The unexpected role of benzotriazole in mitigating magnesium alloy corrosion: A nucleating agent for crystalline nanostructured magnesium hydroxide film

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Benzotriazole (BTA), an effective corrosion inhibitor for Cu or Cu-containing Al alloys, was added to 0.1 M NaCl to study its potential role in suppressing corrosion of the commercial Mg alloy, AMlite. In particular, the impact of pH and BTA concentration was investigated, indicating that BTA was effective at restricting corrosion of AMlite in weakly alkaline NaCl solution, i.e. pH 10.0. The degree of the protection afforded was a function of BTA concentration. The best corrosion inhibition was found in the NaCl containing 15 g/l BTA, however, the mechanism of inhibition involved the insoluble Cu-BTA complex via Cu-N coordination bonds for Cu-alloys. The magnitude of this effect of BTA on Mg corrosion was not anticipated, but effective, with beneficial implications to utilization of Mg alloys as anode materials, where in such cases, when dissolution occurs, the anode can passivate with little change in its potential.

Magnesium (Mg) and its alloys continue to attract attention due to their superior strength-to-weight ratio, electrical conductivity and low density. In particular, Mg alloys are being pursued where weight reduction is desired, such as in transportation and mobile electronics (3C products). Compared to other structural metals which may be protected by a native and stable oxide film, such as titanium (Ti), aluminum (Al), and stainless steel, Mg surfaces are normally covered by a naturally formed loose film comprised of a mixture of oxide, hydroxide and carbonate due to atmospheric CO₂. Such a surface film is un-protective, and particularly unstable in the presence of chloride ions, whilst soluble at near-neutral pH. As such, Mg alloys nominally undergo high corrosion rates when exposed to aqueous or atmospheric environments, limiting their wider application.

To address the corrosion of Mg alloys, a number of methodologies have been developed, including microstructural modification (specific alloying, impurity control, grain size refinement, etc.), and protective coatings for Mg surfaces. The latter has been extensively studied given coatings are much more effective than alloying, with many coating options available to impart corrosion protection. Effective coatings include conversion coatings, electroplated coatings, physical barriers, and PEO coatings, to name but a few. In terms of an economical and wide-scale approach, chromat conversion coatings have proven to be successful, however they are increasingly restricted due to toxicity; whilst appropriate alternatives are yet to translate to large-scale industrial implementation owing to either poor cost-effectiveness or insufficient protection efficiency. Therefore, the development of alternative and simple methods to passivate corrosion of Mg based alloys remains topical.

Whilst a corrosion protection strategy will differ based on the ultimate application, the utilization of corrosion inhibitors is one method to regulate the corrosion of metals, including Mg alloys, for a range of scenarios that may include aqueous exposure, or for incorporation into primers. Benzotriazole (BTA), whose chemical structure is illustrated in Figure 1, has been extensively studied as inhibitor to regulate corrosion kinetics of iron (Fe) and steel., copper (Cu), nickel (Ni), Al, and zinc (Zn) by the formation a protective surface film. After about four decades of investigation, it is well recognized that anodic Cu dissolution is mitigated by the formation of a protective film consisting of insoluble compound of Cu-BTA with a reported low pKsp value of 11.4 in aqueous solution.

Experimental
Preparation of AMlite substrate and BTA containing electrolytes.—High-pressure-die-cast Mg alloy AMlite specimens (in wt %: Mg-12.1Zn-3.5Al-0.3Mn-0.1Ca-0.0029 Fe) were prepared for the electrochemical tests. AMlite substrates, in concert with scanning electron and optical microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy.

Figure 1. Chemical structure of 1,2,3-Benzotriazole (BTA).
supplied by Magontec Pty. Ltd. Specimens of 2.0 × 2.0 × 0.5 cm were used as the substrate material. Specimens were successively ground to a 2000 grit finish with silicon carbide papers and ethanol as lubricant. Prior to immersion in NaCl, AMlite specimens were ultrasonically cleaned in acetone at room temperature for 15 min and then in absolute ethanol for 10 min. 5.84 g NaCl (S7653, Sigma-Aldrich, Australia) was added to 1000 mL deionized water to make 0.1 M NaCl solution. BTA (1.2,3-Benzotriazole, B11400, Sigma-Aldrich, Australia) powder was weighed and introduced into the 0.1 M NaCl solution with concentration varying over the range of 0–15 g/L.

