State-of-the-art hexavalant chromium-free surface pretreatments for aluminium alloys

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INTRODUCTION

At the present time, the phosphoric acid anodising (PAA) process [1] is widely used in America for the pretreatment of aluminium alloys used in 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 environmental problems associated with the ever increasing regulations enforced by both national and local authorities. However, this route has never been favoured in the European aircraft industry due to the superior bond durability offered by chromic acid anodising (CAA) relative to PAA in corrosive environments. Furthermore, CAA has been shown to have twice the anodising throwing power and generally higher peel strengths to that of PAA [3].

As a result of the above, further developments in surface treatments which offer the performance of the standard CAA but without the shortcomings of PAA have been made. One method of increasing the suitability of the PAA process, for example, is to use a combined anodising electrolyte containing both phosphoric and sulphuric acids. Another example is the optimisation of the boric sulphuric acid anodising (BSAA) method [4]. BSAA has been successfully used as a pretreatment to paint adhesion since 1990 [5,6] and with further modifications to the processing parameters has shown excellent bond strength and durability for secondary and primary structural bonding of aerospace alloys [7-9]. 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 [10]. Despite the above, commercial confidence still does not exist in Europe for a complete chromate-free anodising process for adhesive bonding on aircraft structures. This is mainly due to limited full-scale certification of any process for use on either civil or military applications, and to a lesser extent in the automotive industry.

A generic anodising 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 in turn high coating weights, this limits the fatigue performance of any SAA processed aluminium for adhesive bonding usage in its standard specification. 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. To overcome this limiting factor, work has been carried out using SAA hard anodised surfaces with the addition of a further surface modification stage 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 [11,12].

By combining the knowledge of the BSAA work with that of developments in all the phosphoric acid based processes and transferring the technology to a more generic environmentally friendly anodising solution, e.g. SAA, this work aims to produce anodic films which provide equivalent adhesion performance and corrosion protection to that of the currently used CAA oxides without the fatigue issues associated with standard SAA processing.

EXPERIMENTAL

Materials

Substrates chosen for investigation were commercially available 2024-T3 aluminium alloy, both in bare and clad form. In addition, 7075-T6 aluminium in its bare state was used for some studies. The adhesive / primer combination studied was Cytec's FM 73M / BR 127 epoxide system. The FM 73 film adhesive is a toughened general purpose aerospace epoxy. 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.

Sample Preparation

All samples were given a minimum surface pretreatment of degreasing in acetone under ultrasonic agitation. An alkaline clean by submersion for 10 minutes in a proprietary solution of Isoprep 44 was used before subsequent deoxidising. Further to this samples were either treated using the standard 40/50V Bengough-Stuart chromic acid anodise (CAA) or by EPAD plus SAA with or without PAD; further details are given below.

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 10 minutes. Sodium hydroxide solution of 40g/l was used as an alternative deoxidiser, followed by a nitric acid (50:50) dip. All deoxidising treatments were followed by a 3-minute rinse in deionised water prior to anodising. Sulphuric acid anodising (SAA) 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 at a potential of 15V. The 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 then air-dried.

