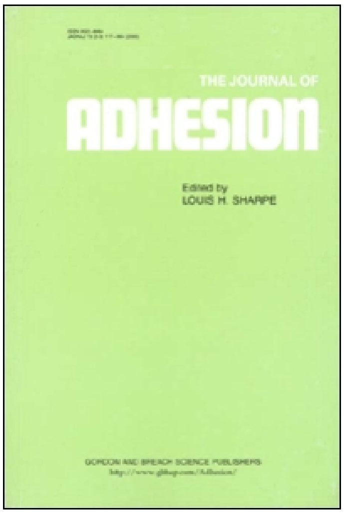

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A Cold Chromate Etch Treatment for some Aluminium Alloys

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A room temperature (cold) modification of the standard FPL chromic acid etching has been studied for three different aluminium alloys. Joints prepared in this way are as strong and durable as those prepared in the usual way at 62°C. The chemistry and morphology of the resulting oxide layers have been studied.

INTRODUCTION

A great deal of effort has been expended during the past 40 years to achieve adhesive bonds between metal adherends which are satisfactory in practical use. Most of this has been for the aerospace industry and the particular aluminium alloys which are used there. Methods have been evolved for the surface treatment of these alloys which lead to bonds which are both adequately strong and are durable particularly in adverse climates. These began with a simple chemical etching treatment in chromic acid which has been improved and is now augmented by electro-chemical anodising often involving phosphoric acid solutions.

At the same time as practical techniques have been evolved so the fundamental scientific rationale has been explored. A great deal is now known about the chemistry and morphology of the surfaces which are produced and which are essential for bonding of the highest quality.

The use of adhesive bonding is now extending into other areas of manufacture where different metals are involved and where it is not practicable to achieve the rigorous conditions achieved in a sophisticated aircraft factory.

The study reported here investigated treatment of aluminium alloys of composition and properties significantly different from those used in aerospace applications and possible simplifications of the techniques of treatment. It follows the work of L. G. Stringer[1] who initiated study and development of a room temperature treatment for aluminium alloy.

MATERIALS

The principal material studied as an adherend was the aluminium alloy DG FVE 232 but two others, NS8 and L71 were also used. Their more important characteristics are:

DG FVE 232—A 2% Mg, 4% Zn alloy, which is weldable and recovers strength by age hardening.

NS8 —A 4–5% Mg, no Zn alloy which is of comparatively low strength but high toughness. It only gains strength by work hardening.

L71 —A 4% Cu aircraft alloy of high strength but which is not weldable.

The adhesive used for all the work was a modified Redux 410. The Redux 410 itself is a conventional two-part cold curing paste adhesive manufactured by Ciba-Geigy and this was modified by adding 0.5% by weight of glass ballotini (105–210 m diameter) to provide glue-line thickness control in the simplest and most efficient way.

At one stage a difference was found between the behaviour and particularly the appearance under the electron microscope of two nominally identical samples of metal. This emphasised the importance of careful control of materials. Variations in storage conditions and handling as well as adventitious contamination can lead to variations in the surface which were not entirely eliminated by the initial cleaning procedures which had been established as standard. Although not adopted in any of this work it is suggested than an initial step of fairly vigorous mechanical scouring would be advisable to eliminate such misleading variations.

Surface treatment and bond testing

Two different surface treatments were used and the results compared; the first was the standard FPL sulphuric acid/dichromate etch at 62°C and the second was a modification of this used at room temperature. The details of these two are:

A. Standard FPL hot etch process

1. Degreased with MoD dichloromethane paint stripper emulsion formulation brushed onto plate and left for 15 minutes. All traces of paint stripper removed under running tap water and left in running water for further 15 minutes. Dried in air oven at 70°C.
2. Immersed in sodium carbonate solution, 80 g/l, at 62°C for 5 minutes. Washed in running tap water for 5 minutes. Dried in air oven at 70°C.
3. Immersed in etch solution at 62 ± 2°C for 30 minutes.
   Etch solution—H_2SO_4 (sg. 1.84) 150 ml
   $Na_2Cr_20_7.2H_20$ 75 g
   Distilled water to 1ℓ.
4. Washed in running water for 5 minutes. Dried in air oven at 37°C.

B. Modified cold etch process

1. Degreased with MoD dichloromethane paint stripper emulsion brushed onto plate and left for 15 minutes. All traces of paint stripper removed under running tap water and left in running water for further 15 minutes. Placed between two sheets of paper towel to remove most of the water.
2. Immersed in sodium carbonate solution, 80 g/l, at room temperature for 1 hour. Washed in running tap water for 5 minutes. Dried in air oven at 37°C for approximately 15 minutes.
3. Immersed in etch solution at room temperature for 4 hours. Etch solution—H_2SO_4 (sg. 1.84) 150 ml
   as before $Na_2Cr_2O_7.2H_2O$ 75 g
   Distilled water to 1ℓ.
4. Washed in running water for 5 minutes. Dried in air oven at 37°C.