**Electrochemical measurements.**— For electrochemical tests, a ‘flat-cell’ (PAR, K0235, Princeton Applied Research, Oak Ridge, TN, USA) containing 300 mL of solution was used with an exposed working electrode area of 1 cm², incorporating a saturated calomel reference electrode (SCE) and platinum (Pt) mesh counter electrode. Potentiodynamic polarization experiments were carried out following 10 min exposure to the NaCl electrolytes at open circuit potential and room temperature. Testing was carried out using a BioLogic VMP-3Z potentiostat (BioLogic Inc., Knoxville, TN, USA). The polarization curves were collected using a scan rate of 1 mV/s to reveal the relative anodic and cathodic kinetics, and to allow an estimate of corrosion current density (i_corr). Any Tafel-type fits were executed by selecting a portion of the polarization curve that commenced >50 mV from corrosion potential (E_corr), and i_corr was subsequently estimated from the value where the fit intercepted the potential value of the true E_corr. Emphasis was given to the cathodic branch, as the anodic branch was often inclusive of a passive window (which is not typical for other Mg corrosion studies).

The anodic current arising from potentiostatic polarization was also recorded, at a constant applied potential of −1.2 V SCE. This potentiostatic potential was selected, as it refers to an anodic polarization, which was applied to elucidate any passivating effect of BTA on the alkalized surface of AMlite.

Electrochemical impedance spectroscopy (EIS) was carried out over a frequency range of 100 kHz to 10 mHz with a sinusoidal amplitude of 10 mV and five points per decade, either following 10 min at OCP or for the given exposure time specified. The EIS data was analyzed using EC-Lab V10.37 software. All tests were carried out in a Faraday Cage.

**Surface characterization following immersion of AMlite specimens.**— The effects of BTA concentration and the pH of 0.1 M NaCl on the resultant surface morphology of AMlite specimens were investigated using scanning electron microscopy (SEM, FEI Nova Nano) and a Celestron digital microscope. The cross-sectional electron micrograph of the passivated surface was realized using a dual-beam Focused Ion Beam (FIB) (FEI Quanta 3D-FEG) employing a gallium-milling current of 3 nA. Surface chemistry was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo K-alpha) having a base pressure of 10⁻⁸ torr and a hemispherical analyzer and the core level XPS spectra for Mg 2p, Al 2p, O 1s, Na 1s, N 1s, and C 1s were recorded. The photoelectrons were generated by a monochromated Al K-alpha (1486.6 eV) primary radiation source (20 kV, 15 mA). Spectra acquired were processed via XPS Peak Fit software and the measured binding energy values were calibrated by the C1s (hydrocarbon C-C, C-H) of 285 eV. The structure and phase composition of various Mg surfaces before and after immersion process were identified by X-ray diffraction (XRD; Philips PW1140), using Cu K-alpha radiation source (k = 1.5418 Å, 40 kV, 25 mA) at a scanning speed of 0.5° min⁻¹ at a 20 range of 10–80°.

**Results**

**EIS measurements.**— Electrochemical impedance spectra were collected for AMlite specimens immediately following 10 min stabilization at the open circuit potential (OCP) during immersion in 0.1 M NaCl with varying BTA concentrations, ranging from 0–15 g/L, and a constant pH value of either 10.0, 7.0 or 3.0. A number of representative OCP curves obtained from AMlite immersed in NaCl with 0–15 g/L BTA additions at pH 10.0, are provided in Figure 2. It is evident that OCP evolution following exposure to NaCl approached a peak value at an immersion time of up to ~150 sec, then OCP subsequently stabilized. The overall impedance as depicted by the Nyquist plot is shown to increase as a function of BTA concentration in the mildly alkaline environment (Figure 3a). The impedance of AMlite specimens approximated doubled (from ~209 Ω cm² to ~379 Ω cm²) with the introduction of a small concentration of BTA (1 g/L) into 0.1M NaCl, compared to BTA-free electrolyte. A further increase in BTA concentration to 5 and 10 g/L substan3ially increases the measured impedance by an order of magnitude compared to the neat NaCl solution; whilst the impedance of AMlite approaches a peak value in the most concentrated BTA solution tested (15 g/L) of ~28003 Ω cm².

