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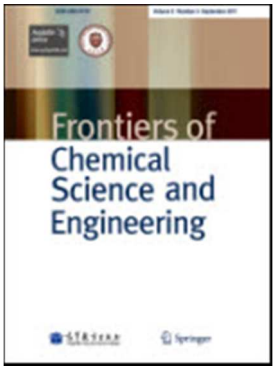

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REVIEW ARTICLE

Towards Cr(VI)-free Anodization of Aluminum Alloys for Aerospace Adhesive Bonding Applications: A Review

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Abstract

For more than six decades, chromic acid anodizing (CAA) has been the central process in the surface pre-treatment of aluminum for adhesively bonded aircraft structures. Unfortunately, this electrolyte contains hexavalent chromium (Cr(VI)), a compound known for its toxicity and carcinogenic properties. To comply with the new strict international regulations, the Cr(VI)-era will soon have to come to an end. Anodizing aluminum in acid electrolytes produces a self-ordered porous oxide layer. Although different acids can be used to create this type of structure, the excellent adhesion and corrosion resistance that is currently achieved by the complete Cr(VI)-based process is not easily matched. This paper provides a critical overview and appraisal of proposed alternatives to CAA, including combinations of multiple anodizing steps, pre- and post anodizing treatments. The work is presented in terms of the modifications to the oxide properties, such as morphological features (e.g. pore size, barrier layer thickness) and surface chemistry, in order to evaluate the link between fundamental principles of adhesion and bond performance.

Keywords Aluminum, Cr(VI)-free, Surface pre-treatments, Anodizing, Adhesive bonding, Adhesion, Durability.

1 Introduction

For many years, hexavalent chromium has been used for the corrosion protection of metals in many industries; aerospace, automotive, maritime and architectural structures are just a few examples for the wide spectrum of applications in which Cr(VI)-based coatings can guarantee the life-long integrity of metallic parts. Unfortunately, Cr(VI) is regarded to be extremely toxic and carcinogenic [1, 2]. This has already being noticed in the first decades of the 20th century [3, 4]. Numerous studies have shown that employees working with chromate-containing compounds risk exposure through skin contact and by inhalation of vapors or dust particles [5, 6]. In the aerospace industry this mostly occurs in the production stage, when the parts are pretreated and painted, during their maintenance or at the end-of life, when these coatings and paints are removed.

In 2006, the Occupational Safety and Health Administration (OSHA) in the U.S. [7], the European Registration, Evaluation, Authorization and Restriction of Chemicals (REACH, EC n°1907/2006) and Restriction of Hazardous Substancespolicies (RoHS) introduced new regulations that strictly limit the use of hexavalent chromium and announced its near future ban. As a consequence, chromates are no longer used in most commercial processes and products. However, the corrosion sensitivity of high-strength aluminum alloys and the required level of performance and safety make its overall replacement in the aerospace industry a very challenging task. In addition, the time it takes to test and qualify new systems for aviation is much longer compared to that in other industries. Therefore, Cr(VI)-based substances are currently still utilized in most aerospace metal pre-treatment, coating and bonding processes.

This paper reviews the state-of-the-art alternatives to *chromic acid anodizing* (CAA), which is the key pre-treatment step to produce anodic oxide films suitable for adhesive bonding. Herein, only the manufacturing of parts aimed for *structural* components are discussed. Although other components of the aircraft are produced in a similar manner, structural components are considered the most critical since they are designed as part of the principal load-carrying structure of the aircraft and they are typically not accessible for inspection and maintenance during its lifetime [8]. As such, these components are subject to the highest engineering standards.

The following section provides background on the main issues and challenges in the pre-treatments of aluminum for structural bonding. Next, section three presents the development of the benchmark CAA process that is currently used in Europe and its major oxide characteristics. The fourth section covers the range of Cr(VI)-free alternatives. In order to identify the key factors that determine the adhesion and durability of these structures, section five critically reviews the main processing parameters, as concluded by reviewing the literature available to date, including recent detailed investigations by the authors. The final section discusses the relation between the main oxide properties and bond performance. This review paper ends with a short summary and conclusion in section six.

2. Structural adhesive bonding in aircraft structures

Adhesive bonding is one of the oldest techniques to join different components, often of dissimilar nature [9]. Bonding is established when the adhesives undergoes physical or chemical hardening reaction (curing) to join the two panels together through surface adherence (adhesion) and internal strength (cohesion) [10]. Adhesive bonding was already used in the first aircrafts, which were made from wood

and continued in the 1940s, when manufacturers started using aluminum [11]. Since then adhesive bonding has become a standard technique to produce the main body (fuselage), wings and other parts of modern aircrafts [12]. Fig. 1 shows the main steps in the production of adhesively bonded components at *Fokker Aerostructures* in the Netherlands.

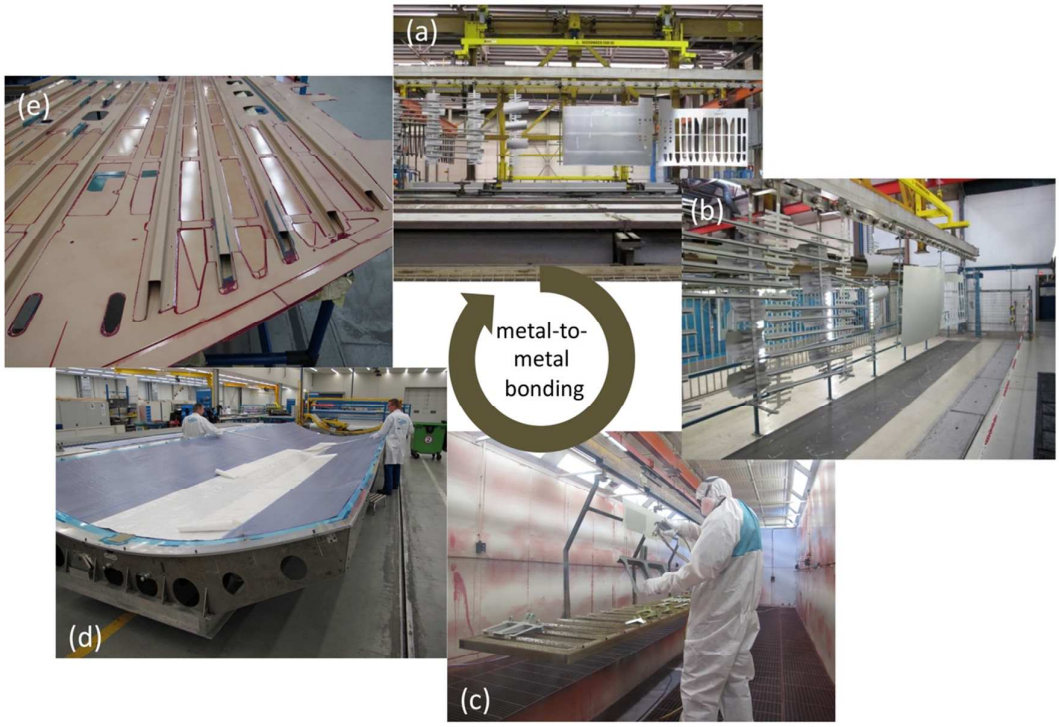

Figure 1 The production of metal-to-metal bonding at Fokker Aerostructures: (a) surface pre-treatment (panels hanging above the anodizing bath), (b) parts drying on the rack after pre-treatment, (c) primer application, (d) adhesive application, (e) a bonded part.

2.1 Durability of the adhesive bond

Ideally, the bonded structure will be able to withstand and carry the high loads that are executed on the structure during use and efficiently transfer and distribute the mechanical stresses over a large surface area. A crucial parameter in maintaining the long-term integrity of the assembly is durability of adhesion under various environmental conditions, such as temperature extremes, varying atmospheric pressures, moisture content and types of aggressive species (e.g. anti-freeze and chlorine ions). These, in combination with the varying mechanical stresses, may lead to early failure [13]. Fig. 2 illustrates the different possible failure mechanisms that can occur within an adhesive joint. They are generally characterized as predominantly cohesive- or adhesive in nature. Cohesive failures take place within the same phase, whereas adhesive failures occur at their interfaces.

Industrial standards generally demand higher adhesion than cohesion strengths. This is desired from an engineering point of view, since cohesive failure related to bulk material properties could be readily considered by design. In the case of metal-to-metal adhesive bonding, this refers to a cohesive failure within the polymeric adhesive (Fig. 2 (A)). Other failure mechanisms (Fig. 2 (B)-(F)) are usually the result of poor bond preparation (processing) and effects of environmental conditions.

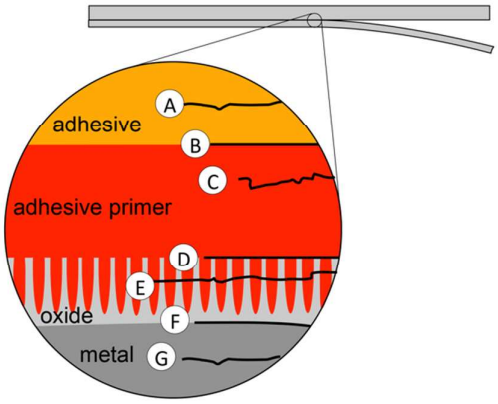

Figure 2 Schematic illustration of the possible failure modes in structural adhesive joint: (A) cohesive fracture of the adhesive film, (B) interfacial disbonding between adhesive and primer, (C) cohesive fracture of primer layer, (D) interfacial disbonding between primer and anodic coating, (E) fracture within anodic oxide coating and (F) corrosion of aluminum substrate at metal/oxide interface and (G) failure of the metal substrate.

One of the key issues concerning bond durability is the permeability of water molecules. Moisture from the environment can enter the bonded system by bulk diffusion through the adhesive, by interfacial diffusion along the interface between the adhesive and the oxide, and by capillary action through cracks or defects. Zanni-Deffarges and Shanahan [14] compared diffusion rates in bulk and bonded epoxy adhesive to show that capillary effects near the oxide-polymer interface can significantly enhance the diffusion rate of water in bonded joints. Once reaching the bond line, moisture can hydrate the oxide. This leads to the formation of oxyhydroxides, a weaker form of oxide with a larger volume [15]. Ultimately, this can lead to cohesive fracture within the hydrated oxide (Fig. 2 (E)). Alternatively, the presence of water at the interface can displace the previously formed bonds between the oxide and the resin, leading to delamination by de-adhesion (Fig. 2 (D)). Another dangerous failure mode is *bondline corrosion* (Fig. 2 (F)). It occurs when a relatively pure aluminum clad layer is present, which function as a sacrificial anode to the base materials. Also this type of failure is facilitated by the diffusion of water and other corrosion-initiating species (e.g. chlorine ions). Once bondline corrosion is initiated, it is characterized by disbonding at the interface followed by localized corrosion.

Pure aluminum metal has an inherent corrosion resistance due to the presence of a relatively uniform and thin oxide layer that protects the underlying metal [16]. This is caused by the high affinity of aluminum towards oxygen. Whenever the fresh metal surface is exposed to the atmosphere as, for example, in case of mechanical damage a new oxide layer will be formed. In dry conditions, this oxide film is typically a dense barrier layer of amorphous alumina (Al_2O_3) that is only 2 to 3 nm thick. In humid environments, this oxide will be covered by a more permeable hydrated aluminum hydroxide ($Al_2O_3 \cdot xH_2O$) at the outer surface. In that case the thickness of this layer can reach up to 10 nm [16]. These thin oxide layers are stable over a fairly broad range of pH ($4 < pH < 8.5$), providing aluminum with sufficient protection for various commercial purposes. At both lower and higher pH values this layer is not stable and it will dissolve [17].

Nevertheless, aluminum in aerospace applications is mainly used in its alloy form. The most commonly employed types of aluminum in the aerospace industry belong to the 2xxx and 7xxx alloy series. Within these families, AA2024-T3 and AA7075-T6 are the most used ones to date. The main alloying elements include copper (Cu), magnesium (Mg) and manganese (Mn) in AA2024 and zinc (Zn), magnesium (Mg),

copper (Cu) and silicon (Si) in AA7075. [18]. These heat-treatable alloys develop their strength by precipitation hardening. As a consequence, the microstructure of these alloys is very complex, presenting several second phase and intermetallic particles. The addition of alloying elements, though essential for mechanical properties, can have detrimental consequences on to the substrate's corrosion resistance. The electro potential differences between local areas of compositional differences can lead to galvanic coupling and selective dissolution of the more active element. The most common type of corrosion in aluminum alloys is pitting corrosion due to second phase particles in the matrix acting as cathodes or grain boundary precipitation causing precipitate-free zones. These phenomena are especially pronounced in AA2024-T3, which contains relatively high amounts of copper, a nobler element to aluminum. These localized attacks can proceed to considerable depths within the substrate and may lead to grain fallout when proceeding along grain boundaries. Detailed mechanisms of localized corrosion of AA2024-T3 under chloride conditions can be found elsewhere in the literature [19-21].

Additionally to their corrosion sensitivity, the surface of the substrate in its 'as-received' state is not suitable for bonding. Metallurgical processing, including heat treatment and rolling, modifies the uppermost layers of the alloy surface. Fig. 3 presents a schematic illustration of these layers, which displays both compositional and structural changes, including smaller grains, enrichments in secondary particles (dispersoids) and higher concentration of Mg and Zn [22]. Additionally, the high shear forces applied during rolling are able to break and fold some of the surface oxides into the substrate. Altogether, this result in a so-called 'near-surface deformed layers' (NSDL), which present significant different electrochemical and mechanical properties compared to the bulk material. [23]. Hence, removing these NSDL should be the first step in any type of further processing.

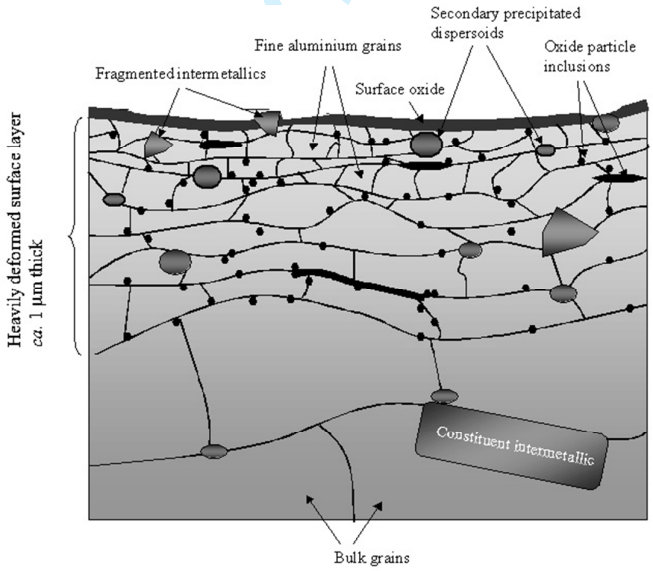

Figure 3 Schematic illustration of the modified composition of the aluminum alloy surface present after metallurgical processing [22].

3. Chromic acid anodizing (CAA)

In order to avoid the previously mentioned types of failure and to ensure long-term safety, bonded metal-to-metal assemblies must be carefully prepared. Surface pre-treatment has emerged as the most important step to provide the desired surface characteristics for bonding and minimize the effect of

surface heterogeneities, as the NSDL. The main pre-treatment schedule that is currently applied in the aerospace industry is illustrated in Fig. 4. It consists of four major steps: degreasing, pickling (or etching), anodizing, and primer application, all currently relying on Cr(VI)-based chemicals. In between two subsequent steps the surface is thoroughly rinsed in water. The following subsections describe each step of this pre-treatment scheme in terms of how it modifies the surface properties and its historical context.

