to the formation of derivatives with molecular substitution [18].

Phosphate Application The application of phosphate coating for paint-based application normally comprises five successive operations: cleaning, rinsing, phosphating, rinsing, and chromic acid rinsing. Some of these operations may be omitted, combined, or integrated in one operation: for example, rinsing after cleaning with water at 71–82 °C and before phosphating since hot water is an additional cleaner. However, ambient temperature rinses are now often used. Hexavalent chromic acid rinse can be replaced by phosphoric acid or other recent alternatives [3].

Phosphating methods may be applied to an aluminum surface by either immersion or spray, or a combination of both. Application is by immersion at 125–140 °F for 1–4 minutes, or spraying at 125–160 °F for 30 seconds to 2 minutes. There is a trend to use zinc phosphating coating processes for automobile bodies using a combination of spray and immersion. Occasionally, a surface may be coated by brushing or wiping [3]. Product selections should be restricted to moderate service environments. Bath life is limited due to the low tolerance for accumulating aluminum [15]. Zinc phosphate coatings applied via spray are easily deposited on aluminum surfaces, provided fluoride ion is present in the bath [3].

Simultaneous Phosphating of Steel and Aluminum It is possible to phosphate steel and aluminum at the same time. In this case, rich solutions in zinc and nickel phosphate perform better than ordinary solutions. Also, the presence of HF and/or simple or complex

fluorides is essential. The steel surface should be larger than that of aluminum in certain cases, and the aluminum surface should not exceed 10–15% of the total phosphate surface [18]. However, in processing a metal mix of aluminum, steel, and galvanized steel, separate fluoride additions to the bath are required if the metal mix consists of greater than 10% aluminum. Coating weights range from 0.27 to 2.2 g/m² (25 to 200 mg/ft²) [3].

Phosphating of Al–Mg–Si Alloy Surface In vehicle body construction, extrusion alloys based on Al–Mg or Al–Mg–Si are most commonly used. Whereas the Al–Mg alloy does not suffer corrosion or paint adhesion problems using standard methods of application, subsurface corrosion can be troublesome with, for example, Al–0.4Mg–1.25Si alloys, especially when a machined surface is involved. This has been observed in the salt spray condensate water test and in atmospheric corrosion accelerated by NaCl. The underlayer filiform corrosion often starts in the direction of machining, after which it transforms into a broad frontally advanced action [20].

The performance of paint coated aluminum in the salt spray test is excellent. A major improvement in corrosion resistance to filiform corrosion is obtained when the Al–Mg–Si alloy surface, after machining, is etched in caustic soda by nitric–sulfuric acids before being phosphated to give a crystalline coating using a fluoride-containing, low-zinc method. The low-zinc phosphate coatings are, with respect to their corrosion resistance, markedly superior to normal zinc phosphating coatings. The low-zinc system produces coatings with a higher proportion of Zn₂Fe(PO₄)₂ (phosphophillite) [20].

14.3.2. Chromate–Phosphate Treatments

Chromate–phosphate coatings were the first pretreatment specifically developed for aluminum in 1945. Their products have performed excellently for the architectural metal and beverage can industries, since the coating does not contain Cr⁶⁺. However, the demand for beverage cans is in decline and the high-performance top coats no longer require the strong performance of chromate-based pretreatments. Effectively, the excellent top coat paints, such as silicone fluoropolymers and powder coats, can minimize the performance requirements for the prepaint treatments. Advances in electocoat application technology are also proving beneficial [15].

The concentration limits of phosphate, fluoride, and hexavalent chromium ions, in the aluminum chromate–phosphating bath, can be expressed as: PO₄³⁻, 20–100 g/L; F⁻, 2–6 g/L; and CrO₃, 6–20 g/L. The F⁻/CrO₃ (anhydrous) ratio should be controlled in the range 0.1–0.4. The pH is usually below 2.

Part of the aluminum can form F₃Al, which leads to formation of relatively soluble complexes such as (AlF₆)³⁻ in combination with fluoride ions in the bath. Addition of HF is very critical to attack the aluminum surface, initiate the phosphating process, and precipitate the formed aluminum fluoride compounds as a mud for disposal. In every case, the aluminum compounds act as inhibitors of the process; they should be continuously removed, otherwise the zinc phosphate layer will not be as pure and homogeneous as desired [18].

Chromate–phosphate treatment can be applied by spray or immersion. Immersion times range from 30 seconds to 3 minutes at 110–130 °F, whereas spraying is done for 15–45 seconds at 95–130 °F. These baths produce crystalline or amorphous coatings of 15–1000 mg/ft². The film is iridescent to grayish green. Thickness can be significant, from 2.5 to 10 μm (0.1 to 0.4 mil). The chromium phosphate films are composed principally of

hydrated chromium phosphate (CrPO_4), Cr_2O_3 , and aluminum oxides. A typical air-dried coating is composed of 50–55% chromic phosphate, 17–23% aluminum phosphate, 22–23% water, and a trace amount of fluorides [15].

The corrosion performance of chromate–phosphate films is generally very close to chromic acid anodizing films and that of chromate oxide films. This treatment is recommended for severe and long-term service conditions. Because of its excellent performance, the American Architectural Manufacturers Association (AAMA) has designed it as a standard prepaint treatment and it is recommended also by U.S. military specifications [15]. In reality, this level of corrosion prevention is ideal for conversion coating.

Chromate Oxide Coatings with Superior Corrosion Performance These coatings were introduced in the early 1950s and are now widely used for domestic appliances, aircraft and electronic equipment, and continuous coil coating of architectural aluminum. Normally a chrome oxide bath consists of three principal constituents: acid chromates (H_2CrO_4), etchants (HF), and accelerators or complexing agents. The original accelerator, $\text{Fe}[(\text{CN})_6]^{3-}$, was replaced by $(\text{MoO}_4)^{2-}$ because of environmental considerations. Paint-based coatings can be applied by spray, immersion, or brush at 25–60 °C (80–140 °F) for 15–45 seconds. Longer times are needed for bare corrosion protection coatings, which are applied by immersion. The formed iridescent yellow to brown color film is very adherent, amorphous, and mixed with metallic oxide corrosion products. The film thickness range is 0.13–1 μm (0.005–0.04 mil) and coating weights are from 15 to 100 mg/ft^2 . The coating consists of chromium oxides covered with an absorbed monolayer of the accelerator [5, 15, 21].

Chromate oxide films are versatile and more widely used than the chromate–phosphate treatments, where parts are too long or assembled with dissimilar metals. They also have superior performance ratings compared to chromate–phosphate coatings. Without paint, the films have twice the salt spray resistance of a chromate–phosphate coating. They can stand very severe service conditions and comply with military specification MIL-C-554 and AAMA 605.2 [15].

Alkaline Chromates These treatments are as old as the described phosphate treatments. Alkaline chromates are primarily solutions composed of 2–3% sodium carbonate and 0.5% potassium dichromate. Immersion times range from 10 to 20 minutes at 95 °C (180–200 °F) at pH 10–11. This carbonate/dichromate ratio is critical to provide consistent coating action. Thin, gray, and porous films are 1–2.5 μm (0.04–0.1 mil) thick and coating weights are 1.077–5.38 g/m^2 (100–500 mg/ft^2), made up of aluminum oxide and dispersed chromate oxides. Maximum corrosion resistance is achieved by sealing in hot 5% potassium dichromate [15].

No-Rinse Chromate Processes These processes are finding application in the coil coating of aluminum. Adhesion and corrosion protection properties are equivalent to conventional processes. The applied solution is composed of Cr^{6+} and Cr^{3+} as well as other ingredients, such as F^- or PO_4^{3-} . Some formulations include organic compounds. For most paint applications, the coating weights range from 0.054 to 0.269 g/m^2 (5 to 25 mg/ft^2) [5].