When tests were conducted in neutral (Figure 3b) and acidic (Figure 3c) NaCl solutions, the Nyquist plots for AMlite specimens markedly differ from those in the slightly alkaline NaCl. With lower electrolyte pH, the impedance (and hence dissolution) of AMlite was concomitantly influenced. Firstly, it is prudent to note that in BTA-free NaCl, AMlite demonstrates the highest impedance (resistance to corrosion) at neutral pH (7.0), followed by that at acidic and alkaline pH, indicating the stability of the naturally formed Mg(OH)₂ film in 0.1 M NaCl is a function of pH, say, pH 7.0 > pH 3.0 > pH 10.0 (refer to the black lines with square symbols in Figure 3). The reason why in BTA-free NaCl that AMlite is more corrosion resistant at pH 7.0 as opposed to pH 10.0 is attributed to the composition of AMlite being rather different to that of pure Mg, with 12.1 wt% Zn in AMlite, which can dissolve under conditions where Zn dissolution is favored.26 Conversely, in the case of pure Mg, Mg dissolves as a linear function of the pH of NaCl solution, as reported by Ralston et al.,27 where decreasing pH favors accelerated corrosion. Secondly, it is noted that any increase in BTA concentration appeared to lower the impedance when the bulk original electrolyte pH was neutral or acidic.

To study the formation mechanism of the protective film on the AMlite surface in the presence of BTA in weakly alkaline NaCl (0.1 M, pH 10.0), long-term EIS was recorded at 30 min intervals for 24 h, along with the immersion of AMlite in 15 g/L BTA containing 0.1 M NaCl. It should be noted that the first EIS data was recorded after 40 min stabilization at OCP. Such a time point was adopted mainly to differ from the EIS measurements depicted in Figure 3a, which were conducted after 10 min pretreatment and running for approximately 29 min. Figure 4a illustrates a time dependent response of the overall impedance at frequencies corresponding to 1 Hz over the 24 h exposure period. The characteristic Nyquist plot for AMlite
Figure 3. Nyquist plots for Mg alloy AMlite after 10 min OCP stabilization in 0.1 M NaCl as a function of BTA concentration and pH (A, 10.0, B, 7.0 and C, 3.0). The inset image magnifies the semi-circles in the high frequency range in (A).

following 40 min immersion in 0.1M NaCl at pH 10.0 and OCP is presented in Figure 4b. The Nyquist plot exhibits two time constants over the studied frequency range (at high and moderate frequencies, respectively), and an inductive loop at low frequency. The EIS data were simulated using the equivalent circuit presented in the inset of Figure 4b, which was proposed by King et al.,28,29 to faithfully represent the corrosion process for Mg in NaCl. The apparent good agreement between the experimental data and fitting indicates the suitability of the chosen equivalent circuit, which has more recently been validated for Mg alloys by Bland et al., using inductively coupled plasma (ICP) analysis.30

With 40 min immersion, the EIS data (the first Nyquist circle as annotated in Figure 4a) indicates a significant decrease in impedance, when compared to the case of 10 min immersion (from $\sim 30000 \Omega \cdot \text{cm}^2$ to $\sim 1280 \Omega \cdot \text{cm}^2$, as presented in magenta with star symbols in Figure 3a). It is evident, after such a decrease in impedance, that the total impedance of AMlite increases with immersion time in 0.1M NaCl at pH 10.0 (Figure 4a); meanwhile, the characteristic evidence of a diffusion limited response (typified by a Warburg-type response) becomes apparent, which is indicative of systems where corrosion protection is occurring, such as conversion coated Mg.5 The impedance data are interpreted further in the discussion below.

Potentio-dynamic and -static polarization.— To investigate the effect of BTA concentration on the anodic and cathodic kinetics of AMlite in 0.1 M NaCl at varying pH, potentiodynamic polarization measurements were performed over the potential range extending to $+1.0 \text{ V vs OCP}$. The calculated corrosion potential ($E_{\text{corr}}$) and corrosion current density ($i_{\text{corr}}$) values are provided in Table I. With respect to performance in the mildly alkaline NaCl solution containing 0 g/L or 1 g/L BTA, anodic current increases steadily with applied potential, indicating a rather rapid dissolution of AMlite. The further addition of BTA at concentration greater than 1 g/L was seen to retard both the anodic reaction kinetics, which leads to the reduction in $i_{\text{corr}}$ and also to the presence of an apparent passivation region whereby passivation

