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BOND DURABILITY PERFORMANCE - THE AUSTRALIAN SILANE SURFACE TREATMENT

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Abstract

The Royal Australian Air Force (RAAF) has produced its own Engineering Standard on Composite Materials and Adhesive Bonded Repairs (RAAF ENG STD C5033) as a consequence of procedure and process deficiencies contained in the manufacturers' Structural Repair Manuals. The surface preparation principles underpinning this standard were established during the development of the Australian silane surface treatment. This paper examines the purpose of each step in preparing the adherend for bonding and its effect on the durability performance. In addition, the durability performance and locus of failure of bonds can be described in terms of a two step model. The first step involves controlled moisture ingress by stress-induced microporosity of the adhesive in the interfacial region. The second step determines the locus of fracture through the relative dominance of one of three competitive processes, viz: oxide degradation, polymer desorption, or polymer degradation. A key element of the model is the control exercised over porosity by the combined interaction of stress and the relative densities of strong and weak linkages at the metal to adhesive interface. The model has the potential for development as an engineering management tool.

Introduction

Adhesively bonded repairs at Royal Australian Air Force depots (deeper level repairs) are conducted under conditions quite different to those that are used in the manufacture of bonded components. Repairs are conducted on existing structure, which limits the range of preparation and processing procedures and the tools that can be applied to the component. Many bonded repairs are not routine, the facilities may be primitive, access to the repair site may be poor and there may be very little control of the environment. The adhesive curing process is often carried out using vacuum bag methods which places the curing adhesive under a negative pressure instead of the positive pressure recommended by the manufacturer.

A survey of defect reports⁽¹⁻³⁾ conducted at one RAAF Unit has shown that 53 per cent of defects were related to adhesive bond failure. Some bonded repair designs and application procedures have little chance of success and can, in some cases, decrease the service life of components⁽³⁾. The RAAF produced its own Engineering Standard on Composite Materials and Adhesive Bonded Repairs

(RAAF ENG STD C5033)⁽⁴⁾ as a consequence of procedure and process deficiencies contained in the manufacturers' Structural Repair Manuals⁽³⁾. These steps were taken to improve the credibility of bonded repair technology and to assist with the management of the technology in the RAAF fleet. The surface preparation principles underpinning this standard were established during the development of the Australian silane surface treatment⁽⁵⁾.

It is well known that adherend surface preparation is critical to the formation of a durable adhesive bond⁽⁶⁾. Baker⁽⁵⁾ and his team at the Defence Science and Technology Organisation (DSTO) established that a solvent degrease, followed by a manual abrasion, a grit-blast and an application of organo-silane coupling agent produced a tough durable bond with selected thermoset epoxy film adhesives. This is now widely known as "The Australian silane surface treatment"⁽⁷⁾. Subsequent research has examined a range of influences over bond durability⁽⁸⁻²³⁾ and void formation in the bond⁽²⁴⁻²⁹⁾. The Australian silane surface treatment procedure was investigated by Kuhbander and Mazza⁽⁷⁾ in an extensive study of the process variables in the grit-blast plus epoxy-silane plus chromate primer treatment, with the conclusion that the process parameters used for the Australian silane surface treatment were, in general, optimal.

This paper compares the Australian silane surface treatment with three other surface treatments used for repair. A range of issues affecting bond strength and durability for adherends treated with the Australian silane surface treatment procedure are presented and evaluated. The paper further develops a model capable of explaining the dependence of bond durability on surface treatment. Finally a revolutionary approach to ensuring the airworthiness of bonded structure which considers the importance of adherend surface treatment on bond durability is discussed in the context of the RAAF Engineering Standard C5033.

Materials and Tests

The evaluation of the Australian silane surface treatment covered a range of aircraft aluminium alloys and adhesives. The data reported here focuses on two aluminium alloys (clad and unclad 2024 T3) and two film adhesives (Cytec FM[®]73 and FM[®]300). The surface treatments for the alloys are reported in detail elsewhere⁽²²⁾ and are summarized, with the nomenclature used, in Table 1.

| Nomenclature | Treatment |
|--------------------|---|
| "as received" | As supplied from the alloy manufacturer. |
| SB+wipe(MEK) | A solvent degrease with Kimwipe® tissues soaked in MEK followed by a Scotch-Brite® abrade (with MEK lubricant) and debris removal with Kimwipes® soaked in MEK. |
| SB+wipe(water) | A solvent degrease with Kimwipe® tissues soaked in MEK followed by a Scotch-Brite® abrade (with water lubricant) and debris removal with Kimwipes® soaked in water. |
| GB | The SB+wipe(water) treatment followed by a grit blast with 50 micron alumina powder at a grit impact density of 1.2 g cm ⁻² . |
| SB+wipe(MEK)+SCA | The SB+wipe(MEK) treatment followed by a dip in aqueous organo-silane coupling agent (SCA). |
| SB+wipe(water)+SCA | The SB+wipe(water) treatment followed by a dip in SCA. |
| GB+SCA | The GB treatment followed by a dip in SCA. |

Table 1 The nomenclature and a summary of steps constituting the Australian silane surface treatment.

The solvent degreasing step involves wiping the surface with tissues which are free of both lanolin and lint (Kimwipe® or Chicopee® tissues). A unidirectional wiping action is used to sweep solvent and contaminant to the edge of the area being degreased. Abrasion to remove persistent contaminant and weathered oxides is conducted with industrial Scotch-Brite® pads. These are an open mesh polymeric material with abrasive particles incorporated. Again abrasion is unidirectional. Kimwipe® or Chicopee® tissues are used in the debris removal step. Inspection to assess the effectiveness of degreasing is conducted with a "water break" test⁽²²⁾.

