Corrosion inhibition of AZ31 Mg alloy with aqueous vanadate was studied and has been attributed to the pH dependence of vanadate speciation. Immersion in tetrahedral coordinated vanadate species, present in neutral and alkaline solution, was shown to decrease corrosion current density and increase the breakdown potential, both of which were enhanced with longer immersion times. Exposure to octahedral coordinated vanadate, predominant in acidic solution, only slightly decreased corrosion current density. An acidic solution was adjusted to alkaline conditions and samples were immersed in the adjusted alkaline solution. Inhibition of these samples was weaker than that of samples immersed in initially alkaline solutions. Anodic inhibition was observed on samples treated in solutions containing tetrahedral species. SEM images showed that vanadate formed a film across secondary particles and the Mg matrix, and provided qualitative evidence that inhibition efficiency increased as the pH increased. XPS results indicated that film formation was associated with the reductive adsorption of vanadium oxoions. Exposure at pH 5.0 produced a film predominated by V(IV). Exposure at pH values of 7.7 and higher, however, produced a film containing predominantly V(V). Raman analysis confirmed the formation of a vanadate film on the Mg surface after exposure at all pH values.

Mg alloys have attracted great attention due to their high strength/weight ratio, good thermal conductivity and other physical properties. They have been widely used in the automotive industry, as aerospace components, and in the field of electronics. However, Mg alloys have high chemical activities, and are susceptible to corrosion, especially galvanic corrosion arising from interactions with more noble materials such as steel. Their active corrosion behavior is a barrier to wider applications. Therefore, protection under corrosion, especially galvanic corrosion arising from interactions with more noble materials such as steel, is a critical issue. Their active corrosion behavior is a barrier to wider applications. Therefore, protection under corrosion, especially galvanic corrosion arising from interactions with more noble materials such as steel, is a critical issue. Many corrosion mitigation methods have been reported, including alloying, surface modification, coatings, and inhibitors. Birbilis et al. studied the effect of numerous alloying elements on the corrosion kinetics of Mg, graphically presenting the effect of anodic and cathodic kinetics on over 30 alloying elements. These detailed studies of alloying elements provided beneficial information for the fabrication, modification and development of corrosion-resistant Mg alloys. Surface modification of Mg alloys includes anodizing, hot diffusion, laser treatment and other treatments that affect the surface, but do not change the original mechanical properties of the alloy. Surface modification can increase polarization resistance and reduce the localized galvanic interactions that arise from the heterogeneous structure found in these alloys. Conversion coatings are another effective method to improve the corrosion resistance of Mg alloys. These coatings can provide excellent protection of the substrate. Common conversion coatings include those based on chromatophores, phosphate, fluoride, and rare earth metals. Extensive attention has also been given to the development of environmentally friendly inhibitors such as phosphate, fluoride, carbonate and silicate. These anionic inhibitors can form a protective layer or film on the surface via precipitation reactions with Mg(OH)₂. The requirement of the presence of aqueous Mg(OH)₂ indicates that these precipitation processes require at least some initial corrosion, leading to a somewhat slow inhibition process. The reliance on some initial corrosion and the accompanying delay of inhibition is also observed in rare earth metal inhibitors on AA2024 and is discussed in detail elsewhere. Chromate can be quickly and readily reduced by active surface elements such as Mg.

Williams et al. propose that chromate provides strong inhibition on Mg surfaces through the reduction of chromate to form a protective Cr(OH)₃ hydroxide film. Similar to chromium, the oxides of vanadium are stable under multiple oxidation states, suggesting an analogous possible inhibition mechanism with vanadium oxoions on Mg. Previous work has shown that vanadates can be readily reduced by active elements such as Mg. Vanadate speciation, however, is complex and strongly dependent on solution pH and concentration. The effect of vanadate speciation on corrosion inhibition of Mg alloys and details on the inhibition mechanism are not well discussed in the literature.

In this work, the inhibition performance of different vanadate species on AZ31 was studied, and the oxidation state of vanadium in the surface film was characterized. Furthermore, the inhibition mechanism of vanadate was analyzed and is discussed.

