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ABSTRACT In spite of regulations aimed at the reduction of the amount of chromium VI in waste streams, chromic acid anodising (CAA) is still widely used in the aerospace industry because a suitable replacement has not yet been found. An alternative should provide good corrosion protection, good adhesive bonding properties and be applicable to all aluminium alloys used in the aerospace industry. Furthermore, the fatigue properties should not be reduced more than by chromic acid anodising. Phosphoric sulphuric acid (PSA) anodising proved to be a possible alternative for CAA for 2XXX series alloys. Its applicability to 7XXX series alloys is discussed in the present paper. The most promising anodising parameters were selected from a large matrix of conditions, based on the microstructure and thickness of the anodic layers obtained on clad 7075-T6. The fatigue properties and corrosion protection capabilities were evaluated for the selected PSA anodising process in comparison to chromic acid anodising. Because the process parameters differed from those of the PSA process established previously for 2XXX series alloys, the selected process was also tested on 2024-T3 and evaluated with respect to microstructure and corrosion protection capabilities. The constant amplitude fatigue behaviour was found to be equal for PSA and CAA treated aluminium. The corrosion protection by PSA anodic layers was not as good as that of CAA anodic layers, which can be explained largely by the differences in thickness of the anodic layers. After application of a chromate-free primer, both anodising processes provided equal protection against corrosion.			



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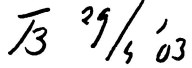

Phosphoric sulphuric acid nodising: an alternative for chromic acid anodising in aerospace applications?

L. Velterop

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Phosphoric Sulphuric Acid Anodising: An Alternative for Chromic Acid Anodising in Aerospace Applications?

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Abstract

In spite of regulations aimed at the reduction of the amount of chromium VI in waste streams, chromic acid anodising (CAA) is still widely used in the aerospace industry because a suitable replacement has not yet been found. An alternative should provide good corrosion protection, good adhesive bonding properties and be applicable to all aluminium alloys used in the aerospace industry. Furthermore, the fatigue properties should not be reduced more than by chromic acid anodising.

Phosphoric sulphuric acid (PSA) anodising proved to be a possible alternative for CAA for 2XXX series alloys. Its applicability to 7XXX series alloys is discussed in the present paper.

The most promising anodising parameters were selected from a large matrix of conditions, based on the microstructure and thickness of the anodic layers obtained on clad 7075-T6. The fatigue properties and corrosion protection capabilities were evaluated for the selected PSA anodising process in comparison to chromic acid anodising. Because the process parameters differed from those of the PSA process established previously for 2XXX series alloys, the selected process was also tested on 2024-T3 and evaluated with respect to microstructure and corrosion protection capabilities.

The constant amplitude fatigue behaviour was found to be equal for PSA and CAA treated aluminium. The corrosion protection by PSA anodic layers was not as good as that of CAA anodic layers, which can be explained largely by the differences in thickness of the anodic layers. After application of a chromate-free primer, both anodising processes provided equal protection against corrosion.

Keywords: anodising, chromate-free, phosphoric-sulphuric acid, corrosion, fatigue, aluminium

Introduction

Aluminium is widely used in the aerospace industry because of its high specific strength and stiffness and excellent corrosion resistance. The corrosion resistance can be further improved by anodising the aluminium components followed by application of epoxy primers and paint coatings. The best adhesion of primers and coatings is obtained for porous anodic aluminium oxide layers as compared to bare aluminium or non-porous anodic aluminium oxide. Such porous anodic oxide layers also provide excellent adhesion for structural adhesive bonding.

The anodising process that is being used most often in the European aerospace industry is Chromic Acid Anodising (CAA). This process results in layers with good adhesive properties, good corrosion resistance and limited reduction of the fatigue strength^{1,2}. However, owing to the toxicity and carcinogenic nature of hexavalent chromium (chromium VI), legislation will



For all anodising conditions the microstructure and thickness of the anodic layer were determined and compared to those of CAA anodic layers. The adhesive properties of all anodic layers were evaluated with climbing drum peel tests (according to ASTM D1781) on fresh specimens and on specimens exposed to salt spray (according to ASTM B117) for 6 – 30 weeks. CAA anodised Alclad 2024-T3 was used as backing plate material. The chromate containing primer BR127 (produced by Cytec) and the autoclave-curing adhesive film AF163-2K (produced by 3M) were used for bonding of the test specimen to the backing plate.