Grit-blasting in the laboratory was conducted using a venturi style nozzle operated at a working distance of 50mm and a gas pressure of 350kPa, delivering 50 micron alumina particles (White Industries AP106®) at a rate of 0.5g s⁻¹⁽¹⁴⁾. The nozzle was raster scanned to produce a grit impact density of 1.2 g cm⁻². This impact density is defined as a "standard" grit-blast. Similar grit impact densities and velocities can be obtained with the pressurized canister style of grit-blast unit used by the RAAF⁽¹⁴⁾. It is essential for the propellant gas and the

alumina powder to be clean and dry to minimize the potential for surface contamination⁽⁴⁾.

A 1% aqueous solution of the organo-silane coupling agent (SCA), γ glycidoxy-propyl-trimethoxy-silane, was applied by dipping the prepared adherends, except for experiments where alternative methods and tools are specified.

Drying was conducted in an isothermal oven, either at 110°C for 1 hour, or at the temperature and time specified.

As part of the bond durability evaluations, the performance of the Australian silane surface treatment was compared with surface treatments described in the repair manuals of two manufacturers as shown in Table 2.

| Nomenclature | Treatment |
|--------------|---|
| MDPP | The Macdonell Douglas® specification A1-F18AC-SRM-250 (AT)0007 00 change 4, which uses a Pasajel® etch and primer applied with cheesecloth. |
| BEA | The Boeing® aircraft specification 737-300 SRM51-70-09, which uses a hydrofluoric acid etch and Alodine®. |
| GB+P | A grit-blast followed by a Pasajel® etch, a rinse and dry (to assess the performance of the Pasajel® without primer). |
| FPL+PAA | Forest Products Laboratory etch followed by Phosphoric Acid Anodization, which represents the best practice for a factory process ⁽³⁰⁾ . |

Table 2 The nomenclature and description of several comparative surface treatments.

In some experiments the aluminium alloy adherends were degreased and ultramilled without lubricant using a Cambridge Instruments tungsten carbide blade attachment to a Jung Polycut E microtome as described in a previous reference⁽²⁰⁾. In some experiments the blades were ground to produce a flat-faced sawtooth profile with base angles of 60°, 120° and 180° (as illustrated in Figure 8). These specimens are designated by the nomenclature; ultramilled angle°.

The ASTM mechanical tests used included the D1876 180° T-peel, D1002 lap-shear, D3165 lap-shear, D1781 honeycomb peel and the D3762 Boeing wedge durability test. Since durability is very sensitive to surface treatment⁽⁶⁾, results using the Boeing wedge test dominate the reporting in this paper.

Surface analysis of adherend surface condition and fracture surfaces was conducted using X-ray photoelectron

spectroscopy (XPS) as described elsewhere^(13, 20). Electron microscopy was performed with a JEOL 6400 Field Emission Scanning Electron Microscope (FESEM). Void measurements were conducted as described elsewhere^(27, 29).

Comparison of Repair Treatments

Figure 1 shows the crack growth rate curves from Boeing wedge durability tests where the unclad 2024 aluminium adherends were treated with either the Australian silane surface treatment (GB+SCA), the MacDonnell Douglas MDPP treatment, the Boeing BEA treatment or the Pasajel® GB+P treatment. The durability performance of the Australian silane surface treatment compares favourably with all three reference repair procedures. Durability experiments conducted with other aluminium alloys and either FM®300 or FM®73 adhesive, are not reported in detail here, but results suggest that there is considerable variability in performance of the MDPP, BEA and GB+P treatments. In each case the GB+SCA performs as well or better than these treatments. The authors believe that the variability of the MDPP, BEA and GB+P durability performance results from inherent deficiencies in the processes and in particular, to sensitivity to operator technique.

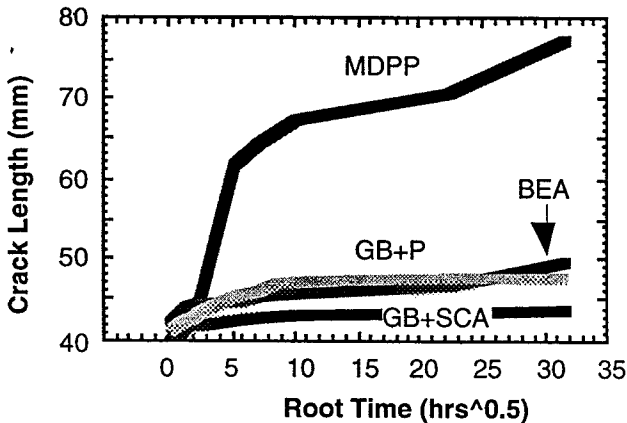


Figure 1 Crack growth rate curves from Boeing wedge durability tests conducted in condensing humidity at 50°C for unclad 2024 aluminium adherends and Cytec FM®300 adhesive, showing the effect of four repair surface treatments. Three of these treatments are used at RAAF bases and one is a commercial aircraft procedure.

The Australian Silane Surface Treatment

Figure 2 shows the crack growth rate curves from Boeing wedge durability tests for clad 2024 aluminium adherends treated successively with each step used in the Australian silane surface treatment. The adhesive used was Cytec FM®73. The FPL+PAA treatment is included in Figure 2 as a benchmark since it represents the best practice for a factory process⁽³⁰⁾.