The main investigation of mechanical strength and durability resulting from various surface treatments used the Boeing Wedge Test.[2] In each instance plates of prepared alloy 5″ × 5½″ were joined with the modified Redux 410 adhesive, hand spread at a covering of 200 g m^{-2} leaving 0.2″ uncoated along one short edge. The joined plates were placed under a 4 kg dead load for 24 hours at room temperature and were then post-cured at 50°C for 8 hours without any load. These double plates were cut into 1″ × 5½″ specimens using a carborundum cutting wheel with water lubricant running in a special jig. Into the 0.2″ gap, now in a 1″ edge, a mild steel wedge, 1″ × 1″ × ½″ with a 30° angular

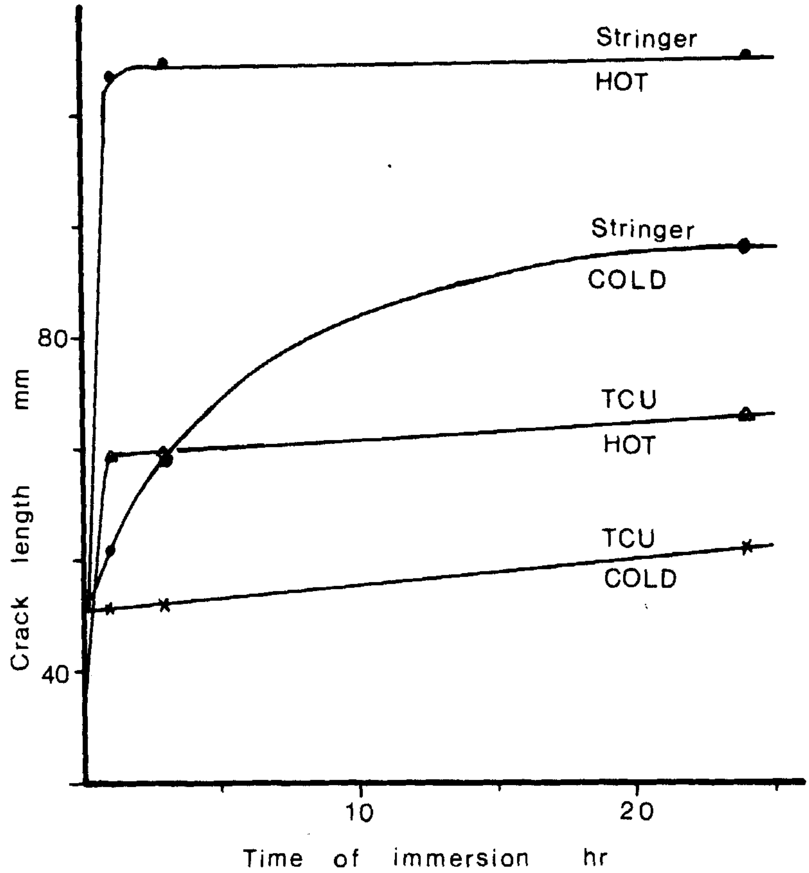

FIGURE 1 Crack lengths from Boeing Wedge Test with alloy DG FVE 232 with hot and cold etch treatments. Results from Stringer and from this investigation (TCU).

edge, was driven home into the end of the specimen using a 4 lb hammer.

The specimens were then left for one hour and the initial crack tip position was established with a low powered magnifier and was marked with a scriber on both edges. They were then immersed in water at a controlled temperature and after appropriate time intervals were withdrawn, and the new positions of the crack tips were established and marked. At the end of the immersion routine the positions of the crack tips were measured using a travelling microscope. Generally three replicate specimens were used in each case so that each distance measured was reported as the mean of six measurements: two edges of three different specimens.

Comparison of hot and cold etching

The first stage of the investigation was to repeat the work of Stringer using the two basic treatments with alloy DG FVE 232 and at the same time extend it to study the effect of the temperature of immersion during the testing.

The results of this Series I are shown in Table I and the results for immersion at 40°C are shown in Figure 1 compared with similar results reported by Stringer.[1]

TABLE I

Series I: Comparison of effects of hot and cold etching of Alloy DG FVE 232 upon durability in water at different temperatures

	Total crack length (mm) after immersion for:			
Water temperature	0 hr	1 hr	3 hr	24 hr
Hot etch				
Room temperature	40.9 ± 0.9	85.9 ± 4.1	89.7 ± 2.1	89.7 ± 2.1
40°C	33.9 ± 0.9	59.4 ± 1.6	59.9 ± 1.7	63.1 ± 1.5
50°C	52.5 ± 0.6	60.6 ± 1.2	66.3 ± 1.3	broken
Cold etch				
Room temperature	43.4 ± 3.5	43.4 ± 3.5	43.4 ± 3.5	43.5 ± 3.5
40°C	45.4 ± 1.2	45.5 ± 0.8	45.8 ± 0.9	51.0 ± 1.6
50°C	43.5 ± 0.4	48.4 ± 0.4	50.5 ± 0.9	broken

