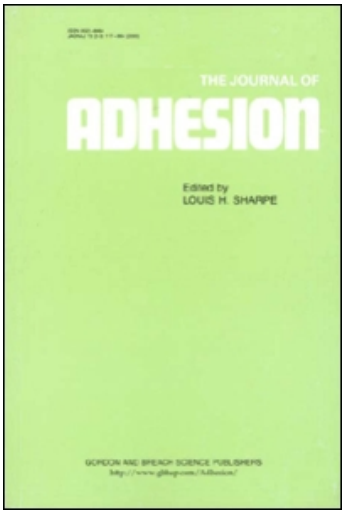

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Influence of Chemical Pretreatments on Surface Morphology and Bondability of Aluminium

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Influence of Chemical Pretreatments on Surface Morphology and Bondability of Aluminium†

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Wettability combined with a strong oxide layer are needed for adhesive bonding and these properties can only be examined by making joints with an adhesive and testing them. The best test for this purpose is the climbing drum peel test. Surfaces must be pickled and anodized. The acids used for pickling influence the anodized structure and chromic-sulphuric acid mixture followed by anodizing in chromic acid gives optimum results. Metal pickled in sulphuric acid shows lower peel strength on bonding. Electronmicrographs show a clear relation between surface morphology and bondability and a fine etchpit structure within coarser etchpits gives the most desirable structure. Low strengths are associated with either weak oxide or a weakened aluminium surface.

I INTRODUCTION

Structural adhesive bonding of aluminium alloys is an important method in the aircraft industry. It is widely known that proper treatment is necessary to obtain a reliable adhesive bonded joint. Not only is an initial high bond strength required but also durable strength is needed in the long service life of an aircraft. Because an aluminium alloy is always covered with an oxide layer, the bondability depends on the quality of this layer. For this reason the wettability of the surface is a necessary but not a sufficient requirement for a high bond strength, because a weak oxide layer may reduce the joint strength considerably. Rupture is found in this case near the interface of adhesive and metal.

It is often difficult to tell whether an adhesional failure or an interfacial

† This paper was presented at the Tenth Annual Conference on Adhesion and Adhesives held at The City University, London, England, April 1972.

failure has occurred, even with a microscope. Sophisticated techniques need to be used to investigate fracture surfaces in the case of failure at weak boundary layers. Non-destructive test methods that measure the quality of a surface are not yet available and destructive methods must be used to investigate joint quality.

To assess the quality of a pretreated surface it is necessary to make an adhesive joint and one is then dependent on test specimen design, the adhesive used on test conditions. To investigate the strength of the boundary layer, test specimens must be used which load the boundary layer by building up high stresses near it. For this, adhesives with a high modulus are required because high stress concentrations exist near the crack tip. A low modulus adhesive is less sensitive to surface quality and for this reason a poor surface quality may not be detected initially but perhaps after years of service life, due to moisture attack and bondline corrosion. The climbing drum peeling test is therefore used on surface quality investigations and a high sensitivity is obtained in the range from low to high bond strength values.

The main two pretreatment systems used throughout the work are pickling and pickling with additional anodizing. In both cases, however, the adhesive is applied to an oxide layer which may vary in strength, thickness and mode of formation.

In the present work cohesional failure at low strength levels of the anodically deposited layer were observed in many cases on test specimens. Sulphuric acid anodized lap joint specimens bonded with Redux were found to fail always within the anodic layer. Chromic acid anodized specimens occasionally failed in the anodic layer, mostly on nonclad material. Cross sections of the fracture surface easily show this type of fracture with light microscopy and Figure 1 shows such a cross section. On pickled specimens a rupture within the oxide layer is not easily visible, due to the very thin oxide layer.

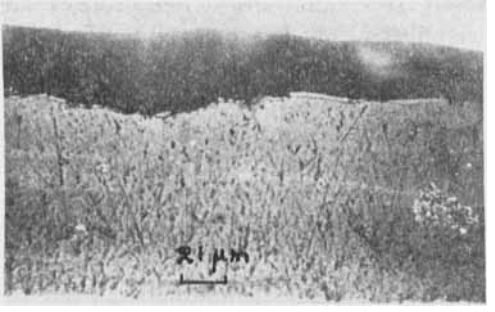

FIGURE 1 Cross-section of fracture surface: Failure in chromic acid anodic layer during peel test.

