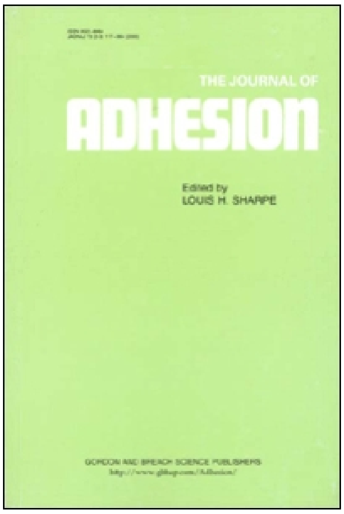

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The Adhesively Bonded Aluminium Joint: The Effect of Pretreatment on Durability†

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The interface in aluminium bonded structures can be revealed by ultramicrotomy and subsequently studied by transmission electron microscopy. By these means, the more usual surface pretreatments encountered, have been characterised in depth.

A similar examination has been effected following exposure of bonded joints (floating roller peel specimens) to 85% relative humidity at 70°C. Although a drop in peel performance is noted over the exposure time, interfacial examination reveals little damage to the adhesive or adherend. Possible mechanisms for bond strength reduction are discussed: subtle undermining of the alumina film and disruption of physico-chemical bonds across the interface. Both are initiated by moisture reaching the alumina film, either passing along the interface itself or travelling through the adhesive matrix. Also considered are the effects of surface pretreatment and "oxide" penetration, by the adhesive, on durability.

The effect of priming the adherend surface prior to bonding, using a heavily strontium chromate filled adhesive primer, is mentioned and its possible influence on durability is briefly discussed.

KEY WORDS Phosphoric acid anodisation; chromic acid anodisation; FPL etching; adherend roughness; environmental attack; oxide morphology; durability and structural bonding.

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INTRODUCTION

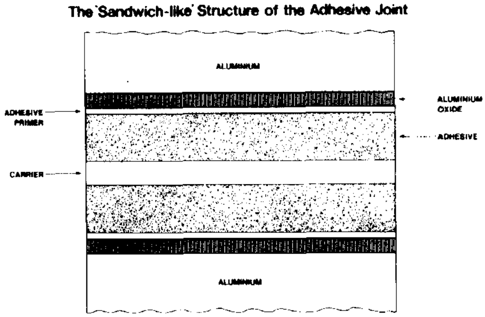
When studying the adhesive joint in depth, the use of scanning electron microscopy (SEM) to identify areas of interest, both on the substrate as well as on the adhesive fracture surface, is now customary. However, such areas can be further characterised by revealing the adhesive/adherend interface *via* ultramicrotomy[1] with subsequent observation by transmission electron microscopy (TEM). This combination of techniques has already been established as a valuable tool in gaining a deeper insight into the nature of interfaces within bonded joints.[2,3,4]

Earlier work[3,4] has characterised the substrates generally encountered in aluminium bonded structures; this has laid the base for a more detailed examination of the joint itself. The early data on one of the many aspects requiring precise characterisation, namely the effects of "hot/wet" environments on the adhesive joint, are reported here.

THE ADHESIVE JOINT

The adhesive joint used in this work is represented schematically in Figure 1; the various components are detailed below:

Aluminium	2024-T3 ALCLAD (Composition—Table I).
"*Oxide*"	Developed through pretreatments outlined later in this section.



CIBA-GEIGY

FIGURE 1 Schematic representation of the bonded aluminium joint.

TABLE I
Composition of ALCLAD 2024-T3

	Percentage composition	
	Core	Cladding
Copper	3.8–4.9	0.1
Magnesium	1.2–1.8	—
Manganese	0.3–0.9	0.05
Iron	0–0.5	0.7
Silicon	0–0.5	
Chromium	0–0.1	—
Zinc	0–0.25	0.1
Others (individual)	0–0.05	0.05
Others (total)	0–0.15	0.15
Aluminium	Rest	Rest

Primer	Both primed and unprimed substrates were examined. The primer, when used, was an experimental epoxy/phenolic system, heavily pigmented with strontium chromate and curing fully in 30 minutes at 120°C.
Adhesive	Experimental, toughened epoxy film adhesive, curing at 120°C.
Carrier	An open, knitted fabric manufactured from Nylon 6.

When bonding structural components, the adherends are usually pretreated to ensure that the adhesive is applied to a clean, stable surface to enable as effective a bond as possible to develop. However, economic and end-use considerations often mean that a less-than-optimum form of pretreatment, and occasionally none, is used. The most common forms of aluminium pretreatment encountered, and used in this work, are listed below:

i) "Light" abrasion using Scotchbrite® or wire wool.

ii) "Heavy" abrasion using an alumina grit blast.

iii) Potassium dichromate/sulphuric acid pickle to DTD 915b (ii)[5] or in accordance with the Forest Products Laboratory process.[6]

iv) Potassium dichromate/sulphuric acid pickle, followed by chromic acid anodising (CAA) to DEF STAN 03-24/1.[7]

v) Phosphoric acid anodising (PAA) to BAC 5555.[8]

ENVIRONMENTAL EXPOSURE

Ideally, natural environmental exposures should be used. However, within the limited time-scale that can be afforded to such an analysis, an artificial environment has to be created which accelerates the natural weathering effect. Thus, floating-roller peel specimens[9] were exposed to a minimum 85% relative humidity environment at 70°C for 30 days. Peel strengths were determined every 10 days, but specimens for characterisation work were only taken after 0 (Control) and 30 days exposure.

