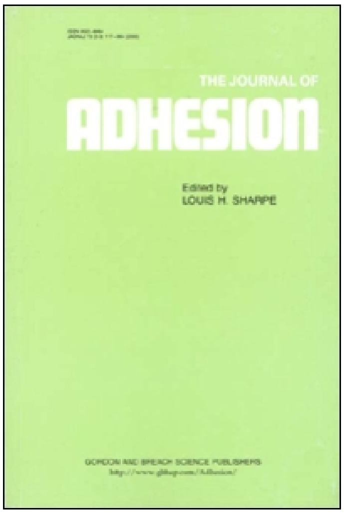

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Recent Trends in Surface Treatment Technologies for Airframe Adhesive Bonding Processing: A Review (1995-2008)

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Recent Trends in Surface Treatment Technologies for Airframe Adhesive Bonding Processing: A Review (1995–2008)

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Proper surface treatment technologies are prerequisite for achieving long-term service capability through the adhesive bonding process. However, the current surface treatment technologies used in the adhesive bonding process for aluminum alloys depend on materials that are undesirable from an environmental- or safety perspective. Suitable alternatives in the aerospace industry are the subject of much interest: non-chromate anodizing, silane, sol-gel, laser, plasma, and ion beam enhanced deposition of Al_2O_3 film. These approaches can eliminate, or greatly reduce, the undesirable hazardous materials and have been proven to deliver comparable bonding performance. In some cases these alternative processes may even outperform established processes, such as chromic and phosphoric acid anodizing.

Keywords: Adhesive bonding; Aluminum alloy; Bonding performance; Environmentally-friendly; Surface treatment

1. INTRODUCTION

To date, airframe assemblies are generally dependent on riveting by either longitudinal lap or circumferential butt joints [1]. Each fastener hole, however, acts as a stress concentrator where subsequent widespread fatigue damage (WFD) may be caused in the airframe

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structures [1–4]. This limitation often leads to either lower design stresses or reduction in maintenance inspection intervals [4].

Recently, there have been several alternative innovations in airframe assembly, including friction stir welding [5], laser welding [6], and adhesive bonding [7]. In particular, the adhesive bonding process has been used in the manufacture of aircraft structures and components for 30–40 years [7,8]. Modern metallic bonded structures using longitudinal lap joints in commercial aircrafts were introduced with the advent of the Airbus A300 [9]. This technique is currently migrating from secondary to primary structural applications as one of the most interesting ways to fasten structural parts with a high level of confidence. For example, structural adhesive bonding is mainly used for attaching stringers and/or tear straps to the fuselage and wing skins, to stiffen the structures against buckling. It is also applied to skin-to-core bonding in metallic honeycomb structures, such as elevators, ailerons, spoilers, and so on [7,10]. Details of the historical use of adhesive bonding processes on commercial aircraft can be found in the published literature [7,11–13]. This technique can offer advantages over conventional mechanically fastened joints; simplified design, weight reduction, fatigue resistance capability, aerodynamic smoothness, high structural stability, and so on. But additional technical challenges are also needed to provide engineering authorization that should be addressed in the bonded repairs: (a) qualification of materials and/or adhesive bonding process, (b) understanding of bond failure, and (c) substantiation of bond durability [14]. In particular, a critical key issue in certification involves establishing the long-term durability of the adhesively bonded joint against environmental exposure, which is generally not considered in mechanically fastened joints. The combined effects of moisture and thermal exposure, leading to hygrothermal aging, result in interfacial adhesive failure with a low joint strength [7,8,13].

Early experiences in bonding techniques demonstrated that surface treatment prior to bonding is the single most critical step which can not be disregarded, even for tertiary-loaded structures, since it is essential to achieve long-term service capability [8,15]. Thus, the proper production steps should be clearly defined before any bonding process is implemented. A particular surface treatment tends to modify the substrate surface by delivering the following features: free from contamination; wettable with either primer or adhesive; highly roughened; and mechanically and hydrolytically stable [15].

A confounding factor that prevents the complete understanding of adhesion mechanisms is the concept of the interphase zone which would be created on a treated surface area as shown in Fig. 1 [16].

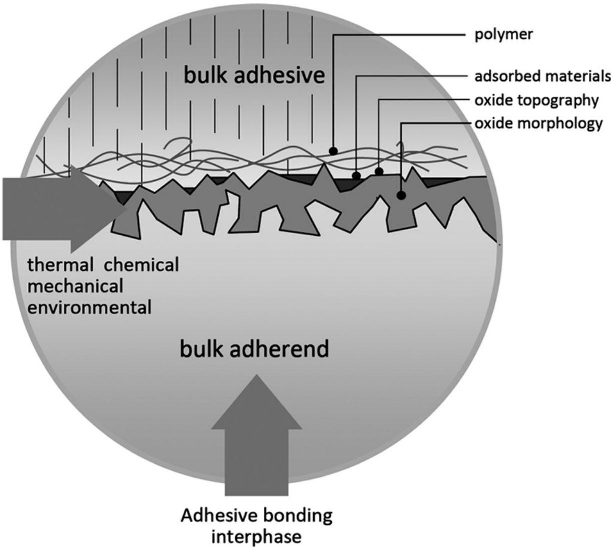


FIGURE 1 Schematic view of the representative adhesive bonding interphase (reproduced from Drzal *et al.* [16] with permission from Taylor & Francis).

The micro-structural composition of the interphase zone plays a major role in the load transfer mechanisms and capabilities of adhesively bonded joints. Even though considerable studies on these topics have been performed, joint durability is still not well correlated with fundamental adhesion mechanisms [15–18]. This is mainly due to the fact that the interphase zone is a very complex phenomenon since it involves multidisciplinary knowledge, such as bulk properties, gradient properties of treated surface, surface chemistry, and other relevant subjects.

The several review works have highlighted the different aspects of surface treatment technologies for aluminum alloys as exemplified by Critchlow and Brewis [15], Oosting [19], and Baldan [20]. Critchlow and Brewis [15], in 1996, reviewed the surface treatment technologies of adhesive bonding processes by including support for the following: general information on treatments, data collection based on the bond performances (*i.e.*, environmental durability), and interpretation of performance data, with different adhesion mechanisms, in detail. Oosting [19], in 1995, was concerned with an in-depth examination of various types of surface treatment technologies used prior to structural adhesive bonding. Baldan [20], in 2004, studied in detail the factors affecting the bonding strength and environmental durability of adhesively bonded joints. It should also be noted that Oosting [19] and Baldan [20] suggest that the study of adhesively bonded joints typically involves consideration of issues such as joint geometries, their loading conditions, materials (structural adhesive and adherend), and temperature/moisture effects.

In the field of adhesive bonding processes, it is important to consider the detrimental effects of processes on the environment, for example, the use of strong acids and hexavalent chromium. This consideration forces industries to develop and use environmental friendly surface treatment technologies as replacements for the standard acid etching and anodizing (primarily chromic and phosphoric) processes [19,21].

The primary objective of this paper is to provide the current state and recent trends in surface treatment technologies for airframe adhesive bonding processes that need to be addressed from the viewpoint of adhesively bonded structure research. The published literature for the past 14 years has been reviewed and summarized to identify the current technological developments with ongoing research efforts. Experimental data recorded have been related by subsequent cross-referencing. Each of them is briefly addressed in the following discussion.

2. SURFACE TREATMENTS FOR ADHESIVE BONDING

2.1. Aluminum Alloys

Generally, commercial aerospace sectors have utilized two aluminum alloys, *i.e.*, Al-Cu-Mg (2000 series) and Al-Zn-Mg-Cu (7000 series) for producing aircraft structures such as skins, bulkheads, and longerons, etc. [7,12]. Although the bonding technique for aerospace alloys is the focus of this review, the processes described in the next sections are commonly applicable to the majority of aluminum alloys. Major aluminum alloys used in the aircraft structures, their specifications, and temper conditions are given in Appendix Table A1.

2.2. Surface Treatment Technologies

As summarized in Table 1, the diverse range of treatments available for surface modification can be split into several broad groups: (1) mechanical (abrasion and grit blasting), (2) chemical (acid etching), (3) electrochemical (anodizing), (4) coupling agent (silane and sol-gel), and (5) novel dry surface treatments (laser texturing, plasma-sprayed, and ion beam enhanced deposition of Al_2O_3). Each treatment could be

TABLE 1 Summary of Surface Treatments on Aluminum Alloys (1995 Onwards)

Treatments	Nature of treatments	Reference sources
Grit-blast with alumina particle	Mechanical	19,21–42,46
Cryoblasting	Mechanical	28
Forest product laboratory (FPL) – including chromic acid etching	Acid etching	21–23,25,26,28,31–33,39,41,43–47,49,51
Sulfo–ferric etching (P2)	Acid etching	44,48
Phosphoric acid anodizing (PAA)	DC-anodizing	19,22–24,26,28,31–34,38,39,43,44,46–55,64
Chromic acid anodizing (CAA)	DC-anodizing	19,21,24,36,54,56,57
Phosphoric-sulphuric acid anodizing (PSA)	DC-anodizing	57,58
Boric–sulphuric acid anodizing (BSAA)	DC-anodizing	21,54,59,60
Sulphuric Acid Anodizing (SAA)	DC-anodizing	47,48,51
AC phosphoric acid anodizing (AC-PAA)	AC-anodizing	18,43,51
AC sulfuric acid anodizing (AC-SAA)	AC-anodizing	18,43,45,47,51
Silane	Coupling/ oxidation	22,24,25,29,30,31,35–37,39,40,50,52,61–65
Sol-gel	Coupling/ oxidation	34,38,41,42,46,48
Excimer UV laser (Laser)	Mechanical	30,34,35,66–69
Plasma-sprayed coating (Plasma)	Ablation/ oxidation	32,36,56,70–73
Ion beam enhanced deposition (IBED)	Ablation/ oxidation	33

introduced as a stand-alone technique, but is more often combined in sequences with rinsing and/or drying at the end of each step. Thus, their compatibilities must be also investigated and justified. This review identified examples of proven engineering practices for surface treatment technologies, which have been used to address selected technical details.

