

FAILURE MECHANISMS IN ADHESIVELY BONDED ALUMINIUM: AN XPS AND PEELS STUDY

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Abstract

The morphology and chemistry of the failure of adhesively bonded PAA treated aluminium alloy (2014A) has been investigated by XPS and TEM/PEELS. Tapered double cantilever beam joints were tested in wet cyclic fatigue and specimens prepared for analysis from the crack tip region and from areas ahead and behind the crack tip (i.e the unfractured and the fatigue fractured and water exposed regions). The failure at the crack tip is shown by both XPS and EFTEM to be very close to the oxide/adhesive interface, but in adhesive phase. Behind the crack tip, the failure surface is devoid of adhesive residues and some oxide hydration is observed. An observation made at regions well removed (10 – 15 mm) from the crack tip indicates that mechanical damage of the hydrated layer occurs as a result of the cyclic fatigue displacement. These results indicate that hydration is a post failure event for the system under study in this work.

1. Introduction

The use of polymeric adhesives in primary structures has been limited, due to the relatively poor understanding of long-term durability upon exposure to hostile conditions, the most hazardous being aqueous environments [1-3]. The present study investigates the durability of aluminium alloy and epoxy-film adhesive joints and “wet” conditions, through the use of fracture mechanics and surface analytical techniques.

The surface pre-treatment under investigation in this study is phosphoric acid anodising (PAA). Anodising in phosphoric acid is the preferred surface treatment for structural bonding in the North American aerospace industry [4]. The choice of phosphoric acid over other electrolytes for anodizing is related to the considerably slower hydration rate of the phosphated oxide formed during anodisation, which makes this oxide layer environmentally stable [5-8].

2. Experimental Details

Materials

An aerospace grade of aluminium alloy was employed (2014A). The adhesive used was a hot-curing rubber-toughened epoxy, which was based upon a dicyandiamide-cured diglycidyl ether of bisphenol-A. The product code for this adhesive was XD[®] 4236-2, from Huntsman Advanced Materials.

Surface Pretreatments & Fracture Mechanics Tests

The phosphoric acid anodising (PAA) surface pre-treatment was employed for the aluminium alloy prior to adhesive bonding and was undertaken in accordance with the relevant standard, BAC 5555 [9].

Full details of the preparation and testing of the joints used for the fracture-mechanics tests are given elsewhere [10,11], so a short summary only is given here. The adhesive fracture energy, G_c , was determined using monotonically-loaded tests carried out on an adhesively-bonded tapered double-cantilever beam (TDCB) specimen using an Instron tensile testing machine. Further to these tests, cyclic fatigue tests were conducted on Instron machines in both a “dry” environment of $21 \pm 1^\circ\text{C}$ and 55% relative humidity and a “wet” environment of distilled water at $21 \pm 1^\circ\text{C}$. The adhesively-bonded tapered double cantilever beam (TDCB) specimen was used to obtain the relationship between the rate of fatigue crack-growth per cycle, da/dN , as a function of the maximum strain-energy release rate, G_{\max} , applied during a fatigue cycle. From this relationship we can determine the threshold strain-energy release rate, G_{th} , below which no cyclic fatigue crack growth occurs. In this investigation, samples used for surface analysis were obtained after cyclic-fatigue tests.

Electron Spectroscopy and Microscopy Studies

Before joint preparation, the substrate surfaces were examined using XPS and then the failure surfaces taken from the TDCB joints were also examined. The XPS analyses were undertaken using a Thermo VG Scientific Sigma Probe system which employs a monochromatic aluminium K_α X-ray source. After initial survey spectra were completed and the peaks identified, high resolution spectra were recorded for the elements detected.

The use of transmission electron microscopy for the study of adhesive joints has not been that widespread due to the difficulties associated with the highly specialised preparation of thin slices from metal/adhesive joints, utilising a process called ultramicrotoming. Of particular interest is the interphase region, which includes the metal substrate, the oxide layer and the adhesive. Once these samples have been prepared using a “C. Reichert OmU3” ultramicrotome [12], they were studied using a Philips CM200 (200keV, LaB₆ filament) TEM, fitted with a Gatan Imaging Filter (GIF2000) parallel electron energy-loss spectrometer (PEELS). Energy-filtered images revealing chemical distribution maps were acquired and processed using Digital MicrographTM.

