The Locus of Environmental Crack Growth in Bonded Aluminium Alloy Joints

A. J. Kinloch[a]; L. S. Welch[b]; H. E. Bishop[b]

[a] Ministry of Defence Procurement Executive, Propellants, Explosives and Rocket Motor Establishment, Waltham Abbey, Essex, England [b] Atomic Energy Research Establishment, Harwell, Oxford, England

PLEASE SCROLL DOWN FOR ARTICLE

The Locus of Environmental Crack Growth in Bonded Aluminium Alloy Joints

A. J. KINLOCH

Ministry of Defence Procurement Executive, Propellants, Explosives and Rocket Motor Establishment, Waltham Abbey, Essex, England.

L. S. WELCH and H. E. BISHOP

Atomic Energy Research Establishment, Harwell, Oxford, England.

The locus of crack growth in epoxy/aluminium-alloy joints exposed to water at 60°C has been investigated using X-ray photoelectron spectroscopy and electron microprobe analysis. The surface pretreatment to which the aluminium alloy is subjected prior to bonding is shown to influence both the subsequent joint durability and the locus of crack growth.

INTRODUCTION

The use of structural adhesives, based typically upon epoxy resins, to join aluminium-alloys to themselves and to other materials in widely employed throughout industry, particularly in aerospace applications. Such adhesive joints are frequently expected to withstand prolonged exposure to aqueous environments. However, under these conditions joints have, in the past, been susceptible to environmental attack which has led to premature failure.

Over the last few years there have been considerable advances[1] in our knowledge concerning the parameters which affect the attack by

penetrating moisture. For example, the degree of susceptibility exhibited by joints has been correlated directly with the type of substrate surface pretreatment employed. This observation has led to several mechanisms being proposed to account for environmental failure. One mechanism envisages the adhesive layer adjacent to the metal oxide being hydrolysed by water, the initial chemical structure of this layer and its subsequent hydrolytic stability being affected by the nature of the oxide present. A second proposed mechanism considers that the adhesive/metal oxide interface is the locus of environmental attack and that different oxides, having different chemical and physical structures, lead to interfaces possessing very different susceptibilities to attack. A third mechanism suggests that the oxide layer itself becomes hydrated and that the hydrated oxide is mechanically weak and fractures prematurely, different oxides generated by the various surface pretreatments possessing different resistances to hydration. In particular it has been suggested that the presence of relatively small amounts of elements such as copper[2] and magnesium[3,4] in the oxide may affect adversely its stability whilst the presence of phosphates may assist greatly in ensuring that the oxide is resistant to hydration[5].

If the mechanisms of environmental attack in bonded aluminium-alloy joints when exposed to water are to be established, then clearly the locus of environmental crack growth must be identified precisely. This is the objective of the present paper.

EXPERIMENTAL

Materials

The aluminium alloy employed was BS.5251 (previous specification: NS4) and its bulk composition is given in Table I. The material was used in the form of strips, of size approximately $120 \times 25 \times 2$ mm. Prior to adhesive bonding they were pretreated by chromic-acid etching, chromic-acid anodising or phosphoric-acid anodising, as described in Appendix 1.

The adhesive employed was a two-part system consisting of an epoxy resin, based upon a diglycidyl ether of bisphenol A, cured with an amine hardener.

TABLE I

Bulk Composition of BS.5251

Element	Atomic %
Al	Rem
Cu	0.04
Mg	1.8/2.7
Si	0.5
Fe	0.25
Mn	0.25
Zn	0.08
Cr	0.15
Ti and others	0.1

Specimen preparation

Two pretreated strips were bonded together and, to crosslink the adhesive, the resultant joint was subjected to a cure schedule of 24 hours at 23°C followed by 24 hours at 60°C. A wedge was then driven carefully into the joint for a fixed distance and the position of the crack tip noted. The test method is shown schematically in Figure 1. The joint was then immersed in distilled water at 60°C from which it was removed periodically for the measurement of crack tip advance. After about seven hours immersion the joint was taken out and the strips pulled completely apart. Areas of the strips where environmental crack growth had occurred were then cut out for subsequent examination.
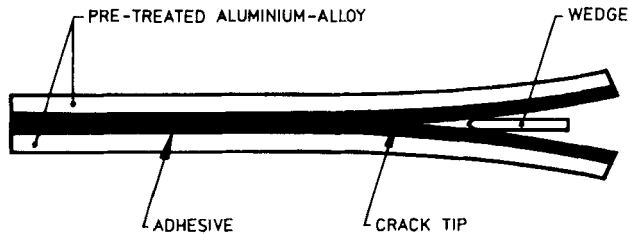

FIGURE 1 Wedge-test crack-growth specimen.

