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Fluoride-Induced Interfacial Adhesion Loss of Nanoporous Anodic Aluminium Oxide (AAO) templates in aerospace structures

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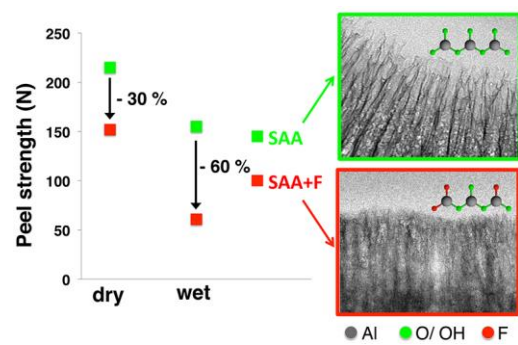
ABSTRACT

Nanoporous anodic aluminum oxides (AAOs) are used as templates in various technological applications, including load-bearing aircraft structures. But in spite of their popularity, the important aspects that control their (dis-)bonding to an organic coating are not fully understood. To study the mechanisms behind the negative effect of fluorides on AAOs adhesion we employed both porous- and barrier AAO specimens. These were prepared by anodizing in sulfuric acid (SAA) or a mixture of phosphoric- and sulfuric acid (PSA), with- and without post-anodizing immersion in NaF. Experimental results indicate that chemical surface modifications, as concluded from X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS), are dependent on the initial oxide composition. A partial replacement of surface hydroxyls (OH) by fluorine on SAA leads to adhesion loss due to removal of these stable sites for oxide-to-adhesive interfacial bonding. Conversely, fluoride-assisted dissolution of surface phosphates in PSA compensates for fluoride adsorption by revealing new OH groups. As the net OH fraction remains similar there is no further adhesion loss under water-ingress. The surprising reduction of dry adhesion is contributed to an interplay between surface energy changes affecting the type of attractive forces across the interface, as well as the loss of fine surface features, as seen by transmission electron microscopy (TEM) cross-section images.

Keywords

Aluminium, Anodizing, Adhesion, Fluorides, Nanotemplates

TOC



INTRODUCTION

Anodizing of is one of the most prominent industrial surface treatments used to produce durable protective anodic aluminum oxide (AAO) films with many desirable engineering properties such as corrosion and wear resistance. Anodizing can produce both barrier and porous layers, but porous oxides are by far more industrially important, as their porosity serves as an excellent base for further surface finishing such as sealing, painting, adhesion, electroplating or certain decorative functions ¹. Such anodized products can be found in packaging, architecture, electronics, lithography or automotive and aerospace components. In recent years anodizing has also become one of the simplest available commercial methods to produce templates for the fabrication of nanostructured materials ². By controlling the process parameters such as the electrolyte properties (composition, concentrations) and the anodizing conditions (voltage, time, temperature) this process enables the production of nanotemplates and a wide range of dimensions. Advances in nanotechnology have further driven the development of countless specialized procedures to produce AAO nanotemplates with complex geometries for specialized technological applications such as sensors, catalysis, molecular membranes, MEMS and biomedical devices ³⁻⁴.

But despite their popularity, the important aspects that control (dis-) bonding between the AAO templates and organic coatings are not fully understood. While some of the previous mentioned applications require a strong and durable interfacial bonding between the two phases, others will benefit from a more inert nature of the AAO mold. In the absence of additional treatments, the interfacial properties of porous AAO's are inherent to the chosen electrolyte and final morphology. The most crucial aspect that determines the structure and interfacial properties of these porous AAO's is the surface pre-treatment ⁵. The first step in this process is cleaning the aluminum surface from external contaminations such as grease and inks. Hereafter, the top few microns of the surface material are etched to remove surface layers from

manufacturing induced damage and near-surface artifacts ⁶. Anodizing in an acid electrolyte generally follows this step, resulting in a duplex nanoporous oxide layer.

This array of pre-treatment steps is generally based on aqueous solutions that often contain different additives for acceleration of surface reactions and bath stabilization. Historically in the aerospace industry, chromic acid was the main ingredient in most etching solutions ⁷. However, in the attempt to avoid this toxic substance, many wet etching solution now contain fluorides, as these have been used for more than a decade for the activation of aluminum (and other metals) in the production of chemical conversion layers ⁸. The presence of F⁻ ions enables metal activation by dissolution and replacement of certain O²⁻ lattice anions ⁹ or by forming surface complexes ¹⁰. The mechanism of chemical dissolution consists of the formation of an Al-F complex by adsorption of the free fluorides, which later desorb from the surface towards the bulk solution. From all metals studied by Cerezo et al. ¹¹, the influence of surface hydroxyls on the formation of the conversion coating was most dominant for aluminum, and the dissolution in this case was solely attributed to fluoride interaction with surface hydroxyls.

Several publications have even considered adding fluorides to the anodizing bath of aluminum and aluminum alloys ¹²⁻¹⁵. They report a beneficial increase in the film growth rate at low to moderate fluoride concentrations. At higher concentrations, chemical dissolution was dominant and affected the film morphological features. The resulting anodic oxides contained incorporated fluorides through the entire film, as fluorides migration rate under the influence of the electric field is about double the rate of O²⁻ ions migration ¹⁶. So far, these investigations focused on the relation between fluoride additions and the final oxide properties.

Aircraft manufacturers have noticed that fluoride contamination in their pre-treatment or rinsing baths is detrimental for the subsequent adhesion between the anodized aluminum components.

To our knowledge, the only previous study to mention the effect of fluorides on the adhesion of anodic oxides was completed in 1979 by Venables et al.¹⁷. The authors claimed that fluoride contamination removes the protrusions previously made by sulfuric-chromic acid etching, leaving a thin and flat surface oxide that does not provide mechanical interlocking with the applied organic resin. Yet, in a recent publication we have shown that flat oxides can adhere to an epoxy adhesive, with their level of adhesion depending on surface chemistry and the adhesive composition¹⁸⁻¹⁹. With this new knowledge and with the increasing importance of fluorides ions in Cr(VI)-free surface treatments, this study aims to investigate the fundamental mechanisms behind the loss of adhesion caused by fluorides. Two types of porous anodic aluminum oxide (AAO) structures from our previous work²⁰ were selected for this case study: a PSA oxide that exhibits a high level of adhesion and a moderate SAA that could possibly be improved by pore opening. By employing porous- and barrier AAO specimens for both chemical characterization and mechanical tests in this study we are able to make a distinction between contributions from morphological and chemical surface modifications.

EXPERIMENTAL SECTION

Materials and sample preparation

Barrier AAO Specimens for barrier-type anodizing were cut from a 0.3 mm thick sheet of pure aluminum (99.99%, Hydro). To remove the surface imperfections, and to provide a flat substrate suitable for high-resolution surface analysis and quantification, all barrier-type specimens were electropolished in a mixture of 80 vol.% ethanol and 20 vol.% perchloric

acid according to the details described in ²¹. Galvanostatic anodizing was performed with SM120-25 power-supply (Delta Elektronika). A three-electrode cell filled with 400 mL solution was used with two AA1050 aluminum cathodes. SAA specimens were prepared in 10 g/L H₂SO₄ at 0.2 A and 35 °C for 4 s. PSA was prepared in the same conditions, with 40 g/L H₃PO₄ and 10 g/L H₂SO₄. After anodizing, the substrates were thoroughly rinsed with running demineralized water for 30 s and subsequently ultrasonically rinsed for 3 minutes. Anodizing conditions were pre-selected to yield barrier-type anodic oxides by stopping the oxide growth at the end of the region in which the voltage increases linearly with time which is associated with the formation of a barrier layer ²². The samples were then cut in half and one part was immersed in 25 g/L NaF solution for 5 minutes. The samples were then rinsed with running demineralized water for 30 s and ultrasonically rinsed for an extra 5 minutes to remove any unbound ions.

