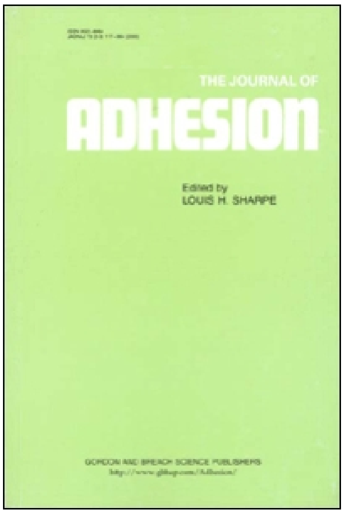

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Davies, R. J. and Ritchie, M. D.(1992) 'Future Design Concepts for the Development of New Pretreatments of Aluminium Alloy/Metal Matrix Composites for Adhesive Bonding', The Journal of Adhesion, 38: 3, 243 — 254

To link to this Article: DOI: 10.1080/00218469208030458

URL: http://dx.doi.org/10.1080/00218469208030458

J. Adhesion, 1992, Vol. 38, pp. 243–254
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Printed in the United Kingdom

Future Design Concepts for the Development of New Pretreatments of Aluminium Alloy/Metal Matrix Composites for Adhesive Bonding*

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(Received October 4, 1990; in final form March 26, 1992)

The present paper is concerned with the identification of reasons for the environmental failure of adhesive joints using aluminium alloy substrates and the potential for improvement in performance by the development of modified anodising treatments. The attention of the work is focused on the behaviour of the oxide region of the joint and its potential influence on overall bonding performance. The scanning electron microscope (SEM) is used to study the oxide region within aluminium alloy adhesive joints which have been prepared by phosphoric acid anodising (PAA) and chromic acid anodising (CAA). Static stress durability tests are used to assess the performance of the joints and the resulting failure surfaces were investigated. Finally, the importance of the presence of a "micro-composite" interphase consisting of anodic oxide penetrated by adhesive, in the joint, is advanced and its significance in future pretreatment design outlined.

KEY WORDS aluminium alloy substrates; adhesive joints; chromic and phosphoric acid anodising; durability; micro-composite; pretreatment design.

INTRODUCTION

A great deal of research has been conducted on the adhesive bonding of aluminium alloys and the main consensus that has arisen is that some form of pretreatment of the aluminium prior to bonding is essential for durability performance.[1,2] However, the exact reasons as to why different pretreatments of aluminium substrates result in various degrees of bonding performance still eludes the adhesion scientist.

Many theories have been advanced to explain why a particular pretreatment of aluminium results in superior or inferior performance of an adhesive joint. These vary from macrosurface roughness factors,[3] surface oxide chemistry,[4] surface oxide hydration resistance[2] and weak layers within the oxide.[2] Other factors resulting from the use of adhesives with surface oxides have also been investigated cover-

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*Presented at the Thirteenth Annual Meeting of The Adhesion Society, Inc., Savannah, Georgia, U.S.A., February 19–21, 1990.

ing wettability,[5] homogeneity of the adhesive properties in the joint[6] and adhesive chemistry.[7]

However, there has been a trend in recent years to investigate thoroughly the oxide morphology produced by the empirically developed pretreatments of aluminium for adhesive bonding.[8-12] This trend has focused investigations into how the oxide morphology produced by the pretreatment of aluminium, coupled with adhesive penetration into porous oxides, could profoundly affect adhesive joint performance.[13] Such investigations have resulted in the concept of a "composite" interfacial region created within the adhesive joint. This composite region was proposed to have mechanical properties between that of the adhesive and the oxide, resulting in increased joint performance.[13,14] This idea is distinctly different from Davis and Venables hypothesis that porous surfaces may promote stronger adhesive joints, by the mechanism of mechanical interlocking.[15]

In an attempt to build on the previous work conducted on morphological influences of the surface oxide on adhesive joint performance, the following investigation looks at three main factors within an aluminium alloy adhesive joint that possibly affect performance. Firstly, the micro-structure of the oxides produced by chromic and phosphoric acid anodising and methods that can be applied to adapt further the micro-structure for adhesive bonding purposes. Secondly, the degree of adhesive penetration within the PAA, CAA and modified oxides. Thirdly, the development of a simple mathematical model to indicate the potential influence of oxide morphology and adhesive penetration of the oxide on the stress conditions within the joint at the critical interfaces.