Figure 4. Time-dependent impedance response of Mg alloy AMlite in 0.1 M NaCl containing 15g/l BTA at pH 10.0. (A) Traditional Nyquist impedance plots collected over a period of 30 min to 24 h, as indicated by the dash red arrow, in which some selected time intervals (30 min, 12 and 24 h, plus initial 10 min OCP stabilization were annotated; and (B) Nyquist plot and corresponding fit collected over a period of 30 min (plus 10 min OCP stabilization). The equivalent circuit given in the inset was used to do data fitting and analyze the corrosion behavior of AMlite in 0.1 M NaCl containing 15 g/L BTA.
Table I. Evaluated $E_{corr}$ and $i_{corr}$ values of AMlite immersed in 0.1 M NaCl at different pH and containing various BTA.

| BTA conc. (g/L) | 0     | 1     | 5     | 10    | 15    |
|----------------|-------|-------|-------|-------|-------|
| $E_{corr}$ (Vsce) | $-1.46 \pm 0.01$ | $-1.47 \pm 0.03$ | $-1.53 \pm 0.03$ | $-1.57 \pm 0.01$ | $-1.47 \pm 0.01$ |
| $i_{corr}$ ($\mu$A.cm$^{-2}$) | $32.1 \pm 3.8$ | $22.4 \pm 5.2$ | $6.8 \pm 2.0$ | $11.8 \pm 1.4$ | $2.3 \pm 0.2$ |

$pH$ 7.0

| $E_{corr}$ (Vsce) | $-1.50 \pm 0.05$ | $-1.55 \pm 0.02$ | $-1.49 \pm 0.01$ | $-1.49 \pm 0.02$ | $-1.45 \pm 0.01$ |
| $i_{corr}$ ($\mu$A.cm$^{-2}$) | $43.9 \pm 3.1$ | $146.9 \pm 12.9$ | $270.5 \pm 24.4$ | $221.0 \pm 9.6$ | $72.9 \pm 14.0$ |

$pH$ 3.0

| $E_{corr}$ (Vsce) | $-1.43 \pm 0.01$ | $-1.44 \pm 0.02$ | $-1.52 \pm 0.01$ | $-1.43 \pm 0.01$ | $-1.49 \pm 0.03$ |
| $i_{corr}$ ($\mu$A.cm$^{-2}$) | $64.6 \pm 4.2$ | $134.8 \pm 10.8$ | $290.2 \pm 10.8$ | $117.56 \pm 16.7$ | $26.8 \pm 3.2$ |

Figure 5. Potentiodynamic polarization curves as a function of concentration of BTA and pH (A, 10.0, B, 7.0 and C, 3.0).

breakdown is observed at $-1.1$ V$_{SCE}$ and $-0.9$ V$_{SCE}$ for the case of 5 and 10 g/L BTA respectively (Figure 5a). A pronounced passivation phenomenon (defined by the arrow in Figure 5a) was obtained in the 0.1 M NaCl containing 15 g/L BTA with extended passivation region to $-0.7$ V$_{SCE}$, indicating a remarkable passivation upon AMlite.

Contrary to the passivation observed at pH 10.0, the neutral (pH 7.0) or acidic (pH 3.0) NaCl did not reveal any such passivation (Figures 5b and 5c). The characteristic form of the anodic polarization curves (i.e. rapid dissolution of Mg matrix with applied potential) remains similar with that of the addition of BTA. The exception to this was a minor level of apparent inhibition of anodic kinetics was evident for AMlite when tested in 0.1 M NaCl containing 15 g/L BTA at neutral pH, supported by the presence of a narrow passivation window with a breakdown event $\sim 100$ mV above OCP. In general, the presence of BTA in 0.1 M NaCl for both pH 3.0 and 7.0 accelerated the cathodic reaction kinetics and consequently led to a higher corrosion rate of AMlite.

