# Interfacial properties and stability in bonded aluminium

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The localized interfacial region between an aluminium substrate and an epoxy adhesive has been extensively investigated. It has been found that a transitional region exists between the substrate surface and the bulk adhesive in which the physical and/or chemical properties of the polymer differ from those of the bulk polymer. Different surface treatments prior to bonding are observed to have little effect on the formation of the transitional region. Two types of transitional layers have been identified; one extending up to 1 $\mu$m from the substrate interface, the other generally restricted to 10 nm from the substrate interface. Examination of regions immediately in front of a propagating crack indicate that the interfacial integrity of both an etched-bonded substrate and a pretreated-bonded substrate are maintained. In contrast, regions of the fracture surface behind a propagating crack show the existence of corrosion products on an etched substrate but not on a pretreated substrate.

## 1. Introduction

Adhesive bonding technology depends on the formation of acceptable adhesion between substrate and adhesive and the retention of this adhesion with time. Although adhesion can be affected by varying the substrate, surface treatment and adhesive, the precise nature of these interactions is not well understood. These reactions do, however, occur at the most critical location in a bonded joint. Not only must the adhesive forces which are developed be sufficient to withstand the highly localized stresses at the interfaces but also the presence of defects and environmental interactions.

A pre-requisite for the elimination of defects at the interface is that complete wetting is obtained between the adhesive and substrate. Wetting does not, however, automatically ensure significant bonding across the interface; for this purpose adhesive–substrate interaction forces and interpenetration of a roughened substrate surface are considered to be important [1–3].

To ensure the long-term performance of a bonded joint, the surfaces of components are generally treated prior to bonding. The development of these surface treatments generally proceeds using qualitative approaches to relate surface pre-treatments, bond strength and joint durability. Associated with the approach is a large amount of work relating to the chemical analysis of the surface coatings. Subsequent analyses have attempted to infer relationships between the environmental stability of a joint and the local chemical variations and stabilities of the surface layers [4–6].

Although variations within the pretreated layer may be important, a complete understanding must encompass the physical and chemical effects of both the surface treatment and the local adhesive. Recently, the localized interface between the adhesive and substrate has been investigated for a number of materials [7–10]. The majority of the work reported to date has concentrated on examining the interfacial region developed when surface treatments relevant to aerospace applications are used. Such surface treatments often develop relatively rough, thick, porous structures so that a detailed observation of the interfacial structure is difficult. For many commercial applications such treatments are not viable. The current work reports the results of independent investigations using surface treatments which provide a thin porous surface coverage. This has permitted clearer observations of the nature of the bonded interface. Although specifically for systems using non-aerospace adhesives and surface treatments, the results are, however, generally applicable. The boundary structure and chemistry within both the substrate surface and the adhesive overlayer have been examined. Future publications
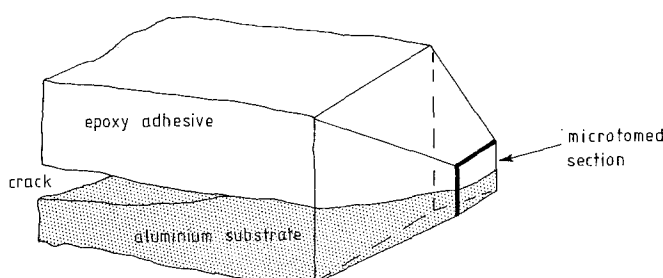


