Magnesium alloys are of great interest because they can be used to manufacture lightweight automotive and aircraft structural materials that reduce vehicle weight and improve fuel efficiency.\textsuperscript{1–3} However, the poor corrosion resistance of Mg is a major challenge.\textsuperscript{4–6} A key contributor to the poor corrosion resistance of Mg is the inability to establish and/or maintain protective surfaces films. Surface films formed on Mg under ambient air and water conditions typically consist of mixtures of Mg(OH)$_2$ and MgO, with small amounts of MgCO$_3$, often also reported.\textsuperscript{7–11} They provide adequate protection under some circumstances, but are particularly vulnerable to disruption by salt species.

The ambient corrosion of Mg differs from many corrosion-resistant structural alloy classes in that the protective surface films can become quite thick, on the order of tens to hundreds of nanometers, rather than the few nanometers typically encountered for protective films on stainless steels, for example. As such, corrosion resistance is influenced not only by classical thin film electrochemical passivity considerations, but also thermodynamic and kinetic considerations typically encountered in thick-film (> 0.5 micron range), high-temperature alloy oxidation phenomena.

Isotopic tracer studies have been widely applied to studies of the high-temperature oxidation of alloys (Al, Fe, Ni, and Zr base; SiC), with significant new insights gained regarding the growth mechanism of the oxide films.\textsuperscript{12–30} Such insights have proven particularly useful for understanding the influence of various alloying additions on film growth, and provide a basis for improved alloy design. For example, tracer studies of Al$_2$O$_3$-forming alloys with and without rare earth element dopants revealed beneficial effects related to more protective, oxygen inward growth mechanisms [e.g. Refs. 13, and 19]. However, a search of the literature did not reveal the application of similar experimental strategies and approaches to the corrosion of Mg alloys. Therefore, the goal of the present work was to use isotopic tracers to study the film growth mechanism on Mg alloys in water. An understanding of the thin-film growth mechanisms would provide an improved fundamental basis to designing more corrosion-resistant Mg alloys, as well as potentially prove useful for other applications of Mg alloys such as hydrogen storage or hydrogen production, where transport of O and H species through films on Mg may be important. As the films that form on Mg involve both oxide and hydroxide phases, $^{18}$O and D ($^2$H) species were used as tracers of water corrosion processes to provide insight into the film growth mechanism.

Experimental

Three materials were selected for study: AZ31B, Elektron 717 (ZE10A type alloy, referred to in this paper as E717 for convenience), and ultrahigh purity (UHP) Mg (Table I). The AZ31B and E717 alloys were selected for study because they were mostly single-phase Mg and represent two major classes of Mg alloys: Mg-Al-Zn type for AZ31B and rare earth (Nd) + Zr + Zn type for E717, with the UHP Mg used as a pure Mg control. Test samples ∼9 mm in diameter and ∼1 to 1.5 mm thick were obtained from all three materials by electric discharge machining, wet ground with SiC paper up to P1200 grit finish, coated with acetone and deionized water, and dried with an air stream. Samples were then stored in a desiccator for at least 24 h prior to the tracer studies.

A companion study\textsuperscript{31} determined film microstructures formed on the UHP Mg, AZ31B, and E717 after 4, 24, and 48 h exposure at room temperature in H$_2$O, and was used to guide selection of tracer water exposure conditions in the present work. The tracer studies were conducted using either H,$^{18}$O ($^{18}$O water for short) and/or D,$^{16}$O (D$_2$O for short) in order to study both oxygen and hydrogen species uptake (for simplicity H refers to $^1$H in this presentation). The $^{18}$O water was obtained as ∼98 atomic percent (at%) $^{18}$O water from Cambridge Isotope Laboratories, Andover, MA USA. Three tracer species sets are involved: $^{18}$O and $^{18}$O$_2$ and H and D.