The effect of polarization scan rate, namely 5, 1 and 0.2 mV/s, on the anodic kinetics of AMlite samples in 0.1 M NaCl containing 15 g/L BTA at pH 10.0, was also investigated. This was done to further investigate the scenario in which high levels of passivation were observed. We also note that 0.1 M NaCl at pH 10.0 that is BTA free is not a passivating solution for AMlite, as clearly observed in Figure 5a. The lowest scan rate of 0.2 mV/s led to alteration in both shape and current density relating to the anodic reaction, and induced a profound decrease in anodic corrosion current density ($i_{corr}$) as indicated by arrow in Figure 6. In addition, the passivation-break-down

Figure 6. Potentiodynamic polarization curves of Mg alloy AMlite after 10 min OCP stabilization in 0.1M NaCl containing 15 g/L BTA and pH 10.0 at discrete scan rates. The dashed blue line with triangular symbols indicates the decrease in anodic current density as a function of scan rate (declining from 5 to 0.2 mV/s).
potential was increased to nobler values, for the slowest scan rate, i.e. 0.2 mV/s. This indicates that the BTA performance is time dependent. This can be stated rather firmly, since nominally for the ‘scan rate effect’ alone, the breakdown potential is artificially elevated when scan rate is more rapid (due to capacitive effects). However, here the highest breakdown potential is at the slowest scan rate, indicating the time (or charge) dependence of the BTA efficacy.

To further electrochemically explore the passivity observed for AMlite in the presence of BTA, potentiostatic polarization was also carried out for a number of conditions. Not all tests are required for presentation herein, however potentiostatic testing was done deliberately to elucidate the mechanism of BTA inhibition. The effective inhibition of AMlite was seen as reported above for weakly alkaline conditions, and it is therefore suggested that the mechanism has a requisite pH. In order to alter surface pH of Mg in situ, it is now well known that alkalization of dissolving Mg surfaces occurs. This phenomenon occurs both due to anodic Mg dissolution itself, but also due to persistent cathodic activity upon anodically polarized Mg surfaces. As such, it was suggested that if an electrolyte of lower pH was used, and Mg dissolved in situ (potentiostatically, with the current monitored) that passivation could be stimulated in situ due to surface alkalization. Consequently, 0.1 M NaCl electrolyte with and without 15 g/L BTA at pH 7.0 was studied. A constant applied potential of $-1.2 \, V_{SCE}$ was applied, based on this being an ‘anodic’ potential from potentiodynamic tests reported (Figure 5). Further, the rationale for choosing this particular potential was that it corresponds to a potential where anodic dissolution proceeds rapidly. As the data illustrate (Figure 7), the BTA-free NaCl electrolyte generated a high and constant anodic current, at $\sim330 \, mA/cm^2$. Meanwhile, under the identical experimental conditions, the addition of BTA at 15 g/L stimulated a powerful inhibition of anodic dissolution. The measured anodic current reduced steadily to the nano-Amp range. This is decisive evidence that a protective surface film was produced in situ during the anodic dissolution of AMlite in the presence of BTA in 0.1 M NaCl at pH 7.0.

**Surface morphology following exposure to NaCl solution.**— Optical images were taken in situ during specimen immersion via a Celestron digital microscope in order to reveal the macro-scale surface morphology with time under various electrolyte conditions, i.e. 0.1 M NaCl containing BTA at 0, 1, 10 and 15 g/L at pH 10.0 (Figure 8). Images of the AMlite sample immersed in BTA-free NaCl were not provided due to the similar surface appearance to the case exposed to 1 g/L BTA. At the onset of immersion, the AMlite surface was partially covered by numerous hydrogen gas bubbles and the lustrous metallic finish evolved to a darker appearance. With time, hydrogen gas was continuously evolved from the surface into the solution. Filiform-like corrosion (indicated by arrows in Figure 8) was identified on the surface of AMlite immersed in the least concentrated BTA (1 g/L) containing NaCl solution for 6 h. Such characteristic filiform-like corrosion phenomena became severe after 12 and 24 h. In terms of the sample in contact with 10 g/L BTA containing NaCl electrolyte, similar signs of localized corrosion were noticeable after 12 h, whilst no corrosion was identified on the AMlite specimen immersed in the 15 g/L BTA-NaCl solution, even after 24 h immersion. It is importantly noted that, at the immersion stage, all specimens formed surface bubbles. However these bubbles did not correspond to noticeable attack for the specimen exposed to 15 g/L BTA for 24 h, on the contrary, an early-on reaction in NaCl with concentrated BTA was an essential precursor to trigger such a passivation effect.

