Aluminum Alloy Corrosion Inhibition by Vanadates

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The inhibition of Al alloy corrosion by vanadates was studied in this work. Vanadium speciation is very complicated and vital to the inhibition efficacy. Critical conditions for decavanadate polymerization from clear metavanadate solutions were investigated. Decavanadate only formed when metavanadate was added to solutions of pH 3 or less. It was not possible to change the pH of a metavanadate solution without forming decavanadates, creating an orange-colored solution. According to $^{51}$V nuclear magnetic resonance, monovanadates were present only in clear metavanadate solutions; orange solutions always contained decavanadates and never contained monovanadates. Orange decavanadate solutions containing 0.5 M NaCl at pH 8.71 exhibited no significant inhibition of the oxygen reduction reaction and increasing decavanadate concentration was detrimental. In contrast, clear metavanadate solutions containing monovanadate exhibited strong inhibition of the oxygen reduction reaction, to a level similar to chromate. At a fixed pH, increased NaVO$_3$ concentration in clear metavanadate solutions increased inhibition efficiency.© 2006 The Electrochemical Society. [DOI: 10.1149/1.2358883] All rights reserved.

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The results of prior studies on corrosion inhibition by vanadates are clouded by a lack of understanding of speciation, the complexity of the hydrolysis of vanadates in aqueous solutions, and the existence of metastable equilibria. The main objective of this work is to understand which vanadate oligomer imparts the best corrosion protection for AA2024-T3. Vanadate speciation as a function of pH and concentration is investigated by $^{51}$V NMR. The influence of decavanadate formation, solution aging, and bulk pH on corrosion inhibition of AA2024-T3 is also addressed.

Experimental

Materials and sample preparation.— Commercially available sodium vanadium oxide, 98% NaVO$_3$, and reagent-grade sodium chloride from Sigma-Aldrich were used. All solutions were prepared with 18.2 MΩ cm deionized water.

To reduce the possibility of composition or heat-treatment artifacts, samples were cut from two different AA2024-T3 panels (nominal composition 3.8–4.9% Cu, 1.2–1.8% Mg, 0.3–0.9% Mn, 0.5% Fe, 0.5% Si, 0.25% Zn, 0.1% Cr, 0.05% Ti, balance Al) that were 1 and 5 mm thick, respectively. The samples were mounted in epoxy resin; ground through 1200 grit SiC papers (Buehler), and polished with 3 and 1 μm diamond paste (Buehler). Ethyl alcohol (<0.2% water) was used as a lubricant during all the surface preparation stages to minimize corrosion damage during grinding and polishing.

Determination of the minimum pH that triggers orange V$_{10}$ polymerization.— As-prepared, NaVO$_3$ solutions remain colorless with a pH that linearly increases with total vanadium concentration (Fig. 1). Acidification with concentrated HCl to adjust bulk pH produces a change in color to orange indicating the formation of decavanadates. The determination of the minimum pH that causes V$_{10}$ formation was investigated. At the same time it was possible to determine whether the bulk pH can be adjusted without introducing color change. Aliquots of colorless 150 mM NaVO$_3$ + 0.5 M NaCl solutions were added to beakers containing exclusively 0.5 M NaCl solutions with initial pH (pH$_0$) varying from 1 to 12. The NaCl solutions were not buffered to avoid any possible complexation between vanadium and the buffer media. Therefore, pH$_0$ was adjusted and measured immediately before mixing. Final NaVO$_3$ concentrations of 100, 50, or 5 mM were obtained by varying the injected volume. The final pH after mixing, pH$_f$, was monitored and determined as a function of pH$_0$.

