Vanadate post-treatments of anodised aluminium and AA 2024 T3 alloy for corrosion protection

S. Liu\textsuperscript{a}, G. E. Thompson\textsuperscript{b} and P. Skeldon\textsuperscript{b}

\textsuperscript{a}Y.C. Solutions, Aberdeen, UK; \textsuperscript{b}Corrosion and Protection Group, School of Materials, The University of Manchester, Manchester, UK

**ABSTRACT**

Porous anodic films formed on aluminium in sulphuric acid were post-treated using various double-dip processes that incorporate a sparingly-soluble, vanadate, corrosion inhibitor. The processes were optimised by investigating the effects of the double-dip order, the rinsing step, the immersion time and the double-dip method. The optimised processes were applied to AA 2024-T3 alloy, which was then exposed to salt spray. V-Cell(III) and V-Zn processes provided corrosion protection similar to that of sealed, sulphuric acid-formed films. A V-Ni process provided increased protection, similar to that of hot water sealed films formed in chromic acid.

**Introduction**

Aluminium alloys are major structural materials in the manufacture of aircraft. For corrosion control, various protective treatments are applied. Common protection schemes utilise chromic acid anodising and application of chromate pigmented epoxy primers.\textsuperscript{2} The combination provides both barrier protection and corrosion inhibition at damaged areas through the use of chromate species. However, the environmental and health impacts of chromates have prompted the search for effective alternative surface treatments.

It has been suggested that sulphuric acid anodising may be a suitable replacement for chromic acid anodising.\textsuperscript{2} However, sulphuric acid films do not contain a corrosion inhibiting component. Baldwin et al. patented a method to improve corrosion resistance after anodising in sulphuric acid utilising a double-dip process, which involved immersion in a solution or gel containing metavanadate ions and then in a solution containing a metal cation.\textsuperscript{2} The precipitation of a sparingly soluble compound within the porous oxide provided a ‘built-in’ inhibitor.

Vanadates have been investigated as corrosion inhibitors in aqueous environments, and also as components of conversion and organic coatings, for a range of metals, including aluminium,\textsuperscript{3–6} magnesium,\textsuperscript{7,8} steel\textsuperscript{9} and zinc.\textsuperscript{10} Work has revealed that crevice corrosion of aluminium can be inhibited in a sodium chloride solution.\textsuperscript{11} Metavanadates have been shown to inhibit oxygen reduction on AA 2024-T3 alloy,\textsuperscript{12,13} although no effect was found with decavanadate.\textsuperscript{13} It has been reported that inhibition does not involve reduction of vanadate.\textsuperscript{14} Inhibition was observed mainly in alkaline conditions when tetrahedrally coordinated vanadate, metavanadate and pyrovanadate were present and the pitting potential was increased.\textsuperscript{15} An increased pitting potential and suppressed dissolution of S phase was reported for a range of copper-containing intermetallic particles with vanadate addition to alkaline sodium chloride solutions.\textsuperscript{16} Mono-vanadates have been found on the matrix of AA 2024-T3 alloy in an acidic solution and a polyvanadate film on intermetallic particles in a basic solution.\textsuperscript{17} The formation of tetrahedrally co-ordinated vanadate was considered to be important to corrosion protection.\textsuperscript{17} Vanadates have been reported to limit corrosion associated with intermetallic particles up to 50°C.\textsuperscript{18}

In the present study, various double-dip processes were applied to sulphuric acid anodised (SAA) aluminium and AA 2024-T3 alloy. First the corrosion inhibition by incorporated vanadate compounds was optimised by investigating the influences of the double-dip order, rinsing step, immersion time and double-dip method on the retention of vanadates in the films. The effectiveness of the optimised processes was then assessed on AA 2024-T3 alloy by salt spray exposure.

**Experimental methods**

**Specimen pre-treatment and anodising**

Specimens of 99.99% aluminium, consisting of rolled sheet of 0.6 mm thickness, and AA 2024-T3 alloy (3.8–4.9% Cu, 1.2–1.8 wt-% Mg, 0.3–0.9 wt-% Mn, 0.5 wt-% Fe, bal. Al), consisting of rolled sheet of 1.5 mm thickness, were used in the study. The specimens were degreased with acetone, etched in 100 g L\textsuperscript{−1} sodium hydroxide solution for 60 s at 60°C, rinsed in deionised water and desmutted in 50 vol.-% nitric acid for 3 min at ambient temperature. Finally, they were rinsed in deionised water and dried in a cool air stream.