Figure 9 illustrates the surface morphology and topography via high-resolution SEM analysis for the AMlite specimens exposed to various BTA-containing NaCl solutions for 30 min and 24 h, respectively. Following only 30 min immersion in the NaCl, the specimen exposed to only 1 g/L BTA, presented the most change of surface morphology. With exposure time extended to 24 h, all surfaces were significantly altered. A surface presenting a non-uniform morphology and coarse agglomerates was derived from exposure to 1 g/L BTA-NaCl solution after 24 h immersion. 10 g/L BTA-NaCl promoted the growth a layer comprising leaf-like particles. The most concentrated BTA obtaining NaCl solution (15 g/L) resulted in the formation of a film comprising fine crystalline compounds with a compact structure. The high-resolution FIB-SEM graph of Figure 10 reveals a characteristic bi-layer structure of the film derived from the immersion process in 0.1M NaCl containing 15 g/L BTA for 24 h. It apparently consists of a dense and thin film (less than 200 nm) adhered closely.
to the substrate as an intermediate, and a top thick (approximately 1.5 μm) and also compact Mg(OH)$_2$ as indicated by XRD and XPS in the following section. The ultra-thin feature of the intermediate film made it a challenge to be detected by XRD but it could be attributed to MgO as reported previously. Such an outer hydrated MgO, i.e., Mg(OH)$_2$ film on top of inner MgO layer, covering the entire AMlite surface, presents a dense structure and high thickness, which all differs from the results by Taheri et al. The surface films developed by Taheri et al. in highly alkaline (pH 14.0) and neutral water solutions consisted of thin MgO layer (50–150 nm thick) with partial or complete coverage by a outer Mg(OH)$_2$ (up to 700 nm in thickness). The significant difference in the film nature determined herein was attributed to the presence of BTA. The thickness of such protective MgO based film, however, is also far thicker than that of BTA-Cu protective film on Cu, ranging from tens of Å to 10 nm, indicating a discrete film formation mechanism.

**XPS and XRD analysis of following exposure to NaCl solution.**

The chemical composition and structural phase analysis of AMlite following 24 h immersion in various NaCl solutions were analyzed and presented for results from XPS (Table II) and XRD (Figure 11). The core-level Mg 2p spectrum for all AMlite surfaces could be resolved into two spectra having binding energy peaks at 49.8–50.1 and 50.8–51.1 eV, which are attributed to metallic Mg and Mg(OH)$_2$, respectively. Oxygen (O) existed in the form of OH in the surface film, as indicated by the characteristic peak value at 531.8 - 531.9 eV. BTA anions were also detected, owing to the presence of a N1s signal with a peak value of 399.5–399.9, in all cases except for the case in which a dilute BTA (1 g/L) solution was used. As the concentration of BTA in the immersion solution increased, this promoted the formation of Mg(OH)$_2$ and BTA anions present at the surface.

Compared to the benchmark XRD pattern derived from pure Mg(OH)$_2$ (analytical powder) as illustrated in Figure 11, the AMlite
surfaces consisted of both characteristic peaks of bulk pure Mg phase and Mg(OH)\textsubscript{2} at 38.1 (101) and 58.5 (110). It is noted that both the quantity and crystallinity of the peaks belonging to Mg(OH)\textsubscript{2} on the treated AMlite surface increases as a function of BTA concentration in NaCl after 24 h immersion.

**Discussion**

*Influence of pH on the passivating role of BTA for AMlite.—* A prevailing claim in terms of corrosion inhibiting function of BTA in the literature advocates the formation of a protective multilayer through chemisorbed BTA\textsuperscript{−} anions onto the surface of Fe, Cu, Zn and Ni as a result of metal-N coordination bonds in aqueous electrolyte.\textsuperscript{13} Studies conclude that pH value of the electrolytes has a negligible impact on the inhibiting effectiveness of BTA for Cu\textsuperscript{13,15}. BTA can coordinate with Cu cations (either Cu\textsuperscript{2+} or Cu\textsuperscript{+}) in the form of BTAH (acidic or neutral pH) or BTA\textsuperscript{−} (alkaline pH) via Cu-N bonding.\textsuperscript{15}

