NOVEL METHODS, INCORPORATING PRE- AND POST-ANODISING STEPS, FOR THE REPLACEMENT OF THE BENGOUGH-STUART CHROMIC ACID ANODISING PROCESS IN STRUCTURAL BONDING APPLICATIONS

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ABSTRACT

The present investigation focuses on novel anodising processes which are being developed for the replacement of the hexavalent chromium containing 40/50V Bengough-Stuart process, with particular emphasis on their resultant performance in structurally bonded systems used in the demanding and harsh environments encountered on operational aircraft. An electrolytic phosphoric acid based deoxidiser (EPAD)has been studied in combination with a standard sulphuric acid anodise. 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 aid structural adhesion in combination with the SAA 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. Single lap shear (SLS) and modified Boeing wedge tests were used to determine adhesion performance. SLS tests were used to determine initial, dry joint strengths whilst wedge test joints immersed in deionised water for up to 100 hours gave a measure of joint durability. Overall, excellent initial joint strengths and durability have been found with both EPAD plus SAA and PAD plus SAA processes suggesting that these environmentally benign treatments may be used as possible drop-in replacements for the currently used hexavalent chromium process. Electron microscopy has been used to investigate the topographical changes introduced to the surface by the various surface pretreatments under investigation to provide an explanation for the observed adhesion test results.

KEYWORDS: aluminium alloy, sulphuric acid anodising, electro-deoxidiser, phosphoric acid dip.

1. INTRODUCTION

Boeing's phosphoric acid anodising (PAA) process [1] is widely used for the

pretreatment of aluminium alloys within adhesively bonded structures; most reported studies have focussed on either 2024-T3 clad or bare or 7075-T6 alloys. 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 in the European aircraft industry 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; giving this solution the ability to produce a more uniform oxide on complex shaped parts when treated areas are not equidistant from the cathode. In addition it is reported that CAA generally gives higher peel strengths, in bonded structures, to that of 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 UK military specifications [11].

Although a number of 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 of aircraft structures. These processes are not generally regarded as performing to CAA standards. This is mainly due to the limited full scale certification of any process for use on either civil or military applications. To a lesser extent this situation can also be applied to the automotive industry.

A generic process not mentioned so far is sulphuric acid anodising (SAA). Historically, this 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, this limits the fatigue performance of any SAA processed aluminium for adhesive bonding 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 surface modification steps to produce more open structures receptive to adhesive or primer penetration. The steps employed include using an electrolytic phosphoric acid deoxidising stage prior to SAA and a phosphoric acid dip (PAD) technique post SAA. The latter has been shown to produce a more receptive surface for adhesive penetration and offer improved bond durability [14,15].

In summary, given 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 electrolytes but with significant pre- and post-anodising stages which modify the SAA oxide to provide structures capable of producing equivalent adhesion performance to that of the currently used CAA oxides without the fatigue issues associated with standard SAA processing.

2. EXPERIMENTAL

2.1 Materials and Processes

The substrates chosen for this investigation were 2024-T3 aluminium alloy in both bare and clad forms. Characterisation was carried out on both bare and clad alloy whilst clad alloy only was used for adhesion tests. 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 ten minutes in a proprietary solution of Isoprep 44 (MacDermid Inc.) before subsequent deoxidising. The Isoprep 44 was heated to $60^{\circ}C$. Substrates were subsequently rinsed in tap water and air dried.

Electrolytic phosphoric 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±0.2V for ten minutes. A sodium hydroxide solution of 40g/l was used as an alternative deoxidiser, the solution was maintained at $60^{\circ}C$ and applied for a period of ten minutes. This was followed by a nitric acid (50:50) dip for a period of approximately two seconds at $23^{\circ}C$. 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 20°C, 26°C or

35°C. Mechanical agitation was used during anodising which was carried out at a potential of 15V for a period of fifteen minutes.

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.

The adhesive / primer combination studied was FM 73M / BR 127 epoxide system from Cytec Engineered Materials Ltd. The FM 73 film adhesive is a toughened general purpose aerospace epoxide, supported by a polyester mat carrier, with a nominal thickness of 0.25mm. 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.