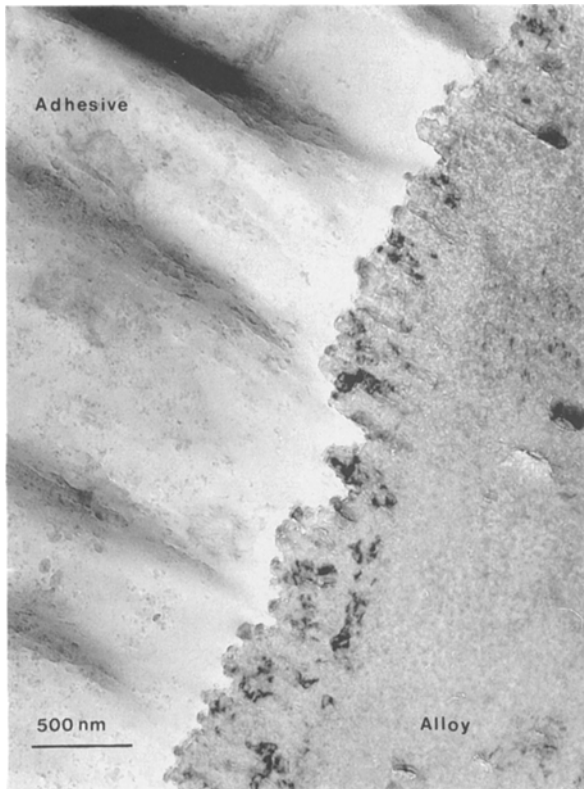*Figure 1* Method of producing microtomed sections ahead of crack tip.

Figure 2 Cross-section of aluminium–epoxy interface.



Figure 3 Interface associated with an etched substrate.

will report the specific effects on joint failure and the chemical variations observed within this region of the bond; the present publication will concentrate on examining the structural characteristics of the interface of a bonded aluminium joint and its stability under different environmental conditions.

## 2. Experimental techniques

In the current investigations adhesive joints were prepared using a commercial Al–Mg–Si alloy. Prior to bonding the surface was lightly abraded to remove surface asperities, vapour degreased and then etched in an acid bath to remove surface contamination. In addition to surfaces having an acid etched structure, specimens were also examined in which a subsequent chemical conversion coating has been applied. Bond-
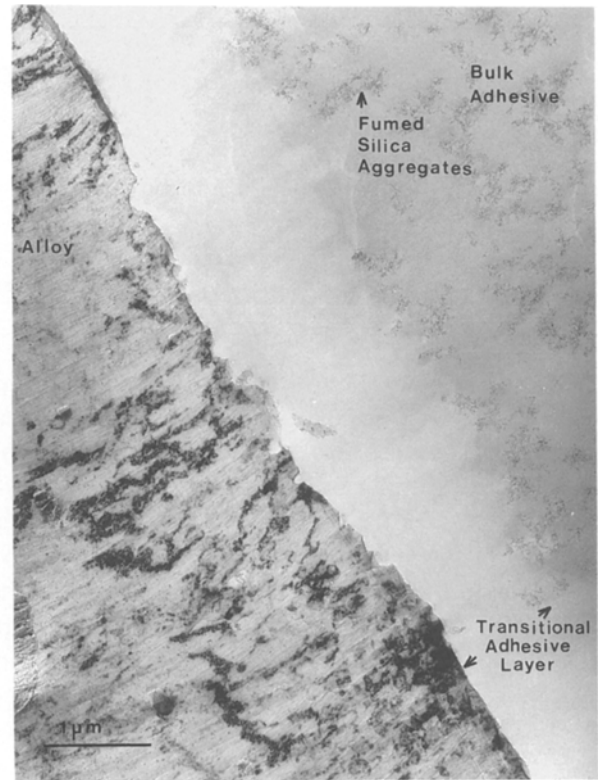
ing was conducted using single-part heat-curing epoxy pastes, one having a cure temperature of 180° C, the other a cure temperature of 120° C. The effects reported here were observed with both adhesives used in the evaluation.

