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Friendlier surface treatments - for metals

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Friendlier Surface Treatments – For Metals

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1 Introduction

With only a few exceptions, some degree of surface treatment is applied to all metal surfaces prior to adhesive bonding. The surface treatment applied will depend upon the requirements of the bond and service conditions that it will see and will generally be chosen on a "fit-for-purpose" basis. The minimum preparation which is usually carried out might include a simple degrease to remove processing aids, such as oils and waxes, and contaminants. However, it is recognised that the current state-of-the-art processes for structural or semi-structural metal bonding are highly complex, multi-stage treatments including conversion coating and anodic oxidation. Alternatives to the commonly-used degreasing processes are sought for many reasons, for example: established processes may not be adequate for difficult-to-remove materials; the processes may use VOCs; they can be carcinogenic or ozone depleting. Regarding the higher treatments, the anodising processes, in particular, are difficult, time consuming and costly to carry out. There are also legislative drivers which make utilisation of the more complex processes, especially those which utilise hexavalent chromium, highly undesirable. Other factors such as energy and chemical disposal costs also deserve consideration when considering the need for environmental or operator "friendly" processes.

This paper will consider a number of alternative friendly surface treatments which might be considered as drop-in replacements for the current industrial standards. The friendlier surface treatments include two simple cleaning methods, namely: seaweed-based cleaners and CO_2 laser ablation. In addition, to cover the spectrum of processes, two novel anodising methods will also be discussed. These are based upon electrolytic phosphoric acid deoxidising plus sulphuric acid anodising (EPAD+SAA) and alternating current-direct current (ACDC) anodising.

2 Alternative Cleaning Methods

2.1 Seaweed-based Cleaner

A layer of organic material present on metal surfaces will, typically, give a water contact angle between 55 and 95°. If the organic layer is effectively removed the contact angle will be reduced to zero. In the present study, contact angle measurements provided a simple method to assess the effectiveness of various cleaning agents. Removal of the organic layer is important because it may constitute a weak boundary layer and because removal of a low energy surface will improve wetting by the subsequently applied organic coating.

The present study considered a range of cleaners on as-received stainless steel; the cleaners are detailed in Table 1. Note that percentages are on a volume basis. Household detergents were moderately effective in removing organic material from the stainless steel as can be seen from the much reduced contact angles, in Table 2, compared with the untreated control. However, they were not as effective as the proprietary metal cleaner Circamax 103.. Of particular interest, Sea Power is a natural detergent based on seaweed and is a product of Natural Technologies International Ltd.

AES data confirmed the effectiveness of the proprietary cleaner in removing organic material. On its own, the seaweed-based detergent was not an effective cleaner but in combination with sodium hydrogen orthophosphate, it gave promising results.

As would be expected, the degree of cleaning increased with treatment time. Ultrasonics also significantly increased the effectiveness of the proprietary cleaner. For a given treatment time, the degree of cleaning was improved with ultrasonic agitation. Conversely, a given degree of cleaning could be achieved more quickly if ultrasonics was applied. The alkaline and acid-based cleaners were shown by AES to also modify the surface oxide by enrichment of the chromium in the surface oxide, the thickness of the oxide layer was reduced by both the alkaline and the acidic etches.

Table 1 – A summary of cleaners studied - Code to treatments

Code No.	Process description
1	Untreated.
2	20% Circamax 103 alkaline cleaning solution 2% Domestic detergent 1 solution
3	2% Domestic detergent 2 solution
4	2% Domestic detergent 3 solution
5	2% NMR Sea Power 100 solution
6	2% NMR Sea Power 100 solution + 1% sodium hydrogen orthophosphate
7	solution 2% NMR Sea Power 100 solution + 1% sodium hydrogen orthophosphate
8	+ 1% sodium metasilicate solution. 0.5% NMR Sea Power 100 solution + 1% sodium hydrogen orthophosphate solution.
9	5% Domestic detergent 4 + 1% sodium hydrogen orthophosphate solution. 1% Domestic detergent 4 + 1% sodium hydrogen orthophosphate solution.
10	20% Circamax 103 alkaline cleaner solution followed by 20% Circamax 115 acid cleaner.
11	2% NMR Sea Power 100 solution + 1% sodium hydrogen orthophosphate solution followed by a 4% sulphuric acid solution