2.2.1. Mechanical Treatments (Abrasion and Grit Blasting)

As a preliminary preparation step in the multi-stage schedules, mechanical abrasion has been used to produce a macro-roughened surface and to remove an undesirable oxide layer, respectively. This method typically involves abrasive scrubbing of the substrate surface with sand paper, 3M Scotch-brite® pad and/or grit-blasting.

In particular, grit-blasting, which uses an alumina grit (50 μm particle size) with clean, dry, propellant air, is employed as a logical surface activation step prior to application of either silane [22,31,35,37, 39,40], sol-gel [38,41,42,46], or plasma [32] to modify the substrate surface for satisfactory bonding results. This mechanical treatment would introduce physico-chemical changes which yield a wettable surface and modify the surface topography, *i.e.*, a macro-roughened surface [27] (see Table 2).

2.2.2. Chemical Treatments (Acid Etching)

Typically, chemical treatment, *i.e.*, acid-etching, is an intermediate production step between degreasing, alkaline cleaning, and electrochemical treatment. Thus, this step should be compatible with post-treatments, *i.e.*, an anodizing process. Three classical acid-etching solutions were introduced to modify the substrate surface of aluminum alloys: chromic-sulphuric acid (CAE), Forest Product Laboratory (FPL), and sulfo-ferric acid (P2) etches. The surfaces treated with acid-etch were consistently reported to be out-performed by anodized surfaces so that the inconsistent results made them unsuitable for stand-alone treatment in primary bonded structures [15].

Forest product laboratory (FPL). Although numerous service bulletins (SB) and airworthiness directives (ADs) have been published due to bond durability problems with FPL, this process, which uses dichromate-sulphuric acid etch, has been the industry standard pretreatment step prior to an anodizing process (PAA) since the mid-1970s [15,74]. The FPL oxide layer consists of porous microstructures (*i.e.*, protrusions, or whiskers), and the surface is passivated with a thin oxide layer of about 40 nm in thickness [75].

TABLE 2 Comparison of Roughness 2024-T3 Produced by Mechanical Treatments

	Surface roughness (R_{av}) ± standard deviation	
Mechanical treatments	Liu *et al.* [41]	Rider [29]
Sanded (180 grit)	1.75 ± 0.06 μm	–
Sanded (220 grit)	–	1.60 ± 0.10 μm
Sanded (240 grit)	1.51 ± 0.05 μm	–
Sanded (320 grit)	–	1.70 ± 0.20 μm
Scotch-brite pad	–	1.10 ± 0.20 μm
Grit-blast	1.78 ± 0.07 μm	1.60 ± 0.10 μm

TABLE 3 Chemical Etch Composition from Ref. [75]

	Optimized-FPL	P2
$Na_2Cr_2O_7 \cdot 2H_2O$ [wt.%]	5.0	15.0^A
H_2SO_4 [wt.%]	26.7	37.0
H_2O [wt.%]	68.3	48.0
Temperature [°C]	65	60–70^B
Time [min]	10	8–15

^{A}$FeSO_4$ instead of $Na_2Cr_2O_7 \cdot 2H_2O$.
^{B}Can also be performed at room temperature.

Sulfo-ferric etch (P2). P2 etch, which uses ferric sulfate in place of toxic sodium dichromate, is a non-chromate acid etch process for the replacement of FPL [44,76–78]. This process is designated as an etch solution method II in ASTM E 864 [76] (see Table 3). The P2 method has proven to be as effective as the well known FPL method by yielding similar topographical features and a somewhat thinner oxide (<37 nm) than FPL [44]. In mechanical evaluation, Griffen and Askins [77] reported that P2 surfaces were equivalent to the standard PAA in lap shear and peel strength (see Fig. 2), but exhibited unsatisfactory durability performance in wedge tests. Digby and Packham [44]

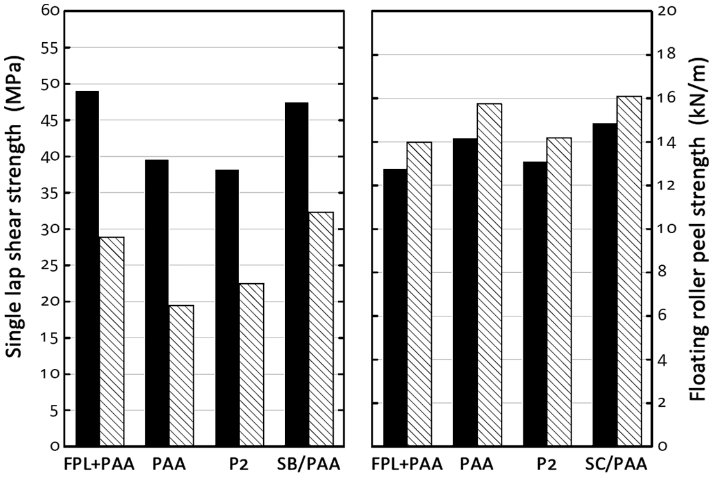


FIGURE 2 Static strength comparisons with EA9628 (Hysol Dexter Inc.) adhesive film by FPL + PAA, only PAA, P2, and Scotch-brite® (SC)/PAA; initial tests at room temperature (■); test at 82°C after 30 days exposure to 60°C/95–100% RH (▧), respectively, (data reproduced from Griffen and Askins [77]).

TABLE 4 DC- and AC-Electrochemical Surface Treatments Prior to Adhesive Bonding

Treatments [Refs.]	Electrolyte (wt.%)	Voltage (V)	Duration time (min)	Temperature (°C)
DC electrochemical treatments				
CAA [19]	2.5–3.0 CrO_3	40.0 ± 1.0/50.0 ± 1.0	35–45	40.0 ± 2.0
PAA [19]	10 H_3PO_4	10.0	20	25.0
BSAA [21]	5.0–10.0 H_3BO_3/ 30.0–50.0 H_2SO_4	15.0 ± 1.0	18–22	26.7 ± 2.2
PSA [58]	10.0 H_3PO_4/10.0 H_2SO_4	18 ± 2.0	15	27 ± 2.0
TFSAA [78]	3.0–5.0 H_2SO_4	15	20	25.0–30.0

Treatments [Refs.]	Electrolyte (wt.%)	Voltage (A/dm^2)	Duration time (s)	Temperature (°C)
AC electrochemical treatments				
AC-PAA [43]	10 H_3PO_4	4.0	30	50.0
AC-SAA [43]	15 H_2SO_4	10.0	12	80.0

assessed the compatibility of preliminary etch solutions, *i.e.*, FPL and P2, with the PAA process: P2 + PAA outperformed FPL + PAA in terms of crack growth and strain energy release rate when wedge specimens were exposed to 50°C/96% RH.

2.2.3. Electrochemical Treatments (Anodizing)

The several electrochemical treatments, *i.e.*, DC- and AC-anodizing, are listed in Table 4. The proprietary materials and exact production steps are slightly dissimilar between organizations. Both chromic acid anodizing (CAA) and phosphoric acid anodizing (PAA) are currently the preferred anodizing processes in the aerospace industries [21,43, 74,75]. Earlier experiences demonstrated that both methods were preferred for metallic bonded structures, but they typically rely on such hazardous materials as strong acid and hexavalent chromium. These limitations will become unacceptable in the near future and the recent alternative non-chromate anodizing (NCA), *i.e.*, boric-sulphuric acid anodizing (BSAA) or phosphoric-sulphuric acid anodizing (PSA), have been developed since the mid-1990s [21,58,78], but neither of them have been fully validated for aircraft applications.

A typical anodic oxide structure is presented in Fig. 3. One obvious characteristic of the anodic oxide is its cylindrical porosity formed just above a thin barrier layer [21]. It is noted that the porous structure can promote the wetting with primer and/or adhesive resins and, subsequently, contribute to bond strength and durability. These porous

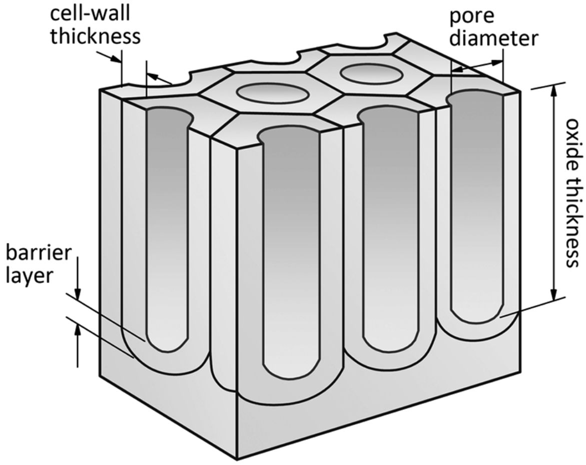


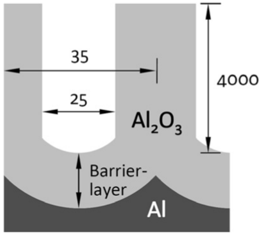
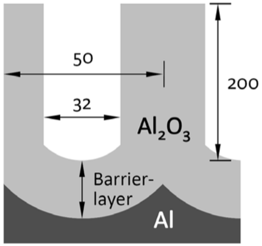
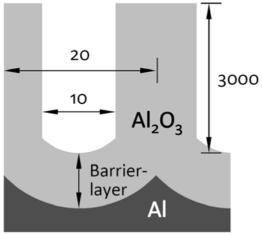
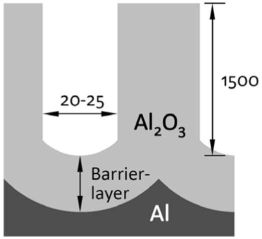
FIGURE 3 Idealized isometric anodic oxide structures (reproduced from Critchlow *et al.* [21] with permission from Elsevier).

oxide layers are controllable for any given operating condition as listed in Table 5. This table shows the effects of anodizing processes on the oxide morphology. Large variations of both thickness and pore size are observed and they can be used to fully understand the formation mechanisms of a porous anodic oxide.