Experimental

0.1 M NaCl was prepared by dissolving reagent grade NaCl in deionized water (resistivity of 18.2 MΩ·cm). 4 mM NaVO₃ was made by adding solid NaVO₃ (98%) to 0.1 M NaCl. This combined solution is referred to as 4 mM NaVO₃ in this paper. The natural pH of 4 mM NaVO₃ was measured as 7.7. The pH of 4 mM NaVO₃ solutions was adjusted to either pH 5.0 or pH 9.2 by the drop-wise addition of either concentrated HCl or NaOH, respectively. A different pH 9.2, 4 mM NaVO₃ solution was prepared by the drop-wise addition of concentrated NaOH to a 4 mM NaVO₃ solution which had first been acidified to pH 5.0. The polymerized octahedral vanadate species formed under acidic conditions cause a color change from transparent (neutral conditions) to orange (acidic conditions). The orange solution produced by these polymerized species persists even upon subsequent alkalinization indicating their stability and a low rate of decomposition. In this work, the term “re-adjusted to pH 9.2” will always be employed in reference to the above described solution which was first acidified creating polymerized orange vanadate species and subsequently alkalinized, resulting in an alkaline solution containing polymerized vanadate species. All other references to a solution at pH 9.2 indicate a solution initially adjusted up without first undergoing acidification. All experiments were conducted immediately after stabilization of the solution pH, which occurred within less than 3 minutes.

Commercial Mg alloy AZ31 was ground using SiC paper (successively up to 1200 grit) with ethanol as the lubricant, polished with diamond paste down to 1 μm, ultrasonically cleaned in ethanol, and dried using compressed hot air.

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Electrochemical measurements were performed in a cylindrical corrosion cell, placed vertically and open to air. The cell was equipped with a central hole in the bottom endplate which permitted face-up exposure of 1 cm² of the working electrode (AZ31) to the cell solution. A standard three-electrode set-up with platinum mesh as a counter electrode and a saturated calomel electrode (SCE) as a reference was employed. All potential values in this work are in reference to an SCE. Anodic polarization measurements were performed starting at −50 mV vs. open circuit potential (OCP) at a scan rate of 0.5 mV/s after different delay times (10, 30 and 60 min) in each solution. The short cathodic branch was utilized to obtain corrosion current density measurements.

Electrochemical Impedance Spectroscopy (EIS) measurements were performed under the same conditions as the polarization experiments (0.1 M NaCl and 4 mM NaVO₃, for each of the four pH conditions). Unlike the polarization experiments, however, these measurements were made on samples after a 60 min free corrosion exposure. Data were collected at 7 points per decade frequency from 100 kHz to 10 mHz with application of a sinusoidal voltage signal with an amplitude of 5 mVrms. EIS measurements were replicated three times.

X-ray photoelectron spectroscopy (XPS) spectra were acquired with a monochromatic 120 W Al Kα source. Survey scans (range of 5 eV to 1400 eV) were performed with a pass energy of 80 eV. O₁s and V₂p spectra were acquired simultaneously (range of 510 eV to 540 eV) with a pass energy of 20 eV. Samples were transferred to the XPS chamber immediately upon rinsing and drying after a 1 hour exposure in 4 mM NaVO₃ solution to minimize any oxidation due to exposure in air. All spectra were calibrated with the 284.6 eV adventitious C₁s signal. Mixed Lorentzian-Gaussian fitting was performed on the O₁s and V₂p peaks. Fitting constraints used for the V₂p peaks were established based on literature values for V₂O₅ and VO₂. For the O₁s peaks, fitting constraints were based on literature values for vanadium oxides and magnesium hydroxides. For V₂p fitting, the area ratio of V₂p3/2 to V₂p1/2 was set as 2:1. For each sample, XPS spectra were collected at two different positions.

Secondary electron microscopy (SEM) was employed to observe the corrosion morphology of AZ31 samples after 1 hour exposure in each of the same solutions, at the OCP. The operating voltage ranged from 10 kV to 20 kV, and the working distance was around 5.0 mm.

