Loughborough University

This item was submitted to Loughborough's Institutional Repository (https://dspace.lboro.ac.uk/) by the author and is made available under the following Creative Commons Licence conditions.

creative commons

COMMONS DEED

Attribution-NonCommercial-NoDerivs 2.5

You are free:

- to copy, distribute, display, and perform the work

Under the following conditions:



Attribution. You must attribute the work in the manner specified by the author or licensor.



Noncommercial. You may not use this work for commercial purposes.



No Derivative Works. You may not alter, transform, or build upon this work.

- For any reuse or distribution, you must make clear to others the license terms of this work.
- Any of these conditions can be waived if you get permission from the copyright holder.

Your fair use and other rights are in no way affected by the above.

This is a human-readable summary of the Legal Code (the full license).

Disclaimer

For the full text of this licence, please go to:
http://creativecommons.org/licenses/by-nc-nd/2.5/

ENVIRONMENTALLY-FRIENDLY SURFACE TREATMENTS

Gary Critchlow*, Keith Yendall, Tim Cartwright and Ian Ashcroft

Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK.
**Email: g.w.critchlow@lboro.ac.uk Tel: +44 (0)1509 222949*

ABSTRACT

The presentation will focus upon both existing and novel developmental processes for the replacement of the hexavalent chromium containing 40/50V Bengough-Stuart anodise (CAA), with particular emphasis on their resultant performance in structurally bonded systems. Two systems of particular interest are based upon a phosphoric acid based electrolytic deoxidiser (EPAD) studied in combination with a standard sulphuric acid anodise and an alternating current-direct current phosphoric-sulphuric (ACDCPSAA) anodise in a benign electrolyte. It has been shown that the EPAD provides an open porous structure in order to enhance adhesion to the modified sulphuric acid anodised (SAA) surface. Additionally, a post anodising (PAD) treatment has been used to further aid structural adhesion in combination with the aforementioned processes. As a control, the standard 40/50V Bengough-Stuart chromic acid anodising (CAA) has been used as a baseline performance indicator in adhesion tests. Adhesion levels have been established using single lap shear and modified wedge test configurations. Overall, excellent initial joint strengths and durability have been found with both EPAD and ACDCPSAA, suggesting that these environmentally benign treatments may be used as possible drop-in replacements for the currently used CAA process.

1 INTRODUCTION

Boeing's phosphoric acid anodising (PAA) process [1] is widely used for the pretreatment of aluminium alloys within adhesively bonded structures. With the replacement of the Forest Products Laboratory (FPL) etch in the anodising line with a hexavalent chromium free alternative [2], this has solved many of the problems associated with the ever increasing regulations enforced by both national and local authorities. However, the PAA route has never been favoured within Europe due to the reportedly superior bond durability of structures formed using chromic acid anodising (CAA) relative to PAA in corrosive environments [3]. Furthermore, CAA has other advantages having been shown to have approximately twice the anodising throwing power and generating higher peel strengths, in bonded structures, compared to PAA [4].

As a result of the above, there is ongoing development of surface treatments which offer the performance of the standard Bengough-Stuart CAA process but without the shortcomings of either CAA or PAA. An example of this is the boric sulphuric acid anodising (BSAA) method, another Boeing patented process [5]. BSAA has been successfully used as a pretreatment to paint adhesion [6,7] and with further modifications to the processing parameters has shown excellent bond strength and durability for secondary and primary structural bonding of aerospace alloys [8-10]. However, it should be noted that the current BSAA specification still requires the use of a dilute chromate hot seal to achieve satisfactory corrosion resistance to salt spray testing as set out by current military specifications [11].

Although a number of other prebond treatments exist [12], there is still a lack of industrial confidence in the current chromate-free anodising and related processes proposed for adhesive bonding. Although this is certainly true of the aerospace industry this philosophy is carried through much of the manufacturing sector including automotive where sulphuric acid anodising (SAA) is preferred due to its increased barrier corrosion protection. Overall, however, all of these processes are not generally regarded as performing as well as CAA . This is, in part, due to the limited full scale certification of any process for use in either civil or military applications. To a lesser extent this situation can also be applied to the automotive industry.

Historically, the aforementioned SAA process has been used for decorative, corrosion protection or wear resistant applications or on non-structurally bonded aluminium parts in aerospace manufacturing. However, due to the relatively thick oxides and consequently high coating weights conventionally deposited using SAA, there is a limit to the fatigue performance of any SAA processed aluminium to standard specifications. Furthermore, despite the ability to achieve good initial bond strengths, adhesion to such processed surfaces has been restricted due to the relatively poor durability that these bonds exhibit under hot humid environmental conditions [12]. Also of note is the high profile application of SAA in automotive bonding, for example, in space-frames [13]. The lack of confidence in this instance manifests in terms of the use of self-piercing rivets used in combination with the adhesive, forming combination or hybrid joints. To overcome this limiting factor, work has been carried out using SAA hard anodised surfaces with the addition of a surface modification using a phosphoric acid dip (PAD) technique. This has been shown to produce a more receptive surface for adhesive penetration and offer improved bond durability [12,14,15].