These results confirmed the pattern of behaviour reported by Stringer although the actual crack lengths obtained were all rather smaller but small differences of technique easily explain that. They also show quite clearly the effect of changing the temperature of immersion of the test. This is not just the acceleration due to increase of temperature but also the change in modulus of the adhesive due to increased adsorption of water at the higher temperature, resulting in greater plastic flow and less brittle fracture.

Effect of period of cold etching

Then the effect was investigated of changing the length of time for which the cold etching (Stage B3) was carried out. The results of this Series II are shown in Figure 2.

From these results it is quite evident that there is no significant variation in the durability of these joints with different periods of cold etching although it is noticeable that the longer the period of immersion the greater is the scatter of results. It would appear that 1 hour is probably a sufficiently long period to achieve a satisfactory treatment—2 hours certainly would be. Apart from the durability, it

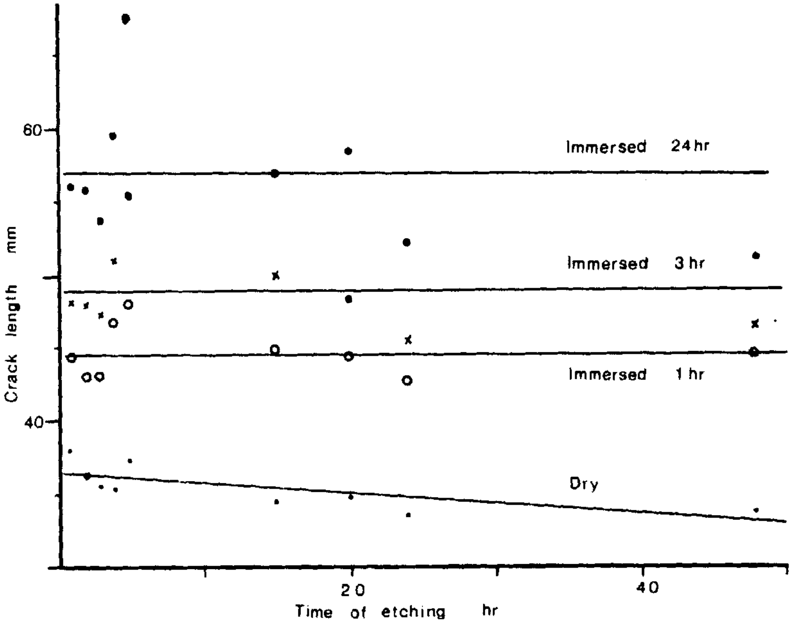

FIGURE 2 Effects of length of time of cold etching of alloy DG FVE 232 upon durability (as measured by crack length) in water at 40°C.

appears that the longer the time of etching the greater is the initial, dry strength; giving a crack length nearly 10% smaller.

Comparison of the mean of these values with those reported in Series I shows shorter initial crack length and a longer final crack length after 24 hours immersion and hence a considerably greater growth in crack length. Although this greater growth in crack length is not unexpected because of the greater cleavage stress from the shorter initial crack length, nevertheless the reason for the difference is not clear but may be due to less expertise in carrying out the tests in Series I. This is borne out by the wide variation in initial crack length obtained with that Series.

Some interest has been expressed in the possible effectiveness of simpler methods of surface preparation and these were briefly explored; firstly, by using the standard cold etching method but omitting the sodium dichromate from the etching solution (*i.e.* using sulphuric acid alone at Stage B3). Secondly, because of claims by

