

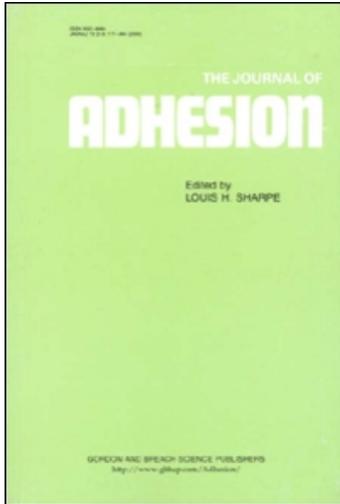
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The Journal of Adhesion

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 Kinloch, A. J. , Bishop, H. E. and Smart, N. R.(1982) 'Surface Analysis and Bonding of Aluminium-Magnesium Alloys', *The Journal of Adhesion*, 14: 2, 105 – 118

To link to this Article: DOI: 10.1080/00218468208074894

URL: <http://dx.doi.org/10.1080/00218468208074894>

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Surface Analysis and Bonding of Aluminium-Magnesium Alloys

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(Received December 4, 1981)

Previous work has used X-ray photoelectron spectroscopy to examine the surface compositions of aluminium-alloy substrates subjected to various surface pretreatments prior to bonding. It was proposed that the presence of magnesium in the oxide structure adversely affected the service-life of adhesive joints when they were exposed to aqueous environments. The present work further explores this correlation by examining a range of aluminium alloys, basically of the same composition except for the level of magnesium in the alloy.

INTRODUCTION

A previous publication¹ discussed the use of a surface sensitive technique, namely X-ray photoelectron spectroscopy (XPS), to investigate the chemistry of aluminium-alloy surfaces which had been pretreated by various methods. The various pretreatments were selected because they were known to lead to adhesive joints possessing vastly different service-lifetimes in moist environments. It had been hoped that the XPS analyses of the variously pretreated alloys would reveal dramatic differences in the chemical nature of the surfaces and thus identify the detailed mechanisms of adhesion and environmental failure. However, although the results contained several interesting features they failed to indicate any such differences. The one intriguing correlation that did emerge was that between the level of magnesium concentration in the oxide layer and the resulting joint durability.

TABLE I

Bulk composition of aluminium alloys (atomic %)

Alloy	Element								
	Al	Cu	Mg	Si	Fe	Mn	Zn	Cr	Ti and others
E1C	Rem	0.05	—	0.5	0.35	0.04	0.04	—	—
NE4	Rem	0.04	1.8/2.7	0.5	0.25	0.25	0.08	0.15	0.1
NE8	Rem	0.04	4.4/5.5	0.4	0.2	0.25/0.5	0.08	0.13	0.1

mass per cent of a curing agent, tri-2-ethyl hexanoate of 2,4,6-tris(dimethylaminomethyl) phenol.

Surface chemical analysis

All the specimens were examined using XPS to obtain a chemical analysis of the uppermost atomic layers. The measurements were made in a Vacuum Generators Escalab System using Al K α X-rays (1486.6 eV) as the photo-excitation 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. Photoelectrons are accepted from the surface and focused on to the entrance slit of a hemispherical energy analyser. Wide energy scans were obtained at a pass energy of 100 eV, from which an elemental analysis could be derived, and higher resolutions were measured for particular peaks using a pass energy of 50 eV. Spectra were recorded and processed employing a mini-computer system. The argon ion source was used to erode the surface by sputtering with argon ions and so reveal a depth profile of the composition material. The erosion rate depends on many factors which differ from surface to surface. An approximate conversion factor of 2 Å/ μ A · min has been employed in the present study.

Auger analysis was conducted using a Vacuum Generators MA 500 System which has a 1000–2000 Å spatial resolution in the scanning mode.

Scanning electron microscopy was performed on both degreased and phosphoric-acid anodised specimens using a Cambridge Stereoscan instrument.