The Mg disks were fully immersed in 5 mL of tracer water at room temperature for the experiments. The tracer exposures were performed by placing the test sample flat on the bottom of a small, plastic beaker half-filled with tracer water and open to ambient air. A cover was placed on top of the beaker (no evaporative loss of tracer water was observed for the exposures). The following experiments

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were performed: 4 h exposure in $^{18}$O water; 4 h exposure in $D_2O$; 4 h exposure in $^{18}$O water + 20 h exposure in $D_2O$; 4 h exposure in $D_2O$ + 20 h exposure in $^{18}$O water. For the 4 h + 20 h sequential exposures the switch in tracer waters was accomplished by moving the test sample immediately from one beaker to another. The sample was removed from the first solution using a plastic forceps, slightly tilted to remove the excess solution from its surfaces, and directly immersed in the second solution without any mechanical drying. This process took no more than 5 seconds, and no physical changes to the samples were observed.

Characterization of the samples from the tracer water exposures, along with as-polished controls, was performed on the top exposed disk surfaces by secondary ion mass spectroscopy (SIMS) using a CAMECA 7f ion microprobe. The samples were initially gold coated prior to SIMS analysis. Due to the thickness of the as-polished films, it was necessary to repolish the original 1200 grit finish to obtain good baseline control data from these samples. This was done to a near-mirror finish using 1 micron diamond paste, sample washed with distilled water and ethanol, and then gold coated for SIMS study. (All of the $^{18}$O water and $D_2O$ water exposed samples were immersed in the tracer water with the 1200 grit polished surface.)

The pressure in the SIMS analytical chamber was $5 \times \times 10^{-9}$ torr. A $\sim$ 45 to 50 nA primary beam of Cs$^+$ was accelerated at 10 kV and rastered over an area of 250 $\times$ 250 $\mu$m using a 100 $\mu$m aperture in the primary column. The secondary column and electrostatic analyzer (ESA) were set to receive ions with 9000 V. A sample voltage offset of 200 V was used during O isotope analysis to eliminate molecular ion interferences, whereas a 0 V offset was used during H isotope analyzes. A 400 $\mu$m field aperture and 150 $\mu$m contrast aperture were used to select ions from the center of the rastered area, with ions effectively obtained primarily from a $\sim$ 75 micron diameter region. Ions were detected at 1800 SEM 1217 electron multiplier coupled with an ion-counting system using an overall deadtime of 37 ns. Two isotopes of oxygen, $^{16}$O and $^{18}$O, and hydrogen, H and D were detected by switching the magnetic field.

In order to optimize detection, oxygen and hydrogen isotopes were analyzed during different analytical sessions, i.e. different sputtering locations on the same sample. Profilometry was used to assess sputter crater depth post analysis. The sputtering rate obtained from the profilometry was estimated to be on the order of $0.8 \times 1.2$ nm/s for all of the samples studied, assuming a linear sputtering rate from film into the underlying Mg metal. However, all data in the present work are presented in terms of sputtering time rather than estimated depth, as the sputtering rates may have varied between film and metal.

It should be noted that a small portion of the SIMS dataset of the present work was presented in reference 31 as a part of the companion film characterization study of the UHP Mg, AZ31B, and E717 in 4, 24, and 48 h water exposures. The data presented was limited to the total H signal ($H + D$) only (no distinction of isotopes) for the 4 h $^{18}$O water + 20 h $D_2O$ exposure sequence and the as-polished controls. No separate data for H, D, $^{18}$O, $^{16}$O, or total O were reported in that work.

Detailed characterization of selected films formed in the tracer waters was also performed using scanning transmission electron microscopy (STEM) analysis. The specimens for STEM analysis were prepared via the focused ion beam (FIB) milling technique by the in-situ lift-out method using a Hitachi NB5000 FIB-SEM. A carbon and tungsten overlayer was deposited to protect the exposed top surface of the film during ion milling. Further details of the sample preparation and analysis methodology are provided in reference 31.

