AC anodising as pre-treatment prior to adhesive bonding of aluminium

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ABSTRACT

Anodising as pre-treatment for structural adhesive bonding has been investigated by wedge testing. The results show that fast hot AC anodising processes may be an environmental friendly and cost-effective alternative compared to traditional DC anodising pre-treatment processes used by the aviation industry. Improved durability and adhesion performance can be obtained by adding a certain amount of phosphoric acid to a sulphuric acid based electrolyte. Degradation in wet environments showed cohesive failure within the adhesive and comparable or even better durability for samples pre-treated by AC anodising in a mixed electrolyte (SPAA) compared to a standard PAA anodising process.

INTRODUCTION

For several decades European and American aviation industry has used anodising as pre-treatment for aluminium surfaces to obtain good durability properties of adhesive joints in service. The good durability properties are explained by good adhesion and corrosion properties resulted by the thin, ductile and protecting oxide films on the aluminium surface after anodising. The process used in Europe is chromic acid anodising (CAA) while Boeing developed a phosphoric acid anodising (PAA) based process including a sodium dichromate sulphuric acid etch (FPL etch) prior to anodising. Due to the hexavalent chromium based chemicals used and international legislation coming the industry needs more environmental friendly processes.

AC anodising in hot acidic electrolytes was developed as a fast pre-treatment process for continuous coil coating [1]. During AC anodising, precipitation of the anodised oxide layer and hydrogen evolution occur simultaneously on the aluminium surface, and no additional degreasing and/or etching stage is necessary due to the cleaning effect obtained by the gas evolution. Based on good experience in coil coating, AC anodising is evaluated as an attractive pre-treatment for adhesive bonding in high volume automotive applications where cost efficient and environmental friendly processes are required.

In the present work, thin film hot AC anodising are compared to regular DC anodising processes, alkaline etching and chromating as pre-treatment for structural adhesive bonding of aluminium.

EXPERIMENTAL

Samples of extruded AA6060-T6 aluminium profiles (2 mm thick and 110 mm wide) were cut in approximately 200 mm lengths for wedge testing. The alloy composition (by weight) was 0.4% Si, 0.2% Fe, 0.5% Mg, 0.02% Mn, 0.006% Cu, 0.01% Zn, 0.01% Ti balanced with Al. The samples were pre-treated using different AC and DC

anodising processes as shown in Table 1. Etched samples were always included as a reference. For comparing, results obtained for chromated samples in a parallel work [2] are included.

The samples were bonded together using epoxy based structural pastes, Araldite 2014 or Betamate XD4600. Spacers were used to control the glue line thickness (0.1 mm). Backing plates in various thickness and strength depending on the adhesive used were added on both sides to control the stiffness of the samples. The sandwich assemblies were machined into four replicas 25.4 mm wide and 154 mm long wedge samples. After introducing the wedges samples were stored at room temperature for 24 hours before the initial crack lengths were measured. Samples were aged in a climate cabinet at 96% RH at 40^{o}C. The crack growth was measured after various time intervals. The microstructures of pre-treated and glued samples were characterised by AFM, FE-SEM and TEM.

Table 1. Pre-treatment prior to adhesive bonding

Pre-treatment	Electrolyte		Current density [A/dm2]	Time	Temperature [°C]
	H_2SO_4 [g/l]	H_3PO_4 [g/l]			
SAA	160		1.5 (DC)	20 min	20
PAA-AC		100	4 (AC)	30 sec	50
SAA-AC	150	50	10 (AC)	12 sec	80
SPAA-10-80	150	50	10 (AC)	12	80
SPAA-20-80	150	50	20 (AC)	30	80
SPAA-10-70	150	50	10 (AC)	12	70
SPAA-20-70	150	50	20 (AC)	30	70
Pre-treatment	**Electrolyte**		**Voltage [V]**	**Time [min]**	**Temperature [°C]**
	H_2SO_4 [g/l]	H_3PO_4 [g/l]			
SAA [1]	160		1.5 (DC)	20	20
PAA [1]		100	10 (DC)	20	25
FPL+PAA [2]		100	10 (DC)	20	25
Chromated [1]	Immersion in Alodine C6100			3	25
Etched	Alkaline etched by immersion in 10 wt% NaOH			2	60