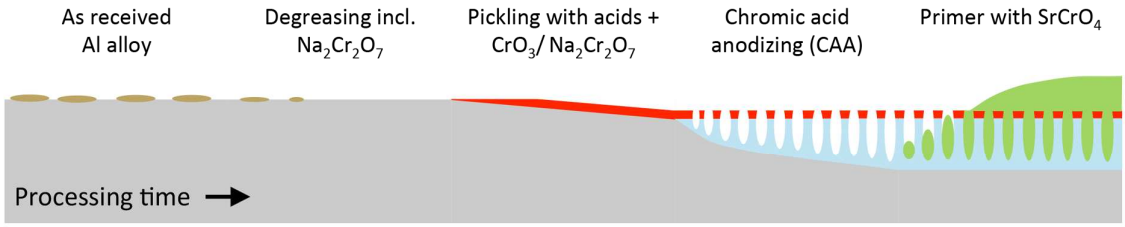

Figure 4 schematic representations of the process steps and the modifications that take place during the complete Cr-based pre-treatment that is currently applied in the European aerospace industry.

Degreasing is the first step in the pre-treatment process and normally the minimum preparation that is carried out prior to any type of metal bonding. Degreasing removes any oils, grease and contaminations that might have been introduced during aluminum manufacturing and processing [24]. This preliminary cleaning is necessary to assure that the following steps will work evenly across the substrate surface [16]. Next, the modified surface layers are chemically removed by **pickling** (also called etching). This can be performed in either acidic or alkaline solutions. The classical pickling solutions are often composed from mixtures of chromic and sulfuric acids and they are generally divided into two types: the FPL- and the CSA etch [25]. The first is the *Forest Products Laboratory* (FPL) process that was developed in the 1950s in the U.S. It consists of immersing the substrate in sodium dichromate ($Na_2Cr_2O_7$) and sulfuric acid solution for 9-15 min at 65°C. The European version of this etch, the CSA pickling, uses lower concentrations of either chromium trioxide (CrO_3) or sodium dichromate ($Na_2Cr_2O_7$) with sulfuric acid at similar temperatures, but longer immersion times (30 min.) [26]. Both methods follow a two-step reaction mechanism. In the first step, hexavalent chromium catalyses the oxidation of aluminum to alumina following Eq. 1. Next, the alumina product is dissolved by sulfuric acid (Eq. 2) [16].

$$2Al + 4H_2SO_4 + Na_2Cr_2O_7 \leftrightarrow Al_2O_3 + Na_2SO_4 + Cr_2(SO_4)_3 + 4H_2O \quad \text{Eq. 1}$$

$$Al_2O_3 + 3H_2SO_4 \leftrightarrow Al_2(SO_4)_3 + 3H_2O \quad \text{Eq. 2}$$

Since the second step is slower than the first one, a thin oxide layer is produced on the surface (as indicated by the red layer in Fig. 4). This oxide is amorphous, with a composition corresponding to alumina (Al_2O_3) and some minor concentrations (~0.5%) of Cr and S impurities. Venables et al. [27] reported that due to surface energy interactions, whiskers-like protrusions extending from the triple grain boundary points extend up to 40 nm from the surface. In their paper, the authors suggest that these branched protrusions already provide sufficient interlocking with the adhesive surface, resulting in an improved adhesion.

Unfortunately, some early in-service failures (mostly of non-bonded structures) occurred in the beginning of the 1960s, as aircrafts manufacturers started using epoxy adhesives instead of phenols [26]. The relatively thin oxide film was thus insufficient to provide reproducible and durable bonds. Consequently, an extra step, anodizing, was added to the pre-treatment schedule. **Anodizing** is an electrochemical process in which the aluminum substrate is artificially oxidized to grow a thick oxide film (up to several μm) [16]. The process derives its name from the fact that the aluminum substrate is

used as the anode in an electrolytic cell. The anode (substrate) is connected to the positive terminal of a DC power supply while a cathode (e.g. Al, stainless steel) is connected to the negative terminal. When the circuit is closed, electrons are withdrawn from the aluminum anode, which facilitate the oxidation of aluminum atoms to aluminum cations (Al^{3+}) at the metal/oxide interface. This is illustrated in Fig. 5. Since the electronic conductivity of aluminum oxide is very low, the anodizing voltage that is applied on the anodic cell encounters a resistance by the existing (natural) oxide film. This leads to a potential drop over the metal/electrolyte interface, which give rise to high electric field over the oxide layer. These electric fields are typically in the order of 10^6 to 10^7 V/m [28], which is high enough to enable oxide growth by ionic migration through the oxide [29]. Since aluminum is anodized in an aqueous electrolyte, adsorbed water at the anode will break down forming negatively charged O^{2-} and OH^-. These anions migrate towards the positively charged anodic substrate. A reaction between Al^{3+} and O^{2-} will leads to the formation of alumina, Al_2O_3, at the metal/oxide interface. Since not all the produced Al^{3+} is consumed by this interface, excess Al^{3+} cations will migrate away from the positively charged anode. Upon reaching the oxide/electrolyte interface, Al^{3+} can react with available O^{2-} forming additional alumina at the oxide/electrolyte interface. Under certain conditions, alumina ions will be directly ejected into the electrolyte. The conversion efficiency and, hence, final film morphology will depend on the balance between oxide growth and oxide dissolution (through direct ejection and chemical attack by an aggressive electrolyte). This in turn, is determined by the nature of the electrolyte and the process conditions, as discussed later.

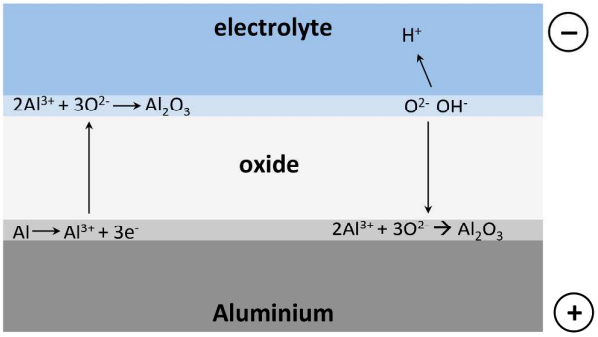

Figure 5 Schematic representation of the aluminum/electrolyte interface, showing the ionic processes involved in oxide growth during anodizing [30].

Chromic acid anodizing (CAA) was incorporated into the pre-treatment schedule in the 1960s. It mainly aimed to improve the overall corrosion resistance by producing a thicker physical barrier between the metal and its environment. Although anodizing can produce barrier- and porous-type oxide morphologies, porous films are preferred for bonding purposes. As illustrated in Fig. 6, porous anodic oxides consist of a compact barrier layer on the bottom and a relatively regular hexagonal porous structure on top [31-34]. These films are created when the anodic oxide is sparingly soluble in the anodizing electrolyte [31, 35]. In Europe, the 40/50V Bengough-Stuart process was adapted, using 2.5-3.0 wt.% chromic acid (CrO_3) at 40 °C [36]. The voltage across the electrolytic bath is initially raised to 40V in the first 10 minutes. This voltage is then maintained for 20 more minutes before it is raised to 50V, where it is kept constant during the last 5 minutes [37]. The higher voltage at the end results in a thicker barrier layer, providing an extra thick barrier for corrosive species [38].

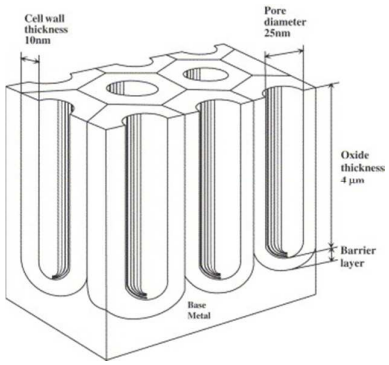

Figure 6 An idealized illustration of the anodic oxide structure formed on clad alloys following the 40/50 V CAA process [36].

This process produces 3-4 μm thick oxide layers on both AA2024-T3 and AA7075-T6 (bare and clad). It is a relatively ductile oxide with very low (0.1-0.3 wt.%) chromium content in the oxide. The oxide is moderately resistant to attack by moisture, although hydration has been reported [24]. This treatment, combined with prior CSA etching, was soon established as an effective pre-treatment for adhesive bonding and become an industrial standard.

In regular manufacturing operations, a certain time interval (several hours up to several months) usually passes between substrate pre-treatment and bonding. During this time, the freshly prepared oxide is susceptible to damage, contaminations, and environmental degradation [39]. This is prevented by the application of a thin layer of **primer** to seal the oxide immediately (within two hours) after the pre-treatments, when surface activity is maximal. Primers are diluted polymeric coatings, usually matching the chemistry of the adhesive. The primer functions as a physical barrier between the pretreated surface and its surrounding. Except for surface protection, primers are also used to promote adhesion. Two contributing mechanisms can be distinguished; (1) improved surface wetting and (2) providing stronger chemical interactions. The first mechanism is driven by the primer's lower viscosity (compared to the adhesive) and the addition of wetting agents. Kinloch et al, [40] compared PAA films that were bonded with- and without primer to show that a primer is able to penetrate deep and completely fill the pores, providing better adhesion. The second mechanism uses coupling agents to form a covalent bond across the inorganic-organic interface. Coupling agents are molecules with dual functionality. They contain organic end- groups such as methoxy (CH_3O-), ethoxy (CH_3CH_2O-) or hydroxyl (HO-) attached to a metallic central atom (e.g. silicon, zirconium or titanium) [41]. Organosilane coupling agents are the predominant chemical type of adhesion promoters. These groups are able to adsorb on the metal oxide surface through hydrogen bonds. Upon curing, a metallosiloxane bonds (Al-O-Si) are formed with the surface oxide [42]. These covalent bonds are much stronger than hydrogen bonds. Any remaining silanol groups will condense with themselves, forming a dense Si-O-Si network. Since Al-O-Si bond can be hydrolysed, the durability of these bonds will be determined by the extent of cross-linking of the Si-O-Si bonds, which will determine the hydrophobicity of the covering siloxane film. Hence, adjusting the chemical composition to tailor the desired film properties is essential. It is important to also match the reactivity of the coupling agent with that of the adhesive [41]. Different studies have demonstrated that silanes are capable to improve interfacial adhesion [40, 43-45], as well as corrosion resistance of coated aluminum [46, 47]. Song and van Ooij [48], for example, have shown that by combining two types of silanes, namely 1,2-bis(triethoxysilyl)ethane (BTSE) and ϒ-aminopropyltriethoxy (ϒ-APS), it is possible

to design a dual functionality interface that would give good corrosion protection and will be compatible with an epoxy adhesive. Since silanes connect via the OH- groups on the substrate, maximizing their amount on the substrate is desired. A study by Franquet et al. [49], showed that chemical pre-treatments affecting the amount of surface hydroxyl groups will in turn affect the silane film uniformity and thickness. Therefore, when silanes are applied, prior surface pre-treatment is still needed.

4. Cr(VI)-free alternatives to CAA

Health and environmental issues, together with the increasing costs associated with the treatment and disposal of solutions containing hexavalent chromium initiated a large number of studies over the past decades. To avoid an exhaustive comparison of the different process parameters, this section will focus on the different methods rather than specific outcomes of the most relevant alternative Cr(VI)-free pre-treatments for structural bonding. For a detailed list of the specific pre-treatments and evaluation techniques, readers are encouraged to consult the review published by Critchlow and Brewis [24].

4.1 Phosphoric acid anodizing (PAA)

For economic reasons, anodizing was initially rejected in the US until Boeing introduced phosphoric acid anodizing (PAA) in 1975, which makes PAA the first commercial alternative to CAA. The PAA process applies 10wt.% phosphoric acid at 21-24 °C. Anodizing is conducted at constant voltage of 10-15 V for 25 minutes. The PAA oxide is considerably thinner (typically 0.5 to 2 μm) and more porous than the CAA film [50]. However, it has an advantage, since the composition of the outer part of the film corresponds to non-hydrated $AlPO_4$ in the outer layer (see section 5.2), which provides higher resistance to humidity and even to hot water sealing. This resistance is attributed to the stability of the chemical bonds between aluminum and phosphate [51] [52] and, therefore, provides an effective environmental stability during service [53]. Nevertheless, studies show that the corrosion resistance of PAA oxides is inferior to those of CAA, which explains why this process was developed together with the introduction of chromate inhibiting primers. Hence, although the PAA process is Cr(VI)-free it typically requires the additional support of (active) protective coatings that contain corrosion inhibitors. So far, the most effective inhibitors are Cr(VI)-based pigments and the search for Cr(VI)-free alternatives is still in progress. Some green inhibitors are based on inorganic species (including lithium, Cr(III), rare-earths, molybdates and vanadates), while others are base on organic functionalities [54].

4.2 Mixed electrolytes anodizing

In addition to PAA, one of the most popular anodizing electrolytes is sulfuric acid. Conversely to PAA, sulfuric acid anodizing (SAA) generally produces a thick and dens protective layer [55]. Therefore, SAA is commercially applied (mostly in *'hard'* conditions) for decorative and corrosion protection applications. However, the same properties that provides it with excellent corrosion and wear resistance deliver poor adhesion [56]. One method to overcome this limitation is to mix sulfuric acid in the anodizing bath with the more aggressive phosphoric acid, thereby providing the conditions to produce an intermediate oxide structure with morphological dimensions comparable to CAA. The process, named phosphoric-sulfuric acid anodizing (PSA) was developed by Kock et al. [57]. The first PSA process contains equal amounts of sulfuric- and phosphoric acids (100 g/l). Similar to PAA, phosphates are found in the outer layer of the oxide [58], providing an additional hydration resistance. Recent investigations by the authors covered a broad range of process parameters: different concentrations of phosphoric and

sulfuric acids, together with ranging temperature and duration in the search for the optimal PSA conditions [59]. Oxide films with wide morphological variations (e.g. pore size of 5 to 60 nm and layer thicknesses of up to 6 µm) were prepared by changing the anodizing conditions (especially phosphoric acid concentration and electrolyte temperature). These conditions were found important for the performance of the bond, as tested by dry and wet floating roller peel tests. Currently, the PSA process is considered a viable alternative to CAA and will be implemented at Fokker Aerostructures in the near future.

Already in the 1960s, a mixture of tartaric and sulfuric acid anodizing (TSA) was suggested by Kape [60]. Unfortunately, the resulting porosity is relatively low and adhesives cannot easily permeate into the oxide layer. Hence, the analogous TSA process is mainly used in *non-structural* applications. The role of tartaric acid, according to a study by Curioni et al. [61] is reducing the current density and thereby reducing the oxide growth rate, so that the of the final film thickness is lower than for normal SAA. More interestingly, however, an improved corrosion resistance is observed. This resistance is explained by a "buffering effect" that tartarate ions remnants in the oxide are providing. During anodizing, tartaric acid can combine with aluminum cations to produce aluminum tartrate, a compound that is highly soluble in the acidic anodizing solution but with relatively low solubility in water. During subsequent rinsing, the pH is rapidly increased and relatively large amounts of aluminum tartrate may precipitate at the pore walls. As a consequence, if the oxide is exposed to a corrosive environment during its use, aluminum tartrate may re-dissolve, producing a local buffer, thereby limiting the susceptibility to localized corrosion. Even further improvements in the corrosion resistance of TSA films were registered after hot water sealing [62] and by the addition of molybdate salts into the anodizing bath [63].