Barrier AAOs for floating roller peel testing were prepared from AA2024-T3 alclad (clad layer AA1230) aluminum test panels of 250x95x1.6 mm and 300x95x0.5 mm for the thick and thin sheets, respectively. Before anodizing, specimens were degreased, alkaline etched and desmuted. Degreasing was achieved by wiping the panels with ethanol. This was followed by a 2 min. alkaline etching with 40 g/L P3 Almecco 51 (from Henkel) at 35°C and a 1 min. pickling with 35 vol.% HNO₃ at RT. After each step, the panel was thoroughly rinsed with running demi-water, followed by 1 min. immersion rinsing in an agitated beaker of fresh demi-water. Anodizing at the same conditions as above, but at 5mA/cm² was performed for 8s. Although the current density is lower than for the model specimens, the time is doubled, so that the final barrier layer thickness should be similar. After anodizing, the panels were rinsed and dried with compressed air. The panels were then bonded (without primer) with FM 73 epoxy film adhesive (from Cytec Engineering Materials) within 10 minutes after the pretreatment of the thin panel was completed. After bonding, the panels were stored in a

sealed plastic bag for up to 24 hours before curing. Curing following the manufacturer instructions was achieved using a Joos hot plate press at 6 bar and 120°C for 75 minutes. Sample preparation method and configurations for the different tests are illustrated in Fig. 1.

Porous AAO Industrial porous specimens were prepared from AA2024-clad sheets. Sulfuric acid anodizing (SAA) panels were anodized in 25 g/L H₂SO₄ for 30 minutes at 21 V and 35 °C, with 2 g Al³⁺/L present in the electrolyte. Phosphoric sulfuric acid anodizing (PSA) panels were anodized for 30 minutes at 28 V and at 35 °C in a mixture of 40 g/L H₃PO₄ and 10 g/L H₂SO₄, also with 2 g Al³⁺/L. The less than optimal SAA conditions (concentration, temperature and time) were preselected to determine if post-treatment can improve wet adhesion strength, while the PSA conditions were preselected to determine if a high level of performance, as reported in our previous study ²⁰. Post-treatment was performed in 50 g/L NaF for 5 and 10 minutes at 25 °C for PSA and SAA, respectively. After treatments, the sheets were applied with phenolformaldehyde primer Redux 101 that was cured at 120°C. Subsequently they were autoclave bonded with epoxy adhesive AF 163 at 125°C and 6bar. Porous oxide samples are denoted: pSAA, pPSA, pSAA+F and pPSA+F (in which the p stands for ‘porous’) thought the paper in order to differentiate them from barrier samples). It is of importance to note the AF163 adhesive results in higher peel strength values than FM73 adhesive (approximately +10%). Additionally the peel strip with pPSA and pPSA+F was 0.8 mm instead of 0.5mm, which results in higher peel strength as well (approximately +40%). Sample preparation method and configurations for the different tests are illustrated in Fig. 1.

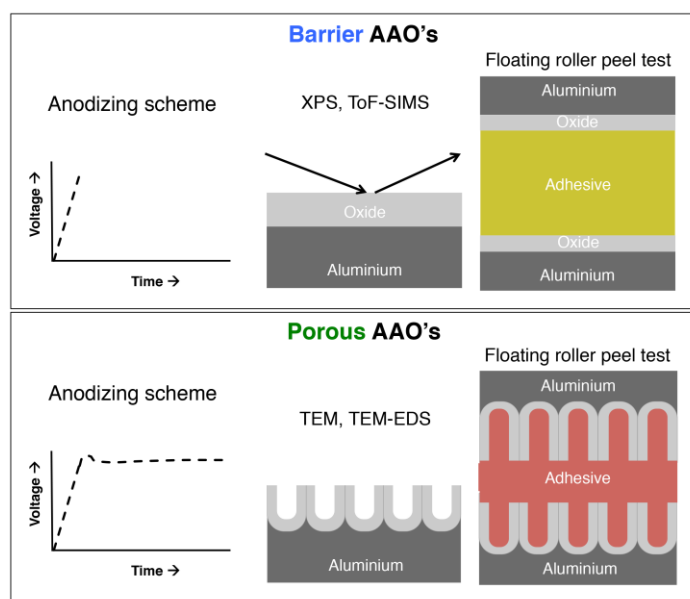


Figure 1: Schematic illustration of the preparation methods, morphologies and analysis configurations for the two different types of samples that were employed in this study.

Analysis methods

X-ray photoelectron analysis (XPS) XPS spectra were collected using a PHI5600 photoelectron spectrometer (Physical Electronics) with an Al $K\alpha$ monochromatic X-ray source (1486.71 eV of photons). The vacuum in the analysis chamber was approximately 5×10^{-9} Torr during measurements. High-resolution scans of the Al2p, O1s, C1s, P1s S2p, and F1s photoelectron peaks were recorded from a spot diameter of 0.8 mm using pass energy of 23.5 eV and step size 0.1 eV. Measurements were performed with a takeoff angles of 15° with respect to the sample surface. Reproducibility of XPS measurements was verified by triplication of the measurements on at least two different specimens (and at a take-off angle of 45°).

Data was analyzed with PHI Multipak software (V9.5.0.8). Prior to fitting, the energy scale of the XPS spectra was calibrated relative to the binding energy of adventitious hydrocarbons (C-C/C-H, Fig. 2(e)) in the C1s peak at 284.4 eV. Curve fitting was then done after a Shirley-type background removal, using mixed Gaussian (80–100%) – Lorentzian shapes.

Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) ToF-SIMS measurements were performed with a TOF.SIMS⁵ (ION-TOF GmbH). Both positive and negative secondary ion spectra were obtained using a 30 keV Bi₃⁺ primary ion beam operated at high current bunched mode with 0.41 pA target current. The total ion dose was kept below the static limit of 1×10^{13} ions cm⁻² analysis⁻¹ on an analysis area of 100x100 μm² at 128 x 128 pixels. Three random positions were analyzed on each sample, both in positive and negative mode, to validate that the obtained spectra were reproducible and characteristic for the sample. Reported intensities were normalized using the total ion count. The mass accuracy of a peak assignment or so-called deviation (in ppm) is calculated by dividing the absolute difference between experimental and theoretical mass by the experimental mass.

Scanning and Transmission Electron Microscopy (SEM and TEM) Cross-sections of selected porous-type anodized specimens were cut using a diamond saw and embedded in an epoxy at room temperature. The cross-sections were then ground and polished down gradually and finished using a 1 μm diamond paste. Lamella for TEM characterization were then prepared by focused ion beam milling using a Ga liquid metal ion source, and in-situ lift out from the interface of the adhesive joint using Helios Nanolab 600 dual beam, FEI coupled to an Omniprobe™ micromanipulator. The lamellas of approx. 1 μm thickness were further thinned down for electron transparency to an approx. thickness of 120 nm, and low energy milling (2 keV) was finally performed to remove any high energy ion beam milling induced artifacts and damage to the samples.