A high scatter of test results at the lower strength levels of bonded joints is due to the possibility of low values from poor surface quality whilst an upper limit is set by the fairly constant strength of the adhesive.

To find criteria for a bondable surface by means of non destructive measurements, more knowledge of the surface was needed and a long term investigation was started some years ago on reproducible pretreatments. The reproducibility was based on visual observations of direct surface replicas of pretreated specimens and it was found that pretreatment to give optimum peel strength was more reproducible than a surface with poor bondability.

A normal pretreatment sequence consists of two or three basic treatments: alkaline cleaning; pickling; anodizing; the last being not always used.

We found that pickling is influenced by the alkaline cleaning, and anodizing by the method of pickling. However, the method of alkaline cleaning is only significant if followed by mild deoxidizing such as is used for pretreatment for spot welding and no reference will be made to this effect.

II SURFACE MORPHOLOGY OF PICKLED ALUMINIUM

The pickling treatment as a surface preparation for adhesive bonding is always carried out in a mixture either of sulphuric and chromic acids or sulphuric acid with sodium dichromate.

A typical etch pattern is always found on pickled specimens by means of the electron microscope. On hydrofluoric-nitric acid and sulphuric acid pickled material large etchpits with smooth surfaces are found, as is shown in Figure 2. Similar surface morphology is found after cold deoxidizing (i.e., chemical removal of oxide scale) in chromic-sulphuric-hydrofluoric acid mixtures. A smooth etched surface gives low peel and lap joint strengths, whilst a microscopically rough surface, obtained by more effective etching, gives high adhesive bond strength values.

Observations on pickled specimens showing high peel strength after short pickling periods, followed by exceptionally low strength after longer periods increasing again after extended pickling, made a systematic investigation necessary in which lap joint and peel strength values were correlated with surface morphology. In this investigation the following factors were varied: concentration of sulphuric and chromic acids; bath temperature and time of pickling. Carbon replicas were taken from the pretreated surfaces, while lap joint and peel strength after Redux bonding were recorded. A survey of the surface configurations showed residual oxides, smooth surfaces, subgrain boundary etchpatterns and microscopic etchpits.

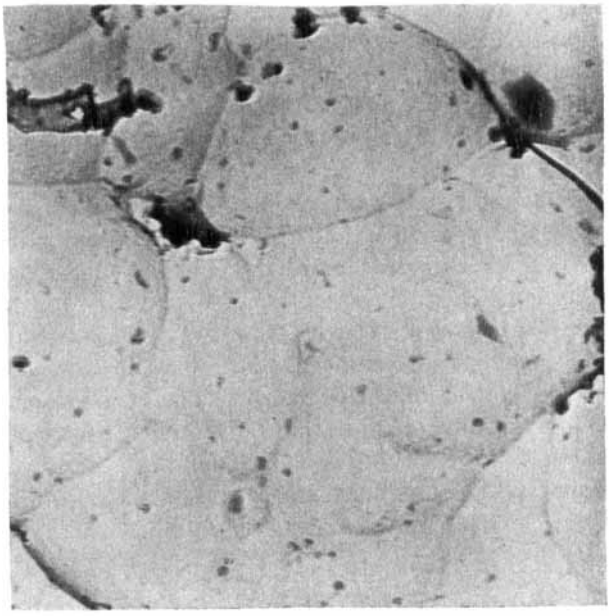

FIGURE 2 Surface morphology of aluminium pickled in hydrofluoric and nitric acid. Lap joint strength with Redux adhesive; 2.5 kgf/mm².

