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Cerium Dibutylphosphate as a Corrosion Inhibitor for AA2024-T3 Aluminum Alloys

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The suitability of cerium dibutylphosphate [Ce(dbp)] as a corrosion inhibitor for AA2024-T3 aluminum alloy in sodium chloride aqueous solutions has been investigated. Weight loss tests combined with electrochemical assessment have been used to evaluate the degree of protection and determine the inhibition characteristics of this compound. It was found that Ce(dbp) offers superior protection when compared to CeCl3, with no discernable corrosion products, significant pitting, or evidence of replated copper on the surface. Cathodic polarization indicated inhibited oxygen reduction reaction kinetics consistent with reduced Cu replating. Corrosion protection seems to be enhanced at higher Ce concentrations, suggesting the inhibiting film is more readily deposited when some corrosion takes place. X-ray photoelectron spectroscopy analysis of the surface confirmed the presence of both Ce(III) and Ce(IV). Focused ion beam secondary-ion mass spectroscopy (SIMS) analysis clearly indicated the presence of a 500 nm thick cerium-containing layer on the surface of the alloy after 10 days immersion in the inhibited solution. A strong phosphorus signal was also detected in the SIMS experiment. Toxicity testing using the EC-50 test suggested that cerium dibutylphosphate is able to fulfill the basic requirements for consideration as an environmentally friendly corrosion inhibitor.

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Studies of the corrosion and stability of aluminum and its alloys are of considerable interest due to their technological importance, especially in aircraft and defense applications. The very mechanism which leads to their favorable mechanical properties (i.e., the presence of intermetallic strengthening phases) also leads to their significant corrosion susceptibility. When exposed to corrosive environments, these phases or the adjacent alloy matrix can be prone to localized attack, resulting in pitting, stress corrosion, corrosion cracking, and corrosion fatigue. 

To date, corrosion inhibition for aluminum alloys has relied extensively upon the highly effective hexavalent chromium compounds. However, the toxicity and carcinogenic properties of the hexavalent chromium ion have caused severe restrictions to be imposed on its use by international environmental standards. As a result, new environmentally benign corrosion prevention technologies are being evaluated. A relatively recent line of research has dealt with the development of new inhibitor compounds, designed according to the principles of green chemistry. This research has been focused on the use of rare-earth metal compounds as an alternative for chromates. Cerium salts have been shown to provide protection for aluminum alloys against corrosion. In addition, many organic compounds that are benign to the environment are currently being investigated as potential corrosion inhibitors for aluminum alloys, in particular using combinations of organic anions and inorganic anodic inhibitors to create hybrid inhibitors.

A recent concept developed by Forsyth and co-workers envisions the coupling of a rare-earth metallic element with an organic inhibitor containing multiple functional groups, in order to produce a multifunctional inhibitor with potential synergism effects between the two components. To date this work has concentrated primarily on the use of organocarboxylates coupled to rare-earth metals for use as inhibitors for mild steel. The possibility exists to create a hybrid inhibitor with mixed inhibition functions and a low critical inhibitor concentration for protection of aluminum alloys. This organophosphate was chosen with the idea that phosphates and phosphonates have been employed in corrosion inhibition formulations for aluminum alloys. The work presented in this paper focuses on the multifunctional inhibitor cerium dibutylphosphate [Ce(dbp)] and investigates its mechanism of inhibition for aluminum alloy AA2024-T3. Weight loss tests combined with electrochemical techniques have been used in order to determine the degree of protection. Surface characterization including X-ray photoelectron spectroscopy (XPS) and focused ion beam secondary-ion mass spectroscopy (FIB-SIMS) was used to establish the fate of cerium and phosphorus ions and therefore identify some features of the inhibition mechanism.

** Experimental

Alloys and test solutions.—The material used in the electrochemical corrosion tests was the commonly used aerospace wrought aluminum alloy AA 2024-T3. The nominal composition is 3.8–4.9 wt % Cu, 1.2–1.8 wt % Mg, 0.3–0.9 wt % Mn, 0.5 wt % Fe, 0.5 wt % Si, 0.25 wt % Zn, 0.15 wt % Ti, 0.1 wt % Cr, and 90.9–93.2 wt % Al.