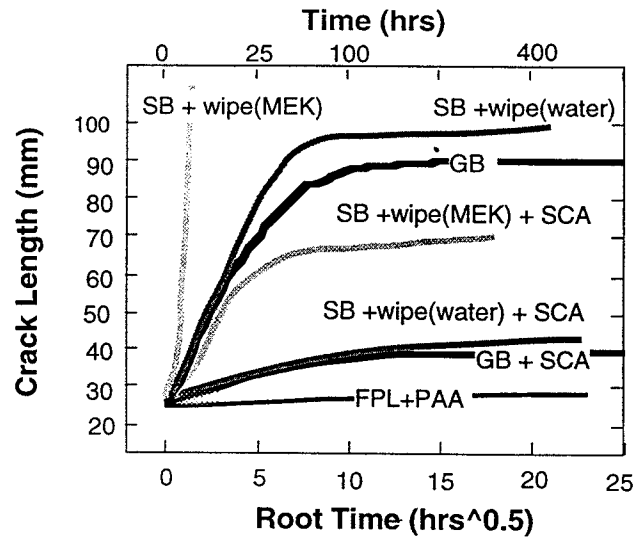


Figure 2 Crack growth rate curves from Boeing wedge durability tests conducted in condensing humidity at 50°C for clad 2024 aluminium adherends and Cytec FM®73 adhesive, showing the effect of abrasive surface treatments and organo-silane coupling agent. The FPL + PAA is a factory treatment used as a benchmark.

It is clear that the use of solvent soaked tissues to remove debris from an abraded surface (SB+wipe(MEK)) leads to very rapid failure. The use of water soaked tissues after abrasion (SB+wipe(water)) improves the durability almost to the level of the GB treatment. However, this level of durability is considered to be unsatisfactory for aircraft applications. The RAAF Engineering Standard C5033 recommends the grit-blast treatment because it minimizes the opportunity for recontamination of the surface from soiled tools⁽²²⁾. The application of the organo-silane coupling agent further improves bond durability, but there is a memory of the previous mechanical and chemical treatment used to prepare the substrate.

Figure 3 shows the composition of the fracture surfaces of the failed Boeing wedge durability tests described in Figure 2. The SB+wipe(MEK) leads to failure at the adhesive to metal oxide interface, which is reported to be due to residual contaminant deposited from the MEK as it evaporates⁽¹⁷⁾. By contrast, failure occurs in the oxide film for the SB+wipe(water), the GB and the SB+wipe(MEK)+SCA treatments. The rate of crack growth for these treatments is similar (Figure 2) and leads to the proposition that the mechanism of moisture ingress and the reaction kinetics leading to a domination of the fracture by oxide degradation are probably similar. In the case of the organo-silane on those substrates which themselves provide good bond durability (i.e. SB+wipe(water)+SCA and GB+SCA), the fracture moves back to the interface containing the polymer and the oxide. However, in this case, the fracture contains both oxide and polymer phases, indicating a mechanism which leads to an

improvement in the durability of the oxide rather than weakening the polymer interface.

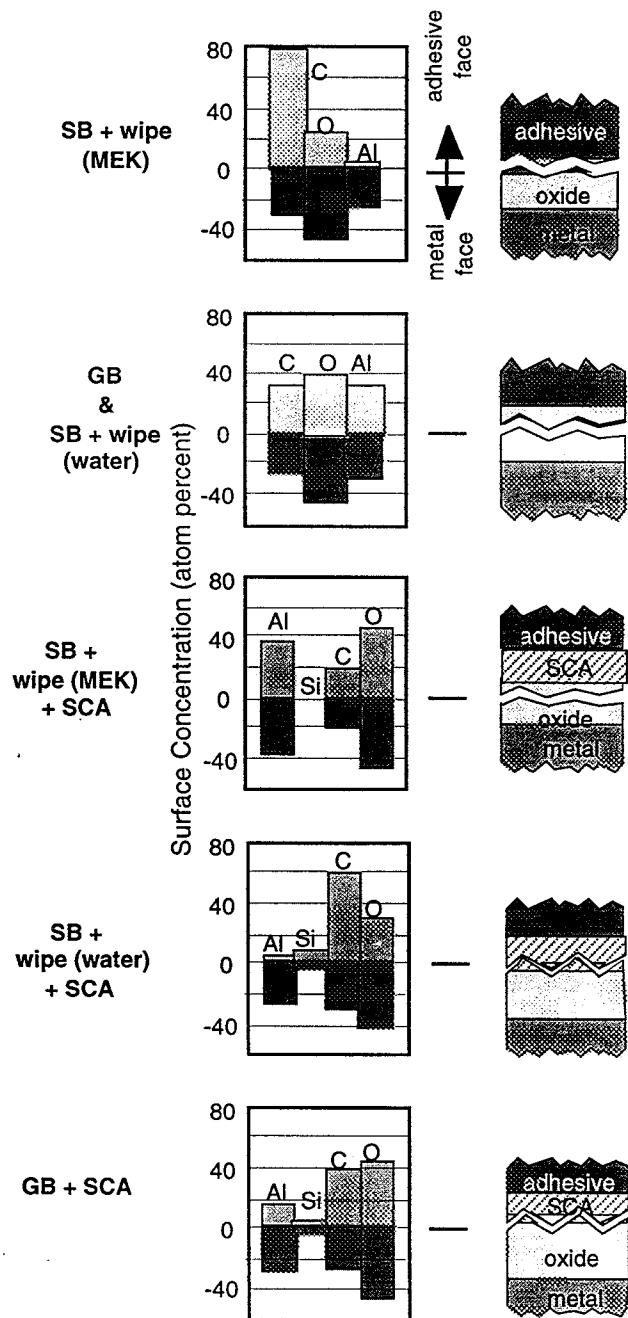


Figure 3 Surface compositions of both fracture faces measured with XPS for the same durability specimens shown in Figure 2. The inferred locus of fracture is also shown.