4.3 Two-step anodizing

Relying on this TSA advantage, a new type of processes has emerged, which combines two-step anodizing. In this case TSA anodizing follows PSA to provide a duplex oxide with both corrosion resistance and adhesion capabilities. The resulting structure shown in Fig. 7 (a) is reported to be suitable for adhesive bonding of structural components [64].

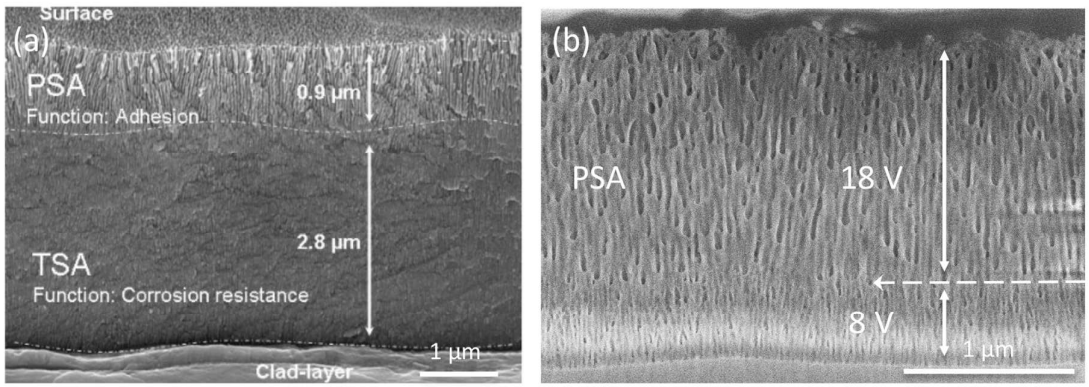

Figure 7 Cross section of the anodic oxide produced on 2024-T3 clad by (a) TSA+PSA process [64] and (b) PSA dynamic anodizing, with voltage decrease from 18 V to 9 V [65].

Similar process is the boric-sulfuric acid anodizing (BSAA) that has been patented by Boeing as an alternative to CAA [66]. The oxide structure resembles SAA, but with finer pores and more uniform

hexagonal arrangement compared to CAA, showing promising results [67]. Zhang et al. [68] report an improvement in bonding and durability of panels created by the BSAA process by the addition of phosphoric acid to the anodizing electrolyte. The process is reported to result in bigger pores, improving primer penetration and extending oxide durability. Because boric acid is also hazardous, using it as a replacement is not generally desired, especially since it may be subject to future regulations.

Similarly to two-step anodizing, dynamically changing the anodizing voltage/current during the process can be used to vary the oxide morphology across its thickness. A SEM cross section of such an example is shown in Fig. 7 (b), possibly providing an alternative for a two-step anodizing process. In an investigation by van Put et al. [65] this complex oxide morphology was formed by an instantaneous voltage decrease during anodizing. Since the pore size is linearly related to the applied voltage, an instantaneous decrease from 18V to 9V forces the formation of new pores with smaller diameters below existing larger pores. As a result, a distinct border between the two morphologies is formed (indicated by the arrow in Fig. 7 (b)). Conversely, applying a voltage increase did not produce the reverse morphology and a transition layer was formed by partly dissolving the walls of smaller pores after the sudden change.

4.3 Electrolytic deoxidation

Earlier study by Venables et al. [27] have shown that fine oxide protrusions produced by the FPL etch on top of a PAA oxide are beneficial for good adhesion. This is desired from adhesion point of view, because protrusions, even just nanometers long, create an additional reinforcement by interlocking with the resin. Likewise, Yendall and Critchlow [69] suggests a method that applies electrolytic phosphoric acid deoxidizer (EPAD) before anodizing. In that respect EPAD replaces the FPL etch in producing an open top layer that comes into contact with primer/adhesive (Fig. 8). They found that this method improves the mechanical properties of the bond depending, however, also on the anodizing temperature used for SAA. In this case, it is important to keep in mind that the choice of electrolyte and applied temperature will also affect the resulting morphology. As discussed later in sections 5.1 and 5.4, if the anodizing conditions are too aggressive, the EPAD layer may (in part or completely) dissolve during subsequent anodizing.

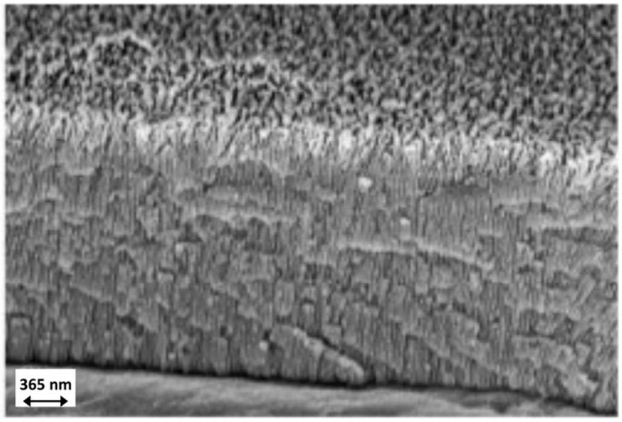

Figure 8 Cross section of AA2024-T3 clad after EPAD and SAA [69].

4.4 AC Anodizing

An interesting alternative applies alternating current (AC) instead of the traditional direct current (DC) for anodizing. AC anodizing was originally developed for high-speed coil applications in the automotive industry [16]. Relatively elastic oxide layers are developed by treatment at higher temperatures and higher anodizing currents. Both sulfuric- and phosphoric acid processes have been reported, with the conditions listed in Table 1. Though developed as a continuous process, batch operation is also possible.

Table 1 Anodizing parameters [70].

Parameter	H_3PO_4	H_2SO_4
Acid concentration, wt.%	10	15
Temperature, °C	50	80
Time, min.	12	30
Current, A/dm^2	4	10

As in other AC processes, hydrogen evolves on the surface of the anode during the cathodic cycle. This is sufficient to remove organic contaminants as well as natural present oxides, so that separate steps for cleaning and deoxidizing prior to anodizing are not required, thereby drastically reducing the amount of processing tanks [70]. Since the resulted oxides are thin, their performance is comparable to the etching rather than anodic oxides [71]. Hence, a U.S. patent by Critchlow et al. [72] suggests applying a two-step process that includes subsequent AC and DC PSA anodizing in the same bath. This combination produces an oxide film that has a thin porous outer layer (less than 1 μm) and a relatively thick (up to 8 μm) uniform inner layer to yield an optimal combination of corrosion protection by the dense inner layer, and adhesion provided by the porous outer layer.

4.5 Anodizing with post-treatments

Correspondingly, a post-treatment immersion of the relatively dense anodic oxide in a dilute acidic or alkaline solution will produce the desired morphology by chemically attacking the oxide to partly dissolve it and open the pores. Both Arrowsmith and Clifford [73] and Yendall and Critchlow [69] applied phosphoric acid dip after SAA (or BSAA) anodizing to report an improved short and long-term durability of the produced bonds. The narrow pores close to the substrate are considered to provide the corrosion resistance, while the etched top layer is able to better interlock with the primer/adhesive. In order to avoid over-etching, the time, nature and concentration of the etching solution should be controlled [74]. Such post-anodizing step is not new to the aviation industry, which frequently applies post- anodizing immersion in boiling water to seal the porous oxide layer when it serves as a protective coating against corrosion instead of a receptive surface for bonding.

An interesting alternative to a post-treatment dip concerns anodizing combining positive and small-negative voltages. The negative charge at the end of the normal anodizing cycle leads to dissolution of the oxide by hydrogen ions attracted to the temporary negative pole [75]. In this case, the dissolution is done in the same bath as anodizing, reducing the need for an extra processing and rinsing bath.

4.6 Non-anodizing processes

As previously mentioned, immersion in hot water is often used to seal off the anodic pores. Treatment in boiling water (and even water at 40 and 50 °C, [76]) leads to hydration of the present Al_2O_3 and to the formation of a pseudoboehmite (AlOOH) oxide. Although sealing the pores openings is not desired from a bonding perspective, boiling water treatment has been suggested as a stand-alone treatment to replace anodizing. The hydrated form of oxide has been reported to provide many benefits, besides it being an inexpensive alternative: a highly-porous morphology with a large surface area [77], increased number of surface hydroxyl groups [78] and a low contact angle [79]. Oxide morphology will depend on the temperature and the duration of the treatments. Three representative morphologies are presented in Fig. 9. After just 30 s of immersion the surface oxide exhibits a cellular structure with thin ridges (approx. 10 nm wide) that provide large porosity. As the treatment time is extended, cell walls develop into distinct plates (of increased thickness) that are oriented normal to the surface. When the time is extended up to 4 hours, the cell walls significantly thickness, producing a distinctive and much less porous structure [80]. Unfortunately, this type of oxide is brittle and mechanical tests often show an early cohesive failure within this pseudoboehmite layer [77, 79]. Although in some cases, the combination of prior grit blasting and the addition of a silane layer was shown to reproduce results comparable to the benchmark used (CSA+PAA), its level of success is highly sensitive to alloy composition [80]. Hence, boiling water treatment generally does not compare with the durability of anodized-based oxide layers.

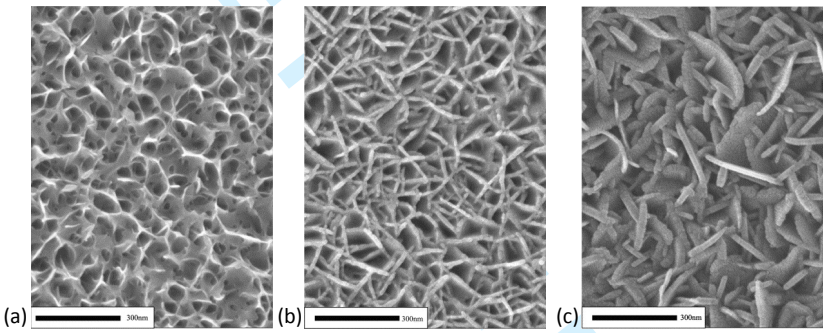

Figure 9 High-resolution SEM micrograph after boiling water treatment on AA2024-T3 clad for 30 s (a), 60 min (b) and 240 min (c), edited from [80].

A similar option consists of a steam treatment [81, 82]. A study by Ud Din et al. [83] have shown that oxide layers with thicknesses comparable to anodic oxides can be produced. Depending on treatment parameters and steam chemistry, layers of few nanometers up to 3 μm can be formed. The addition of acidic components (citric or phosphoric acids) to the steam enables the growth of thicker layers and help in the corrosion protection (especially due to incorporation of phosphates).

5. Parameters affecting the anodic oxide film properties

Considering the list of alternative methods in section 4, it appears that most processes are based on similar electrolytes that apply different preparation conditions to produce certain desired oxide properties. Hence, it is important to understand which key parameters control the anodizing process and how these, in turn, change the oxide film characteristics.

5.1 Electrolyte type

The nature of the electrolyte is one of the main parameters to determine the oxide properties, such as morphology and chemistry (as discussed in section 5.2). The pore size is a direct function of the

electrolyte as found by Keller et al. [84]. Interpore distance and barrier layer thickness are also affected, but to a lesser degree. The pore size generally increases in the order SAA < TSA < CAA< < PSA< PAA [85].

5.2 Incorporation of anions

Besides the ionic species (Al^{3+} and O^{2-}/OH^-) that are responsible for oxide growth, any ion species that is present in the solution may be affected by the electric field. Since the anode is positively charged during anodizing, negatively charged species from dissociating acids will migrate towards the oxide, leading to the incorporation of impurities into the oxide. The extent of incorporation is determined by the nature of the electrolyte solution, the applied conditions and the film type. A range of surface analysis techniques, including Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and glow discharge optical emission spectroscopy (GDOES) [86, 87] have been applied to measure the concentration and distribution of electrolyte-derived impurities in the film. These studies show that the migration of electrolyte species varies from one electrolyte to the other. Table 2 lists the concentration of anions within the most common anodizing electrolytes. It demonstrates that almost anion-free films are formed in chromic acid, while other anions of alternative electrolytes contribute to a much higher relative composition. Since most electrolyte anions migrate at slower rates than the O^{2-} ions, a relatively pure alumina region is formed close to the aluminum/oxide interface [88]. This is indicated in Fig. 10 that displays a comparison of the resulting oxide composition in SAA and PAA. Sulfate anions can migrate into the inner most part of the cell wall, resulting in a duplex oxide composition. Phosphate anions, on the other hand, exhibit a triplex structure with maximal concentration in the region near the interface with the electrolyte. In the mixed PSA (Phosphoric- sulfuric acid anodizing) electrolyte, the incorporation of phosphate on *barrier-type* oxide indicated that the phosphate incorporation in the mixed electrolyte is somewhat inhibited, and phosphates remained close to the oxide/resin interface [58].

Table 2: Percentage of incorporated anions in the porous oxide layer [85].

Electrolyte	H_2CrO_4	H_3PO_4	$H_2C_2O_4$	H_2SO_4
Anion concentration (at.%)	0.1 – 0.3	6 - 8	2 - 3	10 - 13

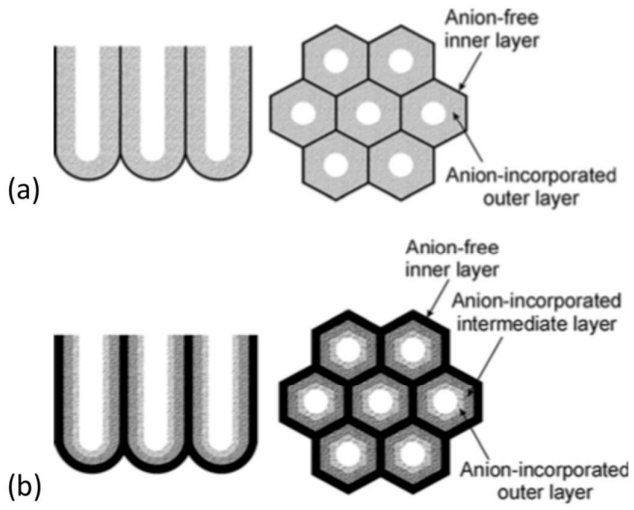

Figure 10: Schematic representations of the sectional and plan views of, respectively, the duplex (a) and triplex (b) structures of porous alumina cell walls formed in sulfuric and phosphoric acids, respectively [85].

Compared to barrier layers, porous film generally contain a higher anion content in the oxide structure [85]. This is explained by the fact that the electric field at the barrier layer is not uniform, so that the semi-spherical shape of the pore base results in a much higher electric field close to the electrolyte/oxide interface, which in turn supports easier incorporation of anions. In addition, the long-term exposure of the oxide walls to the electrolyte readily allows for active penetration of the acid.

Anion incorporation has an effect on the properties of the oxide film, such as the mechanical (e.g. flexibility and hardness) the chemical properties and the space charge [89]. Thompson and Wood [90] reported a transition from solid to gel-like material moving across the cell walls towards the pore interior, with the thickness of this layer depending on the electrolyte, the voltage or current density, and the temperature. Another example is the resistance to hydration that is provided by oxides produced in phosphoric acid. This resistance has been contributed to the presence of $H_2PO_4^-$ ions in the anodic films. These anions can be further decomposed to proton, H^+, and HPO_4^{2-}, thereby retarding the hydration of alumina [68]. The applied electrolyte also seems to have an influence on the water content of the film. Although no water is found in the bulk of oxides formed in acid electrolytes, chemical adsorption (chemisorption) of OH^- groups and water molecules at the outer layer is reported [91]. This can, according to findings on chemically grown aluminum oxides, affect the extent in which the oxide interact with organic molecules and resins [92].