For the corrosion tests, a control solution of 0.001 M NaCl was prepared from analytical grade reagent (Analar) and distilled water. This concentration of NaCl was used as it allowed discrimination between different inhibited solutions and still led to measurable corrosion rates on un inhibited specimens. The corrosion inhibitor Ce(dbp)3 was prepared at the concentrations shown in Table I. Compound preparation was as described elsewhere.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular weight</th>
<th>Concentration</th>
<th>pH of as-prepared solution</th>
<th>Corrosion rate after 7 days (mg/dm2 day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(dbp)3</td>
<td>767.682</td>
<td>50 ppm</td>
<td>0.07</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>100 ppm</td>
<td>0.13</td>
<td>5.6</td>
<td>2.69</td>
</tr>
<tr>
<td></td>
<td>200 ppm</td>
<td>0.26</td>
<td>5.8</td>
<td>2.26</td>
</tr>
</tbody>
</table>

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mula of the dibutylphosphate anion is shown in Fig. 1. All test solutions were open to air in a controlled laboratory atmosphere of 18 ± 1°C.

Coupons preparation.—A two-stage chemical cleaning procedure as per MIL-C-55415 was used for surface preparation of the AA2024-T3 test coupons. This involved degreasing of the coupon surfaces by immersion in an agitated alkaline cleaner for 5 min, followed by a tap water wash. The surface oxide was subsequently removed by 5 min of immersion in an agitated Deoxidizer 6 solution, followed by another water wash. The water-break test was employed to check for the cleanliness of the sample surfaces after cleaning.

Corrosion rate tests.—The weight-loss specimens were cut to dimensions 25 × 25 mm from 2.0 mm thick AA2024-T3 aluminum alloy sheet. Constant immersion corrosion tests were performed in accordance with ASTM G31-93 and ASTM G1-90. Corrosion rates were determined by measuring the weight loss of the aluminum alloy specimens after exposure using an electronic balance accurate to five decimal places. All corrosion tests were done in duplicates, or triplicates when practical.

Open-circuit potential (OCP) measurements and potential polarization measurements.—Cyclic potentiodynamic polarization (CPP) tests were done to determine the degree of protection against pitting corrosion provided by the inhibitor and to establish the nature of the corrosion provided by the inhibitor and to establish the nature of the corrosion mechanism. Electrochemical data were obtained using a conventional three-electrode cell, consisting of a platinum mesh counter auxiliary electrode (1 × 1 in.), a saturated calomel electrode (SCE) reference electrode with a luggin capillary filled with saturated KCl, and AA2024-T3 alloy as working electrode. A BES model EG&G Princeton Applied Research Versastat, with CorrWare corrosion software of Scribner Associate was used for the potentiodynamic measurements. Scans were performed 1 h after immersion and at a rate of 0.1667 mV s⁻¹ starting from the OCP, and proceeding separately in the cathodic and anodic directions to 1.2 V from the OCP. Additional CPP scans were also performed in a more aggressive salt solution (0.1 M NaCl) using a EG&G VMP2z system with a maximum voltage and current capability of 20 V and 400 mA, respectively, controlled by EC-Lab v9.01 software. Experiments were performed in nonaerated solutions for periods between 30 min and 24 h immersion. Cyclic potentiodynamic polarization was carried out over a potential range of −200 to 200 mV vs OCP. The reverse scan was terminated at −200 mV. Potential ramp rate was 0.1667 mV s⁻¹, as outlined in ASTM G59-97.

Cyclic voltammetry (CV) to assay copper replating and the oxygen reduction reaction (ORR) on copper electrodes.—AA2024-T3 coupons prepared as described in the Coupons Preparation Section were corroded in 0.001 M NaCl with and without 200 ppm of Ce(dbp), for 24 h and 10 days, then washed with deionized water and air dried prior to the CV tests. All chemicals used were reagent grade (Alfa Aesar), and solutions were prepared using 18.2 MΩ reverse osmoses water. The CV tests were performed in chloride- and copper-free pH 8.4 borate buffer solution (8.17 g/L Na₂B₄O₇·10H₂O + 7.07 g/L H₃BO₃) under deaerated conditions with nitrogen purging before and during the experiment.