Chromic acid anodizing (CAA). The CAA process has proven to give a relatively thick and amorphous oxide layer compared with the PAA process [43]. It was developed as an effective method for adhesive bonding with long-term durability performance in service [15,19,21, 43]. This method has been typically used in the European aerospace industry [21,43]. The standard involves chromic-sulphuric acid deoxidizing followed by chromic acid anodizing (specified as standard by DEF STAN 03-24/3) [21]. In the anodic process, a two-step constant current density consists of a first hold at 40 volts DC followed by a second hold at 50 volts DC as would be necessary for a higher constant current density [19,21]. Notwithstanding the remarkable durability data in corrosive environments, the use of chromate treatment processes is being restricted due to recent environmental policy.

Phosphoric acid anodizing (PAA). PAA is currently the preferred anodizing option for primary bonded structures in the United States. Boeing developed the PAA process and allowed its application to Boeing fleets since the 1970s [74]. The standard in accordance with either Boeing's BAC 5555 [80] or ASTM D 3933 [81] has proven to

TABLE 5 Comparison of Oxide Morphology According to DC Electrochemical Treatment

Treatments	CAA [21]	PAA [79,83]	BSAA^{A} [21]	PSA [58]
Oxide thickness	4000 nm	200 nm	3000 nm	1500 nm
Pore diameter	25 nm	32 nm	10 nm	20–25 nm
Cell wall thickness	10 nm	18 nm	10 nm	–
Schematic view of oxide structure [nm] (not to scale)				

yield the most reactive surface for structural adhesive bonding. In this process, FPL-etch is used as a pretreatment prior to anodizing.

The PAA-treated anodic oxide is highly porous with open cell diameter of approximately 32 nm in height on top of a much thinner barrier layer [19,82,83]. The PAA oxide thickness is typically reported in the range from 200 to 400 nm with a much thinner barrier layer of about 10 nm [19,75,83]. The PAA-treated surface can exert strong capillary forces on the primer and adhesive when they are applied, thereby drawing the polymer into the structure to form a very strong interlocking interphase [75]. The performance of the PAA process could be confirmed by the records in the earlier literature since the 1980s; PAA provided either equivalent or better durability results than CAA in most experimental trails [84–87]. However, similar static strength results [21,38,58] were also measured in lap shear strengths as listed in Table 6.

Boric-sulphuric acid anodizing (BSAA). As mentioned above, PAA treated surfaces were consistently reported to offer good initial strength and durability. Poor corrosion resistance was also observed due to the thin anodic oxide with a highly porous structure [54]. The BSAA process which uses a mixture of two electrolytes, *i.e.*, boric and sulphuric acids, was developed by Boeing as a replacement for the established CAA process [21]. This process requires low operating temperature (26.7°C) and voltage (15 volts) with reduced production time compared with the established CAA [21]. The BAC 5632 [88] involves deoxidizing with tri-acid solution, *i.e.*, sodium dichromate, sulphuric, and hydrofluoric acid, followed by the application of boric

TABLE 6 Comparison of DC-Anodizing Processes on Static Strength with BR127/FM73 Film Adhesives (Data Reproduced from Critchlow *et al.* [21], Mazza *et al.* [38], and Matz *et al.* [58])

Treatments	Lap shear [MPa]	FRP [kN/m]
CAA [21]	39.75*	–
PAA [38]	42.72**	15.65†
BSAA [21]	40.25*	–
PSA [58]	43.20***	10.56‡

*Lap shear with 10 mm overlap and 20 mm width.

**ASTM D 1002, shear strength of single-lap joint (metal-to-metal).

***EN 2243-1, structural adhesives, single-lap joint (with 3 M Scotch-Weld® AF163 adhesive).

†ASTM D 3167, floating roller peel resistance of adhesives.

††EN 2243-2, structural adhesives, peel metal-to-metal.

and sulphuric acid anodizing. The parts were subsequently dried in warm air at 75°C prior to primer application.

Standard BSAA anodic film yields relatively small pore diameter (10 nm) compared with the well-defined CAA film (25 nm) as listed in Table 5. Currently, the BSAA process is only recommended for non-structural bonding, or painting systems, due to the relatively low bonding performance [54]. The BSAA process has been modified by several research groups, for example [21,59]. The required surface topography and equivalent mechanical stability in strength and durability could be achieved when the following process variations were instituted: electrolytic phosphoric acid deoxidizer (EPAD) [21]; anodizing temperature in the BSAA bath [21,59]; and additional post treatment using a post-anodizing dip (PAD) [21].

Phosphoric-sulphuric anodizing (PSA). Another non-chromic anodizing option, *i.e.*, the PSA process, was elaborated and verified by DaimlerChrysler Aerospace Airbus [58]. The electrolyte used is a mixture of phosphoric acid and sulphuric acid at an intermediate 18 volts DC [58]. This process requires nitric acid deoxidizing prior to PSA treatment. The PSA-treated surface produces an oxide structure of about 1500 nm in thickness with somewhat narrow porous structures in the range from 20 to 25 nm in pore diameter [57]. The shorter duration and simplicity of this process has motivated its application in the aerospace industry [58].

Sulphuric acid anodizing (SAA). SAA, which is generally suitable for both protective and subsequent painting purposes, is another option to yield a wide range of oxide thicknesses on most aluminum alloys. According to MIL-A-8625 [89], two types of SAA were introduced: Type II (conventional) and Type IIB (thin film). The second type of SAA, referred to as thin film sulphuric acid anodizing (TFSAA), was introduced as a non-chromate alternative for adhesive bonding processes [74,78]. This process is similar to BSAA, except for the elimination of boric acid in the electrolyte [78]. Although the replacement of established treatments with TFSAA is under consideration, this process is cost effective and does not utilize toxic materials.

AC anodizing. Recent research work in Norway (SINTEF Materials Technology and Norwegian University of Science and Technology) put emphasis on the possibility of developing a special anodizing process, *i.e.*, hot AC anodizing [18,43,51]. This alternative is a highly feasible, robust, and environmentally friendly process, which is free from the hexavalent chromium found in the conventional CAA. A distinct difference from DC anodizing is hydrogen gas generation on the treated

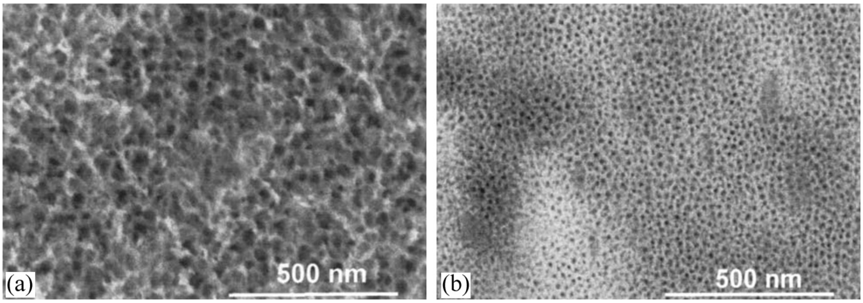


FIGURE 4 FE-SEM cross-section images of anodized oxide layers on extruded AA6060-T6; (a) FPL + PAA, (b) AC-SAA (reprinted from Bjørgum *et al.* [43] with permission from Elsevier).

surface during the hot AC anodizing process. The cleaning effect introduced by gas evolution offers additional advantages, *i.e.*, elimination of preliminary degreasing and/or acid-etch step [43,51]. Bjørgum *et al.* [43] showed the similarity in the anodic oxide morphology, composition, and on the role of process variation, *i.e.*, current density, electrolyte, temperature, and time (see Fig. 4). As shown in Fig. 5, the durability results with both AC-SAA and AC-PAA, as measured in the wedge test (40°C/96% RH), were comparable with the standard

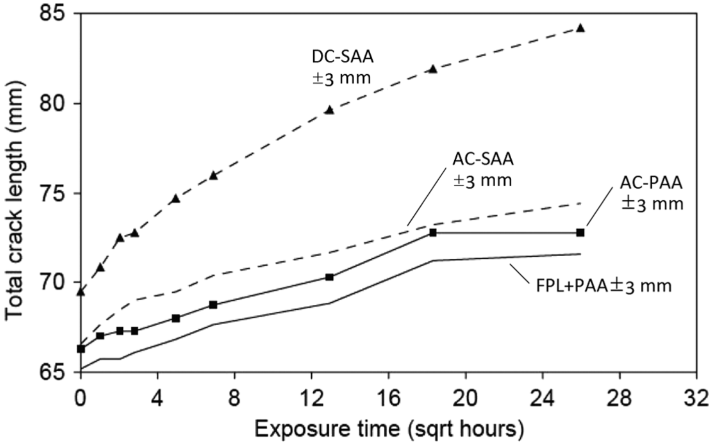


FIGURE 5 Wedge durability test results according to the DC- and AC-anodized AA6060-T6 bonded with a 180°C cure Betamate® XD4600 (Dow Automotive) epoxy adhesive (reprinted from Johnsen *et al.* [51] with permission from Elsevier).