In a recent publication by the authors [58] we have quantified the relative amount of O^{2-}, OH^-, PO_4^{3-} and SO_4^{2-} species at the surface of *barrier-type* PAA, SAA, PSA and CAA oxides using X-ray photoelectron spectroscopy (XPS). Results show that the surface chemistry of anodic oxides is highly affected by the incorporation of anions. Phosphates were the highest with 40 % of the surface species and no hydroxyls at the applied conditions. Sulfate concentration is lower at 15 % and a negligible amount of anions in CAA. It was confirmed that the incorporation of phosphate and sulfate anions comes at the expense of surface hydroxyls. Consequentially, we investigated how variations in the chemical species at the oxide surface after anodizing affect the interaction with an organic resin. In the first instate, this was studied using molecules that represent typical aerospace adhesives. Results show that bonding with two phenol-based molecules and amine molecule both proceeds through the surface hydroxyls. However, interactions with some molecules were sensitive to chemical changes while others did not. Next, mechanical peel tests with barrier-type anodic oxides that were bonded with an industrial epoxy adhesive. We concluded that the bonding mechanism was not affected by anion incorporation, only its extent. Since phosphate and sulfate incorporation reduces the amount of hydroxyls available for interactions, anodizing in these electrolytes was considered inferior from a chemical interactions point of view [93].

5.3 Potential / current density

At steady state growth, a dynamic equilibrium exists between pore base dissolution at the oxide/electrolyte interface and oxide growth at the metal/oxide interface. Studies have shown that the major film characteristics (pore diameter *d*, cell diameter *c* and barrier layer thickness *b*, as indicated in Fig. 11) are directly related to the applied potential [84, 94]. This is explained by the fact that stationary film formation occurs at a constant rate, which is determined by the average field over the oxide [95]. Higher potential values will result in thicker barrier layers, larger cells, and wider pores. The thickening of the barrier layer was found to show an almost universal relation, growing at 1.3-1.4 nm/V for

barrier-type films and about 1.2 nm/V for the barriers under porous films, with only small deviations as a function of the temperature and the electrolyte type [85].

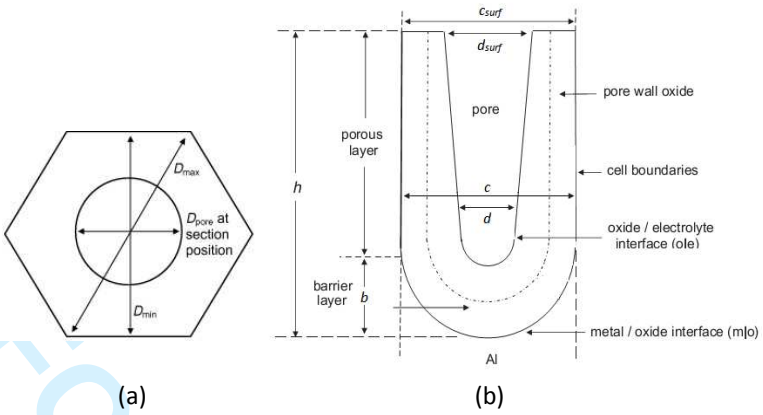

Figure 11: Schematic representation of an ideally hexagonal columnar cell of a porous anodic alumina film [95].

Any tendency of a pore to become too big or too small will be compensated by its curvature that will, accordingly, adjust field strength [96]. If during the anodizing process, a large variation in potential is induced, the oxide film will adapt itself to the new applied conditions. This observations, together with a 'recovery effect' was reported by Curioni et al. [97], using cyclic polarization measurements. The recovery effect is the elapsed time before the steady-state characteristic conditions of the new voltage are attained. It will depend on the potential variance, as well as the bath conditions (electrolyte, temperature). Dynamically varying the anodizing potential during the treatment was used by van Put et al. [65] in order to change the pore size across the oxide thickness, creating complex oxide morphologies. This may explain the gradient of voltage that is applied during the conventional 40/50V CAA anodizing process, providing wider pores at the bottom of the film and thickening the barrier layer. This is an interesting observation that can be used as opportunity in developing new processes.

5.4 Temperature and time

Another significant variable in the anodizing conditions is the electrolyte temperature. A higher bath temperature will enhance local dissolution at the pore base. This, in turn, will result in an increased local current density, which will increase the ionic transfer and oxide formation rates [98]. Aerts et al. [99] have shown that a higher rate of oxide dissolution, due to the aggressiveness of the electrolyte at higher temperatures, have increased the porosity in sulfuric acid anodizing (with a constant convection) from 4% at 5℃ to 32% at 55℃. Dissolution effects are mainly noticeable at the outer layer of the oxide, leading to pore broadening [100]. Upon extended anodizing times, aggressive electrolytes will cause excessive chemical dissolution. Since the oxide is only growing from within the metal, the outer part of the film is in contact with the electrolyte for a longer time period and therefore suffers from the most chemical attack. This phenomenon induces pore widening at the outer surface, which affects the general shape of the pores. This is why cone-shaped pores are often reported; with the pore diameter at the pore base (d in Fig. 11 (b)) generally exhibiting a linear correlation to the anodizing voltage, while pores at the surface (d_{surf} *in* Fig. 11 (b)) are frequently larger [59]. Interestingly, controlling the electrode temperature can have a larger influence on oxide formation than changing the electrolyte temperature [101]. Hence, physical bath properties, such as convection-based heat transfer should be considered.

At high anodizing temperatures and longer times, dissolution has an even larger influence on oxide morphology. An example is shown in Fig. 12 for different electrolyte temperatures and dwell time. At relatively lower temperatures and shorter times whiskers are formed on top of the hexagonal oxide structure. These are created by extended dissolution and thinning of the pore walls. At some critical point, these filaments are so long and thin, that they will collapse, forming a so-called 'bird's nest' structure on top of the oxide film (Fig. 12 m-o).

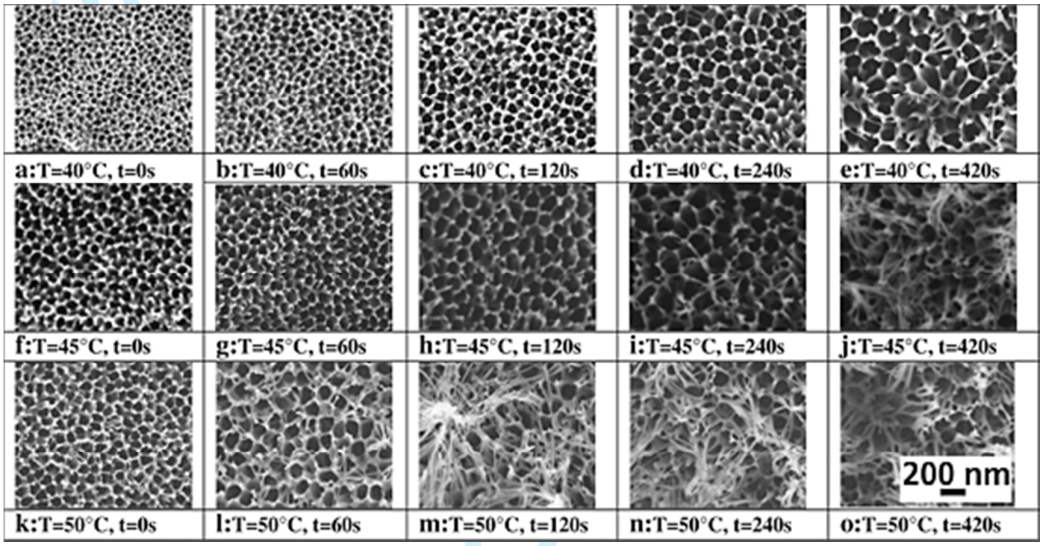

Figure 12: SEM of the oxide layer depending on the bath temperature and the dwell time - surface views (anodizing potential E = 50 VSCE) [102]. Longer time and higher temperatures lead to their collapse and the formation of a 'bird's nest'.

5.5 Pre-texturing

Studies have shown that surface features produced by prior steps are related to pore initiation and development. Following the previously discussed growth mechanism, geometrical (near-)surface features like the rolling lines, scratches and rolled-in oxides locally increase the curvature and therefore present preferential regions for pore initiation and development. It has been shown by Terryn [103] that such features can even pre-impose the alignment of pores to develop certain orientation. This is especially relevant when the step prior to anodizing produces characteristic surface features. If a highly-regular pore arrangement is required, as in the production of alumina template for nanostructure fabrication, a two-step anodizing (with intermediate dissolution of the oxide) is used to produce a well-ordered structure, in which the first anodizing step is used to texture the surface [85]. Since this method is both time-consuming and expensive, pre-texturing by anodizing is generally not applied in the aerospace industry.

5.6 Alloy composition

The presence of alloying elements has an effect on the anodizing potential, as well as the oxide morphology. Since elements in solid solution will change the resistance to current flow, the purer the aluminum, the more resistance to ionic transport [104].

It is generally also observed that the same process conditions can yield completely different forms of anodic films on bare and clad aluminum substrates. Fig. 13 shows a comparison between the CAA 40/50V anodic oxide on clad and bare AA20204-T3. The high purity clad alloy shows a relatively regular columnar structure while no evidently regular structure is observed on the bare material, which resembles a sponge-like structure. This difference is attributed to the presence of second phase particles and alloying elements with a different potential than that of the matrix [69, 105, 106]. Alloying elements with more negative potential will oxidize with aluminum and enter the anodic oxide, while nobler alloying elements like Cu do not. Cu concentration will then rise, leading to enrichment at the metal/oxide interface, immediately beneath the oxide film [107, 108]. It has been shown by Garcia-Vergara et.al [109] that cyclic oxidation of copper in the enriched layer below the barrier layer results in oxygen generation that leads to gas evolution and lateral porosity, resulting in the irregular anodic oxide structure that is produced on bare A2024-T3. Correspondingly, similar process conditions may lead to different oxide weight and morphology on different aluminum alloys.

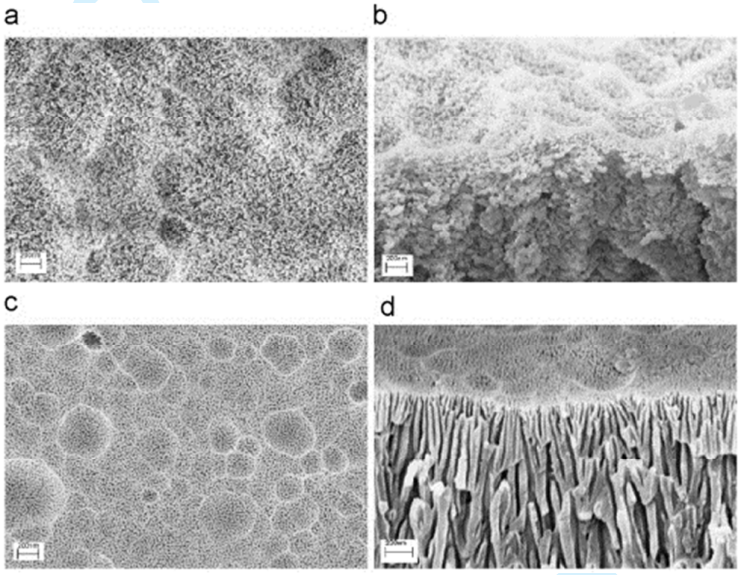

Figure 13: CAA 40/50 V processed, 2024-T3 bare: plan view (a) and cross-section (b), 2024-T3 clad: plan view (c) and cross-section (d). Reprinted from [69], Copyright (2016), with permission from Elsevier.

6. The relation between oxide properties and adhesion

The two main oxide properties that are influenced by the different process parameters are oxide composition and morphological features. Yet, it appears that the main objective in the development of Cr(VI)-free processes so far was to reproduce the CAA morphological features using different types of processes. One of the longest, yet, on-going discussions in the literature concern the adhesion modes. Various theories exist to explain adhesion between different materials: diffusion, electrostatic interactions, weak boundary layer, mechanical interlocking and physical chemical adsorption (or interactions) [110]. Amongst these theories adsorption and mechanical models are considered most relevant for metal/polymer bonding.

Different authors argue that the high level adhesion that is achieved with porous anodic oxides is mainly due to mechanical interlocking [27, 111-113]. However, studies on both chemical and anodic oxides have shown that oxide chemistry also plays a vital role in the nature and type of interaction with the organic resin [92, 114-117]. In an effort to separate the two contributions, a study by the authors using

FM 73 epoxy adhesive shows that significant initial adhesion strength can be achieved without mechanical interlocking and independent of the type of electrolyte. The measured dry peel strengths were in the same level of the dry strengths measured for porous oxides with a relatively small pore size (up to 20 nm). However, porous oxides with wider pores performed better. Above approximately 25 nm pore size, tests showed no further improvement in dry peel strengths [59]. According to these observations, it is not possible to conclude which is the dominating adhesion mechanism. Both mechanical interlocking and a larger contact area could provide this improvement in strength.

Conversely, the stability of the interface under water ingress was found to be highly dependent on the oxide chemistry and anodizing conditions, especially the electrolyte type, concentration and temperature. Chemistry effects were correlated to the amount of surface hydroxyls, which were found to be the reacting entities between the oxide and the resin [116], while morphological considerations were mainly attributed to changes in the surface roughness [59]. Nevertheless, bond strength and durability both appear to be closely related to the ability of the oxide and the resin to form a cohesive interphase. Although mechanical interlocking is considered to contribute, there is no conclusive evidence for its dominance.

Another important aspect in bond durability is the resistance to bondline corrosion. It appears that increasing the oxide porosity and surface roughness will improve adhesion. However, as also claimed to PAA, one of the main challenges is to provide a high level of corrosion resistance in a very porous system. Consequently, failures due to bondline corrosion were observed with PSA test panels produced at relatively aggressive conditions and lower voltages [59]. Oxides produced in the same conditions (electrolyte, temperature and time), but at higher voltage did not fail. This seems to indicate that the presence of thicker barrier-layer that is formed at higher voltages may be playing a significant role. Furthermore, this is the reason why many studies combine the production of a receptive open structure at the outer layer, while aiming to provide better corrosion protection by a denser inner layer. Nevertheless, a recent (unpublished) investigation of the authors indicates that the corrosion resistance of the interface is also largely determined by the chemical composition of the adhesive. Hence, the chemical nature of the oxide *and* the adhesive should be considered.

7. Summary and Conclusions

The required bond performance and durability, together with the corrosion sensitivity of aerospace aluminum alloys, have led to the development of a multi-step pre-treatment process that is carefully designed to provide the desired surface characteristics for bonding and corrosion resistance. In this pre-treatment, the use of Cr(VI)-based chemistries currently still has a crucial role. The importance of finding a replacement is evident by the large amount of literature available on this subject. It is, however, also clear that the success and versatility of Cr(VI)-based applications is one that is very difficult to duplicate. While many Cr(VI)-free alternative options exist and much is known about the relation between the principal process parameters and oxide properties, maximizing bond performance and corrosion resistance is not straightforward. The fact that both atomic- and molecular interactions, as well as mechanical interlocking are crucial for the formation of interfacial bonds are now beginning to be reflected in practical and industrial research. Hence, it is of pivotal importance to adjust both oxide chemistry and morphology in order to produce the desired oxide characteristics. It remains of great academic and industrial interest to continue to gain further fundamental understanding on how adsorption and mechanical adhesion mechanisms contribute to the final bond performance.