Based on the results of these experiments the process window was determined and optimum PSA anodising conditions were identified. For the next stage of the investigation (microstructure, fatigue and corrosion) CAA and PSA anodising using the optimum process conditions were applied. CAA anodising was used as reference.

The CAA conditions were 100 g/l CrO₃, 20 min. at 40 V + 5 min. at 50 V, 40 °C.

Microstructural analysis

The microstructures of CAA and PSA anodic layers on Alclad 2024-T3, bare 2024-T3 and clad 7075-T6 were investigated with SEM (Scanning Electron Microscopy). The layer thickness and pore-size distribution were determined and the three-dimensional pore structure was assessed.

Pore sizes were determined automatically, using digital image analysis, for 6 high resolution SEM images per specimen. The number of pores per pore-diameter interval was determined for each specimen.

For certain military applications, sealing of the pores of the anodic layer is required to improve the corrosion resistance of anodised aluminium. Therefore hot water sealing was evaluated for the optimum PSA anodising condition. Hot water sealing was performed by immersing anodised specimens in demineralised water at 97 – 100 °C for 10 – 12 minutes.

Corrosion tests

The corrosion resistance of PSA anodised aluminium was determined from an intermittent salt spray test according to ASTM G85-94 Annex 2. This MASTMAASIS corrosion test (Modified ASTM Acidic Acid Salt Intermittent Spray) is more severe than the continuous salt spray test described in ASTM B117, and is used frequently for evaluation of the corrosion properties of modern aluminium aircraft alloys. The test essentially consists of periodically spraying 5% NaCl solution buffered with acetic acid to pH = 3. One cycle consist of spraying for ¾ hour, purging with dry air for 2 hours and soaking at high relative humidity for ¾ hours. The cabinet temperature was 35 °C instead of the specified 49 °C. The lower temperature was chosen because exposure at 49 °C is too severe for primed or painted samples.

The specimens were rectangular sheets of 50 x 150 mm² with scribelines according to ASTM D1654. The core metal was exposed in the scribelines. The substrate materials used were Alclad 2024-T3, bare 2024-T3 and clad 7075-T6. CAA and PSA anodising were applied. One set of specimens was anodised and dried, a second set of specimens was provided with the



chromate-free Aviox CF primer (produced by Akzo Nobel) after anodising. A chromate-free primer was chosen to avoid protection against corrosion by chromates, which could obscure differences between the different anodising processes.

Every two weeks the specimens were inspected visually during a dry purging period. After exposure for six weeks (anodised specimens) or nine weeks (anodised and primed specimens) the specimens were rinsed in tap water, dried and photographed. In addition metallographic cross-sections were made to determine the depth of the corrosion attack.

Fatigue tests

S–N fatigue curves were determined for CAA and PSA anodised specimens (using the optimum PSA anodising conditions found in the process window determination). The specimens were flat and waisted, $K_t = 1.06$, and were made of clad 7075-T6, machined before anodising.

Constant amplitude fatigue tests at a stress ratio of $R = 0.1$ were done in a 100 kN Amsler Vibrophore HFP high frequency resonance machine. The tests were performed at room temperature and a test frequency of 75 Hz. Tests ended at specimen failure or after reaching 10^7 cycles. Fatigue crack initiation locations were identified for the failed specimens, using optical microscopy and SEM.

Results and discussion

Process window determination

Many of the anodising conditions chosen for the test matrix to determine the anodising process window resulted in burning. The current density was too high for these conditions, which resulted in high heat generation and a local temperature rise. Other conditions resulted in dissolution of the anodic layer. Stable anodising conditions that can be used in production were found for the lowest temperature (22 °C), where the current density was lower, see table 1.