FIB-prepared lamellas were then transferred to a Tecnai T20 G², FEI for TEM analysis, operating at 200 keV. Bright field images of the films' morphology were recorded for comparison. The local composition of the anodic oxide and the relative concentrations of

the resin in the porous structure were also measured using an X-ray energy dispersive spectrometer (EDS, Oxford 80 mm² X-Max SDD detector) coupled to the TEM. Quantification of the obtained EDS data was performed using Aztec™ TEM EDS software.

Floating roller peel tests Floating roller peel tests were performed according to ASTM D3167-03a²³. The bonded panels were cut into 25 mm wide samples using a diamond saw. After fixing the test panels in the apparatus, the unbounded end of the specimen was attached to the lower head of the testing machine. The thin panel was peeled off from the thicker panel with a speed of 100 mm/min. The peeling load versus head movement (or load versus distance peeled) was recorded. All tests were performed at ambient temperature. The first half of the specimen was peeled under dry atmospheric conditions. Water containing surfactant was then applied to the crack-tip and the second half was peeled under wet conditions.

RESULTS AND DISCUSSION

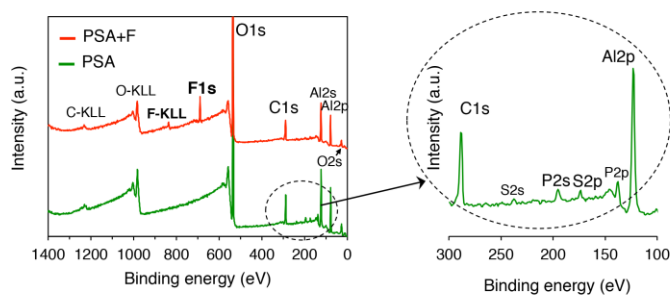
Surface Chemistry of Barrier AAO

Barrier-type oxides were employed to characterize changes in the chemical surface composition using XPS and ToF-SIMS. Fig. 2 (a) displays the XPS survey spectra of PSA oxide before- and after 5 minutes of immersion in NaF solution followed by 3 minutes of rinsing. The main elements in the PSA spectrum in Fig. 2 (a) are: O, Al, C, P and S (no P in SAA spectrum). Besides carbon that arises from atmospheric contamination, all other elements observed are inherent to the anodized oxide. The spectrum after immersion in NaF solution (Fig. 2 (a)) contains, in addition to the previously mentioned elements, 2-4 at. % of fluorine for both SAA and PSA. No Na was detected in any of the specimens. High-resolution spectra (HRES) of O1s, Al2p, C1s, P2s, S2p and F1s were recorded to evaluate changes in the binding states of the surface elements. Examples of the typical HRES

photoelectron peaks are shown in Fig. 2 (b) from PSA+F surface. The average measured binding energies (BE) are listed in Table 1.

The full-width at half maximum (FWHM) of the $O1s$ envelope is changing from 2.8 to 2.6 ± 0.1 eV for SAA and SAA+F, respectively. FWHM of 2.8 and 2.7 ± 0.1 eV were recorded for PSA and PSA+F, respectively. No changes in the FWHM were recorded for $Al2p$ (1.7 eV). Sulfur and phosphor are found at 169.7 eV and 191.5 eV, respectively. These binding energies correspond to sulfates and phosphates²¹. The average binding energy of fluorine $F1s$ was 685.3 ± 0.1 eV with FWHM of 2.2 eV. The binding energy for F in the ionic bond AlF_3 is 687.8 eV with FWHM of 3.0 eV²⁴. According to the Eh-pH diagram (HSC Chemistry V6), AlF_3 is also not stable in the alkaline conditions that were applied in this study. The thermodynamically stable species are F^- and $AlOOH$ (Fig. S1 and S2 in the supporting material). Hence, the lower binding energy of fluorine on the SAA and PSA oxides indicates a weaker nature of interaction between the anodic surface and the fluoride ions. To evaluate relative changes in the chemical composition of the surface groups, HRES data was fitted into the subcomponents shown in Fig. 2 (b), following the method described in Abrahimi et al.²¹. The results are listed in Table 1. Fitting the different groups and calculating the relative amount of surface hydroxyls (while accounting for the contribution of surface contamination) reveal that there is a reduction in the amount of surface hydroxyls on SAA+F oxide compared to SAA (therefore the narrower FWHM of $O1s$) and minor reduction in the sulfate content. Conversely, PSA+F has a larger amount of surface hydroxyls compared to PSA, as well as a reduced number of phosphates, with no change in the relative amount of sulfates.

(a) Survey Spectra



(b) High-Resolution Spectra

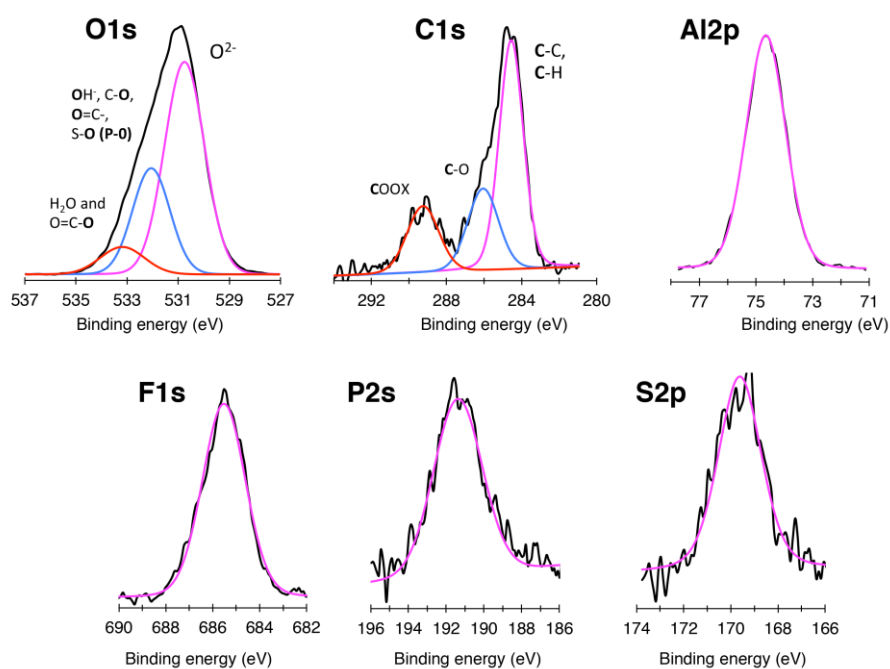


Figure 2: (a) XPS survey spectra for PSA before- (red line) and after 5 min. immersion in 50 g/L NaF (PSA+F, green line) and (b) example of a high-resolution XPS spectra for O1s, C1s, Al2p, F1s, P2s and S2p. Fitted peaks for individual species are marked with colored lines, while the measured spectra are shown in black lines. Peak dimensions were scaled for presentation purposes.

Table 1: Average binding energies (± 0.2 eV) from at least two separate XPS measurements and the calculated relative percentage of surface species. Subpeak assignments corresponds to: (1) C-C/ C-H, (2) C-O, (3) COOX, (1) O^{2-} , (2) OH^- , C-O, O=C- and S-O, (3) H_2O and O=C-O.