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REVIEW ARTICLE

Towards Cr(VI)-free Anodization of Aluminum Alloys for Aerospace Adhesive Bonding Applications: A Review

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Abstract

For more than six decades, chromic acid anodizing (CAA) has been the central process in the surface pre-treatment of aluminum for adhesively bonded aircraft structures. Unfortunately, this electrolyte contains hexavalent chromium (Cr(VI)), a compound known for its toxicity and carcinogenic properties. To comply with the new strict international regulations, the Cr(VI)-era will soon have to come to an end. Anodizing aluminum in acid electrolytes produces a self-ordered porous oxide layer. Although different acids can be used to create this type of structure, the excellent adhesion and corrosion resistance that is currently achieved by the complete Cr(VI)-based process is not easily matched. This paper provides a critical overview and appraisal of proposed alternatives to CAA, including combinations of multiple anodizing steps, pre- and post anodizing treatments. The work is presented in terms of the modifications to the oxide properties, such as morphological features (e.g. pore size, barrier layer thickness) and surface chemistry, in order to evaluate the link between fundamental principles of adhesion and bond performance.

Keywords Aluminum, Cr(VI)-free, Surface pre-treatments, Anodizing, Adhesive bonding, Adhesion, Durability.

1 Introduction

For many years, hexavalent chromium has been used for the corrosion protection of metals in many industries; aerospace, automotive, maritime and architectural structures are just a few examples for the wide spectrum of applications in which Cr(VI)-based coatings can guarantee the life-long integrity of metallic parts. Unfortunately, Cr(VI) is regarded to be extremely toxic and carcinogenic [1, 2]. This has already being noticed in the first decades of the 20th century [3, 4]. Numerous studies have shown that employees working with chromate-containing compounds risk exposure through skin contact and by inhalation of vapors or dust particles [5, 6]. In the aerospace industry this mostly occurs in the production stage, when the parts are pretreated and painted, during their maintenance or at the end-of life, when these coatings and paints are removed.

In 2006, the Occupational Safety and Health Administration (OSHA) in the U.S. [7], the European Registration, Evaluation, Authorization and Restriction of Chemicals (REACH, EC n°1907/2006) and Restriction of Hazardous Substancespolicies (RoHS) introduced new regulations that strictly limit the use of hexavalent chromium and announced its near future ban. As a consequence, chromates are no longer used in most commercial processes and products. However, the corrosion sensitivity of high-strength aluminum alloys and the required level of performance and safety make its overall replacement in the aerospace industry a very challenging task. In addition, the time it takes to test and qualify new systems for aviation is much longer compared to that in other industries. Therefore, Cr(VI)-based substances are currently still utilized in most aerospace metal pre-treatment, coating and bonding processes.

This paper reviews the state-of-the-art alternatives to *chromic acid anodizing* (CAA), which is the key pre-treatment step to produce anodic oxide films suitable for adhesive bonding. Herein, only the manufacturing of parts aimed for *structural* components are discussed. Although other components of the aircraft are produced in a similar manner, structural components are considered the most critical since they are designed as part of the principal load-carrying structure of the aircraft and they are typically not accessible for inspection and maintenance during its lifetime [8]. As such, these components are subject to the highest engineering standards.

The following section provides background on the main issues and challenges in the pre-treatments of aluminum for structural bonding. Next, section three presents the development of the benchmark CAA process that is currently used in Europe and its major oxide characteristics. The fourth section covers the range of Cr(VI)-free alternatives. In order to identify the key factors that determine the adhesion and durability of these structures, section five critically reviews the main processing parameters, as concluded by reviewing the literature available to date, including recent detailed investigations by the authors. The final section discusses the relation between the main oxide properties and bond performance. This review paper ends with a short summary and conclusion in section six.

2. Structural adhesive bonding in aircraft structures

Adhesive bonding is one of the oldest techniques to join different components, often of dissimilar nature [9]. Bonding is established when the adhesives undergoes physical or chemical hardening reaction (curing) to join the two panels together through surface adherence (adhesion) and internal strength (cohesion) [10]. Adhesive bonding was already used in the first aircrafts, which were made from wood

and continued in the 1940s, when manufacturers started using aluminum [11]. Since then adhesive bonding has become a standard technique to produce the main body (fuselage), wings and other parts of modern aircrafts [12]. Fig. 1 shows the main steps in the production of adhesively bonded components at *Fokker Aerostructures* in the Netherlands.

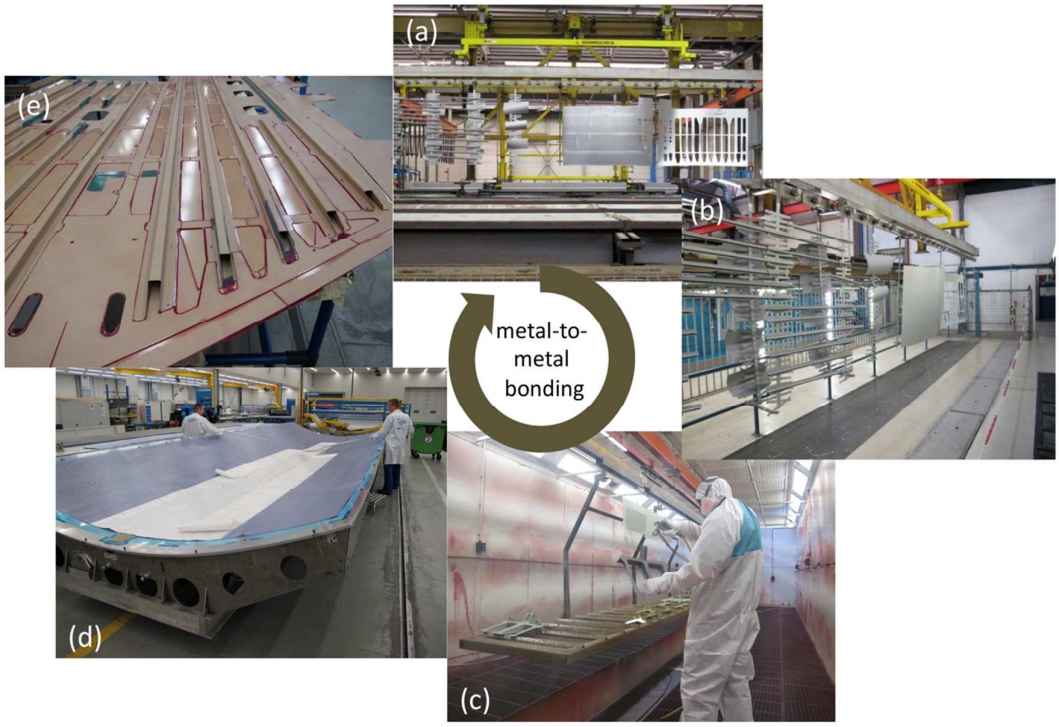

Figure 1 The production of metal-to-metal bonding at Fokker Aerostructures: (a) surface pre-treatment (panels hanging above the anodizing bath), (b) parts drying on the rack after pre-treatment, (c) primer application, (d) adhesive application, (e) a bonded part.

2.1 Durability of the adhesive bond

Ideally, the bonded structure will be able to withstand and carry the high loads that are executed on the structure during use and efficiently transfer and distribute the mechanical stresses over a large surface area. A crucial parameter in maintaining the long-term integrity of the assembly is durability of adhesion under various environmental conditions, such as temperature extremes, varying atmospheric pressures, moisture content and types of aggressive species (e.g. anti-freeze and chlorine ions). These, in combination with the varying mechanical stresses, may lead to early failure [13]. Fig. 2 illustrates the different possible failure mechanisms that can occur within an adhesive joint. They are generally characterized as predominantly cohesive- or adhesive in nature. Cohesive failures take place within the same phase, whereas adhesive failures occur at their interfaces.

Industrial standards generally demand higher adhesion than cohesion strengths. This is desired from an engineering point of view, since cohesive failure related to bulk material properties could be readily considered by design. In the case of metal-to-metal adhesive bonding, this refers to a cohesive failure within the polymeric adhesive (Fig. 2 (A)). Other failure mechanisms (Fig. 2 (B)-(F)) are usually the result of poor bond preparation (processing) and effects of environmental conditions.

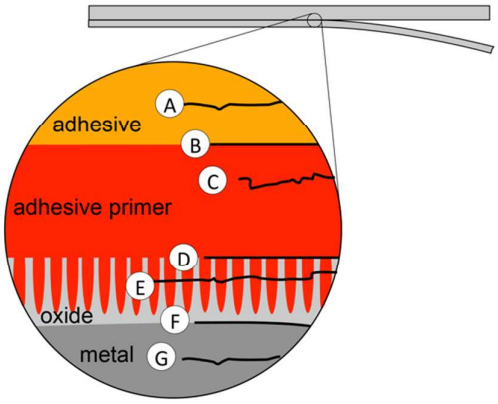

Figure 2 Schematic illustration of the possible failure modes in structural adhesive joint: (A) cohesive fracture of the adhesive film, (B) interfacial disbonding between adhesive and primer, (C) cohesive fracture of primer layer, (D) interfacial disbonding between primer and anodic coating, (E) fracture within anodic oxide coating and (F) corrosion of aluminum substrate at metal/oxide interface and (G) failure of the metal substrate.

One of the key issues concerning bond durability is the permeability of water molecules. Moisture from the environment can enter the bonded system by bulk diffusion through the adhesive, by interfacial diffusion along the interface between the adhesive and the oxide, and by capillary action through cracks or defects. Zanni-Deffarges and Shanahan [14] compared diffusion rates in bulk and bonded epoxy adhesive to show that capillary effects near the oxide-polymer interface can significantly enhance the diffusion rate of water in bonded joints. Once reaching the bond line, moisture can hydrate the oxide. This leads to the formation of oxyhydroxides, a weaker form of oxide with a larger volume [15]. Ultimately, this can lead to cohesive fracture within the hydrated oxide (Fig. 2 (E)). Alternatively, the presence of water at the interface can displace the previously formed bonds between the oxide and the resin, leading to delamination by de-adhesion (Fig. 2 (D)). Another dangerous failure mode is *bondline corrosion* (Fig. 2 (F)). It occurs when a relatively pure aluminum clad layer is present, which function as a sacrificial anode to the base materials. Also this type of failure is facilitated by the diffusion of water and other corrosion-initiating species (e.g. chlorine ions). Once bondline corrosion is initiated, it is characterized by disbonding at the interface followed by localized corrosion.

Pure aluminum metal has an inherent corrosion resistance due to the presence of a relatively uniform and thin oxide layer that protects the underlying metal [16]. This is caused by the high affinity of aluminum towards oxygen. Whenever the fresh metal surface is exposed to the atmosphere as, for example, in case of mechanical damage a new oxide layer will be formed. In dry conditions, this oxide film is typically a dense barrier layer of amorphous alumina (Al_2O_3) that is only 2 to 3 nm thick. In humid environments, this oxide will be covered by a more permeable hydrated aluminum hydroxide ($Al_2O_3 \cdot xH_2O$) at the outer surface. In that case the thickness of this layer can reach up to 10 nm [16]. These thin oxide layers are stable over a fairly broad range of pH ($4 < pH < 8.5$), providing aluminum with sufficient protection for various commercial purposes. At both lower and higher pH values this layer is not stable and it will dissolve [17].

Nevertheless, aluminum in aerospace applications is mainly used in its alloy form. The most commonly employed types of aluminum in the aerospace industry belong to the 2xxx and 7xxx alloy series. Within these families, AA2024-T3 and AA7075-T6 are the most used ones to date. The main alloying elements include copper (Cu), magnesium (Mg) and manganese (Mn) in AA2024 and zinc (Zn), magnesium (Mg),

copper (Cu) and silicon (Si) in AA7075. [18]. These heat-treatable alloys develop their strength by precipitation hardening. As a consequence, the microstructure of these alloys is very complex, presenting several second phase and intermetallic particles. The addition of alloying elements, though essential for mechanical properties, can have detrimental consequences on to the substrate's corrosion resistance. The electro potential differences between local areas of compositional differences can lead to galvanic coupling and selective dissolution of the more active element. The most common type of corrosion in aluminum alloys is pitting corrosion due to second phase particles in the matrix acting as cathodes or grain boundary precipitation causing precipitate-free zones. These phenomena are especially pronounced in AA2024-T3, which contains relatively high amounts of copper, a nobler element to aluminum. These localized attacks can proceed to considerable depths within the substrate and may lead to grain fallout when proceeding along grain boundaries. Detailed mechanisms of localized corrosion of AA2024-T3 under chloride conditions can be found elsewhere in the literature [19-21].

Additionally to their corrosion sensitivity, the surface of the substrate in its 'as-received' state is not suitable for bonding. Metallurgical processing, including heat treatment and rolling, modifies the uppermost layers of the alloy surface. Fig. 3 presents a schematic illustration of these layers, which displays both compositional and structural changes, including smaller grains, enrichments in secondary particles (dispersoids) and higher concentration of Mg and Zn [22]. Additionally, the high shear forces applied during rolling are able to break and fold some of the surface oxides into the substrate. Altogether, this result in a so-called 'near-surface deformed layers' (NSDL), which present significant different electrochemical and mechanical properties compared to the bulk material. [23]. Hence, removing these NSDL should be the first step in any type of further processing.

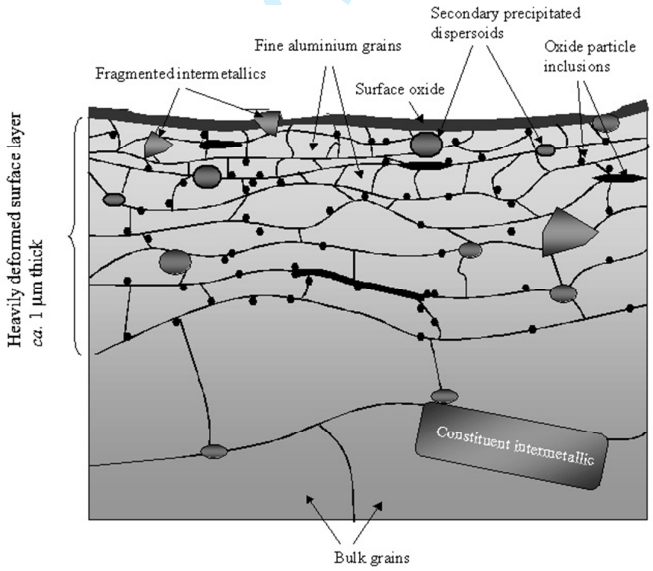

Figure 3 Schematic illustration of the modified composition of the aluminum alloy surface present after metallurgical processing [22].

3. Chromic acid anodizing (CAA)

In order to avoid the previously mentioned types of failure and to ensure long-term safety, bonded metal-to-metal assemblies must be carefully prepared. Surface pre-treatment has emerged as the most important step to provide the desired surface characteristics for bonding and minimize the effect of

surface heterogeneities, as the NSDL. The main pre-treatment schedule that is currently applied in the aerospace industry is illustrated in Fig. 4. It consists of four major steps: degreasing, pickling (or etching), anodizing, and primer application, all currently relying on Cr(VI)-based chemicals. In between two subsequent steps the surface is thoroughly rinsed in water. The following subsections describe each step of this pre-treatment scheme in terms of how it modifies the surface properties and its historical context.

