Hot AC Anodising as a Cr(VI)-free Pre-treatment for Structural Bonding of Aluminium

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ABSTRACT

Hot AC anodising has been evaluated as pre-treatment for aluminium prior to structural adhesive bonding. Phosphoric and sulphuric acid hot AC anodising showed very promising adhesion promoter capabilities with durability comparable with the best standard DC anodising procedures. AC anodising does not required etching prior to anodising and offers a pre-treatment time down to 20 seconds. The interface/interphase between the aluminium substrate and the adhesive was investigated in order to get a better understanding of the involved adhesion mechanisms and to explain the long-term properties. The alkaline medium formed at the oxide layer/adhesive interface has been shown to induce a partial dissolution of the oxide layer leading to the formation of metallic ions which diffuse in the adhesive (EPMA measurements). The effect of diffusion of the Al ions on adhesion and joint durability is still uncertain but studies showed that pre-bond moisture affected the joints durability and to some extent the diffusion length, specially for DC anodised samples. So far no direct correlation could be established between the diffusion length d and the joints durability but new trials with better control over the elapsed time between bonding and adhesive curing are expected to help getting a better understanding of the involved mechanisms.

INTRODUCTION

Adhesive bonding of aluminium in the aerospace industry has a successful history spanning several decades. The automotive industry is a major target for the use of structural adhesive bonding into volume consumer products. Here one can illustrate successful applications of adhesive but there is still some way to go before structural bonding of aluminium can be applied in a volume production vehicle.

Adhesive bonding of aluminium requires a surface pre-treatment, in order to improve the adhesion and to ensure the durability of the joint. The processes developed by the aircraft industry, are time consuming and quite expensive. The need for short pre-treatment times in high

volume vehicle manufacture and the phasing out of existing Cr(VI) containing pre-treatments for environmental reasons presents a challenge.

The two most common processes used for anodising aluminium prior to adhesive bonding are chromic acid anodising and phosphoric acid anodising. Both of which contain chromates at some stage in the treatment and the presence of Cr(VI) is undesirable from an environmental point of view. The growing use of aluminium in the automotive industry combined with adhesive bonding as replacement for welding and riveting has motivated recent work to develop new pre-treatment methods. Hot AC anodising has been used for a while in coil coating but its performance as pre-treatment prior to structural adhesive bonding were not well documented.

EXPERIMENTAL

Aluminium profiles (AA6060) have been anodised with standard DC and hot AC anodising in both phosphoric acid (PAA) and sulphuric acid (SAA). The main advantage with hot AC anodising is the reduction of the pre-treatment time from more than 15 minutes down to 20 seconds. The pre-treatments were tested to study how the bond strength and durability are affected by the anodised layer structure. Lap-shear samples were bonded using the two component epoxy adhesive Araldite 2014. The samples were tested both after

bonding and curing and after accelerated ageing testing (filiform corrosion test and acetic acid salt spray test). The lap-shear samples were exposed 100 days in the different environments before mechanical testing. Wedge testing was also used to evaluate the durability of the joints in high humidity.

In order to get a better understanding of the formation and the structure of the interphase between the anodised layer and the adhesive, FT-IR and EPMA (Electron Probe Micro Analyser) investigations have been performed.

Samples and Pre-treatment

Extruded profiles of alloy AA6060, provided by Hydro Aluminium have been used in that study. Samples have been pre-treated with standard DC anodising (PAA and SAA) and hot AC anodising (PAA and SAA). The anodising conditions are summarised in Table 1. Standard anodising conditions were used for DC PAA and SAA. The DC PAA pre-treatment has anodising parameters in agreement with the PAA process developed by Boeing and can be considered as the regular or standard PAA. Prior to DC anodising the samples are degreased in acetone, alkaline etched and desmutted in nitric acid. In the case of hot AC anodising, however, the aluminium surface is not etched prior to anodising.