Joint preparation and testing

Immediately prior to joint preparation and testing the aluminium-alloy substrates were treated as described in Appendix 1, adhesive was spread on the treated faces and two rods were pressed lightly together to form a coaxial butt

joint. Small lengths of copper wire, previously inserted in the adhesive near the centre of the joint, were employed to control the adhesive thickness to 0.5 mm (this technique has been shown not to affect significantly the joint strength).^{8,9} To crosslink the adhesive the joint was subjected to a cure schedule of 96 hours at 23°C, 1¼ hours at 100°C and 2½ hours at 180°C, followed by a slow cooling period.

The joints were then immersed in distilled water at 60°C. At intervals, joints were removed from this environment, kept at 22°C, 55% R.H. for about half an hour, and then fractured in tension at 22°C and a strain rate of $4.0 \times 10^{-2} \text{ s}^{-1}$.

RESULTS

XPS analysis

Quantitative analyses were obtained from the XPS spectra by measuring the area of the most intense peak for a particular element and applying the appropriate sensitivity factor, mainly taken from Wagner's work.¹⁰

The results of the analyses are shown in Tables II to IV. The small nickel signal comes from the specimen holder and should be ignored. The analyses quoted are representative of the surface composition but the absolute numbers may be subject to substantial systematic errors.¹¹ By assuming simple Poisson statistics it is possible to calculate the statistical error in the elemental concentrations. This error is quoted for some of the results in Tables II to IV. For very small peaks, such as the silicon 2s and 2p peaks the error may be as much as 100%.

All the specimens displayed a carbon-rich layer probably consisting¹² of aliphatic hydrocarbons acquired during handling and from atmospheric contamination adsorbing onto the high-energy oxide surface. There is no correlation between the alloy or pretreatment and the surface levels of carbon.

The binding energy for the Al (2p) peak is ~ 74 eV for aluminium in the oxidised state but ~ 72 eV in the metallic state. For all the alloys and pretreatments the peak position before ion bombardment was ~ 74 eV, indicating aluminium oxide as would be expected. This was the only position observed for the Al (2p) peak from the anodised surfaces, even after prolonged ion bombardment and confirms previous work⁶ which has shown that a relatively thick oxide layer, about 4000 Å deep, is formed by this pretreatment. On the other hand, an Al (2p) peak at ~ 72 eV was observed upon analysis of the degreased surfaces after a light bombardment. The oxide layer on these surfaces was estimated to be only about a hundred angstroms or so thick, in agreement with the previous results.¹

Copper is only present in the bulk material at very low concentrations (~ 0.05 atomic %) and is not generally detected in the oxide layers. Manganese

TABLE II
XPS analysis of EIC alloy

Argon ion bombardment		Atomic % (approximate error in parentheses)									
Charge ($\mu\text{A} \cdot \text{min}$)	Approx. depth (\AA)	O	C	Al	Mg	Zn	Cl	N	Si	P	Others
Degreased											
0	0	33.5 (0.5)	42.5 (0.7)	20.9 (0.7)	—	0.5 (0.1)	1.7 (0.4)	0.9 (0.3)	—	—	Ca—tr
10	20	32.6	19.7	46.7	—	—	0.9	—	—	—	Na—0.1
20	40	27.8	17.4	53.8	—	—	—	1.0	—	—	—
50	100	18.3 (0.5)	18.5 (1.2)	63.2 (1.1)	—	—	—	—	—	—	—
Phosphoric-acid anodised											
0	0	42.2 (0.8)	32.7 (0.8)	15.9 (0.7)	0.5 (0.15)	—	0.4 (0.2)	1.6 (0.6)	1.2 (0.8)	4.1 (0.5)	Na—0.7, Ca—0.7
10	20	49.6	12.3	25.1	0.5 (0.15)	—	1.8	—	3.1	5.1 (0.7)	Na—0.7, K—0.6
50	100	52.5	6.9	28.7	0.4 (0.1)	—	0.5	—	4.6	4.0 (0.9)	Na—0.5, Ca—1.3, K—0.6
150	300	54.3	5.1	32.7	0.4 (0.15)	—	tr	1.5	3.1	1.4 (0.6)	Na—0.6, Ca—0.9
350	700	54.8	4.1	34.8	0.4 (0.15)	—	tr	1.0	3.3	tr	Na—0.3, K—0.3, Ca—1.0
750	1500	56.5	3.7	34.5	—	—	—	—	3.8	tr	Na—0.3, Ca—0.6 Ni—0.2
1150	2300	56.8 (1.0)	3.0 (0.8)	36.1 (0.9)	0.2 (0.1)	—	—	—	2.0 (1.0)	—	Ca—0.8, K—0.5 Ni—0.6