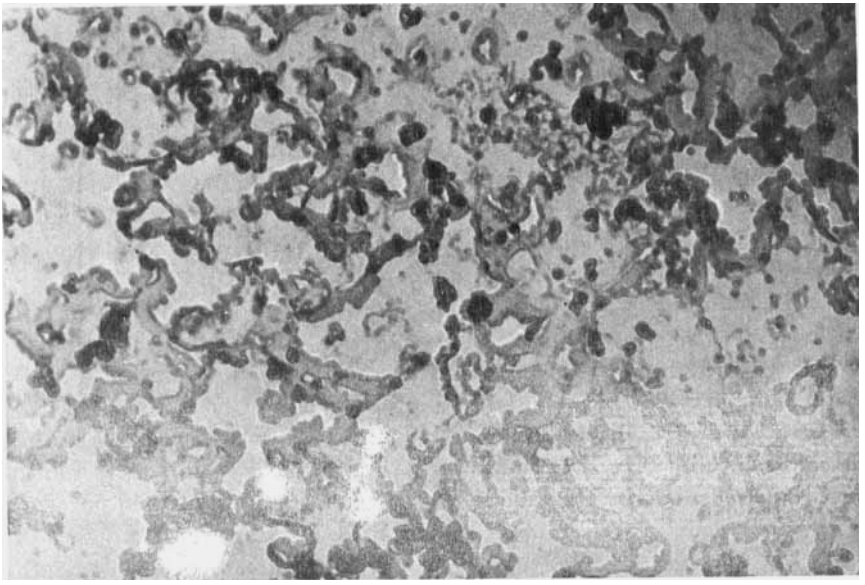

FIGURE 3 Pickled aluminium surface with residual oxides.

Surfaces with residual oxides as in Figure 3 gave a mean peel strength of 10 kgf/2.5 cm but with a large scatter ranging from near zero up to 22.5 kgf/2.5 cm. Surfaces with a smooth configuration as in Figure 4 resulted in an extremely low mean value of 2.5 kgf/2.5 cm with little scatter. Surfaces showing an apparent subgrain boundary etch which can be seen in Figure 5 showed a preferential attack in a kind of network structure and gave a mean peel value of 5 kgf/2.5 cm with a scatter ranging from near zero to 15 kgf/2.5 cm. Microscopically small etchpits shown in Figure 6 gave a mean peel value of 20 kgf/2.5 cm with a scatter of 13–25 kgf/2.5 cm. Whilst similar results were found after sulphuric acid-sodium dichromate pickling, the main difference between the two pickling systems was a high mean value of 12.1 kgf/2.5 cm coupled with a high coefficient of variation with sulphuric-chromic acid pickling compared with a mean value of 10.4 kgf/2.5 cm and a much lower coefficient of variation given by sulphuric acid-sodium dichromate treatment.

Another interesting result was found on correlating lap joint and peel strengths, for which calculated regression lines are shown in Figure 7. Low peel strength does not always result in low lap joint strength. From the scales on this diagram it is clear that the climbing-drum peeling test is far more discriminating than the lap joint test.

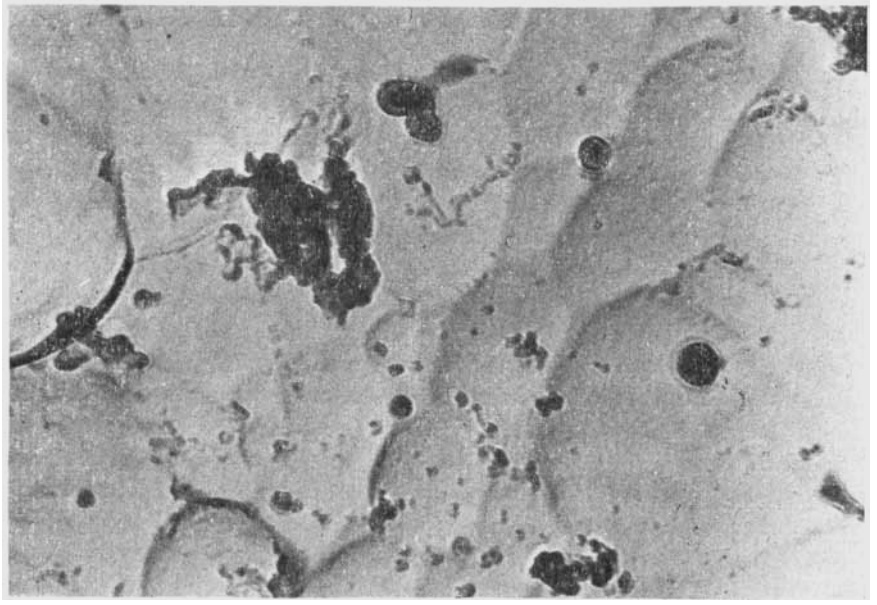

FIGURE 4 Pickled aluminium surface with smooth appearance.