Raman spectra were acquired with 514 nm excitation on a Raman microscope equipped with a 50X objective (NA = 0.75), power of 0.75 μW at sample, and an integration time of 10 s. Prior to Raman analysis, samples were exposed for 15 hours in 4 mM vanadate solutions with pH values of 5.0, 7.7, and 9.2. Samples were rinsed in DI water and air dried for >24 hours after immersion and before analysis. The extended exposure time used for Raman analysis was required to obtain strong and clear spectra.

In 0.1 M NaCl, the corrosion potential of AZ31 remained approximately constant, ~−1.51 V SCE at all three delay times and at all three pH values. At the two higher pH values (7.7 and 9.2), the corrosion potential values were all significantly lower than those observed in the NaVO₃ solutions for all delay times. Similarly, the corrosion potential values observed at a pH of 5.5 were significantly lower in NaCl than in NaVO₃ with both the 10 and 30 minute delay. With a 60 minute delay, at a pH of 5.5, however, the corrosion potential was approximately the same (~−1.49 V SCE) regardless of whether the sample was in NaCl only or NaVO₃ (plus NaCl). The samples immersed in the re-adjusted pH 9.2 solution all displayed corrosion potential values higher than those in the pH 5.5 or 7.7 solutions (regardless of delay time) and potential values similar to the pH 9.2 solution at all delay times.

With regard to breakdown potential values, little change was seen with 10 and 30 minute delay times in the 0.1 M NaCl solution, regardless of pH. However, at all pH values in the NaCl solution, with a 60 minute delay, the breakdown potential increased ~50–60 mV. In general, with each immersion time, the breakdown potential values were significantly lower for samples immersed in NaCl versus NaVO₃, with the gap between the two conditions increasing as pH increased. It is noteworthy though that, as with corrosion potential, the samples immersed at a pH of 5.0 with a 60 minute delay behaved similarly in both NaCl only and in NaVO₃.

No significant clear trends associated with pH were observed in corrosion current density in 0.1 M NaCl for the 10 and 30 minute delay experiments. With a 60 minute delay, however, the current density clearly increased when moving from pH 5.0 to 7.7 (~2.8 μA/cm²) and then decreased ~3.6 μA/cm² when the pH increased to 9.2. The data (and error bars) for these data (Fig. 4), show that at the neutral and higher pH values and at all three delay times, the corrosion current density in the NaCl solution was significantly higher than that observed in the 4 mM NaVO₃ solutions, regardless of delay time imposed in the NaVO₃ solution (excluding the re-adjusted pH 9.2 solution). Likewise, at a pH of 5.0, samples in NaCl clearly displayed higher corrosion current density values with 30 and 60 minute delay times, however, with a 10 minute delay time there was no significant difference between samples immersed in either of the two solutions. Overall corrosion current density was suppressed in the presence of all vanadate species with increased suppression observed at the higher pH values (for all delay times).

Setting aside the control NaCl data and comparing corrosion potential values only for samples immersed in the NaVO₃ solutions provides the following information. At a pH of 5.0, no trend was seen with immersion time, however there was a wide range of values (60 minute delay was the lowest at ~−1.49 V SCE and 30 minute delay was the highest at ~−1.43 V SCE). At the higher pH values, the corrosion potential values were similar regardless of delay time, with the pH 9.2 values being only slightly higher than the pH 7.7 values, all averaging around 1.45 V SCE. Corrosion potential values were slightly more dispersed in the readjusted pH 9.2 solution (range of 20 mV), but still similar to the regular pH 9.2 values, although the sample immersed in the readjusted pH 9.2 solution with a 60 minute delay did display the highest corrosion potential value of ~1.42 V SCE.

Breakdown potential values increased with pH in NaVO₃ solutions, although the values for the readjusted pH 9.2 solution were slightly lower than in the regular pH 9.2 NaVO₃ solution. Furthermore, breakdown potential values displayed a significant increase with delay time at the higher pH values (including the readjusted pH 9.2 solution). At a pH of 5.0, although there was a considerable increase observed with a 10 minute delay versus a 30 minute delay, the 30 and 60 minute data were virtually indistinguishable. Both the 30 and 60 minute pH 5.0 data were over 30 mV lower than the 60 minute delay data obtained at the higher pH values.