The structure associated with the interfacial region of substrate alloy, surface and adhesive was examined using TEM of ultra-microtomed sections across the interface. Microtoming was conducted under several different conditions; in consecutive sections under different conditions, similar effects were observed so that the phenomena under investigation are not considered to be effects resulting from specimen preparation. Specimens were microtomed to approximately 10 to 20 nm in thickness and examined in a Jeol 2000FX over a range of accelerating voltages between 200 and



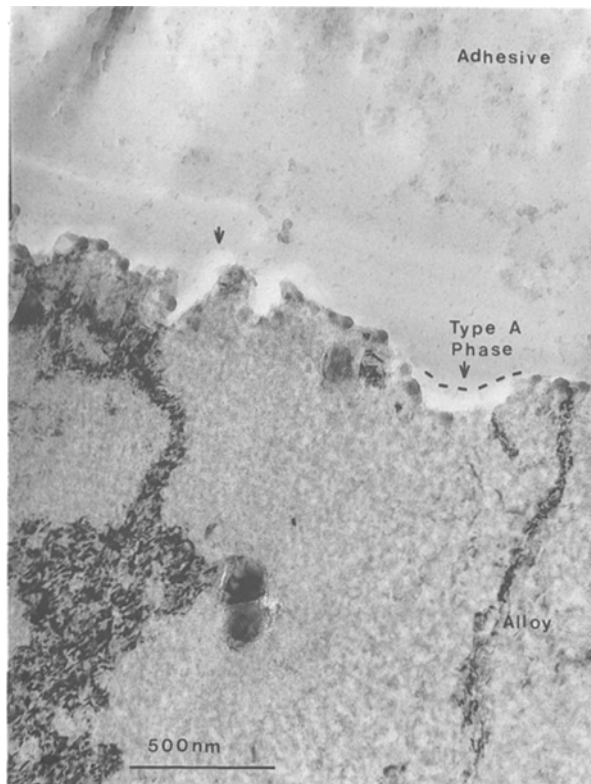Figure 4 Epoxy–aluminium interface for a pretreated substrate.

*Figure 5* Type A phase adjacent to aluminium surface.

80 kV. Under the operating conditions, no structural breakdown of the adhesive was observed to occur.

The influence of environment on the interface structure and stability was examined using SEM of bulk specimens and TEM of microtomed sections from specimens previously tested for crack growth resistance [11]. Microtomed sections were prepared from regions adjacent to the crack tip and at varying thicknesses across the specimen (Fig. 1) thus enabling a specific examination to be made regarding the effect of water at the interface on bond disruption and its effect on failure.

## 3. Results and discussion

The interface of a bonded joint between a simple etched substrate and an epoxy adhesive is shown in Fig. 2. To obtain the conditions necessary to develop adequate adhesive-substrate interactions it is essential that the adhesive and substrate must be in intimate contact with one another. If complete surface coverage is not developed during the curing cycle, defects will remain at the interface and there will be no opportunity for bonding to occur. In the current work, it is evident that complete wetting of the interface is obtained because the relatively rough surface topography of the interface is completely covered with adhesive (Fig. 2).

Although wetting is an initial requirement in providing bonding, it is also essential that an adhesive penetrates what may be a porous surface treated layer. If penetration of a porous layer is not achieved, the porous medium at the interface becomes a defect resulting in a loss in bond strength. In addition, the presence of a porous medium at the interface may provide a preferential pathway for water diffusion into the joint thereby enhancing subsequent failure. The surface treatment used in the present study has been identified as producing a porous coverage of the substrate approximately 30 nm thick [12]. Examination of sections through joints pretreated prior to bonding has shown that, as with an etched substrate, the surface is completely covered by the adhesive but, when examined in detail, penetration of the porous layer is in evidence.

Further examination of the boundary structure shows effects not normally anticipated. The interface between an etched or pretreated substrate and an epoxy resin is not simply one of substrate and adhesive but can be more adequately described in terms of a multi-layered structure (Figs 3 and 4). Features within the adhesive away from the interface are visible, and close to the substrate–adhesive interface local perturbations in the electron transparency of the adhesive are evident. These features are observed on bonds using both an acid-etched surface and a pretreated surface. The only differences in interface structure that occur between the etched and pretreated samples relate to the presence of the thin pretreatment layer itself.