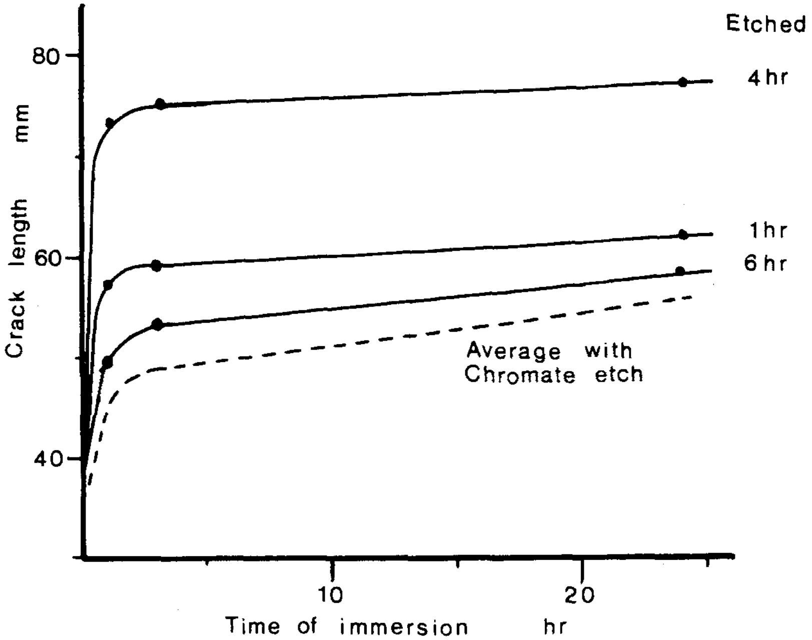

FIGURE 3 Effect of length of time of cold etching in *sulphuric acid alone* of alloy DG FVE 232 upon durability (as measured by crack length) in water at 40°C.

Tennyson Smith[3] that satisfactory and durable joints can be made with degreasing alone and no chemical treatment, a few joints were made with adherends which had been given the cold treatment up to Stage 2 only.

The results from etching with sulphuric acid alone (Series III) are shown in Figure 3 with the average result from Series II for comparison. This shows that these joints etched in sulphuric acid alone are clearly less durable, although they have reasonable initial strength and the differences are not as great as might have been expected.

The joints which had been simply degreased and not etched at all failed completely in less than one hour in water at 40°C, as did also joints made with entirely untreated, as received, metal.

Comparison of different alloys

A series of tests were carried out with the two other alloys, NS8 and L71, using the standard hot and cold etching techniques.

The results of these tests, Series IV, are given in Table II together with the best values for DG FVE 232 extracted from the previous tables for ease of comparison.

TABLE II

Series IV: Comparison of effects of hot and cold etching of three alloys upon durability in water at 40°C

	Total crack length (mm) after immersion for: 0 hr	1 hr	3 hr	24 hr
NS8				
Hot etched	31.0 ± 0.4	41.9 ± 0.6	45.0 ± 0.6	57.8 ± 1.3
Cold etched	28.3 ± 0.3	41.1 ± 0.4	44.2 ± 0.7	59.5 ± 0.6
L71				
Hot etched	37.8 ± 0.6	49.7 ± 0.9	54.3 ± 0.5	62.3 ± 0.7
Cold etched	38.3 ± 1.0	49.3 ± 0.9	52.3 ± 0.9	58.0 ± 1.1
DG FVE 232				
Hot etched	33.9 ± 0.9	59.4 ± 1.6	59.9 ± 1.7	63.1 ± 1.5 (Series I)
Cold etched	34.4 ± 0.5	44.7 ± 0.6	48.9 ± 1.0	56.9 ± 1.6 (Series II Mean)

For the two alloys examined here for the first time there seems to be little difference between the two etching techniques; indeed for NS8 the cold etching gives rather better results than the hot etching.

In this they differ in their behaviour from the alloy DG FVE 232. It might be conjectured that this is associated with the presence of zinc in DG FVE 232 which is one of the major chemical differences and this was explored and is discussed later.

Chemical composition of alloys and their surfaces

Both because of differences in behaviour of nominally identically samples of the same material and because Kinloch[4,5] had demonstrated that the presence of magnesium in the surface layers of an alloy produced joints of decreased durability, it was decided to explore the composition of the surfaces of the materials being used. Three techniques were used successively; firstly, EDAX in the electron microscope, largely because this was immediately and freely available and there was considerable experience with it. Secondly, ESCA was used and finally Auger Spectroscopy in conjunction with ion etching was used.

EDAX

Using an accelerating voltage of 40 keV gave information from a layer about 1 μm thick. This must correspond to at least 10^3 atomic layers and would penetrate considerably beyond any reasonable oxide layer (200–800 Å see later). However, it will give the general composition and may give some indication of any enrichment or impoverishment of minor constituents in the surface.

All three of the alloys were examined, and for each one three conditions were used:

i. the completely untreated surface, as received;
ii. with the surface removed by filing to expose the bulk material;
iii. after the full treatment according to the regime for cold etching for 4 hours.

The results of these are given together with the values from specifications in Table III.

Each result quoted is the mean of three determinations, each of which was made at a different place on the specimen.