	C1s (eV)			O1s (eV)			Al2p (eV)	S2p (eV)	P2s (eV)	F1s (eV)	Cal. OH ⁻ (%)	Calc. SO ₄ ²⁻ (%)	Calc. PO ₄ ³⁻ (%)
	1	2	3	1	2	3							
SAA	284.8	286.2	289.3	530.8	532.2	533.2	74.4	169.4	-	-	23	3	-
SAA+NaF	284.7	286.2	289.2	531.0	532.1	533.2	74.5	169.6	-	685.2	14	2	-
PSA	284.8	286.4	289.4	531.1	532.3	533.5	74.7	169.5	191.6	-	14	2	4
PSA+NaF	284.8	286.3	289.4	530.8	532.0	533.2	74.3	169.8	191.5	685.6	16	2	2

Positive and negative ToF-SIMS spectra were acquired to obtain a better understanding of the effect of fluorides on the chemical composition of the different oxides. Selected fragments of interest are shown in Figs. 3-5 and a detailed fragment list is given in Table 2. Peaks at nominal masses 96, 79 and 122 m/z were identified as SO_4^- , PO_3^- and $AlPO_4^-$ respectively (Fig. 3 a-c) and confirm the presence of sulfates and phosphates, in agreement with the previous XPS analysis. Fluorides are found only on PSA+F and SAA+F, as shown by fragments as F^- , $AlOF^-$ and $AlOF_2^-$, which are found at nominal masses 19, 62 and 81 m/z respectively (Fig. 3 d-e).

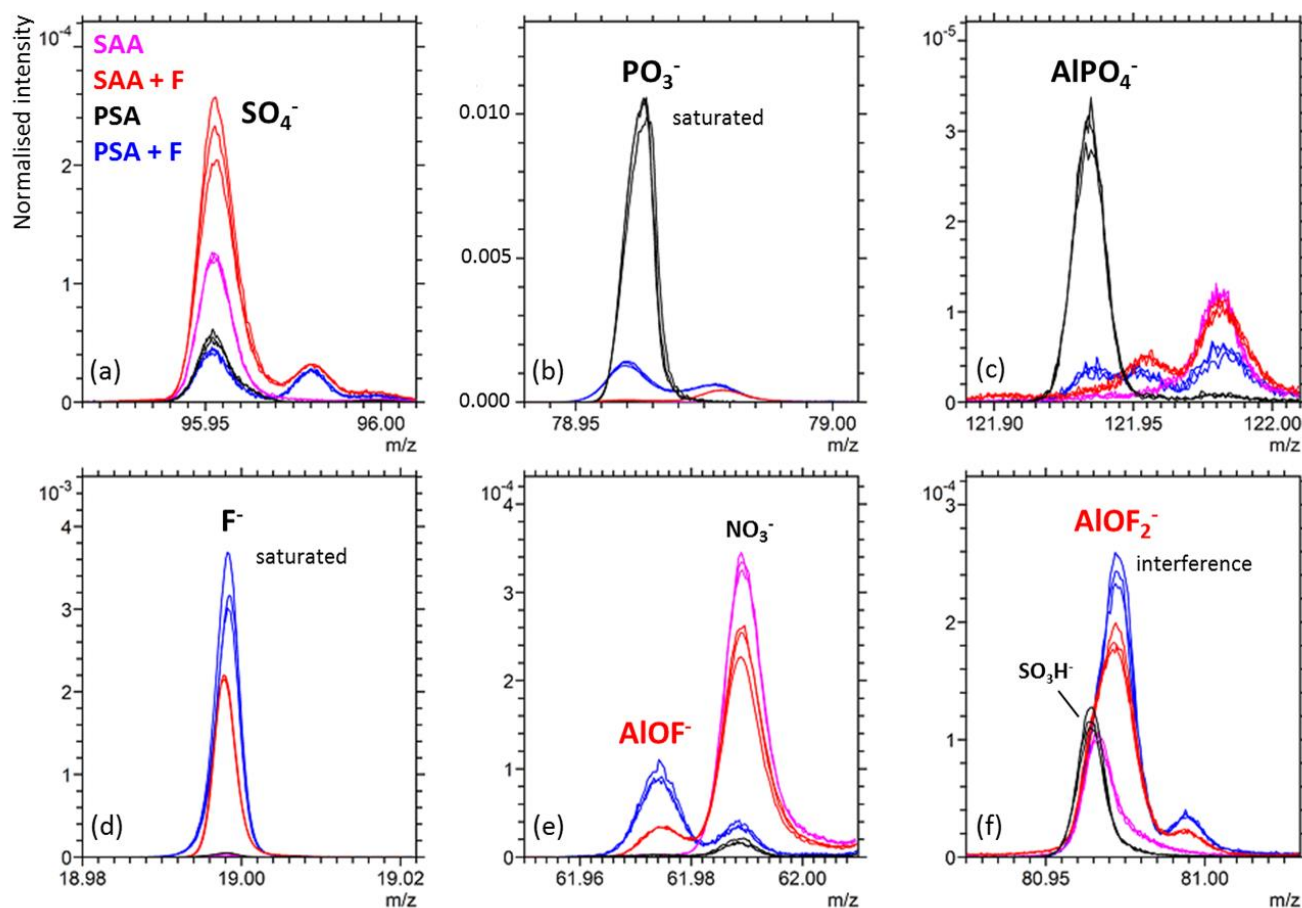


Figure 3: a comparison of the (normalized) measured ToF-SIMS spectra of fragments showing the presence of sulfates and phosphates (a–c) and fluorides (d–f) on the surfaces of the different barrier- AAO's (overlay of 3 spectra per sample).

Fragments as AlOF^- and AlOF_2^- show that fluoride ions interacted with the anodic surface, but do not clarify whether the fluorides are bonded to oxygen or to aluminum. In a higher mass range, fragments were found that give insights into bonding configurations. Peaks at nominal masses 197, 199, 201, 203 and 205 m/z were identified as $\text{Al}_3\text{O}_7\text{H}_4^-$, $\text{Al}_3\text{O}_6\text{H}_3\text{F}^-$, $\text{Al}_3\text{O}_5\text{H}_2\text{F}_2^-$, $\text{Al}_3\text{O}_4\text{HF}_3^-$ and $\text{Al}_3\text{O}_3\text{F}_4^-$ respectively (Fig. 4 (a)), and form a series of fragments in which surface hydroxyl groups are gradually replaced by fluorides. This is illustrated by their proposed chemical structures that were added next to the spectra. $\text{Al}_3\text{O}_7\text{H}^-$ is a fragment that can be considered saturated with hydroxyl groups, while $\text{Al}_3\text{O}_3\text{F}_4^-$ is a

fragment that is fully fluorinated. For ease of reference, fragments will be denoted as 0F, 1F, 2F, 3F and 4F, depending on the number of fluorides they contain. Fig. 4 (b) shows a bar graph in which normalized peak areas are plotted for fragments 0F to 4F. For SAA, only 0F was found present in its mass spectrum, with a normalized intensity more than double the intensity found for 0F in SAA+F. On the other hand, the intensity distribution in SAA+F shows a maximum for fragment 1F, directly followed by 2F. As such, the observations presented in Fig. 4 clearly demonstrate the partial replacement of surface hydroxyls by fluorides on SAA+F, in which fluorides bond directly with aluminum. The general trend is different for PSA and PSA+F. The dominance of fragments 1F, 2F and 3F in the spectrum of PSA+F shows that, in a similar manner to SAA+F, fluorides bond directly with aluminium. However, relative to PSA, the normalized intensity of hydroxyl fragment 0F is significantly higher for PSA+F. This is in accordance with the previous XPS results and demonstrates that fluoride adsorption on PSA+F did not occur through replacement of surface hydroxyl groups.