Contamination

Organic contamination present on the adherend can lead to a weak interface between the adhesive and the adherend. The consequences are most acutely apparent in a loss in bond durability (Figure 2 - SB+wipe(MEK)).

The contact angle for a water droplet on a prepared surface is sensitive to both the presence of hydrophobic contaminant and the degree of roughness of the surface⁽⁶⁾. Figure 4 shows that the contact angle between a 5 μ l drop of distilled water and a prepared aluminium surface decreases with each step of the Australian silane surface treatment process. Figure 4 also shows that contaminant re-adsorption on a prepared surface can influence wetting. The rate of this re-adsorption will depend strongly on the environment in which the bonding is conducted. The rate of surface degradation will be greater at an operating air-base, where AvturTM fuel fumes are present, than in a laboratory environment.

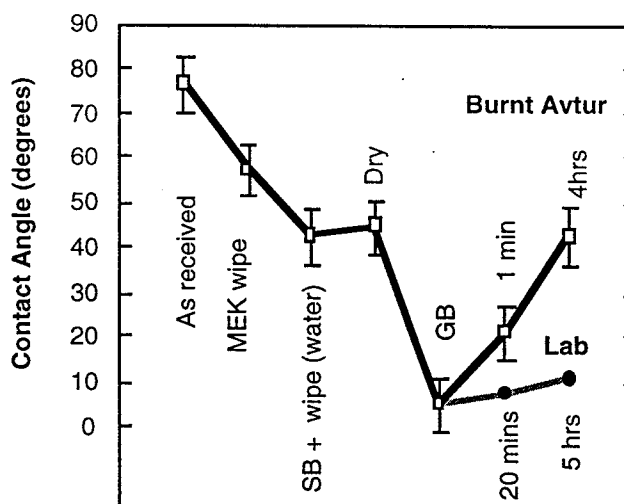


Figure 4 The contact angle for clad 2024 aluminium following the surface treatments defined in the text and following exposure to burnt AvturTM fumes or a laboratory environment.

| Treatment | C 1s concentration atom percent | |
|---------------------|---------------------------------|----------|
| | sample A | sample B |
| As received | 50 | 36 |
| MEK wipe | 31 | 30 |
| SB with MEK | 24 | - |
| SB with water | - | 24 |
| tissue wipe (MEK) | 27 | - |
| tissue wipe (water) | - | 24 |
| grit-blast | 19 | 19 |

Table 3 Carbon 1s concentration on 2024 clad aluminium alloy following the surface preparation steps described. Sample A was abraded with MEK lubricant and wiped with MEK soaked Kimwipe[®] tissues. Sample B was abraded with water and wiped with water soaked Kimwipe[®] tissues.

The carbon 1s level determined by XPS is used as a measure of surface contamination. Table 3 shows that the carbon concentration decreases with each pre-silane step of the Australian silane surface treatment. The Scotch-brite® abrasion leaves a higher carbon concentration than the grit-blast because of the transfer of some of the polymer carrier in the Scotch-brite® to the surface during abrasion. The removal of debris with MEK-soaked tissues after the Scotch-brite® leaves a slightly higher carbon concentration than for removal with water-soaked tissues because the MEK dissolves some organic residues from the tissues, distributes them across the surface, then evaporates, leaving additional organic contaminant on the surface. For this reason, the RAAF ENG STD C5033 insists that solvent only be used for initial degreasing and never as part of later surface preparation steps^(4, 22).

Surface analyses of degreased and abraded surfaces indicates that several atomic layers of hydrocarbon contaminant are present on the surface^(13, 20). Models developed to interpret Angle Resolved XPS data indicate that the contaminant is distributed as islands across the surface⁽²⁰⁾. The island configuration allows hydroxyl moieties on the adhesive to make contact and bond with hydroxyls on the metal oxide in those regions not covered by contaminant. The size and distribution of the islands will depend on the mode of deposition. Residual contaminant deposited in the presence of evaporating MEK solvent is expected to be more uniformly distributed across the adherend surface than contaminant deposited in the presence of water⁽¹⁷⁾. Whilst the difference in carbon 1s concentration between the SB+wipe(MEK) and the SB+wipe(water) is relatively small (Table 3) the effect on durability is substantial (Figure 2). This indicates that the distribution of contaminant appears to be more important than overall concentration in determining the bond durability. The application of a coupling agent to the surface is designed to enhance the effectiveness of the hydroxyl terminations on the metal oxide in linking with the adhesive. This improvement in bond effectiveness is reflected in the significant improvement bond durability shown in Figure 2. However, the memory of the durability performance for the SB+wipe(MEK) and SB+wipe(water) treatments indicates that the distribution of contaminant on the adherend, prior to the application of the SCA, plays a significant role in the ability of the SCA to form effective bonds with the hydroxyl terminations on the metal oxide.

Re-contamination of the surface with hydrocarbons can have a dramatic influence on the durability of the bond. Figure 5 shows crack growth curves for wedge durability tests conducted on clad 2024 adherends deliberately contaminated with Avtur™, either before or after the application of organo-silane coupling agent. The bands shown for GB and GB+SCA represent the range of durabilities obtained from at least five test batches. It is clear that re-contamination between the grit-blast and the application of the organo-silane coupling agent decreases

bond durability whereas contamination after the organo-silane application has little effect. This is consistent with the proposition that surface contaminant adsorbed on the aluminium oxide reduces the number of sites available for atomic bonding with the organo-silane and thus degrades the effectiveness of bonding. It also appears that contaminant deposited on a crosslinked organo-silane layer is absorbed into the adhesive during cure with little apparent effect on bond durability.

