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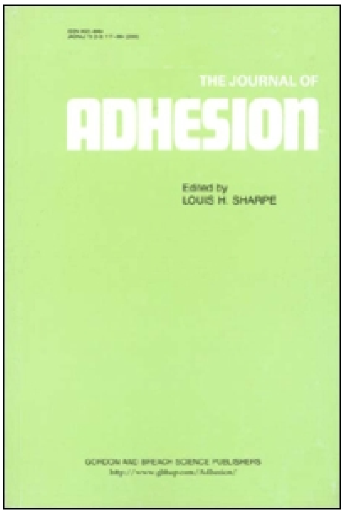

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Surface Analysis and Impact Testing of Chromate-Phosphate Treated Aluminium Alloys

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To cite this Article Maddison, A. and Critchlow, G. W.(1996) 'Surface Analysis and Impact Testing of Chromate-Phosphate Treated Aluminium Alloys', The Journal of Adhesion, 55: 3, 273 — 284

To link to this Article: DOI: 10.1080/00218469608009952

URL: http://dx.doi.org/10.1080/00218469608009952

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J. Adhesion, 1996, Vol. 55, pp. 273–284
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Surface Analysis and Impact Testing of Chromate-Phosphate Treated Aluminium Alloys

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(Received April 23, 1995; in final form July 25, 1995)

An investigation has been carried out to monitor the development of a chromate-phosphate conversion coating on aluminium adherends. Characterisation in terms of both the chemical and morphological changes induced with treatment time show this process to be capable of producing a reasonably uniform, highly micro-rough, thick, mixed oxide structure. Impact test results have been collected for exposed and unexposed joints utilising a range of differently-treated adherends. Chromate-phosphate conversion coating is demonstrated to be capable of giving much improved durability results compared with degreased-only controls when tested by impact.

KEY WORDS: Chromate-phosphate; conversion coating; chemical changes; morphological changes; micro-roughness; mixed oxide structure; durability; AES; XPS; SEM; fracture surfaces; impact; water.

INTRODUCTION

In certain applications the dynamic behaviour of bonded structures may be of critical importance. For example, the collapse of vehicle bodyshells in collision must be controlled in order to minimise deceleration forces on passengers. It follows that, under impact conditions, adhesive bondlines must remain intact to facilitate energy absorption by the plastic deformation of component panels if adhesive bonding is to be acceptable for structural applications on vehicles.

The impact test geometries specified in BS and ASTM methods use thick adherends and are often unrepresentative of real engineering structures. Alternative configurations, based on *T*-peel joints and box-sections, have sometimes been utilised.[1,2] In previous durability studies, the present authors employed short-diffusion-path lap

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* Corresponding author.

joints.[3] A similar approach has been adopted in the current work to study the effects of surface treatment conditions on impact behaviour.

The pretreatment method studied is a chromate-phosphate conversion process developed for high volume automotive applications.[4] The treatment studied in the present work is similar to the "Alcan process"; being rapid and inexpensive it is better suited to volume manufacturing applications than other more elaborate pretreatments. Furthermore, the conversion coating treatment permits subsequent weld-bonding. This is not the case with some anodic oxides.

EXPERIMENTAL

Aluminium alloys 5251 and 5083 were chosen as adherends since these are of industrial interest (Bulk composition by weight; 5251 alloy- 0.1–0.5% Mn, 1.7–2.4% Mg, 0.15% Cu, 0.4% Si, 0.5% Fe, balance Al; 5083 alloy- 0.7% Mn, 4.4% Mg, 0.15% Cr, balance Al). The adherends were 1.6 mm thick. The selected adhesive was 3M 7823 G, a single component, toughened epoxide, cured for 30 minutes at 180°C.

The following surface treatments were used:

(i) Solvent degrease plus alkaline clean (Oakite NST®, 5%, 10 min @ 50°C), and;
(ii) As above, followed by chromate-phosphate conversion treatment using a proprietary solution of Bonderite 705 (Brent Chemicals). The HF concentration was increased for room temperature (@ 22°C) operation in accordance with the manufacturer's recommendations. Treatment times were varied.

Perforted lap shear coupons, measuring 35 × 20 mm, were pretreated as described and bonded in the single lap shear configuration using the adhesive modified by a 1% addition of 160 μm ballotini for bondline control. All joints were immersed in water at 75°C, for up to 7 days. Impact testing was performed on a variable mass pendulum instrument adjusted to provide an initial impact velocity of $3.5\,\mathrm{m\cdot s^{-1}}$.