Surface analysis

The specimens were first examined visually and in a low-power optical microscope.

To provide information about the chemical groups present in the first few atomic layers of the fracture surfaces X-ray photoelectron spectroscopy (XPS) was used. When X-rays irradiate a surface, photo-

electrons are ejected from the atomic core levels, and these electrons originate within the first few atom layers of the surface. The kinetic energies of the photoelectrons are analysed in a hemispherical energy analyser. Spectra are recorded as the number of photoelectrons emitted *vs.* kinetic energy. XPS can give two types of information. The areas under photoelectron peaks are proportional to the relative surface concentrations of the elements on the surface, and thus a semi-quantitative analysis of the average composition of the surface layer is possible. Also, the detailed shapes and positions of the peaks give information about the chemical states of the elements. One problem with an insulator is surface charging which has the effect of moving the whole energy spectrum, but it is usually possible to overcome this problem, for example, by calculating energy differences for relevant peak positions. Measurements were made in a Vacuum Generators Escalab I System. Al K_α X-rays were used as the photoexcitation source and were incident on the sample at approximately 45° to its surface. An argon ion gun was mounted on the system, also at approximately 45° to the sample, and was used to erode the surface by bombardment with 5 keV argon ions. Ion bombardment can be used either to remove the contamination layer normally present on a sample after exposure to ambient atmosphere, or to produce a depth profile into the material.

To investigate the spatial distribution of elements in the fracture surfaces electron probe microanalysis (EPMA) was employed. The electron probe measurements were made using a Cameca Camebax electron microprobe, in which the sample was irradiated at normal incidence by a 10 keV electron beam. The X-rays emitted from a surface are analysed either by an energy dispersive (EDS) detector which can detect characteristic X-rays from elements of atomic number 11 and above, or by a wavelength dispersive (WDS) detector which can detect elements of atomic number 5 and above. With an incident 10 keV electron beam both the depth and the spatial resolutions are between 0.5 to 1 μm, and elemental maps of surfaces can be obtained. In addition, film thicknesses can be estimated by varying the beam energy. The samples were coated with carbon to prevent charging of the surfaces.

RESULTS and DISCUSSION

Fracture studies

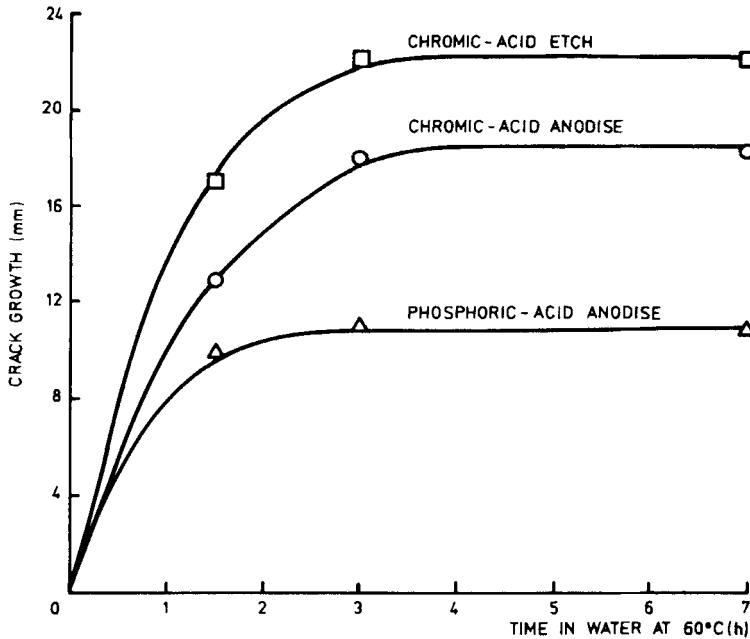The amount of crack growth that occurred in the joints in water at

FIGURE 2   Crack growth versus time in environment of water at 60°C for the wedge joints. Three different surface pretreatments employed.