The layer-type structure generated at the interface of an epoxy-bonded joint can be seen to be associated
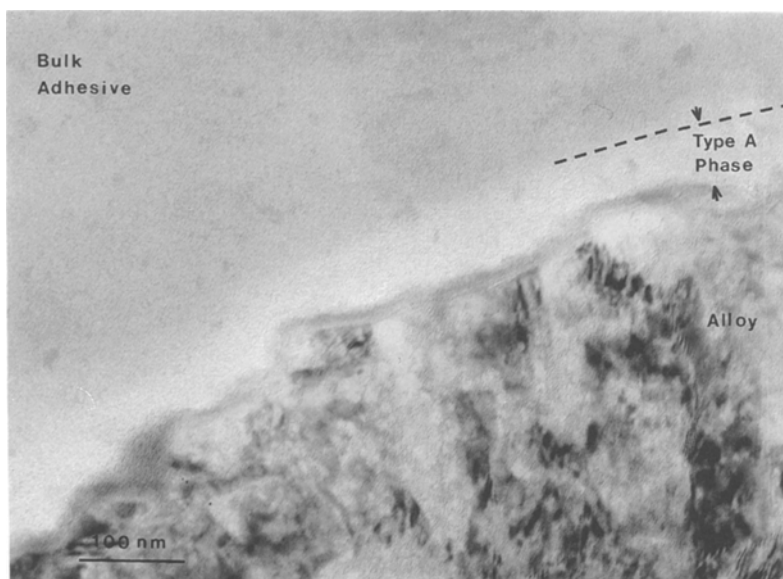


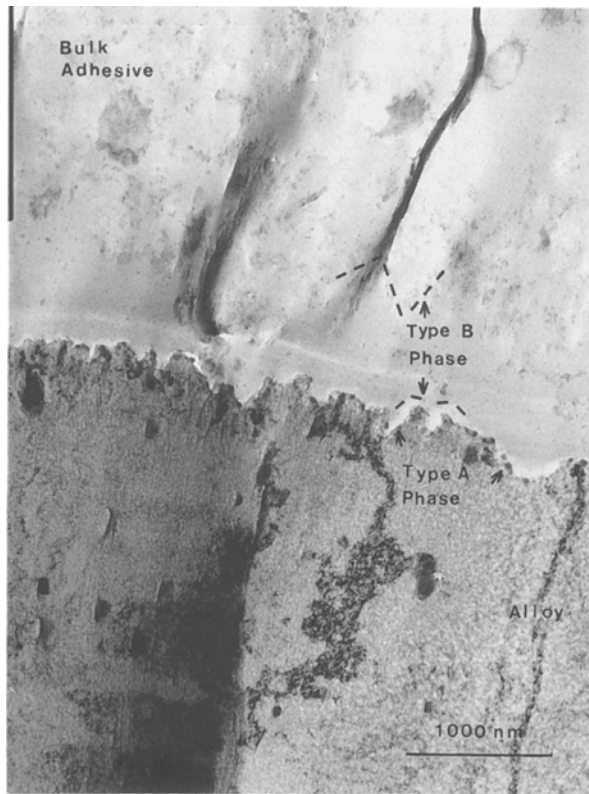*Figure 6* Type A phase extending approximately 50 nm into the epoxy.

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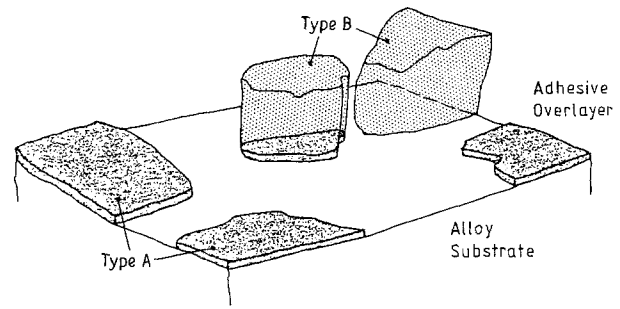Figure 7 Type B phase extending approximately 0.5 μm into the epoxy.