Electrochemical tests.— All electrochemical tests were carried out using either a Gamry PC3/300 or a VoltaLab PGP-201 potentiostat in a three-electrode array. A platinum mesh counter electrode and a standard calomel reference electrode (SCE) were used in all experiments. A Luggin capillary filled with an agar-agar gel made with 0.5 M NaCl was used in all tests. Samples were cleaned and degreased with ethyl alcohol before testing. Each experiment was repeated at least in triplicate. Cathodic polarization experiments were carried out in solutions that were bubbled with air for 1 h prior to the experiment and stirred during the experiment to generate a more reproducible limiting current for the ORR. The potential sweep started 10 mV above the open circuit potential (OCP) and was stopped when the current density reached ~2 mA/cm$^2$. A scan rate of 1 mV/s was used and the total exposed area was approximately 1 cm$^2$. Corrosion rate at OCP was assessed from the polarization resistance ($R_P$) determined using the linear polarization technique (LPT). The potential was scanned at 5 mV/s over a range ±15 mV relative to the OCP. LPT measurements were repeated each 30 min for 24 h.

Long-term OCP exposure.— Samples were immersed in chloride solution containing decavanadate or metavanadate solution for 14 days. The solutions were renewed every 24 h to reduce the effects of changes in pH or speciation.

Results and Discussion

Determination of the minimum pH that triggers V$_{10}$ formation.— The objective of these experiments was to determine the critical conditions (i.e., initial pH and final vanadate concentration) that cause decavanadate formation, as evidenced by a change in color from clear to orange. The injection of the concentrated clear 150 mM NaVO$_3$ solution was made slowly and recorded with a digital camera. Figure 2 shows the pH$_f$ as a function of pH$_0$. The color change associated with V$_{10}$ formation was only triggered for pH$_f$ ≤ 3, independent of final vanadate concentration. Interestingly, for 100 mM and 50 mM final vanadate concentrations, pH$_f$ was equal to 8.4 independent of pH$_0$ for 3 < pH$_0$ < 12. For 5 mM total vanadate, pH$_f$ was equal to 7.6 independent of pH$_0$ for 4 < pH$_0$ < 12. In other words, to create vanadate solutions of concentration 5 mM or higher with pH less than 7.5, the vanadates must be mixed with solutions having pH less than 3–4. Since this pH range is above the pH for color change, a direct implication of these findings is the practical impossibility of adjusting the pH of clear NaVO$_3$ solutions, without producing a change in color and speciation. Therefore, previous studies that investigated inhibition by vanadates at pH 7 actually used solutions containing decavanadate.$^{29,30}$ Exact speciation
of these solutions are addressed below. Once formed, however, orange decavanadate solutions can be adjusted to high pH without completely depolymerizing the V as formed during acidification. Therefore, it was possible to analyze and compare clear metavanadate and orange decavanadate solutions at a common pH only at high pH. Here solutions were adjusted to pH 8.71, which corresponds to the as-dissolved pH of 100 mM NaVO₃.

The fact that a local environment with a pH ≤ 3 triggers formation of decavanadates not only has direct implications in sample preparation procedures, but it might also impact coating schemes based on vanadates. The case of an epoxy coating containing a metavanadate pigment can be used as a simple example. If a scratch through the coating is exposed to an aggressive electrolyte, release of a vanadate species from the coating to the damaged area will occur. If the pH of the electrolyte is lower than 3, released metavanadates will polymerize to form decavanadates. In such a case, decavanadates will have to protect the exposed bare metal from further corrosion. On the other hand, if the pH of the aggressive electrolyte is greater than 4, metavanadates will be the species released and present in solution.

Nuclear magnetic resonance spectroscopy (NMR).—⁵¹V NMR was used to determine quantitatively the speciation of vanadate solutions. Decavanadates were prepared by first acidifying clear metavanadate solutions to pH 4 and then readjusting to pH 8.71. Since decavanadate solutions are not thermodynamically stable in these conditions, solutions were prepared immediately before NMR analysis.

Typical ⁵¹V NMR spectra for a 100 mM decavanadate solution and a 100 mM metavanadate solution adjusted to pH 8.71 are shown in Fig. 3a and b. The peaks are labeled based on assignments reported in the literature.⁵²,⁵³,⁵⁴,⁵⁵,⁵⁶ NMR peaks are proportional to the species concentration.⁵⁷ Cumulations of the peak areas of spectra such as those in Fig. 3a and b from both decavanadate and metavanadate solutions of varying concentration are given in Fig. 3c and d, respectively. In both cases, the sum of n times the area under the peaks, where n = 1, 2, 4, 5, or 10, linearly scaled with total vanadium concentration, thereby proving the validity of the peak assignment and providing a calibration of the method.