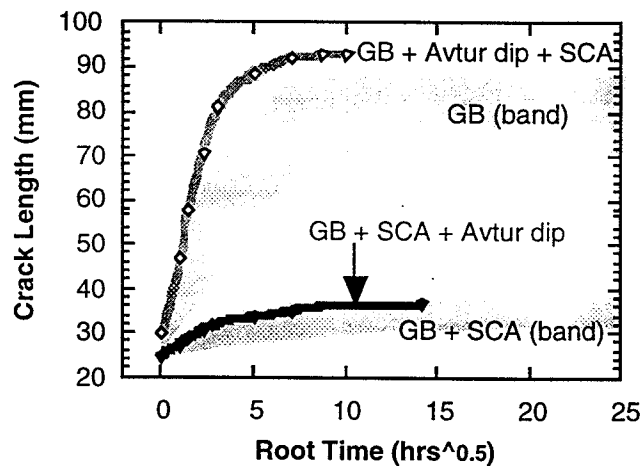


Figure 5 Crack growth rate curves from Boeing wedge durability tests conducted in condensing humidity at 50°C for clad 2024 aluminium adherends and Cytec FM[®]73 adhesive, showing the effect of the sequence of the introduction of Avtur™ contaminant. The bands of GB and GB+SCA results are shown for comparison.

| Contaminant | Crack Length (mm) | |
|------------------------|-------------------|------|
| | 0hr | 50hr |
| No applied contaminant | 26 | 33 |
| C8 (Octane) | 28 | 39 |
| C12 (Dodecane) | 29 | 39 |
| C16 (Hexadecane) | 28 | 39 |
| C18 (Octadecane) | 51 | 100 |

Table 4 Crack lengths from Boeing edge durability tests measured at 0 and 50 hours of exposure to condensing humidity at 50°C for contaminated clad 2024 aluminium adherends treated with SCA and bonded with Cytec FM73[®] adhesive. The adherends were contaminated between the grit-blast and the application of SCA.

Durability experiments were conducted on specimens for which the adherends were contaminated with members of a homologous series of aliphatic hydrocarbons, after the grit-blast. The results of experiments, shown in Table 4, indicate that the more waxy materials, i.e. above C₁₆, have a significant effect on durability, whereas the liquid

hydrocarbon contaminants, i.e. C_{16} and below, have little effect. The lighter fraction aliphatic hydrocarbons appear to be more easily displaced from the surface by the fluid adhesive as it attempts to form atomic bonds with the hydroxyl terminations on the oxide present on the adherend.

The tools used to apply the organo-silane coupling agent can introduce organic contaminant and decrease the durability of the bond²². It is essential to consider the application tool as a potential source of contaminant transfer to the surface, but it is surprising how little attention is given to tool management.

Surface Morphology

Abrasion is performed to remove loosely bound oxides, strongly attached contaminants (e.g. baked grease) and to decrease residual contaminant. Figure 6 (a) shows that the process of abrasion creates a surface with furrows and residual metal debris. Grit-blasting is conducted to prepare a consolidated, fresh, active surface using media where the potential for the introduction of contaminant is low. Figure 6 (b) shows that the grit-blast forms craters in the surface through the impact of the soft aluminium with fine alumina particles. Metal deformation is more dominant than metal removal and pre-existing debris is consolidated into the surface^(10, 14).

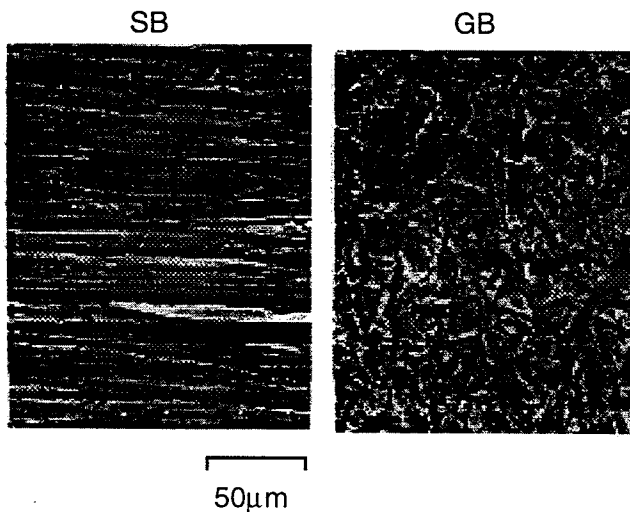


Figure 6 Optical micrographs of clad 2024 aluminium (a) abraded with Scotch-Brite® pads and (b) abraded with Scotch-Brite® and grit-blasted with 50µm alumina powder.

Inspection of the quality of a grit blasted surface is performed visually and for aluminium surfaces prepared with fine grit, optical reflectance characteristics are a good indicator of the severity of grit-blast^(14, 23). A grit impact density greater than 0.6 g cm^{-2} , is required to ensure complete coverage of the surface with grit impacts⁽¹⁴⁾ and hence maximum removal of surface contaminant. Figure 7 shows that a grit impact density of greater than full coverage leads to overfolding of the soft aluminium surface

and the formation of cavities which can trap volatiles. Unless such a surface is thoroughly dried for at least an hour at 110°C , the volatiles released during cure of thermoset resins under vacuum bag conditions, can lead to high void densities in the adhesive^(24, 27, 29). The optimum grit impact density is thus approximately 1 g cm^{-2} . Trials have shown that trained operators can consistently obtain grit impact densities in this range using visual inspection only⁽¹⁴⁾.