3. Cyclic Fatigue Fracture Mechanics Studies

Previous work by the authors [13] has shown that the rate of crack growth is far more rapid in the presence of the aqueous environment, compared to that in the "dry" environment of 55% RH. Significantly, the threshold value G_{th} for the PAA joints is reduced by 25%, from the measured "dry" value of 175Jm^{-2} to the "wet" value of 130Jm^{-2} , therefore significantly reducing long term durability. These reductions in the fatigue performance of the PAA joints in the "wet" environment are accompanied by the locus of failure in the threshold crack growth zone becoming completely interfacial in character, as judged from a simple visual assessment, as opposed to the cohesive failure in the adhesive layer obvious in the dry tested samples; therefore electron spectroscopy (XPS and PEELS) was carried out to see if the visual assessment of the locus of failure was correct.

4. Mechanisms of Environmental Attack

In order to identify the exact locus of joint failure and to attempt to elucidate the mechanisms of environmental failure for the adhesive joints in a "wet" environment, we used a combination of SEM, TEM and XPS. In all cases, the examples taken for analysis were removed from the regions of the TDCB specimens where values of the threshold value of G_{th} had been ascertained (as shown in Figure 1).

SEM and XPS surface analyses conclude that PAA tested in dry conditions fails cohesively, accompanied by relatively high values of G_c and G_{th} , respectively. However, in the "wet" tests, the PAA visually failed by crack growth along the adhesive/oxide interface, accompanied by a relatively increased lower value of G_{th} . The XPS data (Figure 2), taken from the crack-tip in the threshold zone (at position 3 on Figure 1), suggests that the visually-identified "metal" side of the fracture is composed of mainly adhesive residues. In some XPS analyses, aluminium and phosphates were detected close to the crack-tip, indicating either an interfacial failure or post failure hydration of the substrate. Thus the conclusion is that in the failure region analysed by XPS (Figure 2), failure is cohesive within the adhesive with a vanishingly thin layer of adhesive remaining on the PAA treated substrate. To investigate this hypothesis further, TEM/PEELS studies were carried out on a similar sample. The aim of this part of the investigation is twofold; to confirm the porous nature of the PAA layer and establish that the adhesive has penetrated the oxide to form a *microcomposite* interphase between the adhesive and the underlying aluminium alloy. The presence of any thicker adhesive residues will reinforce the observation made by XPS.

From the EFTEM investigations (Figure 3), we note that the pores of the oxide layer are filled with adhesive and therefore cannot readily act as sinks for water sites which might bring about subsequent oxide hydration. TEM (Figure 4) has also shown that there is no evidence of a significant thickening or coarsening of the oxide layer due to exposure of the joint to the aqueous environment. Such a strong bond reduces local stress concentrations, but water may still be able to attack via microvoids left in the

oxide/adhesive layer, where the phosphate “fingers” form in a 20nm layer above the main hexagonal deep pore structure of the PAA-formed oxide. Such a “finger” region is clear on TEM images and appears less dense than the rest of the 400-500nm thick oxide layer, but the integrity of the microcomposite interphase appears good in this region so this is thought to be unlikely. All EFTEM data of Figure 3 and 4 show a well developed interphase region with no evidence of the adhesive separating from the anodized substrate. Thus the initial assessment of the locus of failure by XPS is confirmed in that separation occurs close to the oxide/adhesive interface but in the adhesive.

In the post-crack region the story is rather different, and Figure 5 shows fibrils of the main oxide remaining just after the crack has grown past this point (position 4 on Figure 1); carbon, indicative of the presence of the adhesive is measured in levels around the EELS detectability limit (<3%). This is understood as gross hydration of the anodic film leading to the displacement of the adhesive following failure. The absence of the part of the oxide layer, particularly the fibrils, can also be attributed to mechanical damage caused in the cyclic-fatigue testing process whereby the crack opens and closes as it grows. Therefore the oxide morphology has been partially destroyed by the time the crack has grown by 10-15mm to position 5 (fig 5 right). One can speculate that the main point of weakness of the anodic layer is in the “fingers” grown on top of the main hexagonal structure and that the failure path is close to this oxide layer interface but just in the adhesive layer. The EFTEM elemental distribution map (Figure 5) from position 4 shows no sign of carbon residue from the adhesive, which may also have been dislodged by the fatigue process, especially as the hexagonal structure oxide layer is expected to be much longer (~500nm) and by position 5 after the crack has grown away the “fibrils” have completely dislodged by the harsh cyclic fatigue process.