TABLE III
XPS analysis of NE4 alloy

Argon ion bombardment		Atomic % (approximate error in parentheses)									
Charge ($\mu\text{A} \cdot \text{min}$)	Approx. depth (\AA)	O	C	Al	Mg	Zn	Cl	N	Si	P	Others
Degreased											
0	0	37.6 (0.7)	33.7 (0.8)	20.5 (0.7)	3.3 (0.25)	0.3	1.0 (0.3)	1.0 (0.4)	2.6 (0.4)	—	Na—0.1
10	20	42.8	9.0	43.4	4.8	—	—	—	—	—	—
20	40	33.3	8.6	53.6	4.5	—	—	—	—	—	—
Phosphoric-acid anodised											
0	00	37.6 (0.5)	39.5 (0.5)	16.5 (0.5)	—	—	1.6 (0.3)	1.1 (0.3)	1.9 (0.6)	1.6 (0.3)	Ni—0.2
100	200	48.8	12.3	36.9	1.1 (0.2)	—	—	—	—	—	Ni—0.9
250	500	45.4 (0.8)	7.7 (0.8)	41.9 (0.8)	0.6 (0.1)	—	—	—	—	—	Na—0.2

TABLE IV
XPS analysis of NE8 alloy

Argon ion bombardment		Atomic % (approximate error in parentheses)									
Charge ($\mu\text{A}\cdot\text{min}$)	Approx. depth (\AA)	O	C	Al	Mg	Zn	Cl	N	Si	P	Others
Degreased											
0	0	18.3 (0.6)	66.1 (1.2)	5.6 (1.0)	1.8 (0.25)	—	1.5	2.1	3.1	—	Ni—1.5 (0.2)
10	20	28.3	43.9	16.4	3.7 (0.25)	—	1.5	1.6	1.9	—	Ni—2.7
20	40	27.8	40.6	19.6	6.2	—	0.8	1.5	—	—	Ni—3.5
50	100	22.9 (0.8)	35.1 (1.1)	28.7 (1.2)	4.3 (0.3)	—	1.3	0.9 (0.6)	—	—	Ni—6.8 (0.3)
Phosphoric-acid anodised											
0	0	38.9 (0.4)	37.1 (0.5)	18.4 (0.5)	0.4 (0.1)	—	—	1.6 (0.4)	0.3	2.7 (0.4)	Cu—0.1, Sn—0.1, Ni—0.6
10	20	47.6	19.4	27.0	1.4	—	—	tr	tr	2.9	Ni—1.2, Sn—0.2, Cu—0.3
50	100	47.8	19.3	26.8	1.4 (0.1)	—	—	tr	tr	2.9 (0.5)	Ni—1.6, Sn—0.1, Cu—0.1
150	300	50.8 (0.5)	11.7 (0.6)	34.7 (0.35)	0.9 (0.1)	—	—	tr	—	—	Ni—1.9, Sn—tr Cu—tr

and chromium are also not detected in the oxide layers. Zinc is present at less than 0.1 atomic % in the bulk and is only detected as surface contamination. Surface enrichment of silicon occurs on some surfaces but no pattern is apparent. The anodised surfaces usually had a greater concentration of trace elements, which were presumably deposited during the various aqueous treatment stages involved in this method. The chlorine found on many of the surfaces probably arises from residues remaining from the solvent degreasing, which involves a chlorinated solvent and is used in both pretreatments.

Phosphorus was detected only on the anodised surfaces but was rapidly removed by argon ion bombardment. The largest amount of phosphorus was found on the anodised E1C alloy, *i.e.* ~ 4 to 5 atomic % but only a trace was present at a depth of approximately 700 Å. Auger analysis showed that the phosphorus was present as a phosphate, PO_4^{-3} . Both these observations are in agreement with recent results reported by Sun *et al.*¹³ The anodised NE4 and NE8 alloys were both found to have appreciably lower levels of phosphorus.