Figure 8 Schematic representation of the transitional regions observed at an aluminium–epoxy interface. Type A transitional phase, generally < 10 nm thick; Type B transitional phase, generally < 1.0 μm thick.

with variations principally within approximately 1 μm of the substrate surface. In this region the adhesive exhibits a variation in electron transparency compared to that found within the bulk adhesive thus reflecting a change in the local adhesive state at the interface. In general, this transitional region between bulk adhesive and substrate alloy has been found to give rise to two types of transitional phases, simply termed here types A and B. First, at the immediate interface between the substrate surface and approximately 10 nm into the polymer, type A phases exist (Figs 5 and 6). Secondly, within approximately 0.5 μm of the interface, a second transitional phase, type B, may exist (Fig. 7).

Extensive investigations of microtomed sections from numerous locations within a bond do, however, reveal that variations in the transitional interphases may exist. Some locations revealed the absence of the type B phase but the presence of the type A phase. Alternatively, areas were also observed in which no transitional interphases were apparent.

The incidence of type A and type B phases over a surface may be visualized with the aid of Fig. 8. Areas exist in which type A and type B phases are both present, a type A phase only is present or no transitional phases are apparent. Vertical sections through bonds containing such a distribution of phases would be consistent with the observations made here.

Previous investigations into the nature of thin surface film coverages [13–16] have always assumed that transitional interfacial phases exist over the whole surface. The techniques used to study these phenomena require, however, that the effects occur over a large area such that variations on the scale of those observed here would be masked.

The exact reason for the variability of these phases is not currently fully understood. It is, however, commonly accepted that different types of bonding can occur between substrate and adhesive, for example, covalent or electrostatic. Microscopic structural and/ or chemical variations in the substrate surface may enhance certain types of bonding in which stronger electrostatic interactions may result from the presence of specific thin metal oxide films. Equally specific



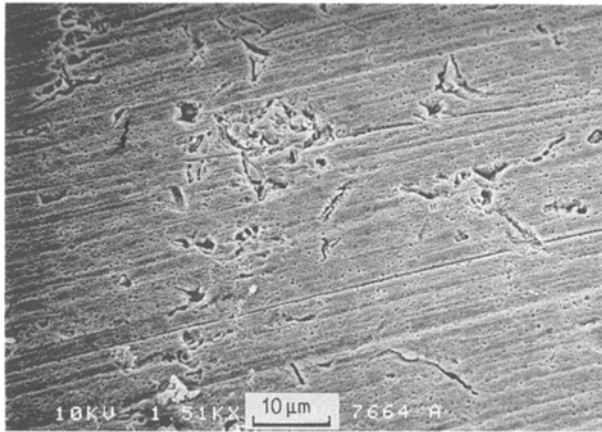Figure 9 Interface region showing fumed silica depletion and absence of Type A and B phases.

*Figure 10* Pretreated surface prior to exposure.



*Figure 12* Etched surface prior to exposure.

components of the adhesive will be more susceptible to the different types of bonding so that variations in the local polymer conformation and chemistry at the interface result.

At present it is not clear whether the transitional phases within the adhesive represent a local chemical or conformational difference. A preliminary examination of the transitional regions may suggest that they are associated with the local absence of fumed silica aggregates. Although instances are evident where such local depletions arise (Fig. 9), particles are also observed within the transitional layers. A more detailed examination reveals that the principal changes are associated with changes in the resin itself (Figs 3 and 7). Brockmann *et al.* [7] have suggested that chemical gradations may exist due to the smaller, more reactive molecules in a resin penetrating surface boundaries more readily than larger, less reactive molecules. Similarly conformational alignments of molecules at the surface may also arise. The attachment of polymeric chains to a surface substrate may occur via specific reactive functional groupings such that a local molecular alignment occurs. In conjunction, local steric hindrance of chain motion may impose a structural alignment in the polymer at the interface. Alternatively, the curing process may begin preferentially at an interface and lead to the formation of localized residual stresses at the interface which may, in turn, affect the local polymer orientation.