14.3.3. Chromate Alternatives

Discharge of Cr(VI) into natural environments must be avoided; therefore molybdates should replace chromates in certain applications [2]. The advent of chromate replacements

for aluminum alloys began in the late 1970s. As regulations became increasingly stricter, commercial, academic and, government facilities have relied on a collaborative effort to come up with novel innovations for the corrosion protection of aerospace aluminum alloys. More elaborate coating formulations have failed to produce the level of protection that chromates provide; therefore researchers have moved to more advanced technologies for improved protection. Some of the newer alternatives include low-temperature cationic plasma deposition, sol-gel and ceramic coatings, and various inorganic and organic inhibitors and conducting polymers, including some based on double helical structures. Although ultimate protection has not been achieved by one single technique, it is believed that a combination of the most promising alternatives will provide the desired protection [4].

The use of phosphochromatation instead of chromatation should be considered with great care since some Cr^{6+} in the phosphochromatation layer has been proved to be present even with thorough rinsing of the treated material. A possible solution is a conversion coating using zirconium but the corrosion resistance is still unacceptable [22]. It has been postulated that a conversion coating based principally on potassium permanganate as the primary component is an acceptable alternative to chromate. Manganese oxides are by far the most closely related to chromic oxides in terms of similar chemical properties [23].

Nonchromate Systems A report has been issued by the U.S. Air Force comparing the corrosion resistance performance of selected fully nonchromate systems to the standard chromate-containing coating system. A total of 12 fully nonchromated systems, consisting of both experimental and commercially available products, were tested on 76 mm \times 152 mm (3 in. \times 6 in.) aluminum alloy AA2024-T3 panels and compared to the performance of the standard chromate system. The salt spray test (ASTM B117-94), filiform corrosion test (ASTM D2803), pull-off strength (PATTI) test (ASTM D4541), and electrochemical impedance spectroscopy (EIS) measurements were considered. The data identified two fully nonchromated systems—MSZ/WEP/APC and MSZ/EEP/APC—that demonstrated promising performance in all tested areas comparable to that of the standard chromated aircraft coating system [24].

The surfaces of the panels that were to receive an MSZ coating underwent the surface treatment method used at Warner-Robins ALC according to MIL-C-10578D. The CCC pretreatment was applied using the MIL-C5541E process specification by immersion for a period of 3–5 min to generate a coating weight between 0.430 and 0.645 g/m² (40–60 mg/ft²). MSZ is a water-based, commercially available mixed silane–zirconate sol-gel, AC-131, with the Boegel EP-II trademark. The material was mixed according to the manufacturer's instructions (AC-131) and left for a 30 min dwell time. The application was spray-applied to upright coupons during several passes to ensure that the coupon was drenched for not < 30 s, but not > 2 min. The thickness of the films, measured by scanning electron microscopy (SEM), ranged from 0.6 to 0.9 μm [24].

The two evaluated nonchrome epoxy primers were: WEP, a commercial water-based nonchromated epoxy primer, PRC CF EW AE048A/B, meeting the specifications in MIL-PRF-85582, type I, Class N with the Eco Prime Trademark; and EEP, an experimental epoxy primer, 02-GN-083. The top coat was APC, product 99-GY-001 Color 3673, meeting MIL-PRF-85285D specifications. Analysis of the experimental data showed the ability of some of the fully tested nonchromate coating systems to provide corrosion protection comparable to that of the chromate control system (CCC/MIL-PRF-23377H/APC), but only when the criterion of a clean scribe is overlooked as stated in MIL-PRF-23377H for Class N primers. After 2000 h of exposure in the salt spray test, nonchromate systems with the MSZ

surface treatment, and either WEP or EEP primer, demonstrated comparable corrosion protection [24].

Cerium Salts as Inhibitors Some of the most promising chromate replacement inhibitors are derived from cerium salts. They are believed to control the cathodic reaction by precipitating cerium hydroxide ($\text{Ce}(\text{OH})_3$) at local regions of high pH. Aldykiewicz et al. [25] studied the effects of cerium chloride on aluminum alloy 2024-T3 using in situ current density mapping. They concluded that there was a preferential Ce deposition over the copper-rich regions, which were associated with increases in pH due to O_2 reduction. Mansfeld et al. [26] modified a process that incorporated cerium, which was originally introduced by Hinton to inhibit corrosion of high-strength aluminum alloys. The process involves immersion of the alloy in hot $\text{Ce}(\text{NO}_3)_3$ followed by anodic polarization in Na_2MoO_4 and final immersion in hot CeCl_3 [4]. In 0.5 N NaCl, treated samples were reported to have pitting potential (E_{pit}) values 200 mV higher (more noble) than the untreated samples. The increase in E_{pit} is indicative of the system reaching a more noble state. The process yielded excellent corrosion resistance for the aluminum alloy 7000 series and marked improvements for the aluminum alloy 2000 series using this process. Cerium compounds are also being incorporated into sol-gel coating systems, which are new candidates for aluminum pretreatments and primers [4].

Sol-Gel Processes Sol-gel processing is a method in which thin oxide films can be deposited on a substrate at much lower temperatures than traditional ceramic processing methods. A variety of metal alkoxides, salts, or nitrates can be used as precursors for the oxide synthesis. Upon deposition, the coating undergoes hydrolysis and condensation to form a continuous three-dimensional oxide matrix. The oxide layer acts as an inert, hydrophobic barrier layer. The intrinsic stresses and processing conditions for one-coat systems limit the film thickness to less than 1 μm . Film thickness of $>1 \mu\text{m}$ can be obtained by combining additives into the sol-gel or by creating multicoat systems. Due to the limited film thickness, sol-gel coatings are used as the substrate pretreatment [4].

Although one would expect a thicker film to provide better protection, the opposite is true for sol-gel films due to the tendency for cracking to occur in single-coat films greater than 1 μm . A more realistic approach for defect-free film formation is being taken by combining the various metal oxides with organic segments to form what are called *ceramers*. They are synthesized using organic functionalized metal alkoxides that promote reaction between an organic group and the inorganic alkoxide. Ceramer systems are potential chromate replacements because the increased flexibility of the coating thickness for ceramers is higher than that for traditional sol-gel coatings, which expands their use [4].

It has been stated by Hamdy et al. [27] that ceramic coatings based on salts like vanadia, ceria, silica, and molybdates prepared by sol-gel are promising future treatments for aluminum surfaces. The surface preparation (etching followed by oxide thickening in boiling water) prior to sol-gel treatment was found to have a marked influence on corrosion protection of AA6061-T6. Molybdate treatment showed the best corrosion resistance after 30 days in 3.5% sodium chloride solution due very probably to the formation of a compact film of molybdenum oxide with buffer action that rejects chloride ions [27].

Hamdy [28] studied the corrosion protection of aluminum composite AA6061-T6–10% Al_2O_3 by silicate/ceria treatments. One of the suggested treatments is oxide thickening in boiling water for 1 h followed by treatment in a solution containing a mixture of 10 mL sodium silicate (4 g/L) + 10 mL CeCl_3 (1000 ppm) for 2 h. It was found that the

corrosion resistance was improved due to the formation of protective oxide films, which act as a barrier to oxygen diffusion to the metal surface. Cerate, and not silicates, plays the main part in the passivation process. EIS studies showed that etching before silicate/cerate treatment has a negative effect on the corrosion resistance that could be due to the increased distribution of silicon and that excludes the more efficient cerium oxide from the active centers [28].

Cerium Chloride Treatment Hamdy [29] stated that a surface preparation is essential for the corrosion protection of aluminum composite AA6061-T6–10% Al_2O_3 . Preetching followed by oxidethickening was proposed before the treatment in pure solution of 1000 ppm of cerium chloride (CeCl_3 for 3 h or 1 day). Corrosion behavior was monitored using electrochemical impedance spectroscopy (EIS) and dc polarization techniques during immersion in 3.5% NaCl solution for up to 60 days. XPS and SEM techniques were used to examine the corrosion performance of different pretreatments.

Studies showed that preetching in 0.01 N KOH for 15 minutes plays an important role to inhibit the active sites, reject the chloride ions from the surface, form a silicon-rich surface, and increase the ability to distribute cerium uniformly on the surface. The oxide thickening step in distilled boiling water for 1 h following pickling is highly recommended. It is postulated that the mechanism of corrosion has been changed from simple adsorption on the surface treated directly with cerium chloride to absorption of cerium through the pores of the thick Al oxide layer [27].