Mechanical properties of unprimed joints

The peel profile for the exposed specimens is shown in Figure 2; this reveals the differences in the peel strengths of the control specimens and the reduction in peel properties after 30-days exposure. The full

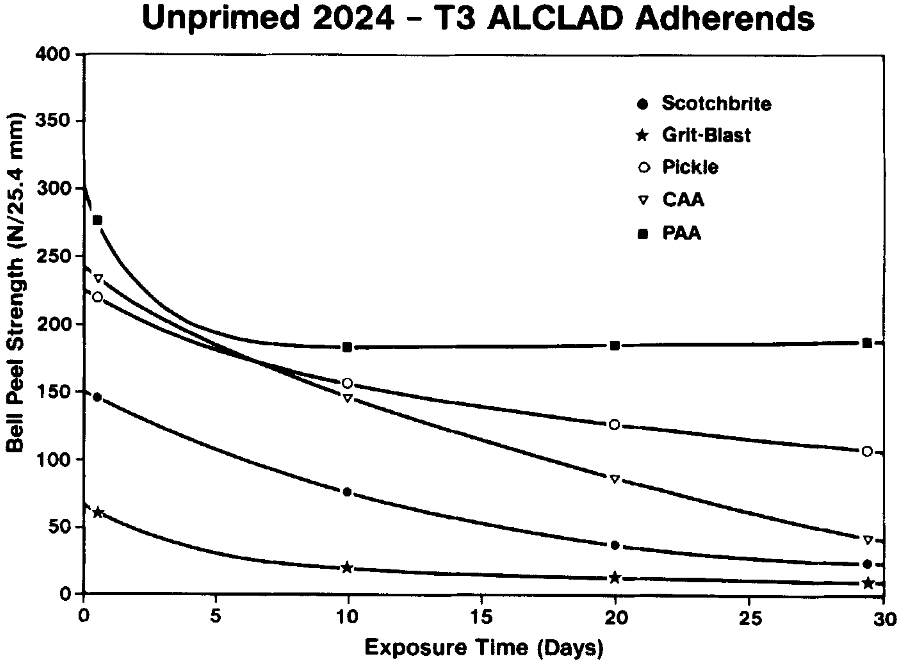


FIGURE 2 Peel strength versus exposure time at 70°C and 85% R.H. for various substrate surface pretreatments used. [Maximum scatter for any set of joints: ±15 N].

Characterisation of the abraded substrate surfaces by SEM.

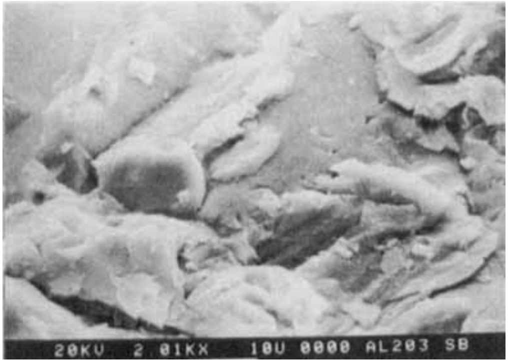


FIGURE 3 Pretreatment: Alumina grit-blast.

extent to which the mechanisms of initial adhesion and subsequent bond degradation, as shown by the reduction in peel strength, are related, awaits detailed clarification. However, the early indications are now considered further.

Controls: Figure 2 clearly shows that the peel values generated fall into two groups; those where the substrates had been abraded and those where chemical pretreatment had been used.

Examination of the adherend surface, the adhesive fracture surface and the adhesive/adherend interface provides a possible explanation for the varied behaviour. SEM analysis of abraded substrates (Figures 3 and 4) shows the potential dangers of using such pretreatments prior to bonding; during pretreatment, although

FIGURE 4 Pretreatment—Scotchbrite 96 abrasion.

Characterisation of the unexposed bonded joint—abraded substrates.

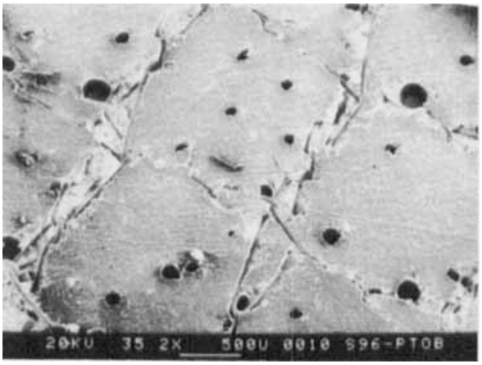


FIGURE 5 Scanning electron micrograph of the adhesive fracture surface showing air-blisters in the glueline (Scotchbrite).

the weak, air-formed film is removed, the aluminium cladding (5% of total plate thickness) is partially cut open, producing a relatively rough surface to which a significant amount of aluminium detritus is loosely attached. Further, in the case of Scotchbrite-abrasion, discrete pieces of the abrading material remain embedded in the surface (Figure 4). SEM examination of the fracture surfaces shows significant areas of apparent adhesion failure to the peeling face, as well as evidence of air blisters in the glueline (Figure 5). Analysis of

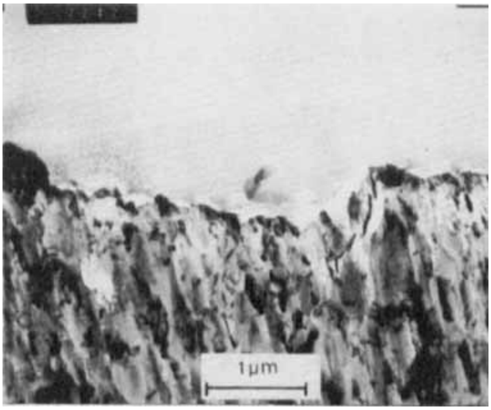


FIGURE 6 Transmission electron micrograph of a section through the bonded joint (Scotchbrite abraded adherends)—poor wetting of the substrate is evident.