Table 2 -Summary of contact angle data

Pretreatment Code	Ultrasonics	Contact angles after x minutes in cleaning solution				
		0	2	5	10	20
1	-	89				
2	√		14	11	9	5
2	-		23	14	17	10
3	√		-	36	37	-
4	√			31	22	-
5	√		-	42	28	-
6	√		-	72	83	-
7	√		53	36	23	16
8	√		33	19	10	13
9	√		50	41	17	20
10	√		15	12	30	30
11	√		54	21	20	15

2.2 CO_2 Ablation

TEA CO_2-laser ablation has been studied to establish its effectiveness for the cleaning of hot dipped galvanised (HDG) mild steel. This laser-based process was demonstrated to be more effective than double-degreasing with ultrasonic immersion in acetone for the removal of organic contamination from a previously oily surface. In addition, the TEA CO_2-laser was shown to modify both the near surface chemistry and the topography; the precise modifications being dependent upon the degree of treatment used.

Importantly, in bond durability trials, the changes introduced to the laser-treated HDG surface were shown to provide equivalent or better joints compared with degreased adherends; see Tables 3 and 4. In the same durability trials, a commercially-available phosphate-based, wet chemical treatment was shown to provide bond durability significantly inferior to the TEA CO_2-laser. In contrast, a chromate-based process gave markedly superior bond durability.

Table 3. Initial joint strengths (kN) of SLS joints as a function of surface treatment

Treatment	Joint strength (kN), ± 1 standard deviation
Double degrease	4.4 ± 0.08
Gardobond 250	4.5 ± 0.22
Gardobond 4504	4.5 ± 0.23
Gardobond 250+4504	3.6 ± 0.11
TEA CO_2-laser treatment – 10 pulses	3.9 ± 0.31
TEA CO_2-laser treatment – 20 pulses	4.0 ± 0.56
TEA CO_2-laser treatment – 30 pulses	4.1 ± 0.22

Table 4 - Mean times-to-failure, t_f, of SSLS joints immersed in water at 60°C at applied loads of 0.2 and 0.5 kN as a function of surface treatment

Treatment	Applied Load (kN)	Mean t_f value (h) ± 1 standard deviation
Double degrease	0.2	163 ± 32
	0.5	85 ± 12
Gardobond 250	0.2	90 ± 16
	0.5	27 ± 7
Gardobond 4504	0.2	235 ± 36
	0.5	172 ± 6
Gardobond 250+4504	0.2	198 ± 53
	0.5	27 ± 7
TEA CO_2-laser treatment – 10 pulses	0.2	177 ± 38
	0.5	37 ± 11
TEA CO_2-laser treatment – 20 pulses	0.2	217 ± 30
	0.5	79 ± 30
TEA CO_2-laser treatment – 30 pulses	0.2	162 ± 30
	0.5	58 ± 18

3 Alternative Anodising Methods

Anodising of aluminium alloys provides a surface that is corrosion resistant and which may be receptive to applied organic layers. Such functionality is achieved by engineering a hydrated oxide film with controlled nanometre-scale porosity within an adherent coating measuring typically 2 to 3.5 micrometres in thickness. The 20-30 nm diameter (Φ) pores created during chromic acid anodising (CAA), for example, enable interphase formation with the organic layer giving excellent adhesion whilst the oxide present provides barrier corrosion protection. Idealised anodic oxide structures, such as those produced on clad aluminium alloy surfaces, are generally of uniform pore diameter with depth, albeit with some lateral branching possible. There is, however, a conflict between the requirement for good corrosion resistance, which dictates a compact pore structure with thick cell walls and small diameters, and adhesion, which requires good interlocking and a large pore diameter. The former case is satisfied by the sulphuric acid anodising (SAA) based processes with Φ ~ 5 nm and the latter by phosphoric acid based processes where Φ ≥ 50 nm. The CAA process, in some respects, provides a compromise.