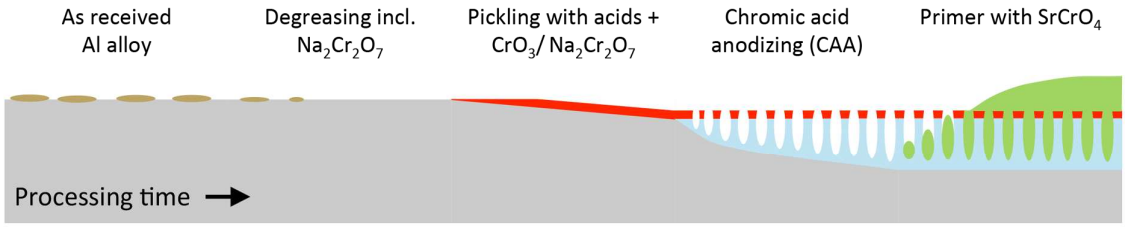

Figure 4 schematic representations of the process steps and the modifications that take place during the complete Cr-based pre-treatment that is currently applied in the European aerospace industry.

Degreasing is the first step in the pre-treatment process and normally the minimum preparation that is carried out prior to any type of metal bonding. Degreasing removes any oils, grease and contaminations that might have been introduced during aluminum manufacturing and processing [24]. This preliminary cleaning is necessary to assure that the following steps will work evenly across the substrate surface [16]. Next, the modified surface layers are chemically removed by **pickling** (also called etching). This can be performed in either acidic or alkaline solutions. The classical pickling solutions are often composed from mixtures of chromic and sulfuric acids and they are generally divided into two types: the FPL- and the CSA etch [25]. The first is the *Forest Products Laboratory* (FPL) process that was developed in the 1950s in the U.S. It consists of immersing the substrate in sodium dichromate ($Na_2Cr_2O_7$) and sulfuric acid solution for 9-15 min at 65°C. The European version of this etch, the CSA pickling, uses lower concentrations of either chromium trioxide (CrO_3) or sodium dichromate ($Na_2Cr_2O_7$) with sulfuric acid at similar temperatures, but longer immersion times (30 min.) [26]. Both methods follow a two-step reaction mechanism. In the first step, hexavalent chromium catalyses the oxidation of aluminum to alumina following Eq. 1. Next, the alumina product is dissolved by sulfuric acid (Eq. 2) [16].

$$2Al + 4H_2SO_4 + Na_2Cr_2O_7 \leftrightarrow Al_2O_3 + Na_2SO_4 + Cr_2(SO_4)_3 + 4H_2O \quad \text{Eq. 1}$$

$$Al_2O_3 + 3H_2SO_4 \leftrightarrow Al_2(SO_4)_3 + 3H_2O \quad \text{Eq. 2}$$

Since the second step is slower than the first one, a thin oxide layer is produced on the surface (as indicated by the red layer in Fig. 4). This oxide is amorphous, with a composition corresponding to alumina (Al_2O_3) and some minor concentrations (~0.5%) of Cr and S impurities. Venables et al. [27] reported that due to surface energy interactions, whiskers-like protrusions extending from the triple grain boundary points extend up to 40 nm from the surface. In their paper, the authors suggest that these branched protrusions already provide sufficient interlocking with the adhesive surface, resulting in an improved adhesion.

Unfortunately, some early in-service failures (mostly of non-bonded structures) occurred in the beginning of the 1960s, as aircrafts manufacturers started using epoxy adhesives instead of phenols [26]. The relatively thin oxide film was thus insufficient to provide reproducible and durable bonds. Consequently, an extra step, anodizing, was added to the pre-treatment schedule. **Anodizing** is an electrochemical process in which the aluminum substrate is artificially oxidized to grow a thick oxide film (up to several μm) [16]. The process derives its name from the fact that the aluminum substrate is

used as the anode in an electrolytic cell. The anode (substrate) is connected to the positive terminal of a DC power supply while a cathode (e.g. Al, stainless steel) is connected to the negative terminal. When the circuit is closed, electrons are withdrawn from the aluminum anode, which facilitate the oxidation of aluminum atoms to aluminum cations (Al^{3+}) at the metal/oxide interface. This is illustrated in Fig. 5. Since the electronic conductivity of aluminum oxide is very low, the anodizing voltage that is applied on the anodic cell encounters a resistance by the existing (natural) oxide film. This leads to a potential drop over the metal/electrolyte interface, which give rise to high electric field over the oxide layer. These electric fields are typically in the order of 10^6 to 10^7 V/m [28], which is high enough to enable oxide growth by ionic migration through the oxide [29]. Since aluminum is anodized in an aqueous electrolyte, adsorbed water at the anode will break down forming negatively charged O^{2-} and OH^-. These anions migrate towards the positively charged anodic substrate. A reaction between Al^{3+} and O^{2-} will leads to the formation of alumina, Al_2O_3, at the metal/oxide interface. Since not all the produced Al^{3+} is consumed by this interface, excess Al^{3+} cations will migrate away from the positively charged anode. Upon reaching the oxide/electrolyte interface, Al^{3+} can react with available O^{2-} forming additional alumina at the oxide/electrolyte interface. Under certain conditions, alumina ions will be directly ejected into the electrolyte. The conversion efficiency and, hence, final film morphology will depend on the balance between oxide growth and oxide dissolution (through direct ejection and chemical attack by an aggressive electrolyte). This in turn, is determined by the nature of the electrolyte and the process conditions, as discussed later.

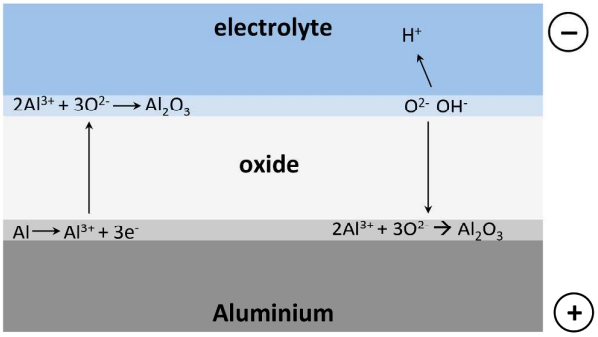

Figure 5 Schematic representation of the aluminum/electrolyte interface, showing the ionic processes involved in oxide growth during anodizing [30].

Chromic acid anodizing (CAA) was incorporated into the pre-treatment schedule in the 1960s. It mainly aimed to improve the overall corrosion resistance by producing a thicker physical barrier between the metal and its environment. Although anodizing can produce barrier- and porous-type oxide morphologies, porous films are preferred for bonding purposes. As illustrated in Fig. 6, porous anodic oxides consist of a compact barrier layer on the bottom and a relatively regular hexagonal porous structure on top [31-34]. These films are created when the anodic oxide is sparingly soluble in the anodizing electrolyte [31, 35]. In Europe, the 40/50V Bengough-Stuart process was adapted, using 2.5-3.0 wt.% chromic acid (CrO_3) at 40 °C [36]. The voltage across the electrolytic bath is initially raised to 40V in the first 10 minutes. This voltage is then maintained for 20 more minutes before it is raised to 50V, where it is kept constant during the last 5 minutes [37]. The higher voltage at the end results in a thicker barrier layer, providing an extra thick barrier for corrosive species [38].

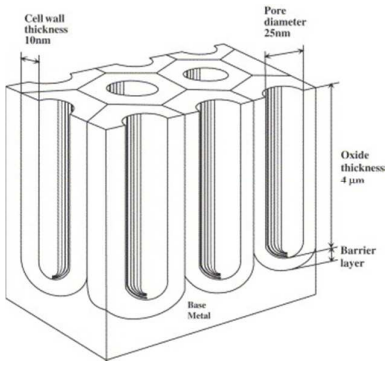

Figure 6 An idealized illustration of the anodic oxide structure formed on clad alloys following the 40/50 V CAA process [36].

This process produces 3-4 μm thick oxide layers on both AA2024-T3 and AA7075-T6 (bare and clad). It is a relatively ductile oxide with very low (0.1-0.3 wt.%) chromium content in the oxide. The oxide is moderately resistant to attack by moisture, although hydration has been reported [24]. This treatment, combined with prior CSA etching, was soon established as an effective pre-treatment for adhesive bonding and become an industrial standard.

In regular manufacturing operations, a certain time interval (several hours up to several months) usually passes between substrate pre-treatment and bonding. During this time, the freshly prepared oxide is susceptible to damage, contaminations, and environmental degradation [39]. This is prevented by the application of a thin layer of **primer** to seal the oxide immediately (within two hours) after the pre-treatments, when surface activity is maximal. Primers are diluted polymeric coatings, usually matching the chemistry of the adhesive. The primer functions as a physical barrier between the pretreated surface and its surrounding. Except for surface protection, primers are also used to promote adhesion. Two contributing mechanisms can be distinguished; (1) improved surface wetting and (2) providing stronger chemical interactions. The first mechanism is driven by the primer's lower viscosity (compared to the adhesive) and the addition of wetting agents. Kinloch et al, [40] compared PAA films that were bonded with- and without primer to show that a primer is able to penetrate deep and completely fill the pores, providing better adhesion. The second mechanism uses coupling agents to form a covalent bond across the inorganic-organic interface. Coupling agents are molecules with dual functionality. They contain organic end- groups such as methoxy (CH_3O-), ethoxy (CH_3CH_2O-) or hydroxyl (HO-) attached to a metallic central atom (e.g. silicon, zirconium or titanium) [41]. Organosilane coupling agents are the predominant chemical type of adhesion promoters. These groups are able to adsorb on the metal oxide surface through hydrogen bonds. Upon curing, a metallosiloxane bonds (Al-O-Si) are formed with the surface oxide [42]. These covalent bonds are much stronger than hydrogen bonds. Any remaining silanol groups will condense with themselves, forming a dense Si-O-Si network. Since Al-O-Si bond can be hydrolysed, the durability of these bonds will be determined by the extent of cross-linking of the Si-O-Si bonds, which will determine the hydrophobicity of the covering siloxane film. Hence, adjusting the chemical composition to tailor the desired film properties is essential. It is important to also match the reactivity of the coupling agent with that of the adhesive [41]. Different studies have demonstrated that silanes are capable to improve interfacial adhesion [40, 43-45], as well as corrosion resistance of coated aluminum [46, 47]. Song and van Ooij [48], for example, have shown that by combining two types of silanes, namely 1,2-bis(triethoxysilyl)ethane (BTSE) and ϒ-aminopropyltriethoxy (ϒ-APS), it is possible

to design a dual functionality interface that would give good corrosion protection and will be compatible with an epoxy adhesive. Since silanes connect via the OH- groups on the substrate, maximizing their amount on the substrate is desired. A study by Franquet et al. [49], showed that chemical pre-treatments affecting the amount of surface hydroxyl groups will in turn affect the silane film uniformity and thickness. Therefore, when silanes are applied, prior surface pre-treatment is still needed.

4. Cr(VI)-free alternatives to CAA

Health and environmental issues, together with the increasing costs associated with the treatment and disposal of solutions containing hexavalent chromium initiated a large number of studies over the past decades. To avoid an exhaustive comparison of the different process parameters, this section will focus on the different methods rather than specific outcomes of the most relevant alternative Cr(VI)-free pre-treatments for structural bonding. For a detailed list of the specific pre-treatments and evaluation techniques, readers are encouraged to consult the review published by Critchlow and Brewis [24].

4.1 Phosphoric acid anodizing (PAA)

For economic reasons, anodizing was initially rejected in the US until Boeing introduced phosphoric acid anodizing (PAA) in 1975, which makes PAA the first commercial alternative to CAA. The PAA process applies 10wt.% phosphoric acid at 21-24 °C. Anodizing is conducted at constant voltage of 10-15 V for 25 minutes. The PAA oxide is considerably thinner (typically 0.5 to 2 µm) and more porous than the CAA film [50]. However, it has an advantage, since the composition of the outer part of the film corresponds to non-hydrated $AlPO_4$ in the outer layer (see section 5.2), which provides higher resistance to humidity and even to hot water sealing. This resistance is attributed to the stability of the chemical bonds between aluminum and phosphate [51] [52] and, therefore, provides an effective environmental stability during service [53]. Nevertheless, studies show that the corrosion resistance of PAA oxides is inferior to those of CAA, which explains why this process was developed together with the introduction of chromate inhibiting primers. Hence, although the PAA process is Cr(VI)-free it typically requires the additional support of (active) protective coatings that contain corrosion inhibitors. So far, the most effective inhibitors are Cr(VI)-based pigments and the search for Cr(VI)-free alternatives is still in progress. Some green inhibitors are based on inorganic species (including lithium, Cr(III), rare-earths, molybdates and vanadates), while others are base on organic functionalities [54].

4.2 Mixed electrolytes anodizing

In addition to PAA, one of the most popular anodizing electrolytes is sulfuric acid. Conversely to PAA, sulfuric acid anodizing (SAA) generally produces a thick and dens protective layer [55]. Therefore, SAA is commercially applied (mostly in *'hard'* conditions) for decorative and corrosion protection applications. However, the same properties that provides it with excellent corrosion and wear resistance deliver poor adhesion [56]. One method to overcome this limitation is to mix sulfuric acid in the anodizing bath with the more aggressive phosphoric acid, thereby providing the conditions to produce an intermediate oxide structure with morphological dimensions comparable to CAA. The process, named phosphoric-sulfuric acid anodizing (PSA) was developed by Kock et al. [57]. The first PSA process contains equal amounts of sulfuric- and phosphoric acids (100 g/l). Similar to PAA, phosphates are found in the outer layer of the oxide [58], providing an additional hydration resistance. Recent investigations by the authors covered a broad range of process parameters: different concentrations of phosphoric and

sulfuric acids, together with ranging temperature and duration in the search for the optimal PSA conditions [59]. Oxide films with wide morphological variations (e.g. pore size of 5 to 60 nm and layer thicknesses of up to 6 µm) were prepared by changing the anodizing conditions (especially phosphoric acid concentration and electrolyte temperature). These conditions were found important for the performance of the bond, as tested by dry and wet floating roller peel tests. Currently, the PSA process is considered a viable alternative to CAA and will be implemented at Fokker Aerostructures in the near future.

Already in the 1960s, a mixture of tartaric and sulfuric acid anodizing (TSA) was suggested by Kape [60]. Unfortunately, the resulting porosity is relatively low and adhesives cannot easily permeate into the oxide layer. Hence, the analogous TSA process is mainly used in *non-structural* applications. The role of tartaric acid, according to a study by Curioni et al. [61] is reducing the current density and thereby reducing the oxide growth rate, so that the of the final film thickness is lower than for normal SAA. More interestingly, however, an improved corrosion resistance is observed. This resistance is explained by a "buffering effect" that tartarate ions remnants in the oxide are providing. During anodizing, tartaric acid can combine with aluminum cations to produce aluminum tartrate, a compound that is highly soluble in the acidic anodizing solution but with relatively low solubility in water. During subsequent rinsing, the pH is rapidly increased and relatively large amounts of aluminum tartrate may precipitate at the pore walls. As a consequence, if the oxide is exposed to a corrosive environment during its use, aluminum tartrate may re-dissolve, producing a local buffer, thereby limiting the susceptibility to localized corrosion. Even further improvements in the corrosion resistance of TSA films were registered after hot water sealing [62] and by the addition of molybdate salts into the anodizing bath [63].