Similarly, corrosion current density decreased with pH, with the largest decrease occurring between pH 5.0 and pH 7.7. Delay time appeared to play a stronger role in corrosion current density measurements, with increasing immersion times leading to significantly lower current at all three pH values. It is noteworthy that the readjusted pH 9.2 corrosion current density data were quite similar to the corrosion
Figure 1. Anodic polarization curves of AZ31 with different delay times and different pH values in 0.1 M NaCl (a-c) and in 4 mM NaVO₃ (d-g).
current density data at pH 5.0 and not nearly as promising as the regularly adjusted pH 9.2 data.

One noteworthy concern arises with the possibility of the surface reduction of vanadate during anodic polarization, specifically in the short cathodic branch from −50 mV up to OCP. As noted below in the XPS results, vanadate is readily reduced at the OCP on AZ31. Therefore, it is reasonable to assume that any reduction of vanadate on the AZ31 surface occurring in the short cathodic branch would be trivial compared to any reduced film formed upon initial exposure of AZ31 to the aqueous vanadate solution (before application of a potential).

The measured EIS spectra presented a capacitive loop in the high to medium frequency range and inductive loop in the low frequency range (Fig. 5). This response is commonly observed with Mg and Mg alloys under these types of exposure conditions.\(^\text{39-41}\) Polarization values \((R_p)\) were estimated using a method derived from the Kramers-Kronig transforms.\(^\text{42,43}\) According to this method, the polarization resistance can be estimated from the imaginary component of the impedance integrated over the measured frequency domain:

\[
R_p = \frac{2}{\pi} \int_{\ln \omega_{\text{min}}}^{\ln \omega_{\text{max}}} -Z''(\omega) \, d\ln \omega
\]

\[
\simeq 1.466 \int_{\log_{10} \omega_{\text{min}}}^{\log_{10} \omega_{\text{max}}} -Z''(\omega) \, d\log_{10} \omega
\]

In this expression, \(Z''\) and \(\omega\) represent imaginary components of the impedance and angular frequency, respectively. The imaginary component of the impedance was fit in parts such that no more than a third order polynomial expression was used to fit the part and the
Figure 6. Plot of $-Z''$ vs. $\log_{10}(\omega)$ (in Hz) of EIS data obtained in 0.1 M NaCl (natural pH of 5.5) and 4 mM NaVO$_3$, for each of the four pH conditions with polynomial fit (a). Calculated $R_p$ values versus pH of NaVO$_3$ solution, obtained from fitting (b). Each data point represents 3 replicates.

Figure 7. XPS spectra and fitting data of samples after 1 hour exposure in 4.0 mM NaVO$_3$: (a) original XPS data; fitting data for samples exposed at pH 5.0 (b), pH 7.7 (c) and pH 9.2 (d). Raw data, black; Baseline, gold; Fitting, red dash.
curves are shown in Figs. 7b–7d. Based on these fitting constraints and relying on binding energy values from the literature for various vanadium oxides and Mg(OH)²⁺, at pH 5.0, the predominant oxidation state of vanadium found in the film is 4⁺ (67%), with the balance in an oxidation state of 5⁺. For samples immersed at a pH of 7.7 or 9.2, however, vanadium primarily exists in a 3⁺ state with a very small amount at 2⁺. Approximately 94% of the oxygen on the surface of samples immersed at a pH of 5.0 arises from Mg(OH)²⁺, however, that percentage drops to ~71% for immersion at pH 7.7 and ~66% at a pH of 9.2, whereas the percentage of oxygen attributable to vanadium oxides significantly increases.