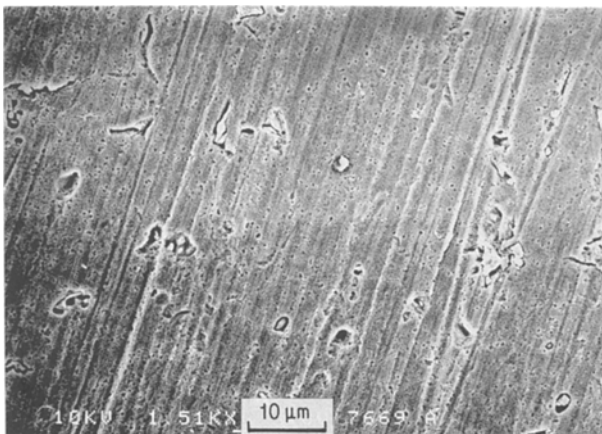Clearly, the existence of transitional layers of

adhesive between a substrate and the bulk polymer can be rationalized in terms of differing chemical and physical states. The precise identification of which mechanism is involved in the present case is to be described elsewhere. The development of local chemical and physical variations, whether these be in the adhesive or substrate, may be expected to influence behaviour of such an interface under environmental exposure and load. Hennemann [17] has recently suggested that differential straining may take place between the various components of the boundary although it is not exactly clear what effect this may have on subsequent joint failure. Clearly the mechanical properties of any transitional layer will affect both the local stress distribution and appropriate failure criterion. Until an exact understanding of the individual transitional layers is possible, it is necessary to investigate the effect of the interface on failure in individual cases.

Previous studies relating to environmentally accelerated failure have concentrated on examining the stability of the substrate surface by exposure to water prior to bonding [18] or by examination of the fracture surface produced after failure in an aggressive environment [3, 19]. Examination of the pretreated surface after prolonged exposure (> 1000 h) to water failed to reveal significant changes in comparison to the surface prior to exposure (Figs 10 and 11). In contrast, exposure of the etched substrate surface resulted in noticeable changes in the substrate topography
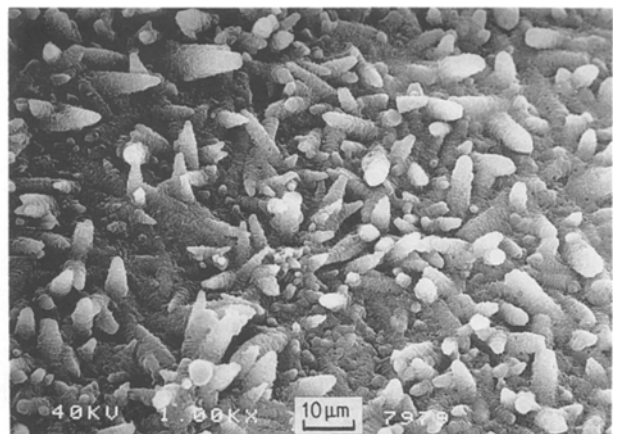


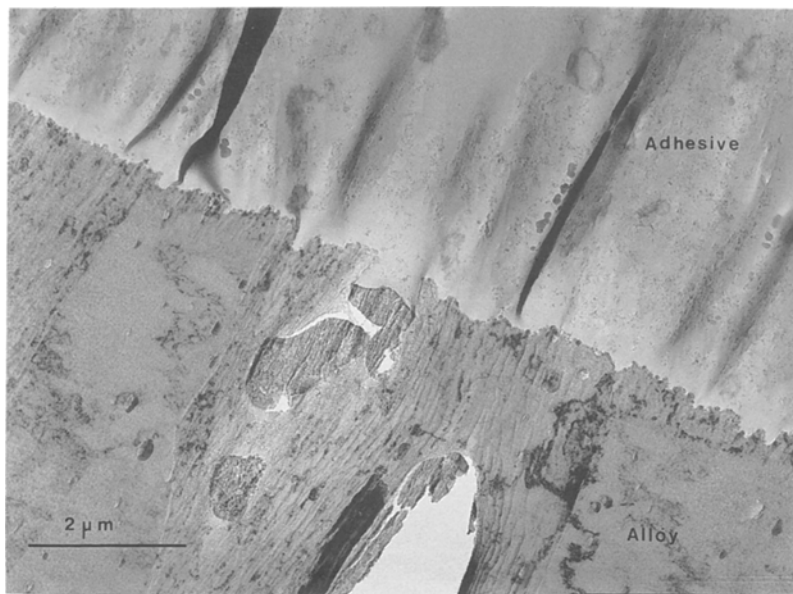*Figure 11* Pretreated surface after 1000 h exposure to water at 60° C.