In the case of decavanadates, the chemical shift, δ, observed for the different oligomers for both decavanadate and metavanadate solutions at pH 8.71. At a fixed pH, the chemical shift of the different oligomers does not vary with incremental concentrations of NaVO₃. Using chemical shift information, it is possible to determine the state of protonation of the oligomers.⁵⁸ Within the experimental error of 0.5 ppm, the results are in good agreement with Heath et al. and Cronin et al.⁵⁹-⁶¹ Nevertheless, the chemical shifts are about 3 ppm more negative than commonly tabulated values. The small discrepancies are probably caused by different experimental conditions such as temperature, ionic strength, and/or pH.⁵⁹-⁶¹ For the clear solutions, the chemical shift of the monovanadate indicates that monoprotonated and diprotonated V⁴⁺ are present. Likewise, for both clear and orange solutions, the chemical shift for the divanadate species indicates that HV₂O₇⁻ and H₂V₂O₇⁻ are at equilibrium. As hypothesized by Heath et al., the slightly more negative chemical shifts for both V₄ and V₅ correspond to an equilibrium reaction between cyclic and linear oligomers.⁵⁸ In addition, for the orange solutions, the position of the three V₅ peaks seems to indicate that the decavanadate species at metastable equilibrium are HV₁₀O₂⁵⁻ and H₂V₁₀O₃⁵⁻.

Inhibition by metavanadate and decavanadate solutions.—The corrosion-inhibiting effects of orange solutions containing decavanate but no monovanadate and clear solutions containing metavanadates (V₁−V₅) but no decavanadate were determined at the fixed pH of 8.71. These solutions will be referred to as orange decavanadate and clear metavanadate solutions, respectively, even though the former solutions also contain some metavanadates. Cathodic polarization curves of AA2024-T3 were measured in orange decavanadate and clear metavanadate pH 8.71 solutions containing 0.5 M NaCl and varying amounts of NaVO₃. Figure 6a compares typical cathodic polarization curves for 100 mM NaVO₃ solutions. A cathodic polarization curve in 0.5 M NaCl with no vanadates is also shown for reference. In the absence of inhibitor, the ORR is not impeded and a limiting current, iₐ, of 25–30 μA/cm² is observed. The iₐ obtained in Cu-containing aluminum alloys is significantly larger than in pure Al or in Al alloys not alloyed with Cu.⁶²,⁶₃ Although not completely understood, it is generally accepted that the presence of Cu contamination in the passive film on the matrix or on intermetallic particles increases conductivity of the oxide, making the diffusion of oxygen the rate-limiting step.⁶₄-⁶₆ In pure Al, the alumina layer acts as an electric isolator, causing electron transfer throughout the film to be extremely difficult. The ability to sustain a large cathodic current makes Al–Cu alloys very susceptible to localized corrosion.⁶₅ Therefore, if a corrosion inhibitor in the
aggressive electrolyte controls the kinetics of oxygen reduction, a diminished corrosion rate is expected.\textsuperscript{9,10,13,14,21,52,55,57,58}

Figure 6a shows that orange decavanadate solutions do not reduce the kinetics of ORR significantly. For a 100 mM decavanadate solution, an average $i_L$ of $8–15\mu A/cm^2$ is observed. The effects of NaVO$_3$ concentration are summarized in Fig. 6b. Comparison of the effects of vanadate on ORR kinetics is complicated by the different shapes of the polarization curves, especially at low potentials. The current density values plotted in Fig. 6b were obtained by extrapolating the linear regions of the cathodic curves to the high potential of $-800$ mV SCE. This is an arbitrary definition and different approaches could have been taken. However, it gives a fair representation of the inhibition efficacy. Higher vanadate concentrations resulted in larger cathodic currents for the orange decavanadate solutions, supporting the concept that decavanadates are poor inhibitors of the ORR. The small amount of inhibition observed in decavanadate solutions is possibly a consequence of the presence of metavanadates such as V$_2$. As the NaVO$_3$ concentration increases, the amounts of V$_{10}$ and V$_4$ increase accordingly, lowering the V$_2$/V$_4$ ratio. It is hypothesized that adsorption of V$_2$ is somehow impeded by the presence of V$_4$ and V$_{10}$, which lowers the inhibition extent by allowing oxygen to adsorb freely on the local cathodes and then reduce.