The magnesium concentration is obviously of considerable interest and hence magnesium depth profiles are shown graphically in Figure 1. The magnesium was detected as oxidised magnesium. The very low concentration on the E1C anodised surface probably arises from the aqueous treatments employed in the anodisation procedure. The degreased surfaces of the magnesium containing alloys, NE4 and NE8, are enriched in magnesium and for both alloys the surface Al : Mg ratios are about 10 : 1, or less, although the bulk ratios are approximately 50 : 1 and 20 : 1 respectively. The concentrations of magnesium in the oxide layers produced by anodising the NE4 and NE8 alloys are considerably lower than those associated with solvent degreasing and generally represent a surface depletion, but in some instances are not significantly different from the bulk Al : Mg ratio.

Surface topography studies

The scanning electron micrographs of all the degreased surfaces were very similar. The surfaces were all relatively rough, with concentric markings and plastic deformation arising from machining clearly visible.

Scanning electron micrographs of the phosphoric-acid anodised surfaces are shown in Figure 2. Differences between the various alloys are readily apparent at the two representative magnifications. For although all the alloy surfaces contain etch pits of the order of microns or so in diameter, the high magnesium NE4 and NE8 alloys possess a number of much larger, and apparently deeper pits. These pits appear to congregate along the ridges of the machining marks, presumably where the greatest strains are present in the substrate surface.

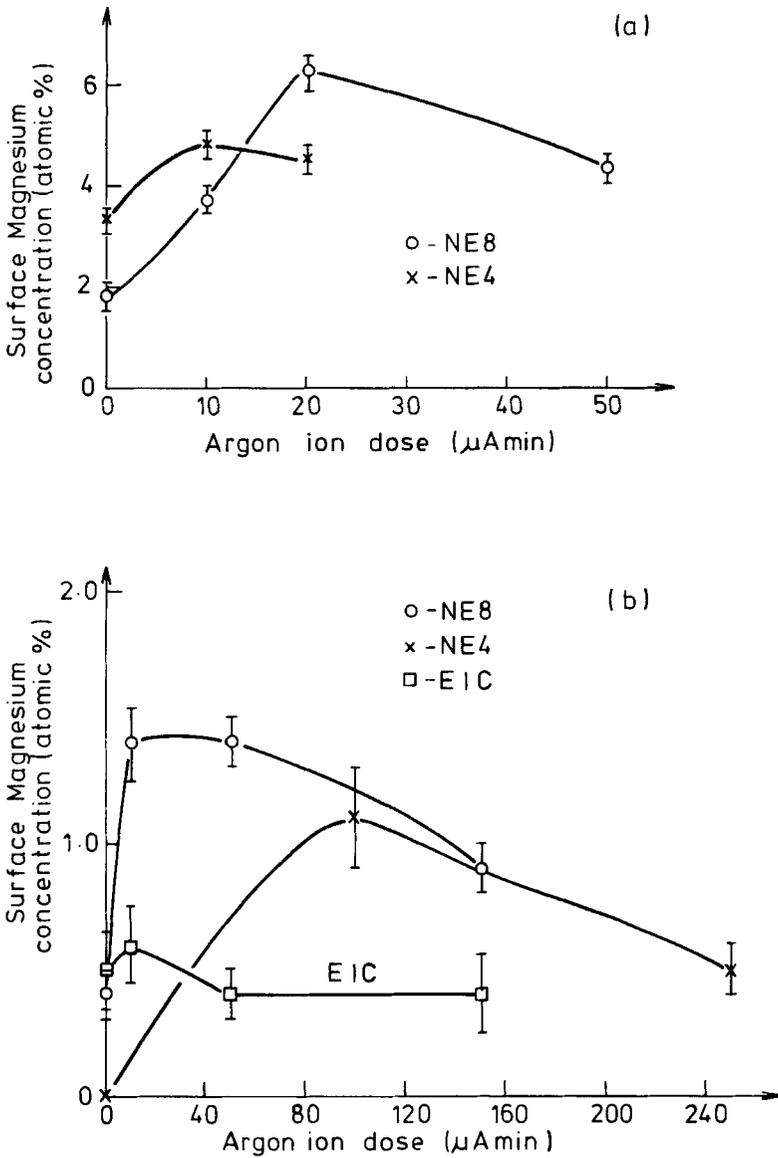


FIGURE 1 Magnesium concentration as a function of argon ion bombardment dose for the various pretreated alloys. (a) Degreased (Note: no magnesium detected in the EIC oxide layer). (b) Phosphoric-acid anodised.