Finally, from this work, the optimisation of future structural aluminium adhesive joints, using aluminium alloy/metal matrix composites, by producing "designer" anodic oxides prior to bonding will be discussed.

EXPERIMENTAL TECHNIQUES

An aluminium-magnesium alloy was employed to British Standard 5251 and had a nominal composition of 2.25% magnesium with the balance being aluminium. The three surface pretreatments used in the work were as follows:

(1) Phosphoric acid anodising (PAA); according to Boeing Aircraft Corporation Specification BAC 5555.

(2) Chromic acid anodising (CAA); according to U.K. Ministry of Defence Standard DEF. STAN. 03-24/1.

(3) Chromic acid anodising (CAA); as 2, followed by immersion in hot orthophosphoric acid.

An epoxy-phenolic based primer (BR 127, supplied by Cyanamid, USA) was applied to the anodised aluminium surface prior to bonding. The adhesive used was an unmodified, single-part epoxy paste adhesive (AV 1566 supplied by Ciba-Geigy, UK) cured for one hour at 150°C. Samples before and after testing were viewed in a Cambridge Stereoscan Model 250 Mk. 2 scanning electron microscope (SEM) by bending the aluminium samples through 180°. The bending of the samples allows the cross-section of surface oxides to be examined.

Durability data on the performance of the PAA and CAA joints was obtained by use of a double cantilever beam test adapted by Davies and Kinloch[13] from the pioneering work conducted by Mostovoy, Ripling *et al.*[16,17] The dimensions of the joints used can be seen in Figure 1 and a pre-crack, 30 mm in length, was created in the adhesive layer. The joints were then placed in a creep-rig apparatus, surrounded by a tank of water at 55°C which enabled the joint to be kept under a constant load. However, as a consequence of the plasticisation effect of ingressing water on the adhesive, crack blunting occurs. To overcome the crack blunting mechanism the load on the joints was increased by 5.6 Kg, every 125 hours. This method eventually induces environmental failure to occur in the interfacial region of the joints. The fracture energy, G, was calculated from:

$$G = P_c^2/2B\{\partial C/\partial a\} \tag{1}$$

where $\partial C/\partial a$ can be found from:

$$\partial C/\partial a = 8(3a^2/h^3 + 1/h)/E_sB \tag{2}$$

where P_c is the critical load, B is the breath of the test-piece, $\partial C/\partial a$ is the partial derivative of the compliance, C, and crack length, a; E_s is the substrate Young's modulus, and h is the thickness of the sample.

RESULTS AND DISCUSSION

In the results of the static stress durability tests given in Figure 2, it is seen that superior durability performance is found from the PAA joints. This observation has been obtained by many other workers comparing the performance of aluminium adhesive joints prepared by the best United States standard (*i.e.* PAA) and the best

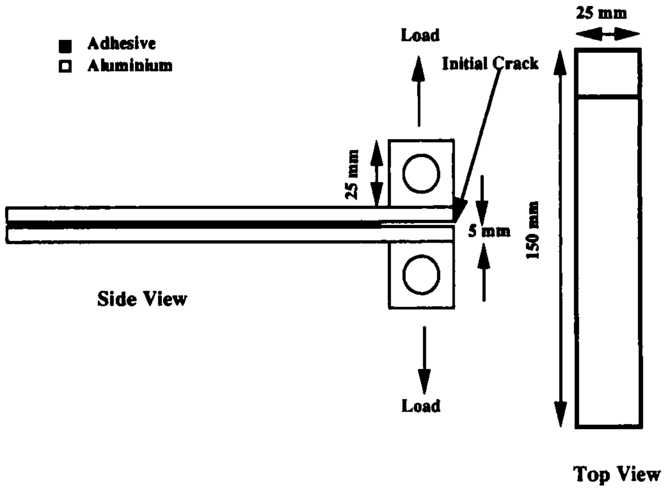

FIGURE 1 Double cantilever Beam (DCB) used for Environmental Testing.