In contrast to the orange decavanadate solutions, a significant decrease in the rate of oxygen reduction was observed in clear metavanadate solutions. The kinetics of oxygen reduction were reduced

Figure 3. Assignment of $^{51}$V NMR peaks and calibration: (a) typical $^{51}$V NMR spectrum for an orange decavanadate solution, (b) typical $^{51}$V NMR spectrum for a clear metavanadate solution, (c) calibration curve for orange decavanadate solutions, and (d) calibration curve for clear metavanadate solutions.

Figure 4. $^{51}$V NMR spectra of 100 mM vanadate solution in different conditions: (a) as-dissolved pH 8.71, (b) acidified to pH 4, and (c) acidified and readjusted to pH 8.71.
by almost 4 orders of magnitude and no diffusion-limiting region was observed (Fig. 6a). In addition, the threshold for hydrogen evolution was shifted toward more negative overpotentials. In further contrast to the orange decavanadate solutions, inhibition performance increased with increasing vanadate concentration (Fig. 6b).

Since the orange decavanadate solutions contain no V1 and the clear metavanadate solutions contain no V10, these results suggest that decavanadates are detrimental or ineffective inhibitors and monovanadates provide the best inhibition. In this regard, the extent of inhibition imparted by monovanadates is similar to that reported for chromates and dichromates in aqueous solutions.21,23,57 These data provide no insight on whether the monomers are adsorbed or reduced at the surface. The mechanisms of inhibition by V1 will be discussed in a future communication. However, it is important to note that the efficacy of vanadate inhibition seems to reach a limiting value in the same range of NaVO3 concentrations where the V1 concentration reaches a limiting value (Fig. 5).

A comparison of the long-term performance of orange decavanadate and clear metavanadate solutions was carried out by analyzing polarization resistance values, $R_p$, extracted by LPT and by optical inspection after OCP exposure. Samples of AA2024-T3 were exposed to aerated pH 8.71 solutions containing 0.5 M NaCl with or without vanadates as indicated. Typical results are shown in Fig. 7. In the absence of inhibitor, $R_p$ varied between 5 and 10 kΩ cm$^2$; and samples were severely pitted after the 24 h experiment. The fluctuation of $R_p$ in the solution without inhibitor is probably associated with the pitting corrosion. An orange decavanadate solution containing 6.26 mM V10 (present in a solution that was initially 100 mM NaVO3) exhibited $R_p$ values that fluctuated between 50 and 300 kΩ cm$^2$ initially. However, after about 5 h, $R_p$ decreased with time to 10–30 kΩ cm$^2$. In contrast, in a clear metavanadate solution containing 1 mM V1, significantly higher $R_p$ values were observed. Polarization resistance typically varied between 300 and 1100 kΩ cm$^2$ and was virtually independent of NaVO3 concentration above 1 mM. The low corrosion rate was sustained during the 24 h of exposure. Samples exposed at OCP to orange decavanadate solutions containing NaCl rapidly developed pits that could be ob-