From an understanding of the role of pre- and post-treatment of anodic oxides it is possible, in principle, to improve upon existing SAA processes in terms of their applicability as stand-alone pretreatments prior to adhesive bonding. This work aims to produce anodic films based upon SAA-containing electrolytes but with significant pre- and post-anodising stages and variable anodising bath conditions which modify the SAA oxide to provide equivalent adhesion performance to that of the currently used CAA oxides without the fatigue and other issues associated with standard SAA processing. Two separate studies will be detailed in the following sections; firstly, the use of electrolytic phosphoric acid deoxidising (EPAD) and phosphoric acid dipping (PAD) on SAA films, and secondly, the application of ACDC phosphoric-sulphuric acid anodising (ACDCPSAA). In the latter case, the intention was to use the porosity associated with AC anodising to create an outer oxide layer, which offers high levels of intrinsic adhesion, and the dense oxide produced by DC anodising to give satisfactory barrier corrosion resistance by preceding DC with AC anodisation in a two stage process. The single electrolyte chosen was a mixture of phosphoric and sulphuric acids. The phosphoric acid content was intended to promote the inclusion of phosphates in the oxide film therefore enhancing the hydration resistance. The large film thicknesses associated with SAA made it attractive in that this electrolyte would be expected overcome the poor barrier corrosion protection offered by PAA alone.

2 EXPERIMENTAL AND RESULTS

2.1 Electrolytic phosphoric acid deoxidising (EPAD)

2.1.1 Materials and Processing

The substrates chosen for this investigation were 2024-T3 aluminium alloy in both bare and clad forms. All substrates were given a minimum surface pretreatment consisting of a degrease in acetone with ultrasonic agitation followed by an alkaline clean by immersion for 10 minutes in a proprietary solution of Isoprep 44 (MacDermid Inc.) before subsequent deoxidising. The Isoprep 44 was heated to 60ºC. Substrates were subsequently hard rinsed in tap water and air dried. Electrophosphoric acid deoxidising (EPAD) was carried out in a 20% (wt) phosphoric acid solution, operated at 30°C with an applied anodic potential of 7.0±2V for ten minutes. A sodium hydroxide solution of 40g/l was used as an alternative deoxidiser, the solution was maintained at 60ºC. This was followed by a nitric acid (50:50) dip for a period of approximately two seconds at 23ºC. All deoxidising treatments were followed by a three minute rinse in deionised water prior to anodising.

Sulphuric acid anodising was carried out in either a low concentration, 40g/l solution or a “standard” concentration of 140g/l, operated at 26°C or 35°C. Mechanical agitation was used during anodising which was carried out at a potential of 15V. The subsequently applied phosphoric acid dip (PAD) was carried out in 20% (wt) phosphoric acid at 30°C for various treatment times. This was followed by a three minute rinse in deionised water and an air dry. CAA was carried out according to a Bombardier Aerospace P.SPEC.410, which consisted of a vapour degreasing using trichloroethylene followed by an alkaline clean in Isoprep 44, as discussed above. An ‘optimised’ FPL etch was then used during the deoxidising stage followed by a three minute rinse in deionised water. Finally, anodising using a bath concentration of 30.5 to 50.0g/l chromic acid at a temperature of 40°C and a 40/50V potential operating cycle for 45 minutes was applied. As previously, rinsing and drying stages were also carried out. Field emission gun scanning electron microscopy (FEGSEM) was carried out on all modified surfaces to determine the topographical changes introduced by the various treatments; FEGSEM results follow.

Adhesion testing was carried out using FM 73M / BR 127 epoxide system from Cytec Engineered Materials Ltd. The FM 73 film adhesive is a toughened general purpose aerospace epoxide. The BR 127 primer is a modified epoxy-phenolic consisting of 10% solids including 2.0% strontium chromate as a corrosion inhibiting additive. The primer is again classified as a general purpose aerospace product. The manufacturers recommended cure schedules were used. A modified Boeing wedge test [15] configuration was used. For the wedge test joints, both the initial crack lengths after stabilisation and subsequent crack extensions, following immersion in deionised water at 60ºC were monitored.

2.1.2 Surface Characterisation-Results

As indicated by field emission gun scanning electron microscopy (FEGSEM), both clad and bare CAA 40/50V treated surfaces had relatively uniform oxide or hydrated oxide films present, with few voids within in the coating. The scalloped texture produced from the deoxidising process is evident on all final anodised surfaces. This is evident at higher magnification on the 2024 alloys, figures 1(a) and 1(c)

A noticeable difference in oxide structure between clad and bare alloys can clearly be seen from Figure 1. The oxide produced on the 2024-T3 clad material being columnar in structure, perpendicular to the metal surface with some branching and termination of columns, as seen in cross-section, Figure 1(d). Also, the expected well defined pores are present on the clad alloy. These pores range from approximately 15 to 30nm in diameter in the surface region. On closer inspection the expected a hexagonal pore arrangement is not present. Furthermore, it is evident that a number of pores have merged with their nearest neighbours to produce the characteristic branching. Previous work [16] has show this oxide structure to also be present on 7075-T6 clad alloy, which has not been studied here. In the case the 2024-T3 bare alloy there is no evidence

of any columnar structure. Instead, there exists a less ordered non-porous formation; see Figure 1(a). This can be further seen in cross-section, where the anodised oxide has a very nodular arrangement resembling an inverted “sponge” in texture comprising a collection of nanospheres of oxide (or hydrated oxide); see Figure 1(b). It is possible that the more densely packed anodic oxide produced on the bare compared with the clad alloy may inhibit the primer/adhesive penetration characteristics in the former case.