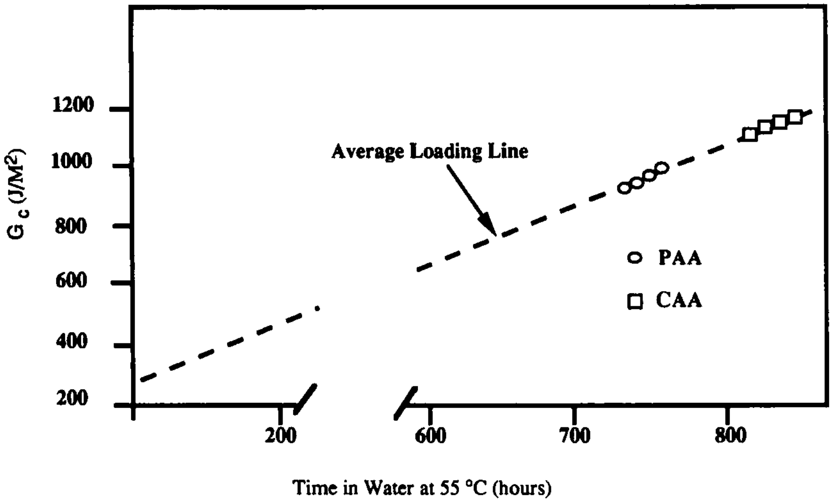

FIGURE 2 Durability Data from DCB Joints; the longer the time to failure the more resistant is the joint to water attack. Initial G applied of 300 J/m is 95% of "dry" G.

European standard (*i.e.* CAA).[1] Nevertheless, both PAA joints and CAA joints give excellent durability performance when compared with many other pretreatments. The factors governing durability performance are unclear. It has been postulated that mechanical keying, hydration resistance of the surface oxide and chemical interactions between oxide and adhesive are major influences on durability performance.[1] However, no one factor or combination of these factors has been able to give a convincing explanation of the superior performance of PAA joints over CAA joints. If the influence of such factors was understood, the possibility of "tailor making" a surface oxide to optimise adhesive bonding performance could exist. Before this can happen a great deal more has to be known about the critical adhesive/oxide interphase. The double cantilever beam (DCB) joint used for durability assessment by Davies and Kinloch[13] has the advantage that failure is initiated in the critical adhesive/oxide interphase.

Viewing the failure surfaces of the DCB joints, small areas of apparent interfacial failure are seen just ahead of the initial crack front, the rest of the failure surface being cohesive (see Figure 3). On closer examination of these small areas of failure using scanning electron microscopy, it was found that all the joints had failed through the oxide region of the joint just below the surface of the oxide (see Figure 4). The hydration of the oxide observed in the failure region has been established to be a consequence of post-failure hydration of the failure surfaces.[13] in order to explain the differences in durability performance between PAA and CAA joints it is necessary to investigate the original oxide morphology and the role of such a structure in an adhesive joint. This is best achieved by the use of electron microscopy.

Figures 5 and 6 show the structure of the PAA and CAA oxides, respectively. The PAA oxide is a 0.6 μm thick porous oxide with a distinctly "columnar-like"

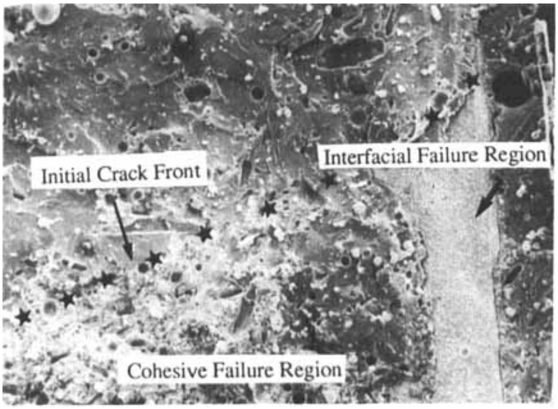

FIGURE 3 Region of Interfacial Failure ahead of front in DCB Adhesive Joints used for Environmental Testing.

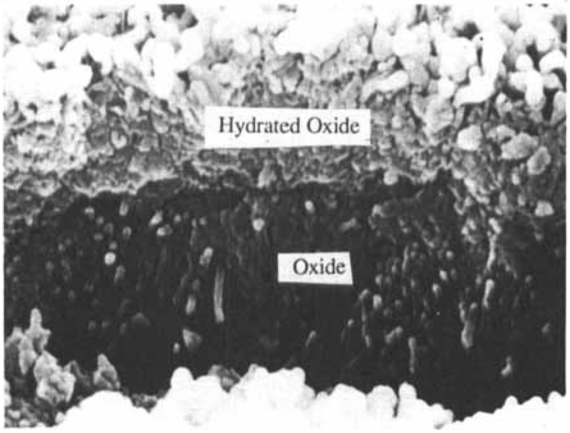

FIGURE 4 Cross Section of CAA Joint Failure Surface in Interfacial Failure Region indicating failure through the Oxide.