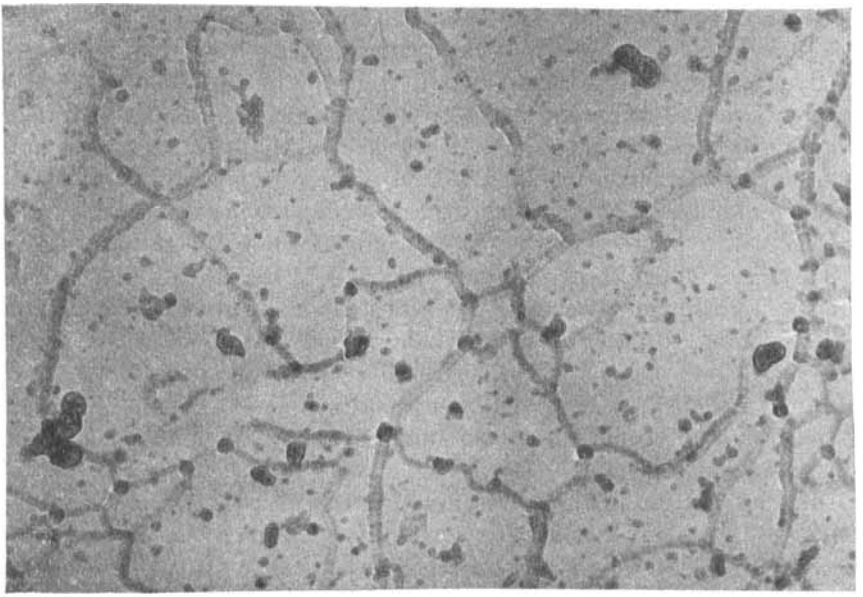

FIGURE 5 Pickled aluminium surface with rough selective etching.

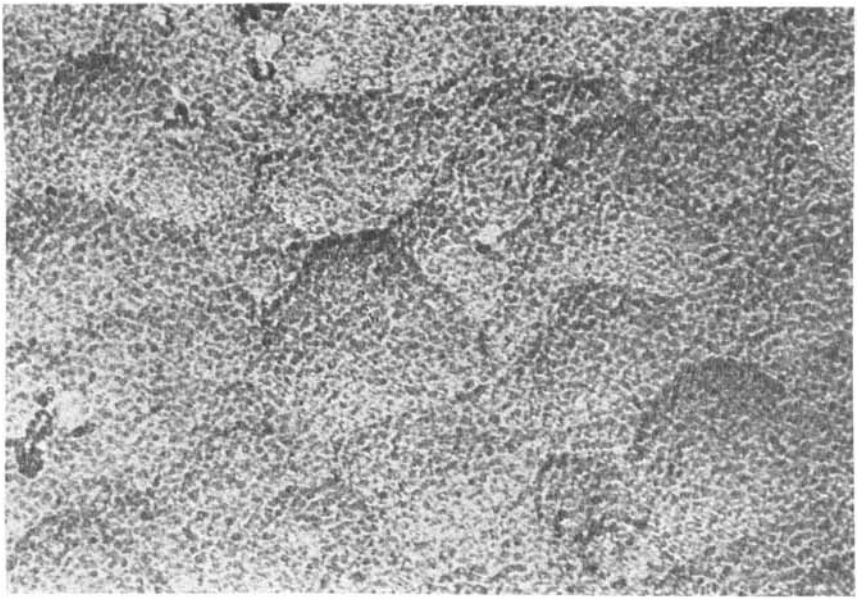

FIGURE 6 Pickled aluminium surface with fine selective etching.

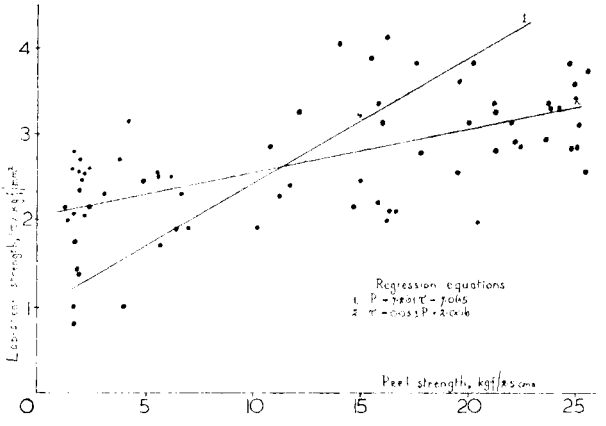

FIGURE 7 Relation between Lap-shear (τ) and Peel (P) strengths.