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Surface analysis was carried out using both Auger (AES) and X-ray Photoelectron Spectroscopy (XPS). AES was carried out using a Varian Auger electron spectrometer operating at a base pressure $< 5 \times 10^{-9}$ torr, with a primary beam energy of either 900 or 3000 eV and a beam current of 0.5 or 1.1 μA, depending on the sample. A spot size approximately 200 μm in diameter was used in all cases. Sub-surface information was obtained by combining AES with argon-ion bombardment using 3000 eV Ar^+ ions with a current density of $75\,\mu\mathrm{A\cdot cm^{-2}}$. XPS was carried out using a VG Escalab MkI instrument with an aluminium X-ray source. Scanning Electron Microscopy (SEM) was carried out on Cambridge Stereoscan 360 and S600 instruments. Scanning Transmission Electron Microscopy (STEM) was carried out on a Jeol GM 100CX. Some samples were gold coated prior to SEM or STEM.

RESULTS AND DISCUSSION

5251 Alloy

AES was used to determine the compositions of the conversion coating film after treatment times of 5, 15, 30 and 60 seconds. Figures 1 to 5 illustrate the compositional

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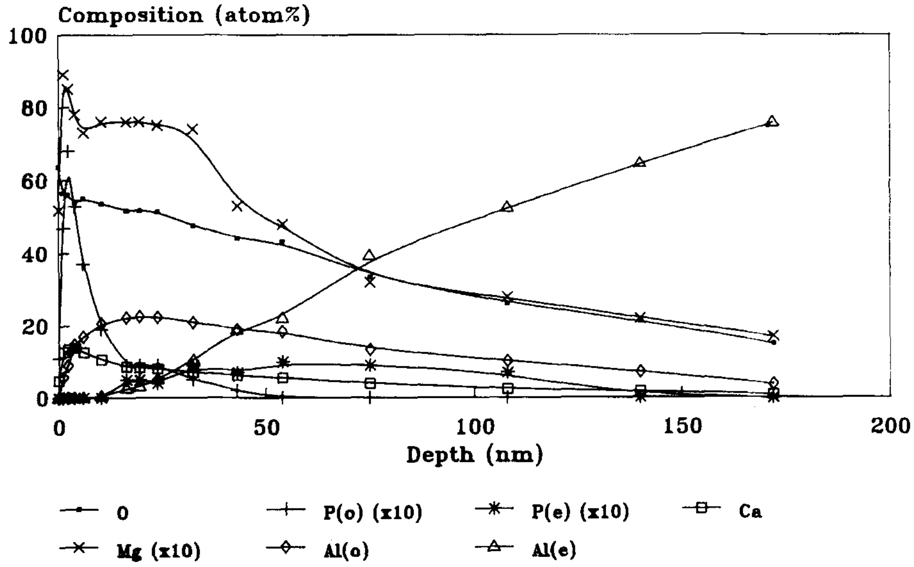

FIGURE 1 AES depth profile from a 5251 alloy coupon degreased plus alkaline cleaned.

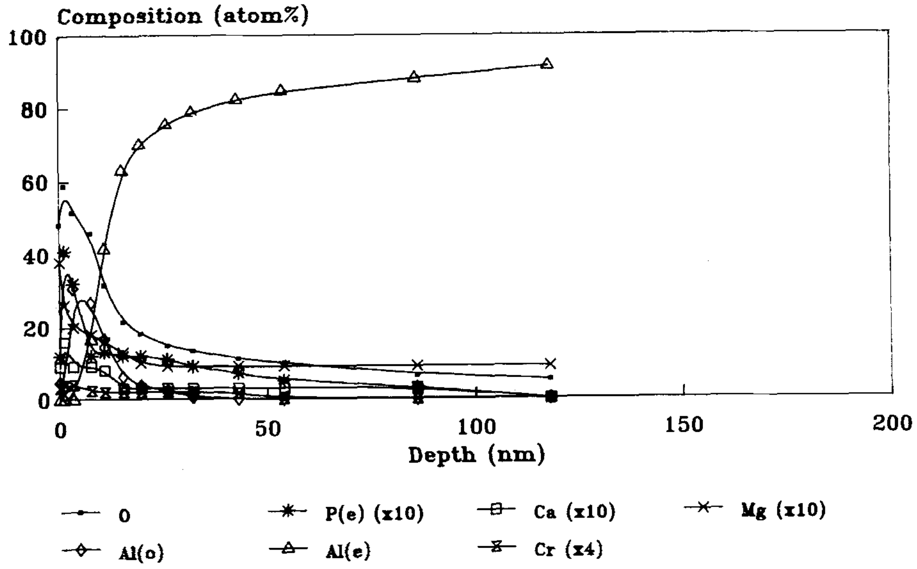

FIGURE 2 AES depth profile from a 5251 alloy coupon after a 5-second conversion coating treatment.

