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Optimisation of Anodic Oxidation of Aluminium for Enhanced Adhesion and Corrosion Properties of Sol-Gel Coatings

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The anodising process for clad and bare AA2024-T3 has been optimised as a surface preparation technique prior to sol-gel coating deposition. The combination of anodised aluminium surfaces and functionally computerised sol-gel chemistry have been investigated to impart elevated corrosion resistance and increased mechanical properties to the aluminium metal. A duplex anodising process has been developed to utilise the natural corrosion resistance properties of sulphuric acid anodising with the adhesion and host properties of phosphoric acid anodising. The novel anodising process and sol-gel sealed surfaces have been characterized using field emission scanning electron microscopy, energy dispersive X-ray spectroscopy. Performance of the sol-gel treated anodic layers is evaluated by neutral salt spray testing, electrochemical impedance spectroscopy and rain erosion testing.

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of significant oxide hydration. In order to achieve both encapsulation of sol-gel materials and unaltered surface hydration, a duplex anodic structure is required. A duplex anodic layer consists of an anodic layer formed from a double anodising process conducted in two different electrolytes. Duplex structures have previously been reported as a result of electro-deoxidising and anodising.\(^{20}\)

To optimise the surface preparation of the aluminium surface, a novel anodising process was developed to produce duplex anodic structures on the surface of aluminium alloys. The process was developed to overcome the limitations between forming voltage for the PAA and SAA treatments so that the parameters of each step could be chosen independently. In this way the PAA layer can be tailored to achieve optimum sol-gel encapsulation while the SAA can be used without sol-gel penetration into the pores, therefore not affecting the oxide layer hydration. The duplex anodic structure has been utilised for sol-gel deposition however it can be used for any applications requiring combined corrosion resistance of SAA layers with the adhesion properties of PAA.

**Experimental**

**Sol-gel synthesis.**—Two sol-gel coatings were synthesised and used as sealers for the anodic layers.

**Phenyl functionalised sol-gel.**—The silane precursor phenyltriethoxysilane (PhTEOS) (98%) was purchased from VWR International Ltd (Irl). Hydrolysis was conducted under acidic conditions by adding 5.2 ml of 0.04 M HNO\(_3\) to 50.6 ml of silane precursor. 30.6 ml of absolute ethanol was immediately added to the mixture and left to stir for 45 minutes. 13.6 ml of de-ionised water was then added dropwise and the solution was left to stir for 24 h before use.

The final molar ratio for the formulation was Silane: Ethanol: Water - 1:2.5:3.5.

**Silane-zirconium hybrid sol-gel.**—A silane-zirconium sol-gel formulation (Si-Zr) developed previously\(^{17,24}\) was also utilised for this work. The silane precursor, 3-(trimethoxysilyl) propylmethacrylate (MAPTMS) (Sigma Aldrich, Irl, Assay 99%) was pre-hydrolysed using 0.01 N HNO\(_3\) for 45 min (solution A). Simultaneously, zirconium (IV) n-propoxide (TPOZ) (Sigma Aldrich, Ireland, Assay ~70% in propanol) was chelated using methacrylic acid (MAAH) (Sigma Aldrich), at a 1:1 molar ratio for 45 minutes (solution B) to form a zirconium complex. Solution A was slowly added to solution B over ten minutes. Following another 45 min, water (pH 7) was added to this mixture. The molar ratio of Si/Zr in the final sol is 4:1 and Si/H\(_2\)O is 1:2. After 24 hours of stirring 3.6-Di-2-pyridyl-1,2,4,5-tetrazine (DPTZ) was added as a corrosion inhibitor at a concentration of 0.3% w/v of MAPTMS precursor.

**Pre-treatment and anodising.**—Unclad AA2024-T3 (Si 0.5%, Fe 0.5%, Cu 0.8-4.9%, Mg 1.2-1.8%, Mn 0.3-0.9%, Cr 0.1%, Zn 0.25%, Ti 0.15% other 0.15%, Al remainder) aluminium panels (150 mm × 100 mm × 0.6 mm) were sourced from Amari (Irl). The panels were degreased in acetone, etched in Novaclean 104 for 45 secs, rinsed and etched in Novox 302 for 90 seconds. Novaclean and Novox were purchased from Henkel (Ger). Acetone, NaOH, HNO\(_3\), H\(_2\)SO\(_4\) and H\(_2\)PO\(_4\) were purchased from Sigma Aldrich IRL.