**Corrosion morphology.**—The observed corrosion morphology on immersed (1 hour) and rinsed AZ31 samples displayed a strong dependence on the presence or absence of NaVO₃ in the immersion solution, as can be seen in Figs. 8a, 8b NaCl at pH 5.5 only; c–i NaVO₃ at noted, different pH values). The filamentous morphology of the corrosion product formed in NaCl solution on the matrix (α-Mg) (shown in Fig. 8a) is attributed to Mg(OH)₂ which is reported to rest on an inner layer of laminar, compact MgO. A similar morphology was observed on secondary particles (β phase) that protrude from the substrate (Fig. 8b), however, it appears to be a more porous structure. Moving to samples immersed in NaVO₃ at pH 5.0 (Figs. 8c, 8d), the filamentous structure is replaced with a film that appears rough and granular, containing numerous gaps and covering both the matrix and secondary phase particles. At a pH of 7.7 (Figs. 8e, 8f), NaVO₃ immersion results in a smoother film over both the matrix and secondary phase particles. Cracks are obvious in the layer, presumably due to dehydration in the SEM vacuum chamber. The surface observed after exposure at pH 9.2 in NaVO₃ (Figs. 8g, 8h) is, arguably, more compact, and contains less cracking, suggesting a more stable film that is not as susceptible to the vacuum conditions. Some pitting, however, is observed around the edges of secondary phase particles. Lastly, the surface of samples immersed in the re-adjusted NaVO₃, pH 9.2 solution display an incomplete film with extensive cracking and gaps.

**Raman spectroscopy results.**—As shown in Fig. 9, the Raman spectra for samples immersed for 15 hours in NaVO₃ solution at the three different pH values and then dried in room air for >24 hours are virtually identical. Spectra of solid V₂O₅, NaVO₃ and V₂O₃ are provided in Fig. 9 for reference. The sample spectra all show a similar spectrum of V₂O₅ and dissimilar from a spectrum of solid NaVO₃. The sample spectra also differ from the Raman spectrum of the V³⁺ oxide, V₂O₅, which does not contain the strong peak at 990 cm⁻¹. Of note is the broad band present between 850 and 950 cm⁻¹ in each of the sample spectra, indicating the presence of amorphous, polymerized vanadate.45–48

**Discussion**

**Inhibition dependence of vanadate speciation.**—The above data show that the addition of vanadate clearly provided corrosion inhibition and that the extent of inhibition was greatly dependent on the pH of the immersion solution. Similar to results observed on aluminum alloys,⁴⁶ optimal inhibition was found with exposure to the tetrahedral vanadate species found at neutral and higher pH values. In this work, this conclusion is supported by the corrosion potential, breakdown potential, corrosion current density, and EIS results, wherein: (1) the best results were observed at a pH of 9.2 and (2) differences observed between the control NaCl solution and NaVO₃ solutions, in general, were minimized under the pH 5.0 conditions. Specifically, the quality of corrosion inhibition as measured by corrosion current density and breakdown potential improved with each increase in pH (within each immersion time frame), and they also improved with each increase in immersion time, indicating a dependence on immersion time in addition to pH. However, the improvements observed with immersion time were similarly present in the control data, and, therefore, may not be associated with the presence/speciation of vanadate.

The morphology results provide additional clear evidence of the superiority of inhibition by the tetrahedral species found at higher pH values. The incomplete porous film formed on the surface of AZ31 exposed at pH 5.0 (Figs. 8c, 8d) would readily permit transport of electrolyte to the surface and provide for the easy release of Mg²⁺ ions and evolving H₂, thereby providing poor corrosion inhibition. This is in contrast to the more compact film formed (in the pH 7.7 and 9.2 solutions) on both the matrix and secondary phase particles in the presence of tetrahedral vanadate (Figs. 8e–8h).
Additional evidence of the importance of speciation can be found in examination of the data obtained from samples exposed in the re-adjusted pH 9.2 solution. This solution was made by acidifying the natural pH 7.7 NaVO₃ solution to a pH of 5.0 (at which point it turned orange indicating the presence of octahedral speciation) and then subsequently raising the pH to 9.2 with NaOH. Although this solution is at the same pH as the clear NaVO₃ solution (tetrahedral speciation) whose pH was raised to 9.2 without first undergoing acidification, the orange color of the re-adjusted solution indicates the predominance of octahedral speciation. This is in agreement with previous NMR analysis of these solutions, which found that transformation from the octahedral to tetrahedral speciation is extremely slow, requiring several hours. These two different pH 9.2 solutions provide a method to distinguish effects due to speciation versus effects due to pH that are unrelated to speciation. Corrosion current density results in the re-adjusted pH 9.2 solution were qualitatively similar to those in the pH 5.0 solution and significantly less favorable than those in the regular pH 9.2 solution. Likewise, breakdown potential values in the re-adjusted solution were lower (for all delay times) than those observed in the regular pH 9.2 solution. Lastly, a comparison of the morphology data in the pH 9.2 solutions, provides clear evidence of superior protection in the regular pH 9.2 solution versus the re-adjusted pH 9.2 solution, Figs. 8g, 8h versus Figs. 8i, 8j, respectively. All of the above provide strong evidence that speciation plays an important role in corrosion inhibition of AZ31 with vanadate and, specifically, that the tetrahedral speciation found under neutral and basic conditions is superior to octahedral speciation.