variations as a function of depth through the oxide. These data give a more detailed analysis of such films than has so far been presented in the literature. For clarity and ease of comparison, surface carbon has not been included in these figures, similarly magnesium has been omitted when present at bulk alloy levels, less than ~2%.

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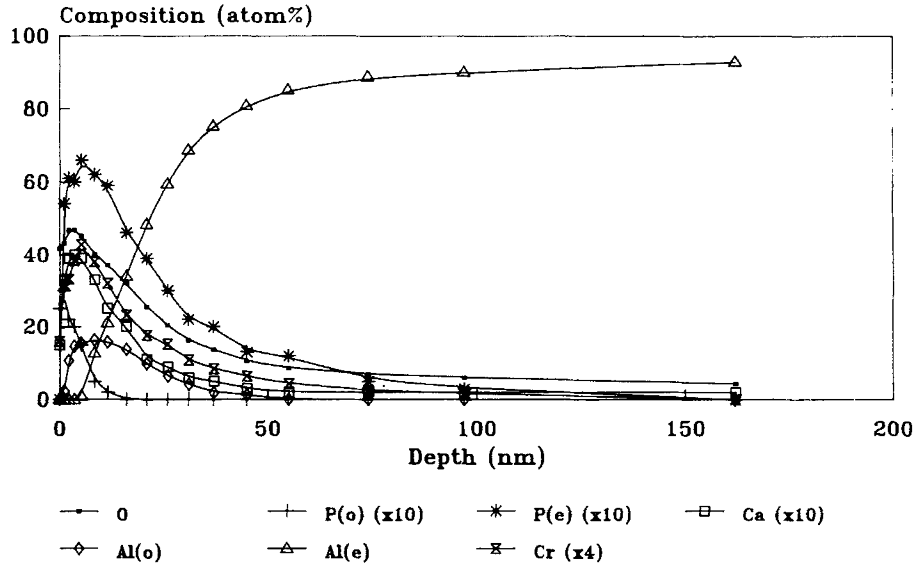

FIGURE 3 AES depth profile from a 5251 alloy coupon after a 15-second conversion coating treatment.

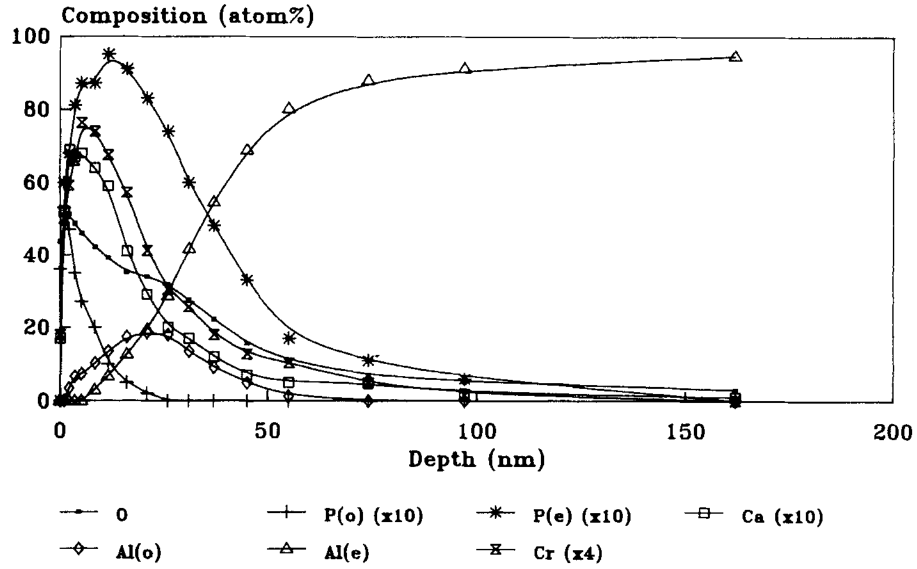

FIGURE 4 AES depth profile from a 5251 alloy coupon after a 30-second conversion coating treatment.