TABLE III
Composition of alloy surfaces by EDAX together with values from specifications, expressed as weight percentage

	Mg	Zn	Cu	Mn	Fe
DG FVE 232					
Specification[6]	2.0	4.0	—	0.25	—
Untreated	5.0 ± 0.2	4.5 ± 0.6	—	0.31 ± 0.01	0.37 ± 0.08
Bulk	4.2 ± 0.1	5.5 ± 0.2	—	0.31 ± 0.01	0.41 ± 0.04
Etched	4.0 ± 0.1	5.4 ± 0.1	—	0.31 ± 0.07	0.58 ± 0.07
NS8					
Specification[7]	4.0–4.9	<0.4	<0.1	0.5–1.0	<0.4
Untreated	8.4 ± 0.04	—	—	0.70 ± 0.04	0.57 ± 0.06
Bulk	7.2 ± 0.04	—	—	0.63 ± 0.04	0.49 ± 0.06
Etched	6.0 ± 0.17	—	—	0.56 ± 0.06	0.49 ± 0.06
L71					
Specification[8]	0.55–0.85	<0.2	3.8–4.8	0.4–1.2	<1.0
Untreated	3.4 ± 0.1	0.49 ± 0.08	8.7 ± 1.9	1.0 ± 0.2	0.68 ± 0.08
Bulk	2.9 ± 0.1	0.29 ± 0.03	6.2 ± 0.2	0.9 ± 0.1	0.54 ± 0.03
Etched	2.6 ± 0.2	0.42 ± 0.01	6.5 ± 0.1	0.9 ± 0.1	0.61 ± 0.06

There are at first sight rather surprising differences of all the experimental results from the specifications. This may well be due to the well established difficulties inherent in deriving absolute values of composition from EDAX results and is entirely in accord with Kinloch's results.[4,5] However, as the Standard Errors of the Means show, each set of results is consistent within itself.

For the alloy DG FVE 232 there is an enrichment of magnesium and a small impoverishment of zinc in the outer layer which are reduced by etching to the value for the bulk material.

For the alloy NS8 there is similarly a greater amount of magnesium in the surface than in the bulk and etching apparently reduces this to a value lower than that in the bulk. There was no zinc detectable in this alloy.

For the alloy L71 again there are higher concentrations of magnesium and of copper in the surface than the bulk and these are reduced by etching to slightly less than that in the bulk. For zinc the total concentration and the changes are all too small to be significant.

Deductions about the surface from these results must be treated with considerable reserve since the EDAX method gives results averaged over a very thick layer of the surface and alterations in the outermost layers will be masked or minimised by lack of change in the deeper layers. Nevertheless, there is consistent evidence that during etching the increased magnesium content is removed.

ESCA

The next step was to examine the surface of one alloy DG FVE 232 by ESCA (or XPS). This method is much more surface sensitive than EDAX and examines a layer only a few (< 10) atoms thick.

The degreased but untreated alloy shows peak corresponding to (Al (2p, 2s), Mg, Zn, Ca and Fe as well as those from O(1s) and c(1s). The large C peak is due to the inevitable contamination which these sensitive techniques always reveal and the Ca peak is probably a residue from the tap-water washing. The Al (2s) peak is at 121 eV which is characteristic of the oxide rather than the metal for which it occurs at 118 eV and similarly the 0 (1s) peak at 517 eV also corresponds to aluminium oxide.

Cold etching for 2 hours removes the two magnesium peaks completely but does not appear to affect the zinc peaks at all and no difference can be detected when the cold etching is continued to a total of 4 hours.

Hot etching for ½ hour and for 2 hours does not appear to give any very different result although the zinc peaks, always quite small, are less easy to discern.

Thus overall the ESCA examination shows that either method of etching, cold or hot, more or less equally removes the magnesium from the surface layer completely; and that hot etching, but not cold, possibly removes some zinc also.

Auger Electron Spectroscopy

A set of six alloy specimens were extensively studied by Auger Electron Spectroscopy and Argon Ion Etching. This spectroscopic method examines a layer only a very few (<5) atoms thick but the Ion Etching allows the surface to be removed in thin layers and allows successive analyses to be made, to build up a concentration/depth profile for various constituents.

The six alloy specimens consisted of the three alloys DG FVE 232, NS8 and L71 each in two states; after cold etching and after hot etching according to the standard procedures already described. Each sample was examined for a range of relevant elements at various depths as the surface was progressively eroded by argon ion beam etching.

Consider first the overall qualitative data obtained after an initial (60 sec $\simeq$ 15 Å) ion etching to remove superficial contamination.

i. All samples showed Al, O, C, N, Cl, Fe and S.
ii. None of the samples showed any Cr or Mg.
iii. All the samples, except cold etched NS8, contained Ca.
iv. All the hot etched samples gave medium signals for Fe while all the cold etched samples gave very weak signals for Fe.
v. Alloy DG FVE 2323 definitely showed a little zinc in the hot etched sample and perhaps a trace in the cold etched sample.

Undoubtedly the C was remaining contamination from the atmosphere and from handling, while the Ca and Cl remained from the washing procedures. The absence of Ca in the case of cold etched NS8 is both unexpected and unexplained. It did however appear in later, deeper spectra from this specimen.

