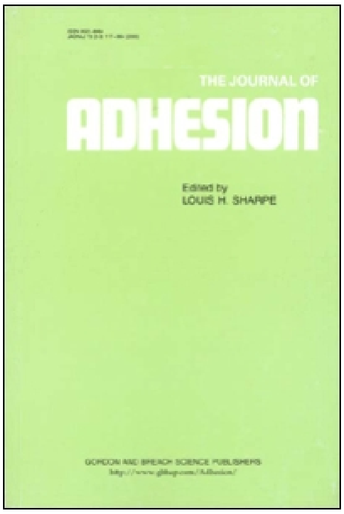

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Bonding and Failure Mechanisms in Aluminium Alloy Adhesive Joints

A. J. Kinloch[a]; N. R. Smart[b]
[a] Ministry of Defence, PERME, Waltham Abbey, Essex, England [b] Atomic Energy Research Establishment, Oxford, England

To cite this Article Kinloch, A. J. and Smart, N. R.(1981) 'Bonding and Failure Mechanisms in Aluminium Alloy Adhesive Joints', The Journal of Adhesion, 12: 1, 23 — 35
To link to this Article: DOI: 10.1080/00218468108071186
URL: http://dx.doi.org/10.1080/00218468108071186

J. Adhesion, 1981, Vol. 12, pp. 23–35
0021-8464/81/1201-0023 $06.50/0

Printed in Great Britain

Bonding and Failure Mechanisms in Aluminium Alloy Adhesive Joints

A. J. KINLOCH
Ministry of Defence, PERME, Waltham Abbey, Essex, EN9 1BP, England

N. R. SMART
Atomic Energy Research Establishment, Harwell, Oxford OX11 0QJ, England

(*Received December 8, 1980*)

X-ray photoelectron spectroscopy and scanning electron microscopy have been used to investigate the surface chemistry of an aluminium-alloy which has been pretreated by various industrial methods commonly employed prior to adhesive bonding. The fracture surfaces of butt joints, consisting of the pretreated alloy bonded with an epoxy adhesive, have also been studied. The analyses have been conducted before and after exposure of the specimens to water, the main hostile environment that structural adhesive joints usually encounter. It is suggested that the concentration of magnesium, in the form of magnesium oxide, on the pretreated aluminium-alloy surface may be an important factor in influencing the durability of adhesive joints.

INTRODUCTION

Throughout industry widespread use is made of epoxy-based adhesives to bond aluminium-alloy and this method of joining almost invariably requires some form of surface pretreatment of the alloys prior to bonding.

Assuming the pretreatment has been sufficient to remove gross contamination, then the initial strength of the resulting joint is usually independent of the pretreatment employed. However, adhesive joints are frequently expected to withstand prolonged exposure to aqueous environments. Under such conditions adhesive joints have, in the past, been susceptible to premature failure and their degree of susceptibility has been directly correlated with the type of substrate surface pretreatment employed.[1,2,3]

However, at the present time it is not really understood exactly which

---

Presented at the International Conference on "Adhesion and Adhesives" of the Plastics and Rubber Institute held at Durham University, England, September 3–5, 1980.

surface chemical and physical parameters are important for imparting good environmental resistance to the adhesive joint. While the adhesion scientist may talk generally about requiring a contamination free, strong, stable receptive surface with the right morphology, the detailed parameters involved, their required values and how logically to obtain them are virtually unknown.

Thus, in the present work a surface sensitive technique, namely X-ray photoelectron spectroscopy (XPS), has been used to investigate the chemistry of aluminium-alloy surfaces which have been pretreated by various methods which are known to result in adhesive joints possessing vastly different service-lifetimes in moist environments. Also studied are the surfaces revealed upon fracture of butt joints, consisting of the aluminium-alloy bonded with an epoxy adhesive. The analyses have been conducted both before and after exposure to water. Four pretreatments commonly used in industry have been considered: solvent-degreasing, grit-blasting, chromic-acid etching and phosphoric-acid anodising.

EXPERIMENTAL

Sample preparation

The aluminium alloy employed was to BS 1474:1969:NE4 and its bulk composition is given in Table I. The material was used in the form of rods, 5 mm in diameter, since this was the size required for the fracture stage attachment on the XPS system. The adhesive employed was a diglycidyl ether of bisphenol A mixed with 9.4 mass per cent of a curing agent, tri-2-ethylhexanoate of 2,4,6-tris(dimethylaminomethyl) phenol.