The results of the microstructural investigation showed that the thickness of the anodic layers increased with increasing sulphuric acid concentration and with increasing anodising time, temperature and voltage⁸. The mean pore size increased rapidly with addition of phosphoric acid up to a concentration of 50 g/l. For higher concentrations of phosphoric acid, the mean pore size depended mostly on the concentration of sulphuric acid, with decreasing mean pore sizes for increasing concentrations of sulphuric acid.

Requirements for the anodic layer thickness are related to the risk of damaging the layer during handling after anodising, and the reduction in fatigue life by the anodic layer. Very thin layers will be easily damaged during handling, while thick layers will cause a large reduction in fatigue life. The pore size of anodic layers affects the mechanical bonding between layer and primer¹. Very large pores will result in insufficient mechanical bonding, while very small pores prohibit full penetration of a primer in the pores. CAA anodic layers have a thickness of 2.5 – 5 µm and pore diameters of about 20 nm. These numbers have proven to be suitable for handling and bonding.



The climbing drum peel test results were good for all anodising conditions: fracture took place in the adhesive, and peel strengths were almost equal. Salt spray exposure caused some reduction in the peel strength for all samples, but only after long exposure times⁸. This decrease in peel strength after exposure is ascribed to ageing of the adhesive. A few specimens showed a drastic decrease in peel strength. These specimens showed bondline corrosion (undercutting of the adhesive by corrosion), which is the most detrimental type of corrosion for adhesive joints¹, on the CAA anodised backing plate. Bondline corrosion was never observed on the PSA anodised test specimens. It should be remembered that a chromate-containing adhesive primer (BR 127) was used for bonding to the backing plate. The chromates in the primer may have reduced the corrosion by the salt-spray exposure.

The optimum PSA anodising condition, resulting in layer thickness and pore sizes equal to CAA for clad 7075-T6, was 100 g/l H₂SO₄, 125 g/l H₃PO₄, 22 °C, 15 V and 20 min..

Table 2: Mean pore diameter and average thickness of the anodic layers.

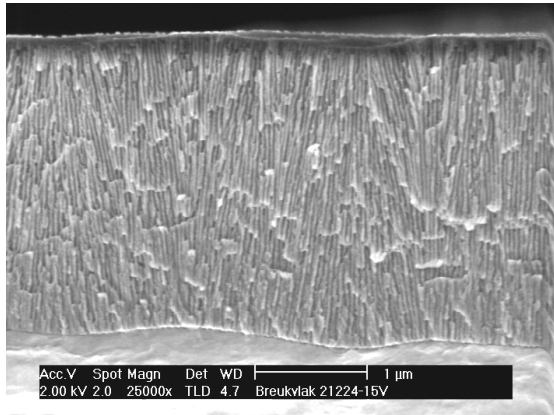
	clad 7075-T6		Alclad 2024-T3		bare 2024-T3	
	CAA	PSA	CAA	PSA	CAA	PSA
thickness (µm)	3.8	2.7	2.3	1.5	3.4	0.9
mean pore diameter (nm)	25-30	20-25	15-20	20-25	--	--

Microstructure

The PSA anodic layers were thinner than the CAA anodic layers for all substrates, see table 2. For the clad substrates the thickness is sufficient, while for bare 2024-T3 the layers are too thin (< 1 µm) to guarantee damage-free handling.

Pore diameters cannot be determined for specimens with rough surfaces. The surfaces of CAA and PSA anodic layers on bare 2024-T3 were very rough and therefore the pore size was not determined for these specimens. The mean pore diameters were determined for CAA and PSA anodic layers on Alclad 2024-T3 and clad 7075-T6 and are shown in table 2. The mean pore diameter is equal for the PSA anodic layers on both substrates, while there was a relatively large difference between the mean pore diameters of the CAA anodic layers. Since the mean pore diameters of the PSA anodic layers were in-between those of the two CAA anodic layers (on 7075-T6 and 2024-T3), mechanical bonding between a primer and the PSA anodic layers is expected to be good.