Table 1. Anodising parameters

Pre-treatment	H_3PO_4 wt%	H_2SO_4 wt%	Voltage (V)	Current density (A/dm^2)	Time	Temperature (℃)
DC PAA	10	–	10	–	20 min	25
DC SAA	–	16	–	1.5 (DC)	20 min	20
AC PAA	10	–	–	4 (AC)	30 s	50
AC SAA	–	15	–	10 (AC)	12 s	80

Oxide layer structure

The anodised films formed in phosphoric and sulphuric acid electrolytes have a hexagonal cell structure. Dimensions of the cell structure (cell size, pore diameter, depth and wall thickness) are governed by the anodising conditions, which determine the porosity of the film. The thickness and the density (porosity) of the anodised film have been determined (see Table 2) with respect to the anodising conditions. Figure 1 shows TEM pictures of cross sections of selected anodised films. As expected, the thickness of the oxide layers and the pore size varied considerably depending on the anodising conditions.

Mechanical testing

Lap-shear

Mechanical testing of lap shear joints has been carried out for both as bonded and as aged samples. A two component room temperature curing adhesive paste (Araldite 2014) has been selected. The tensile test results given in term of maximum strength or stress at break are shown in Figure 2. Ageing of lap joints were carried out by exposure either in a climate cabinet at 40 ℃ and 82% RH or in acidified salt spray at 35 ℃. Tensile test was performed after 50 and 100 days. Results from etched lap-shear specimens (alkaline etching in 10 wt% NaOH, 60 ℃ during 2 min followed by desmutting in HNO_3) have been added as for comparison

Table 2. Thickness and density of the oxide layers formed using the anodising parameters presented in Table 1

Pre-treatment	Thickness (μm)	Density (g/cm^3)
DC PAA	0.62	1.2
DC SAA	5-10	2.7
AC PAA	0.10	1.9
AC SAA	0.18	2.5
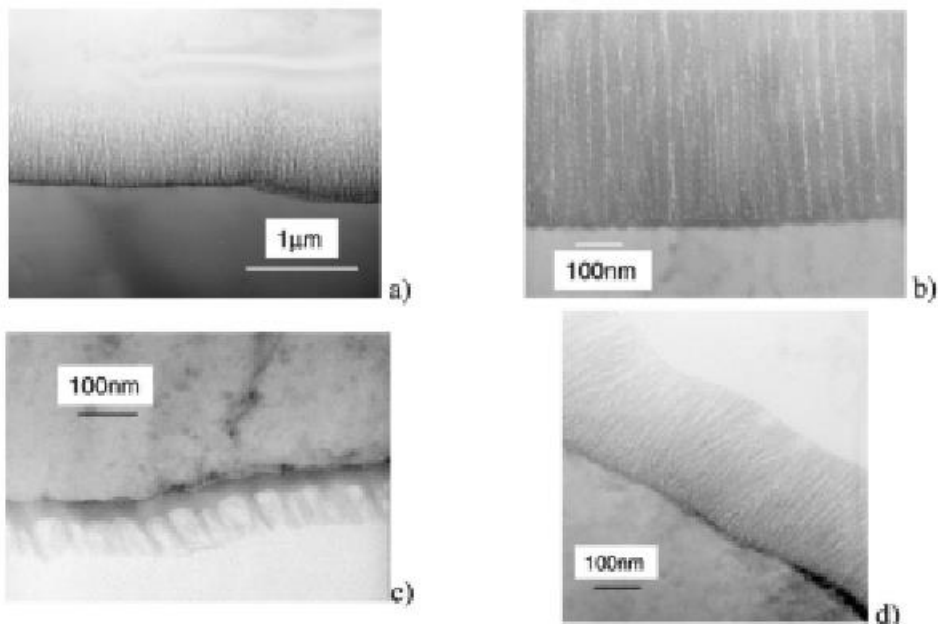
Figure 1. TEM pictures of cross section a) DC PAA b) DC SAA c) AC PAA d) AC SAA.
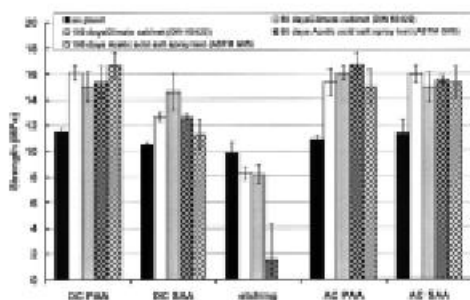
Figure 2. Tensile test results obtained for adhesive bonded AA6060-T6 single lap shear joints (25 mm × 110 mm in size, 20 mm overlap) before and after exposure in either climate cabinet or acidified salt spray.

sake.