AA2024 clad panels with 40 μm of AA1230 (Si 0.2%, Fe 0.5%, Cu 0.03%, Zn 0.03%, Mn 0.03%, Mg 0.005%, Al remainder) were degreased in acetone, etched in 10% NaOH at 40 °C for 50 seconds and rinsed in de-ionised water. The panels were then treated in 50% HNO\(_3\) at room temperature for 90 seconds to remove any intermetallics from the surface prior to anodising.

Anodising solutions were prepared by diluting 98% H\(_2\)SO\(_4\) w/v and 95% H\(_3\)PO\(_4\) in deionised water to a concentration of 25% w/v and 10% w/v respectively. Three anodising procedures were conducted as follows:

1. Phosphoric Acid Anodising (PAA) – 60 min phosphoric acid anodising at constant 40 V.

2. Sulphuric Acid Anodising (SAA) - 20 min sulphuric acid anodising at 1.5 A/dm\(^2\) of aluminium surface area.

3. Duplex Anodising (DA) - PAA process was conducted as per procedure 1). At the end of the PAA cycle the anodising current was immediately reduced to half of its steady state value. As a result the anodising potential gradually decreased. Once the anodising voltage decreased to 10 V the power was turned off. The surfaces were then rinsed in de-ionised water for 10 min to remove any residual electrolyte from the pores. The parts were then immersed in the sulphuric acid electrolyte. AA2024-T3 and Clad AA2024-T3 were anodised for 5 and 2 min respectively at 1.5 A/dm\(^2\) of aluminium surface area.

All anodised samples were rinsed for 20 min in de-ionised water and air dried prior to sol-gel application and testing.

**Sealing in sol gel.**—For the PAA and SAA surfaces the sol-gel solution was applied immediately after rinsing and drying by a dip coating process. The DA surface was hydrothermally sealed in de-ionised water at 95 °C ± 5 for 5 min prior to sol-gel dip coating. In all cases the dip cycle consisted of a 20 minute immersion step in the sol-gel solution following withdrawal at a rate of 10 mm/min\(^{-1}\). The panels were then cured in an oven at 110 °C for 16 hours. Hydrothermally sealed HTS) equivalents of the DA and SAA layers were also produced for comparison.

**Electron microscopy.**—The anodised films were analysed by electron microscopy using a Hitachi SU 70 Field Emission Scanning Electron Microscope (FESEM). Anodic film cross sections were prepared by bending the aluminium sample over 180° to induce micro-cracks in the oxide layer. The cross section of the crack face exhibits the pore structure of the anodic alumina for imaging at 1.5 – 4 kV. For imaging purposes the samples were sputter coated with a 4 nm layer of Pt/Pd using a Cressington 208HR sputter coater.

Dot Map energy dispersive X-ray spectroscopy was conducted using an Oxford instruments INCA X-MAX Energy dispersive X-ray spectrometer attached to the FESEM. Cross sections were prepared by mounting samples in epoxy resin then grinding and polishing to a mirror finish using progressive grades of carbide paper and polished to a 1 μm finish with a diamond solution. The polished cross sections were coated with 5 nm of carbon using a Cressington 208SC Carbon evaporation coating unit. The Si based sol-gels can be identified by analysing the Si species overlapping with the oxide layer species such as O, P and S.

**Electrochemical impedance spectroscopy.**—Electrochemical Impedance Spectroscopy (EIS) was conducted on the anodised and sealed AA2024-T3. EIS was carried out using a Solartron SI 1287/1255B system comprising of a frequency analyser and potentio-stat operated by CorrView and Z Plot software. A 3.5% NaCl solution was used as the exposure electrolyte and the area of the surface exposed was 4.9 cm\(^2\). A single area of each system was exposed and evaluated. All measurements were made at the open circuit potential (E\(_{oc}\)) with an applied 10 mV sinusoidal perturbation in the frequency range 1 × 10\(^{-2}\) to 1 × 10\(^{-1}\) Hz (10 points per decade). It was found that frequencies lower than this range produced data points with significant noise. Before measurements were taken the open circuit potential was allowed to stabilise to maximum perturbation of 5 mV. Prior to each experiment a calibrated dummy cell was used to ensure the correct measurement of the system. A calibrated reference electrode, checked against an unused control electrode, was used for each experiment.