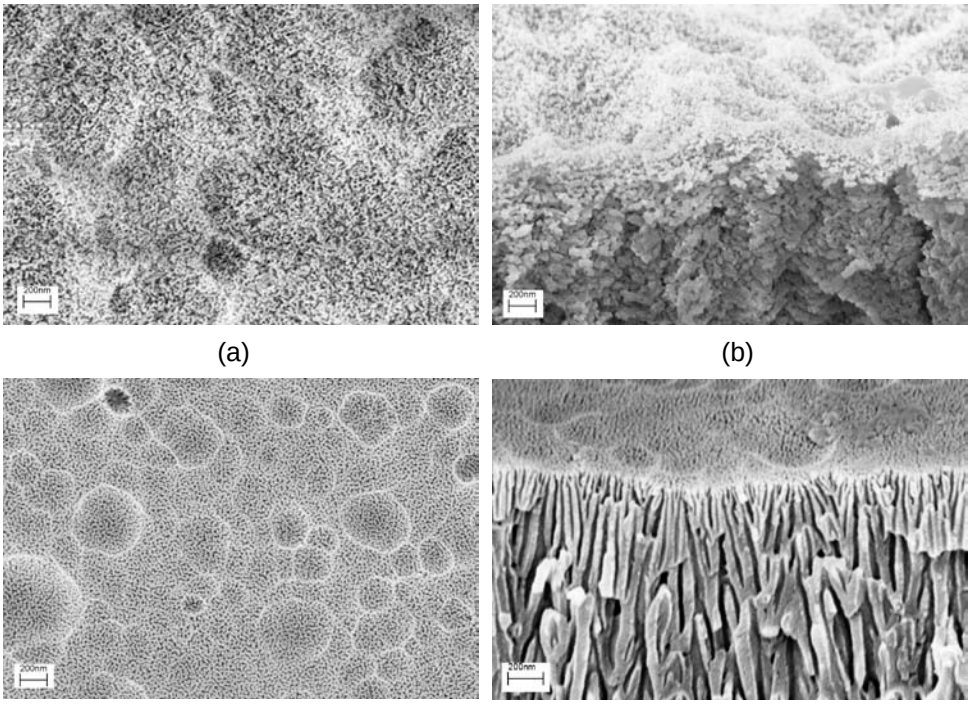
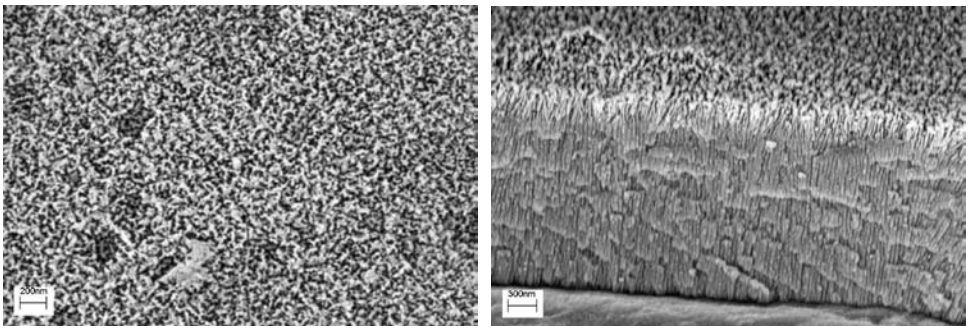


Fig. 1: CAA 40/50V processed, 2024-T3 bare; plan view (a) and cross-section (b), 2024-T3 clad; plan view (c) and cross-section

A feature of interest with the clad material, shown in cross-section, is the way the columns and hence the pores are smaller in diameter and more closely packed at the surface of the film than they are adjacent to the base metal. This many explain why some studies have shown PAA, with its more open pore structure, to have superior bond strength and durability to that of CAA when a primer application is omitted. This then would suggest good penetration of the primer/adhesive system into the oxide is paramount in achieving superior adhesive bonds. In the case of the CAA oxide, the lower viscosity primer can penetrate these pores at the surface whereas a less viscous adhesive is unable to overcome the capillary forces.

The EPAD and SAA processed 2024-T3 clad alloy displays a fibrous surface topography, figure 2(a). In cross-section, figure 2(b), there is a clear duplex oxide evident. The upper oxide film being the result of the phosphoric acid electro-deoxidising. The purpose of this electrodeoxidising stage is to undermine contamination and scale, through an oxide formation and dissolution mechanism in order to leave a clean, uniformly thin compact oxide, ready for subsequent anodising [2]. As shown here, it would appear that an anodic oxide film, approximately 200nm in thickness has remained, which is open and nodular in appearance. This structure has not previously been reported in the literature. One explanation would relate to work carried out by Venables [17] who noted that “an FPL oxide dissolves completely within 30 seconds after immersion in a PAA electrolyte”. If this is also true for a electro-deoxidised oxide when immersed in a PAA solution, then this structure is unlikely to be seen in the final anodised film. The possible difference with this study being the

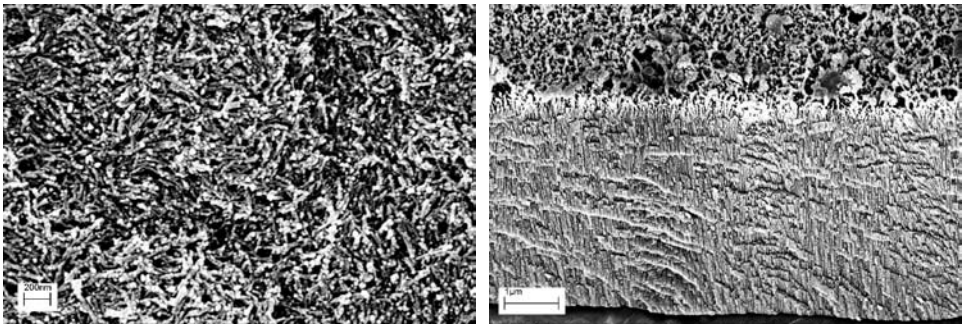
reduced dissolution power of the SAA electrolyte, relative to that of PAA. Such that any oxide produced during the deoxidising stage will remain and any subsequent SAA oxide formation will then be “grown” from underneath the remaining film.