Compositions were based on Al_2O_3, P_2O_5 and Cr_2O_3 reference materials, whilst depth scale calibration was achieved using an etch rate determined by measuring the time taken to etch through a 1000-second conversion coating, the thickness of which was estimated from both SEM and ball cratering.[5] This depth scale calibration procedure

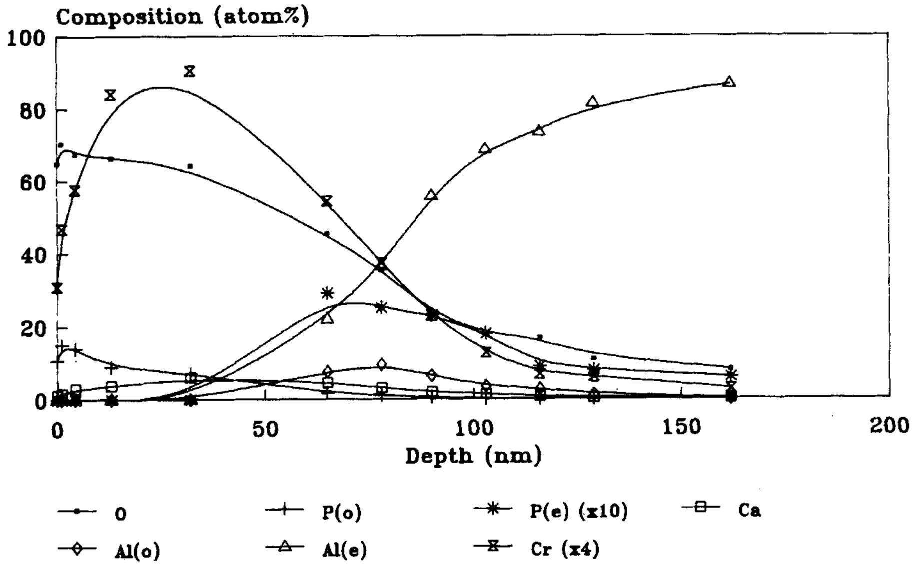

FIGURE 5 AES depth profile from a 5251 alloy coupon after a 60-second conversion coating treatment.

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was undertaken to minimise the errors previously associated with the characterisation of porous coatings on aluminium.[6] From these figures an estimated thickness for the coating present after each pretreatment can be calculated. A compilation of these is given in Table I. In the present work, the average rate of film growth for coating times up to 60 seconds is 86 nm·min^{-1}. This value compares with 96 nm·min^{-1} reported for a chromate-phosphate treatment,[7] which was carried out at 60°C.

In the AES spectra obtained from these samples, two separate oxidation states were observed for both aluminium and phosphorus. These are designated (*o*) and (*e*) in the figures, with (*o*) representing the higher oxidation state. Although electron beam decomposition of phosphorus has been observed in phosphoric acid anodised films on aluminium,[6] there was no evidence of this occuring under the electron beam conditions employed during this investigation. However, ion-beam-induced decomposition cannot be ruled out. If analogies can be made between the phosphoric acid anodic oxide and the converted oxide, then the presence of the higher oxidation state

TABLE I
A compilation of film thickness as a function of growth time

Treatment time (seconds)	Estimated coating thickness (nm)
0	102
5	12
15	22
30	34
60	86

"phosphate" component, $P(o)$, may be expected to impart good hydration resistance properties and, hence, a degree of chemical stability to these films.[8]

Fluorine could be observed, both at the surface and within all of the conversion coated films, at levels up to a few atom percent. The importance of fluorine is stressed in the film formation mechanisms proposed by both Treverton *et al.*[9] and Brown *et al.*[10] There is a disparity between the AES depth profiles in the present work and XPS depth profiles given by Treverton *et al.*[9] In the work by Treverton *et al.*[9] phosphorus levels decrease rapidly with depth, leading to the conclusion that the phosphorus is situated on the surface of the oxide particles which form the conversion coating film. In contrast, in the present work phosphorus is observed throughout the film irrespective of film thickness.

Figure 1 shows that a thick, magnesium-rich oxide is still present after alkaline cleaning in Oakite.® Comparing Figures 1 and 2, it can be seen that this oxide is removed in the initial stages of conversion coating. The developing chromate-phosphate fim can be seen to have a constant growth rate for the treatment times used.