Therefore, all Cu oxidation could be attributed to either surface Cu deposited on the AA2024-T3 surface or intermetallic compounds (IMC) present. Control experiments indicated that the latter was a negligible source of Cu redox peaks in CV.

Voltaammograms were referenced against Hg/Hg₂SO₄, K₂SO₄ (sat.) (MSE) reference electrode and scanned from −1.1 to −0.1 V_MSE back to −1.6 V_MSE at a sweep rate of 1 mV/s. Before each test, the electrodes were potentiostatically held in the test solution at −1.1 V_MSE for 5 min in order to reduce the magnitude of the Al → Al⁴⁺ reaction, so that the copper oxidation and reduction peaks were easier to detect on the AA2024-T3 surface. Three cycles were measured consecutively, with potentiostatic holds between each cycle. This also reduced the background current due to Al oxidation. The resulting voltammograms were compared to the voltammogram of the untreated controls and that of the untreated, uncorroded AA2024-T3, which showed no peaks for copper oxidation or reduction. Visual inspection confirmed that decrease in Cu oxidation and reduction peak heights corresponded to significant reduction in corrosion of AA2024-T3 in the form of pitting and general attack.

The premise that Ce(dbp)₃ acts as a cathodic inhibitor was further investigated by chronoamperometric tests and cathodic polarization on pure Cu. The samples were Cu wires of 150 μm diameter, a Pt/Niobium mesh as a counter, and reference electrode was Hg/Hg₂SO₄. The Cu was wet polished to 1200 before exposure. These samples were first immersed either in borate buffer pH 8.4 for 2 h with the potential being held at −0.875 V_Hg/Hg₂SO₄ or in 0.255 mM Ce (or 200 ppm Ce(dbp)₃) for 68 h with the potential held at −0.875 V_Hg/Hg₂SO₄. This potential value was chosen to mimic the coupled potential of AA2024-T3 Cu rich intermetallics. The sample immersed in the Ce pretreatment was then transferred to a cell with naturally aerated borate buffer at pH 8.4 within less than 4 min (the sample that initially was immersed in borate was not exposed to air, but it was transferred into a different cell, hence it was left at OCP for a short time). Chronoamperometric or cathodic polarization tests were then conducted in the potential regime where ORR is the dominant cathodic reaction. Before starting either of these test the Cu sample was conditioned for 5 min by holding the potential at −0.875 or −0.925 V_Hg/Hg₂SO₄. If the hypothesis regarding cathodic inhibition is correct, then the ORR reaction rates should be reduced after the Ce(dbp)₃ pretreatment.

XPS surface analysis.—XPS analyses were carried out on an uncorroded AA2024-T3 specimen and an AA2024-T3 specimen corroded in a chloride environment with a cerium-based inhibitor present. All specimens were 5 × 5 × 2 mm. A Kratos AXIS Ultra imaging XPS with a monochromatized Al Kα X-ray source (1486.6 eV) operated at 150 W was used. The spectrometer energy scale was calibrated using the Au 4f½ photoelectron peak at binding energy E_b = 83.98 eV. Spectra were charge corrected using the C 1s photoelectron component peak corresponding to C–C species at E_b = 285.0 eV. Survey spectra (wide energy range, typically 0–1100 eV) and high-resolution elemental region spectra were acquired using analyser pass energies of 160 and 20 eV, respectively. The former identifies surface constituents; the latter characterizes the chemical state or states of each of the elements present. The volume of analysis was ~700 × 300 μm × 1 nm.