Molybdate Solutions The effectiveness of the molybdate solutions was reported to be inhibited by the size and solubility of the oxide MoO_2 species. Sporadic pitting potentials of >100 mV led to the conclusion that the oxidizing power of MoO_4^{2-} was not as strong as the dichromate species ($\text{Cr}_2\text{O}_7^{2-}$). The effects of different inhibitors were tested, including molybdates, on the corrosion of aluminum using the power spectral density (PSD) of electrochemical noise measurement (ENM). PSD analysis proved to be an excellent method not only to determine the effectiveness of the inhibitor but also to provide some understanding of the mechanisms of the inhibitor. It was found that molybdates act as oxidizing inhibitors, and the main inhibiting effect was due to an adsorbed layer acting as a barrier to chloride ions [4].

Cerium, Manganese, Vanadium, and Molybdenum Pretreatments The influence of pretreatments of composite AA6061-T6–10% Al_2O_3 on the protection of aluminum by epoxy-treated and coated FLBZ 1074 fluoropolymer top coat was studied by Hamdy et al. [30]. The Ausimont coating system consists of solvent-based epoxy primer (80 μm) clear top coat of FLBZ 1074 (40 μm); FLBZ is the trademark of a fluoro-based top coat produced at Ausimont (Italy). The pretreatments were based on cerium, manganese, vanadium, and molybdenum chemical products [30].

The plastic materials, *Fluoropolymers*, are the most widely used when chemical resistance, stability at high and low temperatures, and good electrical properties are desired. Also, due to the very strong chemical bonding between carbon and fluorine, the fluoropolymers have some special properties, which make them very useful as coatings for equipment in the paint, varnish, and adhesives industries. Eight different types of pretreatments were used as primer before applying the top coat of clear FLBZ 1074 [30].

The epoxy-treated fluoropolymer specimens showed a dramatic increase in corrosion rates under scratched conditions after less than 30 days of immersion in aerated 3.5% sodium chloride solution due to filiform corrosion. The new pretreatments showed

outstanding durability using the salt spray test. No sign of corrosion was observed after 1140 h of exposure to the salt chamber while filiform corrosion took place for the epoxy-treated specimens after only 40 h of exposure. The mechanism of protection using the new treatments depends on formation of a highly protective oxide layer that is efficient to improve corrosion resistance and to maintain the adhesion performance within an acceptable range [30].

Silanes The organofunctional based silanes have been used recently as surface pre-treatments for aluminum and other metals and have the capacity to be used in a variety of ways. Newer developments include the super-primer concept, which is formed of a composite consisting of silanes and organic resins, giving great flexibility in terms of composition and desired properties [31]. The silanes' action on corrosion has been enhanced by neutron scattering techniques. The main property is that they control the corrosion protection due to the hydrophobicity of the coating. If water reaches the surface, metallo-siloxane bonds are not resistant to water since silanes are not good in passivating treatment. They are thin, absorb water, and can be hydrolyzed at low temperatures. If an effective inhibitor package can be achieved that leaches out at a controllable rate, the superprimer can replace the chromate conversion coating and the chromate-containing primer [31].

The bis-silanes, containing OX as alkoxy groups and an amino or ureido as an organofunctional group, and especially silane mixtures have shown protection against both uniform and localized corrosion. Also, a modified silane system can contain an inhibitor with a defect-healing capability. Silanes reduce the corrosion rate of aluminum surface primarily because they replace hydrophilic hydroxyl groups with hydrophobic Al–O–Si groupings and with the action of the remainder of the cross-linked silane film. This is in addition to the improved adhesion to many paint systems because they are covalently bonded both to the metal oxide and to the paint polymer [32].

Huang et al. [33] proposed a novel, environment-protective, water-based metallic coating for aluminum alloys, which mainly contains metal flake, lithium silicate, and silane. The zinc flakes were 0.1–0.2 μm thick and 10 μm in diameter. The coating was sprayed on the finely polished aluminum surface, and then baked for 30 minutes at 200 °C. The film was actually formed by the lithium silicate and silane, which can form an interpenetrating polymer network (IPN) structure by forming Si–O–Si bonds in the larger molecules by means of cross-linking reaction of organosilicone and inorganic silicate. The lithium silicate water glass and silane have many advantages, such as good heat resistance and excellent water resistance. Adhesion and microhardness properties are excellent according to the standards.

In the salt spray test (ASTM B117-2003) (5% NaCl, pH 7 at 25 °C), the coating can endure for 250 h when the coating is 20 μm . The anticorrosion resistance increased with thickness and with the zinc flakes, which made an excellent filling material. Impedance studies found three kinds of electrochemical processes existing during the corrosion process. The zinc filler is attacked first, followed by the integrity of the film as related to the electric resistance and the capacitance of the coating. The last stage of attack is the metal itself, which should be controlled by the diffusion of the aggressive medium to the aluminum alloy–metal coating interface [33].

Cathodic Inhibitors Effective cathodic inhibitors of aluminum in neutral and alkaline solutions such as trivalent cerium acetate and an organic inhibitor such as tolyltriazole have shown promising performance on AA2024-T3 in 3.5% NaCl solution. To control water

solubility of small particles of the chosen inhibitor, the inhibitor was encapsulated with a thin skin of an organic polymer by plasma polymerization. For instance, a plasma-polymerized skin made of a chosen organic compound, such as C_6F_{14} , was deposited on water-soluble salts and did not leach out in flowing water for at least 25 hours. A colorant can be integrated if selected from dyes that are water soluble but become insoluble upon curing [32].

14.4. ANODIZATION

Anodizing is an electrochemical method of converting aluminum into aluminum oxide on the surface of an aluminum piece. Anodized aluminum surfaces resist abrasion and anodizing improves the corrosion resistance of the alloy to weathering and other corrosive conditions. Anodizing is used in every area where aluminum items are produced. Actually, more aluminum is anodized than any other metal, such as titanium and magnesium. As an example, a film 5–7.6 μm thick is normally specified for bright automotive trim and 17–30 μm for architectural product finishes [34].

Anodizing is an electrolytic oxidation process in which the surface of the alloy becomes the anode and is converted into aluminum oxide—an amorphous, thick ($\sim 3\text{--}30\ \mu\text{m}$) layer, bound as tenaciously to the alloy as the natural oxide film (few nanometers thick). Anodic coatings, particularly those applied in a sulfuric acid electrolyte and suitably sealed, are highly effective in preventing discoloration or surface staining of the aluminum-based alloys mentioned previously. In addition, aluminum alloys that are used architecturally are more readily cleaned of atmospheric contaminants if they have been anodically coated. However, anodizing does not provide sufficient protection alone if the alloys themselves are unsuitable for the environment to which they are exposed. Anodic coatings are excellent paint bases [2].

Chromic acid anodization involves the electrochemical growth of an oxide layer where a thin, nonporous oxide layer is formed with a thicker porous layer on top of it. The thickness of the anodized layer is dependent on the applied voltage during film growth, but is usually 0.05–0.1 mil (1 mil = 25 μm) thick. Chromates are introduced in the final stage of anodization by sealing the porous layer with chromic acid (H_2CrO_4). Despite the superior corrosion protection offered by anodization, conversion coatings are preferentially used due to economic benefits [4].

The majority of anodizing processes are “soft”. The current soft type of anodizing is done in chromic or sulfuric acid baths and is used in almost 90% of the production with oxide layers of 5–18 μm produced. Chromic acid anodizing produces a viable base for paint, but environmentally acceptable anodizing solutions are based on sulfuric and phosphoric acids. Hard coating is an excellent resistor and is used when wear resistance is requested and sometimes for corrosion resistance in many aircraft parts and food equipment. The hard type of anodizing (sulfuric acid bath alone or with some additives) produces a thickness on the order of 51 μm [17]. In hard coating, the part’s surface is oxidized with oxygen as anode such that if the coat growth is on the order of 50 μm , 25 μm is below the original surface. It is important that penetration be on the same order as that of the exterior growth (Figure 14.1). Magoxid coat is a ceramic-like surface protection coating [34].