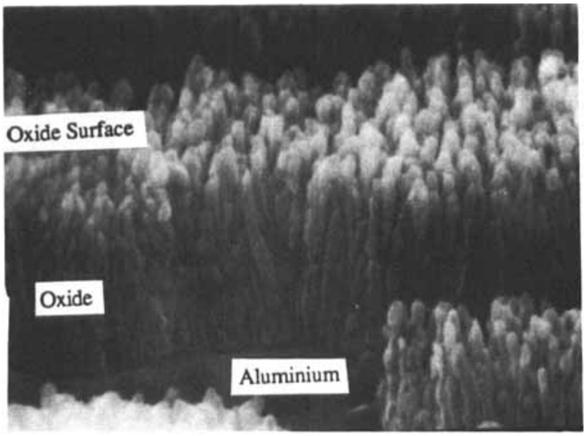

FIGURE 5 Cross Section of the PAA Oxide produced on the Aluminium Alloy.

topography and open pore structure. The CAA oxide is a 3.5 μm thick porous oxide with a complex branching of the oxide cells. As a consequence of the formation of porous oxides on the surface of the aluminium alloy from the anodising pretreatments used, it is possible to envisage that some adhesive penetration into the oxides will occur. In Figure 7, a SEM micrograph shows the cross-section of the oxide region from within a PAA adhesive joint and demonstrates evidence for extensive adhesive/primer penetration into the oxide. This evidence is seen by the changing of the polymeric primer deep in the oxide pores. In the case of the CAA joints (see Figure 8) there is evidence of only limited adhesive/primer penetration into the CAA oxide, as charging of the polymeric material is only seen in the surface regions of the oxide.

Previous work on the extent of adhesive penetration into the porous oxides produced by the pretreatment of aluminium alloys is in disagreement on the true extent of penetration. For example, some workers comment on the complete pene-

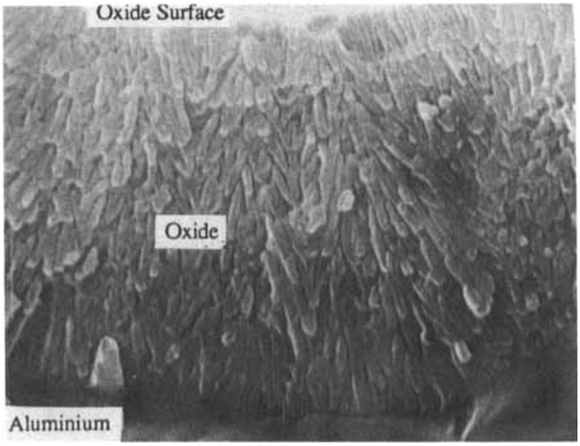

FIGURE 6 Cross Section of the CAA Oxide produced on the Aluminium Alloy.

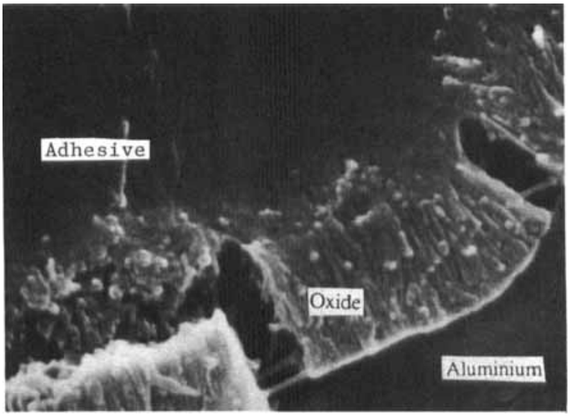

FIGURE 7 Cross Section of the PAA Oxide within an Adhesive Joint demonstrating the creation of a "Micro-Composite" region.