4.3 Two-step anodizing

Relying on this TSA advantage, a new type of processes has emerged, which combines two-step anodizing. In this case TSA anodizing follows PSA to provide a duplex oxide with both corrosion resistance and adhesion capabilities. The resulting structure shown in Fig. 7 (a) is reported to be suitable for adhesive bonding of structural components [64].

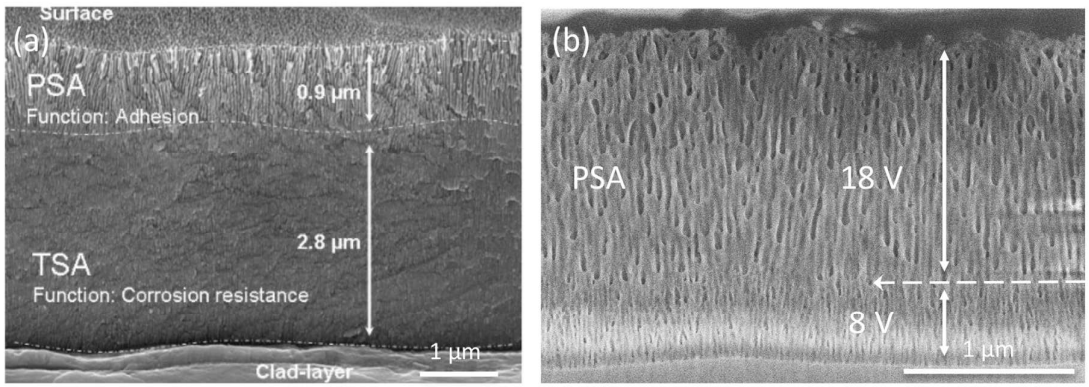

Figure 7 Cross section of the anodic oxide produced on 2024-T3 clad by (a) TSA+PSA process [64] and (b) PSA dynamic anodizing, with voltage decrease from 18 V to 9 V [65].

Similar process is the boric-sulfuric acid anodizing (BSAA) that has been patented by Boeing as an alternative to CAA [66]. The oxide structure resembles SAA, but with finer pores and more uniform

hexagonal arrangement compared to CAA, showing promising results [67]. Zhang et al. [68] report an improvement in bonding and durability of panels created by the BSAA process by the addition of phosphoric acid to the anodizing electrolyte. The process is reported to result in bigger pores, improving primer penetration and extending oxide durability. Because boric acid is also hazardous, using it as a replacement is not generally desired, especially since it may be subject to future regulations.

Similarly to two-step anodizing, dynamically changing the anodizing voltage/current during the process can be used to vary the oxide morphology across its thickness. A SEM cross section of such an example is shown in Fig. 7 (b), possibly providing an alternative for a two-step anodizing process. In an investigation by van Put et al. [65] this complex oxide morphology was formed by an instantaneous voltage decrease during anodizing. Since the pore size is linearly related to the applied voltage, an instantaneous decrease from 18V to 9V forces the formation of new pores with smaller diameters below existing larger pores. As a result, a distinct border between the two morphologies is formed (indicated by the arrow in Fig. 7 (b)). Conversely, applying a voltage increase did not produce the reverse morphology and a transition layer was formed by partly dissolving the walls of smaller pores after the sudden change.

4.3 Electrolytic deoxidation

Earlier study by Venables et al. [27] have shown that fine oxide protrusions produced by the FPL etch on top of a PAA oxide are beneficial for good adhesion. This is desired from adhesion point of view, because protrusions, even just nanometers long, create an additional reinforcement by interlocking with the resin. Likewise, Yendall and Critchlow [69] suggests a method that applies electrolytic phosphoric acid deoxidizer (EPAD) before anodizing. In that respect EPAD replaces the FPL etch in producing an open top layer that comes into contact with primer/adhesive (Fig. 8). They found that this method improves the mechanical properties of the bond depending, however, also on the anodizing temperature used for SAA. In this case, it is important to keep in mind that the choice of electrolyte and applied temperature will also affect the resulting morphology. As discussed later in sections 5.1 and 5.4, if the anodizing conditions are too aggressive, the EPAD layer may (in part or completely) dissolve during subsequent anodizing.

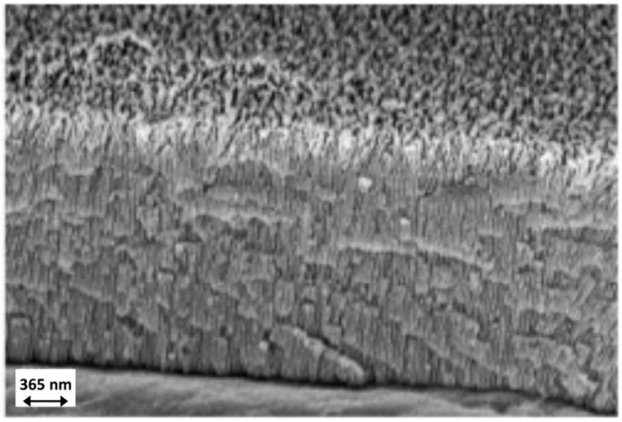

Figure 8 Cross section of AA2024-T3 clad after EPAD and SAA [69].

4.4 AC Anodizing

An interesting alternative applies alternating current (AC) instead of the traditional direct current (DC) for anodizing. AC anodizing was originally developed for high-speed coil applications in the automotive industry [16]. Relatively elastic oxide layers are developed by treatment at higher temperatures and higher anodizing currents. Both sulfuric- and phosphoric acid processes have been reported, with the conditions listed in Table 1. Though developed as a continuous process, batch operation is also possible.

Table 1 Anodizing parameters [70].

Parameter	H_3PO_4	H_2SO_4
Acid concentration, wt.%	10	15
Temperature, °C	50	80
Time, min.	12	30
Current, A/dm^2	4	10

As in other AC processes, hydrogen evolves on the surface of the anode during the cathodic cycle. This is sufficient to remove organic contaminants as well as natural present oxides, so that separate steps for cleaning and deoxidizing prior to anodizing are not required, thereby drastically reducing the amount of processing tanks [70]. Since the resulted oxides are thin, their performance is comparable to the etching rather than anodic oxides [71]. Hence, a U.S. patent by Critchlow et al. [72] suggests applying a two-step process that includes subsequent AC and DC PSA anodizing in the same bath. This combination produces an oxide film that has a thin porous outer layer (less than 1 μm) and a relatively thick (up to 8 μm) uniform inner layer to yield an optimal combination of corrosion protection by the dense inner layer, and adhesion provided by the porous outer layer.

4.5 Anodizing with post-treatments

Correspondingly, a post-treatment immersion of the relatively dense anodic oxide in a dilute acidic or alkaline solution will produce the desired morphology by chemically attacking the oxide to partly dissolve it and open the pores. Both Arrowsmith and Clifford [73] and Yendall and Critchlow [69] applied phosphoric acid dip after SAA (or BSAA) anodizing to report an improved short and long-term durability of the produced bonds. The narrow pores close to the substrate are considered to provide the corrosion resistance, while the etched top layer is able to better interlock with the primer/adhesive. In order to avoid over-etching, the time, nature and concentration of the etching solution should be controlled [74]. Such post-anodizing step is not new to the aviation industry, which frequently applies post- anodizing immersion in boiling water to seal the porous oxide layer when it serves as a protective coating against corrosion instead of a receptive surface for bonding.

An interesting alternative to a post-treatment dip concerns anodizing combining positive and small-negative voltages. The negative charge at the end of the normal anodizing cycle leads to dissolution of the oxide by hydrogen ions attracted to the temporary negative pole [75]. In this case, the dissolution is done in the same bath as anodizing, reducing the need for an extra processing and rinsing bath.

4.6 Non-anodizing processes

As previously mentioned, immersion in hot water is often used to seal off the anodic pores. Treatment in boiling water (and even water at 40 and 50 °C, [76]) leads to hydration of the present Al_2O_3 and to the formation of a pseudoboehmite (AlOOH) oxide. Although sealing the pores openings is not desired from a bonding perspective, boiling water treatment has been suggested as a stand-alone treatment to replace anodizing. The hydrated form of oxide has been reported to provide many benefits, besides it being an inexpensive alternative: a highly-porous morphology with a large surface area [77], increased number of surface hydroxyl groups [78] and a low contact angle [79]. Oxide morphology will depend on the temperature and the duration of the treatments. Three representative morphologies are presented in Fig. 9. After just 30 s of immersion the surface oxide exhibits a cellular structure with thin ridges (approx. 10 nm wide) that provide large porosity. As the treatment time is extended, cell walls develop into distinct plates (of increased thickness) that are oriented normal to the surface. When the time is extended up to 4 hours, the cell walls significantly thickness, producing a distinctive and much less porous structure [80]. Unfortunately, this type of oxide is brittle and mechanical tests often show an early cohesive failure within this pseudoboehmite layer [77, 79]. Although in some cases, the combination of prior grit blasting and the addition of a silane layer was shown to reproduce results comparable to the benchmark used (CSA+PAA), its level of success is highly sensitive to alloy composition [80]. Hence, boiling water treatment generally does not compare with the durability of anodized-based oxide layers.

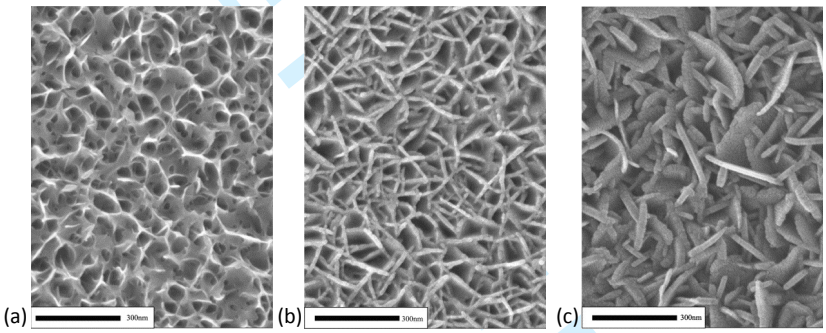

Figure 9 High-resolution SEM micrograph after boiling water treatment on AA2024-T3 clad for 30 s (a), 60 min (b) and 240 min (c), edited from [80].

A similar option consists of a steam treatment [81, 82]. A study by Ud Din et al. [83] have shown that oxide layers with thicknesses comparable to anodic oxides can be produced. Depending on treatment parameters and steam chemistry, layers of few nanometers up to 3 μm can be formed. The addition of acidic components (citric or phosphoric acids) to the steam enables the growth of thicker layers and help in the corrosion protection (especially due to incorporation of phosphates).

5. Parameters affecting the anodic oxide film properties

Considering the list of alternative methods in section 4, it appears that most processes are based on similar electrolytes that apply different preparation conditions to produce certain desired oxide properties. Hence, it is important to understand which key parameters control the anodizing process and how these, in turn, change the oxide film characteristics.

5.1 Electrolyte type

The nature of the electrolyte is one of the main parameters to determine the oxide properties, such as morphology and chemistry (as discussed in section 5.2). The pore size is a direct function of the

electrolyte as found by Keller et al. [84]. Interpore distance and barrier layer thickness are also affected, but to a lesser degree. The pore size generally increases in the order SAA < TSA < CAA< < PSA< PAA [85].

5.2 Incorporation of anions

Besides the ionic species (Al^{3+} and O^{2-}/OH^-) that are responsible for oxide growth, any ion species that is present in the solution may be affected by the electric field. Since the anode is positively charged during anodizing, negatively charged species from dissociating acids will migrate towards the oxide, leading to the incorporation of impurities into the oxide. The extent of incorporation is determined by the nature of the electrolyte solution, the applied conditions and the film type. A range of surface analysis techniques, including Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and glow discharge optical emission spectroscopy (GDOES) [86, 87] have been applied to measure the concentration and distribution of electrolyte-derived impurities in the film. These studies show that the migration of electrolyte species varies from one electrolyte to the other. Table 2 lists the concentration of anions within the most common anodizing electrolytes. It demonstrates that almost anion-free films are formed in chromic acid, while other anions of alternative electrolytes contribute to a much higher relative composition. Since most electrolyte anions migrate at slower rates than the O^{2-} ions, a relatively pure alumina region is formed close to the aluminum/oxide interface [88]. This is indicated in Fig. 10 that displays a comparison of the resulting oxide composition in SAA and PAA. Sulfate anions can migrate into the inner most part of the cell wall, resulting in a duplex oxide composition. Phosphate anions, on the other hand, exhibit a triplex structure with maximal concentration in the region near the interface with the electrolyte. In the mixed PSA (Phosphoric- sulfuric acid anodizing) electrolyte, the incorporation of phosphate on *barrier-type* oxide indicated that the phosphate incorporation in the mixed electrolyte is somewhat inhibited, and phosphates remained close to the oxide/resin interface [58].

Table 2: Percentage of incorporated anions in the porous oxide layer [85].

Electrolyte	H_2CrO_4	H_3PO_4	$H_2C_2O_4$	H_2SO_4
Anion concentration (at.%)	0.1 – 0.3	6 - 8	2 - 3	10 - 13

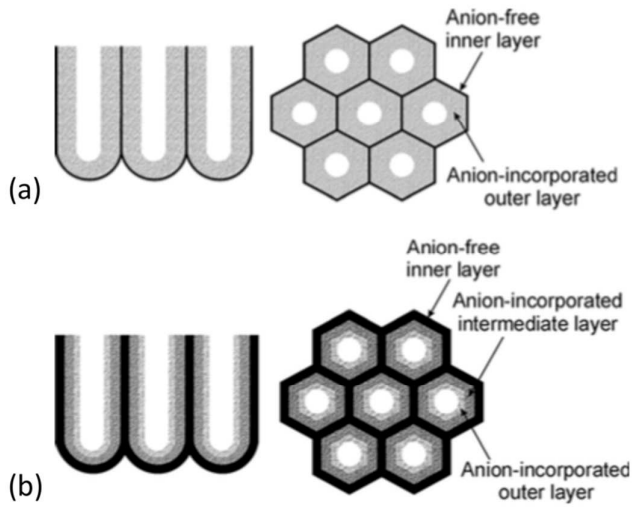

Figure 10: Schematic representations of the sectional and plan views of, respectively, the duplex (a) and triplex (b) structures of porous alumina cell walls formed in sulfuric and phosphoric acids, respectively [85].

Compared to barrier layers, porous film generally contain a higher anion content in the oxide structure [85]. This is explained by the fact that the electric field at the barrier layer is not uniform, so that the semi-spherical shape of the pore base results in a much higher electric field close to the electrolyte/oxide interface, which in turn supports easier incorporation of anions. In addition, the long-term exposure of the oxide walls to the electrolyte readily allows for active penetration of the acid.

Anion incorporation has an effect on the properties of the oxide film, such as the mechanical (e.g. flexibility and hardness) the chemical properties and the space charge [89]. Thompson and Wood [90] reported a transition from solid to gel-like material moving across the cell walls towards the pore interior, with the thickness of this layer depending on the electrolyte, the voltage or current density, and the temperature. Another example is the resistance to hydration that is provided by oxides produced in phosphoric acid. This resistance has been contributed to the presence of $H_2PO_4^-$ ions in the anodic films. These anions can be further decomposed to proton, H^+, and HPO_4^{2-}, thereby retarding the hydration of alumina [68]. The applied electrolyte also seems to have an influence on the water content of the film. Although no water is found in the bulk of oxides formed in acid electrolytes, chemical adsorption (chemisorption) of OH^- groups and water molecules at the outer layer is reported [91]. This can, according to findings on chemically grown aluminum oxides, affect the extent in which the oxide interact with organic molecules and resins [92].