However, ***duplex*** structures offer the advantages of a large pore diameter in the outer layers of the anodic oxide and very small pores in the inner layer close to the metal to give the optimum adhesion and corrosion performance. There are a number of methodologies which might be used to achieve a resultant duplex structure. In the present study we have used two methods namely: electrolytic phosphoric acid deoxidising plus sulphuric acid anodising (EPAD plus SAA), and: alternating current-direct current anodising (ACDC). Both approaches have demonstrated the that they produce ideal bonding surfaces which is reflected in their ability to provide structurally sound joints when bonded using an epoxy primer/adhesive combination to levels equivalent to the existing CAA as indicated in a range of tests.

3.1 Electrolytic Phosphoric Acid Deoxidising plus Sulphuric Acid Anodising (EPAD+SAA)

Figure 1 shows the structure formed using an optimised EPAD plus SAA process. A number of process variables, for example, immersion times and temperatures plus acid electrolyte types and concentrations were considered to achieve this optimised structure. These will be discussed in detail in the presentation.

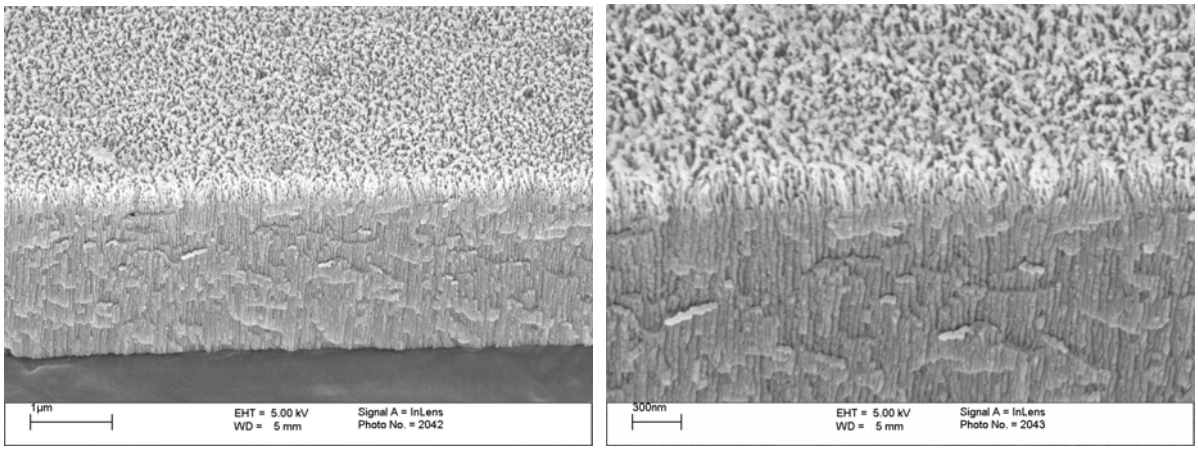


Figure 1 - a. low magnification FEGSEM image to show the through thickness duplex structure of the EPAD plus SAA oxide on clad 2024-T3 aluminium, and; b. the surface region at high magnification.

2024-T3 clad aluminium alloy bonded with the BR127/FM73 primer/adhesive system (Cytec) exposed to 60ºC and tested using the standard wedge test configuration showed comparable results, with optimised processes, to CAA treated controls. In contrast, the SAA only treated aluminium alloy performed very unfavourably in this test due to the lack of primer penetration; see Figure 2.