Table 2: Selected (negative) ToF-SIMS fragments mass, deviation and resolution

Fragment	Mass	Deviation	Resolution
AlOF ⁻	61.9740u	-22 ppm	8992
AlO ₃ H ₂ ⁻	76.9834u	11.4 ppm	8696
AlOF ₂ ⁻	80.9711u	-33 ppm	5806
AlPO ₄ ⁻	121.9359u	3.5 ppm	9049
Al ₂ O ₅ H ₃ ⁻	136.9631u	10.4 ppm	8228
Al ₃ O ₇ H ₄ ⁻	196.9413u	2 ppm	8468
Al ₃ O ₆ H ₃ F ⁻	198.9358u	-3 ppm	7996
Al ₃ O ₅ H ₂ F ₂ ⁻	200.9319u	-1 ppm	8378
Al ₃ O ₄ HF ₃ ⁻	202.9272u	-3 ppm	8586
Al ₃ O ₃ F ₄ ⁻	204.9227u	-4 ppm	8380

It was further investigated whether ToF-SIMS results support XPS analysis regarding surface hydroxyl fractions. A peak at nominal mass 44 m/z, identified as AlOH⁺ (Fig. 5 (b)), could be expected to reflect the variations in hydroxyl fraction among the different oxides. However, in contrast to the XPS results, significantly higher intensities are found for PSA+F, compared to all other oxides. Furthermore, peak intensities of fragments such as Al⁺ (Fig. 5(a)), AlO⁺ (not shown) and AlO₂⁻ (Fig. 5 (c)) are also significantly higher for PSA+F. This suggests a higher concentration of aluminium in PSA+F, which can be explained by the changes taking place at the surface of PSA during NaF treatment. Initially, the PSA surface is mainly covered by aluminum phosphate (and some sulfates), as indicated by Fig. 3 (a-c). During immersion, fluoride-assisted dissolution of surface phosphates is taking place, as seen by the reduced peak intensities of PO₃⁻ and AlPO₄⁻ (Fig. 3 (b-c)) and concluded by XPS

analysis. Consequently, the aluminum (oxide) concentration increases at the surface. In addition, few hydroxyl groups are newly revealed (or created) at the surface. AlOH^+ does not reflect the hydroxyl fraction variations and seems to be strongly influenced by the aluminum concentration. One must be cautious with semi-quantitative interpretations of ToF-SIMS data, as intensities are not merely dependent on actual concentrations, but also on ionization probabilities, which are matrix-dependent. Nevertheless, semi-quantitative interpretation is possible if samples have similar chemistries and secondary ion fragments are properly selected ²⁵. Fragments as AlO_3H_2^- and $\text{Al}_2\text{O}_5\text{H}_3^-$ (found at nominal masses 77 and 137 m/z (Fig. 5 (d-e)) can be considered to be saturated with hydroxyl groups, similar to the 0F fragment in Fig. 4 (a). The intensity distribution of these ‘hydroxyl saturated’ fragments matches quite well with the XPS results. Normalized peak areas are plotted in Fig. 5 (f) and support the theory that the hydroxyl fraction of SAA anodized oxides significantly decreases after NaF treatment, while the hydroxyl fraction of PSA anodized oxides increases after NaF treatment. These results illustrate that the chemical modifications taking place during immersion are dependent on the initial chemical composition.

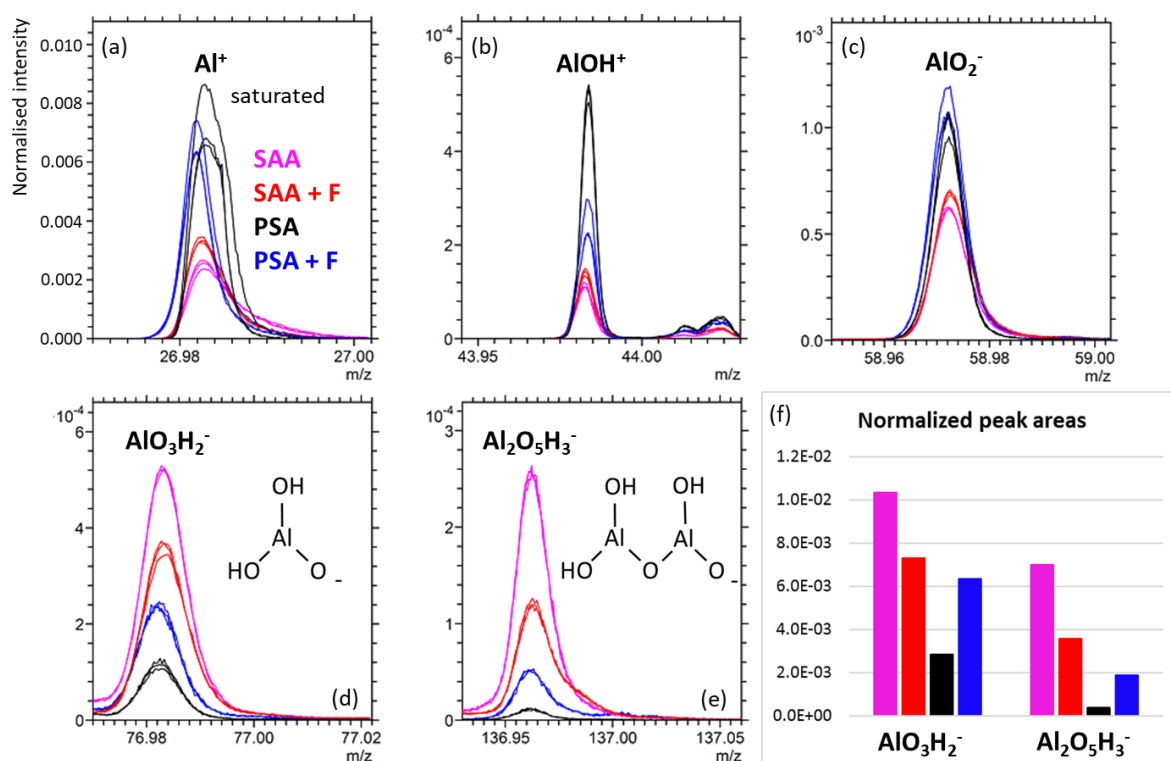


Figure 5: (a-e) a comparison of the (normalized) ToF-SIMS spectra of fragments studied to extract information about the hydroxyl fraction (overlay of 3 spectra per sample). (f) Bar graph showing the intensity distribution of the average (normalized) peak areas of two saturated OH fragments.

Morphological Analysis of Porous AAO

The anodizing conditions and the measured morphological features of the porous AAO are listed in Table 3. Figure 6 (a) and (b) display the TEM cross-section images from the porous specimens pSAA and pSAA+F. Both oxides have comparable thickness, pore diameter and barrier layer thickness (Table 3). The mere distinction between the two morphologies is evident at the oxide/resin interface. The top of the AAO seems to be reduced in density by the NaF treatment and the nano-sized oxide branches visible at the top of pSAA (Fig. 6 (a) and in Fig. S3 in the supporting material) appear to be smoothed out for the

pSAA+F sample (Fig. 6 (b)). Some dissolution of the porous AAO can be expected by the NaF solution due to the pH=11.6 as well as the fluorines [8, 17, 18].