**Neutral salt spray.**—Corrosion resistance testing was conducted in a neutral salt spray environment according to BS EN ISO 9227:2006 with the back and sides of each panel protected with an impermeable electrically insulating tape. The test conditions consisted of a neutral salt fog atmosphere generated from 5 wt% aqueous NaCl solution at 35 ± 1 °C. The panels were placed at an angle of 20° (±5) from the vertical to allow the salt spray to settle on the test face. The panels
were exposed to the corrosive conditions for up to 3500 h. A corrosion rating was assigned after each inspection based on the grid method specified in BS EN ISO 12373-19:2001.

Rain erosion.—To simulate the effect of rain erosion on the anodised and sol-gel sealed surface, a Whirling Arm Rain Erosion test Rig (WARER) was used. Circular test samples were produced from the anodised and sol-gel treated samples by punch and die. The initial sample mass was recorded. Mass measurements were repeated 3 times and taken using an Ohaus Explorer analytical balance with an accuracy of 0.1 mg. Inspection was also carried out for scratches and surface imperfections before testing. An individual test sample was then mounted at the end of the whirling arm. Tests were carried out at 178 ms⁻¹ and weight loss was recorded at four test durations; 15, 30, 45, and 60 min. The total test duration is based on the length of time the droplet system is active. The rainfall rate was 25 mm/h and was monitored by a flowmeter. A cooling system was used to keep the ambient temperature constant during testing. After each test, the coupons were dried with compressed air and the mass recorded again.

Results and Discussion

Anodic layer formation.—SAA treatment of 2024-T3 and clad 2024-T3 alloys have been studied in many publications and the structures and anti-corrosion properties are well documented. DA layers have also been previously reported, however the research to date is limited and the process has not been optimised for sol-gel deposition. The current process produces duplex layers of unique structure as seen in the electron micrograph in Figure 1.

The duplex structure consists of a SAA layer approximately 1 μm in thickness next to the aluminum base metal. This layer exhibits all the natural properties of conventional sulphuric acid anodising such as a small pore diameter as well as surface hydration and auto-sealing. Attached to the surface of the SAA is approximately 2 μm of oxide produced from the PAA process. The oxide exhibits a large pore diameter with a high level of interporosity. This interconnectivity between pores allows better penetration of liquids into the oxide network as the pressure increase within the pores due to the impinging liquid is easily dissipated.

Conventionally the forming voltage of the PAA process is larger than the SAA process. PAA can be conducted up to 200 V while SAA processes generally do not exceed 25 V. The predominant structural effect of the forming voltage is the relative barrier layer thickness with nano-layers formed at approximately 1 nm. The barrier layer has been shown to be a significant feature in the electrochemical response of anodised layers. Due to this difference in forming voltage and subsequent barrier layer thickness, burning and rapid dissolution of the metal can occur during the SAA cycle due to the insulating effect of the previously formed PAA layer. The critical requirement for the formation of DA layer without burning of the aluminum surfaces is the reduction of the barrier layer thickness of the PAA layer prior to the SAA anodising.

After conducting the initial PAA process a porous layer with a relatively thick barrier layer is formed, Figure 2a. The barrier layer formed at the base of the pores is approximately 40 nm in thickness as measured by SEM analysis. It is known that the charge transfer across the barrier is due to ionic conduction of the anodising electrolyte ions as well as Al³⁺ and O²⁻ ions. If the barrier layer thickness is not decreased prior to the SAA process, the application of the second lower steady state anodising potential is not sufficient to allow ionic transfer across the barrier layer. Rather than distributing uniformly across the metal surface, the current will conduct through the point of least resistance. It was found that the process of in-situ electrochemical thinning of the barrier layer (Figure 2b) prior to the second anodising process is critical to prevent burning and dissolution of the metal surface due to large build up of current density at weak spots in the first anodic layer.