Anodic aluminum films are commonly composed of two layers [35]. The film possesses a special morphology corresponding to a hexagonal cell model structure. The porous-type anodic oxide film is shown in Figure 14.2 and can be obtained by anodizing in acid solution.

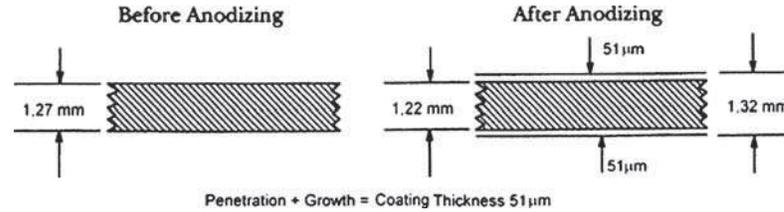


Figure 14.1 Schematic presentation of the effect of hard anodizing on thickness growth and penetration considered as a specific example [17].

The outer layer is characterized as a close packed array of columnar hexagonal cells that are perpendicular to the metal surface and each cell has a central pore that is normal to the substrate surface. At the base of the metal–metal oxide interface, there is the thin hemispherical barrier layer [35].

Morphology of the Film The morphology of the anodized oxide films can be observed by transmission electron spectroscopy and scanning electron microscopy. In TEM oxide films are removed from the metal substrate and thin slices of the vertical sections of oxide films are obtained by the ultrathin sectioning technique. Figure 14.3 shows the vertical section of a porous-type oxide film formed on aluminum in acidic medium [36].

The properties of the oxide layer obtained on aluminum in mixed electrolytes of oxalic acid–sulfuric acid are optimized using experimental design. For this purpose, a four-variable Doehlert design (bath temperature, anodic current density, sulfuric acid, and oxalic acid concentrations) was achieved. In order to maximize the growth rate and the microhardness of the anodic oxide layer and to minimize the effect of this speed on chemical and abrasion resistances of the anodized surface, a multicriteria optimization using a desirability function was conducted. Dissolution rate of the oxide in phosphochromic acid solution (ASTM B680-80) was used to express its chemical resistance. Under the determined optimal anodizing conditions ($C_{\text{ox}} = 12.6 \text{ g}\cdot\text{L}^{-1}$, $10 \text{ }^\circ\text{C}$, $2.6 \text{ A}\cdot\text{dm}^{-2}$, $C_{\text{sul}} = 183.6 \text{ g}\cdot\text{L}^{-1}$), the estimated response values were $0.73 \text{ }\mu\text{m}\cdot\text{min}^{-1}$, $4.38 \text{ g}\cdot\text{m}^{-2}\cdot\text{min}^{-1}$, 481 HV, and $53.3 \text{ g}\cdot\text{m}^{-2}$ for growth rate, dissolution rate, microhardness, and weight loss after abrasion, respectively. The higher abrasion and chemical resistances of the optimum anodic layer can be correlated with its morphology revealed by SEM observations (Figure 14.4). The size of the pores (black spots on the images) is measured using a line

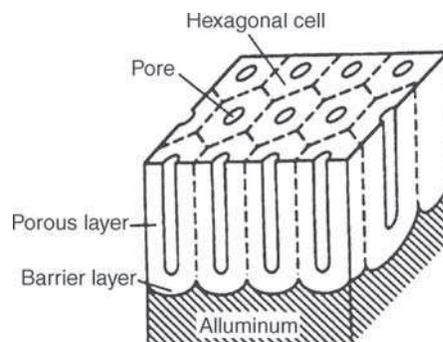


Figure 14.2 Structure of porous-type anodic oxide film formed on aluminum in acid solutions [35].

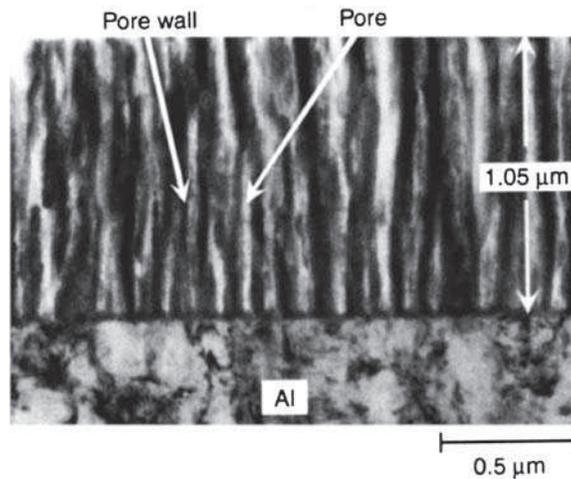


Figure 14.3 A vertical section of the anodized aluminum surface in 0.16 M oxalic acid by TEM showing the pore and its wall after 1 h of immersion at the open circuit potential in the same anodizing solution [35, 36].

profile. Their values range between 7 and 10 nm for the optimized layer. The less porous structure of the optimal anodic aluminum layer is confirmed by higher values of the coating ratios ($R = 1.71$) as compared to that for the nonoptimized samples (1.26 and 1.50) [37].

Coloring Colorings of anodic oxides can be achieved through three options (Figure 14.5): integral coloring, dyeing, and electrolytic coloring. Organic acids, such as oxalic, maleic, or sulfamic acids, can be used. The created anodic color (brown, gray, or black generally) is highly resistant to alteration. Many organic dyestuffs such as Alizaline Blue or Red-S give flashy colors such as gold, blue, or green. Inorganic dyeing through the process of precipitation of low-solubility salts such as PbS in the pores is much more resistant to heat and light but the color range is more limited than that of the organic ones. Electrolytic coloring consists of metal deposition at the bottom of the pore (Ni, Co, Sn, and Cu mainly to color from bronze to maroon to black). Low energy consumption, application for all alloys, and the light-fastness of the finishes are the reasons for using electrolytic coloring instead of integral coloring [35].

Electrolytic Coloring One of the currently used coloring methods of anodized aluminum is electrolytic coloring. During this process, aluminum is first anodized in sulfuric acid

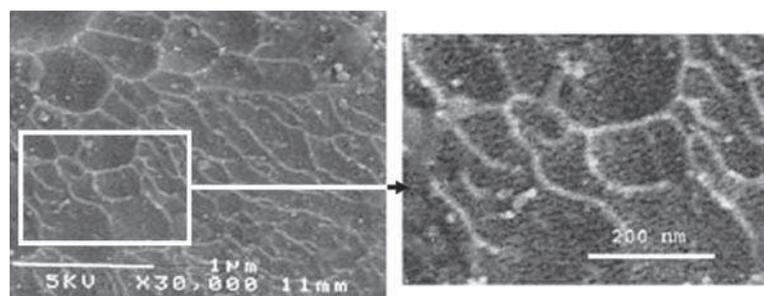


Figure 14.4 SEM top view images of anodic layers elaborated under optimal conditions [37].

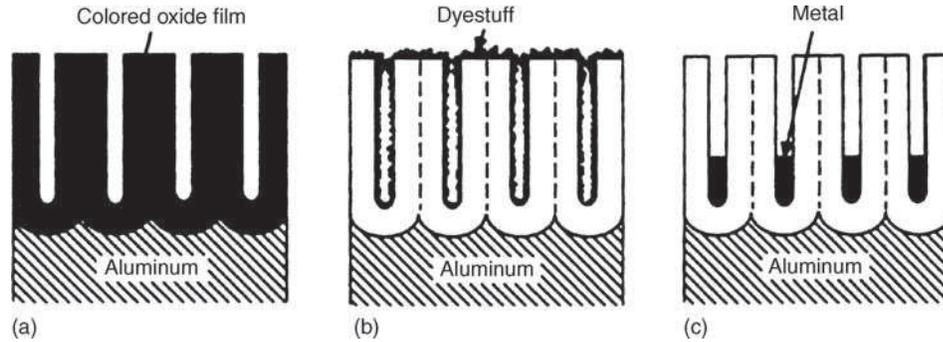


Figure 14.5 Coloring of porous-type anodic oxide films on aluminum by (a) integral coloring, (b) dyeing, and (c) electrolytic coloring [35].

solution, followed by an alternating current electrolytic deposition of a metal (tin, nickel, cobalt, etc.) at the base of the pores of the anodic coating. A very popular commercial bath is the $\text{SnSO}_4/\text{H}_2\text{SO}_4$ one. The ac electrolytic coloring process at $15 V_{\text{rms}}$ in acidic tin sulfate solutions for specimens of AA5083 and AA6111 unheated and heat treated was investigated and compared to pure aluminum. Specimens of AA5083 alloy and AA6111 unheated and heat-treated alloys were anodized in sulfuric acid baths, were electrolytically colored at $15 V_{\text{rms}}$ in acidic tin sulfate solutions, and were compared with those of pure aluminum [38].