(a) (b)

Figure 2: Plan view (a) and cross-section (b) of 2024-T3 clad alloy EPAD and SAA

The underlying film of the duplex oxide, figure 2(b), as mentioned, produced during the SAA stage, displays a columnar structure, similar to that seen for CAA 2024-T3 clad alloy. However, the SAA oxide structure is finer, more even, and non-branching than that of the CAA oxide. In addition, there are fractures, perpendicular to the direction of growth in localised planes, caused during sample preparation. This may indicate some differences in mechanical properties between the SAA and CAA oxides. With the addition of a PAD stage at the end of the EPAD and SAA process, figure 3(a), it can be seen that the PAD has etched away the top surface increasing the available, open topography even further. In cross-section, figure 3(b) the underlying oxide is left unaffected so corrosion integrity should remain unaffected.



(a) (b)

Figure 3: Plan view (a) and cross-section (b) of 2024-T3 clad alloy EPAD, SAA and PAD

A point of interest with PAA oxides is their inability to seal or hydrate in the same way that CAA or SAA oxides are known to, due to the inhibiting phosphate species incorporated in the oxide. As such, it is hoped that the oxide produced during the electro-deoxidising stage will remain “open” and receptive to the adhesive/primer and the underlying SAA oxide will seal to provide substantial corrosion resistance.

2.1.3 Mechanical Testing-Results

The modified wedge test results are presented in figure 4. Taking the CAA 40/50V process as a baseline it can be seen that the initial crack extension, I_0 for all the surface treatments are broadly similar with values close to 25mm. However, when exposed to hot, humid conditions and monitored over set periods of 5, 24 and 100 hours exposure time, differences start to emerge. The CAA 40/50V process developed a total crack extension

of 35mm over the total exposure time of 100 hours. For the 2024-T3 clad alloy deoxidised using sodium hydroxide only the results vary depending on the subsequent anodising treatments. It appears that both the lower temperature, 26°C and also the higher concentration, 180g/l parameters are detrimental to the formed oxide, in terms of a bond durability when combined with the sodium hydroxide deoxidise, even with the use of an additional PAD treatment, with total crack extensions for these surface treatments ranging from 40 to 70mm after 100 hours exposure. The two systems incorporating the sodium hydroxide deoxidise that did show comparable crack extension to that of the CAA 40/50V process where the SAA 40g/l concentration at 35°C and the same parameters with a final PAD treatment, giving total crack extensions after 100 hours exposure of 37 and 34.5mm respectively. In the case of the anodising systems using the electrodeoxidiser, all but the 40g/l concentration, 26°C temperature SAA, showed equivalent bond strength durability to that of the CAA 40/50V process. Using XPS, all anodised specimens showed crack propagation in the region from insertion of the wedge to I_0 to be cohesive failure within the adhesive. Furthermore, a trend emerged where for all crack extensions up to approximately 35mm the failure mode moved from the adhesive towards the primer/adhesive interface. In the case of both the sodium hydroxide deoxidise and SAA 40g/l, 26°C with or without PAD and also the sodium hydroxide deoxidise and SAA 180g/l, 20°C with or without PAD, failure was predominately cohesive within the oxide layer. The above wedge test results suggest that the predominant oxide feature to promote good bond durability is that where the upper 200nm of the oxide film is open and receptive to any adhesive primer application, as in the case of all the pretreatments using the phosphoric acid electrodeoxidiser. However, the underlying oxide still plays a role. From the inferior bond durability of the electrodeoxidised specimens which are then combined with the SAA using 40g/l and 26°C. Here a less dense porous oxide is expected to be formed, in comparison to either a higher temperature or increased concentration anodising bath, where both parameters would be expected to increase the dissolution of the pore walls and produce larger pore diameters. This would indicate that primer penetration needs to be achieved further into the oxide than just the first 200nm. This also holds true for the sodium hydroxide deoxidised and anodised specimens, where in this case the outermost oxide film will be formed during the anodising. Only the increased solution temperature of 35°C is sufficient to provide the open pore structure required for good primer penetration, where an additional treatment of PAD only serves to increase this desired surface feature even further.