### Table I. Chemical shift for the different oligomers present in clear and orange solutions obtained by $^{51}$V NMR.

<table>
<thead>
<tr>
<th>Species</th>
<th>Chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clear</td>
<td></td>
</tr>
<tr>
<td>V1</td>
<td>−545.55</td>
</tr>
<tr>
<td>V2</td>
<td>−569.62</td>
</tr>
<tr>
<td>V4</td>
<td>−581.13</td>
</tr>
<tr>
<td>V5</td>
<td>−589.34</td>
</tr>
<tr>
<td>Orange</td>
<td></td>
</tr>
<tr>
<td>V2</td>
<td>−565.17</td>
</tr>
<tr>
<td>V4</td>
<td>−581.50</td>
</tr>
<tr>
<td>V5</td>
<td>−589.94</td>
</tr>
<tr>
<td>V10</td>
<td>−426.84</td>
</tr>
<tr>
<td></td>
<td>−501.58</td>
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<tr>
<td></td>
<td>−517.97</td>
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served easily with the unaided eye. Figure 8a is an optical micro-
graph of an AA2024-T3 after 14 days in an orange decavanadate +
chloride solution with initial total vanadate concentration of 10 mM.
Very large pits at the surface are evident. In contrast, only small pits
were observed after exposure to clear metavanadate + chloride so-
lutions (Fig. 8b). Interestingly, in both cases, pits were always cov-
ered by a corrosion product that was enriched in vanadium as shown
by EDS (Fig. 8c). The scratches observed in Fig. 8c and d are
common for AA2024-T3 polished to 1 μm diamond paste. Atomic
force microscopy measurements revealed that the scratches are less
than 1 μm deep. Similar results were obtained for samples only
polished to 1200 grit.

Since high-pH orange decavanadate solutions are not at thermo-
dynamic equilibrium, it was of interest to analyze the effects of
solution aging on corrosion inhibition performance. A 100 mM or-
ange decavanadate solution adjusted to pH 8.71 was aged for 10
days. Samples were extracted for $^{51}$V NMR analysis and electro-

Figure 7. Polarization resistance of AA2024-T3 in 0.5 M NaCl solutions
containing no inhibitor, 1 mM $V_i$ or 6.26 mM $V_{10}$.

Figure 8. Optical micrographs of AA2024-T3 after 14 days of exposure to aerated 0.5 M NaCl containing (a) $V_{10}$ and (b) $V_i$. (c) Secondary electron image of
a small pit nucleated after 14 days exposure to $V_i$, and EDS analysis of the corrosion products showing enrichment in vanadium.
chemical characterization after 1, 3, and 10 days. The solution pH decreased slowly over time; therefore, pH was readjusted to 8.71 before the experiments.

The $^{51}$V NMR spectrum shows that after 24 h aging the amount of V10 was reduced and V4 became predominant. However, decavanadate was still present and monovanadate did not form during aging, indicating that the depolymerization to form V1 is not favored under these conditions. After 3 and 10 days no significant changes in speciation were observed. This suggests that the rate of depolymerization is extremely slow. Samples without pH readjustment were also analyzed for comparison. Except for small changes in pH, no significant differences in speciation were found. Consequently, from a practical standpoint, polymerization of V10 is not completely reversible.

Cathodic polarization curves did not show significant variations with aging time of the orange decavanadate solutions. A large limiting current associated with a relatively fast rate of ORR was observed. Similarly, the OCP was 300 mV more positive than the OCP in clear metavanadate solutions. It is interesting that polarization curves in metavanadate solutions were very reproducible, but the scatter for the orange decavanadate solutions was large. The polarization plots shown here represent a lower limit for decavanadate solutions to present conservative results. In many cases currents as large as the limiting current in solutions with no inhibitor added were obtained. Since the main consequence of aging was the rapid formation of V4 species, these findings indicate that inhibition of ORR is not imparted by V10 or by V4. In other words, it seems plausible that the higher molecular weight oligomers do not impart good protection since they cannot lower the rate of O2 reduction.

The effects of incremental pH on speciation of 10 mM clear metavanadate solutions were also investigated by $^{51}$V NMR. Figure 11a summarizes the variation of the concentration of the different oligomers as a function of pH. As pH increased, V1 rapidly became predominant and V5 and V4 peaks diminished. Above pH 9 only signals from V1 and V2 were obtained. Chemical shift vs pH is
plotted in Fig. 11b. In good agreement with Heath et al. and Larson,28,44 the equilibrium for both V1 and V2 shifted toward the deprotonated form at pH > 9. Chemical shift of the higher molecular weight oligomers is virtually independent of pH.28,44

Taking into account these findings, it is possible to analyze the effects of V1 concentration, protonation state, and pH on inhibition. Cathodic polarization experiments in 0.5 M NaCl + 10 mM NaVO3 with different pH were carried out and compared with solutions containing no inhibitor at the same pHs. The exact concentration of V1 and V2 can be extracted from the 51V NMR data (Fig. 11a).