FPL + PAA process [51]. Few data are available on functional outcomes and experience in aircraft construction.

2.2.4. Coupling Agent Treatments

There is an ongoing need to develop environmentally friendly coupling agent techniques, *i.e.*, silane or sol-gel, which can be used with the current generation of materials, *i.e.*, primer and film adhesive. As mentioned before, these approaches demonstrated that the best results were only achieved when the recommended abrasion process, *i.e.*, grit-blasting is applied.

Silane. Current efforts by RAAF (Royal Australian Air Force) and DSTO (Defence Science and Technology Organisation) have successfully led to the development of the Australian silane treatment for adhesive bonding and bonded repairs on metallic structures, by providing a non-toxic, chromate-free treatment with a short production time [29,40,63,90]. The C5033 RAAF Engineering Standard [91] involves grit blasting the aluminum surface with 50 µm alumina grit followed by the application of a 1% aqueous γ-glycidoxypropyltrimethoxy silane (γ-GPS) solution. The thin layer of silane, *i.e.*, about 1.9 nm in thickness (typical 1–5 nm), is deposited onto the metallic surface [39].

Thousands of adhesively bonded repairs using silane techniques have been applied to RAAF military aircraft over the past 25 years [63]. This technique shows excellent long-term durability as listed in Table 7. Rider and Arnott [22] described that the silane layer promotes the hydrolytic stability of the adhesively bonded joint, leading to increased durability in wedge tests. Abel *et al.* [92], using time of flight secondary ion mass spectrometry (ToF-SIMS), demonstrated that a strong Al-O-Si bond was formed between hydrolysed γ-GPS and aluminum surfaces. Abel *et al.* [24] also proposed a wedge crack growth mechanism at the oxide and adhesive interface. The crack growth was propagated through the interface ("*composite-zone*") between oxide, silane, and adhesive in cohesive failure mode, which is considered as an optimum type of failure that occurs primarily in the adhesive layer.

Sol-gel. Another option, *i.e.*, sol-gel, a contraction for solution-gelation, which involves the growth of metal-oxo polymers through both hydrolysis and a condensation reaction to form inorganic polymer networks in thicknesses ranging from 50 to 200 nm as shown in Fig. 6 [35,38]. The Boegel EPII sol-gel agent consists of a dilute aqueous epoxy silane and zirconium alkoxide. This mixture provides a thin inorganic zirconium oxide film incorporated with the epoxy-silane that is applied to the metallic surface [38,74]. In this process, zirconium reacts with the metallic surface to produce a covalent chemical bond,

TABLE 7 Examples of Grit Blast/Silane Applications to RAAF Military Aircraft adapted from DSTO [63]

Aircrafts	Problems	Surface treatments	Structural adhesives	Environmental durability records
C-130E	Stress corrosion cracks in wing stiffeners, 7075 alloy	Grit blast + γ-GPS	AF126*, FM73**	No bond durability problems where bonding carried out as specified over 20 years of service
F-111C	Secondary bending fatigue problems in wing pivot fitting (steel D6ac fastened to aluminum alloy skin)	Grit blast + γ-GPS	FM73	No bond durability failures to aluminum surface over 10 years
F-111C	Stress corrosion cracks in the longeron, 7049-T6 alloy	Grit blast + γ-GPS	EA9321†	Over ten aircraft repaired, no bond durability problems in 8 years
F-111C	Metal-to-metal and sandwich structure repairs	Grit blast + γ-GPS	FM300††, FM73, EA9321	No bond durability failures over 7 years
P-3C	Full depth corrosion damage in horizontal tail, 2075-T6	Grit blast + γ-GPS	FM73	No bond durability problems over around 10 years

*3M™ Scotch-Weld™ Structural Adhesive Film AF126 (3 M Company, USA).

**FM® 73 Toughened Epoxy Film (Cytec Industries Inc., USA).

†Two-component thixotropic paste adhesive Hysol EA9321 (Henkel Aerospace, USA).

††FM® 300 High-Shear Strength Modified Epoxy Adhesive Film (Cytec Industries Inc., USA).

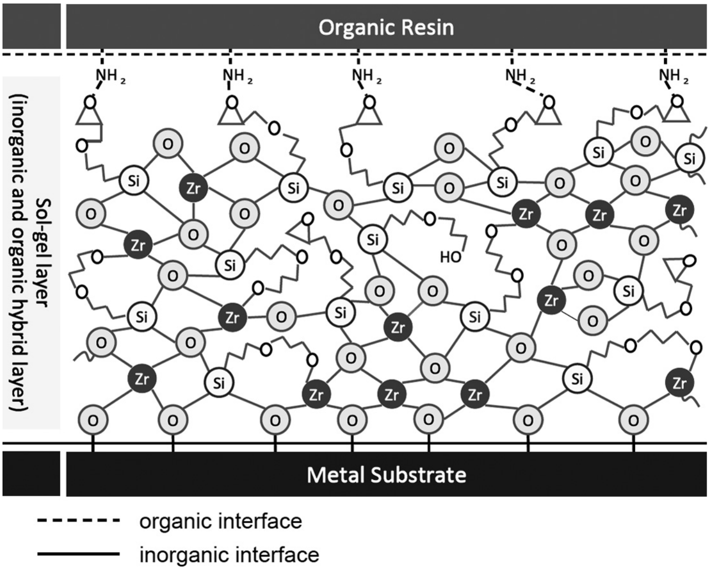


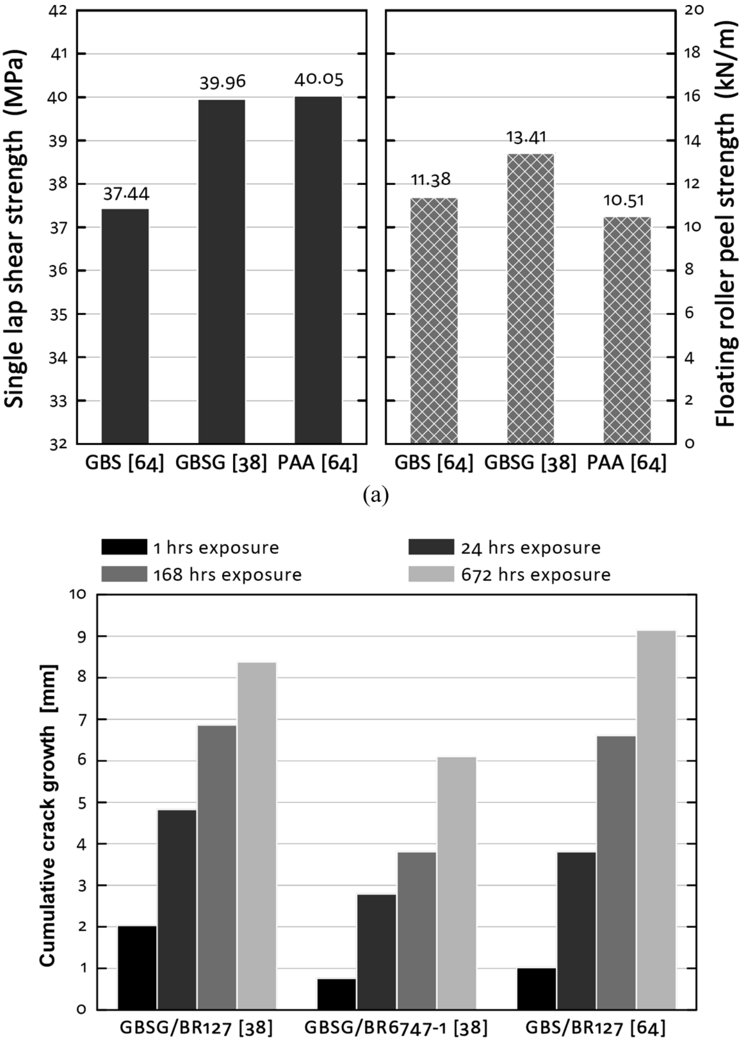
FIGURE 6 Schematic view of representation of a typical sol-gel thin film coating (reproduced from Osborne *et al.* [42] with permission from Elsevier).

while the epoxy-silane offers a reactive organic group for bonding with the adhesive [38,46].

The sol-gel formulation is now commercially available in kit form as AC Tech AC-130 (Advanced Chem. & Technol., Inc., gardengrove, CA, USA) [38,74,93]. This kit is particularly designed to work with the waterborne Cytec® BR 6747-1 primer. BR 6747-1 can completely eliminate the use of volatile organic compounds (VOC), in contrast to the solvent-based standard BR 127 primer (792 g/liter of VOC) [93]. Both coupling techniques yielded comparable results in lap shear and peel strengths, respectively, as shown in Fig. 7 [38,64]. In general, there was a good agreement between joints which perform well in wedge tests with similar exposure conditions; wedge results with GBSG (grit-blast/sol-gel)/BR6747–1 after 28 days exposure showed a crack extension of 6.1 mm, while GBS (grit blast/silane)/BR127 was observed to be 9.1 mm. These test results also highlighted the beneficial effects of waterborne primer followed by GBSG.