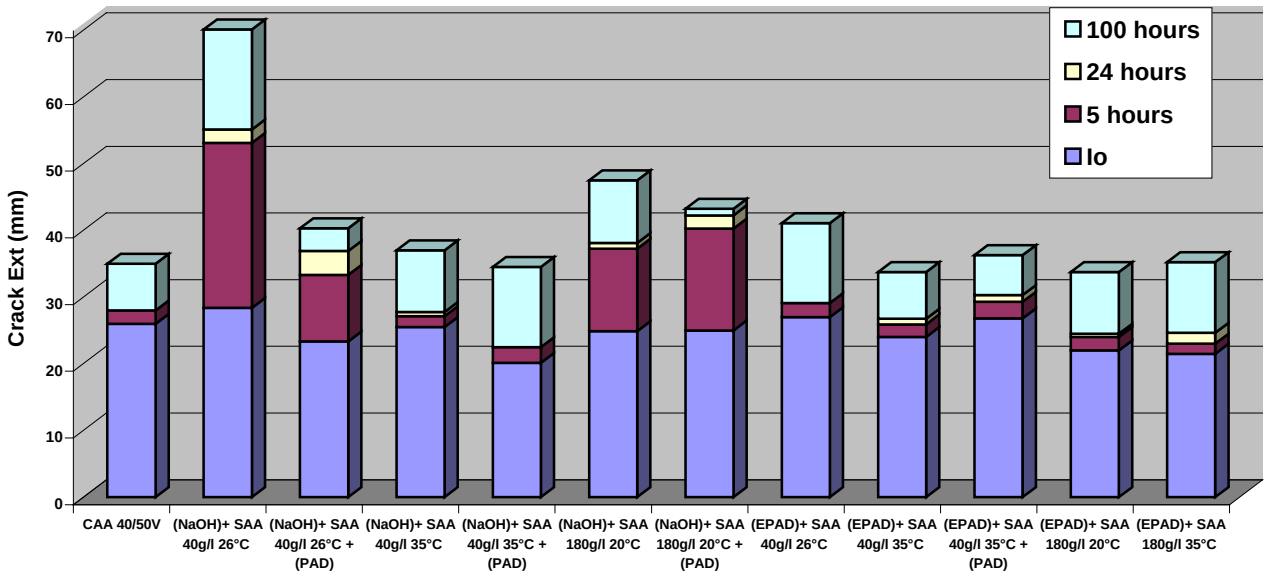


Figure 4: Summary of wedge test crack extensions using 2024-T3 clad alloy

2.2 ACDC phosphoric-sulphuric acid anodising (ACDCPSAA)

2.2.1 Materials and Processing

The same alloys, adhesives and test procedures were used for this part of the study as detailed in *Section 2.1.1*. Extensive trials were carried out to vary the anodising conditions by modifications to the electrolyte, voltages, temperatures and times. Some aspects are summarised below.

2.2.1 AC Film Development

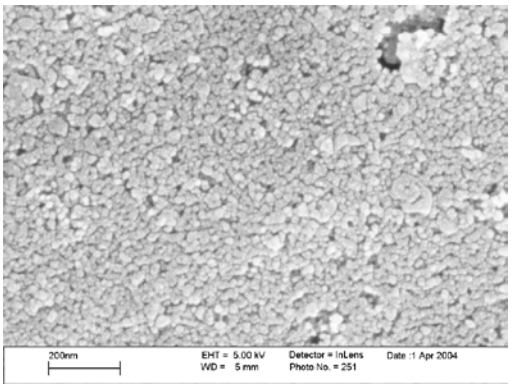
FEGSEM was again used to provide detailed information on the development of the oxide surface as it forms during AC anodising. Figure 5 shows 2024-T3 clad aluminium alloy anodized in a 2.5%SA and 2.5%PA electrolyte. The AC voltage applied was 15 V for periods up to 240 s with plan view FEGSEM images being completed for anodising times of 0 (degreased-only sample), 5, 30, 120 and 240 s. Importantly, after only 5s of AC anodizing a highly modified surface structure becomes apparent, this develops with time to 120 s where the fully porous structure is clearly evident. Pore widening then occurs with time up to 240 s with the final pore diameter very approximately 30+ nm.

Considering other parameters, FEGSEM observation of the morphology of these oxides in cross-section indicates that there are four major variables governing the composition and structure of the oxide. These are; the anodising time, the electrolyte temperature, the applied anodising voltage and the electrolyte composition. Two of these variables, voltage and temperature, form part of the thermodynamic system as they both have a kinetic effect on any reactions taking place. The applied voltage drives the oxidation reaction while the electrolyte temperature has an influence on the solvent power and the electrical conductivity of the electrolyte. An increase in the AC anodising voltage generally increases the thickness of the composite ACDCPSAA oxide. This effect is not without drawbacks, increasing the voltage too much causes localised burning of the oxide film, a highly undesirable effect. The use of alternating current enhances the field assisted dissolution of the anodic film which has a marked effect on the pore diameter of the oxide grown during AC anodising.

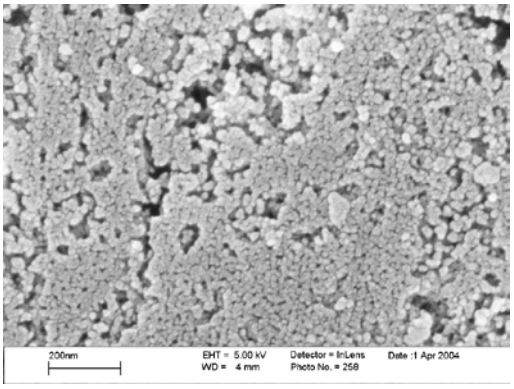
2.2.2 DC Film Development

The inclusion of a DC anodising stage into the process specification is intended to provide the overall oxide film with barrier corrosion protection properties. The initial aim was to grow a DC oxide extending to approximately 1 µm, this value being approximately twice the thickness of the standard PAA process and approaching the thickness of the standard CAA process.