III THE INFLUENCE OF PICKLING ON THE SURFACE MORPHOLOGY AFTER ANODIZING

Adhesive bonding on anodized material is standard practice at FOKKER-VFW. The main reason is to provide corrosion resistance under the adhesive layer. No problems of bondline corrosion have yet been reported of Redux† bonded joints although different results may be found for other adhesives. It is our opinion that the polycondensation process which leads to cure of the adhesive results in a sealing of the anodic layer when the adhesive reaches its maximum penetration. To investigate the influence of the pickling treatment on adhesion after anodizing, panels were pickled in hydrofluoric-nitric acid to obtain poor adhesion and in chromic-sulphuric acid for optimal adhesion.

Bond strength values after anodizing the different pickled panels were compared. If anodic layers without pores were formed, such as is possible in ammonium tartrate, the bond strength is the same on pickled as on pickled and anodized panels. This is shown in Figure 8 for the lap joint strength of Redux bonded panels. If sulphuric acid anodizing is carried out after pickling, the influence of the surface configuration is less pronounced, depending on the type of adhesive used. If Redux bonded panels are tested, only a very small difference is found, due to rupture taking place within the anodic layer. In these circumstances the strength of the anodic layer determines the bond strength and differences to be found are caused by

† A phenolic-polyvinyl formal adhesive; Ciba-Geigy.

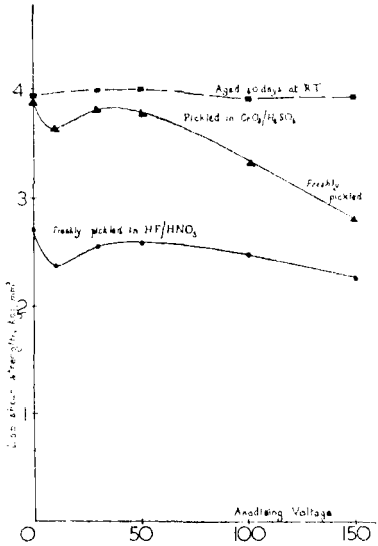

FIGURE 8 Relation of Lap-shear strength to oxide condition modified by anodizing in ammonium tartrate solution.

differences in anodic layer strength or the depth of penetration of the adhesive into the porus oxide.

In the case of adhesive FM 123–5,† large differences were found between sulphuric acid and sulphuric-chromic acid pickled panels and even greater differences in the case of a cold curing adhesive EC 2216.‡

If chromic acid anodizing is carried out after pickling, no differences were reported if bonded with Redux and FM 123–5 but a small difference in the case of a cold curing adhesive. It seems that the optimal pretreatment is by pickling in chromic-sulphuric acids because a kind of anodic layer morphology is formed on the surface followed by anodizing in chromic acid. The oxide layer formed by this anodizing process has sufficient strength to carry the load on the specimens and the process has also a corrective effect if ineffective pickling is carried out. Specimens pickled in sulphuric acid have poor peel characteristics. However, if after sulphuric acid pickling a chromic acid anodizing treatment of one minute is carried out, a high peel strength is achieved. Electron microscopic examination of the anodized surfaces revealed that the surface configuration after pickling is reproduced by the anodic layer, in the case of anodizing in either ammonium tartrate or sulphuric acid solutions. If chromic acid anodizing is carried out, the

† An epoxy-nitrile adhesive carried on woven nylon; Bloomingdale Div., Cyanamid Corp.
‡ An unsupported epoxy-nitrile adhesive; 3M Company.