Barrier layer thinning (BLT) utilises the self regulating nature of the anodising process. By rapidly limiting the current at the end of the PAA process to half of the steady state anodising current, the voltage will gradually decrease from the set 40 V to a lower value. During this decrease in voltage, the self regulating characteristic of the anodising process results in a corresponding thinning of the barrier layer Figure 2b. Once a second steady state anodising voltage is reached, the anodising current can again be halved which results in a further voltage drop and continued barrier layer thinning. This step can be further repeated and by sequentially limiting the current in this way a final steady state voltage of the first anodising process can be lowered below the initial anodising voltage of the second anodising process. The results of a BLT process to 10 V and 2 V can be seen in FESEM images in Figure 3. By lowering the forming voltage to 2 V it can be seen that the barrier layer is almost completely removed. Complete removal of the barrier may however compromise the interfacial adhesion between the anodised layers. Barrier layer thinning to a forming voltage of 10 V is sufficient to allow the second anodising process to proceed and in the present study a single current limiting step was required.

Once the BLT PAA anodised aluminum is immersed in the SAA electrolyte and a potential above 10 V is applied, ionic conduction across the barrier layer will occur. This results in a thickening of the barrier layer and SAA layer pore nucleation initiates. The SAA layer growth then proceeds uninhibited, Figure 2c. The use of an
intermediate BLT step between the first and second anodising processes allows the parameters for each treatment to be chosen independently. This allows a great deal of flexibility in the layer thickness, pore features and chemical nature of the possible duplex structures that can be formed.

**Sol-gel penetration.**—There are many factors that can determine if the sol-gel treatment penetrates the porous anodic layers. PAA layers offer the best possibility of penetration due to the large pore diameter, however if the particle size is sufficiently small the sol-gel colloids can also migrate into the SAA layers. In order to determine the penetration properties of each anodic finish, EDX dot map analysis was used to plot the Si and Al distributions. Figure 4 exhibits the dot maps for the PhTEOS and Si-Zr sol-gel sealed SAA, PAA and DA films on unclad AA2024. The individual layer thicknesses differ from Figure 1, as the alloy is unclad AA2024 as opposed to the clad version in Figure 1.

The PhTEOS exhibits penetration into all surfaces and previous research has shown that the particle size is sufficiently small to allow penetration. On the SAA layer, which contains the smallest pore diameter, it is clear that the PhTEOS sealer has significant penetration into the oxide with Si intensity deteriorating rapidly at approximately 75% of the oxide thickness. The PAA is known to act as an excellent host for sol-gel materials and penetration can be seen again throughout the layer. For the DA layer penetration occurs in the PAA upper layer without evidence of any migration into the SAA base layer probably due to the forced hydration and pore closing between the PAA and SAA layers. In the case of the Si-Zr sol-gel, limited penetration into SAA network occurs. A surface coating only can be distinguished from Figure 4. Similarly to the PhTEOS, the Si-Zr sol-gel penetrates the PAA networks of both the single and duplex anodised layers.

**Electrochemical impedance spectroscopy.**—EIS analysis was conducted on the un-clad 2024-T3 as the electrochemical response is from the copper rich base metal which is more susceptible to corrosion than the clad material.

The impedance and phase shift spectra for the SAA anodisation with sealers, HTS, PhTEOS and Si-Zr, can be seen in Figure 5. The HTS sealed SAA layer exhibits a characteristic single time constant response. Limited hydration sealing of the pores is detected which is consistent with previous work. Both sol-gel sealers display increased impedance values, for all frequencies, indicating increased barrier properties of the sol-gel sealers compared to the HTS equivalent. The SAA PhTEOS system displayed a single time constant response indicating that the contributions from the sol-gel sealer and the barrier layer cannot be distinguished. From the EDX analysis it is known that...
this sealer penetrates the porous network and the EIS response is as a result of the sol-gel/oxide composite layer. PhTEOS sol-gel sealed SAA anodic layers have been previously reported on 3003 and have produced a similar single time constant response.\textsuperscript{26}

In contrast the SAA Si-Zr system exhibited a second time constant. As this sol-gel system acts as a surface coating on the anodic layer, the impedance response likely comprises the response from the surface coating and the barrier layer. The effect of the penetration of the PhTEOS sealer compared to the Si-Zr equivalent can be seen in the low frequency impedance values (< 1 Hz). The PhTEOS system displays higher impedance values, in this frequency region, due to the presence of the sol-gel in the pores.