Under standard electrolytic coloring conditions, the current efficiency for tin deposition was low for all examined materials. This bath provides good throwing power, has fewer tendencies to form complex compounds, is not sensitive to pH variations or bath contamination, and is relatively easy to operate. However, specimens are susceptible to atmospheric oxidation [38].

The current efficiency for tin deposition during electrolytic coloring at standard conditions is much higher for pure aluminum than for alloys. The anodizing voltage seems to influence the amount of tin deposited and the current passed and the effect is less for alloys than for pure aluminum, indicating that, for pure aluminum, the anodizing voltage affects to a greater extent the porosity of the film [38].

The alloy type affects the rate of tin deposition but certain qualitative characteristics and the stages of the electrolytic coloring process are similar for the alloys and pure aluminum. The temper of AA6111 did not affect the electrolytic coloring process, although it influenced the anodizing process. For AA5083, the increase of conductance of the oxide film resulted in an increase of hydrogen evolution with no improvement in tin deposition efficiency as compared with that of the pure aluminum [38].

Sealing The anodic oxidation of aluminum is followed immediately by sealing. The anodized coating can be sealed in hot water and a complete sealing corresponds to 15% weight gain. However, for better adhesion of primers, only a partial seal is recommended, on the order of 5% weight gain due to the adsorbed water. After anodizing, the specimen should be primed as soon as possible but before the freshly formed aluminum oxide adsorbs water and partially seals [39]. Manganese can be employed to alter the response in chemical finishing and anodizing [34].

Sealing of anodic alumina enhances the corrosion resistance of prepared coatings and increases the UV-light resistance of dyes in anodic coatings. Sealing is usually performed by dipping in boiling water. The anhydrous aluminum oxide is transferred to a hydrous one

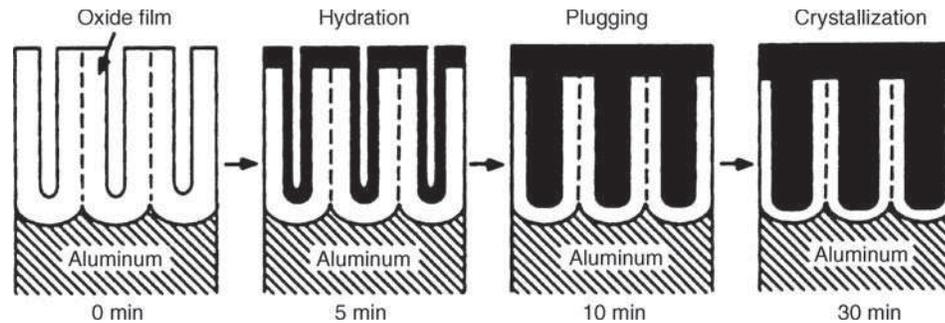


Figure 14.6 Process of pore sealing with hydroxide during dipping in boiling pure water [35].

gaining 1.5–2 molecules of H_2O for every molecule of Al_2O_3 . The volume expansion by the formation of pseudoboehmite causes the pores to be sealed. Sealing for 10 minutes (Figure 14.6) is sufficient to close the pores completely and form a high crystallized form at the outermost part of the oxide film. Pressurized steam allows quick sealing, however, cold sealing in the presence of Ni^{2+} and F^- ions at ambient temperatures is currently used to save energy. Effectively, aluminum–nickel–fluoro complexes are deposited in the pores, blocking them [35].

Cerium Nitrate as Sealer Sealing is conducted in a solution composed of 3 g/L of $\text{Ce}(\text{NO}_3)_3$, 0.3 g/L H_2O_2 , and 0.5 g/L H_3BO_3 having pH = 5, for 2 hours at 30 °C and then the specimen is rinsed with distilled water and dried with air. The thickness of the anodized coating increased approximately 3–5 μm after sealing as examined by an eddy-current thickness indicator; the color of the coating is yellow.

In NaCl solution, the Ce sealing of anodized aluminum alloy 2024 remained passive at the potential range at the open circuit potential in spite of a shift in the active direction of about 530 mV. The sealed anodized film on LY12 alloy was composed of outer and inner layers. By immersing the sample in 3.5 wt % NaCl solution for 6 days, the outer layer of the cerium conversion coat begins to lose its anticorrosive property. The inner sealed cerium layer of the anodized film is not corroded until 60 days of immersion. Thus the inner cerium sealed anodized layer plays a leading role in the corrosion protection of LY12 alloy [40].

Sol-Gel as Sealer Traditional sealing processes, such as hot water sealing, steam sealing, and cold nickel sealing, are well established while other sealing options are being investigated. Among the most promising new sealing methods are those focused on antismutting agents and electrochemical sealing based on the following requirements: corrosion resistance, abrasion resistance, and hardness without posing environmental problems. A promising approach for sealing anodic coatings is to form a protective layer with a sol-gel method. The glass-type layer is especially good for corrosion resistance of anodically oxidized aluminum [41].

The principle of the sol-gel process is to first prepare a sol (i.e., liquid colloidal dispersion) by hydrolysis of organometallic compounds and then have the coating gel (solidify) to form the hard coating. The sintering process finishes the production of the hard seal coat. The characteristics of the developed coating are a function of both the

starting material and the conditions of the hydrolysis reaction. In this process, the coating is created using a colloidal method and a dip technique. The colloidal method of a sol-gel coating preparation means the hydrolysis of an organometallic compound (aluminum butoxide), which is obtained with an excess of stoichiometric water. A 20 minute anodic oxidation to reach a thickness of 10 μm is used for the following sol-gel type of sealing: the sealing is conducted at an operating temperature of 270 °C for 15 min with controlled heating and cooling of 10 °C/min. The samples are dipped into Al_2O_3 sol before the sealing process [41].

Corrosion resistance against atmospheric agents is comparable with hydrothermal sealing and even higher. The thickness of the sol-gel alumina coating, in combination with the other material component thicknesses, can influence the crack formation and the corrosion resistance of the material. A mixture of transition aluminas was identified for sol-gel type of coating, especially the transition $\delta\text{-Al}_2\text{O}_3$. The disadvantage of this process is its high price and decreased abrasion resistance and hardness. In spite of this, for special purposes, this type of sealing is acceptable [41].

Anodization and Plasma Coatings Plasma coatings have two invaluable properties for corrosion protection of metals—a highly cross-linked matrix and excellent adhesion to the metal substrate. Keronite's plasma electrolytic oxidation process transforms the surface of aluminum alloys into a complex ceramic matrix by passing a pulsed, bipolar electrical current in a specific wave formation through a bath of low-concentration aqueous solution. A plasma discharge is formed on the surface of the substrate, transforming it into a hard, dense, ceramic oxide (mainly alumina), without subjecting the substrate itself to damaging thermal exposure. The process forms an ultrahard ceramic layer—from 800 to 2000 HV (Vickers Hardness Test) depending on the alloy and the coating's thickness [42].

The layer is attached to the substrate by a strong molecular bond, ensuring adhesion. The fused ceramic layers closest to the surface provide protection against corrosion and wear. The outer surfaces of the layer are porous and lend themselves well to the application of scratch-resistant, decorative top coats such as paints and lacquers, and can form composite coatings with PTFE (polytetrafluoroethylene, or Teflon), adhesives, or metals. The layer is typically between 10 and 150 μm thick and grows at a rate of around 1 μm minute—partly above the surface and partly below [42].

As an immersion process, it can be used to treat the inner surfaces of complex shapes. The ceramic layer can be adjusted for optimal performance in the chosen application. The process produces a completely uniform layer, even in the case of complex shapes or internal surfaces. The process is compatible with all known aluminum alloys, even those with a high copper content that cannot be treated using hard anodizing [4, 42]. The ceramic can withstand over 2000 hours in salt fog when sealed—a key test for corrosion resistance.