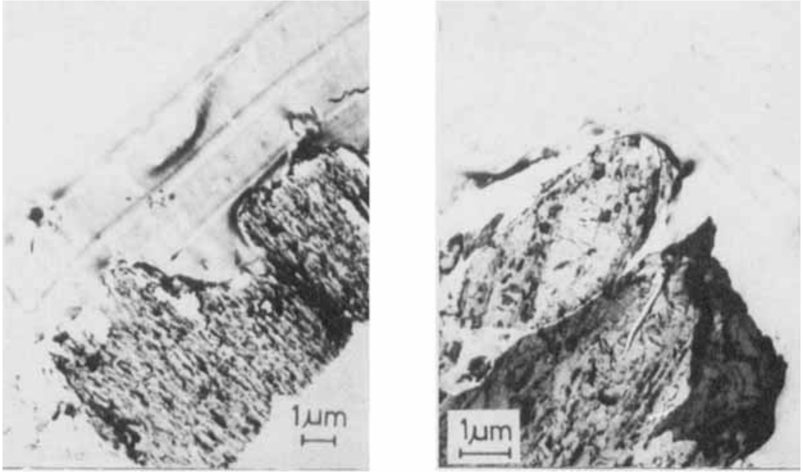


FIGURE 7 FIGURE 8

Transmission electron micrograph of sections through the grit-blasted bonded joint. Figure 7 shows poor wetting and Figure 8 loosely-bound surface detritus.

transmission electron micrographs of ultramicrotomed sections permits one possible hypothesis for the presence of such blisters to be postulated: the surface, as prepared, is too rough. As the adhesive melts and flows during its cure cycle, the air trapped between adhesive and adherend should be displaced allowing the substrates to be fully wetted. Figures 6 and 7 indicate that, because of the high degree of roughness, not all the air has been displaced. This has left air pockets, and consequently macroscopic areas of either no contact or point-contact, between adhesive and adherend. With a film adhesive such as that used here, therefore, mechanical keying of the adhesive into the adherend is not a significant factor.

Figure 8 clearly shows the potential weakening effect on the *unruptured* joint by loosely-bound surface detritus. In addition, a crack is also evident, running through the substrate immediately below the pretreated surface. One of the many possible explanations for this sub-surface fracture, that must be given serious consideration, is that stress-cracking in the adherend is induced by the method of pretreatment itself—in this case, grit-blasting. Figure 9 gives a higher-resolution view of this phenomenon.

All the foregoing suggest that a weak interface exists between

FIGURE 9 Transmission electron micrograph of a section through the aluminium substrate of a grit-blasted bonded joint; it shows the sub-surface cracking.

adhesive and adherend and hence failure should occur at low loads, as indeed is found.

SEM examination of the fractured, chemically pretreated joints (Figures 10–13) shows, as expected from the peel strengths, significant areas of deep cohesive failure within the adhesive.

Characterisation of the unexposed bonded joint. Scanning electron micrographs of the adhesive fracture surfaces for joints produced using chemically pretreated ahherends.

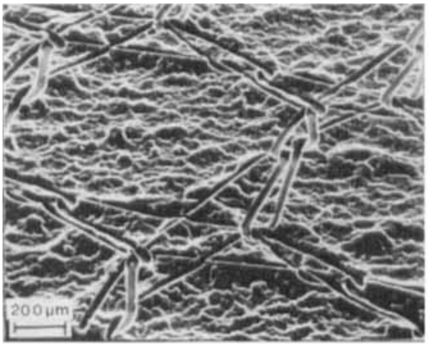


FIGURE 10 Pickled to DTD 915b(ii).

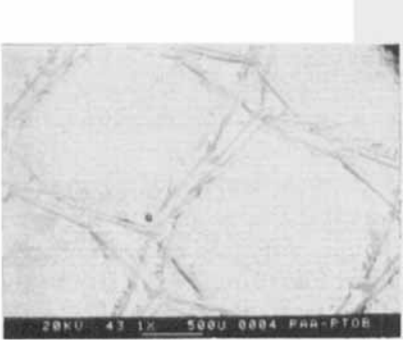


FIGURE 11 Phosphoric acid anodised to BAC 5555.

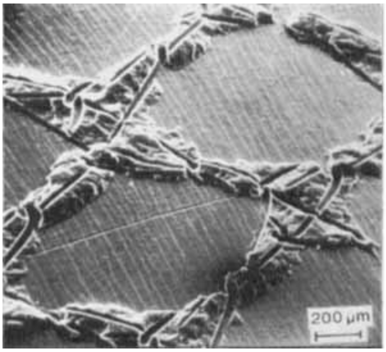


FIGURE 12

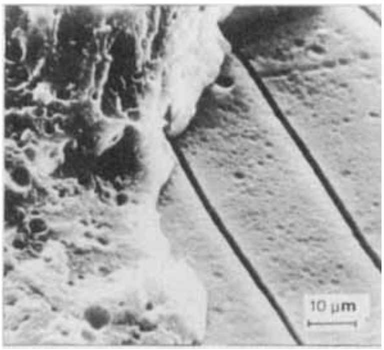


FIGURE 13

Chromic acid anodised to DEF STAN 03-24/1. Figure 13 also shows the induced cracking through the grown oxide film.

Cracks are formed (Figures 12 and 13), at right angles to the peeling direction, through the oxide film grown by chromic acid anodising; this is caused by the joint, as a whole, being bent as it passes through the peel jig. Interestingly, no such cracks are readily evident in the film formed by phosphoric acid anodising which, from its observed structure, would be expected to be more friable.

Use of ultramicrotomy to reveal the chemically pretreated adherend/adhesive interface shows, on examination by TEM, three very different morphologies:

i) Potassium dichromate/sulphuric acid pickled surface (Figure 14): ostensibly finely-spaced, approximately 30 nm high whiskers which, from the evidence in the micrographs, appear to be well-penetrated by the adhesive. These whiskers, which are probably partially-hydrated alumina contaminated by electrolyte species, are developed by transformation of the air-formed film during the immersion process.

ii) Chromic acid anodised surface (Figures 15 and 16): a porous surface film is present which, in the work presented here, was generally 2–4 micrometres thick. The original surface roughness is not significantly enhanced by the anodising process and essentially mirrors the initial surface topography. Although the adhesive wets this surface well, there is no obvious deep penetration of the oxide pores by the adhesive.

Characterisation of the unexposed bonded joint. Transmission electron micrographs of sections through the interface of joints produced using chemically pretreated adherends.