TABLE I

Bulk Composition of NE4 Alloy

Element	Atomic %
Al	94.6
Mg	1·8
Mn	1.0
Si	0.5
Fe	0.5
Zn	0.5
Cr	0.5
Cu	0.2
Ti and others	0.4

For each of the pretreatments (see Appendix I for details) two aluminium-alloy stubs were prepared: one was analysed without further processing and the other was first immersed in distilled water at 60°C for 500 hours. Three butt joints per treatment were fabricated in the following manner. Adhesive was spread over the pretreated ends of two aluminium alloy rods which were then pressed lightly together. The pressure was maintained during the cure cycle of 96 hours at 23°C, $1\frac{1}{4}$ hours at 100°C and $2\frac{1}{2}$ hours at 180°C, followed by a slow cooling period. The joints were subsequently immersed for 0, 500 and 1000 hours in distilled water at 60°C.

XPS analysis

XPS measurements were made in a Vacuum Generators Escalab System using Al Kα X-rays (1486.6 eV) as the photoexcitation source. The spectrometer is housed in a vacuum system which can be evacuated to 10^{-10} torr. The X-ray source and an argon ion source were mounted at approximately 45° to the specimen. The latter source was used to erode the surface by sputtering with argon ions and so reveal a depth profile of the material. Photoelectrons are accepted from the surface and focused on to the entrance slit of a hemispherical energy analyser.

The basis of XPS is that X-rays interact with core electrons and cause ejection of so-called photoelectrons from the atom. Only electrons which are produced within the top few atomic layers will escape from the surface of the material since deeper electrons will dissipate their energy by the various loss processes. The kinetic energy of the escaping electrons is characteristic of the element which emitted them and also depends on the chemical environment of the emitting atom. Consequently, interpretation of precise measurements of kinetic energy can give an insight into the chemical nature of the surface. The number of electrons of a particular energy emitted corresponds to the concentration of a particular element on the surface. By applying experimentally derived sensitivity factors, an elemental analysis of the surface, to an accuracy of $\pm 20\%$, can be derived.

The butt joints were loaded into the fracture stage and fractured by a sharp downward blow parallel to the bonded surfaces. The ambient pressure of 10^{-9} torr increased sharply on fracture of the water-soaked specimens. A residual gas analyser showed that this was due to a release of water vapour.

Scanning electron microscopy

The surfaces under examination were coated with carbon to prevent charging and studied using a scanning electron microscope.

RESULTS

To account for binding energy shifts associated with charging of the surface during XPS analysis all the reported binding energies have been corrected to O1s at 531.5 eV. This corresponds to the O1s position for a thin film of aluminium oxide which should rapidly dissipate any build-up of surface charge. Peak shoulders are quoted as being an approximate percentage of the main part of the peak, as estimated visually. The binding energies quoted are accurate to less than ±0.5 eV.

Analysis of pretreated substrates

Solvent-degreased pretreatment. The results from the XPS analysis are shown in Table II. As may be seen there was a significant amount of carbon (~20 %) on the surface of both the soaked and unsoaked specimens and this level was reduced by ion bombardment. In the case of the unsoaked specimens there was an enrichment of magnesium at the surface with an Al:Mg ratio of about 10:1, compared to 52.6:1 for the bulk composition (Table I). The magnesium's binding energy was approximately 306 eV which is indicative of magnesium oxide. The zinc concentration was also slightly high but that of copper was as expected. After soaking in water magnesium was not detected after removal of 250 Å and there was an increase in the oxide thickness. This latter feature may be deduced from the binding energy of the Al (2p) peak. A peak at ~72 eV corresponds to aluminium in the metallic state whereas the oxidised Al (2p) peak appears at ~74 eV. On the unsoaked surface, after stripping only 20 Å, the signal due to the oxide component was only 60 % of the signal ascribed to metallic aluminium. After soaking no metallic component was detected, even after 260 Å of material had been removed.