Keronite can be used in coating a range of exterior automotive parts, such as roof rails, door handles, door frames, and body panels; interior parts such as seat frames, instrument panel beams and supports, airbag retainers, and mirror brackets; and engine components such as piston crown and ring grooves and clutch rings. When used in engine components, the coating is designed to help improve powertrain performance and efficiency through reduced piston groove wear, better tolerance control, lower friction, and higher combustion chamber temperatures. The coating process reduces the temperature of aluminum pistons by approximately 85 °F [42].

Low-temperature cationic plasma deposition is currently used to create ultrathin hydrophobic barrier coatings on metals. Low-temperature cationic plasma deposition of inorganic or silicon monomers has displayed the best performance for corrosion protection with respect to steel substrates immersed in simulated seawater [4].

Modified Anodizing as Compared to Anodizing and Hard Anodizing Films

Aluminum oxide coatings were deposited on Al–Si alloy substrates to produce hard and corrosion protective films using three different techniques: hard anodizing, anodizing, and modified anodizing. Rectangular coupons (25 mm × 25 mm × 5 mm) of a cast Al–Si alloy were used as the substrate for anodic coating deposition. The composition of this alloy in wt was 15.6% Si, 1.3% Fe, 0.12% other, and Al the balance. The substrates were ground and polished to a surface roughness of $R_a = 0.1 \mu\text{m}$ before washing in water and then drying in air.

During the anodizing process, the substrates (exposed area 6.25 cm^2) were anodized at a constant current density of 0.016 A/cm^2 in 17% H_2SO_4 at $25 \pm 1^\circ\text{C}$ for 15 min and the voltage reached 20 V. The conditions remained the same except the temperature was controlled at $0\text{--}4^\circ\text{C}$ for the hard anodizing (HA) process with a final voltage of 25 V [43]. For the modified anodizing (MA), the substrates (exposed area 17.5 cm^2) were anodized at a constant current density of 0.012 A/cm^2 in 12% NaHCO_3 at $25 \pm 1^\circ\text{C}$ until the voltage increased to 340 V and then switched to a constant voltage (340 V) control mode. The whole process time was 30 min [43].

Oxide coatings were successfully deposited on a cast Al–Si alloy by hard anodizing, modified anodizing, and anodizing techniques. Small cracks and pores near second-phase particles caused by the internal stress are the result of the different film growth rates for the different alloy phases. The different coating features resulted in some differences between the coating hardness and surface hardness. Potentiodynamic polarization tests were conducted to assess the corrosion resistance of the coatings. A microhardness tester was used to measure the coatings' hardness. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis were used to investigate the coating microstructure and chemical composition both before and after corrosion [43].

It was found that the modified anodizing, an environmentally friendly coating method, could produce a hard oxide coating with good corrosion protection for the Al–Si alloy. All coatings provided effective protection for corrosion resistance, while the modified anodizing would be beneficial with respect to development of an environmental friendly process [43].

Pitting Corrosion of Anodized Coatings Moutarlier et al. [44] investigated the pitting initiated in different anodic films on AA2024 alloy. A polarization test in NaCl solution was used to initiate pitting corrosion in anodic layers produced in chromic acid, sulfuric acid, and sulfuric acid containing molybdate species. The mixed electrolyte containing sulfuric acid and molybdate species was studied as a substitute for the chromic acid electrolyte. Corrosion resistance of anodic films formed in sulfuric–molybdate was better when compared to films formed in sulfuric acid, but chromic anodic layers gave the best corrosion performance [44].

The Pitting Potential After anodizing and subsequent sealing, the pitting resistance of aluminum alloys is improved remarkably. The pitting behavior of anodized AA2024 in neutral NaCl solution was investigated using electrochemical methods and SEM [45]. Three stages were observed during potentiostatic polarization of anodized AA2024 in NaCl solution. In the first stage, current decreases with time, following the relation $\log i = -n \log t$, where parameter n indicates the passivation tendency of the alloy. The stage corresponds to the induction time for pitting and increased chloride concentration will shorten the stage. After the induction time, pitting occurs and the current begins to increase

continuously. In the third stage, the current reaches a stable value, and the growth of pits is controlled by an ohmic drop [45]. The relationship between pitting potential of anodic film on AA2024 and chloride concentration in the solution follows the expression $E_p = A - B \log[a_{Cl^-}]$.

14.5. ORGANIC FINISHING

Thermoplastic coatings and *converted coatings*, applied during or after processing, include principally three types of paints: epoxy, polyurethane, and moisture coatings.

14.5.1. Thermoplastic Coatings or Liquors

The resin is in its final form and the coating dries solely by solvent evaporation. The film-forming process is merely the evaporation of the solvent. Examples are vinyls, acrylics, and chlorinated rubbers. If coatings are applied under high-humidity conditions, blushing of the coat occurs and the coat turns white. The blushed surface is porous with poorer resistance characteristics.

14.5.2. Converted Coating During or After Application

All such coatings undergo a chemical or physical change in the process of film formation before, during, and/or after application and they are different from the thermoplastic coatings in that they dry or react in a whole series of steps. There are some conversion coatings that require baking or heating, which are not practical when coatings are to be applied to large existing structures or equipment. The main types of converted coatings are the following [46].

Oil Paints These are very familiar paints that have a drying oil and a resinous varnish or resin as the binder. These usually dry more slowly than the thermoplastic ones, and the various drying stages are considerably more complex. These stages are solvent evaporation, oxidation, thickening, or polymerization. Gelation occurs when the polymers reach a size and concentration that form a continuous network. The paint appears as dry but effectively it contains a considerable quantity of liquid material and may be somewhat soft. The remaining film continues to cure or dry and becomes hard; this can be accelerated by a sunlight or heat mixture. When the films reach their ultimate hardness, they become more porous and loose resistance to moisture and chemicals [46].

Epoxy Coatings Epoxy coatings are created by a conversion process or cross-linking at ambient temperatures. The epoxy resin is mixed with an amine just prior to application. Its drying process consists of solvent evaporation followed by a chemical reaction of the amine and the epoxy resin resulting in cross-linkage. The amine becomes a part of the new polymer since it does not act as a true catalyst. Since this process is temperature-sensitive, and can occur in the absence of air where the cross-linkage takes place, the coating is called *thermoset* and it becomes neither soluble in its original solvents nor as sensitive to softening by heat as expected. There is another conversion reaction that occurs when an epoxy resin reacts with a second resin (e.g., a polyamide resin). In this case, the two resins (the epoxy and

the polyamide) react and cross-link to form a solid resin film. The film is more resilient and elastic than the films formed using the amine epoxy reaction [46].

Polyurethane Coatings Polyurethanes (PUs) form a film through the chemical reaction of acrylic or polyester-modified urethane-based components with isocyanate reactive converter components. It is a conversion reaction and cross-links into a somewhat chemically resistant film. The main function of PU coatings is to improve the finished appearance. This process is not the same as epoxy; it is more humidity and temperature sensitive during the curing process. Excess humidity at this point can lead to loss of gloss, and the formation of a cheesy, nonuniform film, or wrinkling [46].

Moisture Coatings These are characterized by the fact that water from the atmosphere converts the film from a liquid to a solid. This is one of the processes by which moisture-cured PU coatings form. In this case, moisture from the air and/or substrate reacts with a PU resin during the initial evaporation stage, cross-linking it and increasing the molecular size until it becomes solid. The solvent-borne inorganic zinc (IOZ) coatings also require moisture from the air, whereas the waterborne IOZ coatings require carbon dioxide to change the silicate molecule (i.e., sodium, potassium, or ethyl silicate) into a continuous coating by reaction with the zinc pigment [46].

Aluminum is an excellent substrate for organic coatings if it is well cleaned and appropriately prepared. It has long been accepted that the durability of coatings on aluminum is determined first by the preparation of the metal base surface. A suitable preparation of the surface usually starts with degreasing, followed by eliminating existing oxides, forming a base layer, and applying a primer. Since the corrosion resistance of the aluminum base is very good, the resistance of the organic coatings is remarkable even after many years of exposure [47].