Table 3: Anodizing conditions and morphological features as measured on TEM.

Annotation	H ₂ SO ₄ (g/L)	H ₃ PO ₄ (g/L)	Anodizing Temp. (°C)	Voltage (V)	Oxide thickness (μm)	Pore diameter (nm)		Barrier layer thickness (nm)
						[^Top]	[^^Bottom]	
pSAA *	10	-	50	19	5.0	22	8	17
pSAA +F	25	-	35	21	5.4	24	10	22
pPSA *	50	80	35	19	3.0	28	15	20
pPSA +F	10	40	35	28	4.8	34	28	26

*While specimens prepared in exactly the same conditions were not available at the time of TEM observations and analysis, specimens with similar morphological features were selected for morphological comparison. Oxides with these modified anodizing conditions were only used for TEM observations, while panels prepared in the original conditions (with- and without fluoride immersion) were applied in floating roller peel tests.

^Top = in the vicinity of the oxide/resin interface,

^^ Bottom = in the vicinity of the metal/oxide interface

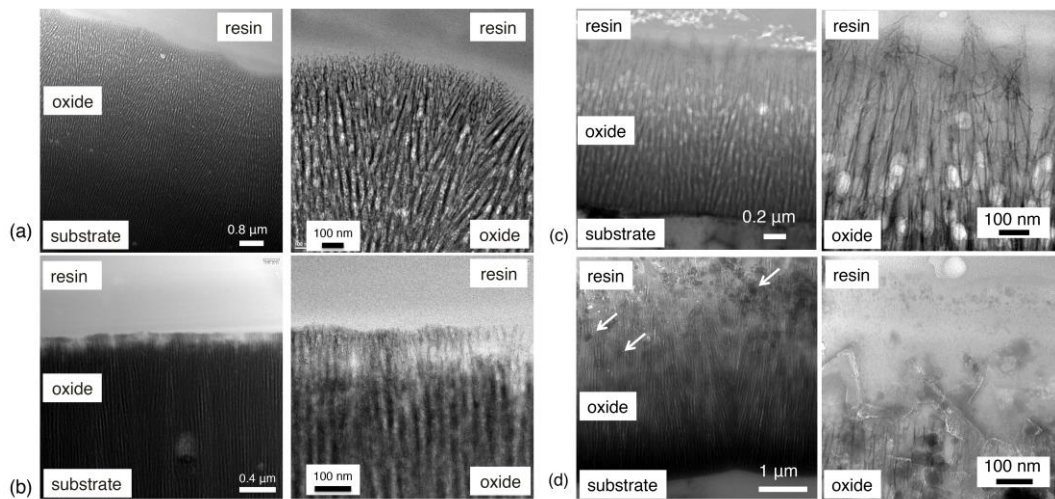


Figure 6: Bright field TEM cross-section images and a higher magnification image from the oxide/resin interface is shown on the right of (a) pSAA, (b) pSAA+F, (c) pPSA and (d) pPSA+F. Black spots in image (d), indicated by the arrows were identified as NaF particles by TEM-EDS analysis.

Figure 6 displays the bright field TEM images of pPSA, and pPSA+F ((Fig. 6 (c) and (d), respectively), prepared in the conditions listed in Table 3. In contrast to pSAA morphologies, pPSA oxides are more porous. This is generally associated with the aggressive nature of phosphoric acid, especially when combined with relatively high electrolyte temperatures²⁰. This results in an open structure with wider and partially dissolved pores in the vicinity of the oxide/resin interface, often leading to the partial collapse of the surface pores leading to a structure that is similar to a “bird’s nest” with nano- and micro porosity. Consequently, pPSA oxide surface presents a rough interface compared to pSAA (Fig. 6 (c)). The differences between pPSA and pPSA+F are also visible at the resin/oxide interface. The general pore structure is similar, however, the very rough features at the top part that were present at pPSA oxide seem to be completely removed by the fluorides in pPSA+F. Fluorides assisted dissolution seems to have almost completely dissolved the upper part of the pPSA oxides, leaving behind an interface with significantly reduced surface roughness and fine features.

Black spots in Fig. 6 (d) can be seen on the oxide, especially at the top part, which obscures some of the morphological features. Plasma cleaning of the thin lamella does not eliminate these features, indicating that they are inherent part of the sample. These were identified by TEM-EDS analysis as NaF particles. It appears that the specimen was not properly rinsed, leaving excess amounts of sodium fluoride in the oxide. Analysis cannot conclusively tell if the presence of NaF in the form of small crystals/particles is inherent to the sample or caused by Ga ion beam induced recrystallization or damage.

X-ray energy dispersive spectrometry (EDS) measurements were also performed on the TEM lamellas. Concentration profiles of all the detected elements are presented in Fig. S4 and Fig. S5 in the supporting material for pSAA and pPSA, respectively. The three different

phases: aluminum, oxide, and resin are clearly distinguished by their different composition. The oxide mainly consists of aluminum and oxygen, with low amounts of electrolyte-derived anions (2-3 wt.% S and about 1 wt.% P in pPSA)²¹. In both oxides, fluorine was hardly detected during TEM-EDS profile measurements. Fluorine at very low concentration (≤ 1.0 wt.%) was detected in pSAA+F by point analysis of various carefully chosen areas along the oxide/resin interface. Conversely, fluorine (approx. 0.2 wt.%) was detected on the pPSA+F oxide (especially in the vicinity of the oxide/resin interface). However, sodium was also detected and this could be due to the presence of the NaF contamination (black spots in Fig. 6(d)).

The organic resin is mostly composed of carbon and oxygen. Inorganic additives such as silicon and bromine were also detected in the resin. About 0.1 wt.% Si was detected only in the resin, while bromine was detected within the oxide, with an increasing concentration towards the oxide/resin interface and a final concentration of 4-10 wt. % within the bulk of the resin. Bromine concentration generally follows the same trend as the carbon profile (Fig. S4 and S5 in the supporting material), providing a clear indication for the presence of resin inside the pores. Hence, the carbon profiles are further used as an indication for the extent of resin penetration. A comparison between the carbon concentration profile in pSAA and pSAA+F, as well as pPSA and pPSA+F are shown in Fig. 7 (a) and (b), respectively. In both cases, the two different specimens exhibit very similar profiles, indicating that resin penetration was not prohibited by the immersion in NaF and the so-called mechanical anchoring was not prevented. Generally, carbon profile concentration in pPSA and pPSA+F is more gradual compared to pSAA and pSAA+F, since the pores are larger and the top of the oxide is thinned.