2.2.5. Dry Surface Treatments

Despite the progress outlined in the above section, several dry treatments for aluminum alloys have been developed to replace the



(a)

(b)

FIGURE 7 Comparisons of bond performance results between GBSG and GBS with 3M AF-163 film adhesive; (a) single lap shear and floating roller peel test results at 21°C, (b) wedge durability test results at 60°C/95–100% RH (data reproduced from Mazza *et al.* [38] and [64]).

conventional chemical wet process: excimer laser texturing [30,34–35, 66–69,94], plasma-sprayed coating [32,36,56,70–73,94], and ion beam enhanced deposition (IBED) [33,94]. These approaches can eliminate, or reduce, the undesirable environmental impacts associated with the currently approved surface treatment technologies which rely on the use of chromate chemistries [94].

Laser texturing was utilized to modify an aluminum substrate's morphology and micro-structure, resulting in an increased bond strength and durability [30,34,94]. In recent years, research performed by the United States Air Force (USAF) Wright Laboratory was undertaken for the USAF to assess the utility of laser beams in surface treatment without the use of solvents or abrasion [34,94]. Surface analysis by Critchlow *et al.* [30] showed that laser ablation treatment modified the aluminum surface by introducing a relatively thin surface oxide layer ($\sim$16 to $\sim$28 nm) and a decrease in the Mg:Al ratio from $\sim$1.5:1.0 to $\sim$0.3:1.0 in the outermost part of the oxide layer. Lap shear and peel strength results for laser texturing were comparable with, or better than, both GBSG and PAA treatments. Wedge crack growth results also were comparable with GBSG and PAA [34].

IBED is a process that cleans and modifies the surface by sputtering with high energy argon ions under vacuum. This process requires a surface activation step, particularly grit-blasting, prior to IBED. Good initial bond strengths were obtained and the improvements in wedge durability compared with PAA were found [94]. Koch *et al.* [33] also demonstrated that IBED had a beneficial effect on the strength and durability of adhesively bonded joints, equal to or better than PAA.

Plasma spray coatings were also used as pretreatments prior to adhesive bonding. Coating thicknesses is in the range of 50 to 75 μm were recommended to maximize the durability properties [94]. In the wedge test, the crack growth data indicated durability better than that obtained with FPL etch, but not as good as with PAA [94]. Davis *et al.* [32] reported that a 60Al-Si/40polyester (by wt.) plasma spray coating could be engineered for specific applications and was better suited for the adhesive bonding process of aluminum substrates, by yielding a performance equivalent to that of the PAA treatment with some epoxy adhesives in the wedge test. Fernandes *et al.* [36] also showed that the coating surfaces offered improved durability in the wedge test compared with grit-blasting, but did not match the performance of the well established CAA treatment. Currently, dry treatment technologies have been studied to a lesser degree, but some researchers have reported comparable properties [32–34,56,94].

TABLE 8 Three Sets of Cytec® Commercially Available Bond Primers for 250°F-Cure Film Adhesives [96]

	BR127	BR6747-1	BR6747-1NC
Solid (wt.%)	10 ± 1%	20 or 30%	20%
VOC level	792 g/liter	0 g/liter	0 g/liter
Chromate (wt.%)	15%	15%	0%

2.4. Bond Primers

A bond primer is an organic liquid used to promote adhesion between the substrate and adhesive and to protect the treated surface against hygrothermal effects [19,95]. The low viscosity liquid is able to penetrate porous and rough surfaces, thereby providing improved mechanical interlocking and protecting a surface against hydrolysis effects, *i.e.*, moisture attacks. Primers may also act as coupling agents, forming covalent bonds between the metal adherend and the adhesive. The compatibility between surface treatments and bond primers is a critical parameter in enhancing the bond strength and durability [19,38,64]. Another issue of bond primers is to compare the performance of conventional primers with the recently developed environmentally friendly primers [38,55]. Cytec BR 127 was one of the industry's standard primers, particularly for 250°F (121°C)-cure film adhesives; however, it contains a large amount of VOCs (792 g/liter), chromates (15 wt.%), and hazardous air pollutants. More recently, waterborne primers such as BR6747-1 and BR6747-1NC were developed to eliminate the VOCs and hexavalent chromium, respectively (see Table 8). Both of them yield comparable performance with the solvent- based BR127 as listed in Table 9 [38,55]. A BR6747-1 was evaluated as the best performer throughout coupon-level tests such as lap shear, floating roller peel, and wedge tests [55].

TABLE 9 Effect of Primers on PAA and GBSG with Commercially Available 250°F-Cure Film Adhesives; Wedge Test Results (24 Hrs Exposure at 60°C and 100% RH)

	PAA/FM73 [55]	GBSG/AF163-2 [38]
BR 127	5.75	4.83
BR 6747-1	5.36	2.79
BR 6747-1NC	5.84	2.79

3. SUMMARY OF PROCESS VALIDATION DATA

3.1. Summary of Surface Analysis

Surface analysis is an important tool for studying adhesion mechanisms. The objective of surface analysis is to understand the requirement of surface treatment to produce strong structural bonded joints. For this reason, three surface characteristics were collected for comparisons to be made between treated surfaces (see Table 10); topography, *e.g.*, surface roughness [19,21,27,33], hydrolytically stable oxide [49,79], and surface wettability, *e.g.*, contact angle measurements [19,21,27].

The strength and durability of bonded joints might be improved by combining the primer with a treated surface which creates a micro-roughened surface topography as shown in Fig. 8(a). A micro-roughened surface is clearly a beneficial factor to maximize the area available for primary and secondary bonding interactions and also to promote the mechanical keying of adhesive with substrate [15,17,52]. The proper surface treatments should leave a thin, uniform oxide on the surface with a low level of contamination. A stable oxide is also important as it can prevent- and/or reduce the formation of weak boundary layers

TABLE 10 Effect of Surface Treatment on Aluminum Alloys

Refs.	Treatments	Alloys^A	Roughness, R_{av} (μm)	Oxide thickness (μm)	Contact angle (deg)
27	Grit-blasting	5251	$1.7 \pm 0.1^*$	NR^B	$28.0 \pm 6.0^*/30.0 \pm 3.0^\dagger$
21	FPL	2024-T3 clad	NR	NR^C	$<10.0^*$
19	PAA	2024-T3	0.47^*	$1.00 \sim 1.40^*$	$3.0{\sim}4.0^\dagger$
21	CAA	2024-T3 clad	0.061^*	$3.00 \pm 0.50^*$	$<5.0^*$
19	CAA	2024-T3	0.57^*	3.40^*	$10.0^*/5.0^\dagger$
21	BSAA	2024-T3 clad	0.053^*	$3.50 \pm 0.50^*$	$<5.0^*$
57	PSA	2024-T3 clad	NR	1.50^*	NR
57	PSA	7075-T6 clad	NR	2.70^*	NR
43	AC-SAA	Extruded AA6060-T6	NR	$0.20^\dagger$	NR
39	Silane	2024 clad	NR	1.9 nm	NR
33	IBED	2024-T3	$0.019^\dagger$	$0.40^\ddagger$	NR
99	Laser	2024-T3	NR	$0.058^\ddagger$	41.6^*

^{A}Chemical compositions of aluminum alloys are listed in Appendix Table A2.

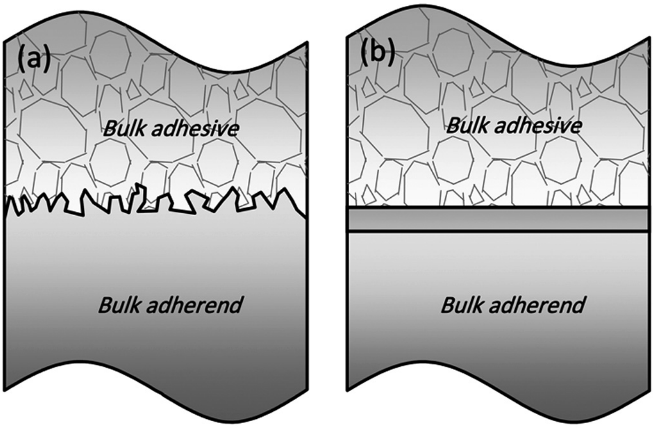
^{B}NR, not reported.

^{C}In typical, oxide thickness of FPL-etch has been reported to be 40 nm [75].

Instruments for surface roughness: *stylus profilometry, or laser depth measuring device (Perthometer), †atomic force microscopy.

Instruments for oxide thickness: *scanning electron microscopy, †transmission electron microscopy, ‡auger electron spectroscopy.

Wetting liquids for contact angle measurements: *water, †diiodomethane.



Mechanical interlocking introduced by; *hills, valleys, pores and crevices, etc*

Adsorption (contact adhesion); *Lifshitz–van der Waals interactions*, which include *London dispersion, Keesom polar, Debye induced polar*

FIGURE 8 Schematic view of the representative adhesive bonding interphase; (a) mechanical interlocking, (b) contact adhesion (reproduced from Berg [97] with permission from Elsevier).

[15,17,20]. Finally, surface wettability by contact angle measurements is indicative of the surface hydrophilicity which enables the adhesive resin to spread on the aluminium surface [15,17,20]. A properly treated surface reduces water contact angle and, as a result, may improve bond strength as shown in Fig. 8(b).