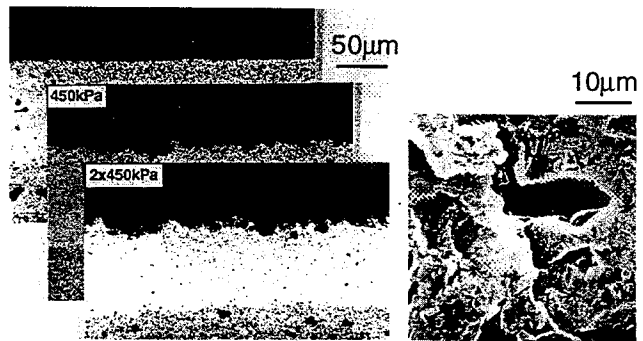


Figure 7 Micrograph cross sections showing (i) no grit blast, (ii) single impact grit-blast and (iii) double impact grit-blast. The micrograph of the double impact grit-blast shows the degree of overfolding and cavities formed.

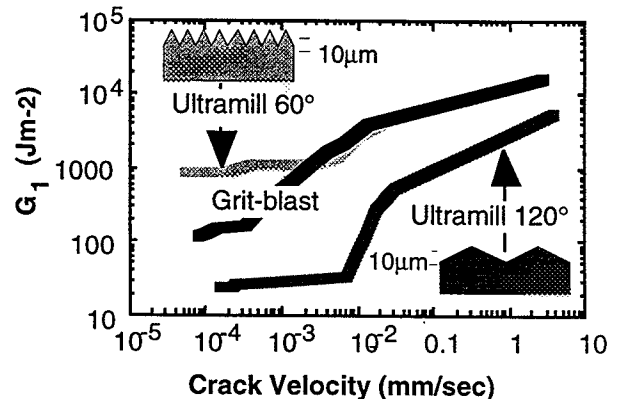


Figure 8 G_1 as a function of crack velocity conducted in condensing humidity at 50°C for clad 2024 aluminium and Cytac FM®73 adhesive, showing the effect of the ultramill profile angle. A comparison with a grit-blast treatment is included.

Figure 8 shows a comparison of the elastic energy release rate, G_1 , as a function of crack velocity for ultramilled surfaces with flat-faced sawtooth profiles with base angles of 60° and 120° and of rough grit-blasted surfaces. (The calculations of G_1 and crack velocity were conducted as described by Venables⁽³¹⁾). Decreasing the base angle of the ultramilled sawtooth clearly improves fracture toughness and bond durability such that the ultramilled specimen with a base angle of 60° has a similar fracture performance to that of the grit-blasted specimen. Surface analysis indicated that the ultramilled adherend had a lower

concentration of hydrocarbon than the grit-blasted adherend. The experiments described in Figure 8 indicated that roughness is essential to high fracture toughness. Increasing the roughness of the surface improves the wettability⁽⁶⁾ and hence the overall number of successful atomic bonds. The increase in energy dissipation during crack formation as a result of a rough surface can be attributed to factors such as: an increase in the surface area (although this is usually less than a factor of 1.5), an increase in the shear stress component, an inhomogeneous micro-stress distribution along the interface and an increase in the size of the plastic zone⁽⁶⁾. Mechanical interlocking is not believed to be a predominant mechanism⁽⁶⁾.

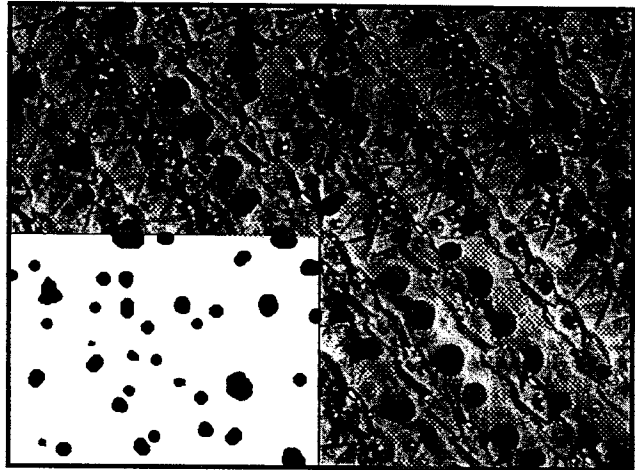
Voids

Moisture uptake in the adhesive and on the adherend during repair bonding at tropical facilities can lead to high void contents in the bond, particularly for repairs conducted using vacuum bag processing. Figure 9 shows photographs of the fracture surfaces of two failed T-peel specimens, manufactured from clad 2024 aluminium adherends with a GB+SCA treatment (thoroughly dried) and Cytec FM[®]300 adhesive. Exposure of the adhesive (4 hours) and the adherend (1 hour) to a tropical environment (70% RH at 30°C) prior to bonding leads to extremely high void contents (Figure 9 (b)) whereas exposure to temperate conditions (50% RH at 20°C) leads to a low void content (Figure 9 (a)). Clearly, the tropical exposure led to sufficient steam to cause a 70 per cent voided area under vacuum bag cure, with a consequential loss in peel strength of over 50%⁽²⁹⁾. These experiments suggest that environmental control of the bonding facility and thorough drying of the adherends is essential.