The anodising cell consisted of a 2 L glass flask fitted with a thermometer and a semi-cylindrical platinum (40 mm length and 35 mm diameter) or stainless steel (127 mm length and 80 mm diameter) cathode. A magnetic stirrer provided vigorous stirring of the electrolyte. The electrolyte temperature was maintained at 20 ± 0.1°C by placing the cell in a thermostatically controlled water bath. Anodising was carried out at a constant current density of 15 mA cm\textsuperscript{−2} in 20 wt-% sulphuric acid using a Good Will Instruments Model GPR-3SH20 power supply.
supply. The anodising time was 10 min for the aluminium and 15 min for the alloy. Specimens were finally rinsed in deionised water and dried in a cool air stream. Control specimens were anodised in chromic acid at 40°C according to the BAe specification ABP 1-1023, Method 1.96, which complies with the DEF STAN 03-24/2, as follows: (i) the voltage was increased from 0 to 40 V in steps of 4 V over a 10-min period; (ii) then held at 40 V for 20 min; (iii) then raised to 50 V in steps of 2 V over a 5-min period; (iv) and lastly held at 50 V for 5 min. The thicknesses of the films formed in the sulphuric acid and chromic acid electrolytes were measured at twelve locations on the anodised specimens using a FISCHERSCOPE eddy current meter; the average values were 5.0 and 2.5 μm, respectively. Prior to use, calibration was carried out with supplied standards, which included an electropolished, non-anodised specimen and anodised specimens with film thicknesses of 2.0 and 25 μm.

### Post-treatments

In order to optimise double-dip processes, all solutions employed were studied individually. The single dip procedures are designated as follows, where solution X is nickel sulphate (NiSO₄), or 10 g L⁻¹ nickel sulphate (NiSO₄), or 10 g L⁻¹ cerium(III) sulphate hydrate (Ce₃(SO₄)₂·6H₂O):

- **(i) X-no rinse process**: immersion in X for 10 min at 40°C, no rinse, followed by drying in air;
- **(ii) X-rinse process**: as (i) but with rinsing in deionised water after immersion in X;
- **(iii) X-H₂O process**: as (i) but with immersion in deionised water for 10 min at 40°C after immersion in X;
- **(iv) H₂O-X-no rinse process**: immersion in X for 10 min at 40°C, no rinse, followed by drying in air;
- **(v) H₂O-X-rinse process**: as (iv) but with rinsing in deionised water after immersion in X.

Double dip processes were carried out by immersion of specimens for 10 min in sodium metavanadate solution at 40°C followed by immersion for 10 min in a metal sulphate solution at 40°C. The specimens were then rinsed in deionised water and dried in air. The effects of rinsing between immersions and the times of immersion in the solutions were also investigated.

#### Hot water sealing

Following anodising, some specimens were sealed in water at 100 ± 0.5°C using glass flasks, equipped with a reflux condenser, placed in a thermostatically controlled isomantle heater. Deionised water of conductivity about 10⁻⁵⁻¹⁻⁶Ω⁻¹ cm⁻¹ and pH 5.5 at 293 K was employed. The water volume to specimen area ratio was ≥125 L m⁻². Sealing was carried out for 10 min for films formed in sulphuric acid and for 5 min for films formed in chromic acid. Lastly, specimens were rinsed in deionised water and dried in a cool air stream.

### Specimen examination

Scanning electron microscopy, with energy-dispersive X-ray (EDX) spectroscopy, was employed to determine film compositions using an Amray 1810 instrument, operated at 20 kV. Analyses were made at three spots on the surface of each specimen from which the atomic ratio of the metal species (vanadium, cerium, nickel or zinc) to aluminium was determined. The mean values of the ratios from the three analyses are presented. The compositional information from the analyses was limited to the outer ≈ 2–3 μm of the film thickness. A typical EDX spectrum is shown in Figure 1 for a specimen treated by a V-Ni double-dip process with rinsing of the specimens between dips. Since mostly small amounts of solution species were incorporated into the variously treated films, peaks in the EDX spectra were low relative to the background noise. Thus, the presented ratios of the metal species to aluminium have an accuracy of about ±25%.