60°C is shown as a function of time in Figure 2 for the three different surface pretreatments. All the joints exhibited environmental crack growth but the extent depended on the particular pretreatment employed. The ranking order for environmental resistance is in agreement with previous work[1,6] and is: phosphoric-acid anodised > chromic-acid anodised > chromic-acid etched.

Optical examination

Optical examination revealed clearly that, although the initially inserted crack was almost in the centre of the adhesive layer, environmental crack growth occurred largely in the interfacial regions. One surface was predominantly metallic in appearance and the other surface contained mainly adhesive. Therefore, for subsequent examination specimens were obtained from the environmental crack growth region from both halves of the fractured joint, i.e., one from the apparently

"metal" side and one from the opposite "adhesive" side. Considering the effects of the different pretreatments in greater detail:

i) *Chromic-acid etched joints:*   The "metal" side had a non-uniform appearance with a number of interference colours visible, due to a surface film of varying thickness in the region of a few thousand Å. This is considerably greater than has been reported[3,7] for the initial oxide thickness produced by this pretreatment, about 300 to 500 Å. The increased thickness results from exposure of the oxide to water and has been observed previously[3]. The typical pitted appearance produced by chromic-acid etching was apparent all over the "metal" side but in a few-places small flakes of adhesive were visible. The "adhesive" side had a matt appearance.

ii) *Chromic-acid anodised joints:*   The "metal" side had a uniform appearance with the occasional spike of retained adhesive. The "adhesive" side was uniform and slightly shiny.

iii) *Phosphoric-acid anodised joints:*   The "metal" side appeared quite different from the previous fracture surfaces in that many adhesive flakes were clearly visible and the "adhesive" side had a torn appearance.

X-ray photoelectron spectroscopy studies

The results from the XPS analysis of the "metal" and "adhesive" sides of the fracture surfaces are shown in Table II. Concentrations of the main elements are listed in terms of atomic % and are calculated from the areas under the peaks combined with atomic sensitivity factors[8].

i) *Chromic-acid etched joints:*   The important result obtained from the joints prepared using this pretreatment is that there was a substantial Al signal present on both the "metal" and "adhesive" sides. Furthermore, the level of Al was maintained as the surface was ion eroded, while the Al binding energy was constant at 74 eV, indicative of aluminium oxide. The carbon level was relatively low even at the outermost surface layer and fell as the surface layer was removed by the ion beam. This suggests that the initial carbon level may have arisen largely from the presence of post-fracture atmospheric contamination, which has been shown[9] to consist of carbonaceous material.

The above results suggest that the locus of environmental crack

growth in joints prepared using chromic-acid etching was largely within the oxide layer but with occasional divergence of the crack into the adhesive layer. However, to check that the oxide detected on the "adhesive" side was not merely transferred to the adhesive *after* environmental crack growth had occurred elsewhere in the joint, a piece of pretreated aluminium-alloy was placed in contact with a specimen of cured adhesive sheet in water at 60°C for about seven hours; *i.e.*, no adhesive bond was established. When the surface of the adhesive sheet was subsequently analysed no aluminium was detected. Thus the aluminium (oxide) signal on the "adhesive" side of the fractured wedge joint did indeed arise from environmental crack growth through the oxide layer.

ii) *Chromic-acid anodised joints:* Table II shows that the results of surface analysis of the fracture surfaces of these joints were very similar to those for the chromic-acid etch pretreatment, and the interpretation is the same.

TABLE II
XPS analysis of fracture surfaces

Specimen	Approximate thickness removed by Argon ion sputtering (A)	Atomic %				
		Al	O	C	N	Mg
Chromic-acid etched						
Metal side	0	23	59	17	0.6	0.6
	20	27	65	6.9	0	1.0
Adhesive side	0	21	57	22	0	0.3
	20	26	61	12	0.2	0.1
Chromic-acid anodised						
Metal side	0	23	64	12	0.1	0.5
	20	30	65	4.1	0.3	0.7
	120	31	65	2.0	0.3	0.8
Adhesive side	0	20	55	23	0.9	0.7
	20	30	62	7.2	0.1	
	120	32	63	3.8	0.1	1.1
Phosphoric-acid anodised						
Metal side	0	17	54	25	1.8	0.2
	20	24	53	19	1.2	0.9
	120	25	52	22	0	0.8
Adhesive side	0	10	36	50	3.5	0.2
	20	13	35	50	1.9	0.2