The impedance and phase shift spectra for PAA sealed anodic layers can be seen in Figure 6. The sol-gel sealers showed an increase in impedance, compared to the PAA blank, in the high frequency range ($\sim 1 \times 10^4$ Hz). As the pores of PAA anodic layers are known to remain open indefinitely\textsuperscript{1} the encapsulation of the sol-gel sealers results in this increase in the impedance compared to the PAA blank. In contrast to the SAA PhTEOS layer the PAA PhTEOS layer exhibits a two time constant response. The barrier layer of the PAA anodic layer will be thicker, due to higher forming voltage than the SAA equivalent, and perhaps this increased oxide thickness results in the discrimination between the sol-gel material and the anodic alumina barrier layer. The low frequency impedance of the PAA Si-Zr layer exhibits lower impedance values than the PhTEOS equivalent. The low frequency impedance (0.1 Hz) of the PAA Si-Zr is equivalent to the PAA blank. The PhTEOS sealer shows higher impedance than both the PAA blank and the PAA Si-Zr sample. This may be due to better penetration of the PhTEOS sol-gel to the base of the pores to the barrier layer.

The impedance and phase shift spectra for DA sealed anodic layers can be seen in Figure 7. The DA HTS samples exhibits a similar response to the SAA HTS sample with a single time constant detected. Significantly, despite the increased thickness of the SAA layer compared to the sulphuric acid formed layer in the DA structure the impedance response are relatively similar. The EIS response in both

Figure 5. Impedance (top) and phase plot (bottom) for SAA sealed samples.

Figure 6. Impedance (top) and phase plot (bottom) for PAA sealed samples.

Figure 7. Impedance (top) and phase plot (bottom) for DA sealed samples.
Figure 8. Plot of impedance as a function of time for PhTEOS treated layers exposed to 3.5% NaCl.

Figure 9. Plot of impedance as a function of time for Si-Zr treated layers exposed to 3.5% NaCl.

Figure 10. Rain erosion performance of anodised and sol-gel sealed systems on clad 2024-T3.

Table 1. Neutral salt spray corrosion ratings of anodic layers on AA2024-T3.

<table>
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<tr>
<th>Treatment</th>
<th>Anodising</th>
<th>Sol-gel</th>
<th>First Cor</th>
<th>TCorr</th>
<th>NSS Duration</th>
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<td>Sol-gel</td>
<td>First Cor</td>
<td>TCorr</td>
<td>24 h</td>
<td>168 h</td>
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<td>50</td>
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<td>12</td>
<td>200</td>
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<tr>
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<td>1</td>
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<td>-</td>
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<td>0</td>
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</table>
been used for comparison. As expected in the unsealed form, the
SAA, PAA and DA surfaces offer little protection with corrosion oc-
curring rapidly. The SAA and PAA layers exhibited pitting corrosion
after 24 h exposure with the DA surface remaining clear of corro-
sion until 72 h exposure. Upon the onset of initial corrosion, pitting
increases rapidly for all of the unsealed anodised surfaces. The pre-
ence of the sol-gel within the pores of the SAA layer appears to have a
negative effect on corrosion prevention with a marginally higher level
of pitting exhibited on the PhTEOS treated surface when compared
to the unsealed SAA. This is possibly due to the effect on hydration
due to the presence of the sol-gel within the aluminum oxide network.
The sol-gel may retard the hydration of the surfaces as has been
previously reported. 1 In the case of the PhTEOS PAA layer there is
a marginal reduction in pitting however the improvement over the
unsealed PAA is negligible. The PhTEOS sealed DA layer exhibited
a marked increase in pitting prevention over the other PhTEOS sealed
anodised finishes. This displays the value in utilising the DA process,
as the natural hydration properties of the anodic layers are retained,
while the sol-gel is also encapsulated in aluminum oxide.

The negative effect of the PhTEOS sealer on the SAA layer during
neutral salt spray was not identified by the EIS analysis. One possible
explanation is the difference in exposure area during the test. The
much larger surface area exposed during the NSS test may be more
indicative of the actual corrosion resistance than the smaller area EIS.
For all samples the discrimination in corrosion resistance is greater by
NSS than EIS indicating that the NSS is possibly a more aggressive
test. The authors also believe that the EIS immersion cycle allows the
natural hydration of the layers to proceed better than the salt fog test.
Additionally, the salt fog test has reported to delaminate and remove
sol-gel coatings attached to anodic layers, 2,3 which may result in a
more aggressive corrosion effect.