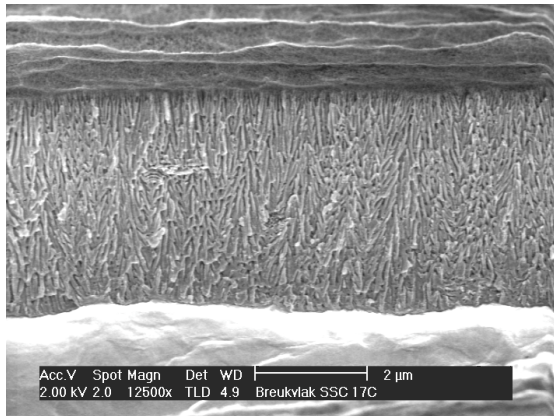
Cross-sections of some of the anodic layers are shown in figure 1. A large difference can be observed between the pore structures on clad and bare aluminium. A smaller difference is seen between CAA and PSA anodic layers on the same type of substrate. PSA anodic layers on clad aluminium have a columnar pore structure with all pores perpendicular to the surface, while the CAA layers have pores at different angles to the surface, see upper and lower left images of figure 1. The PSA anodic layer on bare 2024-T3 is very open, with a dendritic-like pore-wall structure. CAA layers on bare 2024-T3 have no clear pore structure and are denser than PSA anodic layers on the same substrate. The reason for these differences is probably that the



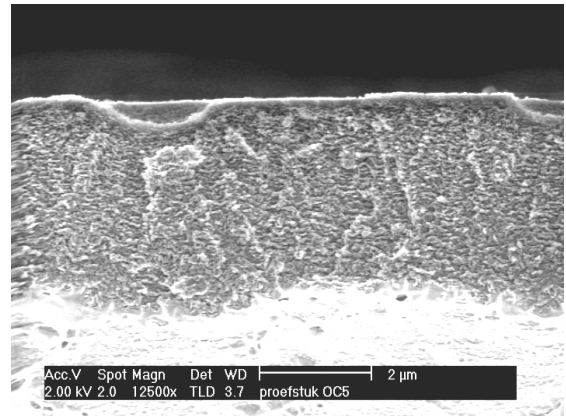
clad 7075-T6 -- PSA



bare 2024-T3 – PSA



clad 7075-T6 -- CAA



bare 2024-T3 – CAA

Figure 1: SEM micrographs of cross-sections of PSA and CAA anodic layers on different aluminium substrates.

alloying elements, precipitates and intermetallic particles disturb the columnar growth of pores on bare aluminium.

Hot water sealing of PSA anodic layers was not possible. Pore closure, as observed for CAA, did not occur for PSA anodic layers. Partial closure of the pores occurred only for bare 2024-T3. However, in view of the very open pore structure and small anodic layer thickness on this substrate, it is expected that the partial pore closure has no influence on the corrosion properties of PSA anodised bare 2024-T3 aluminium.

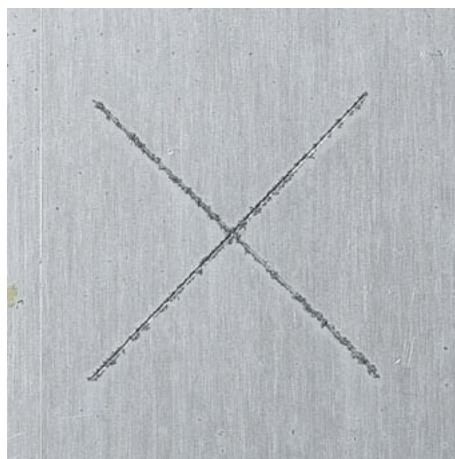
From the microstructural point of view it seems that CAA can be replaced by PSA anodising, although the process parameters must be optimised to give sufficiently thick layers on all substrates. For applications where sealing is required an effective sealing procedure must be found for PSA anodic layers.