TABLE II

XPS analysis of solvent degreased substrate

	Approximate Depth (Å)	Al (2p) Binding energy (eV)	Analysis (atomic %)							
			O	C	Al	Zn	Cu	Mg	Si	Others
Not soaked in water	0	74.3	45	20	25	0·9	0·2	4.1	3.8	
	20	71.95 (sh. 74.85(60 %)	44	7.0	41	0.2	0.1	5.9	1.1	
	120	72.05 (sh. 74.65(5 %))	21	13.9	62	0.2	—	3.6	—	
Soaked in water	0	74.15	59	17.6	21	0.6	0.4	—	1.5	
	20	74.70	61	6.7	30	0.4	0.5	—	1.3	
	60	74.70	61	3.6	33	0.3	0.4	—	2.1	
	260	74.75	61	21	34	—	0.3	—	2.3	

Grit-blasted pretreatment. The results are given in Table III and indicate that there is again a surface enrichment of magnesium in the form of the oxide, but to a lesser extent than on the degreased surface. The Al:Mg ratio for the surface of the grit-blasted alloy is about 15:1. Zinc and copper were also detected and the latter element was certainly present in a greater concentration than predicted from the bulk composition. However, the scanning electron micrographs showed the surface to be extremely rough which complicates the interpretation of depth profiles. The original oxide layer was thicker than on the degreased specimen.

After soaking no magnesium was detected and the oxide thickness increased considerably.

TABLE III

XPS analysis of grit blasted substrate

	Approximate Depth (Å)	Al (2p) Binding energy (eV)	Analysis (atomic %) O	C	Al	Zn	Cu	Mg	Si	Others
Not soaked in water	0	74.55	51	24	22	0.8	0.7	2.5	3.1	Cl-2.0
	20	74.55	49	15	31	0.5	1.4	2.5	0.6	Cl-0.9
	120	74.45 (71.95(90%))	43	17	38	0.2	1.3	1.4	1.5	Cl-0.6
Soaked in water	0	74.00	54	25	14.4	0.4	0.5	4.6	—	Cl-0.8
	20	74.30	59	12	25	0.4	0.5	—	3.4	
	120	74.50	63	3.6	30	—	0.2	—	3.3	
	520	74.55	63	0.5	34	—	—	—	2.6	

Chromic-acid etched pretreatment. The XPS analysis of the aluminium-alloy surface subjected to the chromic-acid etch pretreatment is shown in Table IV. Magnesium was detected as magnesium oxide but there is no significant surface enrichment. Zinc was absent but a trace of copper was detected and it is also interesting to note the high silicon level and the virtual absence of chromium. The level of carbon on the freshly prepared surface of the alloy was extremely high. Finally, the initial oxide thickness was somewhat higher than produced by the above pretreatments and increased on water soaking. The scanning electron micrographs indicated a pitted surface was produced, as illustrated in Figure 1.

Phosphoric-acid anodised pretreatment. The results are given in Table V and show that this pretreatment and the solvent-degreasing method produced the lowest carbon levels on the aluminium-alloy surface. Zinc and copper were absent from the unsoaked sample although magnesium, as magnesium oxide, was detected but there was no surface enrichment. Indeed, the Al:Mg ratio was about 80:1 which was higher than the bulk composition.