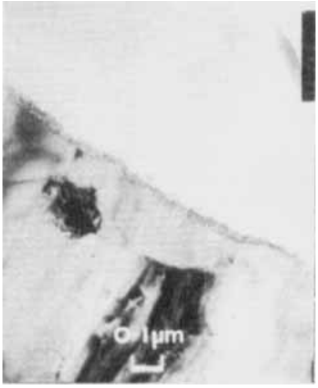


FIGURE 14 Pickled to DTD 915b(ii).

iii) Phosphoric acid anodised surface (Figure 17): again, a porous surface film is present; generally about 0.5–1.0 micrometres thick. Here surface roughness is enhanced due to film material collapse during anodising (caused by progressive thinning of the cell material adjacent to the pore wall); this more open structure is also reported by W. Brockmann *et al.*[10] The degree of roughening, however, is some orders of magnitude less than for the abraded surfaces, which can be seen by the naked eye. The adhesive not only wets well,

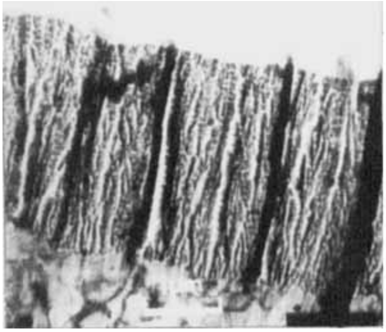


FIGURE 15 Chromic acid anodised to DEF STAN 03-24/1.

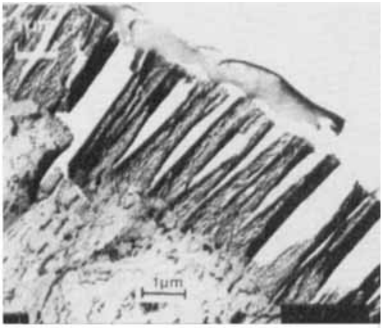


FIGURE 16 Chromic acid anodised to DEF STAN 03-24/1.

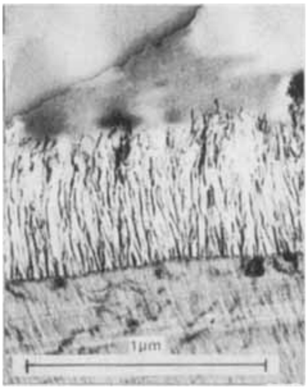
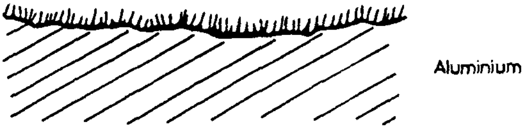


FIGURE 17 Phosphoric acid anodised to BAC 5555.

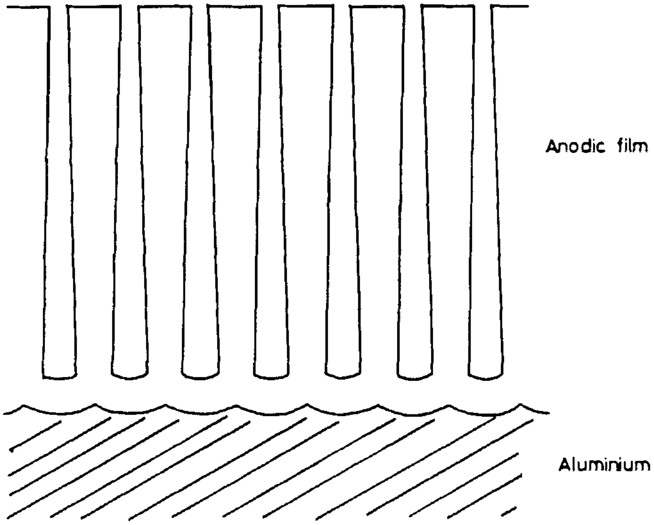
filling the revealed surface cavities, but careful examination of the enlarged micrograph also reveals evidence of pore penetration into the depths of the anodic film; this is confirmed by the work of others.[11]

The use of Auger electron spectroscopy (AES) on the respective anodised samples shows that, whilst there is no evidence, within the detection limits, of any chromium associated with the CAA film, phosphorus is present throughout the section of the PAA film.

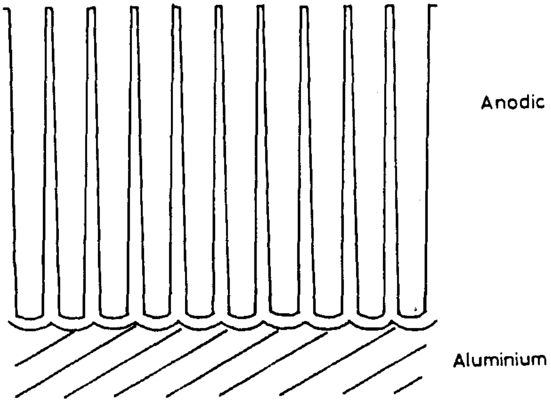
The three chemically pretreated surfaces can, therefore, be visualised, relatively simplistically, from the schematic diagrams below. Within these diagrams only the overriding pore and cell structure has been considered; other details within the section of the films shown—the "feathered"/branched pore structure of the CAA film—have been omitted on grounds of better clarity.



Pickled: "Whisker" film; no enhanced roughness; apparent extensive penetration by the adhesive.



CAA: 2–3 micrometre porous surface film with no significant enhanced surface roughness; no obvious penetration by the adhesive into the film depths.



PAA: 0.5–1 micrometre porous surface film with enhanced surface roughness and incorporated phosphate species; penetration, at least partially, by the adhesive into the film depths.

The interfacial examination has shown that, in all cases, the chemically pretreated adherend is wetted well by the adhesive; this, according to the theories of Zisman[12] should account for the relatively high peel strength levels on the substrates. Any increase in the effective surface area, by surface cavity formation in the case of the PAA adherends and by oxide film penetration in the case of pickled and PAA substrates, does not appear to affect significantly the average metal/metal bond strength for this adhesive. This would indicate that mechanical keying is not an important criterion in obtaining high peel loads. It could, however, explain, at least partially, the consistency of the peel levels for the PAA and pickled specimens as opposed to the slight variability observed on testing the CAA joints.

30-*Day Exposure*: At this time, the peel strength profile (Figure 2) indicates that the influence of substrate pretreatment on environmental exposure is much more varied than for the control experiments.