Specimens post-treated using the V-Ni and V-Zn processes were examined using glow discharge optical emission spectroscopy (GDOES), employing a Jobin-Yvon 5000 RF instrument, with argon at 3 Torr, RF of 13.96 MHz and power of 25 W. Light emissions from O, Zn, Ni, Al and V were monitored at wavelengths (nm) of 130, 335, 341, 396 and 411 nm, respectively. The area of analysis was of 4 mm diameter.

Compositional analysis was also carried out by Rutherford backscattering spectroscopy (RBS) employing 2.0 MeV α-particles provided by the 2.5 MeV Van de Graaff accelerator of the University of Paris. The beam current and beam diameter were 60 nA and 1 mm, respectively, with the beam incident normal to the specimen surface. The particles were detected at 165° to the direction of the incident beam. The data were interpreted using the RUMP program, with the composition of the near-surface regions (~0.4μm thick) determined.

### Salt spray testing

Neutral salt spray testing was carried out according to ASTM B 117. Treated panels were tested for times up to 1248 h. After testing, the panels were rinsed and corrosion was evaluated.

### Results and discussion

#### Reaction in bulk solution

The times for double-dip solutions to precipitate salts were investigated by mixing 200 mL metal sulphate solution and 200 mL sodium metavanadate solution at the concentrations and temperature used in double-dip treatments. Precipitation occurred immediately with cerium(III) sulphate, and after 10
and 30 min with zinc(II) and nickel(II) sulphates, respectively. Yellow, black and green reaction products were filtered from the mixtures with zinc(II) sulphate, cerium(III) sulphate and nickel sulphate solutions, respectively.

Reaction in the pore volume

Figure 1 presents the results of EDX analyses of variously treated films. The V-rinse process, i.e. the first dip of a double-dip process followed by rinsing in deionised water, resulted in an atomic ratio of V:Al of $6.7 \times 10^{-3}$. Following subsequent immersion in nickel, zinc or cerium(III) sulphates, the V:Al ratio was reduced by about 70, 40 and 10%, respectively (Figure 2(a–c), respectively). Nickel and cerium species were deposited, with Ni:Al, and Ce:Al ratios of $3.3 \times 10^{-3}$ and $6.2 \times 10^{-3}$, respectively (Figures 2(a) and 1(c) respectively). No peak for zinc was resolved in the EDX spectra, indicating a Zn:Al ratio of $\leq 1 \times 10^{-3}$. Substituting immersion in water for the vanadate solution (H$_2$O-X-rinse) led to a 75% increase in nickel, negligible effect on zinc and no incorporation of cerium, the last indicating that vanadium species enhanced the uptake of cerium.

The high V:Al and Ce:Al ratios in the film treated by the V-Ce(III) process show that the precipitation has occurred of the sparingly soluble metavanadate by a double decomposition reaction. Following the V-Ni and V-Zn double-dip processes, the amounts of nickel and zinc were similar to or less than those of the H$_2$O-X-rinse process suggesting that double decomposition reactions were insignificant and the species detected were introduced due to adsorption on pore walls.

Effect of rinsing

Figure 3 shows the V:Al ratios from EDX spectroscopy for X-no rinse, X-rinse, X-H$_2$O, H$_2$O-X-no rinse and H$_2$O-X-rinse processes (X = V, Ni, Zn, Ce(III)). The trends for X = V, Ni and Zn were similar, with the highest X:Al ratios for X-no rinse and H$_2$O-X-no rinse. Lower ratios occurred following rinsing or immersion treatments, especially for Zn and Ce(III), indicating that incorporated species can be washed out by rinsing in deionised water, with the remaining species decreasing in the order: V $>$ Ni $>$ Zn $\approx$ Ce.