In a recent publication by the authors [58] we have quantified the relative amount of O^{2-}, OH^-, PO_4^{3-} and SO_4^{2-} species at the surface of *barrier-type* PAA, SAA, PSA and CAA oxides using X-ray photoelectron spectroscopy (XPS). Results show that the surface chemistry of anodic oxides is highly affected by the incorporation of anions. Phosphates were the highest with 40 % of the surface species and no hydroxyls at the applied conditions. Sulfate concentration is lower at 15 % and a negligible amount of anions in CAA. It was confirmed that the incorporation of phosphate and sulfate anions comes at the expense of surface hydroxyls. Consequentially, we investigated how variations in the chemical species at the oxide surface after anodizing affect the interaction with an organic resin. In the first instate, this was studied using molecules that represent typical aerospace adhesives. Results show that bonding with two phenol-based molecules and amine molecule both proceeds through the surface hydroxyls. However, interactions with some molecules were sensitive to chemical changes while others did not. Next, mechanical peel tests with barrier-type anodic oxides that were bonded with an industrial epoxy adhesive. We concluded that the bonding mechanism was not affected by anion incorporation, only its extent. Since phosphate and sulfate incorporation reduces the amount of hydroxyls available for interactions, anodizing in these electrolytes was considered inferior from a chemical interactions point of view [93].

5.3 Potential / current density

At steady state growth, a dynamic equilibrium exists between pore base dissolution at the oxide/electrolyte interface and oxide growth at the metal/oxide interface. Studies have shown that the major film characteristics (pore diameter *d*, cell diameter *c* and barrier layer thickness *b*, as indicated in Fig. 11) are directly related to the applied potential [84, 94]. This is explained by the fact that stationary film formation occurs at a constant rate, which is determined by the average field over the oxide [95]. Higher potential values will result in thicker barrier layers, larger cells, and wider pores. The thickening of the barrier layer was found to show an almost universal relation, growing at 1.3-1.4 nm/V for

barrier-type films and about 1.2 nm/V for the barriers under porous films, with only small deviations as a function of the temperature and the electrolyte type [85].

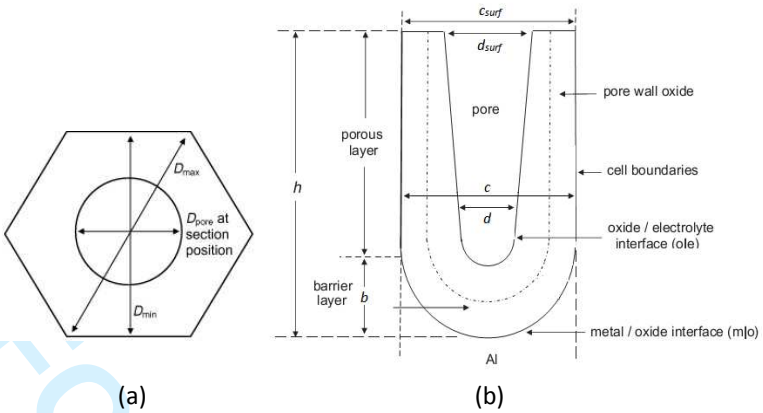

Figure 11: Schematic representation of an ideally hexagonal columnar cell of a porous anodic alumina film [95].

Any tendency of a pore to become too big or too small will be compensated by its curvature that will, accordingly, adjust field strength [96]. If during the anodizing process, a large variation in potential is induced, the oxide film will adapt itself to the new applied conditions. This observations, together with a 'recovery effect' was reported by Curioni et al. [97], using cyclic polarization measurements. The recovery effect is the elapsed time before the steady-state characteristic conditions of the new voltage are attained. It will depend on the potential variance, as well as the bath conditions (electrolyte, temperature). Dynamically varying the anodizing potential during the treatment was used by van Put et al. [65] in order to change the pore size across the oxide thickness, creating complex oxide morphologies. This may explain the gradient of voltage that is applied during the conventional 40/50V CAA anodizing process, providing wider pores at the bottom of the film and thickening the barrier layer. This is an interesting observation that can be used as opportunity in developing new processes.

5.4 Temperature and time

Another significant variable in the anodizing conditions is the electrolyte temperature. A higher bath temperature will enhance local dissolution at the pore base. This, in turn, will result in an increased local current density, which will increase the ionic transfer and oxide formation rates [98]. Aerts et al. [99] have shown that a higher rate of oxide dissolution, due to the aggressiveness of the electrolyte at higher temperatures, have increased the porosity in sulfuric acid anodizing (with a constant convection) from 4% at 5℃ to 32% at 55℃. Dissolution effects are mainly noticeable at the outer layer of the oxide, leading to pore broadening [100]. Upon extended anodizing times, aggressive electrolytes will cause excessive chemical dissolution. Since the oxide is only growing from within the metal, the outer part of the film is in contact with the electrolyte for a longer time period and therefore suffers from the most chemical attack. This phenomenon induces pore widening at the outer surface, which affects the general shape of the pores. This is why cone-shaped pores are often reported; with the pore diameter at the pore base (d in Fig. 11 (b)) generally exhibiting a linear correlation to the anodizing voltage, while pores at the surface (d_{surf} *in* Fig. 11 (b)) are frequently larger [59]. Interestingly, controlling the electrode temperature can have a larger influence on oxide formation than changing the electrolyte temperature [101]. Hence, physical bath properties, such as convection-based heat transfer should be considered.

At high anodizing temperatures and longer times, dissolution has an even larger influence on oxide morphology. An example is shown in Fig. 12 for different electrolyte temperatures and dwell time. At relatively lower temperatures and shorter times whiskers are formed on top of the hexagonal oxide structure. These are created by extended dissolution and thinning of the pore walls. At some critical point, these filaments are so long and thin, that they will collapse, forming a so-called 'bird's nest' structure on top of the oxide film (Fig. 12 m-o).

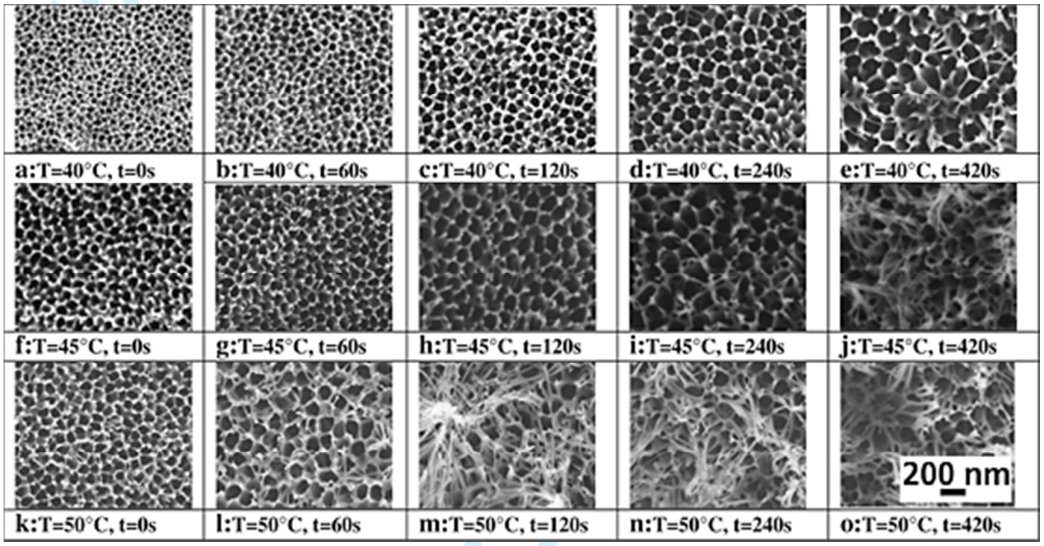

Figure 12: SEM of the oxide layer depending on the bath temperature and the dwell time - surface views (anodizing potential E = 50 VSCE) [102]. Longer time and higher temperatures lead to their collapse and the formation of a 'bird's nest'.

5.5 Pre-texturing

Studies have shown that surface features produced by prior steps are related to pore initiation and development. Following the previously discussed growth mechanism, geometrical (near-)surface features like the rolling lines, scratches and rolled-in oxides locally increase the curvature and therefore present preferential regions for pore initiation and development. It has been shown by Terryn [103] that such features can even pre-impose the alignment of pores to develop certain orientation. This is especially relevant when the step prior to anodizing produces characteristic surface features. If a highly-regular pore arrangement is required, as in the production of alumina template for nanostructure fabrication, a two-step anodizing (with intermediate dissolution of the oxide) is used to produce a well-ordered structure, in which the first anodizing step is used to texture the surface [85]. Since this method is both time-consuming and expensive, pre-texturing by anodizing is generally not applied in the aerospace industry.

5.6 Alloy composition

The presence of alloying elements has an effect on the anodizing potential, as well as the oxide morphology. Since elements in solid solution will change the resistance to current flow, the purer the aluminum, the more resistance to ionic transport [104].

It is generally also observed that the same process conditions can yield completely different forms of anodic films on bare and clad aluminum substrates. Fig. 13 shows a comparison between the CAA 40/50V anodic oxide on clad and bare AA20204-T3. The high purity clad alloy shows a relatively regular columnar structure while no evidently regular structure is observed on the bare material, which resembles a sponge-like structure. This difference is attributed to the presence of second phase particles and alloying elements with a different potential than that of the matrix [69, 105, 106]. Alloying elements with more negative potential will oxidize with aluminum and enter the anodic oxide, while nobler alloying elements like Cu do not. Cu concentration will then rise, leading to enrichment at the metal/oxide interface, immediately beneath the oxide film [107, 108]. It has been shown by Garcia-Vergara et.al [109] that cyclic oxidation of copper in the enriched layer below the barrier layer results in oxygen generation that leads to gas evolution and lateral porosity, resulting in the irregular anodic oxide structure that is produced on bare A2024-T3. Correspondingly, similar process conditions may lead to different oxide weight and morphology on different aluminum alloys.

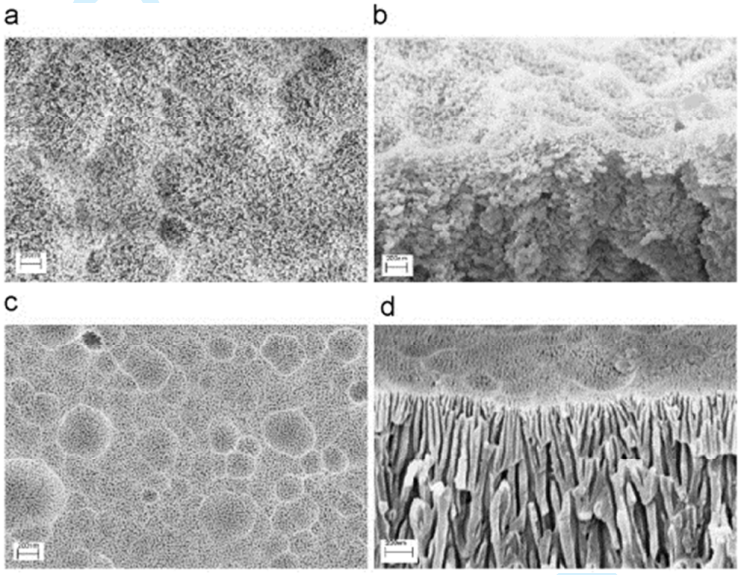

Figure 13: CAA 40/50 V processed, 2024-T3 bare: plan view (a) and cross-section (b), 2024-T3 clad: plan view (c) and cross-section (d). Reprinted from [69], Copyright (2016), with permission from Elsevier.

6. The relation between oxide properties and adhesion

The two main oxide properties that are influenced by the different process parameters are oxide composition and morphological features. Yet, it appears that the main objective in the development of Cr(VI)-free processes so far was to reproduce the CAA morphological features using different types of processes. One of the longest, yet, on-going discussions in the literature concern the adhesion modes. Various theories exist to explain adhesion between different materials: diffusion, electrostatic interactions, weak boundary layer, mechanical interlocking and physical chemical adsorption (or interactions) [110]. Amongst these theories adsorption and mechanical models are considered most relevant for metal/polymer bonding.

Different authors argue that the high level adhesion that is achieved with porous anodic oxides is mainly due to mechanical interlocking [27, 111-113]. However, studies on both chemical and anodic oxides have shown that oxide chemistry also plays a vital role in the nature and type of interaction with the organic resin [92, 114-117]. In an effort to separate the two contributions, a study by the authors using

FM 73 epoxy adhesive shows that significant initial adhesion strength can be achieved without mechanical interlocking and independent of the type of electrolyte. The measured dry peel strengths were in the same level of the dry strengths measured for porous oxides with a relatively small pore size (up to 20 nm). However, porous oxides with wider pores performed better. Above approximately 25 nm pore size, tests showed no further improvement in dry peel strengths [59]. According to these observations, it is not possible to conclude which is the dominating adhesion mechanism. Both mechanical interlocking and a larger contact area could provide this improvement in strength.

Conversely, the stability of the interface under water ingress was found to be highly dependent on the oxide chemistry and anodizing conditions, especially the electrolyte type, concentration and temperature. Chemistry effects were correlated to the amount of surface hydroxyls, which were found to be the reacting entities between the oxide and the resin [116], while morphological considerations were mainly attributed to changes in the surface roughness [59]. Nevertheless, bond strength and durability both appear to be closely related to the ability of the oxide and the resin to form a cohesive interphase. Although mechanical interlocking is considered to contribute, there is no conclusive evidence for its dominance.

Another important aspect in bond durability is the resistance to bondline corrosion. It appears that increasing the oxide porosity and surface roughness will improve adhesion. However, as also claimed to PAA, one of the main challenges is to provide a high level of corrosion resistance in a very porous system. Consequently, failures due to bondline corrosion were observed with PSA test panels produced at relatively aggressive conditions and lower voltages [59]. Oxides produced in the same conditions (electrolyte, temperature and time), but at higher voltage did not fail. This seems to indicate that the presence of thicker barrier-layer that is formed at higher voltages may be playing a significant role. Furthermore, this is the reason why many studies combine the production of a receptive open structure at the outer layer, while aiming to provide better corrosion protection by a denser inner layer. Nevertheless, a recent (unpublished) investigation of the authors indicates that the corrosion resistance of the interface is also largely determined by the chemical composition of the adhesive. Hence, the chemical nature of the oxide *and* the adhesive should be considered.

7. Summary and Conclusions

The required bond performance and durability, together with the corrosion sensitivity of aerospace aluminum alloys, have led to the development of a multi-step pre-treatment process that is carefully designed to provide the desired surface characteristics for bonding and corrosion resistance. In this pre-treatment, the use of Cr(VI)-based chemistries currently still has a crucial role. The importance of finding a replacement is evident by the large amount of literature available on this subject. It is, however, also clear that the success and versatility of Cr(VI)-based applications is one that is very difficult to duplicate. While many Cr(VI)-free alternative options exist and much is known about the relation between the principal process parameters and oxide properties, maximizing bond performance and corrosion resistance is not straightforward. The fact that both atomic- and molecular interactions, as well as mechanical interlocking are crucial for the formation of interfacial bonds are now beginning to be reflected in practical and industrial research. Hence, it is of pivotal importance to adjust both oxide chemistry and morphology in order to produce the desired oxide characteristics. It remains of great academic and industrial interest to continue to gain further fundamental understanding on how adsorption and mechanical adhesion mechanisms contribute to the final bond performance.

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