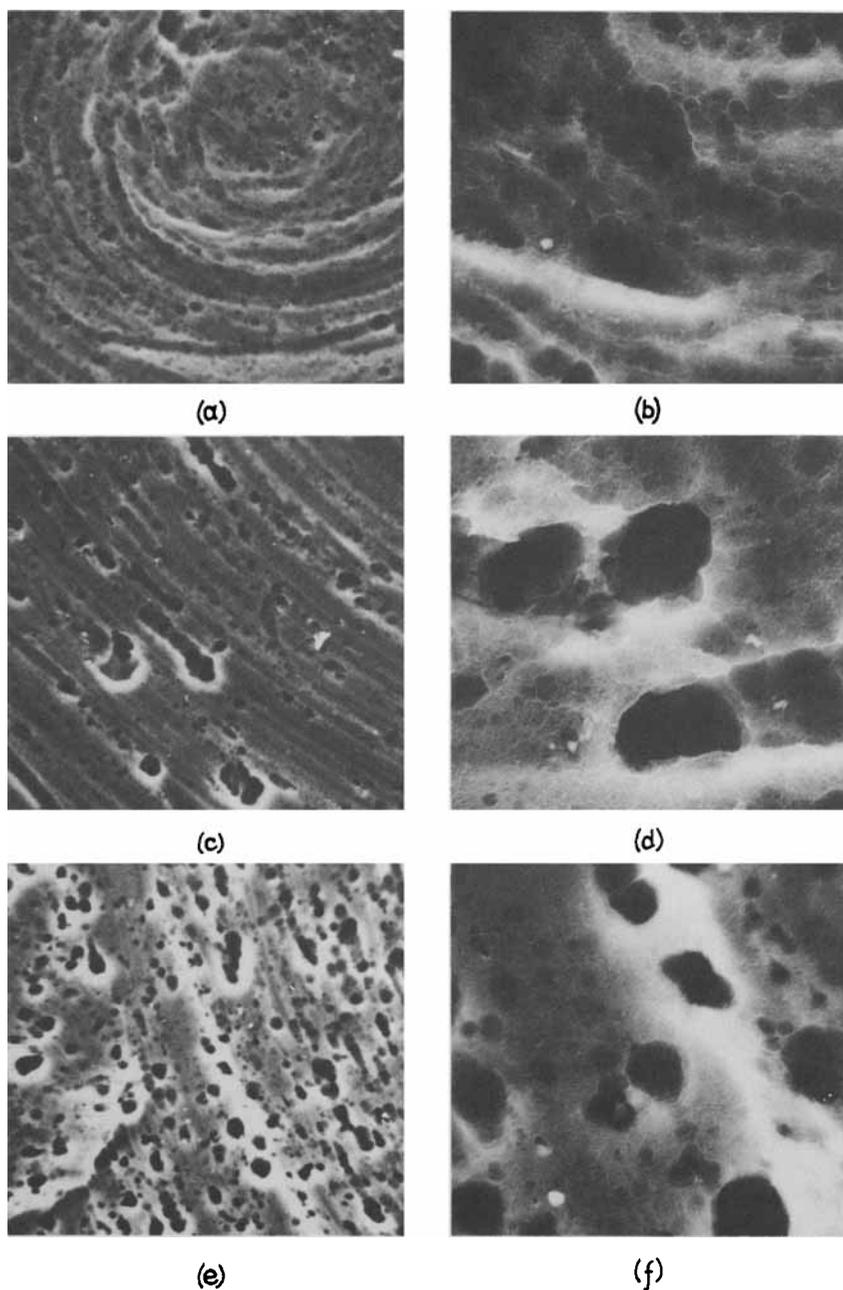


FIGURE 2 Scanning electron micrographs of the phosphoric-acid anodised alloy surfaces.
E1C alloy: (a) $\times 675$ (b) $\times 2700$
NE4 alloy: (c) $\times 660$ (d) $\times 2600$
NE8 alloy: (e) $\times 675$ (f) $\times 2700$