3.2. Summary of Strength and Durability

To support process validation according to the surface treatment, a summary of strength and durability results for the surface treatments is given in Table 11. The most often adopted test method was ASTM D 3762 (Boeing wedge test) [21,22,24,31–34,36,39,46,54], while limited available data for lap shear strength [21,26,28,34,35,38,54,56] or floating roller peel strength [33,34,38] were found in the published literature.

Although wedge durability evaluation does not account for cyclic fatigue loading, the results have proven to be correlated with service performance [8,84,98]. It is much more reliable than lap shear or peel tests [98]. The wedge crack growth mechanism which occurs along the oxide-adhesive/primer interface was suggested by Venables *et al.* [99].

TABLE 11 Effect of Surface Treatment on Bonding Performances

			Surface treatments/Performance ranks							
Refs.	Alloys^{A}	Test method	Grit blast	Etch	CAA	PAA	BSAA	Silane	Sol-gel	Dry
21	2024-T3 clad	Lap shear	4	3	$1^{=}$		$1^{=}$			
28	5251	Lap shear	3	2		1				
56	AA6016	Lap shear			$1^{=}$					1^{*}
26	2014A	Lap shear	3	2		1				
34	2024-T3	Lap shear	3			$1^{=}$				$1^{\dagger}$
35	5251	Lap shear	2					1		$3^{\dagger}$
38	2024-T3	Lap shear			2	1			3	
54	2024	D 3165			$1^{=}$	1	3			
33	2024-T3	D 3167		3		1				$2^{\ddagger}$
25	2014-T6	TDCB fatigue	3	2				$1^{=}$		
26	2014-T6	TDCB fatigue	3	$1^{=}$		$1^{=}$				
21	2024-T3 clad	D 3762			2		$1^{=}$			
22	2024-T3 clad	D 3762	3			1		$1^{=}$		
24	2024-T3 bare	D 3762	4		$2^{=}$	1		$2^{=}$		
31	2024-T3 clad	D 3762	3			1		2		
32	2024-T3	D 3762	4	3		1				$1^{=*}$
33	2024-T3	D 3762				1				$1^{=\ddagger}$
34	2024-T3	D 3762	$2^{=}$			1				$2^{=\dagger}$
36	2024-T3 clad	D 3762	4		1			2		3^{*}
39	2024-T3 clad	D 3762	4	3		1		2		
46	2024-T3	D 3762				2			1	
54	2024	D 3762			$1^{=}$	1	3			
22	7075-T6 bare	D 3762	3			1		$1^{=}$		

^{A}Chemical compositions of aluminum alloys are listed in Appendix Table A2.

$^{=}$Denotes comparable, but slightly inferior to the highest rank; *plasma coating treatments; † laser treatments; ‡ IBED treatments.

-ASTM D 1002 Standard test method for apparent shear strength of single-lap-joint adhesively bonded metal specimens by tension loading.

-ASTM D 3165 Standard test method for strength properties of adhesives in shear by tension loading of single-lap-joint laminated assemblies.

-ASTM D 3167 Standard test method for floating roller peel resistance of adhesives.

-Tapered Double-Cantilever Beam (TDCB) joints.

-ASTM D 3762 Standard test method for adhesive-bonded surface durability of aluminum (wedge test).

During environmental exposure to high temperature and humidity, the oxide hydration results in formation of a weak oxide layer that is easily failed under load. This weak hydroxide layer is consequently, a favorable path for crack propagation. A brief review of the literature is given on the use of wedge-type tests for assessing the environmental durability of adhesive joints [8,39,84,100].

Lap shear and floating roller peel offer shear strength and fracture resistance of adhesive bonded joints as well as quantitative data for design calculations. Shear strength is the most critical engineering property for structural bonded joints; design requirements are typically dominated by shear strength tests [101,102]. The floating roller peel method identifies the relative peel resistance of adhesive bonding under the specified conditions [102]. Moisture, combined with high temperature, is absorbed into the joints, possibly reducing the strength of the interfacial bond between the adhesive and adherend.

The superior performance in bond strength and durability of two standard surface treatments such as CAA [21,24,36,38,56] and PAA [22,24,26,28,31–34,38,39,46] with an epoxy adhesive yields an answer as to why the standard anodizing technologies are still widely regarded as the best aluminum surface treatment technologies for adhesive bonding. Grit-blasting does not deliver good durability [22, 24,31,32,36,39], nor even acceptable initial strength [21,26,28,34]. Acid-etch treatments are only suitable for moderate bond strength requirements [21,26,28], or minimal environmental durability against moist conditions [32,39]. The standard BSAA process showed that the bonding strength and durability were much lower than for the standard PAA and CAA processes, implying that the process was unsuitable for structural bonding [54]. However, the comparable results between BSAA and CAA were expected when a modified anodizing temperature of 35°C was applied [21], because the modified anodizing temperature provides a hydrated oxide directly comparable in structure with the standard CAA process, with the increased, more open, pore size. The new coupling treatments, such as silane and sol-gel, on the whole, yielded durability comparable with PAA [22,24]; evidence that contradicts these results are, however, also available [31,36,39]. Finally, dry treatments, such as laser, plasma, and IBED, were reported to perform similarly to anodizing processes in lap shear [34,56] and wedge testing [32,33]. But these processes led to inconsistent results in wedge durability tests [34,36].

Rose [103] reported that there were several nondestructive inspection (NDI) techniques capable of detecting bond integrity. However, the current NDI techniques only identify extremely poor bonds, which can results from improper preparation (*i.e.*, surface treatment), and from porosities and voids during manufacture [103–105]. A notable limitation with regard to production is that, as yet, there are no reliable, commercially available. NDI techniques for bonded joints [106]. To date, some success has been recorded in the development of new techniques to counter such problems. Potential solutions are going to fall into two major categories: dielectric measurement and acoustic emission [106,107]. In particular, a change in dielectric measurement of adhesively bonded joints is indicative of moisture intrusion in the bond and a corresponding weakening of the structural integrity [107]. However, the potential solutions under both categories require further research before a reliable system can be marketed commercially [17,107,108].

4. CONCLUSION

This paper reviews the recent trends in surface treatment technologies for adhesive bonding processes and presents experimental data obtained in the last 14 years. Such an approach will provide some guidance for adhesively bonded structures, which comes from military and commercial aircraft experiences with educational value for an expanding workforce. It is noted that proper surface treatment is critical for achieving long-term durability against service environmental exposure. Bond integrity is not yet defined either by NDI or quality control methods.

Current surface treatment technologies are typically dependent on several materials that are hazardous to use, and they have large disposal costs. Their suitable alternatives are the subject of great interest in the aerospace industry. Several alternatives, such as non-chromate anodizing, silane, sol-gel, laser, plasma, and IBED processes demonstrate that the potential possibility of shorter duration and simplicity put the aerospace industry in a position to be able to apply these techniques in production. In addition, they are favorable methods when the environmental issue is critical. Bonded joints fabricated using these alternatives offer performance comparable with the current generation of materials (*i.e.*, primers and adhesives). However, the literature shows that these techniques lead to a somewhat lower evaluation due to the incompatibility between these treatments and the primer/adhesive, and this could contribute to lower durability, which is not acceptable for application in primary aircraft structures, such as wings and fuselages. Additional studies are required for full validation for aerospace applications.

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APPENDIX

TABLE A1 Major Aluminum Alloys Used in Aircraft Structures and their Specification and Temper Conditions (Data Reproduced from MIL-HDBK-5H [109])

Alloys (principle alloying elements)	Product forms (specification)	Temper conditions
2014 (Al-Cu)	Bare sheet and plate (AMS 4028 and 4029) Clad sheet and plate (AMS-QQ-A250/3) Forging (MIL-A-22771, QQ-A-367, and AMS 4133) Extruded bar, rod, and shapes (AMS-QQ-A-200/2)	T6, T62, T651, T652, T6510, and T6511
2024 (Al-Cu)	Bare sheet and plate (AMS 4037, 4035 and AMS-QQ-A250/4) Clad sheet and plate (AMS-QQ-A250/5) Bar and rod, rolled or cold-finish (AMS 4120) Extrusion (AMS 4152, 4164 and 4165) Extruded bar, rod, and shapes (AMS-QQ-A-200/3)	T3, T4, T6, and T8
7075 (Al-Zn-Mg-Cu)	Bare sheet and plate (AMS 4044, 4045 and AMS-QQ-A-250/12, 24) Clad sheet and plate (AMS 4049 and AMS-QQ-A-250/13, 25) Forging (AMS 4126, 4147, MIL-A-22771 and QQ-A-367) Extruded bar, rod, and shapes (AMS-QQ-A-200/11, 15) Bar and rod, rolled or cold-finish (AMS 4122, 4123, 4124, 4186 and 4187)	T6, T73, and T76
7150 (Al-Zn-Mg-Cu-Zr)	Bare plate (AMS 4306 and 4252) Extrusion (AMS 4307 and 4345)	T61 and T77

TABLE A2 Chemical Compositions of Aluminum Alloys Identified in the Current Review (in Weight %)

		Composition by weight						
Alloys	Refs.	Si	Cu	Mn	Mg	Cr	Zn	Temper conditions
2014A	[110]	0.8	4.4	0.8	0.5	–	–	T6
2024	[110]	–	4.4	0.6	1.5	–	–	T3
5251	[35]	0.4	0.15	0.5*	2.4*	–	–	
AA6060	[43]	0.43	0.002	0.02	0.51	–	0.01	T6
AA6016	[111]	1.3	0.07	0.07	0.33	0.03	0.02	
7075	[110]	–	1.6	–	2.5	0.23	5.6	

*Maximum.