iii) *Phosphoric-acid anodised joints:*   In the case of the phosphoric-acid anodised joints, the "metal" side of the joints had a relatively high carbon concentration, even after argon-ion profiling to a depth of about 120 Å, confirming the presence of adhesive. The aluminium (oxide) concentration on the adhesive side was comparatively low. Thus, the extent of failure within the oxide appeared to have decreased while the degree of cohesive fracture of adhesive, albeit close to the interface, had increased, compared to the effects of the chromic-acid etched and anodised pretreatments. These observations are in agreement with the superior durability exhibited by joints prepared using the phosphoric acid anodising pretreatment shown in Figure 2.

Electron microprobe analysis

The electron microprobe was employed to obtain topographical images of the "adhesive" side of the fractured joints at higher resolution than was possible with the optical microscope and to determine the thickness of the aluminium oxide that was present on that side.

i) *Chromic-acid etched:*   The surface of the "adhesive" side showed two types of structure which can be seen in Figure 3a, taken from an area where both types co-existed. A higher magnification micrograph is shown in Figure 3b, with the corresponding Al X-ray image in Figure 3c. The layer giving bright contrast is clearly aluminium, resulting from environmental crack growth through the oxide. The magnitude of the aluminium signal indicated that the covering of aluminium oxide was about 2000 Å thick, assuming that it had the density of alumina[10]. A small Al signal consistent with perhaps 20 Å of oxide was measured from the darker area (but 20 Å had already been removed from the specimen by ion bombardment). An oxide thickness of 40 Å is not inconsistent with the results from the XPS analysis on the "adhesive" side.

Thus, as discussed above, the aluminium oxide has become hydrated whilst immersed in water at 60°C and its thickness increased[3] from a few hundred Å to a few thousand Å. Environmental crack growth occurred largely in this hydrated oxide layer. However, the crack wandered from near the oxide/metal interface to near the adhesive/oxide interface, leaving an oxide layer on the "adhesive" side of 40 Å to 2000 Å thickness.
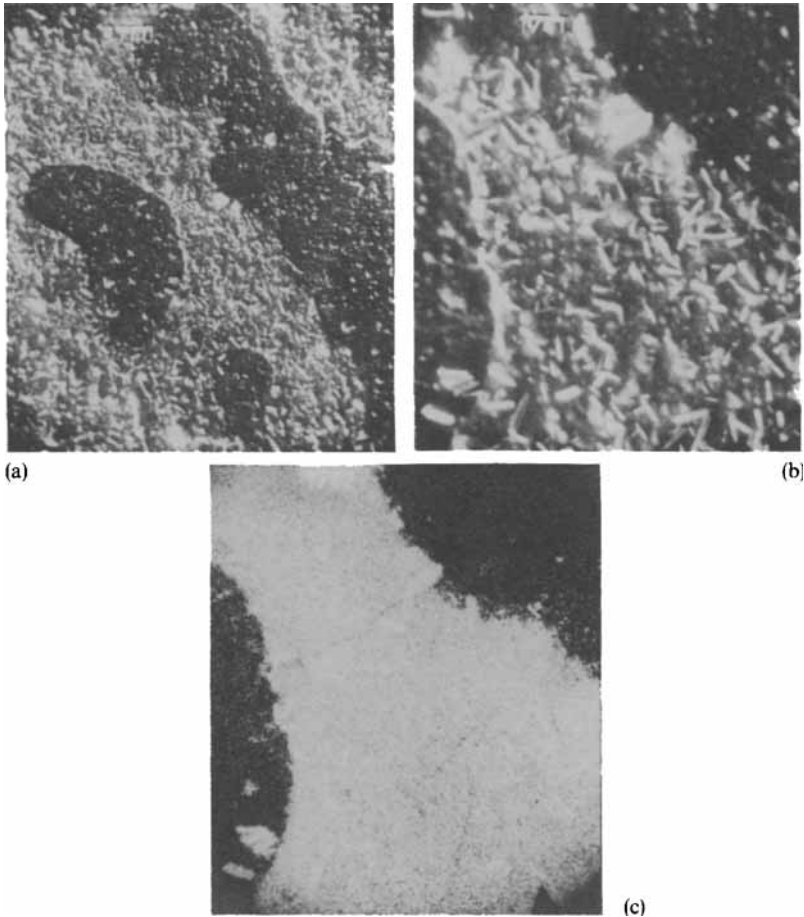
(a)   (b)