*Figure 13* Etched surface after exposure to water.

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typical of corrosion products of aluminium (Figs 12 and 13). Similarly, the examination of fracture surfaces generally shows evidence of corrosion products in the acid-etched case, but none in the pretreated joints. This is similar to the results of other workers [3, 20] who consider failure to be due to environmentally induced transitions in the surface structure. Although such effects may occur it cannot be immediately concluded that this is the cause of joint failure in a bonded joint. To effect failure water must not only diffuse into the joint but also react at the interface to significantly reduce the joint strength. For the average case it can be considered that this process requires several simple successive steps.

(a) Diffusion of water to the site of failure, this may be along a crack or through the polymer bulk.

(b) Diffusion of water ahead of the site of failure.

(c) Reaction to produce a significantly weakened area to allow subsequent failure.

Hence it is difficult to ascertain whether the environmental degradation of the substrate fracture surface is representative of a pre-failure or post-failure interaction. In addition, degradation of a bonded joint by water ingress requires that water diffuses through the adhesive and as such is time dependent. To reach the substrate interface this diffusion must enter either from the sides of a joint, or, if a crack is present within the adhesive through the adhesive towards the interface or along the interface.

To establish a clearer understanding of the way in which water may affect substrate surface stability in the presence of an organic coating, microtomed sections taken from regions adjacent to a crack tip propagated in water were examined. Although it is difficult to produce specimens which represent the exact crack front, progressive sectioning back towards the crack front enabled examination to be made of regions immediately adjacent to the crack front. Micrographs showing these regions for a pretreated and an etched substrate surface are given in Figs 13 and 14 respectively. From these examinations it is evident that the interface between the epoxy and the substrate aluminium is stable in both cases despite the

prolonged exposure to water in this region. Similarly, examination of areas of the fracture surface where adhesive remained attached after failure, found no evidence of changes in either the substrate structure or chemistry. This behaviour contrasts with that observed for exposure of the free surfaces to water environments (Figs 11 and 13) where the development of corrosion products is evident on an etched substrate surface but is inhibited on a pretreated substrate (Fig. 15).

From other work it is clear that water diffusion into a polymer substrate can occur and that it may be more rapid under stress. However, in view of the substrate

surface stability observed when covered with an epoxy layer, environmentally induced substrate transformations may not be the only cause of joint failure. The observations reported here indicate that the interface is not simply a junction between two homogeneous continuums but that significant local variations occur. To provide an accurate rationale for environmentally enhanced joint failure requires an identification of failure locus and a related understanding of the interaction of environment with the various components of the interface. This approach will then enable a fuller understanding of the significance of interfacial reactions to developing both initial bond strength and bond durability to be made.

## 4. Conclusions

1. The interface of a bonded aluminium joint has been observed to consist of a layered structure in which varying interfacial phases may exist.

2. Two types of interfacial region have been identified. Type A phases are restricted to regions within 10 nm of the substrate surface, Type B phases may extend up to 1 $\mu$m from the substrate surface before the characteristics of the bulk adhesive are encountered.

3. Examination of regions immediately in front of a propagating crack indicate that the interfacial integrity of both an etched-bonded substrate and a pretreated-bonded substrate are maintained. In contrast, regions of the fracture surface behind a propagating crack show the existence of corrosion products on an etched substrate but not on a pretreated substrate.

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