For indoor applications, the coating can be applied directly to a clean surface. However, a suitable primer coat, such as wash primer or a zinc chromate primer, usually improves the performance of the finish. For applications involving outdoor exposure, a surface treatment such as anodizing or chemical conversion coating is required prior to the application of a primer and a finish top coat, such as an epoxy urethane or polyurethane. Some new one-step, self-priming polyurethane top coats are also available, as are low volatile organic compound (VOC), high-performance primers such as epoxy polyamide [5]. Chromium-free conversion coatings are emerging to avoid the environmental problems caused by using Cr^{6+} compounds. Zinc phosphating provides a good base for organic compounds and has yielded very good results in the automobile industry with the cathodic electrodeposit coating [34].

The common antifouling paints for steels to prevent growth of algae, barnacles, and other sea organisms are not suited for aluminum. They may contain leachable heavy metals such as lead, arsenic, and copper that can plate on the aluminum surface and initiate galvanic corrosion, and so specific antifouling paints should be chosen for aluminum. For certain applications, the top coat can be replaced by adhesively bonded applied films. These flexible films provide a durable, weather-resistant finish when applied over standard, corrosion-resistant primers [5].

Clear protective coatings (lacquers) are used to provide protection while retaining glossy metallic appearance. All beverage and food containers are coated for prolonged shelf life and to prevent contamination of the food product. The absence of a hole or even a fine

pore in the coating is highly recommended. Clear coatings are used also in the protection of anodized aluminum surfaces on commercial and residential buildings and ease cleaning procedures. Material in coil form can be coated very economically. The strip is first pretreated, rinsed, and dried, and then the paint is applied and baked in one continuous process. As a rule, a primer of about 5 μm is applied followed by a top coat of about 20 μm . Notable examples of organic coatings for aluminum are nonstick coatings on cooking utensils [5, 34], for example, polytetrafluorethylene (PTFE, or Teflon), and pressure-sensitive tapes and/or strippable plastic coatings for temporary protection of aluminum sheets or extrusions used in buildings [5].

Maximum protection depends on inspection and maintenance. Painted jet airliners are stripped of their coating and completely repainted as needed, usually for appearance purposes. Automobiles are repainted as needed usually for appearance or decoration. Dents and scratches in residential siding are rarely repaired, whereas rain-carrying systems such as gutters and down spouts are more frequently replaced than repaired [5].

14.5.3. Coatings Containing Metals More Active than Aluminum

Magnesium use as a pigment presents a possible alternative for the sacrificial protection of aluminum alloys. A Mg-based primer for the protection of aluminum structures, based on this concept, has been developed and tested [48]. An excellent performance of aluminum panels sprayed with this Mg-rich primer in Prohesion testing has been observed. This new class of metal-rich primer can be formulated for the protection of aluminum alloys in analogy to the Zn-rich primer devised for the protection of steel. The Mg-rich primer was made using a stabilized Mg particulate, 30–40 μm in average size, manufactured by Non Ferrum-Metallpulver GmbH, Salzburg, Austria. This particulate consists of Mg covered with a thin layer of MgO, intended to control the reactivity of magnesium and thus prevent further oxidation under dry conditions. Dispersion was made using a silane-modified multilayer/IPN polymer matrix [48].

To provide sacrificial protection, the Mg metal particles in the primer have to be in electrical contact with the substrate and also with each other. The Mg-rich primer was formulated at 50% PVC, approximately near the critical pigment volume concentration (CPVC) of the coating. The electrochemical behavior of Mg-rich primer on AA2024 and AA7075 has been studied via electrochemical impedance spectroscopy (EIS), open circuit potential (OCP), and potentiodynamic polarization. Electrochemical technique studies were complemented by scanning electron microscopy (SEM). Most of the electrochemical tests were made in 0.1 wt% NaCl distilled water. One of the experiments was conducted in Dilute Harrison's Solution, which emulates acid rain and consists of 0.35 wt % $(\text{NH}_4)_2\text{SO}_4$ and 0.05 wt % NaCl in distilled water [49].

Results showed that the Mg-rich primer provides sacrificial protection to the Al substrate by a two-stage mechanism. In a first stage, corrosion of aluminum is prevented by cathodic polarization, whereas at a later stage the precipitation of a porous barrier layer of magnesium oxide was observed. Magnesium had a very negative potential, compared to that of the aluminum alloy, and underwent fast corrosion, with visible bubbling on the surface. The high rate of the cathodic reaction was assessed by measuring the pH, which was approximately 11, on the Mg surface [49].

Corrosion of the Al alloys in 0.1% NaCl resulted in the formation of small pits. The solution pH was approximately 5. At this pH, Al becomes passive, as indicated in the Pourbaix diagram. The presence of inclusions and precipitates, however, can induce

instability of the passive film and lead to localized corrosion, and so can the presence of aggressive ions, such as chlorides. The OCP measurements, however, have shown that the potential of the galvanic couple was lower than that of the bare alloys, and this has to be a result of cathodic protection.

The impedance of magnesium after 1 h of immersion was smaller than that of the bare aluminum substrate by approximately one order of magnitude—a conclusion that is in reasonably good agreement with the results from potentiodynamic polarization. When the Mg-rich coating was applied, the total impedance of the system increased significantly, again in good agreement with the potentiodynamic observations, showing that the sacrificial protection was manifested at a comparatively low Mg oxidation rate [49].

In order to assess the efficiency and protection mechanism at defective areas of the primer, a large scribe was induced with a knife on a coated sample, exposing an area of approximately 1 cm^2 prior to immersion in Dilute Harrison's Solution for 10 days of immersion. Inspection of the scribed area at the end of the experiment by SEM and EDAX revealed the aluminum surface was covered by a precipitate of magnesium oxides. This precipitate was porous and had several flaws; however, this did not correspond to sites of pitting corrosion of aluminum [49].

Unlike zinc, whose hydroxides precipitate at neutral pH, magnesium has a vast pH range over which it remains active. This range includes not only the regions of stability of Al_3^+ and Al_2O_3 , but also overlaps the region of alkaline corrosion of aluminum, up to pH 11. Thus Mg becomes oxidized at a high rate, which could lead to exhaustion of the coating after a relatively short exposure period. Mixing magnesium with polymer significantly decreased the corrosion rate of the metal due to the barrier effect of the polymer and this can extend the lifetime of the coating [49].

In the case of zinc-rich primers for sacrificial protection, the zinc corrosion products precipitate inside the coating, around the zinc particles that originated them, blocking the pores of the coating and therefore increasing its barrier resistance. Magnesium acts in a somewhat different way. Because at the near-neutral pH of the solution the magnesium ions are soluble, they actually diffuse out of the primer layer. Furthermore, because of the high rate of electrochemical reactions, the pH can become quite alkaline at the cathodic sites, particularly if there is a relatively small defect in the primer. When these ions reach the cathodic areas, they will then precipitate as $\text{Mg}(\text{OH})_2$ [49].

The Mg-rich coating used in this work has the capability of protecting alloys AA2024 and AA7075 against corrosion. The effect of magnesium starts with the polarization of aluminum, shifting its potential below the pitting corrosion potential. The consequence of this polarization can be either the prevention of pit nucleation at the exposed aluminum areas, or the inhibition of pit growth for the nucleated pits. During this stage, any defects on the surface will become cathodic, whereas the magnesium particles will be anodic. At the cathodic areas, reduction of hydrogen and possibly dissolved oxygen increases the pH above the threshold for the precipitation of magnesium oxide and the formation of magnesium hydroxide. This precipitation leads to the formation of a porous layer that further inhibits corrosion by a barrier mechanism. The typically high dissolution rate of magnesium is significantly decreased by its incorporation in the polymer [49].