The tensile test results of as cured joints do not indicate any clear effect of variation in the pre-treatment prior to adhesive bonding on initial strength of the lap joints. After ageing, however, the strength of the etched lap joints was significantly lower than the other variants. The DC anodised SAA lap joints showed a slightly lower apparent strength than the other anodising conditions after ageing. Except for the etched variant, the tensile test results indicated increased joint strength as a result of ageing in both environments. The increased strength of the aged specimens can partly be explained by the water absorbed by the adhesive. Water acts usually as plasticiser leading to a more ductile behaviour. This has been observed for the Araldite 2014 and one can refer to the publication by *Lapique and al* for more details. For the etched variant, the loss of strength was most extreme in the acidified salt spray environment. Figure 2 shows that the hot AC anodising, performed either in sulphuric or in phosphoric acid, seems to provide as good durability properties for the investigated lap-shear joints as regular DC anodising in phosphoric acid which is known as a

reference pre-treatment. No effect of increased exposure time from 50 to 100 days is observed in our tests.

Wedge test

This test has proven to be highly reliable in determining and predicting the environmental durability of substrate surface pre-treatments. The test is primarily qualitative, but is very discriminating in determining variations in adherent surface preparation parameters and adhesive environmentally durability. The specimens consist of extruded AA6060 plates (4 mm thick) glued together. The bondline had a controlled thickness of 100 μm. The wedges were introduced between the adhesive bonded aluminium substrates in a controlled manner (1 mm/s). The specimens were stored at room temperature for 24 hours before the length of the initial crack was measured. The specimens were aged at 40 ℃ and 96% relative humidity. At the end of various time intervals, the specimens were removed from the climate chamber and the crack growth measured. The total crack length is reported according to the exposure time. Inspection of the specimen surfaces (after test completion) shows that the initial fracture propagates in the bondline (cohesive fracture). This is a common feature observed on all the specimens, independent of the pre-treatment. The same observation has been reported in the literature. Under exposure, two behaviours have been observed. Depending on the pre-treatment the crack may deviate towards the interface adhesive/substrate leading to an interfacial fracture or keep on propagating in the bondline (see Figure 3).

The pre-treatments providing the best durability include the variants DC-PAA and the hot AC variants PAA-AC and SAA-AC (see Figure 4). The crack propa-
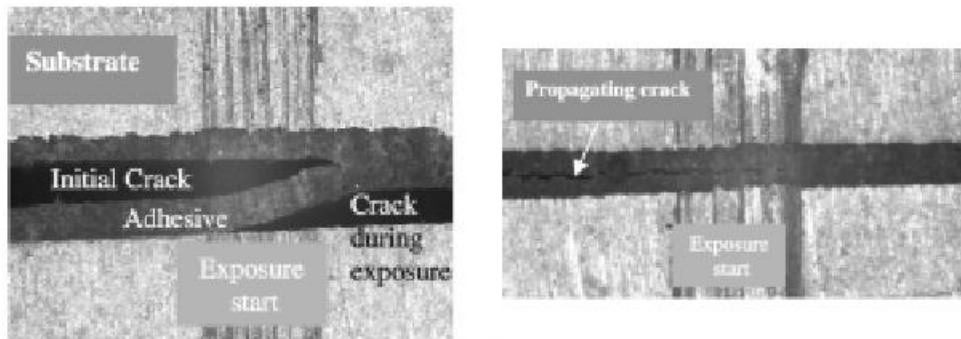
Figure 3. Crack location during exposure (right part of the pictures). While the initial crack (coming from the left) propagated in any cases cohesively, exposure to humidity and hot temperature lead to interfacial fracture for DC-SAA and AC-SAA, whereas DC-PAA and AC- PAA exhibited cohesive fracture.
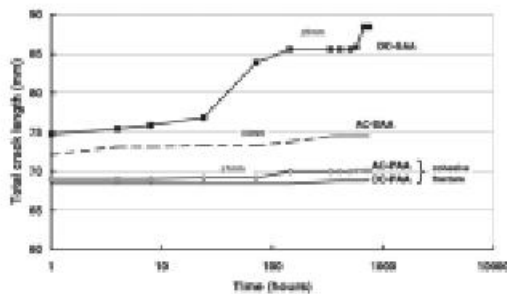