SEM micrographs in Figures 6, 7 and 8 indicate the topography of surfaces prior to bonding. Figure 6 shows that the initial oxide after alkaline cleaning is highly variable in thickness across the surface. Figures 7 and 8 compare the 15- and 60-second treatments and show the developing conversion coating. After a 60-second treatment, a more complete film with fewer cracks is present when compared with the 15-second treatment. Neither of these coatings exhibit the same patchiness in the surface topography that was evident prior to conversion coating. Examination by STEM of

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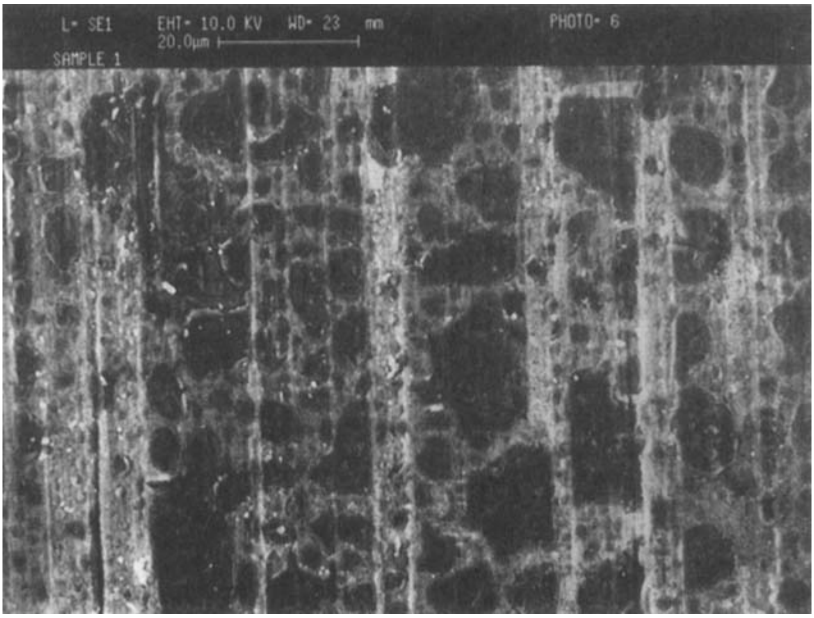

FIGURE 6 SEM micrograph of an alkaline-cleaned-only 5251 alloy coupon.

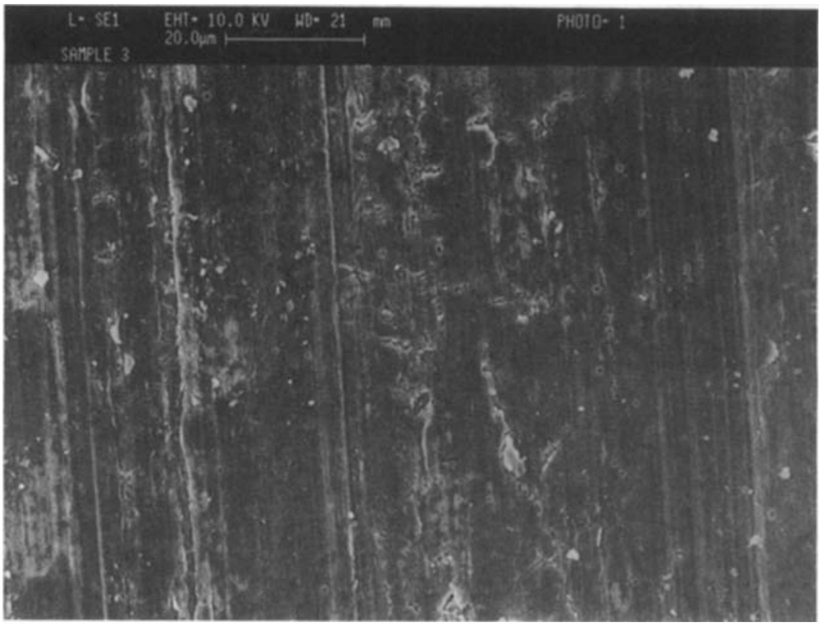

FIGURE 7 SEM micrograph of a 15-second conversion coated 5251 alloy coupon.