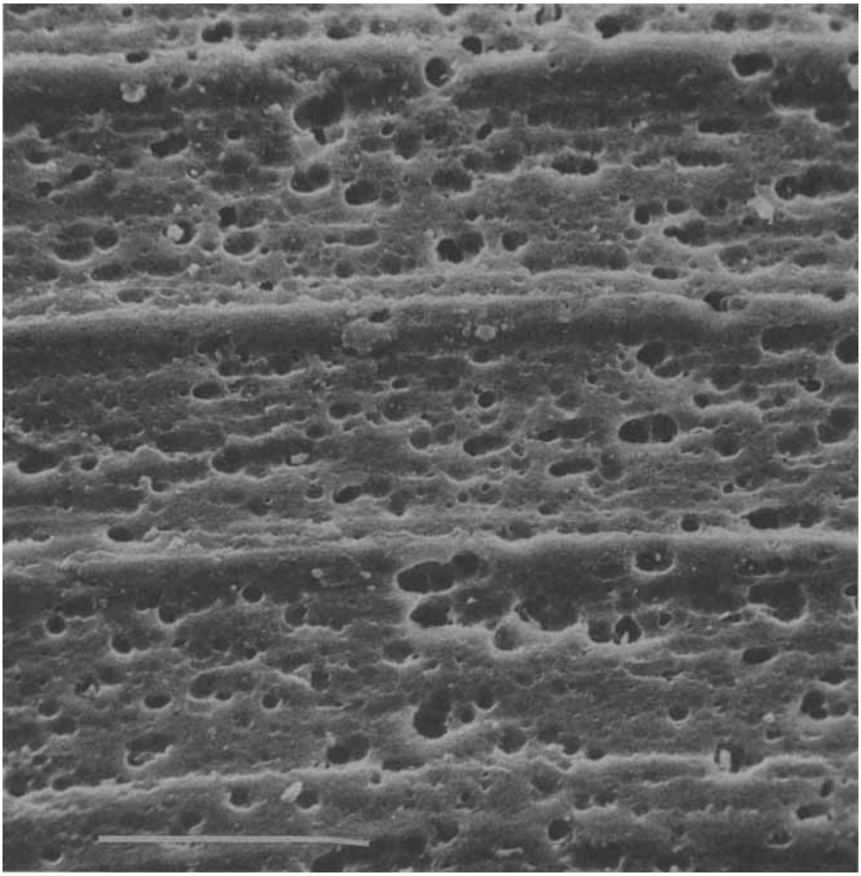

FIGURE 1 Scanning electron micrograph of aluminium alloy surface pretreated using chromic-acid etching method. Bar represents 55 μm.

Silicon was detected but in a much lower concentration than for the chromic-acid etched surface. The level of phosphorus, considering phosphoric-acid was employed in the surface preparation, was low. The oxide thickness was greater than for the chromic-acid etched pretreatment. Previous work[4] has indicated that the phosphoric-acid anodise pretreatment produces a very thick, porous oxide about 4000 Å deep while the chromic-acid etch results in an oxide thickness of only a few hundred angstroms.

After water soaking the main difference was the detection of the elements zinc and copper.

TABLE IV

XPS analysis of chromic-acid etched substrate

	Approximate	Al (2p)				Analysis (atomic %)			
	Depth (Å)	Binding energy (eV)	O	C	Al	Zn	Cu	Mg	Others
Not soaked in water	0	73.9	26	61	6.8	—	—	—	Si 5.4, S 1.2
	60	74.7	28	38	20	—	0.1	0.3	Si 3.6, Fe 0.5
	300	74.4 (72.1(40%))	30	24	34	—	—	0.6	Si 1.5, Fe 0.7
Soaked for 500 hours	0	74.1	54	25	17	0.4	—	—	N 1.2, S 0.4, Cr 0.2, Si 0.5, P 0.8
	20	74.5	59	11	29	0.4	—	tr	Cr 0.2, Si 0.7
	170	74.7	61	6	32	0.3	—	—	Si 0.7, Ca tr.

TABLE V

XPS analysis of phosphoric-acid anodised substrate

	Approximate	Al (2p)				Analysis (automic %)			
	Depth (Å)	Binding energy (eV)	O	C	Al	Zn	Cu	Mg	Others
Not soaked in water	0	74.2	52	23	22	—	—	0.2	Si 0.6, Ni 0.1, Sn 0.1, N 0.5, P 1.3
	10	74.5	58	9.5	30	—	—	0.4	Si 1.0, Sn 0.1, P 0.8
	150	74.7	59	6.0	34	—	—	0.3	P 0.7, Si 0.4, Ni 0.1, Sn 0.1
500 hours soaking	0	74.05	55	21.6	20	0.4	0.1	0.3	Si 0.7, Ni 1.5, Ca 0.3
	4	74.45	59	12	27	0.4	0.3	0.1	Ca 0.2, Si 1.0, Ni 0.1, N 0.5
	12	74.8	65	8.2	25	0.4	0.3	0.2	Ca 0.3, Si 0.9, Ni 0.1
	25	75.0	62	6.9	29	0.3	0.2	0.1	Ca 0.2, Si 1.1, Ni 0.1, N 0.1
	70	75.2	59	7.0	31	0.4	0.1	0.2	Si 1.9, Ni 0.1

Analysis of fracture surfaces of butt joints

Interpretation of the XPS analysis of the surfaces of the fractured butt joints was greatly complicated by two factors. Firstly, the fracture path frequently jumped from at, or near, one interface to the other and consequently photoelectrons from both adhesive and metal interfaces were accepted into the energy analyser. Secondly, charging of the adhesive surfaces caused shifts in the binding energies.