Figure 4. Results of wedge testing of adhesive bonded AA6060-T6 specimens. The measurements incertitude is notified along the curves.

gated very slowly and after exposure of 800 hours, no signification advancement of the fracture front could be measured. Furthermore it has to be noted that the stress level in the specimens was high since the initial crack was short.

DC-SAA offered a good dry adhesion (short initial crack) but provided a relatively poor durability. When exposed, the crack moves to the interface (see Figure 3) and propagates with a rate higher that for the other anodising pre-treatments.

Hot AC anodising either carried out in phosphoric, AC-PAA, or sulphuric acid, AC-SAA, provides as good durability as regular phosphoric acid DC anodising. The good durability properties obtained for the hot AC anodised samples confirms the tensile test results of lap shear joints. It should be added that AC-PAA and DC-PAA exhibited a cohesive fracture mode (see Figure 3) whereas the AC-SAA showed interfacial fracture.

Interphase adhesive-oxide layer

Compared to the tensile test results of as bonded specimens, ageing has resulted in increased joint strength for all the anodising variants. Similar observations have been reported in the literature where the increased joint strength of aged specimens was attributed to the formation of a new and stronger interphase (in addition to the plasticising effect of the water) in the presence of water. *Aralanov and al* observed that the joint strength decrease measured during the first hours of exposure was followed by a spontaneous recovery of the joint strength. They showed that at the beginning of the "recovery regime", aluminium hydroxide is intensively formed both at the initial interface and in the polymer. The high content of hydrox-

ide in the polymer phase was claimed to be related to the fact that diffusion of metallic ions to large distances is possible during the curing of the polymers. After longer exposure, the reconstruction of the interfacial region by the formation of a composite transition region was reported, resulting in a stronger interface. *Roche and al* showed that the high basicity (pH〉 10) of diamine curing agents lead to a partial dissolution of the oxide and/or hydroxide metallic surface. The diffusion of the dissolution products (metallic ions) in the adhesive could explain the high content of hydroxide in the polymer phase in the work of *Aralanov*. The formation of a new interface region in wet conditions proposed by *Aralanov and al* is confirmed by the work of *Kinloch and al* where the role of the interphase in the environmental failure of tapered double-cantilever beam adhesive joint was investigated.

In order to get a better understanding of the mechanisms governing adhesion and durability, the interface between the anodic layer (formed in either sulphuric or phosphoric acid) and epoxy adhesives has been investigated.

Two structural epoxy adhesives Araldite 2014 and Betamate XD4600 were used. In order to study the formation of the interphase at the adhesive/substrate interface, FT-IR spectroscopy and EPMA (Electron Probe Micro Analyser - Microprobe) investigation have been used.

FT-IR analysis

The curing agent of the Araldite 2014 is diethylenetriamine (DETA). The pH of the DETA was measured to be close to 11. Aluminium oxide is not stable at such a pH level and a partial dissolution of the anodised layer is then expected as soon as the adhesive is applied onto the anodised surface. A thin layer of DETA was applied
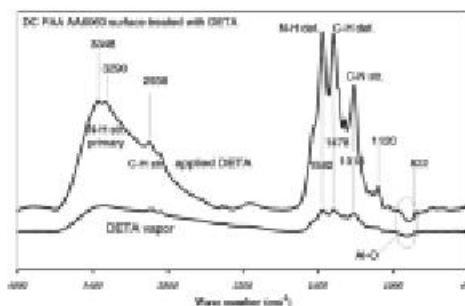
Figure 5. FT-IR spectra of two DC-PAA aluminium surfaces treated with or exposed to DETA.

onto DC-PAA, AC-PAA and AC-SAA pre-treated surfaces. Figure 5 shows FT-IR spectra from two DC-PAA surfaces treated with DETA. The first curve represents the FT-IR spectrum of the surface treated with DETA (thin film) while the second shows the FT-IR spectrum of a surface exposed to DETA vapor. They have in common a decrease of the signal associated to the Al-O bond (890 cm^{-1}). The other peaks are associated to the DETA.