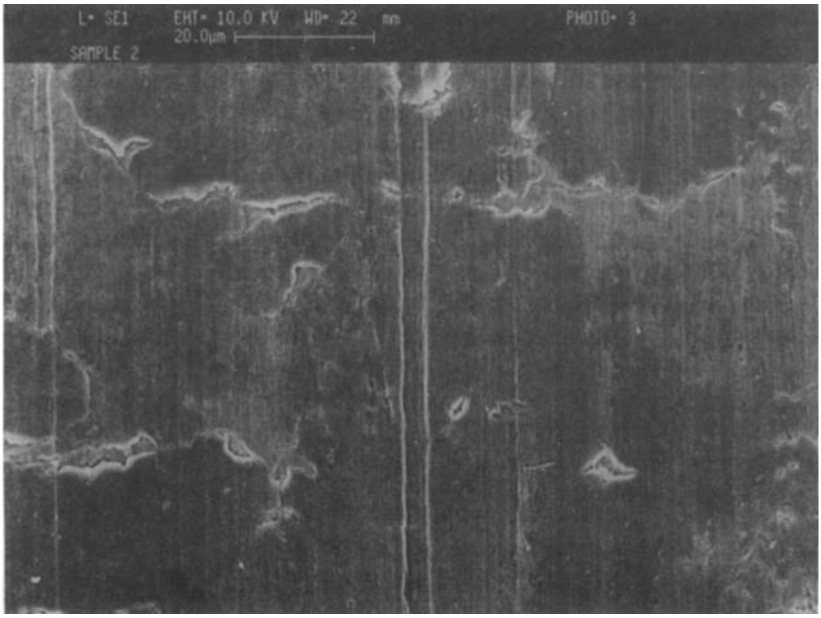

FIGURE 8 SEM micrograph of a 60-second conversion coated 5251 alloy coupon.

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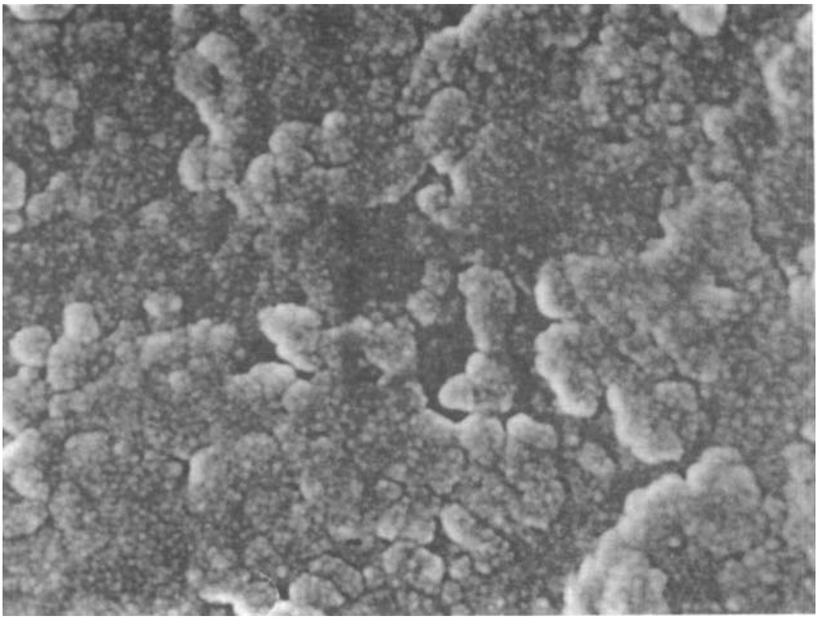

FIGURE 9 STEM micrograph of an alkaline-cleaned-only 5251 alloy coupon (x50 K) magnification).

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the oxide present after the alkaline cleaning stage and after the 60-second coating revealed comparable surface micro-roughness, Figures 9 and 10.

In preliminary bonding trials, using adherends which had been either alkaline cleaned only or alkaline cleaned plus conversion coated (treatment times of up to 60 seconds at room temperature), cohesive failures within the adhesive were observed in all cases. However, after 7 days exposure to water significant losses in energy absorption occurred. XPS was used to determine the locus of failure for both initial and exposed joints. Qualitative results from XPS analysis of fracture surfaces are presented in Table II.

In Table II, A, B and C, D and E, F are the opposing fracture faces revealed after impact testing. Results from surfaces A and B confirm cohesive failure within the adhesive when impact-testing unexposed joints, with Si and O attributable to the ballotini and with C and N associated with the epoxide. In contrast, analysis of fracture surfaces E and F indicates that after exposure to water some cohesive failure is observed within the coating since Al is observed on both surfaces. Analysis of surface C and D indicates a degree of interfacial failure in joints incorporating alkaline cleaned only surfaces, with both Al and Mg observed only on the "metal" side of the failed joint.