5. Conclusions

The adhesive bonding of PAA treated aluminium substrates bonded with a low-viscosity adhesive has been investigated and complete penetration of the porous oxide layer by the adhesive occurs. Thus, water cannot accumulate in unfilled pores and no hydration of the oxide is observed pre-failure. Further, a “microcomposite” interphase is formed between the underlying aluminium-alloy substrate and the adhesive layer. This results in a greatly increased surface area for interfacial bonding compared to a planar interface thus this adhesive system, utilising a PAA surface pretreatment has many advantages over, for example, a grit-blasted and degreased surface pretreatment. At the crack tip, failure is associated with the adhesive phase, with an extremely thin layer of this material remaining on the metallic substrate. Although no gross hydration is observed at this point, such a phenomenon is noted behind the crack tip; some 3 mm behind the crack tip hydration in the form of fibrils is observed but, some 10 – 15 mm behind the crack tip these features have been removed, presumably by the action of the cyclic fatigue process. All surfaces examined by EFTEM from behind the crack tip are devoid of adhesive residues.

XPS coupled with (EF)TEM examination is an extremely powerful tool both to characterise the interfacial and interphasial regions of bonded joints. The EFTEM studies

have confirmed in cross-section the initial observations made by (plan view) XPS analyses.

Acknowledgements

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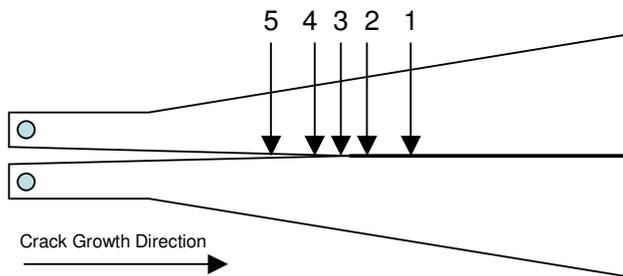


Figure 1. Diagram of TDCB showing locations for XPS and TEM analysis. 1 – Pre-crack, 2 – 3mm Pre-crack-tip, 3 – Crack-tip, 4 – 3mm Post-crack-tip, 5 – Post-crack.

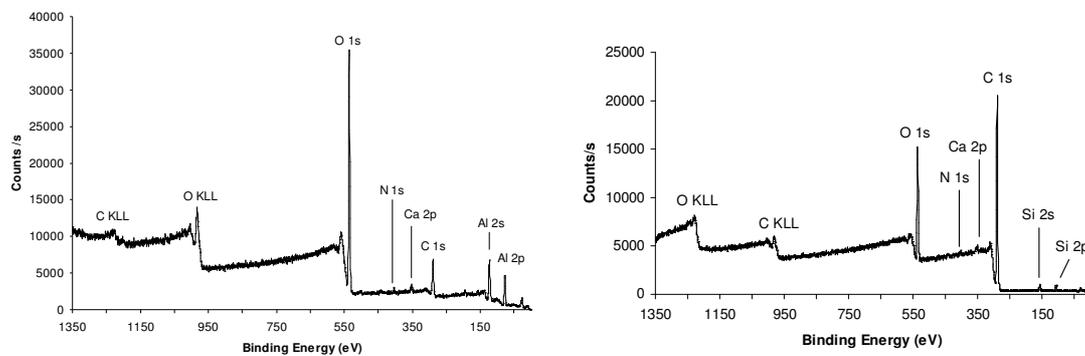


Figure 2. XPS Survey Spectrum (a) PAA Control Specimen. (b) “Metal” Side of post-crack threshold growth zone (position 5 in Figure 1) of PAA-pretreated joint from a “wet” cyclic fatigue test.