The Si-Zr sol-gel displays enhanced pitting corrosion protection
over the PhTEOS sol-gel sealed systems. The increased barrier prop-
erties as well as the inclusion of an active corrosion inhibitor results
in a significant level of protection for all anodising treatments. The
SAA layer in particular exhibits remarkable corrosion resistance with
no evidence of pitting at 3500 h. The absence of pore penetration of
the Si-Zr sol ensures that the natural hydration properties of the SAA
layer are retained unlike the PhTEOS equivalent. Furthermore, the
inclusion of an the tetrazine based corrosion inhibitor may also have
a positive effect on the integrity of the SAA layer as tetrazines are
known to bond to and chelate copper ions. 4 These inhibitors have been
studied as standalone treatments for anodic layers and have shown in-
creased ability to inhibit pitting corrosion. 5 The DA equivalent shows
a higher degree of degradation, when compared to the SAA equiva-
 lent, possibly due to the decreased thickness of the SAA layer. The
worst performing Si-Zr sealed layer is the PAA.

Rain erosion.—Anodising is often used to increase the surface
hardness and abrasion resistance of aluminum alloys. 1 By incorpo-
rating the sol-gel-coating into the aluminum oxide network elevated
mechanical properties are afforded to the sol-gel coating. This will
improve the hardness, abrasion resistance and impact resistance of
the sol-gel coatings. A significant advantage of increased mechanical
performance for the aerospace industry is the decreased effect of rain
erosion. Erosion of aerospace grade aluminum alloys by impinging
water droplets is a significant issue especially during aircraft take-off
and landing. 39,40

Whirling arm rain erosion evaluation of the Si-Zr sol-gel sealed
clad 2024-T3 samples was conducted and the weight loss over the 60
min exposure was recorded as seen in Figure 9. The weight loss for the
sol-gel applied on the SAA is significantly greater than any other
surface tested. From the EDX analysis (Figure 4), it is determined that
the sol-gel forms a surface coating on the SAA surface with limited encapsulation in the porous anodic alumina. Therefore, the
rain erosion and weight loss of this system is of the sol-gel coating
only, which is mechanically inferior to the aluminum oxides produced
from SAA, PAA and DA as well as the sol-gel/alumina composites
produced from sol-gel encapsulation.

This indicates that the encapsulation of the sol-gel coatings in
anodic alumina presents a significant improvement in rain erosion.
The weight loss of the bare anodic layers or sol-gel encapsulated layers
is minimal.

Sol-gel materials have been studied extensively for replacement
of chromate materials as they can act as reservoirs for active corro-
sion inhibitors. However for many sol-gel coating additives there is a
critical concentration after which the additive affects the film forming
properties and integrity of the applied sol-gel film. Excess amounts of
corrosion inhibitors have shown to have a negative effect on film
forming properties of sol-gel coatings. 41–45 By utilising a duplex an-
odic oxide, the active corrosion inhibitors can be incorporated in the
SAA layer at a significantly higher concentration while the sol-gel
can be encapsulated in the porous PAA network. As shown from the
results, the DA layer is particularly suitable for sol-gel sealing. Due
to the low thickness of sol-gel coatings, the PAA layer can be tailored
to result in full encapsulation of the sol-gel coating within the anodic
structure. Furthermore, conventional sealing methods can be applied
to the SAA base layer of the DA structure. This results in elevated
corrosion resistance while also preventing the sol-gel material from
migrating into the SAA pores. This becomes particularly important
with clad AA2024 or non copper containing alloys as the natural
hydration properties of SAA layer is therefore not affected by the
presence of the sol-gel material. The DA process developed can also
be utilised for adhesion and bonding applications while also retaining
a significant level of corrosion resistance on aluminum alloys.

Conclusions

Duplex anodic layers have been developed to achieve sol-gel en-
capsulation in porous anodic alumina to ensure that the natural hydra-
ration properties of anodised aluminium is retained. By encapsulating
sol-gel materials in phosphoric acid anodised aluminium the mechan-
ical properties of the sol-gel coatings are enhanced. By forming a
sulphuric acid anodised layer between the sol-gel/alumoxide composite
and the substrate the combined corrosion resistance is significantly
enhanced. The value of utilising the duplex anodic layers is evident
due to the achievable anti-corrosion performance on corrosion prone
2024-T3, sealed with a simple organically modified silane based sol-
gel. The performance is further enhanced by applying a Si-Zr hybrid
sol-gel with active tetrazine based inhibitor. For all systems the ab-
seence of the sol-gel from the pores of the SAA layers is critical to
allow the natural or accelerated hydration of the systems to proceed.

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