5083 Alloy

As with the 5251, depth profiling using AES was carried out on alkaline-cleaned-only and 1000-second conversion coated surfaces. The results show a thick, magnesium-rich oxide on the alkaline cleaned 5083 surface, similar to that seen on the 5251 alloy. The

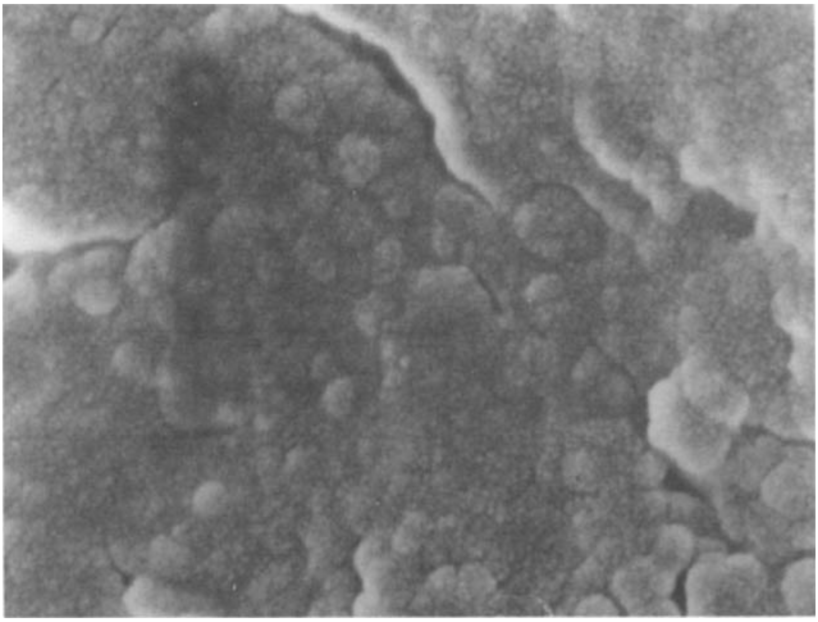

FIGURE 10 STEM micrograph of a 60-second conversion coated 5251 alloy coupon (x50 K magnification).

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TABLE II
Qualitative XPS results from fracture surfaces exposed by impact testing

Fracture surface	Treatment time (seconds)	Exposure	Elements observed
A	60	No	Si, C, N, O
B	60	No	Si, C, N, O
C	0	Yes	Si, C, P, O, Al, P, Mg
D	0	Yes	Si, C, N, O
E	60	Yes	Si, C, N, O, Al
F	60	Yes	Si, C, N, O, Al

thickness of the 1000-second coating on this alloy was measured to be ~ 0.95 μm by the ball-cratering method.[5] SEM examination of this film confirmed its thickness to be approximately 1 μm with a highly fissured coating structure, as illustrated in Figure 11.

Table III presents joint strength data obtained over the range of coating thicknesses produced on the 5083 aluminium alloy both before and after environmental exposure.

After 7 days in water at 75°C, energy absorption retention levels of approximately 30% were achieved on converted surface, compared with the 6% value found with alkaline cleaning only. Severe porosity was observed within the adhesive layer in specimens with the thickest coating. This is associated with the markedly reduced initial performance. It is suggested that evolution of water vapour had occurred from

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TABLE III
Effects of conversion treatment on the energy absorption of both initial and exposed joints

Surface treatment	Energy absorption	
	Initial	Exposed
Alkaline clean only	5.0	0.3
Chromate-phosphate-1 second	6.2	1.7
Chromate-phosphate-10 seconds	5.6	1.6
Chromate-phosphate-100 seconds	4.6	1.6
Chromate-phosphate-1000 seconds	1.2	0.5