Adhesion Testing

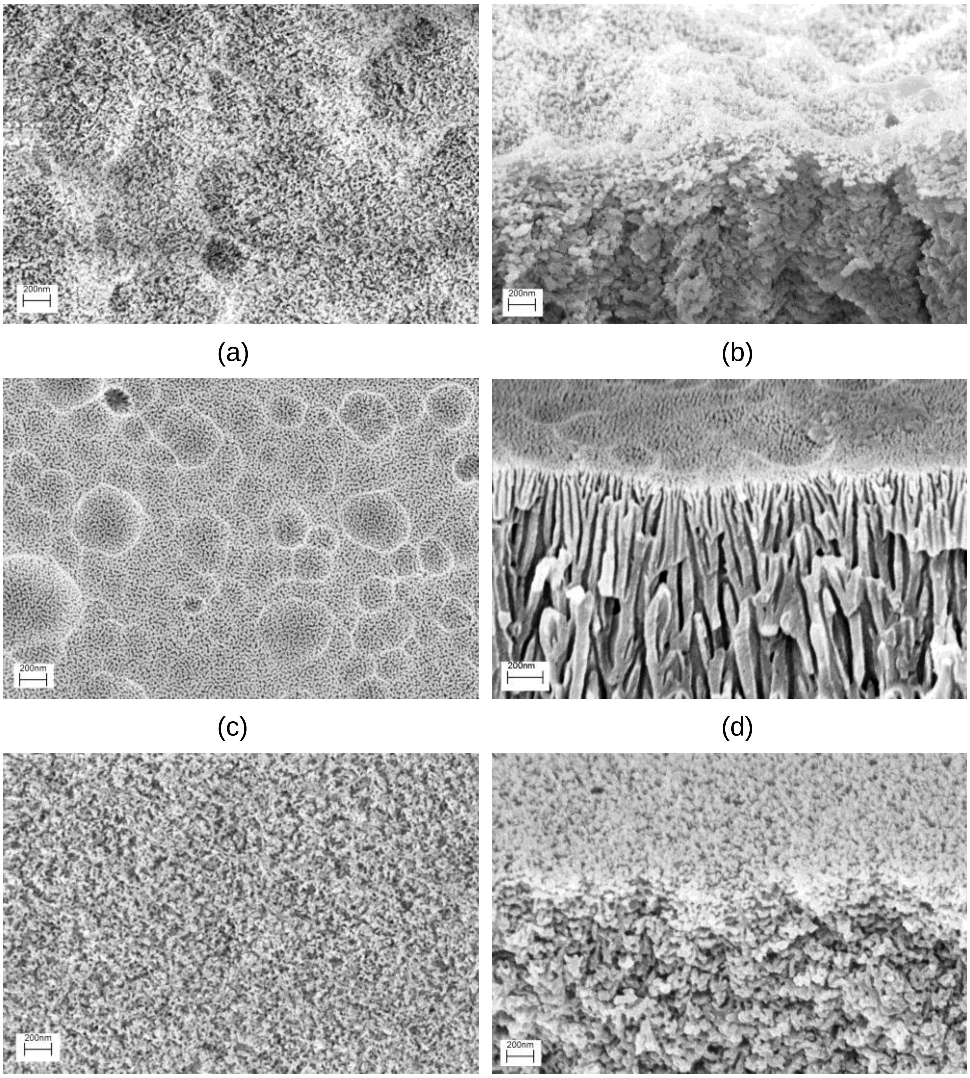
A modified Boeing wedge test [13] and single lap shear (SLS) joints were prepared and tested.

RESULTS AND DISCUSION

Surface Characterisation

All CAA 40/50V treated surfaces demonstrated oxides with relatively uniform, compact films formed, with few voids present in the coating. The scalloped texture produced from the deoxidising process is evident on all final anodised surfaces. This is more evident at higher magnification on the 2000 series alloys, figures 1(a) and 1(c) than for the 7000 series alloy, in which this scalloping is present but not visible at the higher magnification shown, figure 1(e).

A noticeable difference in oxide structure between clad and bare alloys can also be seen from figure 1, such that the oxide produced on the 2024-T3 clad material is columnar in structure, perpendicular to the metal surface with some branching and termination of columns, as seen in cross-section, figure 1(d). Also, well defined pores are present, in the range of 15 – 30nm in diameter.



(a) (b)

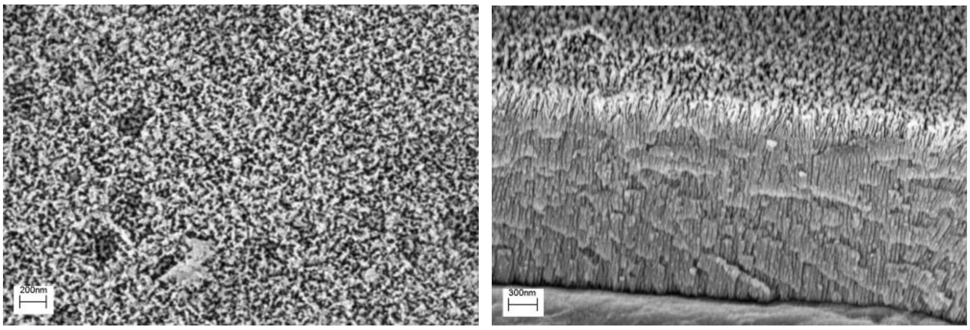
(c) (d)

(e) (f)

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 (d), 7075-T6 bare; plan view (e) and cross-section (d)

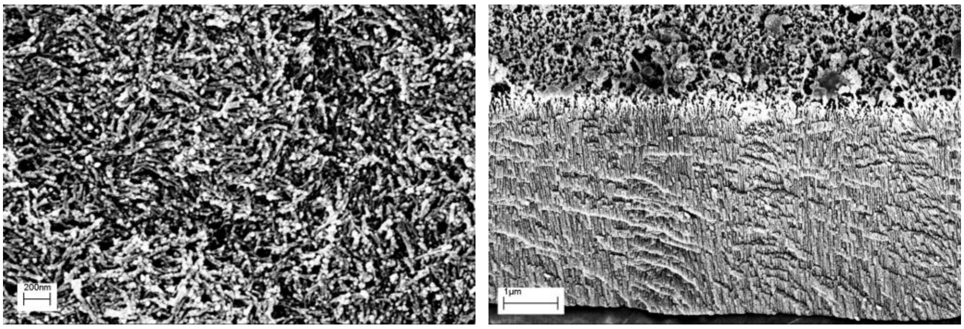
On closer inspection the expected hexagonal pore arrangement is not present, instead a more random array exists. Furthermore, it is evident that a number of pores have merged with their nearest neighbours. Previous work [14] has shown this oxide structure to be present on 7075-T6 clad alloy, which has not been studied here. In the case of both the 2024-T3 bare and the 7075-T6 bare alloys there is no evidence of any columnar structure. Instead there exists a less ordered formation, figures 1(a) and 1(e). This can be further seen in cross-section, where the anodised oxide has a very nodular arrangement resembling a “sponge” in texture, figures 1(b) and 1(f). In addition, the anodic oxide produced on the 7075-T6 bare alloy appears less dense than that of the 2024-T3 bare alloy. This may affect the primer/adhesive penetration characteristics of the oxide relative to the two different alloys.