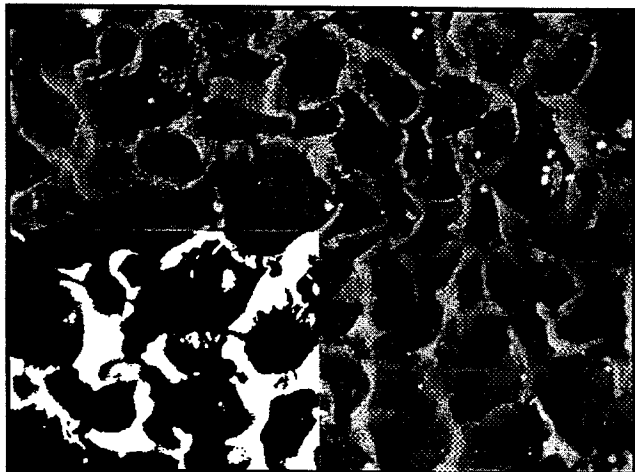
Volatiles present in the adhesive and on the adherend can lead to voids in the adhesive during elevated temperature cure using a vacuum bag^(24, 26 - 29). The adhesive received from the manufacturer contains volatiles and can absorb an equilibrium concentration of water in just over an hour^(27 - 29). The adherend surface can adsorb sufficient moisture to present a significant void problem, particularly in cases of severe grit-blasting⁽²⁴⁾. As described in the section on Surface Morphology, multiple grit impacts and the associated metal deformation leads to over-folding and cavities in the surface which can trap volatiles and water. Some of the water is physisorbed and thus easily removed. The remainder is chemically bound in the surface oxides and may require drying for several hours at temperatures above 110°C to lead to substantial reductions in chemisorbed water^(27, 29). Unless this water is removed, it will continue to evolve during the cure cycle and add to the volatile burden in the adhesive. Experiments in temperate conditions have shown that drying the adherend at 110°C for at least 1 hour is essential to minimize volatile evolution responsible for void formation during the cure phase of the adhesive⁽²⁷⁾.

As a general observation from the limited range of film adhesives studied, the higher temperature curing adhesives tend to show a greater tendency to voiding. This is consistent with the expected increase in vapour pressure at the higher temperatures required to cure the adhesive.

(a)



(b)



1 mm

Figure 9 Photographs of the fracture surfaces of failed T-peel specimens, showing the void content developed as a result of pre-bond exposure to (a) temperate conditions and (b) tropical conditions. Bonds were manufactured using clad 2024 aluminium with a GB+SCA treatment, Cytec FM[®]300 adhesive and vacuum bag cure procedures.

Bond Degradation Model

Adhesion relies on a range of attractive forces between the adhesive and the substrate⁽⁶⁾. The prepared metal surface has an oxide film, with an hydrated outer surface⁽³²⁾. It is generally believed that this surface forms bonds with the

hydroxyl moieties on the organic phase (adhesive, coupling agent or primer)⁽³³⁾. Calculations show that dispersion (London) forces or dipole interactions are more than sufficient to account for observed adhesive bond strengths⁽⁶⁾.

The application of coupling agents to the surface is designed to enhance the effectiveness of the hydroxyl terminations on the metal oxide in linking with the adhesive. In the case of the organo-silane coupling agents, the organic head group is chosen for cross-link compatibility with the adhesive polymers and the silanol groups formed during hydrolysis either react chemically with the hydroxyl groups on the metal oxide surface to form oxirane bonds (M - O - Si)^(6, 32) or form hydrogen bonds with these hydroxyl groups (M - OH...HO - Si)⁽⁶⁾. The exact nature of the interaction remains speculative. The organo-silane forms strong polysiloxane networks which play a significant role in interfacial durability enhancement⁽³²⁾.

A comprehensive view of bond degradation can only be achieved when a detailed model with the capability of explaining all experimental data, can be formulated. The following model assists with an explanation of the sensitivity of bond durability to surface treatment and the subtle changes in locus of fracture observed with surface analysis.

The adhesive bond degradation model shown in Figure 10 is an extension of the model introduced by Arnott and Rider^(17, 20-22). This particular model involves diffusion of moisture to the interface and three competitive degradation reactions, viz: (i) oxide degradation, (ii) polymer desorption or (iii) polymer hydrolysis (Figure 10 (a)). The relative rates of each of these reactions will determine the region in the interface in which degradation will predominate. Moisture ingress into the interfacial region is dominated by the micro-porosity of the bond at that interface. Stress at the interface and the relative densities of strong and weak atomic bonds will determine the porosity (Figure 10 (b)) and hence the rate of moisture diffusion into the crack tip. This interfacial deformation component of the model is based on experimental observations of macro-deformation made with constant displacement rate durability tests⁽¹⁹⁾. The relative densities of strong and weak bonds can be induced chemically, such as through the relative concentrations and distribution of organo-silane coupling agent and contamination. Alternatively, regions that are effectively strong or weak can be induced through locally high or low stresses. Such an inhomogeneous stress field distribution can occur along a rough surface. The concept of strong and weak bonds will be developed further later in this section.

The model is capable of explaining the bond durability data in Figures 2, 5 and 8 and the inferred fracture paths in Figures 3. Bonds manufactured with a SB+wipe(MEK) show very poor durability (Figure 2) and a fracture path at the interface between the metal oxide and the adhesive

(Figure 3). In this case, the weakly bonded region in Figure 10 dominates the interface as a result of the organic contaminant present. Moisture ingress will be rapid under load and polymer desorption appears to be more dominant than oxide degradation as the failure mechanism. Adherends treated with a SB+wipe(water), a GB or a SB+wipe(MEK)+SCA have durabilities in the mid range (Figure 2) and fail within the oxide film (Figure 3). The density of strong bonds (strongly bonded region in Figure 10) have increased leading to lower porosity and a decrease in the rate of moisture ingress under load. The dominant degradation reactions shift from polymer desorption to oxide degradation. In the case of adherends treated with SB+wipe(water)+SCA and GB+SCA, the excellent durability (Figure 2) is accompanied by a shift in the locus of fracture toward the organo-silane interface (Figure 3). This suggests that the SCA has further strengthened the interface leading to a further reduction in moisture ingress under load. The SCA also inhibits the degradation of the oxide by water⁽¹³⁾ and thus will shift the mechanism for bond degradation toward reactions involving polymer desorption and polymer degradation.