Simple visual examination of the ruptured joints (Figure 18) reveals the areas in which significant environmental attack has apparently taken place. This is evident down the length of the joint, parallel and just adjacent to the cut edges (Figure 18C) and occasionally, dependent on pretreatment, extending towards the centre or even across the joint (Figure 18D). This latter tendency is particularly prevalent when abraded substrates are used. From these observations, as well as the determined peel strengths, the chemically pretreated adherends can be rated, in ascending order of

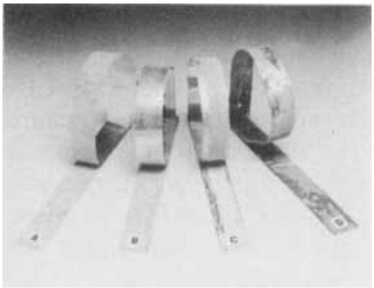


FIGURE 18 Visual examination of ruptured peel joints. A—Unexposed Control; B—30 days exposure: no obvious attack; C—30 days exposure: attack down cut edges; D—30 days exposure: extensive attack.

Characterisation of the environmentally exposed bonded joint.

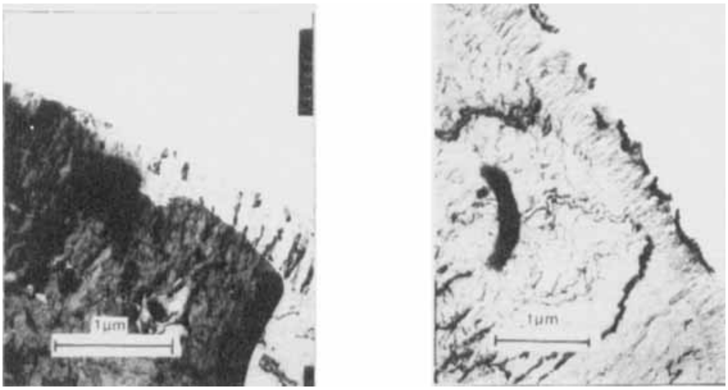


FIGURE 19 Scotchbrite abraded substrate. Essentially adhesion failure.

FIGURE 20 Phosphoric acid anodised substrate. Intermittent, cohesive failure.

Tranmission electron micrographs of sections through the peeling face of the ruptured peel specimen.

environmental resistance: chromic acid anodised < potassium dichromate/sulphuric acid pickled < phosphoric acid anodised.

It should be noted that the initial edge effect is likely to stem from damage to the interface, inflicted when sawing the joint *prior* to exposure. Strong support for this is given by observations of the uncut joint ends, protected by adhesive squeeze-out, which rarely show such attack.

Within these visual areas of bond deterioration, SEM examination suggests, irrespective of surface pretreatment, failure at the adhesive/adherend interface. Significant areas of apparent adhesion failure to the peeling substrate are evident. The so-called pseudoboehmite morphology was clearly seen on these exposed aluminium structures, remote from the unfractured area.

TEM examination of ultramicrotomed sections of the respective adhesive joints confirms the presence of extensive adhesion failure to the peeling face (Figures 19 and 20 are typical of all pretreatments); small areas of cohesive failure in the adhesive can be seen on the chemically pretreated substrates, whilst the abraded adherends appear to exhibit almost total adhesion failure.

Specimens taken in advance of the crack tip (Figures 21–25) *i.e.* in the unruptured, supposedly unstressed area of the joint, show no

Characterisation of the environmentally exposed bonded joint. Tranmission electron micrographs of sections through the unruptured bonded joint after 30 days environmental exposure.

FIGURE 21 Scotchbrite abraded.

FIGURE 22 Alumina grit-blasted.

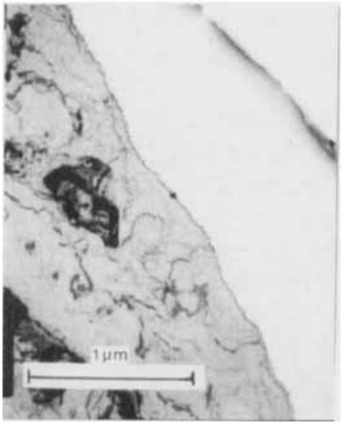


FIGURE 23 Pickled to DTD 915b(ii).

FIGURE 24 Chromic acid anodised to DEF STAN 03-24/1.

evidence of pseudoboehmite formation at the interface. Hence, in this case, the acicular appearance of this well-characterised form of hydrated alumina is formed mainly post-rupture and is not the cause of failure *per se*.

Figures 21–25 show little evidence of significant degradation at

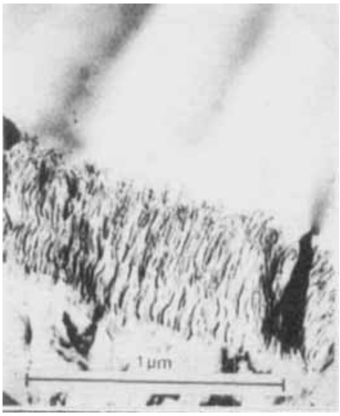


FIGURE 25 Phosphoric acid anodised TO BAC 5555.

the pre-rupture interface, or in the adherend immediately under the interface. It can, therefore, be postulated that the reduction in peel strength is due to an ingress of water either weakening or causing a debonding effect at or immediately adjacent to the adhesive/adherend interface.

There are three possible paths by which water can transport or diffuse through the joint: i) through the adhesive itself, assisted by cracks and voids in the organic matrix or by wicking along the carrier/adhesive interface, ii) through the grown or air-formed film on the adherend surface or iii) along the adhesive/adherend interface. In all cases water ingress would have to start at the exposed joint edges and thus, in view of the length of the diffusion path to the interior of the joint, any immediate attack must start at or closely adjacent to the edge of the bonded area.

When bonded specimens are produced using abraded substrates, this initial edge attack is frequently augmented by rapid ingress into the joint. The areas of non-contact between adhesive and adherend, caused by the over-rough surface and the loosely-attached detritus of pretreatment (Figures 6–8), offer a more direct route through the joint and, hence, water should be able both *to enter and pass into the interior* of the bonded area with relative ease. This would effectively short-circuit the potentially much longer path through the adhesive and, obviously, allow water to be taken up at a much higher rate than along the interface of a well-wetted adherend. The already poor adhesion, due to the nature of the surface and the unsuitability of the air-formed film which is produced rapidly after pretreatment, is thus further reduced both by possible over plasticisation of the adhesive matrix by water and feasibly by the disruption of the physico-chemical bonds (Van der Waal's forces, etc.) across the interface. Both possibilities could well account for the relatively high degree of debonding of the cured adhesive film *to the non-peeling face,* seen after rupture.