14.5.4. Electrodeposited Coatings

An environmentally friendly system that has been proved effective by the automotive industry is electrodeposition of organic resins (e-coat). The unique advantage

of electrodeposition is that a thick (up to several millimeters) coating can easily be deposited on a conducting substrate with good control of the thickness. The deposition process can be modified to undergo either cathodic or anodic deposition, depending on the resin functionality. Cathodic deposition is predominantly used today for corrosion applications because of some inherent disadvantages of the anodic process. Several types of resin have been successfully used for e-coat binders. These binders include acrylics, alkyds, epoxies, polyurethanes, polyamides, and polyesters. Electrochemical evaluation of e-coat systems has been used to demonstrate its excellent barrier properties. Twite and Bierwagen [4] presented data showing the superior barrier protection behavior of polyurethane/blocked isocyanate e-coats on aluminum alloys with and without a chromate conversion coat pretreatment.

14.6. CORROSION TESTING OF COATED METAL

14.6.1. Electrochemical Testing of Coatings

Corrosion monitoring of epoxy-coated aluminum 2024-T3 was carried out by electrochemical impedance spectroscopy methods and electrochemical noise measurements. The epoxy was electrodeposited on the surface of panels with one of following treatments: actone cleaned, alkaline cleaned, or plasma deposition of polytrimethylsilane. The epoxy coating was modified by one of the applied voltages: 100, 150, or 200 V (current-controlled coating). Six selected combinations of the surface treatment and the applied voltage were considered. The corrosive solution was 0.35 wt % ammonium sulfate and 0.05 wt % sodium chloride [50].

EIS and ENM (electrochemical noise measurement) data were collected over a 70 day immersion period on days 1, 7, 14, 60, and 70. For each sample pair, the impedance modulus at a frequency of 1 Hz was used. For ENM, time records of ZRA current and sample voltage were collected at a rate of 0.5 Hz for 128 s to provide the standard deviation of voltage and current. It was possible to conduct repeated measurements for EN over 5 h.

Linear regression analysis was used as the statistical treatment of the collected data to detect the individual contributions relating to the analysis technique. It has been concluded that EIS data can be used to monitor the protective quality of the coating as a function of surface treatment or applied voltage, while ENM data were too noisy. It was also found that a combination of 200 V with alkaline-cleaned aluminum would produce the highest impedance values [50]. Furthermore, there is considerable interest in potentiodynamic polarization techniques to rapidly assess the durability of coated aluminum surfaces that have been painted or given various polymeric or anodic surface treatments.

The use of electrochemical noise measurements to evaluate the corrosion protection as a probe for coated systems has already been studied; however, reproducibility of the results has been examined by Bierwagen et al. [51]. Monitoring is continuous and data can be gathered over a period of days, weeks, months, or even years. The backs and sides of the specimens were coated with a Colophony rosin/beeswax mixture, which is an inert high-resistance protective coating. Although this study considered grit-blasted painted steel with three-coat systems, the results can be extrapolated to coated aluminum or magnesium alloys with certain precautions. Each panel had 50 cm² of paint left exposed to better assess the influence of agitation and temperature. The solution was mainly NaCl (3%) or seawater. The Gaussian value determines the standard deviation based on the mean of all points of the sample, while the robust method bases the standard deviation on

the median of the sample. The reproducibility of the ENMs was good and variations inherent in coating systems manifest themselves as variations in electrochemical properties in nominally identical samples. Different local variations in thickness leading to local structural variation are the most likely reason for the variability in the ENMs and corrosion results [51].

14.6.2. Conventional Testing

Evaluation of the protective ability of coatings is generally made in salt spray cabinets, such as those covered in ASTM B117 and G85 or in the 3.5% NaCl alternate immersion test (G44). Recent investigations, primarily on steel, have established the desirability of including ultraviolet (UV) light as part of the cyclic exposure, since UV light has a degrading effect on paints and other organic coatings. Various cabinet tests to provide UV light are under development, along with a corresponding Annex 5 to ASTM G85. Corrosion resistance of anodized aluminum is evaluated by conventional corrosion tests, such as CASS tests, salt spray tests, and other exposure tests. Galvanic corrosion tests are important because the corrosion rate of aluminum in the active state in contact with other less active or more noble metals can be more dangerous than that of aluminum alone [35] (see Chapter 15).

14.6.3. Corrosion Fatigue of Thermal Spraying of Aluminum as a Coating

We will examine the fatigue behavior of Al alloy 7075-T651 with ductile aluminum applied by a thermal spray process. The coating, deposited by four different commercial arc spray devices (guns), has been characterized. A thermal spray process—arc spraying—for ductile metallic materials was selected to apply 200 μm (nominal) thick aluminum coatings onto Al alloy 7075-T651 substrates. The aluminum coating was produced from four different commercial arc spray guns. Coated specimens, as well as polished and shot-peened specimens, were evaluated under fully reversed uniaxial loading ($R = -1$) at a constant amplitude of ± 225 MPa in accordance with ASTM 466-82. A frequency of 20 Hz was selected to avoid potential frequency-induced heating with a sinusoidal loading wave form applied via a computer-controlled MTS servohydraulic load frame. The different coatings were evaluated also in terms of their microstructure [52].

While the shot peening pretreatment was observed to increase the fatigue resistance of polished specimens, application of the coatings subsequently reduced fatigue life to below that of the original polished coupons. Changes in the residual stress state of the shot-peened surface were identified as the most likely source of these reductions, even though no microstructural changes in the substrate were perceptible. Variations in fatigue life were also observed between the coatings resulting from the four spray guns. The roles of surface roughness and coating delamination in producing these decreases were investigated and stress concentrations resulting from coating delamination were identified as the primary detrimental factor affecting fatigue resistance. The effect of thermal spray coatings on the fatigue behavior of various substrate materials has attracted increased attention in recent years. With the absence of microgaps at the coating–substrate interface, even after the fatigue tests and with the lowest coating roughness, the equipment provided the best fatigue behavior for the Al-coated 7075-T651 Al alloy in this study [52].

14.6.4. Environmentally Assisted Cracking of Metallic Sprayed Coatings

Aluminum alloys play an important role in the manufacturing of air and ground vehicles. However, corrosion damage is often found on structural components subjected to fatigue loading. The alloying provides a large benefit, in terms of the high specific tensile strength (ultimate strength/density ratio), to the aluminum alloy but causes the aluminum alloy to be more sensitive to localized corrosion due to complex microscopic heterogeneities such as secondary phases. Arsenault and Ghali [54] studied thermal spray coating using arc spraying to evaluate the protection against environmentally assisted cracking (EAC) and localized corrosion on aircraft structural Al alloy 7075-T651. EAC and pitting corrosion at the coating–substrate interface are a challenge for thermal spray protective coatings on aluminum alloys under cyclic load and immersion. In this study, EAC was initiated on polished and shot-peened Al alloy 7075-T651 through a four-point bending test under cycling fluctuation load in 3.5 wt % NaCl solution kept at 25 °C in open air (ASTM G39-99) [53].

The applied load was kept under the yield strength (YS) (503 MPa) of 7075-T6 alloy and oscillated between 24% and 40% YS in tension ($R = 0.6$) at a frequency of 0.1 Hz. The selected stress level was sufficiently low to avoid premature coating damage and to allow a single failure mode. The failure mode validates the EAC mechanism such as SCC or corrosion fatigue. This approach has the benefit to initiate intergranular cracking in the aluminum alloy with a fast response, while maintaining the substrate material under elastic deformation. The samples used for EAC evaluation were rectangular in shape, having the dimension of 60.0 mm \times 20.0 mm \times 4.5 mm and machined in the short transverse direction to evaluate the coating protection performance in the most susceptible EAC direction of the 7075 aluminum alloy [54].

This study underlines the impact of coating material on the interface properties, in terms of interface quality (microgap) and adhesive strength. The Al coating shows, for five different surface properties, either lower microgap or higher bond strength than Al–5Mg. Moreover, the surface preparation on Al alloy substrate requires one to remove material mechanically, such as by grit blasting or by deoxidation, in order (1) to provide a low defect interface in order to avoid coating spalling under cyclic load test and (2) to avoid localized corrosion underneath the coating especially when under immersion applications. Both thermal spray anodic Al and Al–5Mg coatings did confer EAC protection to the Al alloy 7075-T651. However, the Al coating conferred the best protection against localized corrosion for the Al alloy 7075-T651 substrate [54].

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