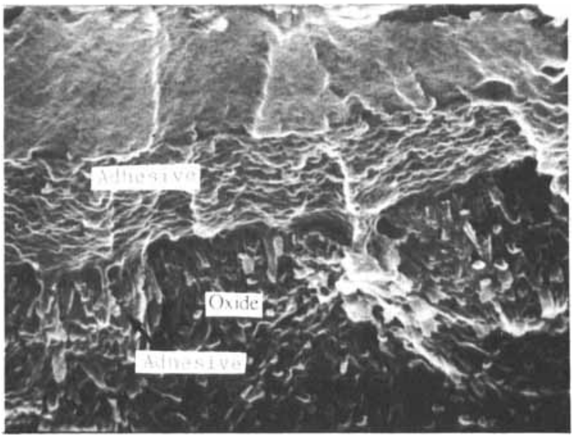

FIGURE 8 Cross Section of the CAA Oxide within an Adhesive Joint showing evidence of adhesive Penetration only in the upper regions of the Oxide.

tration of the PAA oxide,[2] while others only commit themselves to a conclusion of a limited penetration of this oxide.[18]

From the evidence of pore penetration of the adhesive into the various oxides produced by pretreatment, a description of a cross-section of an aluminium adhesive joint as simply adhesive/oxide/aluminium is inadequate. A more accurate description would be adhesive/micro-composite/oxide (barrier layer or unfilled porous oxide)/aluminium, the micro-composite region being an area of polymeric adhesive in a brittle oxide matrix. Thus, one cold hypothesise that it is the extent of the presence of such a micro-composite region within an adhesive joint that is a major contributor both to the strength of the joint and its subsequent durability performance.

Developing the "Micro-Composite" Hypothesis

The effect of adhesive penetration into the oxide will be to change the mechanical properties of the adhesive/oxide interphase. If an aluminium adhesive joint is viewed as simply adhesive/oxide/aluminium, it can be seen, by using known values of elastic moduli ($E_{adhesive} = 3$ GPa, $E_{Al} = 69$ GPa and $E_{oxide} = 350$ GPa), that there is a significant change in modulus at the adhesive/oxide interface. The simplest possible analysis of such a situation is to treat a loaded DCB joint as a cantilever beam in simple bending and to treat the strain as proportional to the distance from the beam centre (the neutral axis). In the critical interphase region of the joint, which is minute compared with the overall joint dimensions, the strain gradient experienced by the adhesive, oxide and aluminium in this region is negligible, *i.e.* close to an iso-strain situation exists. Using such assumptions, it is relatively simple to envisage from the definition of Young's modulus that a considerable stress discontinuity will exist at the adhesive/oxide interface. The presence of a "micro-composite" region within an adhesive joint, identified in this investigation, will decrease this stress discontinuity.

The reduction in the adhesive/oxide stress discontinuity can be demonstrated by using a model of the adhesive joint as a cantilever laminate beam under an end load, shown in Figure 9. Such a beam can be modelled using an extension of the polynomial functions developed for homogeneous materials provided the following boundary conditions can be satisfied:

$$(\sigma_{xy}) = \sigma_{yy} = 0 \quad \text{at} \quad y = \pm h/2 \tag{3}$$

$$-\int_{-h/2}^{+h/2} \sigma_{xy} dy = P \text{ and } \sigma_{xx} = 0 \quad \text{at} \quad x = 0 \; \ldots. \tag{4,5}$$

and at the internal boundaries of the beam, $-c/2$ and $+c/2$ the following must hold, at $-c/2$:

$$(\sigma_{xy})_0 = (\sigma_{xy})_1, (\sigma_{yy})_0 = (\sigma_{yy})_1, (\epsilon_{xx})_0 = (\epsilon_{xx})_1, (\partial^2 u_y/\partial x^2)_0 = (\partial^2 u_y/\partial x^2)_1 \tag{6–9}$$

and at $+c/2$:

$$(\sigma_{xy})_0 = (\sigma_{xy})_2, (\sigma_{yy})_0 = (\sigma_{yy})_2, (\epsilon_{xx})_0 = (\epsilon_{xx})_2, (\partial^2 u_y/\partial x^2)_0 = (\partial^2 u_y/\partial x^2)_2 \tag{10–13}$$

where σ, ϵ and u denote the components of stress, strain and displacement, respectively, and the subscripts 0, 1, 2 refer to the oxide, adhesive and aluminium layers, respectively. The use of partial derivatives of displacements to avoid their explicit expressions is discussed in Zienkiewicz and Gerstner's work.[19] Only one elastic parameter, η_n, formed from the elastic constants, was found necessary to obtain the solution. The Airy stress function (φ_n) and the stress components, in layer n, are:

$$\varphi_n = (12P/\Delta c^2)[a_n cx/2(y + c/2) + (b_n x/4)(y + c/2)^2 + (d_n x/6c)(y + c/2)^3] \tag{14}$$