FIB-SIMS surface analysis.—FIB-SIMS experiments used a finely focused beam of gallium ions from a liquid metal source to sputter the sample. The sputtered ions are collected by a SIMS, separated by their mass-to-charge ratio, and counted to produce high-resolution elemental maps or elemental spectrum. The examined specimen edges were polished prior to analysis and the resulting cross section was profiled, allowing for the evaluation of distinct layers within the surface and their relative thickness, as well as information relating to the chemical composition of these layers. In this instance cerium and phosphorus were specifically targeted. A FEI FIB 200 equipped with a quadrupole-based SIMS instrument.

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**Figure 1.** Chemical structure of the dibutylphosphate anion.
was used. Surface elemental spectrums were obtained using probe currents of 11500 and 350 pA, with probe sizes 5000 and 550 Å, respectively. Data was accumulated over 20 scans with a dwell time of 10 ms. Elemental maps were recorded after narrowing the window of detection to the desired atomic mass unit and calibrated for maximum responses by varying the probe current and size. The detection window was accurate to ±0.4 AMU. A 1 ms dwell time with a resolution of 512 pixels was used.

Toxicity testing.— The toxicity of Ce(dbp)$_3$ was analyzed by Leeder Consulting using the Microtox technique, which measures the toxicity of a compound using bioluminescent marine bacterium Vibrio fischeri as the test organism. EC50 values are determined based on the dosage required to reduce the bacterium population by 50% in the emitted light. The Ce(dbp)$_3$ was supplied to Leeder Consulting in solution form at its maximum solubility; hence, the EC50 value was reported as a percentage. An EC50 value of 25% indicates the bacteria were in a solution diluted 3/4 by the buffer, i.e., 1:4 ratio of supplied solution buffer. An EC50 value of 100% indicates that the bacteria were placed into an undiluted solution. The Ce(dbp)$_3$ sample recorded an EC50 value of >100%, indicating that less than 50% of the bacterium population was affected in the undiluted test solution. This indicates that Ce(dbp)$_3$ has a very low toxicity and may be considered as nontoxic.

Results and Discussion

Corrosion rate measurements.— The corrosion rates calculated after 1, 3, and 6 weeks exposure periods for the inhibited solutions and the control solution are given in Fig. 2. The inhibiting effect of the Ce(dbp)$_3$ appeared to increase markedly with exposure time. After 6 weeks exposure, the corrosion rate was reduced by greater than a factor of 40 for 200 ppm (0.255 mM) Ce(dbp)$_3$. Furthermore, as shown in Table I, it is clear that even low inhibitor concentrations significantly decreased the corrosion rate.

In cases where an alloy is prone to pitting corrosion, weight loss

![Figure 2. Corrosion rates for AA2024-T3 alloy exposed to 0.001 M NaCl (control) and 0.001 M NaCl/200 ppm Ce(dbp)$_3$, after 1, 3, and 6 weeks immersion. Corrosion rates determined from weight-loss specimens as per ASTM G1-90. Individual results for the duplicate experiments are shown.](image)