Joint durability studies

The results from the joint durability experiments are shown in Figure 3 and the error bars indicate the degree of scatter incurred from the four replicates tested at each condition. As may be seen the phosphoric-acid anodised specimens all exhibited far greater durability than the joints prepared from solely degreased substrates. In both cases the joints consisting of the E1C alloy possess a significantly better durability than those employing the NE4 and NE8 alloys and the durability of the NE4 and NE8 joints are generally similar.

In agreement with previous studies^{4,12,14,15} the locus of joint failure was assessed, using optical microscopy, as being cohesive through the adhesive prior to environmental exposure but become increasingly at, or close, to the adhesive/oxide interface as the time immersed in water at 60°C, prior to testing, increased.

DISCUSSIONS AND CONCLUSIONS

The quantitative XPS analysis of the pretreated substrates indicates that the amount of magnesium in the oxide structure on the NE4 and NE8 alloys is similar, despite the former possessing only half the bulk magnesium concentration of the latter. For the E1C alloy, which nominally contained no magnesium in the bulk alloy, a small amount of magnesium was detected in the anodised oxide layer, but not on the degreased oxide, and was probably deposited during anodising pretreatment. The concentration of magnesium was, however, considerably lower than that found on the NE4 and NE8, *i.e.* the magnesium containing alloys.

Comparing the above comments, and the results shown in Figure 1, to the joint durability studies illustrated in Figure 3 immediately reveals that, as stated in the Introduction, a low level of magnesium cannot be the sole criterion for producing a substrate surface with the potential for attaining good durability. For example, if this was the case then a degreased E1C alloy surface would impart a joint durability equivalent, or superior, to the phosphoric-acid anodised E1C joints. This is clearly not true, as previous work⁴ has also indicated. Possible reasons for the greatly improved durability of the joints prepared from the phosphoric-acid anodised substrates compared to the degreased include: (i) the very different oxide thicknesses, and possibly structures; (ii) the presence of phosphate ions in the anodised surface leading to greater stability of the oxide to moisture attacks and weakening; (iii) the different oxide topographies. In connection with this last point it is interesting that, on the anodised surfaces, numerous, deep etch pits were observed only on the NE4 and NE8 alloys. Thus, the increased capacity for a “macro-