### Results

**Film microstructures.**—Cross-section bright field (BF) STEM images for the UHP Mg, AZ31B, and E717 samples after 4 h immersion in $^{18}$O water $+ 20$ h immersion in $D_2O$ are presented in Fig. 1. The films were primarily MgO-based, and consistent with the 4 h and 24 h H$_2O$ formed films and thickness trends for these materials reported in reference 31 (film thickness order: UHP Mg $\geq$ E717 $> AZ31B$). In addition to MgO, the film near surface regions formed in 4 h and 24 h water contained small amounts of Mg(OH)$_2$ and MgCO$_3$, based on X-ray photoelectron spectroscopy (XPS). The films are considered “partially hydrated” as hydrogen was detected throughout the MgO-base films by SIMS, with decreasing intensity moving from the film surface to the underlying alloy (the form of this hydrogen, i.e. intermixed Mg+Mg(OH)$_2$ or H dissolved in MgO is not known). The film formed on UHP Mg (Fig. 1a) varied from $\sim$ 40 nm to 1 micron, the film on AZ31B was relatively uniform in thickness, on the order of $\sim 100$ nm (Fig. 1b), and the film on E717 was typically on the order of $\sim 150$–350 nm (Fig. 1c). The MgO-based film formed on AZ31B in water contained Al distributed throughout the film thickness. The film formed on E717, as well as the underlying alloy, also contained nanoscale Zn$_2$Zr$_3$ precipitates (small bright particles in Fig. 1d). The enrichment of Zn at the film-metal interface was also observed for both the E717 and AZ31B. The thinner films formed on AZ31B and E717 in ambient water from 4 to 24 h, relative to UHP Mg, are attributed to effects of segregation of Al and Zn (AZ31B) and Zr and Zn (E717) to the films and film-metal interface regions (details in reference 31).

The film thickness variations observed in the STEM images, as well as the undulating (non-planar) nature of the water-film and film-alloy interfaces (Fig. 1) complicates interpretation of data obtained in SIMS/isotopic tracer depth profile studies. However, much of this non-uniformity is averaged out as the SIMS data were obtained over a relatively large surface area, primarily from a $\sim$ 75 micron diameter area of a rastered 250 $\times$ 250 micron region. Typically, only one SIMS dataset per sample was obtained. As shown in Appendix for duplicate E717 samples exposed for 4 h in $D_2O$ or 4 h in $^{18}$O water, the H and O species data was consistent, indicating the experimental approach adopted yielded reasonably repeatable results (experimentally checked only for these 4 h E717 samples). The non-uniform nature of film formation on Mg does result in diffuse transitions in the SIMS sputtering profile inward from the film into the underlying metal. The film-metal interface transition is not sharp in the data presented in the next section.

**SIMS isotopic profile studies.**—Figure 2 shows the SIMS data for control 1 $\mu$m diamond polished surfaces for UHP Mg, AZ31B, and E717. Very little $^{18}$O and D were detected in these surfaces (Figs. 2a, 2b), with similar profiles on sputtering for all 3 materials, consistent with the low natural abundance of these isotopes in air and water vapor. The $^{18}$O intensity levels reduced on sputtering to less than 10.

### Table 1. Alloy grain size and chemical composition of UHP Mg, AZ31B, and E717 determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The E717 contains $<0.5$ wt% Nd, the exact level of Nd is considered proprietary.

| Alloy     | Grain Size (microns) | Mg   | Al  | Zn  | Zr  | Mn  | Nd  | Fe  | Cu  | Ni  |
|-----------|----------------------|------|-----|-----|-----|-----|-----|-----|-----|-----|
| UHP Mg    | $>1$ nm              | 99.98 | 0.01 | 0.01 | $<0.01$ | $<0.01$ | $<0.01$ | $0.002$ | $<0.001$ | $<0.001$ |
| AZ31B     | 10 $\pm$ 5          | 95.64 | 3.03 | 1.06 | 0.001 | 0.25 | $<0.001$ | 0.006 | 0.001 | 0.001 |
| E717      | 14 $\pm$ 10         | Bal. | $<0.001$ | 1.18 | 0.25 | 0.007 | $<0.05$ | 0.004 | $<0.001$ | 0.001 |