**Reductive adsorption of vanadate species.**—Corrosion inhibition of aluminum alloy 2024-T3 with vanadate has been extensively studied, wherein the primary mechanism is cathodic inhibition. Specifically, at room temperature, vanadate suppresses the oxygen reduction reaction primarily by forming a physically adsorbed polymerized layer on the alloy surface. At a higher temperature (70 °C), however, reductive adsorption on the aluminum alloy, also resulting in an amorphous, polymerized film, was observed on both the matrix and on secondary phase particles. The Mg content of AA2024–T3 is less than 2%. Therefore, reductive adsorption across the matrix would most likely rely primarily on the oxidation of Al, in addition to oxidation of the small amount of available Mg. In the case of AZ31, however, where vanadate would have ample access to active Mg, reductive adsorption could be expected at room temperature. Indeed, the XPS results discussed above strongly support reductive adsorption at room temperature, and they indicate that speciation plays a role in the reduction and film forming process. Under all pH values, the XPS data indicate a reductive adsorption process. Although the oxidation of the reduced vanadium oxoion film can occur quickly under aqueous conditions and/or exposure to air, the XPS analysis, performed immediately after 1-hour immersions in each of the solutions, can be expected to provide insight into the oxidation state of vanadium in the films formed under the three pH values. The predominance of V⁴⁺ found in the film formed at a pH of 5.0 versus the predominance of V³⁺ (accompanied by a small amount of V²⁺) in the films formed at pH values of 7.7 and 9.2 indicates that the reductive process is either more rigorous and/or results in more stable products at increased pH values.

The above results combined with earlier work with vanadates suggest that reductive adsorption could proceed with ease under all the pH values discussed herein. The predominant vanadate species expected in aqueous solutions under various pH values have been studied in detail. At the pH values employed in this work, 5.0, 7.7, and 9.2, the predominant species are HV₁₀O₁₈⁵⁺ (octahedral), H₂VO₄⁻ (tetrahedral), and HVO₄²⁻ (tetrahedral), respectively. The predominant vanadate species in the orange re-adjusted pH 9.2 solution would be HV₁₀O₁₈⁵⁺. The XPS data indicate that the film formed in the octahedral pH 5.0 solution was either less likely to undergo rigorous reductive adsorption and/or that the reductively adsorbed film was quickly partially re-oxidized. Additionally, the polarization data and the morphology data clearly indicate that the film formed in the pH 5.0 solution was inferior to that formed at pH values of 7.7 and 9.2. Both the redox properties of the available species and the polymerization of those species could be expected to play a role in film formation.