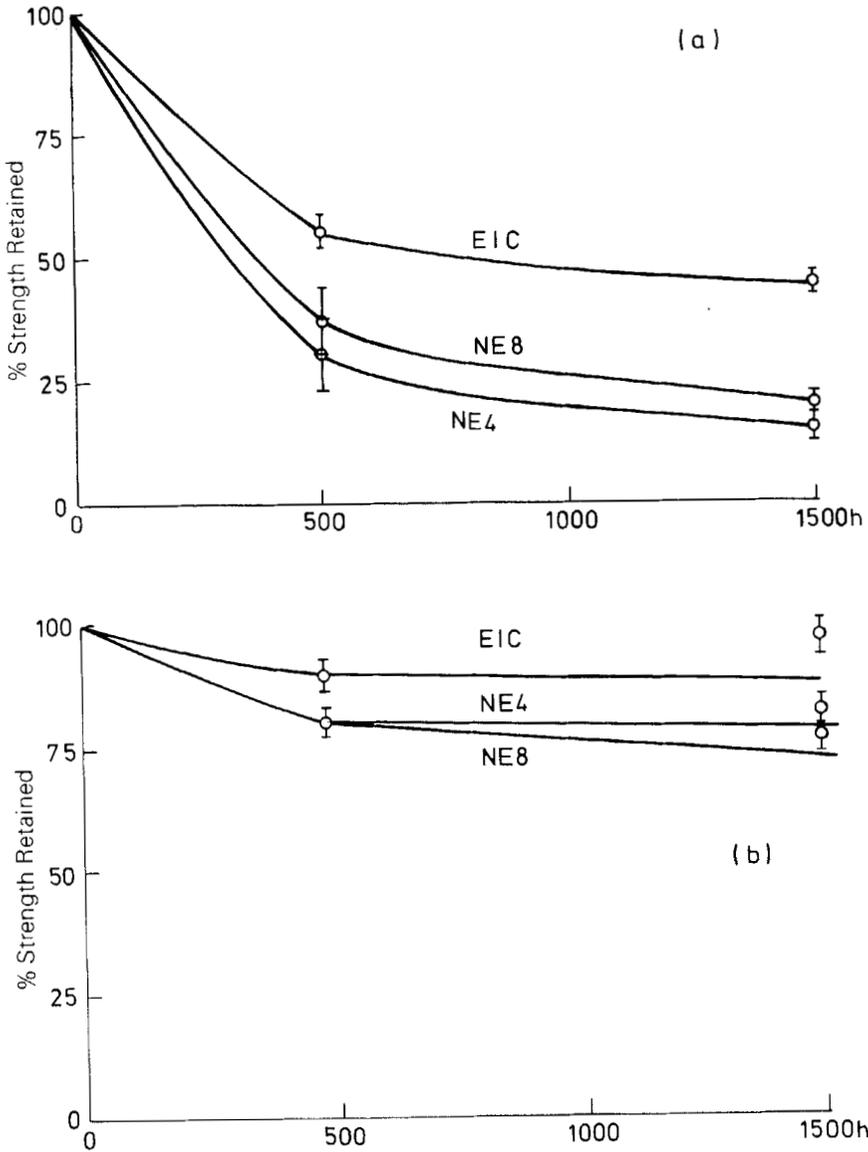


FIGURE 3 The dependence of joint durability upon the substrate alloy and pretreatment. Joints immersed in water at 60°C. (a) Degreased. (b) Phosphoric-acid anodised.

mechanical interlocking" mechanism of adhesion does not appear to correlate directly to improved durability.

However, within each type of pretreatment the concentration of magnesium in the oxide layer does appear to exert an influence on the durability ranking of the joints prepared from the various alloys studied. For each pretreatment the joints consisting of the E1C alloy possessed significantly superior environmental resistance; the E1C alloy always had the lowest concentration of Mg in the oxide structure. The NE4 and NE8 alloys had approximately the same level of Mg in their oxide structures and joints prepared from these alloys possessed similar durabilities. Also, the degreased NE4 and NE8 surfaces had by far the highest magnesium levels and resulted in the most environmentally sensitive joints.

Thus, whilst a low level of magnesium in the oxide structure is obviously not the sole criterion for obtaining good joint durability, the results from the present work confirm the previous conclusion in that high magnesium concentrations are invariably associated with inferior environmental resistance.

Finally, the detailed micromechanisms involved in the environmental attack on aluminium-alloy/epoxide adhesive joints have yet to be firmly established. However, a likely mechanism^{4,16} is that the ingressing moisture causes subtle changes, such as hydration, of the initial oxide which, in turn, results in a mechanical weakening of the oxide. Premature joint failure would then occur at the adhesive/oxide interface or in the weakened oxide layer and Noland⁵ and Venables *et al.*,¹⁷ have furnished evidence for such a mechanism. The presence of even relatively small concentrations of other elements, such as magnesium, would be expected to affect the nature and rate of this mechanism.

Acknowledgements

The authors would like to thank Mr. A. Kosecki (PERME) for obtaining the scanning electron micrographs and Mr. R. W. Atkins (PERME) for assistance in the surface preparation of the alloys.

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APPENDIX 1

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) *Phosphoric-acid anodising* The surfaces were first degreased as described

above and 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 O and then rinsed in cold distilled water and air dried. They were next anodised in a 10% w/w aqueous solution of H_3PO_4 at 10–15 V for 25 minutes at 23°C as according to Boeing Airplane Company Specification (U.S.A.) BAC 5555. The surfaces were then washed in distilled water and allowed to air dry.

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