Results of RBS, which examined larger areas but reduced depths compared with EDX analysis, of V-no rinse and V-rinse films are shown in Figure 4. The spectra reveal scattering from aluminium, oxygen, sulphur and vanadium species in the anodic film. Scattering from vanadium at the film surface occurs at channel 360. Scattering from vanadium within the anodic film is evident between channel 360 and the leading edge of the sulphur signal. This region corresponds to an outer layer of the anodic film of thickness about 350 nm. A comparison of the spectra shows that the amount of vanadium within the film is enhanced significantly when rinsing is not applied to the specimen. The V:Al ratio in the analysed depth was $1.3 \times 10^{-2}$, consistent with the ratio of $1.4 \times 10^{-2}$ from EDX spectroscopy. In contrast, the V:Al ratio for the rinsed specimen was $5.0 \times 10^{-3}$, which is lower than the value of $6.7 \times 10^{-3}$ obtained by EDX spectroscopy, but confirming a depletion of vanadium by rinsing. The spectrum for the non-rinsed specimen shows a small peak from vanadium at the film surface, which corresponds to about $2 \times 10^{15}$ V atoms cm$^{-2}$, which may be adsorbed or chemisorbed residues of the vanadate solution. The results of GDOES analyses, presented later, of specimens subject to a double-dip process with no rinsing after dipping in the vanadate solution revealed a relatively uniform distribution of the vanadium through the whole thickness of the anodic film, indicating that the absence of rinsing increased the vanadium content throughout the film thickness.
Double-dip processes were carried out without the intermediate rinsing step with the aim of increasing the retention of solution-derived species in films. The no-rinse specimens were immersed in the metal sulphate solution after removal from the metavanadate solution, then rinsed and dried in cool air. The V:Al ratios, determined by EDX spectroscopy, in the films are shown in Figure 5 and compared with the ratios for films following the V-no rinse and V-rinse processes and double-dip processes with a rinsing step applied. A no rinse process was either slightly beneficial (V-Zn) or more significantly beneficial (V-Ni and V-Ce(III)) than with rinsing. No rinse processes were also favoured for incorporation of Ce(III), whereas incorporation of Zn and Ni was not enhanced even though the concentration of vanadium species in the films was doubled prior to the second dip (Figure 6). This is because the increased vanadium species were easily leached to the metal sulphate solution within the time required for any reaction within the pore volume. In contrast, the V-Ce(III) process...
introduced a high level of solution-derived species and removal of the rinse significantly increased the retention of both vanadium and cerium species in the films. Schematic diagrams showing the distribution of solution-derived species following the various double-dip processes are illustrated in Figure 7.

**Effect of immersion time**

The effects of the immersion time on the incorporation of species were investigated for each double-dip process by immersing specimens in each of the double-dip solutions for 10, 20, 30 or 60 min, with no rinsing between the two dips. The V:Al ratios in the latter films are shown in Figure 8(a). The V:Al ratio increased from $4.7 \times 10^{-3}$ to $1.0 \times 10^{-2}$ with the increase in the immersion time.

---

**Figure 6.** Atomic ratios of cerium, zinc or nickel to aluminium, determined by EDX spectroscopy, for anodic films generated in sulphuric acid for 10 min and post-treated with various no-rinse double-dip processes: V-Zn process, V-Ni process, and V-Ce(III) process. For comparison, results for rinse double-dip processes (with a rinsing step applied between the successive dips) are also included.

**Figure 7.** Schematic diagrams showing the distribution of solution-derived species following various double-dip processes: (a) immediately after dipping in NaVO₃; (b) after (a) and rinsing with deionised water at room temperature; (c) after (b) and after dipping in Ce₂(SO₄)₃·nH₂O; (d) after (a) and after dipping in ZnSO₄ or NiSO₄.

**Figure 8.** (a) Change of atomic ratios of V:Al with the increase in immersion time following the V-rinse process; (b) change of atomic ratios of V:Al and Ni:Al with the increase in immersion time in each of the double-dip solutions during the V-Ni process; (c) change of atomic ratios of V:Al and Zn:Al with the increase in immersion time in each of the double-dip solutions during the V-Zn process; (d) change of atomic ratios of V:Al and Ce:Al with the increase in immersion time in each of the double-dip solutions during the V-Ce(III) process. The ratios in (a–d) were determined by EDX spectroscopy. For clarity of presentation, error bars are shown in only one of the three curves in each of the figures (b–d).
Figure 8(b) shows that for the V-Ni process the amount of vanadium increased progressively with time; but remained lower than for the control specimens. Conversely, the Ni:Al ratio reached a maximum value of $1.0 \times 10^{-2}$ at 30 min then decreased to $2.1 \times 10^{-3}$ (Figure 8(b)). For these specimens, GDOES analyses were carried out to confirm the trends determined by EDX spectroscopy. The average intensities of optical emissions from nickel and vanadium across the film thicknesses, determined by GDOES, are presented in Table 1; an example of the elemental profiles is presented in Figure 9, which shows that vanadium and nickel are distributed uniformly through the film. In accordance with the EDX spectroscopy, the vanadium intensity increased with the increase in the immersion time from 10 to 60 min, while the nickel intensity reached a maximum after 30 min.