This results seems to indicate that the high basicity of the curing agent leads to a partial dissolution of the aluminium oxide formed during anodising. The same observation was made on AC-SAA and AC-PAA pre-treated surface. In order to study the kinetics of the reaction between the DETA and the Al substrate, FT-IR spectra were recorded with time (Figure 6).

Figure 6 indicates that the dissolution process takes place as soon as the curing agent comes into contact with the surface. In addition, the process is completed within the first minute since no significant difference can be observed in Figure 5. The partial dissolution of the aluminium oxide layer rises a new question. What happens to the dissolved aluminium? It has been suggested in the literature that the metallic ions could diffuse into the adhesive and eventually react to form organo-metallic complexes. EPMA measure-
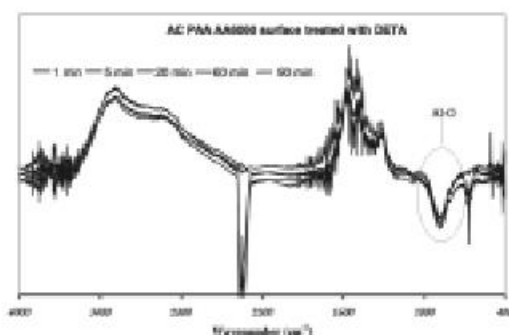
Figure 6. FT-IR spectra of AC-PAA Al surface treated with DETA.

ments were performed to find evidence of the diffusion of dissolved aluminium into the adhesive.

EPMA measurements

A thin film of Araldite 2014 was applied and cured onto a DC-SAA pre-treated aluminium surface. Cross sections were prepared and microprobe analysis performed. An Al mapping through the interface showed an increased concentration of aluminium in the adhesive (Figure 7).

The same Al diffusion was observed with the adhesive Betamate XD4600. The formation of low molecular weight amines during curing (coming from the degradation of the curing agent) has been reported in the literature. In the presence of water they react to produce an alkaline medium in which the aluminium oxide is unstable.

EPMA investigation was performed on DC-SAA, DC-PAA, AC-SAA and AC-PAA coated with Betamate XD4600 where concentration profile of different elements was registered. Concentration of Al, Si, Mg, Cl and Ca were registered and were balanced with O in the oxide layer and C in the adhesive. In addition to look at the pre-treatment effect, the moisture at bonding was controlled. Bonding was performed at 11, 33, 45 and 85% relative humidity. The effect of the pre-bond moisture on the durability of the specimens can be found in a paper published by *Johnsen and al.* Figure 8 shows the concentration profile of Al and O+C in the case of AC-SAA anodising bonded at 85% RH with Betamate XD4600. The measurements were started in the Al substrate, went through the anodised layer and the interface anodised layer/adhesive and ended deep in the adhesive layer.

Figure 9 shows, in addition to Al, the concentration profile of different elements present in the system. While a sharp transition was observed for Mg, Si and Cl when crossing the interface oxide layer/ adhesive, a concentration gradient was measured for Al. This is a clear evidence for diffusion of Al into the adhesive. The same observation was made on AC-SAA,
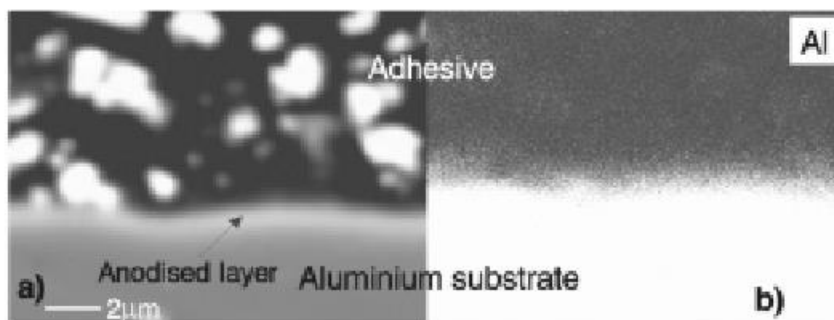