*0.01 wt% Pb detected

*0.001 wt% Nd detected

| Composition weight% (wt%) |
|---------------------------|
| Mg | Al | Zn | Zr | Mn | Nd | Fe | Cu | Ni |
|----|----|----|----|----|----|----|----|----|
| UHP Mg | >1 nm | 99.98 | 0.01 | 0.01 | $<0.01$ | $<0.01$ | $<0.01$ | $0.002$ | $<0.001$ | $<0.001$ |
| AZ31B | 10 $\pm$ 5 | 95.64 | 3.03 | 1.06 | 0.001 | 0.25 | $<0.001$ | 0.006 | 0.001 | 0.001 |
| E717 | 14 $\pm$ 10 | Bal. | $<0.001$ | 1.18 | 0.25 | 0.007 | $<0.05$ | 0.004 | $<0.001$ | 0.001 |
counts per second (c/s) background values, and the D levels to a few c/s (Fig. 2a, 2b).

The $^{16}$O signals in the as-polished surfaces decreased to the $10^3$ to $10^5$ c/s range on sputtering (Fig. 2c). The relatively high residual signal of $^{16}$O likely reflects an inherent small impurity level of oxygen dissolved in the Mg (primarily as $^{16}$O), as well as possible contributions from preferred instrument fractionation of the lighter $^{16}$O vs $^{18}$O. (The reason for the higher residual level of $^{16}$O signal in the as-polished E717 sample relative to AZ31B and UHP Mg in Fig. 2c is not known. It is speculated to possibly be related to a local inclusion or defect in the sampling region, as such differences are not observed in subsequent water-formed films for the three materials and E717 in particular, e.g. Fig. 3c.) The H profiles also exhibited high residual baseline signal intensities, with sputtering into the underlying metal reducing to the $10^3$ to $10^5$ c/s range (Fig. 2d). The relatively high intensity of the H signal is attributed primarily to the background level of H in the SIMS vacuum chamber, with an inherent small impurity level dissolved hydrogen in the Mg (primarily as H) and instrument fractionation of the lighter H vs D also possible contributing factors. Figures 3a, 3c, 3e show SIMS data for UHP Mg, AZ31B, and E717 exposed for 4 h in $^{18}$O water. The sputter profiles of $^{18}$O and $^{16}$O (Figs. 3a, 3c) for UHP Mg, AZ31B, and E717 are qualitatively similar, with moderately deeper penetration of O species (thicker films) for UHP Mg and E717 than for AZ31B, consistent with previously observed film thickness trends for these materials in ambient water exposures. The levels of $^{18}$O and $^{16}$O decreased to similar baseline levels of $<10$ c/s for $^{18}$O and $<10^3$ c/s for $^{16}$O after ~1000 s sputtering for AZ31B and ~2000 s sputtering for UHP Mg and E717 (Figs. 3a, 3c). The fraction of $^{16}$O/$^{18}$O intensity (Fig. 3e) reached peak values of ~0.3 to 0.4 for the UHP Mg, AZ31B, and E717 despite the use of nominally 98% pure $^{18}$O water.

The relatively high concentration of $^{18}$O in the $^{18}$O water-exposed film surfaces is attributed to several factors, including $^{16}$O from the native ambient air-formed films on the samples prior to exposure to the $^{18}$O water (Fig. 2c), the nominal ~2% $^{16}$O impurity in the $^{18}$O water, dissolution of $^{18}$O from ambient air into the $^{18}$O water, possibly participating to some degree in the Mg corrosion reaction, and instrument fractionation effects favoring $^{16}$O over $^{18}$O detection. That said, it is important to note that peak $^{16}$O intensity levels reached 5–7 $\times$ 10$^2$ c/s in the 4 h $^{18}$O water-exposed films (Fig. 3a), compared to baseline residual $^{18}$O levels of $<10$ c/s (Figs. 2a and 3a). This 4 order of magnitude increase shows that profiling of the $^{18}$O derived from exposure to the $^{18}$O water can readily be used to gain insights into the oxygen uptake and growth mechanism of these films.