T3: solution heat-treated, cold worked, and naturally aged to a substantially stable condition.

T6: solution heat-treated and artificially aged.

REFERENCES

[1] Alderliesten, R. C. and Homan, J. J., *Int. J. Fatigue* **28**, 1116–1123 (2006).

[2] Jones, R., Molent, L., and Pitt, S., *Theor. Appl. Fract. Mec.* **49**, 38–50 (2008).

[3] Pitt, S. and Jones, R., *Eng. Fail. Anal.* **4**, 237–257 (1997).

[4] Goranson, U. G., *Int. J. Fatigue* **20**, 413–431 (1997).

[5] Di, S., Yang, X., Luan, G., and Jian, B., *Mater. Sci. Eng. A* **435–436**, 389–395 (2006).

[6] Simmons, M. C. and Schleyer, G. K., *Thin-Walled Struct.* **44**, 496–506 (2006).

[7] Higgins, A., *Int. J. Adhes. Adhes.* **20**, 367–376 (2000).

[8] Davis, M. and Bond, D., *Int. J. Adhes. Adhes.* **19**, 91–105 (1999).

[9] Räckers, B., Bonding Processes at Airbus, in: 2004 FAA Workshop on Adhesive Bonding, Sussex, UK, October 2004. Available at http//:www.niar.wichita.edu.

[10] di Scalea, F. L., Bonomo, M., and Tuzzeo, D., *Res. Nondestr. Eval.* **13**, 153–171 (2001).

[11] Bishopp, J. A., *Int. J. Adhes. Adhes.* **17**, 287–301 (1997).

[12] Petrie, E. M., *Met. Finish.* **106**, 26–31 (2008).

[13] Tomblin, J., Strole, K., Dodosh, G., and Ilcewicz, L., Assessment of industry practices for aircraft bonded joints and structures, Report no. DOT/FAA/AR-05/13, (US Department of Transportation, Federal Aviation Administration, Washington, D.C., 2005).

[14] Tomblin, J. and Davies, C., Bonded Structures Industry Survey, in: 2004 FAA Workshop on Bonded Structures, Seattle, WA, June 2004.

[15] Critchlow, G. W. and Brewis, D. M., *Int. J. Adhes. Adhes.* **16**, 255–275 (1996).

[16] Drzal, L. T., Rich, M. J., and Lloyd, P. F., *J. Adhes.* **16**, 1–30 (1983).

[17] Yang, S., Gu, L., and Gibson, R. F., *Compos. Struct.* **51**, 63–71 (2001).

[18] Johnsen, B. B., "Adhesive bonding of aluminum," Ph.D. Thesis, Norwegian University of Science and Technology (2003).

[19] Oosting, R., "Toward a new durable and environmentally compliant adhesive bonding process for aluminum alloys," Ph.D. thesis, Delft University of Technology, The Netherlands, 1995.

[20] Baldan, A., *J. Mater. Sci.* **39**, 4729–4797 (2004).

[21] Critchlow, G. W., Yendall, K. A., Bahrani, D., Quinn, A., and Andrews, F., *Int. J. Adhes. Adhes.* **26**, 419–453 (2006).

[22] Rider, A. N. and Arnott, D. R., *Int. J. Adhes. Adhes.* **20**, 209–220 (2000).

[23] Kinloch, A. J., Little, M. S. G., and Watts, J. F., *Acta Mater.* **48**, 4543–4553 (2000).

[24] Abel, M. L., Allington, R. D., Digby, R. P., Porritt, N., Shaw, S. J., and Watts, J. F., *Int. J. Adhes. Adhes.* **26**, 2–15 (2006).

[25] Abel, M. L., Adams, A. N. N., Kinloch, A. J., Shaw, S. J., and Watts, J. F., *Int. J. Adhes. Adhes.* **26**, 50–61 (2006).

[26] Hadavinia, H., Kinloch, A. J., Little, M. S. G., and Taylor, A. C., *Int. J. Adhes. Adhes.* **23**, 449–461 (2003).

[27] Harris, A. F. and Beevers, A., *Int. J. Adhes. Adhes.* **19**, 445–452 (1999).

[28] Brewis, D. M., Critchlow, G. W., and Curtis, C. A., *Int. J. Adhes. Adhes.* **19**, 253–256 (1999).

[29] Rider, A., Bond durability of grit-blast and silane treated metallic adherends bonded with room temperature curing adhesives, Report no. DSTO-TR-1187, (Defence Science and Technology Organisation, Australia, 2001).

[30] Critchlow, G. W., Cottam, C. A., Brewis, D. M., and Emmony, D. C., *Int. J. Adhes. Adhes.* **17**, 143–150 (1997).

[31] Rider, A. N., Olsson-Jacques, C. L., and Arnott, D. R., *Surf. Interface Anal.* **27**, 1055–1063 (1999).

[32] Davis, G. D., Groff, G. B., and Zatorski, R. A., *Surf. Interface Anal.* **25**, 366–373 (1997).

[33] Koch, G. H., Todd, G. L., Deutchman, A., and Partyka, R., Nonchemical surface treatment for aluminum alloys, Report no. WL-TR-96–4084, (AFRL Wright-Patterson AFB, Ohio, 1996).

[34] Walters, C. T., Laser surface preparation for adhesive bonding II, Report no. AFRL-ML-WP-TR-2006–4139, (AFRL Wright-Patterson AFB, Ohio, 2004).

[35] Critchlow, G. W., Brewis, D. M., Emmony, D. C., and Cottam, C. A., *Int. J. Adhes. Adhes.* **15**, 233–236 (1995).

[36] Fernandes, J. C. S., Ferreira, M. G. S., Haddow, D. B., Goruppa, A., Short, R., and Dixon, D. G., *Surf. Coatings Tech.* **154**, 8–13 (2002).

[37] Rider, A. and Chalkley, P., *Int. J. Adhes. Adhes.* **24**, 95–106 (2004).

[38] Mazza, J. J., Gaskin, G. B., Piero, W. S. D., and Blohowiak, K. Y., Sol-gel technology for low-VOC, nonchromated adhesive bonding applications, Report no. AFRL-ML-WP-TR-2004–4063, (AFRL Wright-Patterson AFB, Ohio, 2004).

[39] Rider, A. N., *Int. J. Adhes. Adhes.* **26**, 67–78 (2006).

[40] Chalkley, P. and Berg, J. V. D., On obtaining design allowables for adhesives used in the bonded-composite repair of aircraft, Report no. DSTO-TR-0608, (Defence Science and Technology Organisation, Australia, 1998).

[41] Liu, J., Chaudhury, M. K., Berry, D. H., Seebergh, J. E., Osborne, J. H., and Blohowiak, K. Y., *J. Adhes.* **82**, 487–516 (2006).

[42] Osborne, J. H., Blohowiak, K. Y., Taylor, S. R., Hunter, C., Bierwagon, G., Carlson, B., Bernard, D., and Donley, M. S., *Progr. Org. Coating* **41**, 217–225 (2001).

[43] Bjørgum, A., Lapique, F., Walmsley, J., and Redford, K., *Int. J. Adhes. Adhes.* **23**, 401–412 (2003).

[44] Digby, R. P. and Packham, D. E., *Int. J. Adhes. Adhes.* **15**, 61–71 (1995).

[45] Lunder, O., Olsen, B., and Nisancioglu, K., *Int. J. Adhes. Adhes.* **22**, 143–150 (2002).

[46] Osborne, J. H., Blohowiak, K. Y., and Sekits, D. F., Environmentally benign sol-gel surface treatment for aluminum bonding applications, Report no. WL-TR-95–4060, (AFRL Wright-Patterson AFB, Ohio, 1996).

[47] Johnsen, B. B., Lapique, F., Bjørgum, A., Walmsley, J., Tanem, B. S., and Luksepp, T., *Int. J. Adhes. Adhes.* **24**, 183–191 (2004).

[48] Lefebvre, D. R., Ahn, B. K., Dillard, D. A., and Dillard, J. G., *Int. J. Fract.* **114**, 191–202 (2002).

[49] Brewis, D. M. and Critchlow, G. W., *Int. J. Adhes. Adhes.* **17**, 33–38 (1997).

[50] Comyn, J., Day, J., and Shaw, S. J., *Int. J. Adhes. Adhes.* **17**, 213–221 (1997).

[51] Johnsen, B. B., Lapique, F., and Bjørgum, A., *Int. J. Adhes. Adhes.* **24**, 153–161 (2004).

[52] Briskham, P. and Smith, G., *Int. J. Adhes. Adhes.* **20**, 33–38 (2000).

[53] Pires, I., Quintino, L., Miranda, R. M., and Miranda, R. M., *Mater. Manuf. Process* **20**, 175–185 (2005).

[54] Zhang, J. S., Zhao, X. H., Zuo, Y., and Xiong, J. P., *Surf. Coatings Tech.* **202**, 3149–3156 (2008).

[55] Stayrook, J. J., Bellevou, D. L., Manson, R. T., Martinelli, A. A., Ridpath, S., Arnold, J. R., and Gaskin, G. B., Performance of Solvent and Water Based Primers in Epoxy Adhesive Systems, (Naval Air Warfare Center Aircraft Division, Maryland, 1999).