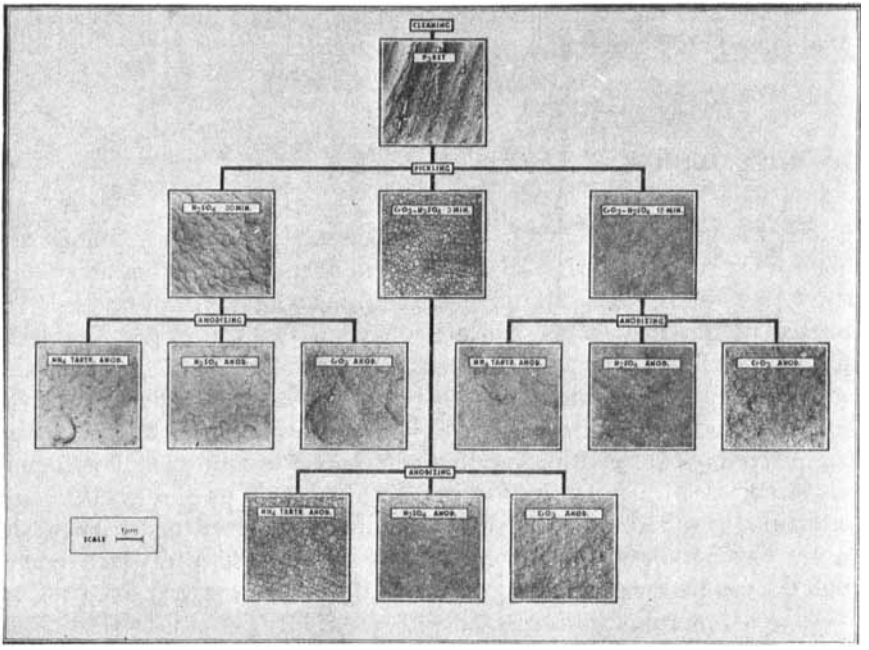

FIGURE 9 Electronmicrographs of surfaces obtained by various combinations of pickling and anodizing.

pores in the anodic layer are visible and the original surface morphology cannot be recognized.

In Figure 9 the micrograph of the pickled and anodized surfaces are given and in Table I results are given of similarly treated panels, tested by the climbing drum method.

TABLE I
Climbing drum peel test results on pickled and anodized panels

Pickled in	Adhesive R	Adhesive F	Adhesive E	Followed by anodization in	Adhesive R	Adhesive F	Adhesive E
Sulphuric acid (not anodized)	5.9	1.3	2.4	Ammonium tartrate	0.4	0.4	1.2
				Chromic acid	13.5	24.5	7.6
				Sulphuric acid	2.3*	11.2	1.1
Chromic and sulphuric acids (not anodized)	18.8	16.0	13.0	Ammonium tartrate	0.1*	10.2	8.4
				Chromic acid	13.6	24.6	10.4
				Sulphuric acid	1.4*	22.1	4.4

Adhesive code: R, Redux, Geigy-Ciba; F, FM 123-5, Cyanamid; E, EC 2216, 3M.
* Failure occurred in oxide layer.

The effects of the surface morphology on the peeling strength is extremely pronounced after pickling.

IV DISCUSSION

From the test results a clear relation between surface morphology and bondability is found. It is also clear that to secure this relation an efficient testing method is necessary and an appropriate adhesive must be used. The surface morphology might indicate a certain type of oxide. A smooth surface as is found after sulphuric acid pickling indicates little local galvanic action and a passive surface covered with a weak hydrated oxide layer, and it is typical that sulphuric acid pickling shows a lower rate of etching compared to pickling with chromic sulphuric acid (a ratio of 1 : 2 is found).

Chromic acid, as a strong oxidizer, seems to activate the local galvanic action on the surface, starting with a kind of filiform attack under the passive layer. This localized attack forms ridges over the surface which branch with the passive areas becoming smaller and smaller. At a very fine structure the optimal morphology is reached with about fifty per cent small cathodic passivated areas, and fifty per cent anodic areas with a strong oxide type as is found after anodizing. One might say that the action is comparable with anodizing but localized with its centre moving over the surface, leaving ridges of a strong oxide behind it. Figure 10 shows this model in diagrammatic form. A stereoscan picture of these ridges could be seen in a stereoscan micrograph but the resolution of the stereoscan did not permit pictures sharp enough for reproduction here. An optimal pickled surface shown at rather less magnification by stereoscan is given as Figure 11.

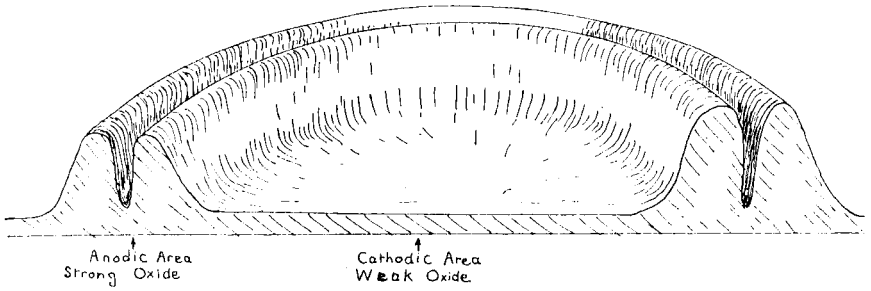

FIGURE 10 Cross sectional model showing oxide pore formation.