2.2 Adhesion Testing

2.2.1 *Wedge Testing*

A number of modifications were carried to the standard Boeing wedge test [15], in terms of sample preparation and testing procedure. Firstly, individual 2.54 x 15.24 x 0.3175 cm coupons were machined before any surface pretreatment was carried out. Coupons were then racked and treated using the required parameters. The treated coupons were then either set aside for characterisation or primed and bonded, as per the manufacturers recommended procedures, prior to mechanical testing.

Once cured, excess edge fillets were polished off so that the bondline could be clearly defined. In addition, controlled insertion of the wedge was carried out using a Hounsfield H20K-W tensometer in compression mode at 50mm per minute. After the wedge had been inserted, a stabilization period of one hour was allowed for crack growth to normalise. The specimens were then immersed in deionised water at 60°C for the duration of testing. All other ASTM procedures were followed [16].

2.2.2 Single Lap Shear (SLS) Testing

Single lap shear (SLS) joints were prepared using 2024-T3 clad alloy only. Individual coupons measuring 7.62 x 2.54 x 0.16 cm were prepared for each test variable. The overlap area measured 2.54 x 1.0 cm. Testing was carried out using a Lloyd HK20 instrument with a 50kN load cell with a crosshead speed of 6mm per minute.

3. RESULTS AND DISCUSION

3.1 Surface Characterisation

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; see Figures 1(a) and 1(c)

In the case of all cross-sections, samples were fractured by bending the processed aluminium alloy through an angle greater the 90° and then looking perpendicular to the fractured surface. 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 in 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 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 [17] has show this oxide structure to also be present on 7075-T6 clad alloy the results of which are not otherwise reported here. In the case of the 2024-T3 bare alloy there is no evidence of any columnar structure. Instead, there exists a less ordered non-porous formation, which has been attributed in aluminium alloys to the influence of the second phase particles on the resultant anodic oxide; 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.

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 may 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. In this and other studies a primer has clearly been used. 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 more viscous adhesive is unable to overcome the capillary forces.

The EPAD and SAA processed 2024-T3 clad alloy displays a fibrous surface topography as illustrated in Figure 2(a). In cross-section, Figure 2(b) shows that there is a clear duplex oxide evident. The upper region of the oxide film being the result of the phosphoric acid electro-deoxidising whilst the inner film is characteristic of the more compact SAA. The purpose of this electro-deoxidising stage is to undermine contamination and scale, through an oxide formation and dissolution mechanism in order to leave a clean, uniformly thin open 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 Davis *et al* [18] 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.

The underlying film of the duplex oxide, as shown in Figure 2(b) 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 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.

3.2 Mechanical Testing

3.2.1 Single Lap Shear

Initial joint strength results, as measured using the single lap shear geometry, showed equally good values, within experimental errors, for all the various anodised joints; see Table 1. Note that typical standard deviations are ± 200N. In contrast, the degreased-only surface treatment gave relatively poor initial joint strengths, with an average value of 3350N and the single FPL acid-etch treatment showed a marginal reduction in joint strength giving 7250N, maximum load to failure, compared to all anodised surface treatments, which were in the order of 8000N.

3.2.2 Wedge Test

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 a value of approximately 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 the results vary depending on the subsequent anodising treatments. The SAA carried out at 26ºC with an acid content of 40g/l gave the worst performance. This process provides a relatively compact oxide.

Indeed, considering the sodium hydroxide deoxidise plus SAA processes, it appears that with both low and high concentration of SAA, the low temperature electrolyte is detrimental to the functionality of the formed oxide, in terms of bond durability, compared with high temperature anodising. In all cases, following a sodium hydroxide deoxidise and SAA, the addition of a subsequent PAD treatment did improve wedge test results significantly. For example, with a SAA electrolyte of 40g/l and 26ºC processing, total crack extensions decreased from approximately 70mm to 40 mm 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 were 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 EPAD, all but the 40g/l concentration, 26°C temperature SAA, showed equivalent bond 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 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 electro-deoxidiser. However, the underlying oxide still plays a role, as seen from the inferior bond durability of the electro-deoxidised specimens which are then combined with the SAA using 26°C and 40g/l, compared with all other SAA oxides with either high temperature or high acid content anodising solution. Here with the 26°C and 40g/l SAA process a more dense, less 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, ideally, 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.