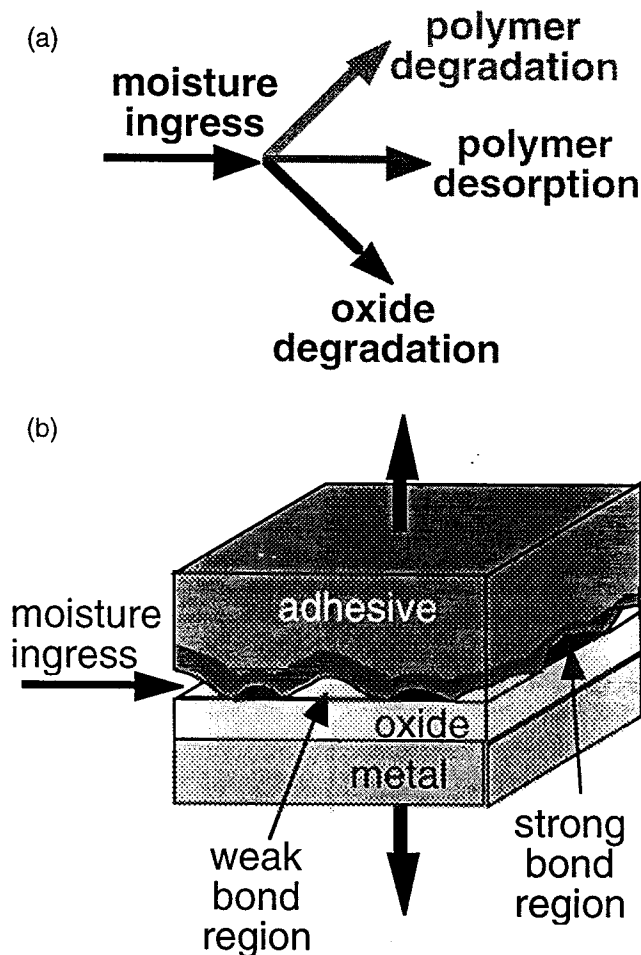


Figure 10 Adhesive bond degradation model used to explain bond durability changes with surface treatment. (a) Moisture ingress and bond degradation paths. (b) Deformation at the bond interface under load.

The bond degradation model in Figure 10 can also qualitatively explain the dramatic changes in fracture energy shown in Figure 8, resulting from changes in the surface roughness profile. In an adhesive bondline of 100 micrometres width and a peak to valley roughness profile of 10 micrometres, the application of a mode 1 opening load will lead to a stress intensity at the peaks which is 20 percent higher than in the troughs, based on calculations using a spring model to describe the adhesive under load³⁴. In addition, bond strengthening and toughening processes, such as an increase in surface area, the addition of shear stress components, and modification of plastic zones, may also be involved. Again, regions that are effectively strong or weak can result from locally low or high stresses respectively. The number, magnitude and distribution of the relatively unstressed and highly stressed (strong and weak) regions will again influence the microporosity at the interface between the metal oxide and the adhesive. Indeed, for a rough surface, microporosity may only be significant in the region of the peaks (and not in the troughs) of a roughened surface thus influencing the rate of diffusion of moisture to the interface over a substantial fraction of the surface.

The adhesive bond degradation model described in Figure 10 may eventually assist in advancing the primitive art of adhesive bond lifeing.

RAAF Engineering Standard C5033

The present approach to the airworthiness of bonded structure expressed through US Federal Aviation Regulations adequately assures structural integrity at the time of manufacture, but does not assure continuing integrity of structural adhesive bonds⁽³⁵⁾. The durability of a structural adhesive bond is most strongly influenced by the adherend surface preparation prior to bonding and, as shown in this paper, can depend critically on the correct application of steps within the procedure. Davis⁽³⁵⁾ argues that it is the process of forming a durable bond which needs to be validated, because current test programs do not assure resistance to interfacial hydration.

There is currently no reliable, quantitative non-destructive inspection method to assess the quality of the adherend surface treatment prior to bonding, nor are there methods to assess the resistance of the bonds to environmental degradation following bond manufacture^(3, 6). Thus, the key elements to the quality and integrity of an adhesive bond are⁽³⁾; (a) a fully qualified procedure, (b) training to ensure a high level of skill of the technicians manufacturing the bond and (c) management systems to ensure that standards are met and procedures are followed. The RAAF Engineering Standard C5033⁽⁴⁾ and associated in-house training courses are based on the firm belief that the most effective way to encourage implementation of the correct standards and procedures is through training based on a thorough understanding of principles. In repair situations, the bonding task is frequently novel and there is always the

potential for unexpected problems. Handling these problems in a satisfactory way depends on the technician having a good knowledge of the consequences of their actions.

Conclusions

The Australian silane surface treatment is designed to minimize organic contaminant, optimize surface topography and provide chemical coupling between the adhesive and the metal oxide present on the adherend. This paper demonstrates the importance of each of these features in optimizing bond durability. It is essential to ensure an appropriately roughened surface with a fresh hydrated oxide surface and a minimum of adsorbed hydrocarbon contaminant. The step between the grit-blast and the application of organo-silane coupling agent is particularly critical. Void formation is due to excess moisture in the bondline during cure but can be controlled through environmental conditioning of the bond facility together with control of the severity of grit-blast and effective drying of the adherend.

This paper also demonstrates a model capable of explaining bond durability behaviour as a function of contaminant concentration and surface roughness. The model involves diffusion of moisture to the interface of a stressed polymer and three competitive degradation reactions, viz: (i) oxide degradation, (ii) polymer desorption or (iii) polymer hydrolysis.

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