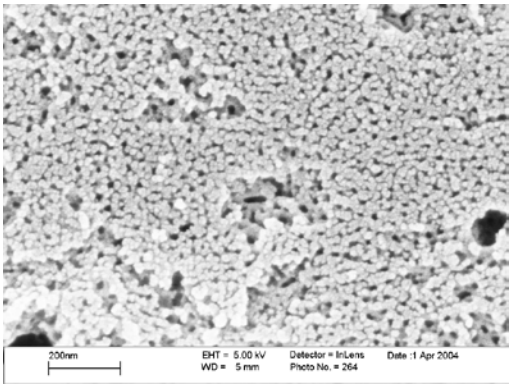
FEGSEM clearly shows that a DC oxide of approximately 1 µm can be easily grown in an electrolyte comprising 2.5% by volume of both phosphoric and sulphuric acids. This figure is achieved by anodising at 20 V DC for 10 min. Coincidently, the thickness achieved after this time appears to be the limiting thickness for this particular electrolyte/voltage combination with no further film thickening occurring by further anodisation. Figure 6 illustrates measurements taken from FEGSEM images.



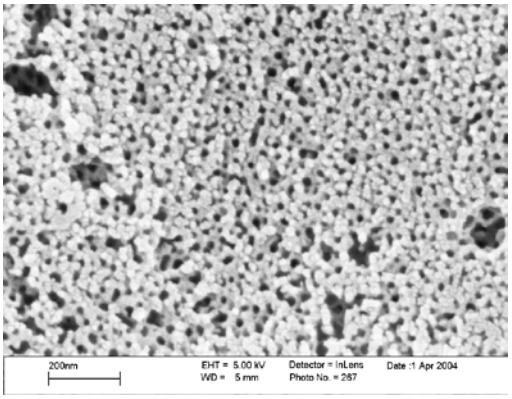
(a) – 5 s



(b) – 30 s



(c) – 120 s



(d) – 240 s

Figure 5 (a – d) – FEGSEM micrographs showing the development the AC anodised 2024-T3 clad aluminium alloy surface with application periods ranging from 0 to 240 s in the phosphoric/sulphuric acid electrolyte

The oxide properties of the various anodising parameters investigated in the DC part of the ACDCPSAA process whilst using a constant electrolyte concentration of 2.5% by volume of each phosphoric and sulphuric acids. The underlying DC anodising component was fixed at 20 V for 10 min. There are two main observations:

1. For the same voltage there is a net increase in film thickness with temperature.
2. For the same voltage there is a net increase in pore diameter with temperature.

These two points provide evidence that there is a possibility to nanoengineer specific surface properties.

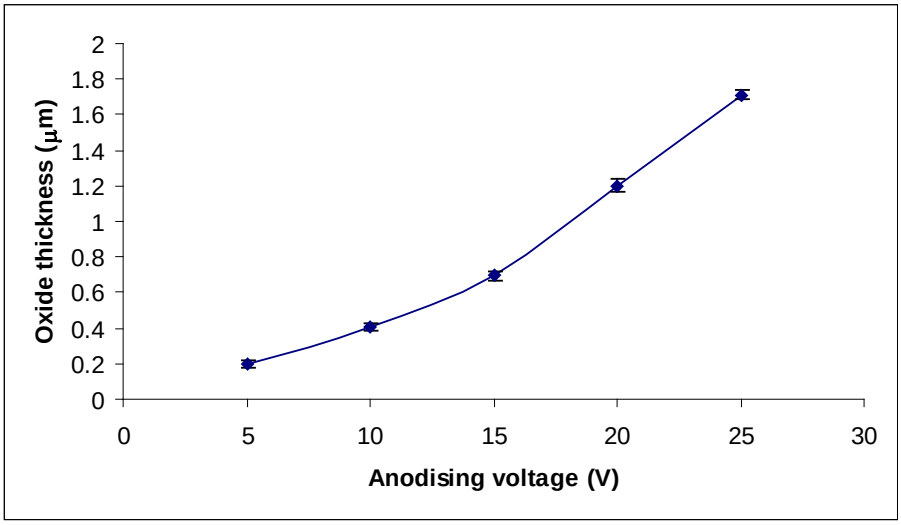


Figure 6 - Graph indicating the DC oxide film thickness on 2024-T3 clad aluminium alloy as a function of the applied anodic voltage for a period of 10 min in the phosphoric/sulphuric acid electrolyte,

2.2.3 Combined ACDC PSAA

A number of observations were made when combining the optimized AC and DC procedures. Firstly, the conductivity of the electrolyte is clearly a function of temperature so as the anodising temperature rises, so too does the conductivity and with it the oxidation rate during anodisation. At 20°C the ACDCPSAA oxide is relatively thin and very compact, whereas with an electrolyte temperature of 35°C, the oxide more than doubles in thickness and takes on an open porous structure which is ideal for adhesive bonding. This increased conductivity and oxidation rate appears to be the root of the problems experienced when anodising at higher temperatures than this. For example at 50ºC there is extensive surface modification as undesirable compounds from the electrolyte are clearly deposited onto the surface, indicated by increased elemental composition of phosphorous and sulphur given by XPS analysis.