4. CONCLUSIONS

- Single lap shear and 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 those which make use of an electrolytic phosphoric acid deoxidiser (EPAD) when combined with a low concentration

sulphuric acid anodising (SAA) solution at an elevated temperature of 35°C, where this system shows equivalent performance to that of the CAA 40/50V process, currently used as a European industry standard.

- The EPAD 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.

ACKNOWLEDGMENTS

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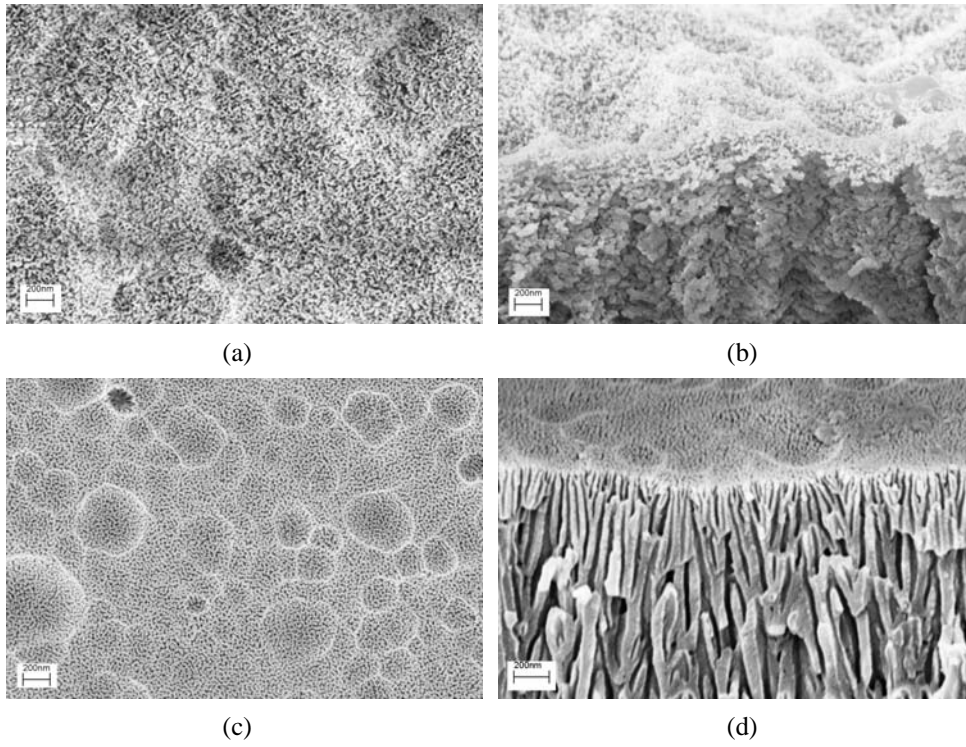
Fig. 1: CAA 40/50V processed, 2024-T3 bare; plan view (a) and cross-section (b), 2024-T3
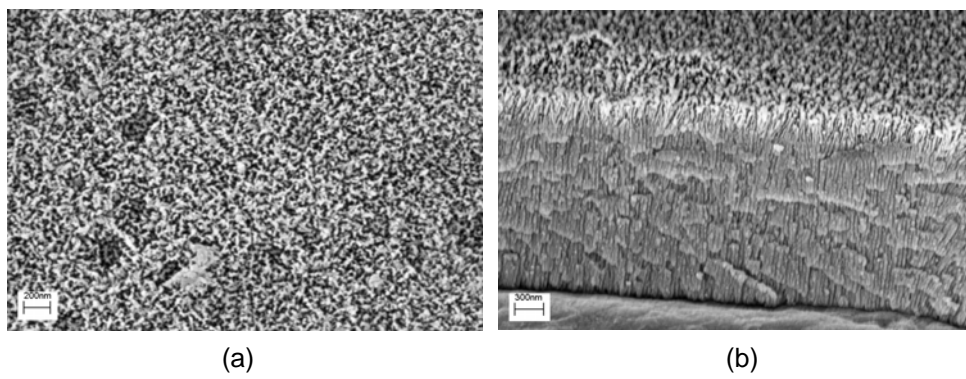clad; plan view (c) and cross-section