Figures 3b, 3d, 3f shows SIMS data for the UHP Mg, AZ31B, and E717 after 4 h exposure in D$_2$O. A relatively small fraction of D/(D + H) intensity signal was also detected these films (Fig. 3f), with a peak fraction value of ~0.2 observed for E717 and only ~0.05 range for UHP Mg and AZ31B. This low ratio is attributed to the high background level of H in the SIMS vacuum chamber, as well as H from the native ambient air-formed films on the samples prior to exposure to the D$_2$O water (Fig. 2d), and instrument fractionation effects favoring H over D detection. As with $^{18}$O, the peak detected D levels reached ~10$^3$ to 10$^4$ c/s (Fig. 3b), compared to baseline levels on the order of a few c/s detected in as-polished surfaces (Fig. 2b). Thus, profiling of the D derived from exposure to the D$_2$O water can also readily be used to gain insights into the hydrogen uptake and growth mechanism of the films. However, unlike the sputter profiles for $^{18}$O in 4 h $^{18}$O water exposure (Fig. 3a), which were similar among the UHP Mg, AZ31B, and E717, the D profiles for 4 h exposure in D$_2$O water are quite different (Fig. 3b). Specifically, the extent and depth of the D profiles in E717 are much greater than in AZ31B and UHP Mg, and the D profile curve is much flatter (and higher intensity) for E717 over the sputtering range examined.

As noted in the experimental section, it was necessary to obtain the $^{18}$O, $^{16}$O and D, H data from different sputtering runs/locations on the samples to optimize $^{18}$O and D detection, respectively, which complicates direct comparison of H and O profiles. However, the SIMS data was obtained over a 75 micron diameter region, which is believed sufficient to average out most, if not all, film thickness variation effects. With that caveat, based on the $^{16}$O and $^{18}$O profiles (from the 4 h $^{18}$O water exposed material, Figs. 3a, 3c and the companion $^{16}$O and $^{18}$O data taken for the 4 h D$_2$O exposed material, Fig. 4a), underlying metal in the 4 h water exposed samples is fully reached in E717 by ~2000 s of sputtering, whereas after 8000 s of sputtering the D fraction in E717 is still 0.1 (Fig. 3f) and the detected intensity levels of D are still on the order of 10$^3$ c/s (Fig. 3b). This indicates extensive penetration of D through the film and into the underlying metal in E717. Similar above background levels of H were also observed for E717 after 8000 s sputtering, Fig. 3d. In contrast, the D signal intensities in UHP Mg and AZ31B after 4 h exposure in D$_2$O reduced to near baseline values of 1–5 $\times$ 10$^2$ c/s after ~2000 s of sputtering for UHP Mg and ~1000 s for AZ31B (Fig. 3b), the sputtering depths at which the $^{16}$O and $^{18}$O profiles also reduce to baseline (Figs. 3a, 3c). This indicates that the underlying metal has been fully reached, and far less (if any) D penetration beyond the film into the underlying metal occurred for UHP Mg and AZ31B after 4 h water exposures, compared to E717.

Two-stage tracer data is shown in Figs. 5a, 5c, 5e for 4 h D$_2$O followed by 20 h $^{18}$O water, and Figs. 5b, 5d, 5f for 4 h $^{18}$O water followed by 20 h D$_2$O. The $^{18}$O was used as a tracer for the 4 h D$_2$O + 20 h $^{18}$O water data to follow oxygen uptake and incorporation into

Figure 1. BF STEM images of the film cross-sections for UHP Mg (a), AZ31B (b), and E717 (c) after 4 h in $^{18}$O water + 20 h in D$_2$O. The dotted red line marks the metal-film interface. Fine precipitates (small bright particles marked by arrows) were evident in the E717 film and underlying alloy, high angle annular dark field image (d).
Figure 2. SIMS data (counts per second vs sputtering time) for as-polished surfaces on UHP Mg, AZ31B, and E717. a) Intensity $^{18}$O signal; b) Intensity D signal; c) Intensity $^{16}$O signal; d) Intensity H signal. Zero sputtering time corresponds to the sample surface.