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 bonded systems. 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.



(a) (b)

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



(a) (b)

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

The EPAD and SAA processed 2024-T3 clad alloy displays an amorphous 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 electro-deoxidising 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 [15] 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 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, 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 point of interest with PAA oxides is their inability to seal or hydrate in the same way 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.

Mechanical Testing

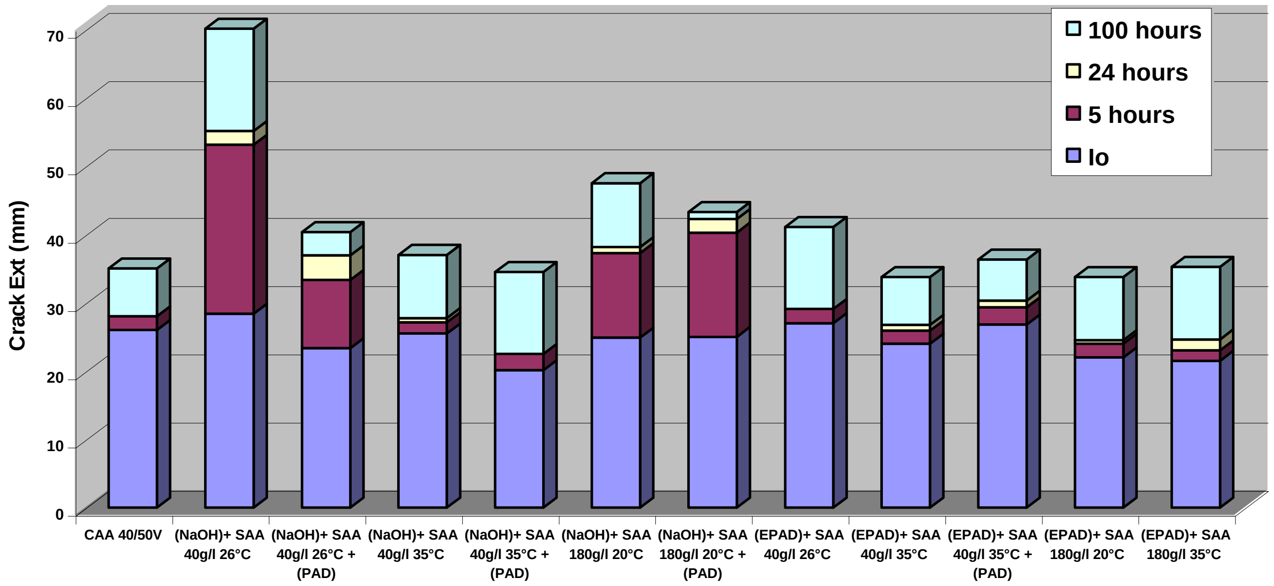
Initial joint strength results, as measured using the single lap shear geometry, showed equally good values, within experimental errors, for all the various anodised joints, Table 1. Note that typical standard deviations are ± 200N. In contrast, the degreased-only surface treatment gave relatively poor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

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

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. However, when exposed to hot humid conditions and monitored over the set periods of time, differences start to emerge. For the 2024-T3 clad alloys deoxidised using sodium hydroxide 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. The two systems using 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.

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



In the case of the anodising systems using the electro-deoxidiser, 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 electro-deoxidiser. However, the underlying oxide still plays a role. From the inferior bond durability of the electro-deoxidised 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.

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; including DC BSAA and those which make use of an electro-phosphoric acid deoxidiser when combined with a low concentration sulphuric acid anodising (SAA) solution at an elevated temperature of 35°C. Equivalent performance to that of the CAA 40/50V process, currently used as an industry standard has been demonstrated.

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 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 aforementioned DC processes are, however, all extremely time and energy consuming. A combined ACDC process using a benign, low concentration phosphoric-sulphuric acid electrolyte, in contrast, performs as well as the CAA with all alloys tested but processing times are extremely rapid. Processing times are reduced by a factor of 5 to 10 compared with the standard CAA.

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