The oxidation of Mg occurring during reductive adsorption would result in basic surface conditions for all three of the pH values explored in this work. It is well established that V⁵⁺ and V⁴⁺ are both easily oxidized to V⁴⁺ in basic solutions. Under all three pH values, the XPS data, however, indicate that reduced vanadium oxoions were stable during the transfer process to the XPS chamber, indicating that they were present at a high percentage during the film forming process. Reasons for the majority presence of V⁴⁺ in the films formed at pH 7.7 and 9.2 versus the majority presence of V⁵⁺ in the film formed at pH 5.0 are not straightforwardly obtainable. Although there are numerous reduction (and re-oxidation) routes the three dominant species could take, it is certain that they are all dependent on pH, with reduction favored as pH decreases and re-oxidation favored as pH increases. The morphology data show that the porous film formed at pH 5.0 would be more subject to changing pH conditions due to its intimate contact with the solution through the numerous pores in the film. On the other hand, it is not unreasonable to assume that the dense films formed at pH 7.7 and 9.2 are providing a barrier that limits contact with the solution, thereby somewhat protecting the reductively formed film from reoxidation. This scenario, supported by the difference in oxidation states observed at different pH values, provides additional evidence that the film formed under the higher pH values is more robust, providing both limited protection of the species within the film, and, more importantly, added protection of the AZ31 surface.

Hydrolysis and condensation reactions for vanadium oxoions are exceptionally complex. As discussed above, although the literature clearly indicates that the polymerization of vanadates within solution (under aqueous conditions) is favored at pH 5.0 (HV₁₀O₁₈⁵⁺) versus the monomers, dimers, and trimers found at pH values of 7.7 or 9.2, no discussion could be found regarding polymerization during film formation on a substrate. Rush and Johnson found that the average number of OH⁻ ions bound per V atom increases from 1.5 for de-cavanadates (pH 5.0) to 2.0 for dimers and trimers (expected along with monomers at pH 7.7) to 3.0 for the monomers that dominate at...
ph 9.2. Presumably, this occurs because as the vanadates bond to each other within solution at low pH, they cannot accommodate as many OH$^-$ ions. The increase in the number of exchangeable ligands found as pH increases could explain the increased density and rigor of the film formed on a substrate at the higher pH values. This scenario is also supported by the results obtained in the re-adj usted pH 9.2 solution. Although the equilibrium process transforming $\text{HV}_3\text{O}_5^{3-}$ (pH 5.0) to $\text{HVO}_4^{2-}$ (pH 9.2) is slow, one would expect to find more $\text{HVO}_4^{2-}$ in the re-adj usted pH 9.2 solution than in the pH 5.0 solution. Indeed, the polarization data and the morphology data showed more inhibition and a more robust film, respectively, in the re-adj usted pH 9.2 solution versus the pH 5.0 solution (both solutions were bright orange, indicating the presence of $\text{HV}_3\text{O}_5^{3-}$).

Combining the Raman data with the polarization and morphology data suggests that the integrity (versus the identity) of the film might be the dominant feature enabling corrosion inhibition. As can be seen in Fig. 5, the spectra of the films formed under all three pH values are virtually identical. Furthermore, they all point to a film consisting of $\text{V}^{5+}$ oxides in a mix of crystalline and amorphous structures. It is not surprising that all the films have been reoxidized−back to the $\text{V}^{5+}$ state, as $\text{V}^{5+}$ is the stable state for vanadium in the presence of air. Unlike the XPS analysis conditions in which the samples were transferred to the analysis chamber immediately after immersion, all these samples had been left under ambient conditions for $\sim$24 hours after immersion and before Raman analysis. The primary difference in the sample spectra versus the $\text{V}_2\text{O}_5$ spectrum is the low, broad band after immersion and before Raman analysis. The primary difference between 900 and 1000 cm$^{-1}$, indicating the presence of amorphous, polymerized vanadate, present under all three pH conditions. Although that band definitively indicates the presence of amorphous, polymerized vanadate, all three sample spectra are strongly dominated by bands associated with crystalline $\text{V}_2\text{O}_5$ or a similar structure. This suggests that the long-term composition of the film is the same or similar regardless of pH. However, based on the polarization and morphology data, the integrity of the film formed at higher pH values is superior.