(c)

FIGURE 3   "Adhesive" side of an environmental fracture of bonded chromic-acid etched aluminium alloy. a. Scanning electron micrograph (× 200) b. Scanning electron micrograph (× 600) c. Distribution of aluminium in 3(b), using electron microprobe analysis.

ii) *Chromic-acid anodised:*   The fracture surfaces of the "adhesive" sides of the joints prepared using chromic-acid anodising were far more uniform than those described above, both topographically and in the distribution of aluminium, which is shown in Figure 4. The oxide layer on the "adhesive" side is estimated to have been of thickness between 400 to 900 Å.
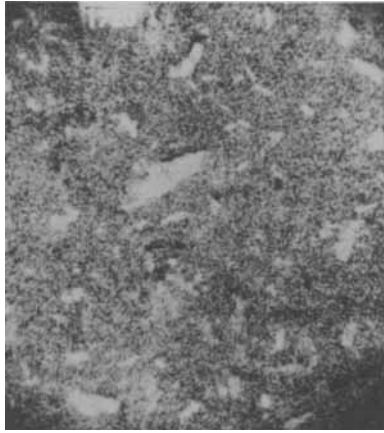
FIGURE 4 "Adhesive" side of an environmental fracture of bonded chromic-acid anodised aluminium-alloy showing the distribution of aluminium using electron micro-probe analysis (× 800).

iii) *Phosphoric-acid anodised:*   Figures 5a and 5b show typical areas from the "adhesive" sides of the joints prepared using phosphoric-acid anodising. Areas which appear to be adhesive are clearly visible and they correlate with the flakes of adhesive present on the "metal" side. However, apart from these observations which confirm that a relatively large amount of crack growth occurred through the adhesive itself, the results shown in Figure 5c indicate that the crack also propagated to a certain extent through the oxide. The Al X-ray image also showed that the thickness of oxide was about 400 Å. These results are in qualitative agreement with the visual and XPS analyses reported above.

CONCLUSIONS

In previous work[9] the examination of the locus of environmental failure in epoxy/mild-steel joints showed clearly that after immersion in water the joints failed by interfacial fracture between the epoxy adhesive and the iron oxide. That is, the interface became the weakest region upon environmental exposure. This was clearly not the case for the joints employing aluminium-alloy. For the epoxy/aluminium-alloy joints the failure path was complex but, in the case of chromic-acid etching and
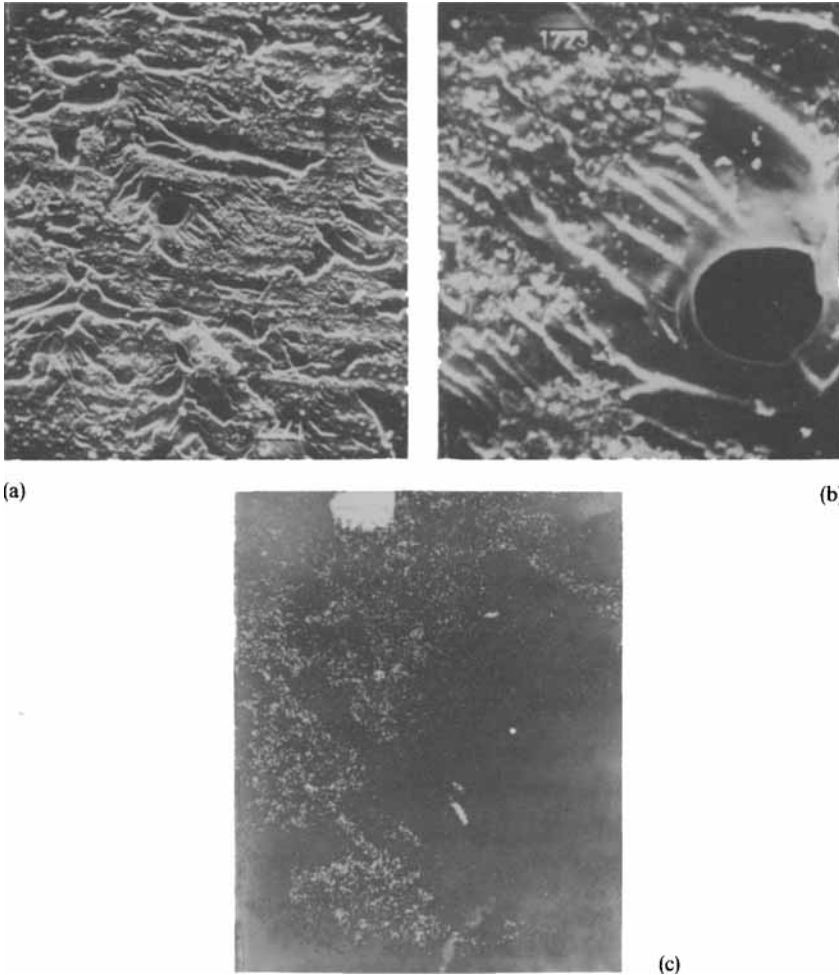
(a)