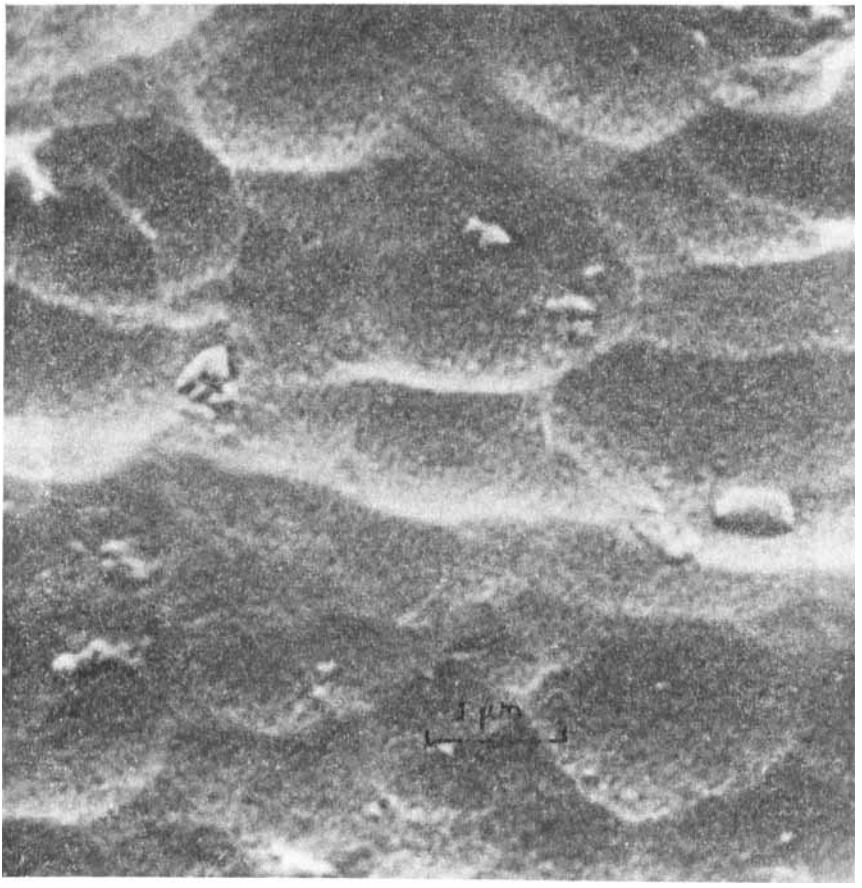

FIGURE 11 Stereoscan micrograph of a fine "etchpit-like" configuration within large etchpits. Shadowed at 45°.

The fine etchpit-like structure is found within the larger etchpits. The importance of this fine surface morphology was apparent from an examination by electron microscopy of replicas from a pickled surface and a fracture surface of a Redux peel test specimen. The adhesive remaining on the surface after breaking the bond was found over a large etchpit which itself was covered with a fine etch pattern.

The word "adhesion" is avoided in this review, because in all cases the poor adhesion is not the cause of the low bond strength. A weak boundary layer, formed by the weak oxide, is probably the only reason why the bond strength is low.