The incorporation of electrolyte species into the outer layers of the oxide also appears to have a time dependency. AES analysis carried out on the composition of AC oxides grown with different application periods, shown in reveals that there is a peak in phosphorous content at 120 s which falls away with increased time. This peak is of paramount importance if the electrochemical corrosion theories concerning the hydration resistance of phosphated alumina, are correct. Linear polarisation shows these theories to be true. An AC anodising period of 2 min seems the optimised value, coupled with an electrolyte temperature of 35°C, gives an oxide structure which has an overall thickness of approximately 2 µm and an outer pore diameter of between 20 nm and 30 nm when subsequently DC anodised at 15 V AC. At this temperature there is no indication of any detrimental surface modification and no smutting of the oxide is visibly apparent, a concern when anodising at 50°C. Higher voltages than 15 V typically cause oxide burning which is highly undesirable and promotes corrosion of the unprotected substrate. Wedge test data demonstrates that these conditions produce acceptable limiting fracture toughness values in the wedge test.

Increasing the temperature to 35°C has the effect of raising the dissolving power of the acid electrolyte as well as the conductivity which leads to a thicker, more porous oxide film. The resultant film is illustrated in Figures 7a and 7b.

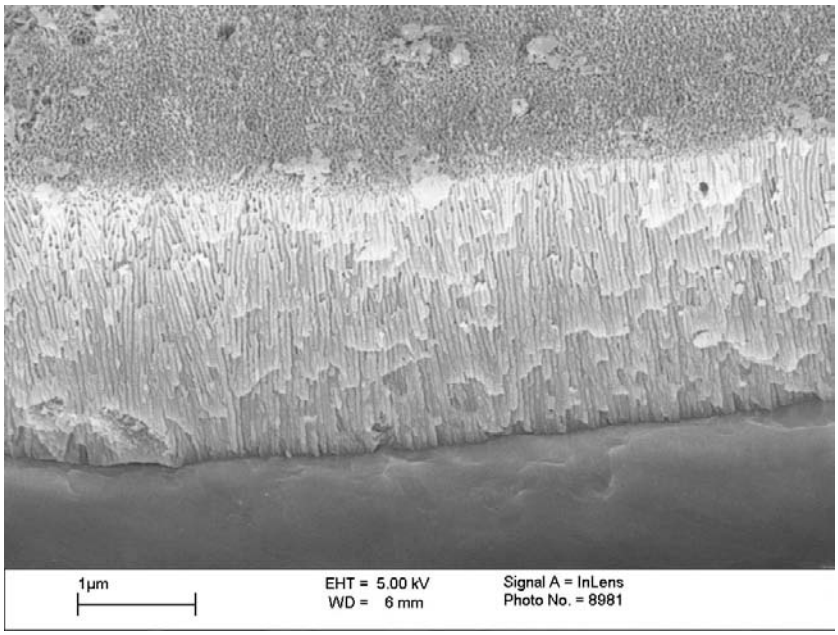


Figure 7a – FEGSEM micrograph of an optimized ACDCPSAA oxide on 2024-T3 clad aluminium alloy

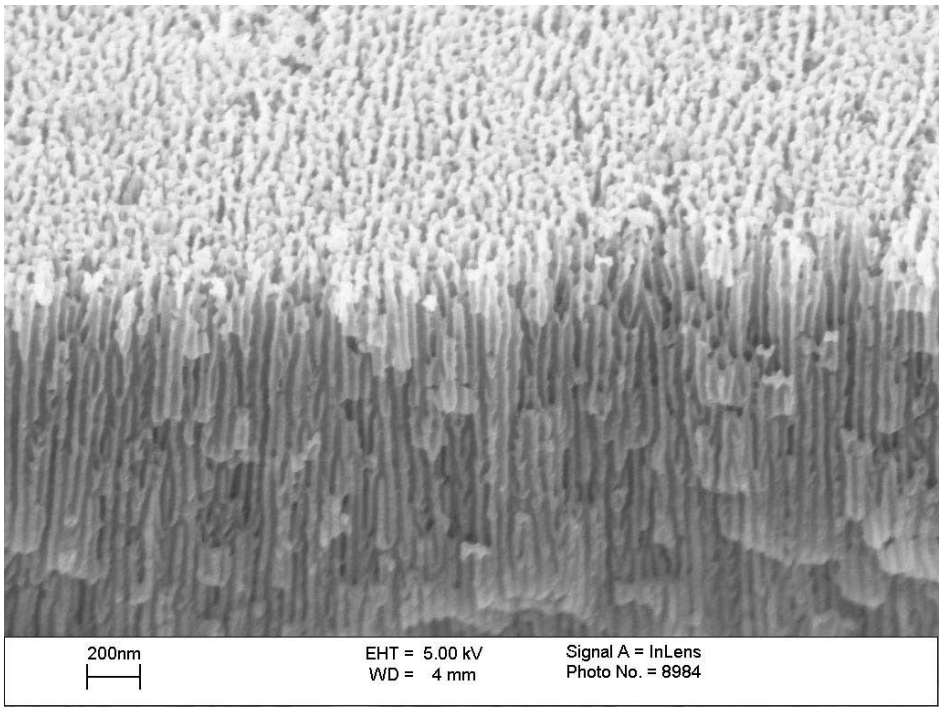


Figure 7b – FEGSEM micrograph showing the outermost region of an ACDCPSAA oxide on T3 clad aluminium alloy

The original intention and motivation for creating the ACDCPSAA process, was to produce a drop-in replacement for CAA For this reason, a viable ACDCPSAA process must perform as well as, if not better than, CAA in adhesion and corrosion tests. In the wedge test, the ACDCPSAA and the CAA prepared joints performed very similarly. Upon inspection, both systems fail cohesively within the adhesive with the limiting fracture toughness value for ACDCPSAA being marginally greater than that for CAA. Extensive adhesion testing has been carried out including dry cyclic fatigue which has shown improved performance of ACDCPSAA compared with CAA.