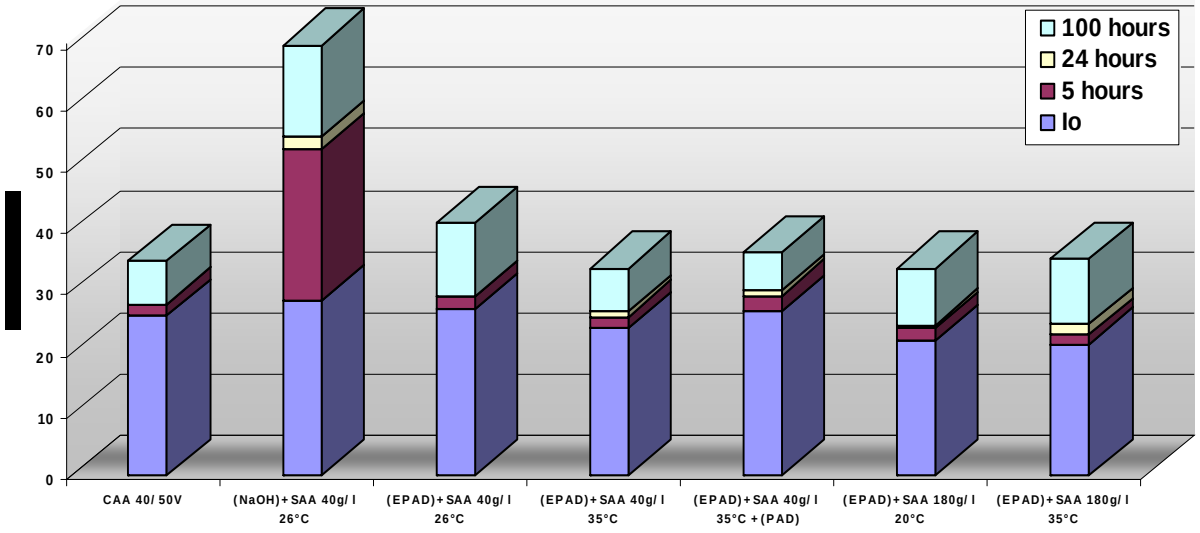


Figure 2 - To show the results of wedge testing with clad 2024-T3 aluminium exposed to deionised water at 60 ºC.

3.2 Alternating Current-Direct Current Anodising (ACDC Anodising).

Figure 3 shows the optimised ACDC structure in cross-section at various magnifications. A range of tests have been conducted using 2xxx (clad and bare), 5xxx, 6xxx and 7xxx (clad and bare) aluminium alloys. These tests include measurement of both adhesion and corrosion performance. In all cases, with all alloys, the ACDC process performed favourably compared with either SAA or CAA controls. Examples of wedge test data are presented in Table 5. Note, however, that peel, butt, lap shear (static exposed and fatigue)

tests have also been carried out, all tests indicating comparable levels of adhesion between ACDC and CAA treated alloys. Similarly, linear polarisation and other corrosion studies have shown that the ACDC process gives comparable corrosion resistance to the CAA. Importantly, the ACDC process is carried out in a weak acid electrolyte containing no hexavalent chromium. Furthermore, the total processing time for ACDC is approximately one tenth of that required to anodise to the standard CAA specification.