(b)

(c)

FIGURE 5   "Adhesive" side of an environmental fracture of bonded phosphoric-acid anodised aluminium-alloy. a. Scanning electron micrograph (× 200) b. Scanning electron micrograph (× 800) c. Distribution of aluminium in 5(b), using electron microprobe microanalysis (× 800).

anodising, appeared to be largely in the oxide layer. The observations that, in the absence of an aqueous environment, crack growth was exclusively in the adhesive and that the oxide layer increased in thickness during environmental exposure supports the suggestion that hydration,

causing weakening of the oxide, is a major mechanism. Indeed, the increase in thickness was apparently greatest for the oxide produced by the chromic-acid etch pretreatment and this pretreatment also resulted in the poorest environmental resistance. Furthermore, the improved durability obtained by using phosphoric-acid anodising as the pretreatment, coupled with the observation that the extent of oxide failure significantly decreased, supports the contention that this pre-treatment resulted in increased oxide stability. This may have been a consequence of the presence of phosphate ions in the oxide structure.[1-4]

Acknowledgements

APPENDIX I

(a) *Chromic-acid-etching:* The surfaces were degreased in trichloro-ethane, washed in an alkaline solution containing sodium carbonate and a detergent, and then etched in chromic acid at 60–65°C for 30 minutes as described in Ministry of Defence (UK), Defence Standard 03–2/1 (1970), Method 0, and finally rinsed in cold distilled water and air dried.

(b) *Chromic-acid anodising:* The surfaces were first treated as described in (a) and then anodised in chromic acid at 38 to 42°C for 40 minutes at 40 V as described in Ministry of Defence (UK), Defence Speci-fication 151 (1965) and finally rinsed in cold distilled water and air dried.

(c) *Phosphoric-acid anodising:* The surfaces were first treated as described in (a) and then anodised in a 10% w/w aqueous solution of H_3PO_4 at 10–15 V for 25 minutes at 23°C according to the Boeing Airplane Company Specification (USA) BAC 5555. The surfaces were then washed in cold distilled water and allowed to air-dry.

References

1. A. J. Kinloch, (Ed) *Durability of Structural Adhesives*, (Applied Science Publ., London, 1983).

2. T. S. Sun *et al.*, *Appl. Surf. Sci.* **1**, 202 (1978).
3. A. J. Kinloch and N. R. Smart, *J. Adhesion*, **12**, 23 (1981).
4. A. J. Kinloch, H. E. Bishop and N. R. Smart, *J. Adhesion*, **14**, 105 (1982).
5. G. D. Davis, *et al.*, *J. Mater. Sci.* **17**, 1807 (1982).
6. J. D. Minford, *J. Appl. Polym. Sci.*, *Appl. Polym. Symp.* **32**, 91 (1977).
7. J. D. Venables *et al.*, *SAMPE Tech. Conf.*, Seattle, Washington. 7–9 Oct, 1980.
8. C. Wagner, *et al.*, *Surface Interface Analysis*, **3** (5) 211 (1981).
9. M. Gettings, F. S. Baker and A. J. Kinloch, *J. Appl. Polym. Sci.*, **21**, 2375 (1977).
10. H. E. Bishop and D. M. Poole, *J. Phys. D*, **6**, 1142 (1973).