Table 1. Optical emission intensities of vanadium and nickel from GDOES analyses of specimens immersed for different times in the double-dip solutions during the V-Ni process. The specimens were not rinsed between the two dips of the V-Ni process.

| Immersion time in each solution (min) | $V$        | $\text{Ni}$   |
|--------------------------------------|------------|---------------|
| 10                                   | 0.13 ± 0.03| 0.03 ± 0.01   |
| 20                                   | 0.14 ± 0.03| 0.05 ± 0.01   |
| 30                                   | 0.14 ± 0.04| 0.07 ± 0.01   |
| 60                                   | 0.19 ± 0.03| 0.02 ± 0.01   |

For the V-Zn process the V:Al and Zn:Al ratios reached values of $8.0 \times 10^{-3}$ and $3.1 \times 10^{-3}$, respectively after 30 min (Figure 8(c)). No further significant change occurred at an immersion time of 60 min. GDOES analyses (Table 2) showed that the average intensity for vanadium in the films increased up to 30 min followed by a small decrease, in agreement with EDX spectroscopy. The intensity of the optical emission for zinc was too low to reliably determine a trend with immersion time.

Table 2. Optical emission intensities of vanadium and zinc from GDOES analyses of specimens immersed for different times in the double-dip solutions during the V-Zn process. The specimens were not rinsed between the two dips of the V-Zn process.

| Immersion time in each solution (min) | $V_{\text{Zn}}$ | $Z_{\text{n}}$ |
|--------------------------------------|-----------------|---------------|
| 10                                   | 0.17 ± 0.03     | ≈0.01–0.02    |
| 20                                   | 0.22 ± 0.03     | ≈0.01–0.02    |
| 30                                   | 0.23 ± 0.04     | ≈0.01–0.02    |
| 60                                   | 0.17 ± 0.03     | ≈0.01–0.02    |

Figure 8(b) shows that for the V-Ni process the amount of vanadium increased progressively with time; but remained lower than for the control specimens. Conversely, the Ni:Al ratio reached a maximum value of $1.0 \times 10^{-2}$ at 30 min then decreased to $2.1 \times 10^{-3}$ (Figure 8(b)). For these specimens, GDOES analyses were carried out to confirm the trends determined by EDX spectroscopy. The average intensities of optical emissions from nickel and vanadium across the film thicknesses, determined by GDOES, are presented in Table 1; an example of the elemental profiles is presented in Figure 9, which shows that vanadium and nickel are distributed uniformly through the film. In accordance with the EDX spectroscopy, the vanadium intensity increased with the increase in the immersion time from 10 to 60 min, while the nickel intensity reached a maximum after 30 min.

For the V-Zn process the V:Al and Zn:Al ratios reached values of $8.0 \times 10^{-3}$ and $3.1 \times 10^{-3}$, respectively after 30 min (Figure 8(c)). No further significant change occurred at an immersion time of 60 min. GDOES analyses (Table 2) showed that the average intensity for vanadium in the films increased up to 30 min followed by a small decrease, in agreement with EDX spectroscopy. The intensity of the optical emission for zinc was too low to reliably determine a trend with immersion time.

For the V-Ce(III) process, the V:Al and Ce:Al ratios changed negligibly for immersion times from 10 to 30 min (Figure 8(d)). Further increase of the times led to significant increases of both vanadium and cerium concentrations. Visual examination revealed parts of the specimen had changed from colourless to brown. Hence, an optimum time of 30 min was chosen.

Generally, increase of the immersion times from 10 to 30 min increased the retention of solution-derived species.
in the films, since the time for species to precipitate sparingly soluble compounds was increased. In addition, significant increase was revealed for the V-Zn and V-Ni process, which involve low precipitation rates as revealed by reaction in the bulk volume. For the V-Ce(III) process, for which precipitation was immediate, an increase in the immersion times from 10 to 30 min had no effect on the uptake of vanadium species. The findings indicate that the optimum immersion time for the V-Zn and V-Ni processes is 30 min.