Corrosion

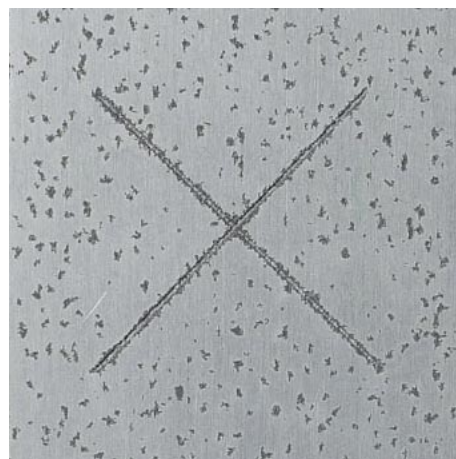
Anodised specimens. After 6 weeks MASTMAASIS exposure the anodised specimens without primer showed corrosion in the scribelines. Most specimens also showed (some) pitting attack. Table 3 summarises the severity of corrosion for all the specimens investigated. Figure 2 shows the surface appearances of the clad 7075-T6 and bare 2024-T3 specimens. The corrosion found on clad 2024-T3 was similar to the corrosion on clad 7075-T6; CAA gave better corrosion protection than PSA.

Table 3: Overview of severity of corrosion attack for all specimens. ++ indicates (very) light corrosion, -- indicates severe corrosion.

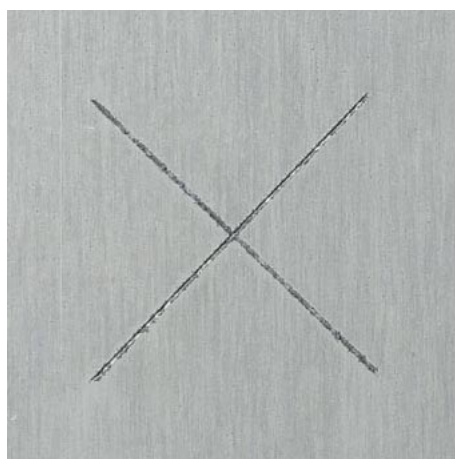
	clad 7075-T6		Alclad 2024-T3		bare 2024-T3	
	CAA	PSA	CAA	PSA	CAA	PSA
scribeline attack	++	++	++	++	-	--
pitting attack	++	+	++	+	+/-	--



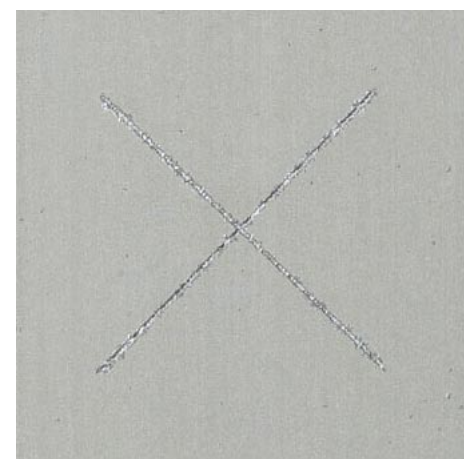
clad 7075-T6 – PSA



bare 2024-T3 – PSA



clad 7075-T6 – CAA



bare 2024-T3 – CAA

Figure 2: Details of the surface appearances of anodised aluminium after 6 weeks MASTMAASIS exposure, showing corrosion at the scribelines and severe pitting attack on bare 2024-T3 after PSA anodising (top right image).



Metallographic cross-sections were prepared to investigate the depth of the corrosion pits and the extent of attack at the scribelines. The depth of deep pits was about 30 – 50 μm for all specimens. The scribelines in clad specimens were protected against corrosion by sacrificial dissolution of the clad layer. The scribelines were severely corroded (corrosion depth about 0.1 mm) on the CAA and PSA anodised bare 2024-T3 specimens.

Anodised and primed specimens. All primed specimens showed the same type and degree of corrosion after 9 weeks MASTMAASIS exposure. Limited attack was found at the scribelines (see figure 3) and small homogeneously distributed blisters on the coated surface. The blisters were observed on all specimens after 4 weeks of exposure and did not increase much in size or number during further exposure.