The polarization curves in the solutions with no inhibitor were identical except for a change in the OCP. All polarization curves in the metavanadate-containing solutions exhibited much lower ORR rates, and there was no clear influence of pH (and thus V1 concentration) (Fig. 12). This suggests that above a critical concentration, most of the local cathodes are blocked by V1 (or a combination of V1 and V2), which greatly reduces the rate of oxygen reduction.

These findings should directly impact the development of new coating systems based on vanadates. To date, most of the work with vanadium compounds was focused on hosting decavanadates in hydroxalcite pigments or in conversion coatings.12,28,30 Since monovanadate appears to be the strongest corrosion inhibitor of the system, any coating scheme based on vanadium should release V1. The electrolyte developed in atmospheric exposure of aircrafts is thought to be neutral to basic,29 which would impede the formation of decavanadate. Special care should also be taken during coating formulation. Since pH < 3 triggers decavanadate formation, the pH of the coating bath has to remain above that critical level. The problem of NaVO3 as pigment is its relatively large solubility, which would end up producing blistering after water uptake. However, Smith et al.28,30 and Nazarov et al.11 produced a variety of vanadate pigments with a lower solubility than NaVO3, by simply reacting NaVO3 with different metallic chlorides such as MgCl2 and SrCl2. This suggests that it could be possible to have control over the release kinetics.

In addition to the effects of vanadates on the OER, the effects of both clear metavanadate and orange decavanadate solutions on the anodic reaction were studied in detail and are the topic of a future communication. However, the effects of clear metavanadate solution on the anodic reaction were significantly smaller than the large reduction in the rate of the OER.

Finally, it is unclear what would happen inside an acidic crevice. However, the absence of crevice attack under masked regions during long-term exposure seems to indicate that the blockage of the local cathodes by monovanadates diminishes any possible anodic dissolution, including crevice corrosion. Nevertheless, a more detailed investigation is still required.

Figure 12. Cathodic polarization curves of AA2024-T3 exposed to 0.5 M NaCl at high pH with no inhibitor or clear metavanadate.

Conclusions

Speciation of vanadate solutions with varying concentrations and pH was studied by 51V NMR spectroscopy and the effects of corrosion inhibition for AA2024-T3 were investigated. The following conclusions can be obtained:

1. Decavanadate only formed when metavanadate was added to solutions of pH 3 or less. The final pH after vanadate addition was independent of the initial pH for initial pH of 3 or greater. Therefore, it is impossible to change the pH of a metavanadate solution without forming decavanadates.

2. Acidification of clear metavanadate solutions to pH 4 or lower polymerized all the oligomers to form V10. Reducing the pH to 8.71 produced a partial depolymerization of V10 to form V104, V4, and V6. Orange solutions always contained decavanadates and never contained monovanadates.

3. Orange decavanadate solutions containing 0.5 M NaCl exhibited no significant inhibition of the ORR and increasing decavanadate concentration was detrimental. Aging of the metastable decavanadate solutions for up to 10 days did not improve protection.

4. Clear metavanadate solutions containing monovanadate exhibited strong inhibition of the ORR, to a level similar to chromate. At a fixed pH, increased NaVO3 concentration in clear metavanadate solutions increased inhibition efficiency.

5. Since the orange decavanadate solutions contain no V1 and the clear metavanadate solutions contain no V10, these results suggest that decavanadates are detrimental or ineffective inhibitors and monovanadates provide the best inhibition.

6. As the pH of clear metavanadate solutions increases, V1 and V2 become the predominant species, but improvement in inhibition was not found.

7. A coating system based on vanadates should be able to release monovanadates. The formation of decavanadates during coating formulation should be avoided.

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