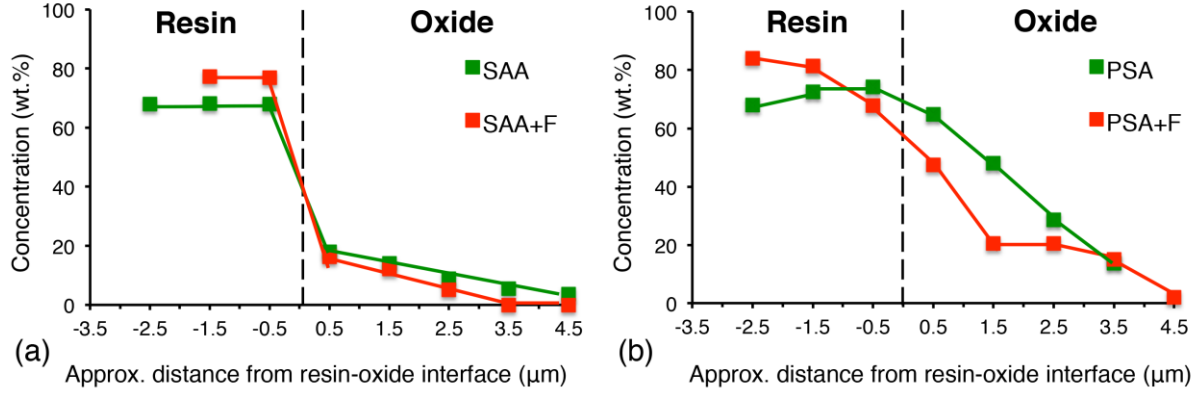


Figure 7: EDS profile showing the carbon concentration across the oxide and resin for: (a) pSAA and pSAA+F, and (b) pPSA and pPSA+F.

Adhesion evaluation by floating roller peel tests

Adhesion of barrier- AAOs

Following the characterization of the oxide properties, floating roller peel tests were performed to evaluate the adhesion strength of the oxides bonded with typical aerospace epoxy resins. By measuring the peel strength of bonded panels with barrier-type oxides we minimize the effect of surface roughness, focusing on the role of surface chemistry in interfacial adhesion. These results are plotted in Fig. 8. Peel measurements on barrier-type oxides bonded with FM 73 epoxy show that only a minor reduction in dry peel strength is found after fluoride treatments. This is in line with previous research in which adhesion strength is effectively independent of the oxide chemistry, obtained by various anodizing treatment and electrolyte temperatures¹⁸. Optimum peel strength with cohesive fracture of the adhesive is obtained with an interface strength that is higher than the yield strength of the epoxy adhesive²⁶. Apparently dry adhesion is even easy to achieve on a flat, featureless, oxide through dipole-dipole interactions and hydrogen bonding, probably because both Al_2O_3 and primers/ adhesives are polar. In spite of the fact that fluorides can reduce the surface

energy²⁷⁻²⁹, a few percent of fluorine on the AAO surface do not cause dramatic reduction in their dry peel strength.

Under wet conditions, on the other hand, there is a three-fold loss of peel strength in SAA+F compared to SAA, while the performance of PSA+F remains similar to PSA. These results are in excellent agreement with our earlier findings which show that the wet peel strength of barrier-type oxides is proportional to the amount of surface hydroxyls¹⁸. The same trend is observed in here, see figure 10 (a): SAA with the largest amount of hydroxyls in this group (OH \approx 23 %, Table 1) exhibits the highest wet peel strength, while all the other oxides (SAA+F, PAS and PSA+F) exhibit similar performance as they contain a similar amount of surface hydroxyls (OH \approx 15 %, Table 1). Because some phosphates that were present on the surface of PSA were dissolved to reveal new surface hydroxyls on PSA+F, as measured by XPS and ToF-SIMS, the net effect of fluoride on the surface chemistry of PSA+F is small. As a consequence, there is no significant change in bond strength under wet conditions and no further adhesion loss is registered.

It is well established that interfacial bonding largely depends on the chemical affinities between the surface and the resin. Hence, chemical modifications to the oxide play important role in determining the type and strength of interfacial bonding³⁰⁻³¹. Studies on surface fluorination have shown that replacement of surface H, OH⁻ and O²⁻ sites by fluorides alter the surface properties significantly^{27-29, 32-33}, but with the few percent fluorine on the AAO surface in this study, no dramatic reduction in wet peel strength is found. As a consequence, the relation between OH% and wet peel strength that was previously found on barrier-type oxides still remains after fluorine treatment (Figure S7 (a)).

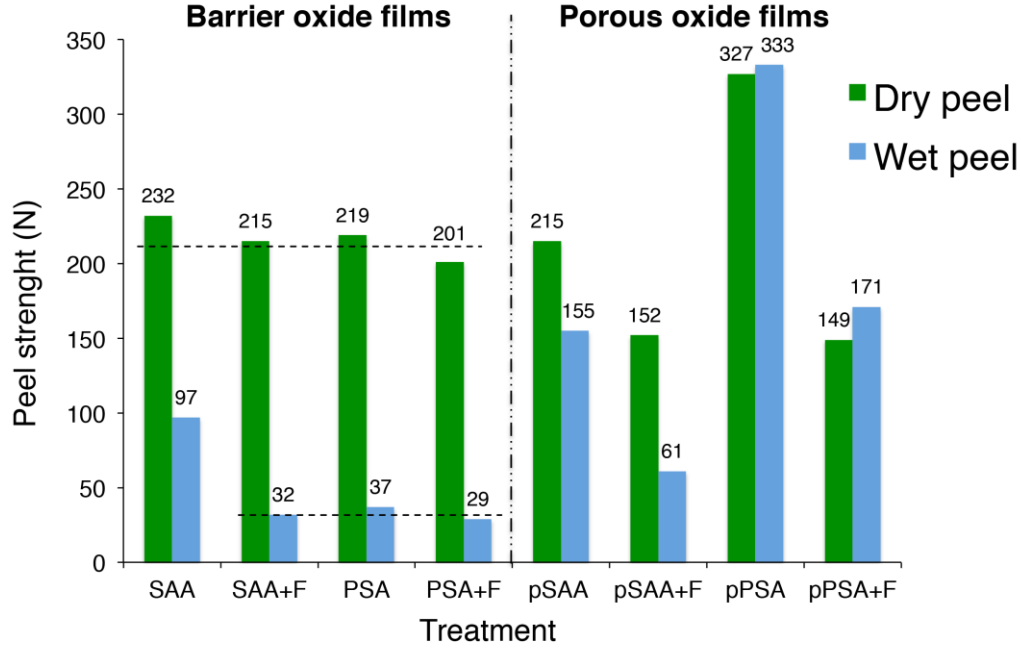


Fig. 8 Peel strength before- and after NaF dip for barrier AAO (a) SAA, SAA+F and (b) PSA, PSA+F and porous AAO (c) pSAA, pSAA+F and (d) pPSA, pPSA+F. Values are the average measured from six specimens.

Adhesion of porous AAOs

Since industrially applied AAO's are porous, their interfacial adhesion is affected by changes in the surface chemistry, as well as changes in the morphology, including differences in the surface roughness. Therefore, their adhesion performance will be affected by changes in both parameters. Peel test results for porous oxides are displayed in Fig. 8 for pSAA and pPSA, respectively. In all cases there is a significant reduction in the bond strength after fluoride treatments, under both dry- and wet conditions. Compared to pSAA, dry peel strength after fluoride treatment (pSAA+F) is reduced by 30% (from 215 N to 152 N), while the wet peel strength is reduced by 60% (from 155 N to 61 N). As the dry peel of barrier AAO was not significantly affected by changes in the surface chemistry due to fluoride treatment, the initial 30% reduction in dry conditions is rather unexpected. In our previous