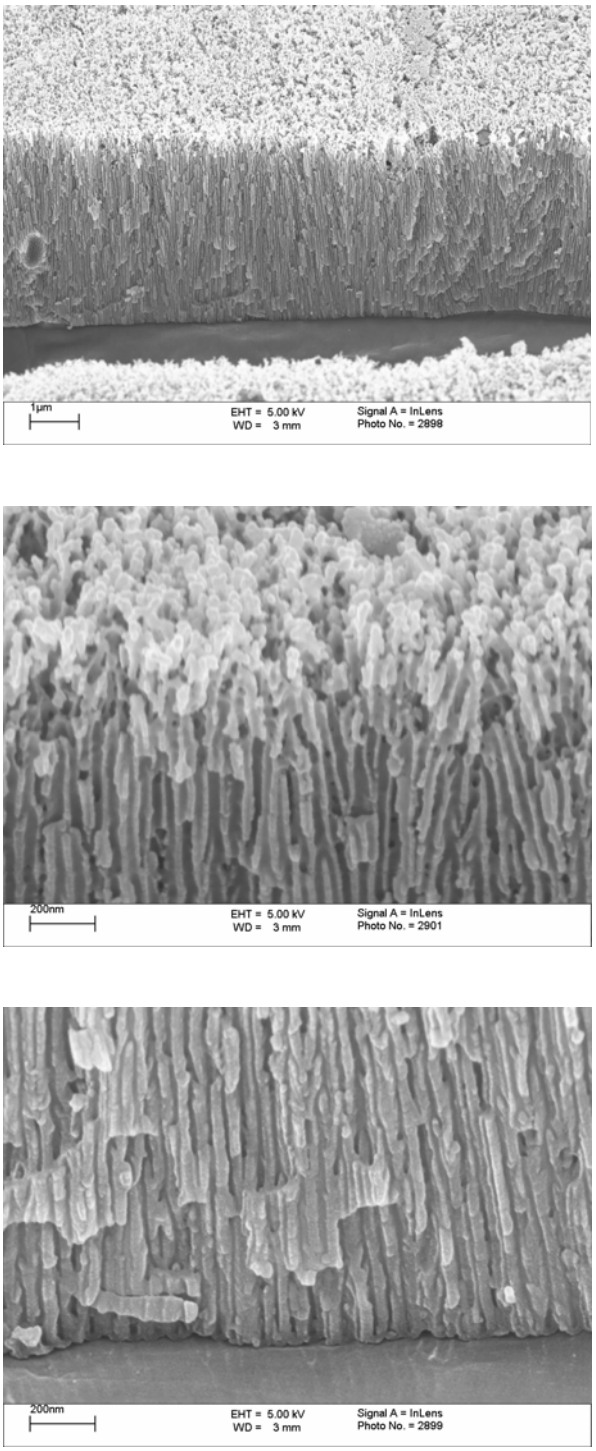


Figure 3 - FEGSEM images to show the structure of optimised ACDC oxides on clad 2024-T3 clad aluminium. Top image shows the through thickness, middle image the outer oxide, bottom image the inner oxide.

AC anodising parameters		Exposure time (h)						
		1	4	8	24	48	72	96
10 V 120 s 35°C	Mean crack length (mm)	33.25	33.25	33.25	35.00	35.38	35.50	35.50
	Σ	0.82	0.82	0.82	0.74	0.75	0.54	0.54
10 V 120 s 50°C	Mean crack length (mm)	31.33	31.50	31.58	32.83	33.33	33.33	33.33
	Σ	0.37	0.41	0.45	1.07	1.18	1.18	1.18
10 V 240 s 35°C	Mean crack length (mm)	31.33	31.42	31.42	33.00	33.33	33.42	33.42
	Σ	0.56	0.69	0.69	0.79	0.95	0.99	0.99
10 V 240 s 50°C	Mean crack length (mm)	33.50	33.67	33.67	34.50	34.83	35.25	35.42
	Σ	0.19	0.25	0.25	0.84	0.45	0.69	0.91
15 V 120 s 35°C	Mean crack length (mm)	31.33	31.67	32.25	33.08	33.25	33.25	33.25
	Σ	0.82	1.25	2.07	1.65	1.57	1.57	1.57
15 V 240 s 35°C	Mean crack length (mm)	31.92	32.17	32.58	33.58	34.08	34.25	34.92
	Σ	0.29	0.56	0.75	1.11	0.90	1.11	1.41
40/50 V CAA	Mean crack length (mm)	31.50	33.10	33.35	33.90	34.45	34.45	34.45
	Σ	0.95	1.09	0.84	1.37	1.90	1.90	1.90

Table 5 - Wedge crack length data to show the influence of varying the AC anodising parameters and electrolyte temperature for the ACDC process; note a 10 m, 20V DC process has been deposited beneath each AC film

4 Summary

- Legislative, H&S and other drivers are currently in place which promote the need for friendly surface treatments.
- The requirements of a particular treatments may vary from a simple degreasing operation to providing complex but well defined surface topography and chemistry to meet the demands of structural bonding.
- A number of drop-in replacements exists today which provide all of the functionality of the industrial standards.