When chemically pretreated adherends are used a more subtle mechanism of attack must operate. The control peel strengths confirm that these surfaces are wetted well by the adhesive. There is, therefore, no such easy route for water to reach the interior of the joint and, indeed, any immediate edge effect is generally rapidly not followed by environmental attack across the bonded area.

Clearly, water eventually penetrates the bonded area since significant reductions in peel strength are observed and it could be argued that, because of the good wetting of the adherend by the adhesive, the dominant diffussion path is probably through the adhesive matrix; the occasional, relatively gross flaw or discontinuity in the bulk resin which allows a faster passage for the water, could well account for the intermittent occurrence of environmental attack in semi-isolated central areas of the bonded joint.

Deep cohesive failure, in the adhesive, is rarely evident in ruptured joints which have previously undergone environmental exposure. This would indicate that the water has caused relatively little damage to the adhesive matrix compared with the more significant processes proceeding at or close to the interface.

In the following, although only PAA and CAA pretreated adherends are specifically considered, it is reasonable to treat the pickled surfaces as behaving somewhat similarly to those anodised in phosphoric acid. However, for pickled aluminium the "pore" depth is only about 3–4% of that of PAA substrates and thus, in this case, the film/metal interface is significantly closer to the outer film surface and hence, could play a more significant role in the mechanism of bond degradation.

The water ingress, once at the interface, may wet the adherend surface and porous structure comprising the anodic film morphology better than the adhesive matrix already in place; the extent of pore wetting will be dependent on the degree of adhesive penetration. In such cases, this wetting of the alumina material may be sufficient, *per se,* for bond deterioration by significantly reducing the Van der Waal forces etc., across the interface. If not, then a subtle transformation of the adjacent alumina film to AlOOH and $Al(OH)_3$, at a rate dependent on the exposure conditions, must be considered.

Speculating further, in situations where the pore volume is not penetrated substantially by the adhesive, wetting of the pore surface and possible build-up of water and other potentially damaging species, within the pore, (either direct from the environment or dissolved out of the cured adhesive matrix, as shown for example, by Brockmann *et al.*[10]) can also be contemplated; a ready transformation of the anodic alumina to hydrated material would be anticipated. Transformation is expected to proceed by penetration of the cell material surrounding the pore, developing a disaggregated alumina zone behind which dissolution and reprecipitation occur. This disruption of the alumina cell, with precipitation of relatively voluminous hydrated material, could contribute significantly to the undermining of the anodic film surface and hence lead to bond deterioration.

Further, should moisture gain access to the pore volume then direct passage to the metal, *via* flaws in the substrate, is a distinct possibility. Once in contact with the metal, water, assisted by damaging species (*e.g.* chloride ions, ammoniacal materials), can enhance corrosion of the substrate, undermining the alumina film. Considering the situation when the adhesive substantially penetrates the porous morphology, any undermining of the alumina (through hydration proceeding into the cell walls) and corrosion of the metal are likely to be significantly delayed.

However, in the present study, where durability has been assessed by exposure to relatively high humidity, examination of the adhesive fracture surface shows no strong evidence for failure through the alumina film and hence, crack propagation should proceed along, or close to, the interface, with intermittent diversions into the immediately adjacent bulk of the adhesive matrix.

Further, hydrated alumina is not readily observed attached to the adhesive fracture surface. This indicates that the degree of any surface transformation does not have to be extensive in order to cause potentially severe bond degradation.

In the work described here, the adhesive, metal adherends, cure cycle and operators have, essentially, been kept constant. Thus, the differences revealed in the resistance to environmental attack by the bonded specimens, prepared using chemical pretreatments, must be due to the pretreatments themselves.

Before these differences can be fully explained, however, the moisture diffusion path, the factors affecting the rate of diffusion and the alumina/moisture reaction must be more fully understood. Some pointers do already exist:

i) As opposed to phosphoric acid anodised surfaces, those produced in chromic acid, although possessing a porous morphology, reveal a macroscopic planar surface in intimate contact with the adhesive but with little pore penetration (Figures 15 and 16).

The outer regions of the PAA film, however, comprise both a coarse and a fine cavity-like structure, due to film collapse; these areas are readily wetted by the adhesive, which also occupies a significant fraction of the internal film volume. Thus, for such anodic films, the moisture diffusion paths are considerably extended, when compared with those for CAA films.

The above argument will also generally apply to the joints where pickled substrates have been used, the adhesive wetting and, to a large extent, penetrating the whisker-like film growth and hence extending the interfacial area and eliminating any real planar interface.

Considering the PAA adherends further, the presence of bound, absorbed and adsorbed phosphates could well mask potential hydration sites, slowing down the damaging transformation to hydrated alumina. However, even in the presence of these phosphates, if hydration does eventually proceed in the outer regions of the anodic film then the transformed areas will be almost fully enveloped by adhesive. In other words, no distinct, weak interphase can develop parallel to the aluminium substrate surface.

In addition, any later corrosion processes in the metal itself are also likely to be delayed because of the penetration of adhesive into the pores.

ii) Although it has been stated that little indication of interfacial damage had been found by TEM/ultramicrotomy examination, there was a specific area where some evidence of hydration existed; on pickled and abraded substrates at the adherend/adhesive interface, in the immediate vicinity of second-phase particles (inter-

Characterisation of the environmentally exposed bonded joint. The effect of intermetallic inclusions on environmental attack. Transmission electron micrographs of sections through the unruptured bonded joints 30 *days environmental exposure.*

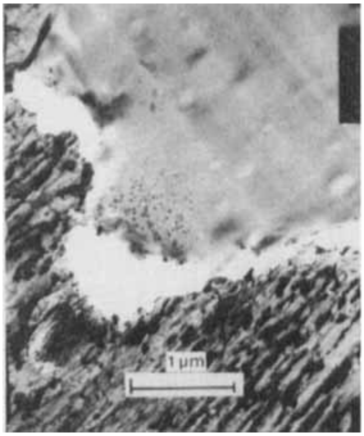


FIGURE 26 Alumina grit-blasted.