Instead, our electrochemical results (Figures 3–5) reveal that BTA plays a critical role in inhibiting corrosion progress of Mg alloy AMlite in conditions approaching alkaline (pH 10.0), indicating some exclusivity to protection being afforded in the presence of an excess of OH\textsuperscript{−}, and, implying a different (unknown) inhibition mechanism. In this context, we aim to rationalize the passivation provided by BTA when there is an excess of OH\textsuperscript{−}. The following equations demonstrate how BTA hydrolysis proceeds in aqueous solution as a function of pH:

\[
\text{BTA} + \text{H}_2\text{O} \rightarrow \text{BTA}^− + \text{[H}_3\text{O}]^+ \quad [1]
\]

\[
f_{[\text{BTA}^−]} + f_{[\text{BTA}]} = 1.0 \quad [2]
\]

\[
pK_{\text{a(BTA)}} = −\log_{10}\left(\frac{[\text{BTA}^−][\text{H}_3\text{O}]^+}{[\text{BTA}]}\right) = 8.2 \quad [3]
\]

\[
pH = −\log_{10}[\text{H}_3\text{O}^+] \quad [4]
\]

The acidic dissociation constant, pK\textsubscript{a} of BTA in water, has been confirmed to be 8.2.\textsuperscript{39} Therefore, according to Eqs. 1–4, the fraction of BTA molecules that have been ionized [BTA\textsuperscript{−}] at pH 3.0, 7.0 and 10.0 is 0.000004, 0.04, and 0.975 respectively. It is evident therefore, that the majority of BTA molecules stay as BTAH when pH is below 7.0 and become BTA\textsuperscript{−} anions by releasing H\textsuperscript{+} from their structure when pH tends to an OH\textsuperscript{−} excess. Considering that BTA only exhibits a corrosion-inhibiting role for Mg alloy AMlite under conditions where the dominant species is the BTA\textsuperscript{−} anion, we discount the formation of a protective layer comprising of a BTAH-Mg complex via an Mg-N coordinating bond. Therefore a dissimilar working mechanism to that reported for Cu/Fe/Ni/Zn is anticipated correlating to the presence of BTA\textsuperscript{−} anions.

*Role of BTA\textsuperscript{−} anions in passivating AMlite.—* Although BTA passivates corrosion of AMlite to varying degrees under in weakly alkaline conditions, we have also demonstrated that the protection is dependent on the concentration of [BTA\textsuperscript{−}] in 0.1 M NaCl (Figure 5a). The electrochemical data herein suggests that in 0.1 NaCl at pH 10.0, the presence of a relatively high concentration of BTA\textsuperscript{−}, e.g. 15 g/L or 125 mmol/L, is beneficial. Such concentrations are higher than those of other typical inhibitors (for example, ethylenediamine tetraacetic acid, p-nitro-benzene-azo-resorcinol, and stearic acid are effective at 5 mmol/L).\textsuperscript{40} Therefore, BTA most likely contributes to surface-property alteration, such as the generation of a protective film. It should be noted that there is some evidence that BTAH additions have a catalytic effect on cathodic kinetics of AMlite at pH 7.0 (Figure 5b) and pH 3.0 (Figure 5c), compared with the control, which might be attributed to the strong adsorption of BTA\textsuperscript{−} onto the noble phases (such as Zn-rich and Al-rich regions). Future work will be conducted regarding monitoring the dependence of E\textsubscript{corr} on immersion time in the presence/absence of BTAH to further elucidate the proposed inhibiting mechanism of BTA more generally.

As seen in Figure 8, we observe the surface of AMlite alters from a metallic finish to a dark appearance with time, indicating the formation of a product or substance on the surface evolving during immersion in NaCl with the presence of 15 g/L BTA. Such a surface darkening effect has been reported for pure Mg and Mg alloys of which dissolution was strongly suppressed by phosphate additions made to a chloride electrolyte.\textsuperscript{1,42} Such findings support the proposed mechanism inhibition of BTA, where the inhibitive film formation, leading to enhanced passivity in chloride electrolyte, requires a certain degree of widespread anodic dissolution when the surface is first immersed.

The high-resolution observations (Figure 9) reveal that a film with uniform and compact morphology existed, comprising fine individual crystals and covering the entire surface of AMlite after 24 h exposure to the NaCl in the case of 15 g/L BTA. This surface film was largely insoluble, and unaffected by the chlorides present, since it was robust and persistent under long-term immersion conditions. The XRD (Figure 11) and XPS (Table II) analysis provides evidence of a highly crystalline Mg(OH)\textsubscript{2} as the dominant phase in this film, most prevalent in the case of 15 g/L BTA, and serving to explain the remarkable corrosion resistance upon AMlite.\textsuperscript{43}
or alkalinized in situ) NaCl solution (Figures 3–7), such that slightly elevated pH is a “catalyst of crystalline Mg(OH)2” films.