Locus of joint failure. The scanning electron micrographs indicated that all the joints where only a degreasing pretreatment was used failed at, or near, the aluminium oxide/adhesive interface. The XPS analysis for the 500 hour water immersion specimen shown in Table VI clearly demonstrates that failure did not occur in the oxide layer, *i.e.* there is no Al (2p) signal generated from the "adhesive" (from visual examination) side of the broken joint.

The unsoaked joints prepared using the other surface pretreatments all fractured by largely cohesive failure through the adhesive layer. After water soaking the locus of failure was at, or near, the interface for the grit-blasted and chromic-acid etched joints. For the latter joints the evidence for this conclusion from the scanning electron microscopy studies is illustrated in Figure 2(a) and (b). The "metal" side of the joint has the same general appearance as the chromic-acid etched aluminium-alloy surface prior to bonding, *cf.* Figures 1 and 2(a). However in Figure 2(a) some of the pits give

TABLE VI

Enrichment of Mg at fracture surfaces

Treatment	Immersion time in water at 60°C (h)	Side	Al (atomic %)	Mg (atomic %)	Al:Mg ratio
Solvent degreased	0	A	16	2.3	7.0
		B	4.7	1.6	2.9
	500	A	14	8.6	1.6
		B	—	—	—
	1000	A	12.1	3.6	3.4
		B	1.5	—	—
Grit-blasted	0	A	3.1	—	—
		B			—
	500	A	12	2.4	5.0
		B	8.6		—
	1000	A	14	1.0	14
		B	7.4	—	—
Chromic-acid etched	0	A	—		—
		B	1.1	—	—
	500	A	6.2	—	—
		B	6.4	—	—
	1000	A	29	0.3	97
		B	17	—	—
Phosphoric-acid anodised	0	A	0.9		—
		B	1.2	—	—
	500	A	11.0	—	—
		B	—	—	
	1000	A	0.6	—	—
		B	0.3	—	—