A further advantage that ACDCPSAA has over CAA is the overall processing time. The standard 40/50 V Bengough-Stuart CAA cycle incorporating a 30 min FPL etch stage takes a minimum of 124 min, including the initial vapour degrease of the parts. The optimised ACDCPSAA process takes a minimum of 32 min including the degreasing stage. This time-saving, potentially represents a four-fold increase in productivity. Other than the actual anodisation being faster, the ACDCPSAA process benefits from the use of only one processing tank, the anodising electrolyte, as no alkaline cleaning or deoxidising is necessary. Industrially, this is a huge advantage as moving large parts from tank to tank on an anodising line is a slow process and adds even more to the overall production time.

3 CONCLUSIONS

- The electro-phosphoric acid deoxidiser has been shown to leave an anodic oxide on the surface of 2024-T3 clad alloy, approximately 200nm in thickness and nodular in appearance. This oxide remains as part of a final duplex oxide layer with the SAA oxide forming the underlying film. This leaves the top surface open and receptive to adhesive primer penetration, while still possessing a more corrosion resistant lower oxide barrier layer.

- The phosphoric acid dip (PAD) further “opens” the top surface by a dissolution mechanism but has limited beneficial effects on bond durability if the surface pretreatment has already produced a receptive oxide surface. However, if used as a post treatment to a sodium hydroxide deoxidised and SAA process, the phosphoric acid dip does enhance the final surface morphology for improved adhesive primer penetration. Again, only by combining the above pretreatments with a low concentration sulphuric acid anodising solution at the elevated temperature of 35°C does the wedge test performance show equivalent crack extensions to that of the CAA 40/50V process.

- The ACDCPSAA provides a different route to producing a duplex oxide. It was thought that the outer porous layer can successfully form an interphase with subsequently applied adhesives or primers whilst the inner more compact layer provides optimised corrosion protection. All tests conducted to date show that such functionality has been successfully achieved using ACDCPSAA.

- Wedge testing has demonstrated that excellent joint strengths and durability can be achieved by using the modified anodising pretreatments investigated in this study. This indicates that these environmentally benign treatments may be possible contenders for use as drop-in replacements for the currently used hexavalent chromium based processes. The best performing alternative systems, studied here, are the ACDCPSAA and those which make use of an electrophosphoric acid deoxidiser (EPAD) and when combined with a low concentration sulphuric acid anodising (SAA) solution at an elevated temperature of 35°C show equivalent performance to that of the CAA 40/50V process,

currently used as an industry standard.

4 ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the Engineering & Physical Sciences Research Council (EPSRC), together with support in terms of both material supply and processing from David Bahrani of Bombardier Aerospace, Northern Ireland, Steve Ward of Cytec Engineered Materials Ltd and Terry Hirst of Goodrich Engine Control Systems Ltd.

5 REFERENCES

1. J.A.Marceau in *Adhesive Bonding Of Aluminum Alloys*, E.W.Thrall & R.W.Shannon (Eds): Vol. 8, No.10, 51-74, Marcel Dekker, New York, (1985).
2. L. E.Tarr and H.H.Holmquist, Proc.*35th International SAMPE Symposium*, 2102-2111, (1990).
3. J.L.Cotter and R.Kohler, *International Journal of Adhesion and Adhesives*, Vol. 1, 23-28, (1980).
4. O.D.Hennemann and W.Brockmann, *Journal Of Adhesion*, 1981, Vol. 12, 297-315, (1981).
5. C.Wong and Y.Moji, US Patent No. 4,894,127 (1990).
6. T.Leland and Y.Moji, *Proc.26th Annual Aerospace / Airline Plating & Metal Finishing Forum & Exposition*, 1-6, (1990).
7. R.Koop, and Y.Moj, *Proc.28th Annual Aerospace / Airline Plating & Metal Finishing Forum & Exposition Conference*, 1-8, (1992).
8. J.Mnich and C.Schoneman, *Proc.38th International. SAMPE Symposium*, 819-828.
9. G.B.Gaskin, G.J.Pilla, D.L.Bellevou, A.A.Martinelli and S.R.Brown, *Proc.26th International SAMPE Technical Conference*, 258-264, (1994).
10. G.W.Critchlow, K.A.Yendall, D.Bahrani, A.Quinn and F.Andrews, *International Journal of Adhesion and Adhesives*, Vol. 26, 419-453, (2006)
11. MIL-A-8626, *Anodic Coatings For Aluminium And Aluminium Alloys*
12. G.W.Critchlow and D.M.Brewis, *International Journal of Adhesion and Adhesives*, Vol. 16, 255-275, (1996).
13. J.Mortimer, Industrial Robot, Vol. 28, 192-198, (2001).
14. D.A.Moth: ARE TM(UMM) 87410, (1987).
15. R.P.Digby, and D.E.Packham, *International Journal of Adhesion and Adhesives*, Vol. 15, 61-71, (1995).
16. *Standard Test Method for Adhesive-Bonded Surface Durability of Aluminium (Wedge Test)*, ASTM D 3762-79.
17. K.A.Yendall, *PhD thesis*, Loughborough University, (2003).
18. G.D.Davis, T.S.Sun, J.S.Ahearn, and J.D.Venables, *Journal of Materials Science*, Vol. 17, 1807-1818, (1982).