the film first formed by 4 h in D$_2$O, which was initially composed almost entirely of $^{16}$O (Fig. 4a). In the same manner, the 4 h $^{18}$O water + 20 h D$_2$O is used to follow the film growth mechanism with the D used as a tracer to follow hydrogen uptake and incorporation into the film first formed by 4 h in $^{18}$O water, which was initially composed almost entirely of H (Fig. 4b).

The $^{18}$O and $^{16}$O profiles after exposure in 4 h D$_2$O + 20 h $^{18}$O (Figs. 5a, 5c) decreased to baseline values after $\sim$3000–3500 s of sputtering for AZ31B and UHP Mg, and $\sim$4000 s for E717. The fraction of $^{18}$O ($^{16}$O + $^{18}$O) intensity (Fig. 5e) plots vs. sputtering depth shows differences among the three materials. The UHP Mg $^{18}$O fraction profile starts at $\sim$0.4, decreases to $\sim$0.32 after $\sim$1000 s of sputtering, and then increases to $\sim$0.37 at $\sim$2000 s of sputtering prior to leveling off at baseline levels at $\sim$3500 s. The AZ31B $^{18}$O fraction shows a sharp initial decrease from $\sim$0.3 to $\sim$0.23 over the first $\sim$750 s of sputtering, followed by a more gradual rate of decrease out to $\sim$2000 s of sputtering, and leveling off at baseline levels at $\sim$3500 s. In contrast, the E717 shows a relatively flat $^{18}$O fraction for the first $\sim$3000 s of sputtering, although with a slight increase and decrease between $\sim$1000 and $\sim$2000 s of sputtering, followed by a decrease to baseline values at $\sim$4000 s.

Unlike the $^{18}$O data from the 4 h D$_2$O + 20 h $^{18}$O exposures (Figs. 5a, 5c, 5e), the D and H profiles after exposure in 4 h $^{18}$O + 20 h D$_2$O (Figs. 5b, 5d, 5f) do not decrease to the baseline levels of a few c/s observed in as-polished materials (Fig. 2b). Rather, the D signals remain above $10^2$ c/s after 5000 s of sputtering for AZ31B and 15000 s of sputtering for E717 (Fig. 5b). The D levels for UHP Mg do approach baseline levels of $<10$ c/s, but only after $\sim$7000–8000 s of sputtering, far deeper than the $\sim$3500 s needed to reach $^{18}$O baseline levels in the 4 h D$_2$O exposure UHP Mg data (Fig. 5a). This observation again indicates preferential penetration of D beyond the film into the underlying metal, particularly for the E717 as is observed after 4 h exposure in D$_2$O alone (Fig. 3b). Similar to the 4 h D$_2$O exposure data (Fig. 3c), the peak D/(D + H) intensity signal fraction (Fig. 5f) reaches the highest value for E717, $\sim$0.23, but only $\sim$0.05 range for UHP Mg and AZ31B. The D fraction profiles in the film regions show a qualitatively similar shape to the corresponding $^{18}$O fraction profiles for UHP Mg and AZ31B, but not for E717 (Figs. 5e, 5f). The UHP Mg D fraction profile (Fig. 5f) shows an initial decrease followed by a decrease to $\sim$2500 s of sputtering and then another decrease and leveling with continued sputtering. The AZ31B showed a sharp, continuous decrease to $\sim$2500 s of sputtering, followed by leveling.
Figure 3. SIMS data (counts per second vs sputtering time) for 4 h $^{18}$O water (a, c, e) and 4 h $D_2$O (b, d, f) exposed UHP Mg, AZ31B, and E717. Intensity $^{18}$O signal; b) Intensity D signal; c) Intensity $^{16}$O signal; d) Intensity H signal; e) Fraction $^{18}$O/($^{18}$O+$^{16}$O), f) Fraction D/(D+H). Zero sputtering time corresponds to the film surface. F-M = film-metal interface.