$$(\sigma_{xx})_n = (12P/\Delta c^2)[b_n x/2 + d_n x/c(y + c/2)] \tag{15}$$

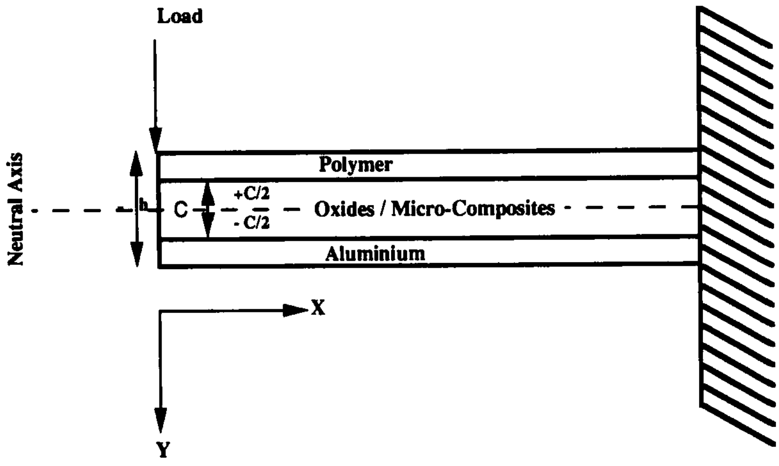

FIGURE 9 A Schematic Diagram of the Laminate Bean as Applied to the Simple Adhesive Joint Model.

$$(\sigma_{xy})_n = (12P/\Delta c^2)[a_n c/2 + b_n/2(y + c/2) + (d_n/2c)(y + c/2)^2] \tag{16}$$

$$(\sigma_{yy})_n = 0 \tag{17}$$

where Δ, a_n, b_n and d_n are functions of the thicknesses of the adhesive, oxide and aluminium layers and the elastic constants, η_n, E_n/E_0 for plain stress or $\{E_n/(1-\nu)\}/\{E_n/(1-\nu)\}$ for plain strain conditions, where ν is the Poisson's ratio, E_n is the modulus of the aluminium or polymer and E_0, the modulus of the oxide.[20] The modulus of the oxide layer within the model was altered using the dimensions of the oxides obtained in the investigation and assuming a honeycomb structure, (see Figure 10). Various degrees of adhesive penetration were used and the resulting moduli calculated by a simple rule of mixtures.[21] The results obtained for PAA and CAA joints are given in Table I and the Table includes results for the cases of both the presence and non-presence of a "micro-composite" region within the joints.

From Table I it is shown that the longitudinal stresses (σ_{xx}) in the adhesive layer next to the oxide can be substantially decreased if the oxide layer is penetrated by the adhesive, creating a "micro-composite" region. Thus it is possible to hypothesise that this reduction in stresses across the critical adhesive/oxide interface is a major factor in determining both initial bond strength and durability performance of such an adhesive joint.

The natural progression of this argument is to see if modifying the CAA oxide, to allow extensive penetration of the adhesive in the oxide, could result in improved performance, as suggested from Table I. One such modification process is the use of a post-etch treatment developed by the U.K. Admiralty.[22] When used on the CAA oxide, it is possible to reproduce the dissolution conditions observed during

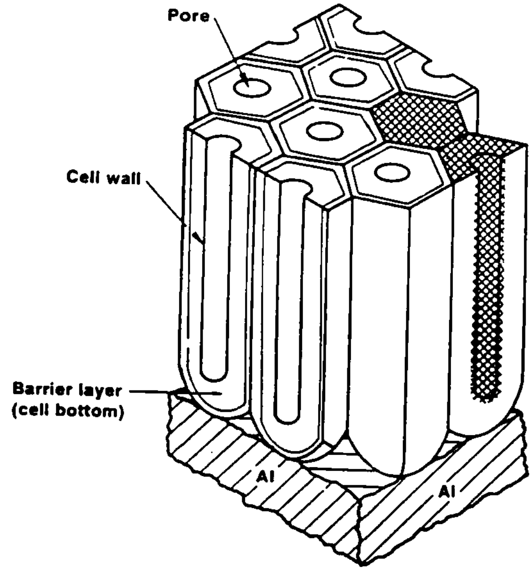

FIGURE 10 Structure of Oxide used to calculate modulus of micro-composite.