Initially, when Mg alloys are exposed to aqueous solution, such as NaCl, the substrate reacts with water and generates an appreciable amount of hydrogen gas bubbles and Mg2+ cations, as indicated by the micrographs in Figure 8. Given the Ksp of Mg(OH)2 at 25°C is 1.8 × 10−11, and [OH−] is 10−4 at pH 10.0, the greatest concentration of Mg2+ cations in solution counts for 1.5 × 10−7 in such conditions. Additional Mg2+ ions generated as a result of Mg dissolution combine with OH− cations and precipitate upon to the substrate surface of Mg alloy as a film comprising mainly Mg(OH)2. Such a surface film is expected to offer a certain protective function against further corrosion but its protective degree relies upon its stability which is determined by its chemical and physical properties (the latter referring to homogeneity, porosity, or crystallinity, etc.). The poor corrosion performance of AMlite in neutral and acidic NaCl is a reflection of the difficulty in formation of a protective Mg(OH)2 precipitated film, regardless of the presence of BTA. However, the excess of OH− creates a favorable set of conditions for quality film formation. This experimental finding can be extended to the case that surface pH elevation is be able to allow BTA to “repair” dissolution / damage sites (as damage sites are locally alkaline) by means of in situ formation of a crystalline Mg(OH)2 film. This was demonstrated in the case of AMlite in neutral 0.1 M NaCl (pH 7.0), subject to anodic potentiostatic polarization, which triggers BTA to function as corrosion inhibitor, though in a different mode as that for Cu, Zn, Fe or Al alloys.12,13 Clearly this revelation will be a beneficial avenue for future work and studies to exploit this phenomenon. For example, one may consider the in situ passivation of Mg may be useful for regulating Mg dissolution in the case of Mg anodes (including Mg in primary batteries) controlling parasitic of Mg may be useful for regulating Mg dissolution in the case of Mg anodes (including Mg in primary batteries) controlling parasitic discharge (often given then moniker of “self corrosion”).

From the empirical work herein, it is conclusive that the highest corrosion resistance imparted to AMlite was attributed to the physical existence of a surface film containing Mg(OH)2 nano-crystals, which was stable in 0.1 M NaCl. The growth of such an Mg(OH)2 film including crystal size, shape and spatial arrangement, architecture, is intimately associated with the presence of BTA+ anions; however no real optimization was presented herein. Further, no alteration of the BTA was pursued, however it is conceivable that several organic substances have ample functionality to facilitate nucleation-inducing substances with customized molecular structure or composition,15,66 to offer perhaps even higher protective (or alternatively, protection at lower inhibitor concentration) in terms of corrosion.15,47–50

Conclusions

The present study has revealed that BTA has the ability to impart significant corrosion resistance to Mg-alloy AMlite in weakly alkaline NaCl, and as a result of surface alkalization due to AMlite dissolution at neutral pH. The mechanism for this protection differs radically from that of BTA in the cases of Cu, Fe, Zn or Cu-containing Al alloys. It is posited that BTA molecules are ionized to BTA+ anions in aqueous conditions where an excess of OH− anions exists (i.e. bulk or locally alkaline) and these molecules interact with the dissolving Mg surface.

The adsorption of BTA− anions have shown to provide favorable nucleation sites to initiate the precipitation of crystalline Mg(OH)2. The crystals were unlike those routinely observed as part of the Mg surface film, instead they were nanostructured and dense assembly of highly crystalline Mg(OH)2, the structure and consequent properties of which varied with the BTA concentration. The developed Mg(OH)2 films imparted a previously unseen corrosion resistance to the AMlite substrate, including a window of passivity which was remarkable. As the formation of the crystalline Mg(OH)2 coating was a function of concentration of BTA anions, so was the subsequent protectiveness. With respect to mechanism, in acidic or neutral conditions, BTA remained in the form of BITA or BTA, which was unable to form BITA-Mg compounds and subsequently form an insoluble BTA catalyzed Mg(OH)2 coating. However, dissolution of Mg and local alkalization were able to induce passivity. This latter concept is particularly important, since it highlights that BTA may play a key role in the electrolytes in which Mg alloys are utilized as anode materials, where the passivation of the anode surface can be controlled.

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