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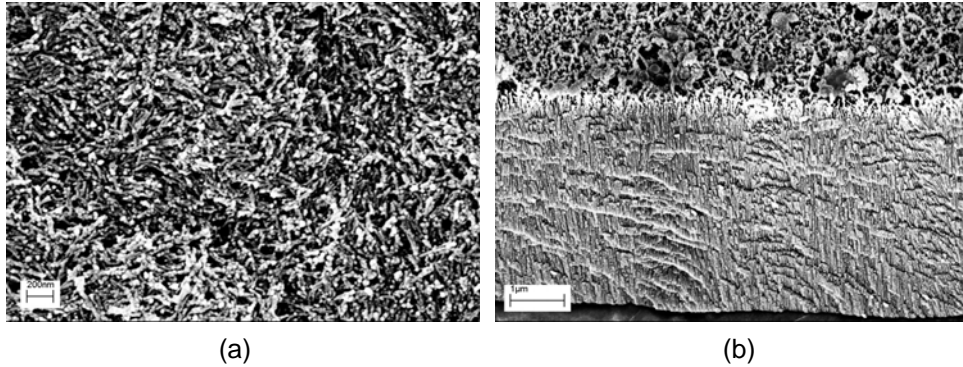
<center>(a)   (b)</center>

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

Table 1: Summary of single lap shear joint strengths – maximum load to failure

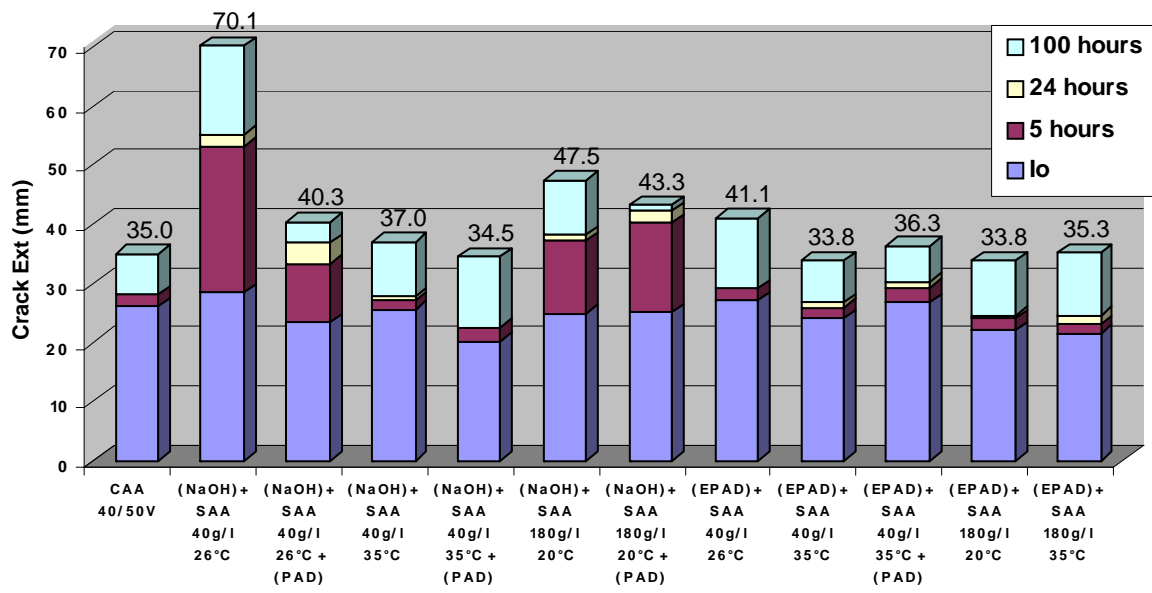| Surface treatment	Force (N)
Degreased-only	3350
FPL etched	7250
Degreased + NaOH + SAA (40g/l : 26°C)	8000
Degreased + NaOH + SAA (40g/l : 26°C) + PAD	7750
Degreased + EPAD + SAA (40g/l : 26°C)	8050
Degreased + EPAD + SAA (40g/l : 26°C) + PAD	7800
Degreased + 'optimised' FPL etched + CAA 40/50V	7900

Figure 4: Summary of wedge test crack extensions using 2024-T3 clad alloy, note figures are averages of 5 replicates and represent final crack extensions after 100 hours