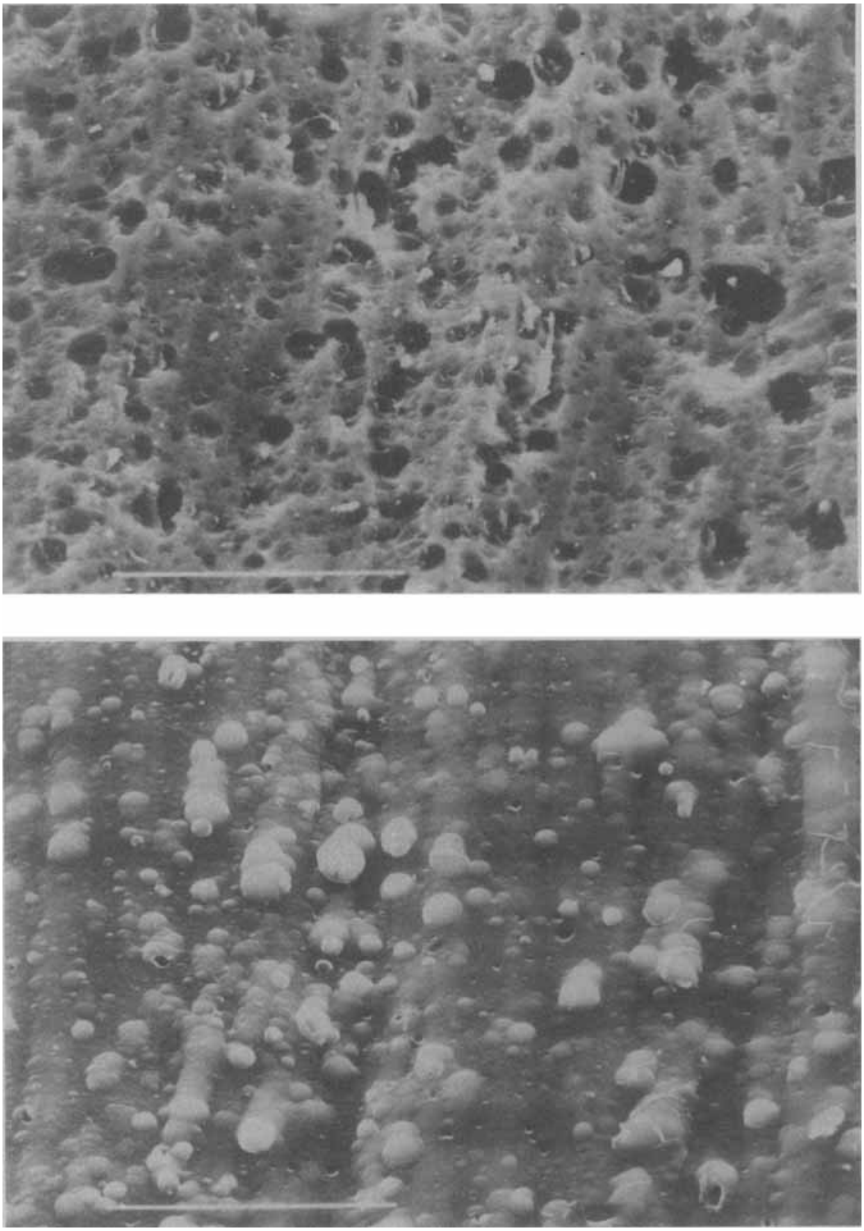

FIGURE 2 Scanning electron micrograph of fracture surfaces of butt joint prepared using the chromic acid etch pretreatment. (a) "metal" side of joint, (b) "adhesive" side of joint. Bar represents 55 μm.

the appearance of containing epoxy adhesive. The "adhesive" side shows clearly that the adhesive has penetrated into the pits during joint formation. Unfortunately, a more precise description of the locus of joint failure from the XPS analysis was not possible because of the problems mentioned above. For the phosphoric-acid anodised samples, joint failure even after immersion for 1000 hours was mainly by cohesive fracture through the adhesive. Where failure was close to the interface it was evident that adhesive remained in many of the pores of the oxide film. XPS analysis confirmed this fracture path from the high carbon level on both sides of the fractured joint and a low total aluminium concentration.

Magnesium concentration on fracture surfaces. The concentration of aluminium and magnesium, in the form of the respective oxides, and the Al:Mg ratio found on the fracture surfaces is given in Table VI. For the bulk aluminium-alloy the ratio was 52.6:1. Thus, as may be seen, the level of magnesium found on the "metal" side of the fracture surfaces was extremely high for the solvent-degreased and grit-blasted pretreated joints. For the chromic-acid etched and phosphoric-acid anodised joints the level of magnesium was zero, or very low, even when a relatively high concentration of aluminium was present on the "metal" fracture surface.

DISCUSSION and CONCLUSIONS

It is well established[1-3,5] that the different pretreatments examined in the present study impart different degrees of environmental resistance to the adhesive joints. In the order of increasing durability: phosphoric-acid anodised > chromic-acid etched $\gg$ grit-blasted > solvent-degreased. Previous work[6-8] has shown that differences in the surface chemistry may influence the subsequent joint durability. It was therefore hoped that the XPS analyses of the variously pretreated aluminium alloy would reveal dramatic differences in the chemical nature of the surfaces. However, the results shown in Tables II to V, although containing interesting features, fail to do so.

Considering firstly the main elements detected, then all the surfaces possessed a relatively high carbon concentration. Its peak position at 285 eV indicated that it may be associated with elemental or hydrocarbon[9,10] and upon ion bombardment the carbon concentration usually fell rapidly. This level of contamination on a carefully cleaned aluminium alloy substrate arises, of course, because an absolutely clean surface has a very high surface free energy and thus will adsorb contaminants like organic adsorbates, nitrogen, etc. from the atmosphere. It is thought[11] that common adhesives, which are relatively polar, displace and absorb such non-polar contamination during the adhesive wetting process. It is noteworthy that the solvent-degreased and phosphoric acid anodised surfaces, at the extreme ends of the environmental resistance spectrum, had the lowest level of contamination.

Considering secondly the elements detected in relatively low concentrations then the phosphoric acid anodise and chromic acid etch pretreatments produced the greatest extent of such elements. However, with the exception of magnesium concentration which is discussed below, no clear correlation with joint durability is evident. The levels of phosphorus and chromium respectively were very low. These levels appear to provide little basis for suggesting that these pretreatments produce a phosphate or chromate rich surface layer which then prevents water inducing mechanical weakening, and eventually fracture, of the oxide layer.