Salt spray testing

The corrosion resistance of anodised AA 2024 T3 alloy, post-treated with the optimised double-dip processes, was evaluated by neutral salt spray testing for times up to 1248 h. Various control specimens of the alloy were also investigated: non-anodised, chromic acid anodised (CAA), SAA, CAA and hot water sealed, SAA and hot water sealed, and SAA and double-dip treated. The results of tests are summarised in Table 3 and optical micrographs of the specimens following testing are presented in Figures 10–12.

After exposure for 1000 h, the non-anodised alloy was severely corroded and many pits were evident on SSA and CAA panels (Figure 10). Sealing improved the corrosion resistance; after 1248 h exposure, only moderate pitting was evident for the SAA-sealed alloy and only two pits were evident for the CAA-sealed alloy (Figure 11). The V-Ce(III) and V-Zn processes provided protection similar to that of hot water sealed, SAA and hot water sealed, and SAA and double-dip treated. The results of tests are summarised in Table 3 and optical micrographs of the specimens following testing are presented in Figures 10–12.

Figure 10. Optical micrographs of the variously treated AA 2024 T3 alloys, following 1248 h exposure to the salt spray (ASTM B 117): (a) SAA and hot water sealed alloy and (b) CAA and hot water sealed alloy.

Figure 11. Optical micrographs of the variously treated AA 2024 T3 alloys, following 1248 h exposure to the salt spray (ASTM B 117): (a) CAA and hot water sealed alloy and (b) SAA and hot water sealed alloy.

Figure 12. Optical micrographs of the SAA AA 2024 T3 alloy post-treated by various double-dip processes following exposure to the salt spray for various times (ASTM B 117): (a) V-Ni process (30 min) after 1248 h exposure; (b) V-Zn process (30 min) after 1248 h exposure; and (c) V-Ce(III) process (30 min), after 1000 h exposure. The specimens were not rinsed between the two dips of the respective processes.
sealed SAA films (Figure 12(c,b)), while the V-Ni process provided protection similar to that of CAA-sealed films (Figure 12(a)). It is noteworthy that the levels of corrosion protection provided by the double dip processes are achieved without the requirement for sealing of the films, and also that the corrosion tests were carried out for much longer than the times often employed for neutral salt spray testing of sealed panels treated by CAA and SAA, usually about 300–336 h.19,20

The protection provided by the double-dip processes is considered to be due to corrosion inhibition provided by vanadate ions that suppress the cathodic reaction12–14 and increase the pitting potential.15 The low solubility of heavy metal vanadates assists the retention of vanadates in the unsealed pores. Hence, vanadates remain available to provide protection throughout the period of the salt spray tests. The reason for the particular effectiveness of the V-Ni process, which was similar to that of a CAA-sealed film, is not clear from the present investigation. It may be related to the solubility of the vanadate species.

Conclusions

(i) Compositional analyses of films post-treated by V-Ce(III), V-Ni and V-Zn double-dip processes indicated that the V-Ce(III) process is most successful in introducing both the metavanadate anion and the metal cation into the pores of anodic films, followed by the V-Zn and V-Ni processes.

(ii) Rinsing of specimens in deionised water between the two dips can reduce the amount of incorporated vanadate and metal cations. In contrast, incorporation is enhanced by increasing the times of immersion in the dip solutions. The optimised treatments comprise immersion for 30 min in each solution with no rinsing between the two dips.

(iii) Films post-treated by the optimised V-Ce(III) process or V-Zn process provide corrosion protection to AA 2024 T3 alloy similar to that of hot water sealed, sulphuric acid-formed films. However, films post-treated with the optimised V-Ni double-dip process confer an increased protection, similar that of anodising in chromic acid and sealing in hot water.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

The authors thank the Engineering and Physical Sciences Research Council (LATEST Portfolio Award: Programme Grant: EP/D029201) for support of this work and the European Community for financial assistance within the Integrating Activity ‘Support of Public and Industrial Research Using Ion Beam Technology (SPIRIT)’, under EC contract no. 227012.

References

1. C. J. E. Smith, K. R. Baldwin, S. A. Garette, M. C. Gibson, M. A. H. Hewins and P. L. Lane: ‘The development of chromate-free treatments for the protection of aerospace aluminium alloys’, 1st International Symposium on Aluminium Surface Science and Technology, Antwerp, Belgium, ATB Metallurgie, 1997, 37, 266–273.