[1]: Alkaline etched prior to [2]: FPL-etched prior to anodising:

RESULTS AND DISCUSSION

Investigations carried out have shown [3,4] that fast hot AC anodising pre-treatments either in sulphuric or phosphoric acid based electrolytes gives durability properties comparable to the DC phosphoric acid anodising process used as pre-treatment of adhesive bonded aluminium by the aircraft industry, as shown by wedge test results for Araldite 2014 adhesive bonded samples in Figure 1. Inspection of investigated sample surfaces showed that the initial fracture propagated in the adhesive. Although etched samples showed good dry adhesion poor durability properties in the wet environment leaded to a total failure within 24 hours of exposure. The pre-treatments providing the best durability include variants DC anodised in phosphoric acid and the AC anodised variants either carried out in phosphoric (PAA-AC) or sulphuric (SAA-AC) acid. This observation was also confirmed exposure of lap-shear joints in corrosive environments [3]. Samples DC anodised in sulphuric acid (SAA) showed a relative poorer durability. Visual investigation of fractured surfaces after wedge testing showed interfacial failure mode of both the etched and the sulphuric acid anodised variants, as demonstrated for etched variant in Figure 1. A preferential cohesive fracture in the adhesive was found for the PAA variants.

Sulphuric acid based electrolytes, however, are generally favourable to phosphoric acid electrolytes when it comes to process cost effectiveness. Thus, the effect of introducing certain amounts of phosphoric acid in the sulphuric acid based AC anodising electrolyte (SPAA processes in Table 1) has been investigated by wedge testing of samples bonded using the Betamate XD4600 adhesive. As shown in Figure 3, the SPAA-20-70 variant provided comparable or even better than the SAA-AC and PAA variants. Inspection of fractured surfaces after testing showed a mainly cohesive failure for the Betamate XD4600 adhesive bonded SAA-AC samples, indicating an improved adhesion compared to SAA-AC samples bonded using the Araldite 2014 adhesive. The failure mode of the SPAA-20-70 variant, however, was cohesive within the adhesive indicating a further increase in adhesion in the presence of phophoric acid in the anodising electrolyte. Introductory studies have shown that good durability and cohesive failure can be obtained for different SPAA processes. For a few variants, however, wedge testing showed a significant poorer durability, as demonstrated for SPAA-10-70 in Figure 4. Visual investigation of fractured surfaces after testing showed interfacial failure for such samples.

Adhesive or partly adhesive fracture of SAA-AC is explained by an oxide more susceptible to hydration and/or smaller pore size resulting in less penetration of adhesive into the SAA-AC anodised film compared to the PAA films. A more open pore structure of PAA-AC compared to SAA-AC is demonstrated by TEM cross sections in Figure 5. Both improved hydration properties and changed oxide structure may explain the improved adhesion properties obtained by adding phosphoric acid to the sulphuric acid based AC anodisng electrolyte. As demonstrated by plane view FE-SEM images in Figure 6 (a) and (b) presence of phosphoric acid in the Ac anodising resulted in increased pore size. A further increase in the pore size can be obtained by increasing the current density or voltage for the AC anodising process, as shown in Figure 6 (b) and (c) for SPAA carried out at 10 and 20 A/dm^2, respectively. A non-continuous thin surface layer partly covering the anodised oxide film in Figure 6 (d) are connected to the poor performance of such samples. High dissolution rates in the warm phosphoric acid containing electrolyte, and/or hydration of the anodised oxide film prior to adhesive bonding may explain these observations. The results, however, show that SPAA-AC processes may be attractive pre-treatment processes for adhesive bonding and organic coatings, both from an economical and an environmental point of view. To avoid the observed phenomenon and for further optimisation of the SPAA process as pre-treatment further investigations are necessary.