Figure 7. EPMA pictures from cross section of DC-SAA anodised Al substrate + adhesive a) back scattered electron picture b) Al mapping.
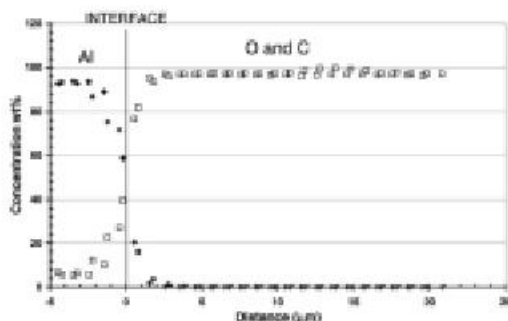
Figure 8. AC-SAA bonded at 85% RH with Betamate XD4600. Typical concentration profile of Al and O+C from the Al substrate to the adhesive, through the interface oxide layer/adhesive.

AC-PAA and DC-PAA samples.

The diffusion length d of Al in the adhesive has been measured, depending on the pre-treatment and the pre-bond moisture. No clear effect of pre-bond moisture on AC anodised specimens had been determined while DC anodised samples exhibited a slightly increased diffusion length with pre-bond moisture. Diffusion lengths up to 15 mm have been measured at high pre-bond moisture. Results reported by *Johnsen et al* showed that the durability of AC anodised bonded specimens was little affected by the pre-bond moisture while a dramatic deterioration of the durability of DC anodised bonded samples was observed. It is at that stage very difficult to conclude on whether there is a correlation between durability and extent of Al diffusion in the adhesive.

Based on our results so far, we believe that there is another important parameter that has not been controlled, namely the elapsed time t between bonding and adhesive curing. t is expected to affect the extent of the dissolution and diffusion of the Al. New trials will be conducted to address this issue.
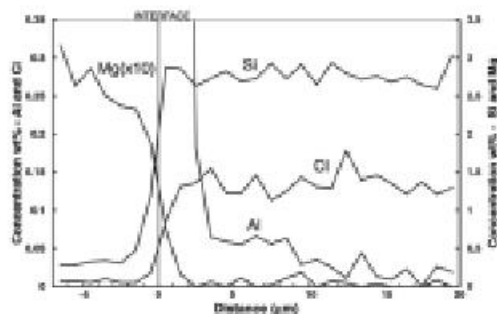

Figure 9. AC-SAA bonded at 85% RH with Betamate XD4600. Concentration profile of several elements present in the system. While a sharp transition is observed for Mg, Si and Cl, a concentration gradient is measured for aluminium.

CONCLUSION

Phosphoric and sulphuric acid hot AC anodising showed very promising adhesion promoter capabilities with durability comparable with the best standard DC anodising procedures. AC anodising does not required etching prior to anodising, reducing then the number of steps in the process. In addition hot AC anodising offers a pre-treatment time down to 20 seconds and is therefore an attractive pre-treatment method. A study of the interface/interphase between the aluminium substrate and the adhesive was conducted in order to get a better understanding of the involved adhesion mechanisms and to explain the long-term properties.

The alkaline medium formed at the oxide layer/adhesive interface has been shown to induce a partial dissolution of the oxide layer leading to the formation of metallic ions which are virtually free to diffuse into the adhesive. EPMA measurements gave indications that such diffusion takes place. The interaction between the metallic ions

and the adhesive is still unknown but XPS analysis may answer this question. The effect of diffusion of the Al ions (and the formation of an interphase) on adhesion and joint durability is still uncertain but studies showed that pre-bond moisture affected the joints durability and to some extent the diffusion length, specially for DC anodised samples. So far no direct correlation could be established between the diffusion length d and the joints durability but new trials with better control over the elapsed time between bonding and adhesive curing are expected to help getting a better understanding of the involved mechanisms.

ACKNOWLEDGEMENTS

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