2. K. R. Baldwin, C. J. E. Smith and P. L. Lane: ‘Treatment of aluminium and aluminium alloys’, U.S. Pat. No. 5,954,893, 1999.

3. H. Guan and R. G. Buchheit: ‘Corrosion protection of Aluminium alloy 2024-T3 by vanadate conversion coatings’, Corrosion, 2004, 60, 284–296.

4. P. Wang, X. Dong and D. W. Schaefer: ‘Structure and water-barrier properties of vanadate-based corrosion inhibitor films’, Corros. Sci., 2010, 52, 943–949.

5. M. Yan, C. A. Vetter and V. J. Gelling: ‘Corrosion inhibition performance of polypyrrole Al flake composite coatings for Al alloys’, Corros. Sci., 2013, 70, 37–45.

6. M. B. Jensena, M. J. Peterson, N. Jadhav and V. J. Gelling: ‘SCM investigation of corrosion inhibition by tungstate- and vanadate-doped polypyrrole/aluminium flake composite coatings on AA2024-T3’, Prog. Org. Coat., 2014, 77, 2116–2122.

7. K. H. Yang, M. D. Ger, W. H. Hwu, Y. Sung and Y. C. Li: ‘Study of vanadium-based chemical conversion coating on the corrosion resistance of magnesium alloy’, Mater. Chem. Phys., 2007, 101, 480–485.

8. L. Niu, S.-H. Chang, X. Tong, G. Li and Z. Shi: ‘Analysis of characteristics of vanadate conversion coating on the surface of magnesium alloy’, J. Alloys Compd., 2014, 617, 214–218.

9. M. F. Morks, P. A. Corrigan and I. S. Cole: ‘Mn–Mg based zinc phosphate and vanadate for corrosion inhibition of steel pipelines transport of CO2 rich fluids’, Int. J. Greenhouse Gas Control, 2012, 7, 218–224.

10. B. L. Hurley, K. D. Ralston and R. G. Buchheit: ‘Corrosion inhibition of zinc by aqueous vanadate species’, J. Electrochem. Soc., 2011, 158, C125–C131.

11. B. R. Shrestha, Q. Hu, T. Baimpos, K. Kristiansen, J. N. Israeliachvili and M. Valtinier: ‘Real-time monitoring of aluminium crevice corrosion and its inhibition by vanadates with multiple beam interferometry in a surface forces apparatus’, J. Electrochem. Soc., 2015, 162, C327–C332.

12. M. Iannuzzi and G. S. Frankel: ‘Mechanisms of corrosion inhibition of AA2024-T3 by vanadates’, Corros. Sci., 2007, 49, 2371–2391.

13. M. Iannuzzi, T. Young and G. S. Frankel: ‘Aluminium alloy corrosion inhibition by vanadates’, J. Electrochem. Soc., 2006, 153, B533–B541.

14. M. Iannuzzi, J. Kovac and G. S. Frankel: ‘A study of the mechanisms of corrosion inhibition of AA2024-T3 by vanadates using the split cell technique’, Electrochim. Acta, 2007, 52, 4032–4042.

15. K. D. Ralston, S. Chirant, T. L. Young and R. G. Buchheit: ‘Corrosion inhibition of aluminium alloy 2024-T3 by aqueous vanadate species’, J. Electrochem. Soc., 2008, 155, C350–C359.

16. K. D. Ralston, T. L. Young and R. G. Buchheit: ‘Electrochemical evaluation of constituent intermetallics in aluminium alloy 2024-T3 exposed to aqueous vanadate inhibitors’, J. Electrochem. Soc., 2009, 156, C135–C146.

17. B. L. Hurley, S. Qiu and R. G. Buchheit: ‘Corrosion inhibition of Zinc by aqueous vanadate species’, J. Electrochem. Soc., 2014, 161, C125–C131.

18. J. Li, B. Hurley and R. Buchheit: ‘Inhibition performance study of vanadate on AA2024-T3 at high temperature by SEM, FIB, Raman and XPS’, J. Electrochem. Soc., 2015, 162, C219–C227.

19. DEF Stan 03-25: Sulphuric acid anodising of aluminium and aluminium alloys, 2003.

20. DEF Stan 03-25: Sulphuric acid anodising of aluminium and aluminium alloys, 1997.