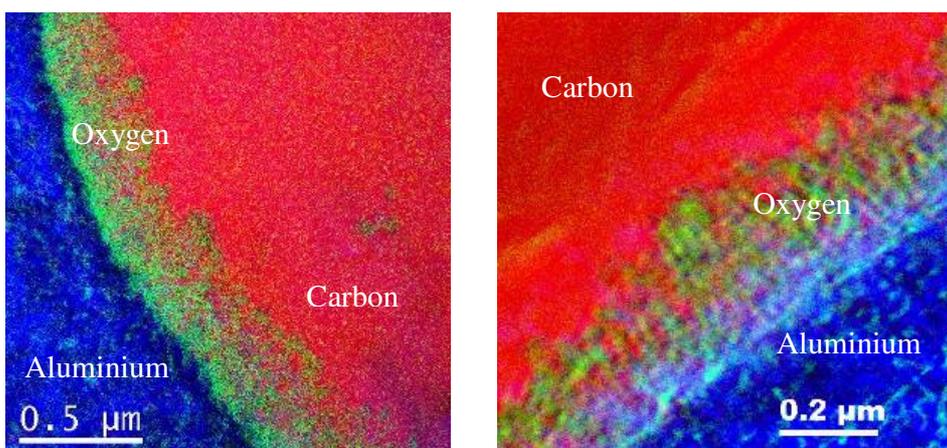


Figure 3. Composite EFTEM elemental distribution map of the interphase region of a PAA-pretreated joint from a “wet” cyclic fatigue test. Blue: aluminium; green: oxygen; and red: carbon. Left: Pre-crack (position 1 shown on Figure 1) Right: 3mm pre-crack tip

(position 2 on Figure 1). The images show a good penetration of the adhesive into the oxide interphase region.

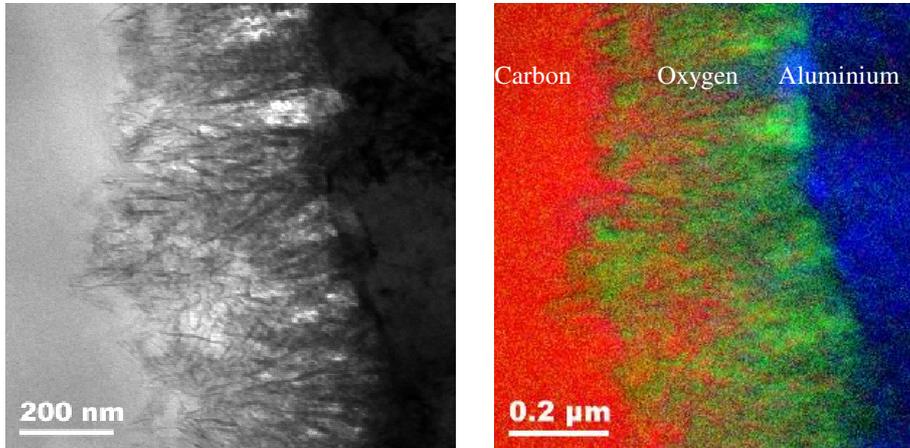


Figure 4. Images at Crack Tip (position 3 on Figure 1) showing that the adhesive (carbon) clearly penetrates the pores of the PAA-produced aluminium oxide layer. Left: TEM bright field image showing the hexagonal packed structure and anodic "fingers". Right: Composite EFTEM elemental distribution map of the interphase region of a PAA-pretreated joint.

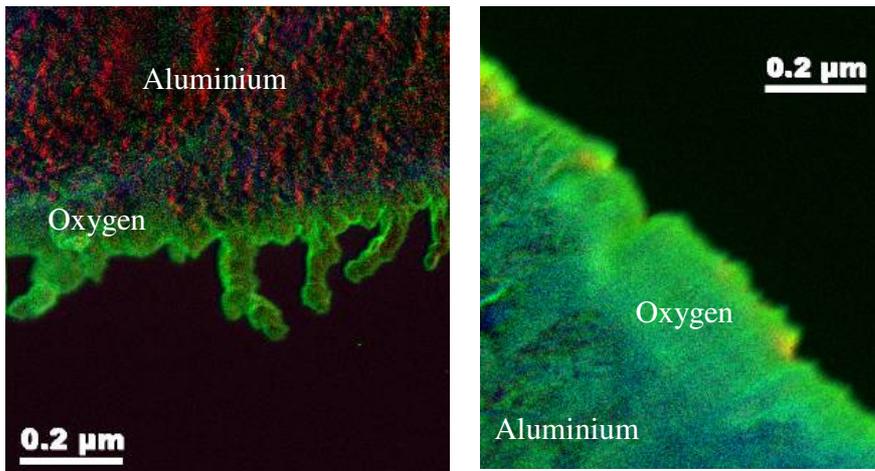


Figure 5. Composite EFTEM elemental distribution map of the interphase region of a PAA-pretreated joint from a "wet" cyclic fatigue test. Left: 3mm post-crack-tip (position 4 shown on Figure 1) showing remaining "fibrils" and possible hydration. Right: Post-crack (position 5 shown on Figure 1) indicating the cyclic fatigue has destroyed the "fibrils" that were present in the oxide layer.