Upon drying the specimens, the blister disappeared (figure 3). Cross sections of the specimens revealed that the blisters were caused by de-bonding within the primer or delamination at the interface between primer and anodic layer. The corrosive attack underneath the blisters was very

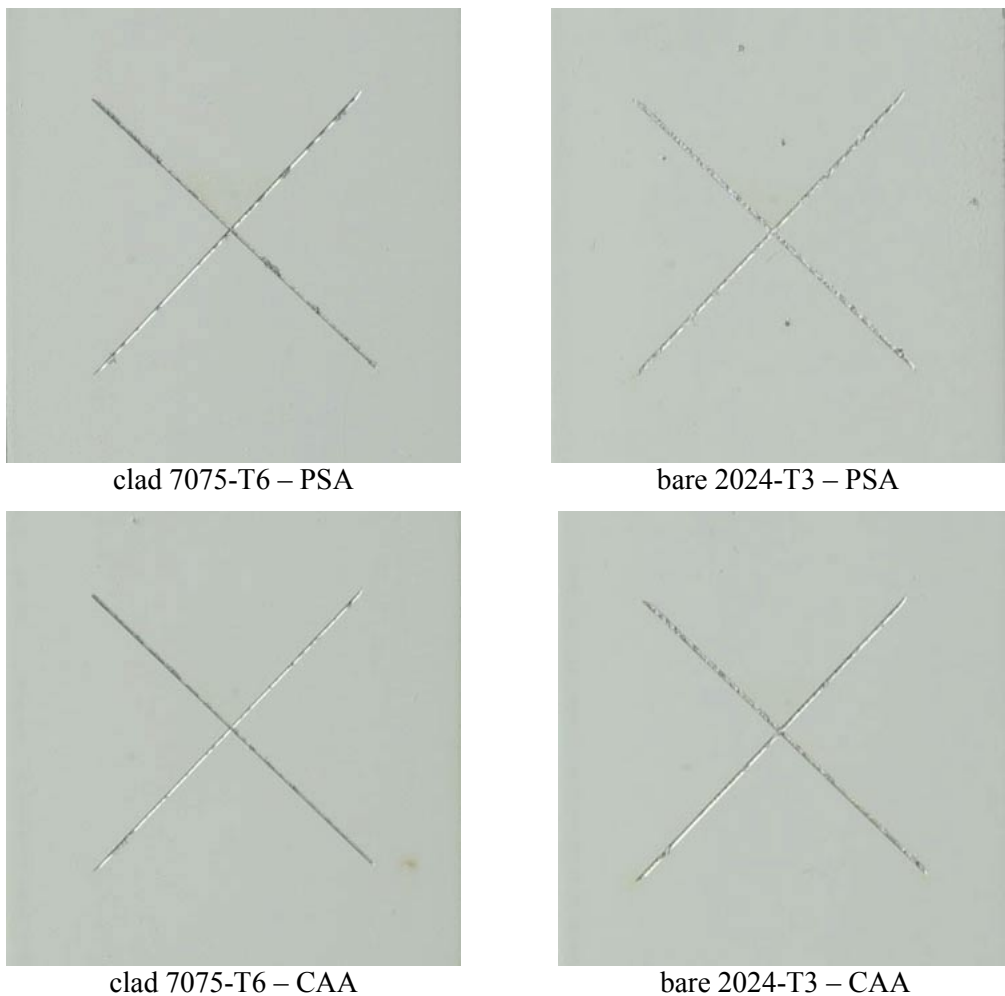


Figure 3: Details of the surface appearances of anodised and primed aluminium after 9 weeks MASTMAASIS exposure, showing negligible difference between the PSA anodised and CAA anodised samples.

limited. A well-adhering (impermeable) top-coat will reduce the transport of water to the coating – substrate interface and may thereby reduce blister formation and increase the life-time of the substrate – coating system.

Application of the primer diminished the differences between the different substrates and the different anodising conditions (figure 3).