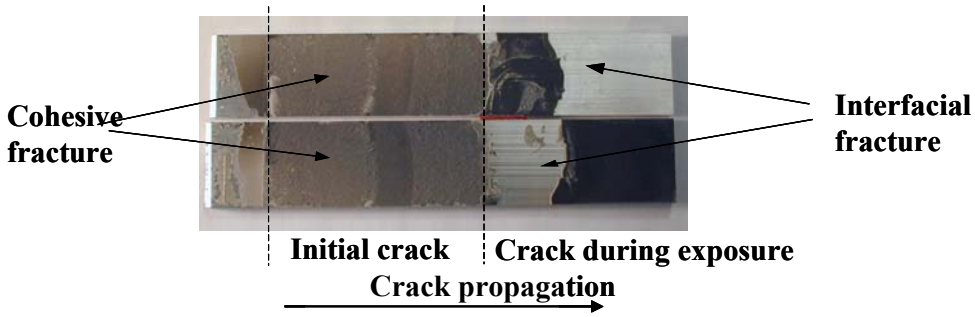

Figure 1. Surface fracture of a wedge tested etched AA6060-T6 sample bonded with Araldite 2014.

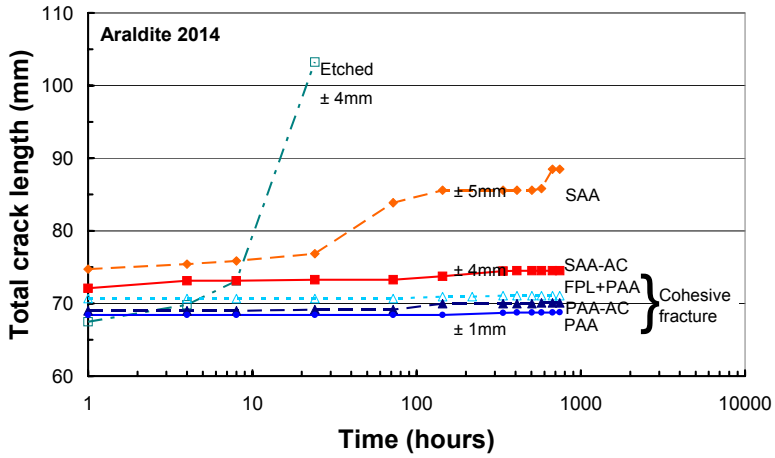

Figure 2. Wedge testing results of AA6060-T6 samples bonded with Araldite 2014.

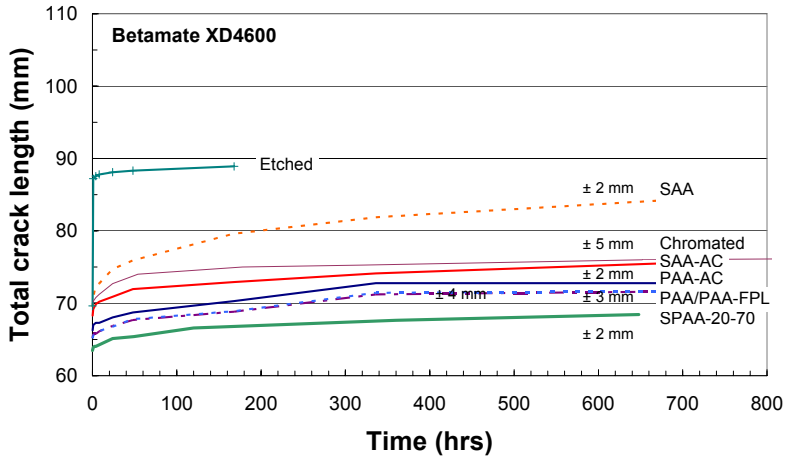

Figure 3. Wedge testing results for AA6060-T6 samples bonded with Betamate XD4600.