![Figure 3. Optical images of AA2024-T3 coupons exposed for 7 days in (a) 0.001 M NaCl, (b) 0.001 M NaCl/200 ppm Ce(dbp)$_3$, and (c) 0.001 M NaCl/97 ppm CeCl$_3$·7H$_2$O. These concentrations were chosen as they represented the solubility limit in neutral pH for Ce(dbp)$_3$ and the equivalent concentration of Ce$^{3+}$ in the latter case. (d) 42 day exposure to control solution and (e) AA2024-T3 coupons exposed for 42 days in 0.001 M NaCl/200 ppm Ce(dbp)$_3$ solutions. As a comparison of the inhibition effectiveness of dbp alone, (f) 0.01 M NaCl/6754 ppm Na-dbp has been included.](image)
measurements may sometimes be misleading, thus visual inspection of the specimens was carried out. Figure 3a-c shows typical specimens after exposure for 1 week to solutions of 0.001 M NaCl, 0.001 M NaCl with 200 ppm $\text{Ce(dp}b\text{)}_3$, and 0.001 M NaCl with 97 ppm 0.13 mM $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$. It is evident that $\text{CeCl}_3$, while being recognized as a good cathodic inhibitor, still leads to some degree of pitting on the surface, whereas the specimen exposed to a similar concentration of $\text{Ce(dp}b\text{)}_3$ remains pristine. A comparison of the surface after 42 days exposure in uninhibited and 0.26 mM $\text{Ce(dp}b\text{)}_3$ inhibited solutions is also shown in Fig. 3d and e. Again, a near-pristine surface is seen after this extended exposure to the rare-earth organic inhibitor. An occasional pit was seen to form at early stages on duplicate specimens but this did not appear to continue to grow with continued immersion. Thus, the combination of $\text{Ce}^{3+}$ with the dibutylphosphate anion in the form of $\text{Ce(dp}b\text{)}_3$ compound provides substantially more protection than an equivalent amount of $\text{Ce}^{3+}$ alone. As with other organic inhibitors, while high concentrations of Na(dp) give reasonable inhibition of AA2024, shown in Fig. 3f, the low level of dp anions provided here would not be beneficial, and indeed a straight combination with equivalent concentrations $\text{CeCl}_3$ with Na(dp) as for 200 ppm concentration of the $\text{Ce(dp}b\text{)}_3$ compound leads to poor protection (data not shown). The clear suppression of pitting compared with $\text{CeCl}_3$ is also suggestive of the decrease of the electrochemical reactions at or near the intermetallics, as has been noted previously.

**OCP measurements and potential polarization measurements.**—The OCP measured over 24 h is shown in Fig. 4. The behavior of the OCP for the control and inhibited system seem to be very similar over the initial few hours, followed by a steady fall in the OCP in the inhibited sample compared with the seemingly sudden and random oscillations in the OCP for the uninhibited control, probably attributable to pitting on the electrode surface. At longer time periods of over 20 h the OCP for the inhibited sample was noticeably more noble than the control. This was also seen when the sample was immersed in a higher concentration of NaCl (0.1 M) such that the inhibitive action was more clearly seen. Repeated measurements of OCP as a function of time suggested that the anodic shift occurs anywhere from a few minutes up to an hour following immersion in the inhibited solution. Initial OCP values were somewhat inconsistent and varied by up to 200 mV, most likely due to the heterogeneous nature of the substrate metal.

Figure 5a shows potentiodynamic scans for a $\text{Ce(dp}b\text{)}_3$-inhibited solution. In the absence of this inhibitor (i.e., control sample) anodic dissolution takes place without any sign of passivation. It is likely that the pitting potential is near the OCP, indeed the pitting potential of AA2024-T3 follows the relationship $E_{\text{pit}} - \text{AA2024-T3} = -0.684 - 0.1083 \times \log(\text{Cl}^{-}, \text{molar})$, yielding a pitting potential of $-0.360 \text{ V vs SCE}$ in 0.001 M NaCl solution. In contrast, the inhibited solution displays a small but distinct change of anodic slope from $E_{\text{corr}}$ to $-400 \text{ mV}$ (i.e., an increase in the anodic slope), consistent with a suppression of the anodic reaction and with the rise of OCP. However, it appears that once the surface film has been