research on porous AAOs practically all the studied anodizing pretreatments resulted in good dry adhesion, unless the pores were too small for the primer to fully penetrate and fill the pores¹⁸⁻²⁰. When pores are not properly filled, it results in a lower contact surface for bonding and the negative impact of these unfilled cavities is effective at dry peel as well as wet peel strength. Although both surface chemistry and oxide morphology have been affected by the NaF immersion, as shown by TEM images, still a proper filling of the pores had been confirmed with the carbon profile measured by TEM-EDS. Hence, the dry peel strength of the porous AAO's after fluoride immersion appears to deviate from this general trend, as shown in Fig. S7 (a) in the supporting information. In the absence of extended surface roughness, it is most likely that the surface chemistry of the porous oxides after NaF immersion will play a more significant role than for barrier oxides. Replacing hydroxides with fluorine can lead to a reduction in the surface energy²⁷⁻²⁹ and negatively affect depletion/wetting between the primer and the porous oxide³⁴. Consequently, the attractive interface forces as created by surface hydroxides, such as dipole-dipole and hydrogen bonding, are replaced by much weaker van der Waals forces due to the presence of the fluorides. These much weaker interfacial bonds require an extremely high surface area to collectively play a decisive role in interfacial interactions, as in the famous Gecko example and its man-made imitations³⁵⁻³⁹, a parameter that is clearly missing after fluorides-assisted dissolution of the fine features at the top surface of the pores. Additionally, the difference in adhesion could be explained by the use of a phenol-formaldehyde primer with the porous oxides, compared with an epoxy adhesive that was used with the barrier oxides. A phenol-formaldehyde is expected to give less adhesion than an epoxy, a parameter that previously did not play a significant role in dry porous oxides with rough interface¹⁸⁻²¹. Furthermore, there can also be a geometric effect, since load transfer between adhesive and porous anodic oxide is primarily by shear at pore surfaces. While usually the shear strength of an interface is

lower than the tensile normal strength ²⁶, as applicable with featureless barrier type oxides, any of above adhesion reductions will consequently be more affective on porous oxides. Further research is needed to identify the dominant cause of this reduction.

Under wet conditions, we expect to measure a reduction in the peel strength of the porous oxide pSAA+F due to partial replacement of surface hydroxyls by fluorides, as established for the barrier oxide SAA+F. Indeed, the relative wet peel strength reduction from 155N to 61N for pSAA versus pSAA+F is in agreement with the relative wet peel strength reduction from 97N to 33N for SAA versus SAA+F. This implies that for both SAA oxide types the wet peel strength is dominated by surface hydroxides and similar quantitative adhesion loss can be explained by the partial replacement of surface hydroxides by fluorides.

When we previously compared the peel strength of porous AAOs in dry conditions with wet conditions ²⁰, it was observed that properly filled oxide pores with sufficient dry adhesion have failed in wet conditions when produced by less than optimal anodizing parameters (chemicals and electrolyte temperature) that produced low nano- and micro surface roughness ²⁰. While with barrier type oxides a poor wet adhesion is obtained with PSA due to relatively low OH concentrations, typically with porous oxides higher wet peel strengths are obtained with PSA than with SAA. This difference can either be explained by possible differences in surface chemistry between barrier oxides and porous oxides, or the high surface area with nano-fibrils created by PSA. Typically with barrier oxides practically no oxide dissolution has occurred within the 4-8s of pre-treatment, while with porous oxides a substantial part of the surface has been dissolved with PSA due to the presence of phosphoric acid in the anodizing electrolyte, as shown by van Put et al. ⁴⁰. While with pSAA a reasonable amount of surface hydroxyls is formed by anodizing, still an increase strength can be obtained in moisture resistant adhesion by immersion in H₃PO₄ solution, as shown by Yendall et al. ⁴¹.

Considering the good wet peel values obtained with phosphoric sulfuric acid anodizing (as well as high temperature sulfuric acid anodizing [11]), the oxide dissolution does not only affect the surface morphology but may also yield an increased concentration of surface hydroxyls. Therefore, pPSA oxides typically deliver excellent peel strength in both dry and wet conditions. After NaF treatment, however, both dry and wet peel strength of pPSA+F are significantly reduced. The surprising reduction of dry adhesion is contributed to an interplay between surface energy changes affecting the type of attractive forces across the interface, as well as the loss of fine surface features, as seen by transmission electron microscopy (TEM) cross-section images, as was also described with pSAA+F. The slight difference in wet environment compared to dry conditions is negligible (49% and 55%, respectively). Since chemical analysis shows that the net effect of fluorine adsorption on the surface chemistry of PSA+F is small, we do not expect adhesion reduction of its porous equivalent to be occurring due to OH loss, as in pSAA+F. More likely, both peel strength values are dominated by the reduced surface polarity and effective surface area after NaF immersion. The relative adhesion loss on pPSA+F compared to pSAA+F in wet conditions (approximately 50%), confirms this hypothesis. The somewhat reduced effect with pPSA+F can be explained by the replacement of surface phosphates by new OH groups.

CONCLUSIONS

The mechanism of surface chemical modification caused by NaF post-treatment immersion was clarified by XPS and ToF-SIMS chemical analysis of barrier-type AAOs. Measurements reveal that surface hydroxyls are partially replaced by fluorides, but that the impact on oxide composition depends on the initial surface chemistry. While the amount of surface hydroxyls on SAA+F is significantly reduced due to fluorides adsorption, dissolution of surface

phosphates in PSA+F (which previously dominated the PSA surface composition) reveals new OH groups that compensate for fluorine adsorption and therefore, the net OH fraction remain similar (and even somewhat increases). Morphological modifications, as revealed by TEM images show that NaF immersion caused dissolution of the nano-fibrils at the top AAO surface. However, carbon concentration profiles measured by TEM-EDS are similar to the ones before NaF immersion, indicating that primer is still able to fill the pores.

In spite of the fact that fluorides can reduce the surface energy, a few percent of fluorine on the AAO surface do not cause dramatic reduction in dry adhesion of flat, featureless AAOs, probably because both Al_2O_3 and primers/ adhesives are polar. Reduced dry adhesion, on the other hand, is measured on the porous equivalent. This adhesion loss is probably caused by interplay of multiple parameters, including: surface energy changes affecting the type of attractive forces across the interface, as well as the loss of fine surface features that contribute to an extended surface area and (nano-) roughness. Further research is needed to identify the dominant cause.

It is more difficult to obtain water-resistant adhesion in which the number of OH groups is of great importance for stable bonding, even for a partially fluorinated AAO surface. By replacing water-stable OH surface interaction sites with fluorides, a significant loss of bond strength of SAA+F is measured under water ingress for both barrier- and porous oxides.

This study expands our knowledge on the different mechanisms that contribute to adhesion of AAOs and, for the first time, unambiguously distinguish contributions from interfacial chemistry in porous AAOs. The results demonstrate a clear relation between interfacial modifications on the nano- scale and macroscopic interface strength. Hereby we hope to encourage further research on similar systems of industrial relevance, as a better fundamental understanding can lead to further improvements of durable adhesion.

SUPPORTING INFORMATION

Fig. S1 in the supporting information displays an example of fibrils on top of SAA oxide. Fig. S2 and Fig. S3 display the chemical concentration profiles of all the elements measured on TEM cross-sections that are shown in Fig. 6. Fig. S4 and S5 show the Eh-pH diagrams that were made for F-Al-H₂O and Al-F-H₂O systems at 25 g/l NaF and 25 °C (calculated using HSC Chemistry version 6). Fig. S6 displays barrier AAO's specimens after floating roller peel tests, showing the different failure modes. Fig. S7 exhibits a comparison between the peel strength measured in this study to the general trends of porous oxides that were discussed in the previous paper²⁰.

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