TABLE I
The magnitude of interfacial stresses in the critical interphase region using the simplified adhesive joint model

Pretreatment	No adhesive penetration of the oxide layer	Micro-composite
PAA	1) 456 MPa 2) 89 MPa	1) 52 MPa 2) 89 MPa
CAA	1) 418 MPa 2) 82 MPa	1) 47 MPa 2) 83 MPa

Longitudinal Stresses at: 1) the adhesive/oxide interface
2) the oxide/aluminium interface

phosphoric acid anodising to produce a structure that is very similar in appearance to the PAA structure, with the important difference that it is much thicker (see Figure 11). Observing the cross section of such a structure in an adhesive joint, it is found that an extensive "micro-composite" region is created. Figure 12 demonstrates the extent of the resulting "micro-composite" region with evidence of adhesive penetration at the very bottom of the modified CAA oxide within an adhesive joint. Recent durability work conducted by the U.K. Admiralty[18] on modified single lap shear joints, prepared using this modified CAA oxide, resulted in significant improvements in durability performance over standard CAA joints.

As a consequence of the work conducted so far, and the evidence emerging, the programme is continuing in order to quantify accurately the true effect of surface oxide morphology on the final performance of an adhesive joint. This work is developing methods to measure accurately the moduli of separated surface oxides and corresponding "micro-composites" that result within a joint. This will allow the refining of mathematical models to assess accurately the potential effect of varying surface oxide morphology on the mechanical properties of the interphase region. Such a development will be of particular importance in designing pretreatments

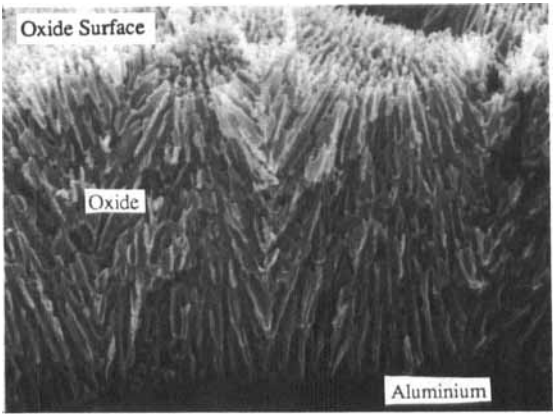

FIGURE 11 Cross-Section of modified CAA Oxide.

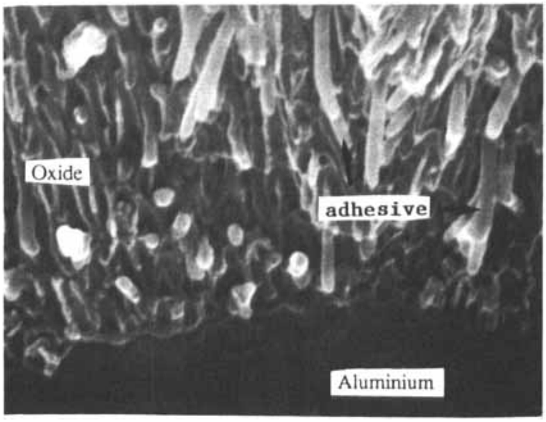

FIGURE 12 Lower Regions of Modified CAA Oxide within an Adhesive Joint showing extensive Adhesive Penetration in the region.

for the emerging aluminium/metal matrix composites. New pretreatments for such materials need to take account of the possibility of exposed ceramic particles or fibres on the surface and the corresponding effect on surface oxide morphology.

CONCLUSIONS

The results obtained in this investigation demonstrate that adhesive penetration occurs in the porous surface oxides created by phosphoric and chromic acid anodising of aluminium alloys. The extent of this penetration is determined by the oxide morpholoy produced. In the case of the PAA oxide extensive penetration results and only partial penetration is evident within the CAA oxide. However, the CAA oxide morphology can be modified to allow extensive adhesive penetration to occur. From the data obtained from the durability tests there would seem to be some correlation between the extent of adhesion penetration into the surface oxide and resulting durability performance. All of this evidence supports the "micro-composite" hypothesis and its positive influence on the mechanical properties of the critical interphase region of an adhesive joint.

Acknowledgements

The authors gratefully acknowledge the support and advice given by Mr. D. A. Moth of the Defence Research Agency, Maritime Division, Poole, Dorset, U.K. and Mrs. Gwen Harrison for help in preparing the manuscript.

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