The strong, sharp peak present at 990 cm$^{-1}$ in the Raman spectra arises from $\text{V} = \text{O}$ in vanadates containing $\text{V}$-O-$\text{V}$ linkage. This is in contrast to a film formed on the matrix of AA2024T3 at $\sim$ pH 8 in 0.1 M NaCl + 0.1 M NaVO$_3$, which provided only a weak spectrum indicating the presence of some amorphous, polymerized vanadate and also some monovanadates, indicating very low coverage. Lesniak and Griffith found that the strong $\text{V} = \text{O}$ peak typically appears between 900 and 1000 cm$^{-1}$ in compounds that contain V-O-V linkages, whereas a $\text{V} = \text{O}$ peak presenting between 1020 and 1040 cm$^{-1}$ (observed in spectra of the treated AA2024-T3) can be attributed to monomeric vanadate units. These contrasting results support a very different film forming mechanism on AZ31 versus AA2025-T3, most likely due to the rigorous reductive adsorption process accompanying film formation on AZ31.

Although the mechanism by which a reductive adsorption film forms is unclear, a clue could lie in the speculation of reduced vanadium oxoions. Both $\text{V}^{5+}$ and $\text{V}^{4+}$ form oxocations in solution, whereas $\text{V}^{5+}$ forms oxoanions. The monomer, dimer and trimer vanadate species discussed above (tetradehdral speciation) that were more able to accommodate OH$^-$ ligands than the decamers found at lower pH would, therefore, also be more likely to undergo deprotonation at higher pH, leaving an anionic species that would be more receptive to bonding with the oxocations of $\text{V}^{5+}$ and $\text{V}^{4+}$. This scenario accommodates both the enhanced film formation on AZ31 versus AA2025-T3 and the production of a more robust film on AZ31 at higher pH values.

Reductive adsorption, of course, is accompanied by the dissolution of Mg. Evolution of H$_2$ gas was observed during all of the above immersion tests. In this way, it behaves similarly to chromate conversion coatings which depend on the reductive adsorption of chromate to create a mixed Cr$^{3+}$/Cr$^{6+}$ oxide film on aluminum alloys and a Cr$^{3+}$-hydroxide film on Mg. Whether vanadate can eventually provide a protective, reductively adsorbed film that essentially stops the dissolution of Mg is not addressed in this work, although it is certainly a possibility. Additionally, supplementary inhibitors such as phosphate and carbonate could possibly be added to achieve synergistic inhibition performance, as these anions would be expected to combine with generated Mg$^{2+}$ to form protective precipitates on the surface. Incorporation of these precipitates into the vanadate film could serve to enhance the ability of the film to prevent dissolution of the Mg surface beyond the initial film forming process.

**Conclusions**

A variety of analytical methods were employed to study the pH dependence of aqueous vanadate corrosion inhibition on Mg alloy AZ31.

1. Corrosion inhibition of AZ31 by vanadates is dependent on the vanadate species present in the solution. Tetradehdral vanadate, which exists in neutral and alkaline solution, provides inhibition of anodic reactions, increasing breakdown potential, decreasing corrosion current density, and increasing polarization resistance. Limited inhibition by octahedral vanadate is observed.

2. Active Mg provides a strong driving force for the reduction of vanadates in solution, resulting in an inhibition mechanism different from that observed on aluminum alloys.

3. Reductive adsorption of vanadium oxoions under neutral and alkaline conditions results in a film containing $\text{V}^{5+}$ and some $\text{V}^{4+}$, in the short term. Reductive adsorption of vanadium oxoions under acidic conditions results in a film containing $\text{V}^{4+}$, also in the short term. Under all pH conditions, the reduced vanadium is reoxidized to $\text{V}^{5+}$ upon exposure to air.

4. Corrosion inhibition by vanadate is attributed to a protective, reductively adsorbed film formed on the surface, comprised of vanadium oxides and magnesium hydroxides. Films formed under acidic conditions (octahedral speciation), are porous and non-continuous, while films formed under neutral and acidic conditions (tetradehdral speciation) are dense and continuous.

5. Reductive adsorption and polymerization on AZ31 may be enhanced by the ionic nature of vanadium oxides which exist as anions in the $\text{V}^{2+}$ state and cations in the $\text{V}^{5+}$ and $\text{V}^{4+}$ state. Additionally, the tetradehdral speciation of vanadates present at pH 7.7 and 9.2 could be more receptive to bonding than the octahedral speciation of vanadates present at pH 5.0. This can be attributed to the ability of tetradehdral species to accommodate more exchangeable OH$^-$ ligands.

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