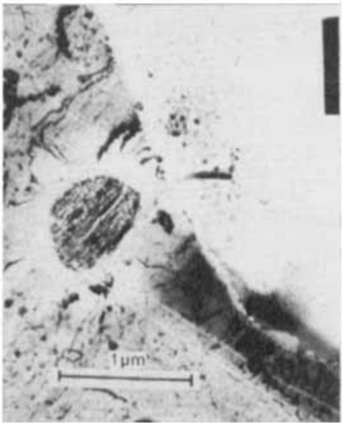


FIGURE 27 Pickled to DTD 915b(ii).

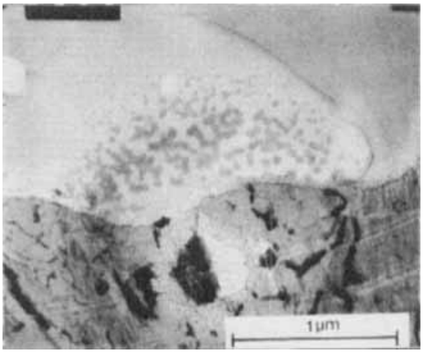


FIGURE 28 Pickled to DTD 915b(ii).

metallics) in the aluminium cladding. If such inclusions are resident at or very close to the surface (i.e. at locations where they are readily revealed by pretreatment) then they may exert an influence on the performance of the joint under environmental exposure; the evidence, from the micrographs, suggests that the inclusions should probably be no deeper than 4–5 nm and hence such an effect should be limited to joints where the adherends have either been mechanically abraded or chrome/sulphuric acid pickled. This has, indeed, been found; Figures 26–28 show the enhanced local degradation of surface films in the presence of those intermetallic inclusions.

If water, containing any dissolved electrolyte species, reaches the interface, then, as the intermetallics are essentially of the $FeAl_3$ type (Figure 29) the possibility of galvanic corrosion, with the adjacent aluminium matrix serving as the anode, must be considered. However, a further possible cause for this interfacial degradation could be weak (in the bonding sense), readily hydrolyseable films developing above the inclusion itself; as the interface recedes there is the possibility of new intermetallics being revealed and an easier environmental pathway being opened up to them.

Although requiring further clarification, this effect must be put into perspective. The cladding contains a *maximum* 0.7 wt% iron and not all the inclusions will be sufficiently close to the surface to exert an influence. Thus, this mechanism of bond strength reduction is not considered to be dominant, under the conditions employed in the present investigation. However, any local surface degradation caused as a result of the presence of intermetallics may facilitate the passage of water along the interface, which would then, indeed, have a significant effect on joint durability.

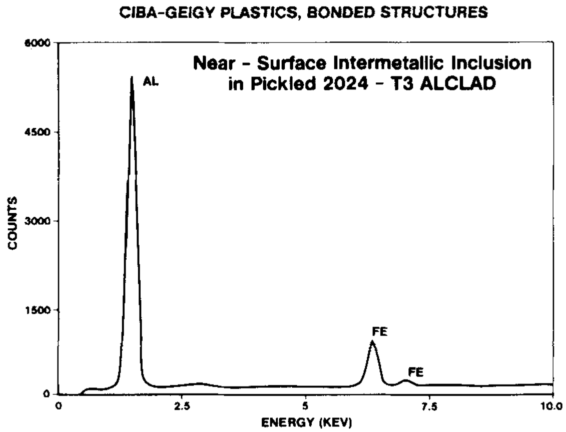


FIGURE 29 X-ray dispersive analysis of a typical metallic inclusion. This confirms the $FeAl_3$ structure.

Mechanical properties of primed joints

Work has commenced on this examination and is already showing results of considerable interest. With abraded adherends, it appears that the primer wets and fills the smaller troughs and craters of the convoluted surface and assists in "fixing" some of the loosely-bound surface detritus (Figures 30 and 31).

For the chemically pretreated substrates, the question of primer penetration of the film surface through the pores is of major importance. It is thought that there is little difficulty in the case of pickled adherends. Figure 32 shows that some component, at least, of the primer does penetrate the PAA film. This has been confirmed using an organotitanate labelled primer;[13] titanium was detected largely throughout the porous film morphology. This same work has also shown that some component of the primer does partially penetrate the CAA film; titanium was detected down to about one-third of the pore depth.

The peel strength profile (Figure 33) shows, once again, the marked difference between specimens prepared with abraded substrates and those using chemical pretreatments.

Characterisation of the unexposed bonded joint having primed substrates. Transmission electron micrographs of sections through the interface of bonded joints—various surface pretreatments.

FIGURE 30 Scotchbrite abraded.

FIGURE 31 Alumina grit-blasted.

Both show better wetting-out of the substrate surface than for the unprimed case—air gaps can, however, still be seen.

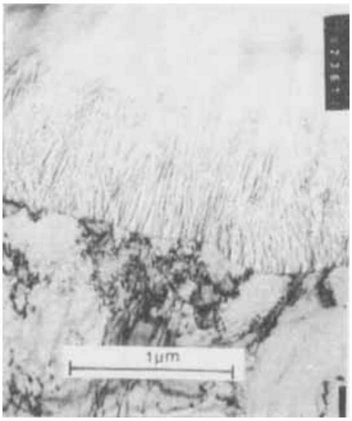


FIGURE 32 Phosphoric acid anodised to BAC 5555.

For the abraded adherends, some improvement in durability is to be expected through the presence of the primer and its pigment particles. The latter, in addition to extending the diffusion path of water, produce soluble chromate species which, upon migration to the air-formed film surface, will hinder hydration. Further, if corrosion in the vicinity of intermetallic and second-phase material is a significant factor in bond degradation, then chromate species are highly effective inhibitors of aluminium corrosion. However, all these factors may be largely outweighed by the still restricted wetting of adherends with complex geometries; this would appear to be confirmed by the peel profile which shows relatively rapid bond deterioration.