In contrast, the D fraction for E717 started at 0.1, and then increases with sputtering depth to $\sim$0.23 at $\sim$4500 s of sputtering, followed by a decrease to $\sim$0.05 just past 10,000 s of sputtering.

Master plots of $^{18}$O and D fraction data for all exposure conditions for each material are shown in Figures 6–8. The $^{18}$O fraction values in 4 h $^{18}$O water + 20 h $D_2$O (Figs. 6a, 7a, 8a) reaches 0.15 to 0.4 range (highest for UHP Mg, lowest for AZ31B), which is comparable to the peak $^{18}$O fractions in the 4 h $D_2$O + 20 h $^{18}$O water (Fig. 5e). However, background $^{18}$O fraction values are reached after $\sim$1000–1500 s of sputtering for the 4 h $^{18}$O + 20 h $D_2$O data (Figs. 6a, 7a, 8a) vs.
Discussion

Figure 9 shows schematic ideal theoretical tracer fraction profiles from references 13, 17, 19, and 33 devoted to two-stage, sequential tracer studies of $^{18}$O incorporation during high-temperature oxidation of alumina-forming alloys. The plots assume initial formation of the oxide scale in $^{16}$O gas, followed by introduction of $^{18}$O gas. The $^{18}$O fraction from 0 to 1 is plotted vs. the depth from the gas-oxide interface inward to the oxide-metal interface, at which point the profile stops, i.e. the profiles do not include diffusion into the underlying metal because oxygen has little solubility in the alumina-forming Fe- and Ni-base alloys this was originally developed for. These schematics also assume that the $^{18}$O fraction reaches a value of 1, and that approximately 50% of the total oxide scale thickness is formed in the initial exposure step in $^{16}$O gas, and 50% of the oxide thickness is formed during the second $^{18}$O step.

This approach should also be qualitatively applicable to tracer data for both $^{16}$O and $^{18}$O species in the water-formed films on Mg of the present work. However, several differences from the ideal limiting cases should be noted for Mg in water. First, the peak $^{18}$O fraction in the $^{18}$O water exposures of the present work were in the range of only $\sim$0.15 to 0.4, with peak D fractions even lower at $\sim$0.05 to 0.2. As discussed in the results section, this is likely due to $^{16}$O and H species present in the initial air-formed film on the Mg, with additional contributions from the nominal $\sim$2% $^{18}$O impurity in the $^{16}$O water, dissolution of $^{18}$O from ambient air into the $^{16}$O water possibly participating to some degree in the Mg corrosion reaction, and instrument fractionation effects favoring the lighter $^{16}$O and H over $^{18}$O and D detection. In the case of hydrogen, the high background level of H in the SIMS vacuum chamber also likely contributed to the low peak D fractions values observed. However, as also previously noted, the signal intensities for $^{18}$O and D species in films formed in the tracer waters were over 10^4 c/s higher than the baseline values detected in as-polished surfaces, which is considered more than sufficient to act as tracers.

The nonuniform and undulating nature of water-formed films on Mg (Fig. 1) also pose some complications for analysis. The present analysis assumes little to no oxygen diffusion into the underlying metal for Mg in water. An assessment of relative film thickness contributions from the 4 h step 1 exposures to the 20 h step 2 exposures can be obtained by comparing the $^{18}$O fraction plots for 4 h $^{18}$O water exposure to 4 h $^{16}$O water exposures shown in Figs. 6a, 7a, and 8a. For the UHP Mg base, near zero $^{18}$O fraction are reached after sputtering for $\sim$2000 s in 4 h $^{18}$O water and $\sim$4000 s in 4 h $^{16}$O + 20 h $^{16}$O water exposure in Fig. 5f. For UHP Mg, baseline near zero $^{18}$O fraction are reached after sputtering for $\sim$2000 s in 4 h $^{18}$O water and $\sim$4000 s in 4 h $^{16}$O + 20 h $^{16}$O water. Similarly, for AZ31B the values are $\sim$1000 s vs. $\sim$3500 s and for Et717, $\sim$1800–2000 s vs $\sim$4000–4500 s. Thus, $\sim$25–50% of effective total film thickness in the sputtering profiles can be attributed to the step 1 tracer exposure, which is reasonably close to the 50% assumed in the ideal schematics of Fig. 9.