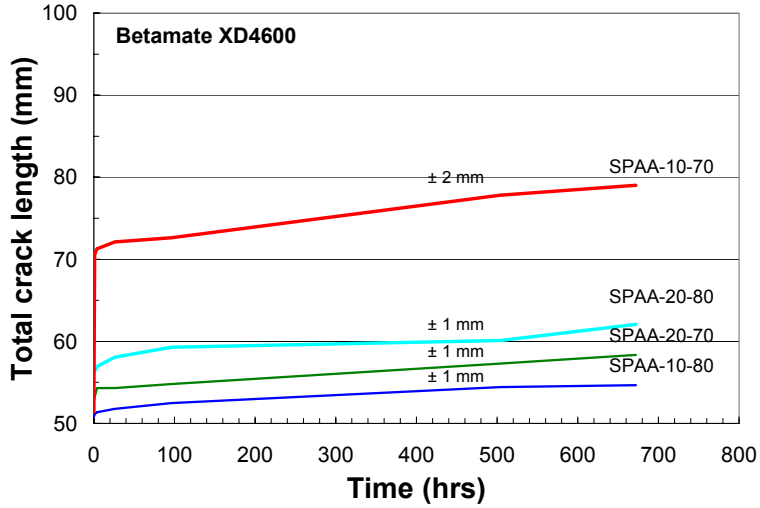

Figure 4. Wedge testing results for AA6060-T6 samples bonded with Betamate XD4600.

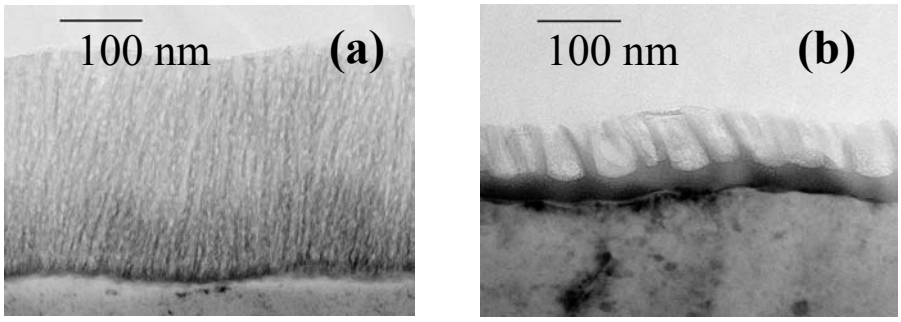

Figure 5. TEM cross-sections of (a): SAA-AC and (b): PAA-AC oxides on AA6060-T6.

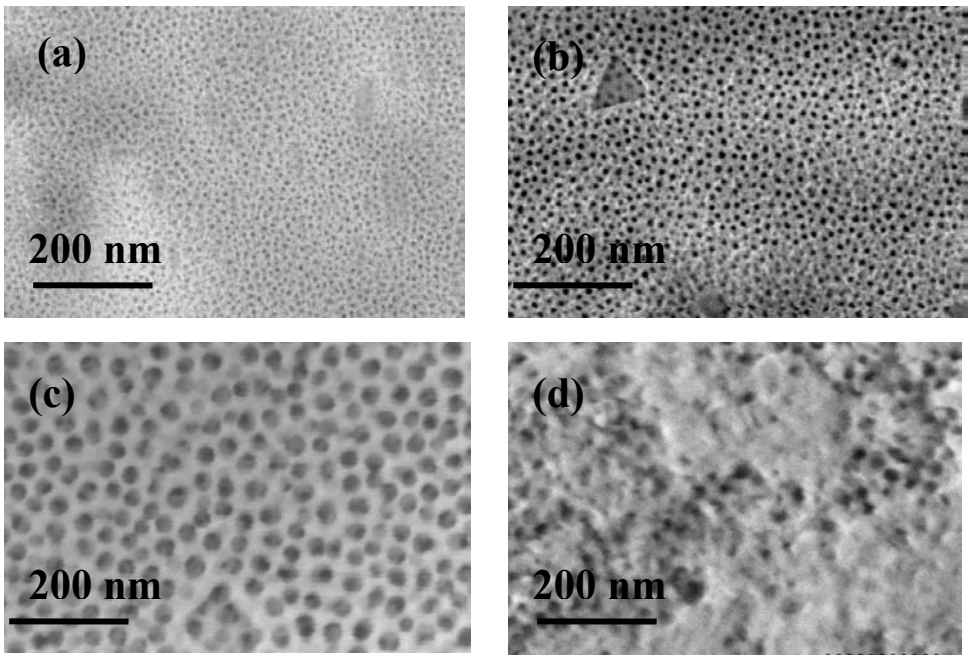

Figure 6. FE-SEM plane view images of anodised oxides on AA6060-T6, (a): SAA-AC (b): (SPAA-10-70 and (c): SPAA-20-70. (d): a partly covered anodised surface of a SPAA variant.

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