Anodised versus anodised and primed specimens. Comparison of the anodised specimens after 6 weeks of MASTMAASIS exposure with the primed specimens after 9 weeks shows that the chromate-free primer provided good protection against corrosion of the scribelines, presumably by the effect of a non-chromate corrosion inhibitor.

Anodised material, tested in intermittent salt spray environment, showed differences in corrosion between PSA and CAA anodising. These differences were absent for anodised and primed material. This shows that the thickness and structure of an anodic layer are less important for the corrosion resistance when a primer is applied, provided that the structure of the anodic layer results in good adhesion of the primer. Application of a top-coat or an adhesive will improve the corrosion protection of the primed material. Therefore the differences in corrosion resistance between PSA and CAA anodised material will be negligible for anodised and primed (and painted) material.

Summary. The corrosion experiments on anodised specimens showed that CAA anodic layers provided better corrosion protection than PSA anodic layers for all substrates investigated. The differences correlate well with the thickness of the layers, indicating that a thick layer provides better protection than a thin layer. As expected, the presence of a clad layer provides additional corrosion protection of the core material. The corrosion protection by PSA anodic layers is considered insufficient, especially for bare 2024-T3.

After application of a primer, both anodising processes provide similar protection against corrosion. Hence, CAA can be replaced by PSA anodising as pre-treatment for priming and painting.

Fatigue

The fatigue tests showed identical results for both PSA and CAA anodising. The S–N curves shown in figure 3 coincide and the fatigue cracks initiated at the same locations. The fatigue crack initiation locations were:

- the milled and anodised side for specimens tested at maximum stresses above 225 MPa;
- the corner of the specimen, and often also at the clad surface, for specimens tested at maximum stresses below 225 MPa.

Some of the specimens tested at maximum stresses below 225 MPa showed true multiple site initiation. Some other specimens showed secondary crack initiation, whereby the propagating crack caused initiation of new cracks in front of the crack tip. In all these cases cracks initiated in the clad layer.



For specimens tested at high maximum stresses (>225 MPa) cracks initiated at “cavities” in the milled surface. Such cavities were found in all specimens analysed with SEM, also in those tested at lower stresses, but caused crack initiation only in the specimens tested at high maximum stresses. The depth of the cavities (about 30 μm) was much larger than the depth of milling tracks (only a few μm). The anodic layer was present in the cavities, indicating that they were there before anodising. Therefore it is assumed that the chromic-sulphuric acid etching prior to anodising caused the cavities.

Summarising, from the fatigue point of view CAA can be replaced by PSA anodising.

Conclusions

For unprimed (unpainted) components the corrosion protection of phosphoric sulphuric acid anodising is insufficient, probably because the anodic layer was thinner than with chromic acid anodising.

Phosphoric sulphuric acid anodising can replace chromic acid anodising as pre-treatment for painted 2XXX and 7XXX series aluminium components. Fatigue life and corrosion sensitivity of phosphoric sulphuric acid anodised and primed aluminium are the same as for chromic acid anodised and primed aluminium.

Acknowledgements

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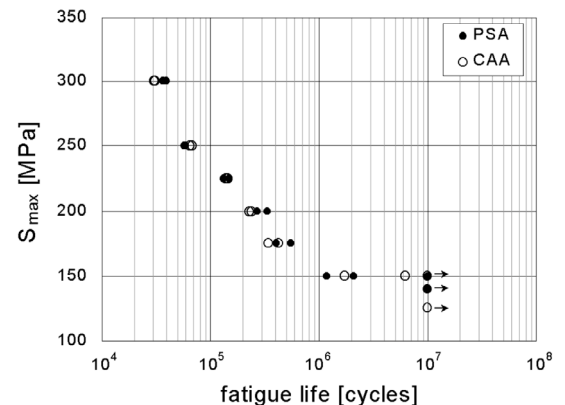


Figure 4: S-N fatigue curves for CAA and PSA anodised 7075-T6 clad showing equal fatigue lives. $R = 0.1$, $K_t = 1.06$.



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