The results for the magnesium concentrations are especially intriguing. Firstly, the level of magnesium, present as magnesium oxide, is in the order: solvent-degreased > grit-blasted $\gg$ chromic-acid etched > phosphoric-acid anodised. Secondly, for the solvent-degreased and grit-blasted prepared surfaces there is a surface enrichment of magnesium. This has been observed previously[12] for the former pretreatment on a different alloy and this combination also resulted in an adhesive joint possessing poor durability.[13] The magnesium rich surface layer is thought[12] to arise during the heat treatment given to the alloy during its manufacture. When Al/Mg alloys are oxidised in oxygen then magnesium oxide is preferentially formed at the surface of the aluminium oxide.[14, 15] This enrichment does not occur on chromic-acid etched or phosphoric-acid anodised surfaces. This indicates that the mechanism of fresh oxide formation, induced by these pretreatment methods, results in a completely different distribution of elements in the oxide layer. Upon water immersion the magnesium concentration decreased and this may be a result of a thicker aluminium oxide layer; the oxide thickness increased upon water immersion. Alternatively, the magnesium may have been removed by a leaching process although the MgO is a very insoluble species (0.0086 g/1 in hot water) and hence this mechanism seems unlikely.

Thirdly, unlike previous studies,[16] using steel substrates, the XPS analysis of the fracture surfaces from the butt joints failed to reveal in precise detail the exact locus of fracture after environmental attack. Although the present work has shown environmental failure in aluminium-alloy/epoxy adhesive joints does indeed involve a fracture path at, or very close to, the interface. However, the role of magnesium in influencing the joint durability was substantiated. The poor pretreatments both resulted in a low Al:Mg ratio on the "metal" side of the fractured joint.

Thus, it is suggested that the concentration of magnesium, in the form of magnesium oxide, on the pretreated aluminium alloy surface may be an important factor in influencing the durability of adhesive joints.

Acknowledgements

The authors would like to thank Drs. H. Bishop and M. Gettings for useful discussions and Mr. V. Moore and Mr. A. Kosecki for the scanning electron micrographs.

APPENDIX I

Surface pretreatments

(a) *Solvent-degreasing*

The surfaces were subjected to a liquid- and vapour-degreasing bath of trichloroethane and then allowed to dry in air.

(b) *Grit-blasting*

The surfaces were degreased as described above and then subjected to grit-blasting with 180–220 mesh alumina and then again degreased.

(c) *Chromic acid etching*

The surfaces were first degreased as described in (a), then washed in an alkaline solution containing sodium carbonate and a detergent, 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.

(d) *Phosphoric-acid anodising*

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

References

1. J. D. Minford, *Adhesives Age* **21** (3), 17 (1978).
2. A. J. Kinloch, *J. Adhesion* **10,** 193 (1979).
3. J. C. McMillan, *Developments in Adhesives*, **2,** ed. A. J. Kinloch, (Applied Science Publ., London, 1981), to be published.
4. J. D. Venables *et al.*, *Appl. Surf. Sci.* **3,** 88 (1979).
5. J. D. Minford, *Treatise on Adhesion and Adhesives* **3,** ed., R. L. Patrick, (Marcel Dekker, New York, 1973), p. 79.
6. M. Gettings and A. J. Kinloch, *J. Mater. Sci.* **12,** 2511 (1977).
7. J. M. Chen *et al.*, *Proc. 22nd Nat. SAMPE Sympos.*, 1977, p. 25.
8. M. Gettings and A. J. Kinloch, *Surf. Interf. Analysis* **1,** 189 (1979).
9. F. R. McFeeley *et al.*, *Phys. Rev.* **B9,** 5268 (1974).
10. U. Gelius *et al.*, *Phys. Scripta* **2,** 70 (1970).
11. A. J. Kinloch, *J. Mater. Sci.* **15,** 2141 (1980).

12. T. S. Sun, *et al.*, *Appl. Surf. Sci.* **1**, 202 (1978).
13. N. T. McDevitt, W. L. Baun and J. S. Solomon, *J. Electrochem. Soc.* **123**, 1058 (1976).
14. B. G. Goldstein and J. Dresner, *Surf. Sci.* **7**, 15 (1978).
15. T. Rönnhult, U. Rilly and I. Olefjord, *Mat. Sci. Eng.* **42**, 329 (1980).
16. M. Gettings, F. S. Baker and A. J. Kinloch, *J. Appl. Polym. Sci.* **21**, 2375 (1977).