Similarly, for the chemically pretreated substrates, an improvement in durability is anticipated. Generally, the primer or its components penetrate the pore volume, thereby enhancing the area of contact. Consequently, hydration by water—contaminated or otherwise—contained within the porous morphology, is hindered for the reasons outlined previously (for adhesive penetration of the oxide film morphology); released chromate species should also limit hydration to voluminous film material. Additionally, and importantly for the primer/adhesive situation, the bond between the respective organic phases is relatively diffuse (when observed by high resolution microscopy—Figure 34) implying no built-in plane of

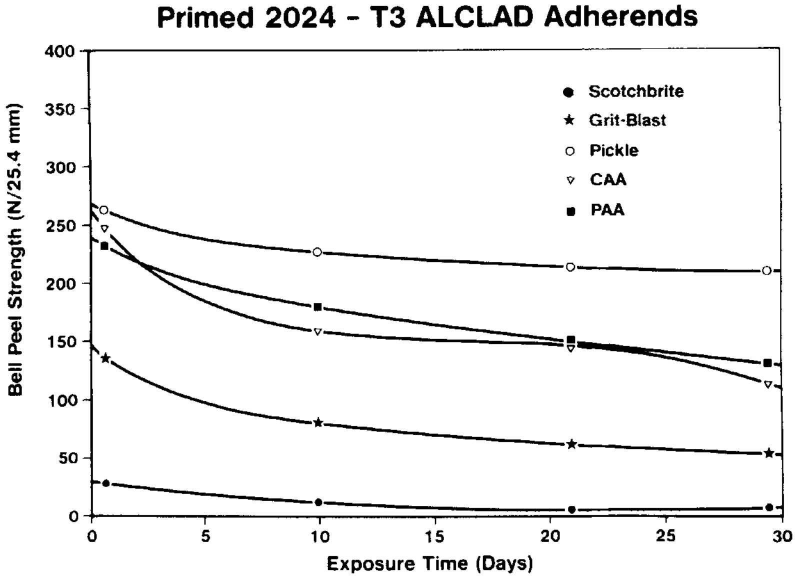


FIGURE 33 Peel strength versus exposure time at 70 Deg C and 85% R.H. for the various substrate surface pretreatments used; all adherends were primed prior to bonding.

[Maximum scatter for any set of joints ±10 N].

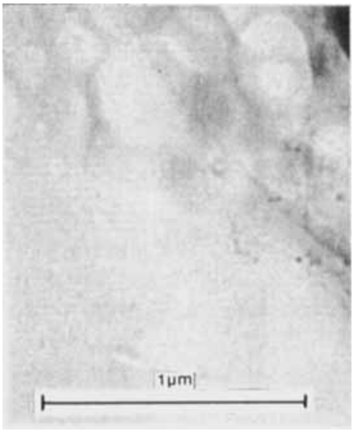


FIGURE 34 Transmission electron micrograph of a section through the glueline. This reveals the relatively diffuse nature of the primer (upper) and adhesive (lower) interface/interphase.

weakness at this further interface. This is confirmed by the visual evidence where, once again, failure is generally at or very close to the primer/adherend interface or just in the adhesive and *not* at the boundary between primer and adhesive.

Finally, if good wetting of the adherend surface coupled with adhesive/primer penetration of the oxide film morphology is the key to limiting the environmental attack on the bonded joint (by increasing the diffusion time of water to the interface), then it would be expected that:

i) There should be little difference in durability between primed or unprimed joints using PAA adherends.

ii) Priming CAA substrates should improve joint durability towards that of the PAA system.

iii) If the primer can seal off the intermetallics from ready access to moisture ingress, then an improvement in durability is to be expected on priming pickled adherends.

The early results are, essentially, in support of these statements.

CONCLUSIONS

The following conclusions can be drawn from the work reported here:

1) For good wetting of the adherend, and hence good adhesive strength levels, chemically pretreated substrates appear essential. The surface convolutions and loosely-bound detritus, produced by mechanical abrasion, lead to low levels of intimate contact, weak interfacial layers and stress-cracking in the adherend; all contribute to poor bond strength.

2) The needle-like oxide morphology formed on pickled substrates and the rough, porous anodic oxide layer grown in phosphoric acid appear to be well penetrated by the adhesive; although porous, the CAA film does not appear to be significantly penetrated by adhesive.

3) A significant level of incorporated and adsorbed phosphate is found throughout the PAA film. Within the detection limits of AES, no parallel is evident for the CAA or pickled substrates,

although anion (chromate) adsorption on exposed surfaces is expected.

4) On unprimed substrates, the effect of pretreatment on the resistance to environmental attack can be rated, in ascending order; grit-blasting and "light" abrasion < chromic acid anodising < pickling < phosphoric acid anodising.

5) Initial rapid moisture attack at the joint edge is certainly enhanced by and possibly due to damage inflicted whilst sawing the specimens.

6) The morphologically characterised pseudoboehmite form of hydrated alumina appears to be formed only *after* rupture and hence is not thought to be the cause of environmental failure *per se*.

7) Environmental attack appears either to disrupt the physicochemical bonds across the interface or to undermine the interface itself, rather than weakening the adhesive matrix.

8) Penetration of the adhesive into the depths of the oxide film is important in that it effectively increases the length of the interface at the same time as eliminating a true planar boundary between adhesive and adherend. Thus, for pickled and PAA adherends, once water reaches the interface, there is no continuous passage for moisture between adhesive and adherend—effectively hindering any possible bond disruption. Should transformation of the alumina film, to its hydrated form, take place then any area attacked will be isolated by the surrounding adhesive. Both will limit the development of a continuous, weak interphase.

For CAA adherends, a planar interface exists with little adhesive penetration into the pores; any environmental attack can, therefore, proceed more rapidly both causing bond disruption and having the potential for the undermining of the anodic film surface.

9) If water can reach the surface film/metal interface, through flaws or by means of intermetallic sites, then corrosion is feasible, unless limited by the presence of primer. The result again would be an undermining of the pre-developed "oxide" films. This would be particularly relevant where the developed film is relatively thin—*i.e.* on abraded or pickled adherends.

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