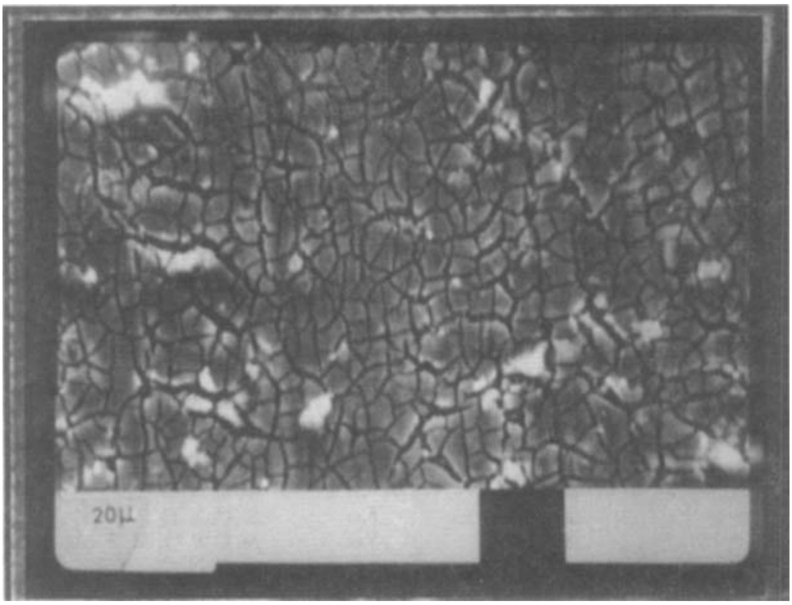

FIGURE 11 SEM micrograph of a 1000-second conversion coated 5083 alloy coupon.

the thick chromate-phosphate film at elevated temperatures. It is recognised that further work needs to be undertaken to confirm this mechanism.

Of particular interest is the cohesive failure observed within the 1000-second film after exposure. SEM revealed areas where detachment of the coating had occurred, as indicated in Figure 12. AES analysis carried out in such a region showed the film to be much thinner than that present on the unbonded sample. This is confirmation of failure within the coating after what might be regarded as an excessively long treatment time. Similar analyses of coatings of intermediate thickness are in progress in order to extend our understanding of the relationship between coating composition and dynamic behaviour after exposure to adverse environments.

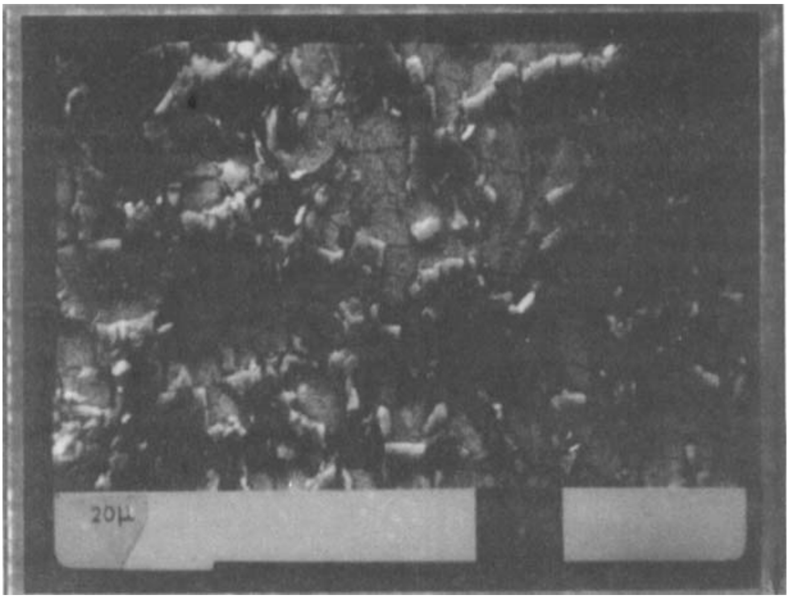

FIGURE 12 SEM micrograph of the metal fracture face after a 1000-second conversion coating treatment, exposure and impact testing.

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CONCLUSIONS

Surface characterisation of chromate-phosphate treated aluminium alloy coupons shows that the removal of the surface oxide is followed by controlled film formation. The surface film comprises a highly complex oxide structure which is relatively uniform in its coverage, highly micro-rough and thick, up to ~ 1 μm. These conclusions are in good agreement with those obtained by other workers investigating the effects of chromate-phosphate treatment on commercially pure (99.5%) aluminium.[9,10] It has been established that (as with crack propagation, peel and static shear tests) the impact behaviour of bonded aluminium is significantly influenced by surface treatment and environmental exposure.[11–16] The chromate-phosphate treatment investigated was shown to improve markedly the durability of adhesive bonds to aluminium alloys, although there is evidence that cohesive failure of the coating may occur, particularly once reasonable process tolerances are exceeded. Comparative trials using adherends treated with a "high performance" treatment, for example, the Boeing Aircraft Co., BAC5555 phosphoric acid anodise, need to be carried out to evaluate fully the performance of this treatment. More extensive durability trials utilising these adherends and surface treatments exposed to harsh service environments are in progress.

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