[56] Alexander, M. R., Zhou, X., Thompson, G. E., Duc, T. M., McAlpine, E., and Tielsch, B. J., *Surf. Interface Anal.* **30**, 16–20 (2000).

[57] Velterop, L., Phosphoric sulphuric acid anodising: An alternative for chromic acid anodising in aerospace applications, Report no. NLR-TP-2003–210, (National Aerospace Laboratory NLR, Amsterdam, 2003).

[58] Matz, C. W., Hilling, B., Kelm, W., and Kock, E., Phosphoric Sulfuric Acid Anodizing (PSA) – A Heavy Metal Free Alternative for High Quality Surface Pretreatment of Aluminum, in: 83rd Meeting of the AGARD Structures and Materials Panel, Florence, Italy, September 1996.

[59] Domingues, L., Fernandes, J. C. S., Cunha Belo, M. D., Ferreira, M. G. S., and Guerra-Rosa, L., *Corros. Sci.* **45**, 149–160 (2003).

[60] Song-jiang, M., Peng, L., Hai-hui, Z., Chao-peng, F., and Ya-fei, K., *Trans. Nonferrous Met. Soc. China* **18**, 825–830 (2008).

[61] Johnsen, B. B., Olafsen, K., and Stori, A., *Int. J. Adhes. Adhes.* **23**, 155–163 (2003).

[62] Underhill, P. R., Rider, A. N., and DuQuesnay, D. L., *Int. J. Adhes. Adhes.* **23**, 307–313 (2003).

[63] Rider, A. and Vodicka, R., Proposed framework for a risk-based approach for the environmental certification of adhesively bonded repairs, Report no. DSTO-RR-0282, (Defence Science and Technology Organisation, Australia, 2004).

[64] Mazza, J. J., Avram, J. B., and Kuhbander, R. J., Grti-blast/silane (GBS) aluminum surface preparation for structural adhesive bonding, Report no. WL-TR-94–4111, (AFRL Wright-Patterson AFB, Ohio, 2003).

[65] Nolting, A. E., Underhill, P. R., and DuQuesnay, D. L., *Int. J. Fatigue* **30**, 178–187 (2008).

[66] Spadaro, C., Sunseri, C., and Dispenza, C., *Radiat. Phys. Chem.* **76**, 1441–1446 (2007).

[67] Li, R., Ferreira, M. G. S., Almeida, A., Vilar, R., Watkins, K. G., McMahon, M. A., and Steen, W. M., *Surf. Coatings Tech.* **81**, 290–296 (1996).

[68] Wong, R. C. P., Hoult, A. P., Kim, J. K., and Yu, T. X., *J. Mater. Process Tech.* **63**, 579–584 (1997).

[69] Galantucci, L. M., Gravina, A., Chita, G., and Cinquepalmi, M., *Compos: Part A* **27**, 1041–1049 (1996).

[70] De Iorio, I., Leone, C., Nele, L., and Tagliaferri, V., *J. Mater. Process Tech.* **68**, 179–183 (1997).

[71] Carrino, L., Napolitano, G., and Sorrentino, L., *Int. J. Adv. Manuf. Technol.* **31**, 465–473 (2006).

[72] Anagreh, N., Dorn, L., and Bilke-Krause, C., *Int. J. Adhes. Adhes.* **28**, 16–22 (2007).

[73] Polini, W. and Sorrentino, L., *Appl. Surf. Sci.* **214**, 232–242 (2003).

[74] Voast, P. V. and Blohowiak, K., Critical Materials & Processes Bonded Joint Issues, in: 2004 FAA Workshop on Bonded Structures, Seattle, WA, June 2004.

[75] Davis, G. D. and Venables, J. D., *Surface Treatments of Metal Adherends*, (Elsevier, Amsterdam, 2002), 1st ed., Vol. 2, Ch. 21, pp. 947–1008.

[76] ASTM Standard E 864–98, *Standard Practice for Surface Preparation of Aluminum Alloys to be Adhesively Bonded in Honeycomb Shelter Panels*, American Society for Testing and Materials, Philadelphia, 1988.

[77] Griffen, C. and Askins, D. R., Non-chromate surface preparation of aluminum, Report no. AFWAL-TR-88–4135, (AFRL Wright-Patterson AFB, Ohio, 1988).

[78] (www.metalast.com). METALAST International, Inc., METALAST® Technical Bulletin

[79] Smith, T. and Lindberg, G., *Surf. Tech.* **9**, 1–29 (1979).

[80] Boeing Process Specification, BAC 5555, *Phosphoric Acid Anodizing of Aluminium gor Structural Bonding*.

[81] ASTM Standard D 3933-98, Standard Guide for Preparation of Aluminum Surfaces for Structural Adhesives Bonding (Phosphoric Acid Anodizing), American Society for Testing and Materials, Philadelphia, 1988.

[82] Venables, J. D., *J. Mater. Sci.* **19**, 2431–2453 (1984).

[83] Brockmann, W., Hennemann, O. D., and Kollek, H., *Int. J. Adhes. Adhes.* **2**, 33–40 (1982).

[84] Sargent, J. P., *Int. J. Adhes. Adhes.* **25**, 247–256 (2005).

[85] Kinloch, A. J., Welch, L. S., and Bishop, H. E., *J. Adhes.* **16**, 165–177 (1984).

[86] Cotter, J. L. and Kohler, R., *Int. J. Adhes. Adhes.* **1**, 23–28 (1980).

[87] McGarel, W., Farnham, H. A., and McGuckin, R., *Int. J. Adhes. Adhes.* **6**, 89–92 (1986).

[88] Boeing Process Specification, BAC 5632, *Boric Acid–Sulfuric Acid Anodizing*.

[89] Anodic coatings for aluminum and aluminum alloys, MIL-A-8625.

[90] Rider, A., Williams, I., Shum, Ed., and Mirabella, L., Environmental durability trial of bonded composite repairs to metallic aircraft structure, Report no. DSTO-TR-1685, (Defence Science and Technology Organisation, Australia, 2005).

[91] Royal Australian Air Force Engineering Standard for Composite Materials and Adhesive Bonded Repairs, No. C5033 Issue 1. Department of Defence, Australia.

[92] Abel, M. L., Watts, J. F., and Digby, R. P., *Int. J. Adhes. Adhes.* **18**, 179–192 (1998).

[93] (www.actechaero.com). Advanced Chemistry & Technology, Inc., AC-®130 Metal Prebond Surface Treatment

[94] Mazza, J. J., Advanced Surface Preparation for Metal Alloys, in: 83rd Meeting of the AGARD Structures and Materials Panel, Florence, Italy, September 1996, pp. 10-1–10-12.

[95] Bishopp, J. A., Parker, M. J., O'Reilly, T. A., *Int. J. Adhes. Adhes.* **21**, 473–480 (2001).

[96] (www.cytec.com). Cytec Engineered Materials Inc., Technical Datasheet

[97] Berg, J. C., *Semi-empirical Strategies for Predicting Adhesion*, (Elsevier, Amsterdam, 2002), 1st ed., Vol. 2, Ch. 1, pp. 1–73.

[98] ASTM Standard D 3762-03, Standard Test Method for Adhesive-Bonded Surface Durability of Aluminum (Wedge Test), American Society for Testing and Materials, Philadelphia, 2003.

[99] Venables, J. D., McNamara, D. K., Chen, J. M., Ditchek, B. M., Morgenthaler, T. I., Sun, T. S., and Hopping, R. L., *Nat. SAMPE Tech. Conf.* **12**, 909 (1980).

[100] Underhill, P. R. and DuQuesnay, D. L., *Int. J. Adhes. Adhes.* **26**, 88–93 (2006).

[101] Pate, K. D., *Applications of Adhesives in Aerospace*, (Elsevier, Amsterdam, 2002), 1st ed., Vol. 2, Ch. 25, pp. 1129–1192.

[102] ASTM Standard D 3167-03, Standard Test Method for Floating Roller Peel Resistance of Adhesives, American Society for Testing and Materials, Philadelphia, 2003.

[103] Rose, J. L., *Ultrasonic Inspection of Adhesive Bonds*, (Elsevier, Amsterdam, 2002), 1st ed., Vol. 1, Ch. 18, pp. 699–724.

[104] Bond, D. A., The Effect of Environmental Moisture on the Performance and Certification of Adhesively Bonded Joints, in: 2004 FAA Workshop on Bonded Structures, Seattle, WA, June 2004, available from: http//:www.niar.wichita.edu.

[105] Davis, M., Best Practices in Adhesive Bonding, in: 2004 FAA Workshop on Bonded Structures, Seattle, WA, June 2004, available from: http//:www.niar.wichita.edu.

[106] Barnes, T. A. and Pashby, I. R., *J. Mater. Process Tech.* **99**, 72–79 (2000).

[107] Munns, I., *Mater. World* **3**, 527–529 (1995).

[108] Munns, I. J. and Georgiou, G. A., *Insight* **37**, 941–952 (1995).

[109] Department of Defense, Military handbook: Metallic materials and elements for aerospace vehicle structures. MIL-HDBK-5H, USA 1988.

[110] *American Society for Metals, Metals Handbook Ninth Edition*, (ASM International, Ohio, 1979), 9th ed., Vol. 2, Ch. 1, pp. 1–204.

[111] Andreatta, F., Turco, A., de Graeve, I., Terryn, H., de Wit, J. H. W., and Fedrizzi, L., *Surf. Coatings Tech.* **201**, 7668–7685 (2007).