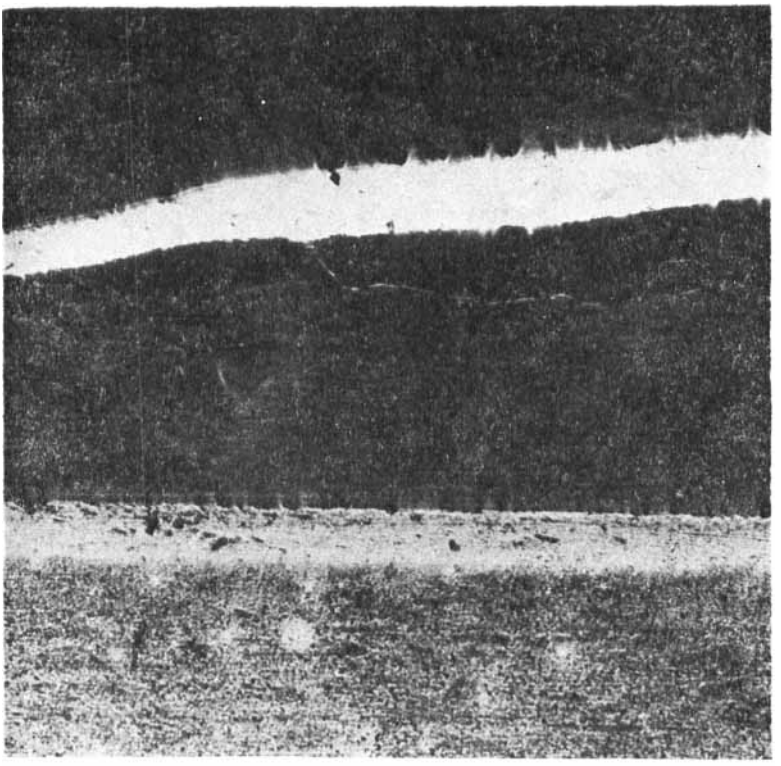

FIGURE 12 Anodic layer failure of sulphuric acid anodized peel test specimen: Note the flowlines in the adhesive near the crack tip.

More investigation is needed to find the real importance of the surface morphology on adhesive bond strength.

Some macroscopic cases of weak boundaries found in practice are:

i) *A weak anodic layer.* This may cause low bond strength if high modulus adhesives are used as illustrated in Figure 12.

ii) *Intergranular attack during pickling.* This was found to give low peel values after Redux bonding, due to intercrystalline failure and is shown in Figure 13.

iii) *A smeared weakened aluminium surface.* This has been found after a treatment of an aluminium surface with abrasive pads. Low peel strength was ascribed to rupture of the metal. A fracture surface of a peel test specimen showed a large number of aluminium particles on the adhesive.

It should be noted that the replicas given in this report are direct carbon

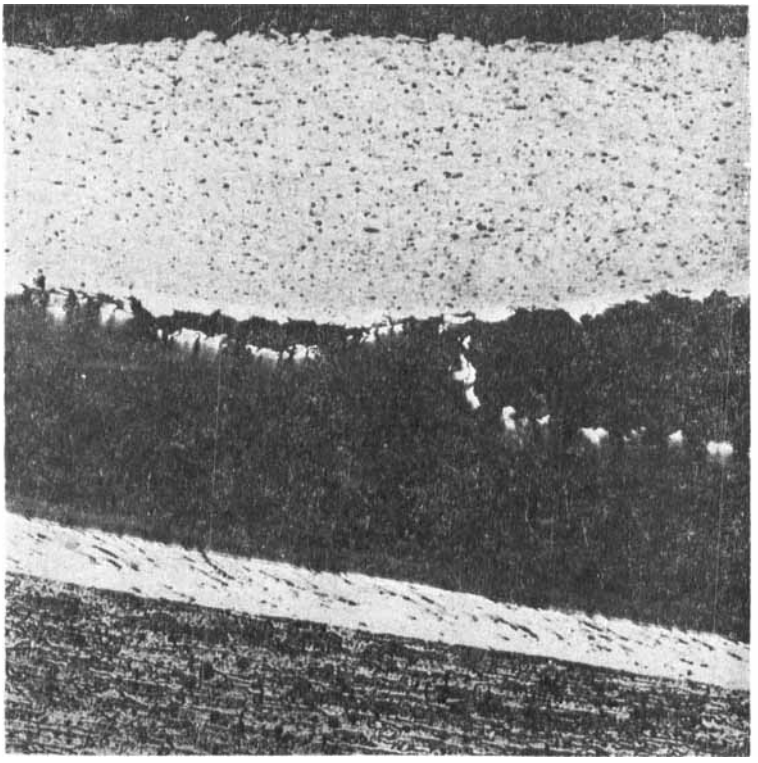

FIGURE 13 Failure caused by intergranular attack during pickling of aluminium-magnesium alloy.

replicas, shadowed with platinum-iridium under an angle of about 30°. It is clear that the appearance of the surface morphology is strongly influenced by the replica technique. A promising method of surface morphology study is by replicas of carbon evaporated perpendicularly on the surface and removed from it by mercury-chloride or brom-methanol. This gives an extraction replica of the oxide film under a carbon cover.