**Figure 4.** OCP scan over 24 h in a 0.001 M NaCl solution. A fresh electrode was prepared for each scan.

**Figure 5.** (a) Potentiodynamic scan for AA2024-T3 electrode scanned from OCP in the anodic direction and toward the cathodic. A fresh electrode was prepared for each sweep direction. Scans were performed at 0.1667 mV/s. (b) A CPP scan for AA2024-T3 from $-200 \text{ mV cathodic of OCP}$ after 30 min immersion in a 0.1 M NaCl solution. A comparison is shown between (b) inhibited and (a) uninhibited solutions.
destabilized under the forced anodic conditions, the inhibitor is no longer able to suppress the anodic reactions. The additional suppression of the cathodic current densities relative to a control sample leads to the conclusion that this inhibitor is most likely acting as a mixed inhibitor. Given that the effects of this inhibitor are more dramatic at longer times as observed in the weight loss and OCP measurements, the slight difference in the electrochemical measurements in this particular experiment may be due to the short exposure time of AA2024-T3 to the inhibitor solution. However, the CPP plot shown in Fig. 5b suggests predominantly cathodic inhibition in this system with a substantial decrease in $i_{\text{corr}}$ when the alloy is exposed to 0.1 M NaCl. This particular experiment intrinsically changes the surface at the outset of the experiment; by beginning the polarization scan 200 mV cathodic of OCP we determine that cathodic processes occur which lead to pH changes. The subsequent increase in surface pH is likely to cause hydrolysis of the rare-earth inhibitor compound and possible thickening of the resultant inhibitive film. In effect, these changes reflect the longer term behavior of the alloy in the Ce(dbp)$_3$-containing solution where slow hydrolysis naturally occurs, thereby leading to a thickening of the film, as shown in surface characterization experiments discussed below. Thus, in this experiment, it appears that the cathodic currents are suppressed significantly, although the anodic character of the inhibitor is not evident in this experiment. Longer term immersion (between 6 and 24 h, not shown) prior to CPP measurement leads to a still stronger suppression in cathodic currents.

Recent measurements using microcell electrochemistry on individual aluminum alloy phases support this behavior.$^{28}$ Another interesting electrochemical affect which confirms the significant corrosion inhibition of this compound is discussed below.

Assessment of replated copper during corrosion of AA 2024-T3 and ORR suppression on copper.— Low magnification images of alkaline-etched, untreated, precorroded, and pretreated [in 0.05 M Ce(OAc)$_3$ solution] then corroded (in 0.05 M NaCl solution) AA2024-T3 specimens are shown in the literature.$^{24}$ The characteristic reddish brown color of copper or copper(I) oxide is apparent in the case of the alkaline-etched and specimens precorroded in 0.05 M

![Figure 6. CV data (a) 24 h and (b) 10 days. The copper oxidation peaks are clearly absent in the sample corroded in the 200 ppm Ce(dbp)$_3$0.001 M NaCl solution but are quite distinct when no inhibitor is present (control).](image)
amperogram for a 150 or 2 h in pH 8.4 borate buffer solution. For comparison the theoretical chro-
dramatically enhanced in the Ce-compared to the uninhibited specimens. Moreover, this effect was
this low level of inhibitor significantly reduced the Cu oxidation
lent 10 day exposure in Ce-compared to the uninhibited specimens. Therefore, when we consider the visual
ance is seen after corrosion in 0.001 M NaCl with 200 ppm
peaks increase significantly due to corrosion, these peak heights
served in an NaCl contaminated solution is substantiated.

**XPS characterization.**— Figure 8 presents the survey spectrum of the XPS analysis of an uncorroded bare AA2024-T3 aluminum alloy specimen. The Al 2p and Cu 2p XPS spectra of the bare specimen after exposure for 7 days to the 0.001 M NaCl control solution are shown in Fig. 9. Surface analysis revealed that the predominant elements in the surface layer of the uncorroded specimen were Al, Cu, and Mg, with the binding energies and the concentrations given in Table II. The binding energies of these elements suggested they were present in the form of their oxides, i.e., Al$_2$O$_3$, CuO, and MgO. This was in agreement with a total oxygen content of 40.57 atom %. After 7 days of full immersion in the corrosive medium, the XPS surface analysis showed a decrease in the aluminum content. By contrast, the copper percentage rose from 0.13 to 1.59%, while magnesium was no longer observed on the specimen surface. The binding energy for aluminum indicated that it was present as Al$_2$O$_3$, whereas for copper it suggested that this element could have been on the surface either as CuO or as Cu(OH)$_2$.