The absence of any trace of Cr shows both that there is no chemical incorporation of chromium into the surface structure and that the washing procedures have been sufficiently effective to remove all traces of the etching solutions. This does not support the view at one time advanced that trace quantities of chromium remaining in the surface are important both as corrosion inhibitors and in improving the durability of the adhesive joint.

There were small amounts of iron in the specifications of all the alloys and these had been found in the EDAX analysis. The longer acid treatment in the cold etching may have removed more of this iron than the shorter, hot etching treatment, although this does not seem very likely. A more probable explanation is that iron from impurities in the etching solution is absorbed into the oxide to an extent dependent upon the structure of this film.

Now consider the changes revealed as the ion etching progressed and the layer analysed became nearer to the bulk metal. Generally, there was a decrease in the concentration of all the elements except aluminium which, as would be expected, increased. The only exceptions to these were:

(i) the nitrogen concentration remained almost constant in the hot etched DG FVE 232,

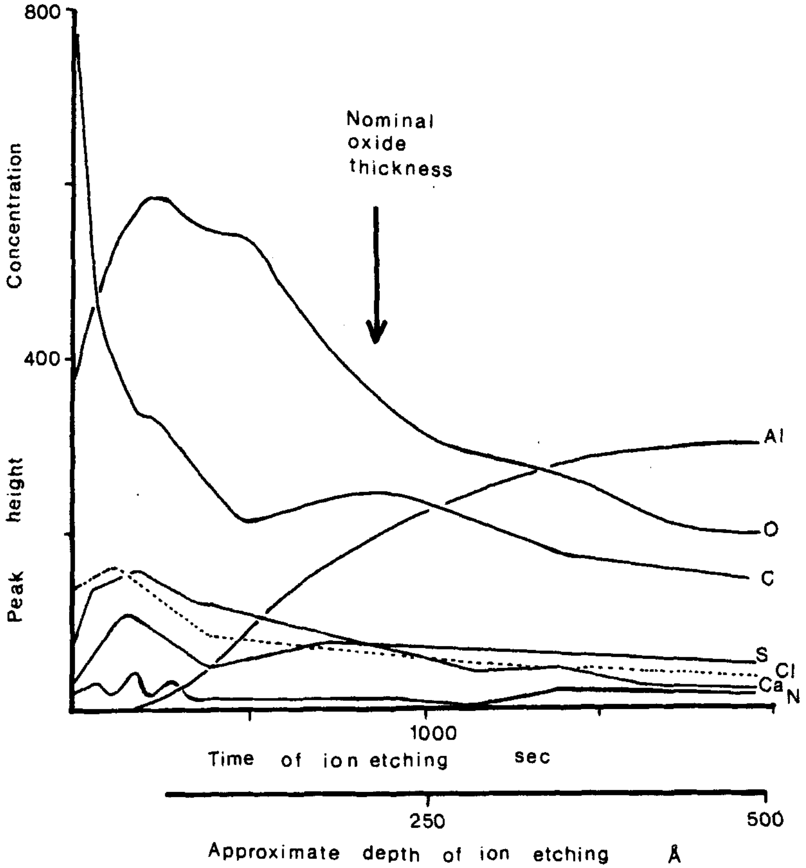

FIGURE 4 Concentration profiles of elements in alloy DG FVE 232 after hot etching as indicated by Auger Electron Spectroscopy and Ion Etching. Nominal thickness of the oxide film indicated.

(ii) the iron concentration in cold etched DG FVE 232 increased as the bulk metal was approached.

These effects are generally illustrated by the concentration profile which is given for various elements in hot etched DG FVE 232 shown as Figure 4.

A careful investigation was made to estimate the comparative thickness of the oxide films produced by the two treatments on each of the alloys. Of course there is no clear-cut and unique boundary and there are two conventions used to establish a position for a formal interface. It may be considered to be at the intersection of the graphs of peak height for aluminium metal (at 1396 eV) and for aluminium oxide (at 1378 eV); or it may be considered to be at the mid-point between the maximum and minimum of peak heights for oxygen. These two conventions do not give very different values and in the present investigation the latter convention was used. The ion etching was done with a target current of 20 Å and with a beam energy of 4 kV which gives an erosion rate of the order of 15 Å per minute. This indicated oxide film thicknesses which are shown in Table IV.

TABLE IV
Thickness of oxide films on alloys resulting from cold and hot etching procedures; established from AES spectra

Sample	Eatch time to reach metal-oxide inteface Seconds	Approximate thickness of oxide layer Å
DG FVE 232		
Cold etched	720	200
Hot etched	840	220
NS8		
Cold etched	1200	320
Hot etched	540	150
L71		
Cold etched	3120	830
Hot etched	1620	430

The general pattern emerging, as can be seen in Figure 4, is of a very thin organic layer covering the oxide film—as would be expected. Most of the other elements estimated are present in the oxide layer and do not extend to any significant extent into the bulk of the metal.