The XPS surface analysis of the AA2024-T3 specimens that had been exposed for 7 days to the 0.001 M NaCl solutions containing the Ce(dbp)$_3$ compound revealed that, on all coupons, the main constituents of the surface layer were cerium, aluminum, silicon, oxygen, and carbon, with the notable absence of Cu, which is consistent with copper replating data discussed above. Surprisingly, however, no phosphorus was found. This could be because this element is not present uniformly on the top surface or is present at very low levels on the surface. The presence of P is confirmed, however, via FIB-SIMS experiments discussed in the following section. The high-resolution Ce 3d spectra recorded for the sodium chloride solutions containing CeCl$_3$ and Ce(dbp)$_3$, respectively, are

**Figure 7.** Chronoamperometric test of Cu (150 μm diam wire) at -1.225 V in pH 8.4 borate buffer after 68 h pretreatment in 0.2547 mM Ce [Ce(dbp)$_3$] or 2 h in pH 8.4 borate buffer solution. For comparison the theoretical chronoa-

**Figure 8.** XPS survey spectrum of an uncorroded bare AA2024-T3 aluminum alloy specimen indicating the presence of various alloying elements on the surface.
shown in Fig. 10. Analysis of these spectra indicates the coexistence, in the uppermost layers of the surface film, of both oxidation states of cerium, i.e., Ce\(^{3+}\) and Ce\(^{4+}\). This suggests that the cerium-rich layer may consist of a mixture of oxide/hydroxide of Ce\(^{3+}\) and Ce\(^{4+}\), i.e., CeO\(_2\), Ce(OH)\(_x\) \(x=3,4\), and CeO(OH)\(_x\) \(x=1,2\).

It is acknowledged that the Ce oxidation state is extremely sensitive to the quantity of dissolved oxygen and the pH of the solution. Therefore, it is possible for Ce to exist in both valence states at or near the metal surface. According to Hinton et al.,\(^{10,25,30,31}\) the presence of H\(_2\)O\(_2\) is necessary for the oxidation of Ce\(^{3+}\) to Ce\(^{4+}\) and is formed as an intermediate species during the cathodic reduction of oxygen. The yellow coloration specific to Ce\(^{4+}\) has not been detected on our specimens. Because Ce\(^{4+}\) would be expected to be located on the cathodic precipitates, however, this coloration would be undetectable because of their microscopic size.\(^{12}\) Moreover, the valence of Ce in the film may vary depending on the time of exposure to the corrosive environment. Davenport et al.\(^{32}\) found Ce\(^{4+}\) only after about 7 days immersion in a NaCl solution containing Ce compounds. Balasubramanian,\(^{33}\) in his work on electrochemical deposition of cerium hydroxide on aluminum, found that anodic deposition resulted in an oxide phase comprised of Ce\(^{4+}\), whereas cathodic deposition results in the formation of a Ce\(^{3+}\) hydroxide.

The XPS surface analysis data, obtained on a corroded specimen after 7 days of exposure to the control solution, indicate preferential dissolution of Mg and Al. The corroded surface was also found to be rich in copper, which is consistent with the theory of Mg-rich precipitates dealloying and copper redistribution across the corroding surface, postulated by some authors.\(^{3,34-36}\) Thus, the Ce(dbp)_3 inhibitor is seen to suppress dealloying, with the XPS data supporting the findings from the copper replating experiments.

**FIB-SIMS analysis.**—Figure 11 shows the secondary electron image of a specimen bombarded with a high-energy gallium beam for a short duration (typically 5 min). The specimen was exposed to an aqueous chloride solution containing 200 ppm Ce(dbp)_3 for 10 days. A surface film approximately 500 nm thick is clearly visible in this image. The two inserts in this figure represent the cerium maps obtained from the SIMS measurement for specimens exposed for 24 h (inset a) and 10 days (inset b). The magnification has been reduced compared with the main image in order to clearly see the interfacial region rich in cerium ions. After 24 h the thickness of this cerium-rich layer is approximately 300 nm, while it approaches 500 nm after 10 days, consistent with the thickness of the surface film. This data gives us direct confirmation that the cerium is incorporated into a protective surface film with dimension within the submicrometer range.

A phosphorus map could not be obtained using the same procedures as for the cerium maps. Instead, full atomic mass spectrums under different beam strength conditions were collected. Figure 12 gives the full spectrum across the entire edge and a strong phosphorus signal is detected, confirming its presence in the film. However, when the beam strength is changed, a more complex mass spectrum was observed and the phosphorus signal was significantly diminished. This more complex mass spectrum is likely to be a result of organic chemical fragments that are ejected from the metal surface upon bombardment with gallium ions; the nature of these
fragments may well be dependent on the beam strength. Nevertheless, the presence of the strong phosphorus signal together with the presence of complicated mass fragments provides evidence of the incorporation of the organic component of the Ce<br>3 inhibitor in the surface film.

Conclusions

Ce<br>3 appears to be a promising benign inhibitor for the protection of high-strength aluminum alloys against corrosion in aqueous chloride media. Comparison of the results obtained from Ce-containing systems with those using Na-organic compound systems suggests that the inhibitive effect of Ce<br>3 is due to the combination of the rare-earth and the organic component. While the corrosion rate and electrochemical measurements have confirmed the dramatic inhibiting effect of this compound, the surface characterization has shown the presence of a submicrometer film (300–500 nm) which contains both the cerium ion [Ce(III) and Ce(IV)] as well as phosphorus. The FIB secondary image and cerium map suggest relatively uniform coverage after long exposure, although it is likely that the deposition of the inhibiting film is actually rather heterogeneous given the heterogeneous morphology of the AA2024-T3 substrate. The evidence of Ce(IV) may suggest that CeO2 is present at the intermetallics, as suggested by Ref. 37, while the Ce(III) may be incorporated as an oxide/hydroxide and/or some complex bimetallic compound incorporating the dibutylphosphate moiety, as observed for the Ce–Fe carboxylate combinations.19 In the latter case, the inhibitor system is proposed to retain some clustered units (as opposed to individual dissolved ionic species) due to only the partial hydrolysis of the Ce-organic bonds. These dangling bonds are then free to coordinate with aluminum ions and thereby form Al/Ce-based bimetallic compounds which deposit on the aluminum alloy surface, leading to protective insoluble films. The evi-

Figure 10. (a) XPS high-resolution Ce 3d spectra shows the spectrum of the Ce(dbp)<sub>3</sub> compound containing the characteristic twin repeating peaks of Ce<br>3 at 882–886 eV and 900–904 eV. (b) The same Ce 3d region taken of a AA2024-T3 alloy after 7 day exposure to 0.001 M NaCl/200 ppm Ce(dbp)<sub>3</sub>. The additional peaks indicate the presence of Ce<br>4.
dence in the case of the steel for bimetallic complexation, and the significant improvement in the surface protection of the aluminum alloy in this work, allows us to hypothesise that bimetallic Al–Ce–phosphate compounds are present. Further hydrolysis of this surface film with ongoing exposure and local pH changes will ultimately lead to a CeO(OH)/Ce(OH)₃ deposit. The model discussed here is under further investigation using advanced surface characterization techniques including micro-Raman and time-of-flight SIMS spectroscopy.

The combination of the two components in the Ce(dpβ)₃ compound appears to lead to mixed control, with a thin protective film covering the aluminum alloy surface, as shown by XPS and FIB-SIMS. The copper replating experiments together with XPS confirmed that the Ce(dpβ)₃ compound in chloride solutions leads to a reduction in surface dealloying and hence, a reduction of copper on the metal surface. The lower water solubility of this compound may allow its incorporation as a controlled release compound in coatings. Work is currently underway to investigate the performance of this compound in epoxy primer coatings as well as to understand more deeply the inhibition mechanism.

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References


Figure 11. Secondary electron image obtained from FIB experiment for an AA2024-T3 specimen following exposure of 10 days to 0.001 M NaCl/200 ppm Ce(dpβ)₃. (Inset a) SIMS map for Cerium after a 24 h exposure (length scale = 2 μm). (Inset b) SIMS map for Cerium after a 10 day exposure (length scale = 1 μm).

Figure 12. Full atomic mass spectrum from 20 to 150 AMU. This figure clearly shows the presence of phosphorus being bombarded from the edge surface of the coupon exposed for 10 days.