For the alloy DG FVE 232 the oxide layer is of approximately the same thickness whether it is etched by the hot or by the cold process.

For the alloys NS8 and L71 the cold etching processes give oxide layers approximately twice as thick as the hot etching process does, although the actual thickness for the two alloys are quite different.

The nitrogen concentration, although fairly small, shows a systematic change between the two etching processes and is significantly greater in each of the cold etched samples than in the corresponding hot etched samples. This effect is observed with all the alloys (including

DG FVE 232 where there is no difference in the thickness of the oxide) and strongly suggests a difference in the structure of the oxide films. The cold-formed films, being generally thicker, are diffuse so allowing a greater penetration and adsorption of nitrogen than the thinner, more compact layers produced by the hot etching process.

The two main constituents of these alloys which were of particular interest were magnesium and zinc, and it was very desirable to have concentration profiles for these, especially for magnesium in alloys DG FVE 232 and NS8 and for zinc in DG FVE 232. However, no magnesium could be detected in the Auger spectra at any depth, although it was detectable in the ESCA spectra. This evidently means that the surface had been denuded of magnesium, at least to the depth to which it had been ion etched, which varied from 500 Å to 1500 Å for the different specimens.

The concentration profiles for zinc in DG FVE 232 both cold and hot etched were rather erratic, no clear differences appeared, and no useful conclusions could be drawn.

Morphology of surfaces

It had been the original intention to study the morphology of the various surfaces by transmission techniques of electron microscopy using replicas of the surfaces in order to take advantage of the high resolution achieveable with these techniques. Considerable efforts were made but all attempts failed to remove the various types of replica from the etched surfaces. The adhesion of the films (carbon or plastic) to the metal was just too great. Thus all the morphological studies were made by straightforward Scanning Electron Microscopy (SEM) with a Jem 100B electron microscope which, in fact, yielded a very considerable amount of information.

The surface of the alloy principally studied, DG FVE 232, as received and without any treatment was quite variable. Some specimens had a covering of irregularly sloped flakes a few micrometres across which it has been suggested are hyroxide. This flakey appearance remained after etching for 4 hours at room temperature but was removed by etching for ½ hour at 62°C or 48 hours at room temperature. Other specimens had a more or less smooth appearance on which the only features were adventitious debris. With this appearance, the surface was removed and the underlying structure was reavealed in considerably shorter periods, 4 hours at room temperature was frequently, but

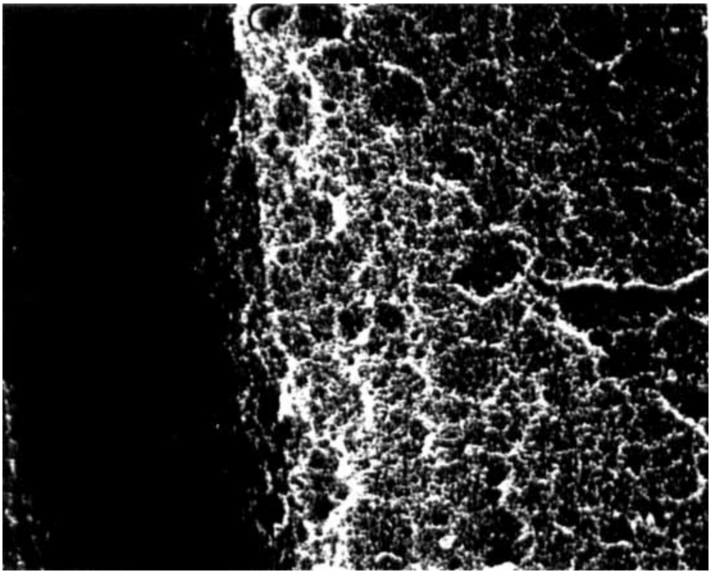

FIGURE 5 Photomicrograph × 10 K, platinum coated, of alloy DG FVE 232 cold etched.

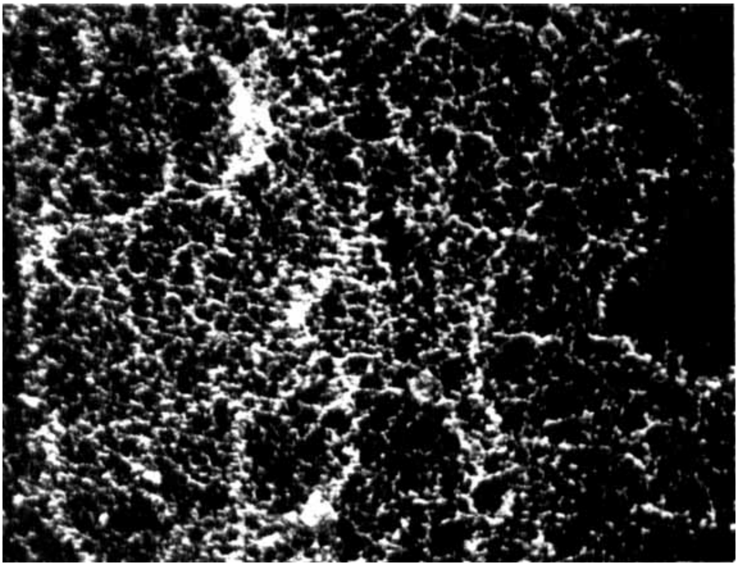

FIGURE 6 Photomicrograph × 30 K, platinum coated, of alloy DG FVE 232 cold etched.

not invariably, sufficient. Whatever the initial surface, once that had been removed then attack was clearly preferentially along the grain boundaries of the metal. All this was clear from examination either with uncoated specimens or after coating with a layer of evaporated gold and at a magnification × 1k.

To achieve a fuller understanding of the fine structure of the surface it was necessary to use platinum instead of gold for the coating, and to have the electron microscope itself in particularly good adjustment.

Stereoscopic pairs of electron micrographs of alloy DG FVE 232 which had been etched for 4 hours at room temperature and coated with platinum taken at a tilt of 12° and at × 10k and × 30k clearly showed a cellular structure with protrusions from their edges. These cells were very approximately hexagonal and 300-6000 Å across. This corresponds quite closely to that reported by Venables[9] for aluminium either FPL etched or phosphoric acid anodised where the cells are quoted as approximately 400 Å across. By good fortune one pair of these micrographs at a × 10k revealed a grain face which was inclined fairly sharply away from the main horizontal plane of view. This showed the whiskers standing out from the surface and very approximately 1000 Å long. This is similar to the structure described for aluminium surfaces which have been phosphoric acid anodised rather than FPL etched for which the whiskers are only approximately 400 Å long. These micrographs are shown in Figures 5 and 6.

Pairs of micrographs with alloy DG FVE 232 which had been etched for ½ hour at 62°C showed a structure which was generally similar but far less distinct and no information about the size of the whiskers could be deduced. Stereoscopic electron micrographs were prepared for the other two alloys but inadequate definition was achieved for useful conclusions to be drawn.

CONCLUSIONS

The first conclusion quite clearly is that for the adhesive joint properties of all three alloys examined, NS8, L71 and DG FVE 232, the results achieved after etching for 4 hours at room temperature are at least as good as those obtained by the conventional etching for ½ hour at 62°C. Moreoever this 4 hours can probably be reduced to 2 hours without any adverse result.

The improved durability with DG FVE 232 etched at room temperature instead of at 62°C, which Stringer reported,[1] is confirmed but the extent of this improvement was clearly less.

For alloys NS8 and L71 the oxide films produced by cold etching were twice as thick and absorbed significantly more nitrogen that the films produced by hot etching. For alloy DG FVE 232 the thickness of oxide films was not significantly different but the pattern of adsorption of nitrogen was similar to other alloys. This suggests that in every case, there is a difference in structure of the oxide films and that those formed by cold etching are more diffuse and less dense.

In considering the chemical composition of the surfaces, the most significant element is magnesium. The EDAX results all indicate that for the untreated alloys there is some enrichment of magnesium in the surface which has resulted from the well known behaviour of the alloys when they were first cast. This is supported by the ESCA results for alloy DG FVE 232.

Etching, either hot or cold, removes magnesium from the surface layers completely. This is shown by the ESCA results for alloy DG FVE 232, by the AES results for all three alloys, and is not inconsistent with the EDAX data. It is only for alloy DG FVE 232 that full concentration profiles from AES and Ion Etching are available and for that no magnesium can be detected down to 800 Å when cold etched, or 500 Å when hot etched (the limits of ion etching for these specimens). This result is surprising because the normal thickness of the oxide film is about 200 Å, but certainly no peaks can be seen in either of the spectra at 1117, 1142 or 1183 eV which correspond to magnesium. This must imply that the etching not only removes the original oxide coating but also attacks and removes magnesium particles from the surface of the metal to a considerable depth. As the new oxide layer is deposited so these lacanae will be filled. The existence of these "pockets" of oxide will correspond with the extension of some proportion of oxygen into the metal below the nominal boundary which is evident from the concentration profiles.

In the one alloy in which zinc is present in significant amounts, it appears to be virtually evenly distributed in depth and the chromic acid etching removes it uniformly and non-selectively.

Similarly, in the alloy which contains copper in significant amounts, there is no evidence for marked segregation or non-uniform removal by acid etching.

The oxide produced by cold etching of alloy DG FVE 232 has a hexagonal cellular structure with protruding whiskers. There is some indication that it more closely resembles that which Venables[9] describes from phosphoric acid anodising than that from FPL etching but the evidence is not conclusive.

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