In the case of the D fraction data, the situation is more complex as the data obtained indicate extensive penetration of D/H into the underlying metal, particularly for the Et717 alloy, which is not assumed to occur in the ideal schematic tracer profiles of Fig. 9. An estimate of the UHP Mg, AZ31B, and Et717 film-metal interface location for the 4 h $^{18}$O water + 20 h $^{16}$O water exposures is marked in Fig. 5f. Only the portion of the D fraction curve within the film itself should be used for comparison with the ideal schematic tracer profiles of Fig. 9.

With these points in mind, relative to the schematic theoretical tracer fraction profiles shown in Fig. 9, Fig. 5e which shows the $^{18}$O fraction for exposure of 4 h $^{16}$O + 20 h $^{18}$O water, and Fig. 5f which shows the D fraction for exposure of 4 h $^{18}$O water + 20 h $^{16}$O water can be used to gain insight into the film growth mechanism by oxygen and hydrogen, respectively. This is because the detection of $^{18}$O and D in the film can be attributed unambiguously to the 2nd, 20 h exposure step with $^{18}$O water and $^{16}$O water, respectively, given enrichment intensity levels from $<10$ c/s background for $^{18}$O and D without tracer water exposure to $10^2$–$10^4$ c/s range when exposed to the tracer waters (Figs. 2, 3).
Figure 5. SIMS data (counts per second vs sputtering time) for 4 h D$_2$O + 20 h $^{18}$O water (a, c, e) and 4 h $^{18}$O water + 20 h D$_2$O (b, d, f) exposed UHP Mg, AZ31B, and E717. a) Intensity $^{18}$O signal; b) Intensity D signal; c) Intensity $^{16}$O signal; d) Intensity H signal; e) Fraction $^{18}$O/(16O+18O); f) Fraction D/(D+H). Zero sputtering time corresponds to the film surface. F-M = film-metal interface.
Figure 6. Fraction $^{18}\text{O}/(^{18}\text{O}+^{16}\text{O})$ (a) and Fraction $D/(D+H)$ (b) master plots for UHP Mg. Conditions include: as-polished (AP, red), 4 h $^2\text{H}_2\text{O}$ (purple), 4 h $^{18}\text{O}$ water (orange), 4 h $^2\text{H}_2\text{O} + 20$ h $^{18}\text{O}$ water (black), and 4 h $^{18}\text{O}$ water + 20 h $^2\text{H}_2\text{O}$. Zero sputtering time corresponds to the film surface.

Figure 7. Fraction $^{18}\text{O}/(^{18}\text{O}+^{16}\text{O})$ (a) and Fraction $D/(D+H)$ (b) master plots for AZ31B. Conditions include: as-polished (AP, red), 4 h $^2\text{H}_2\text{O}$ (purple), 4 h $^{18}\text{O}$ water (orange), 4 h $^2\text{H}_2\text{O} + 20$ h $^{18}\text{O}$ water (black), and 4 h $^{18}\text{O}$ water + 20 h $^2\text{H}_2\text{O}$. Zero sputtering time corresponds to the film surface.

The film that formed on UHP Mg (Fig. 5e) shows a “dip” in the $^{18}\text{O}$ fraction profile (decrease, increase, and decrease with sputtering time) that appears most consistent with the schematic theoretical profile shown in Fig. 9e for mixed film growth involving oxygen inward and metal outward transport along different paths. (Fig. 9f for mixed growth along similar transport paths is also a possible fit for UHP Mg; however peak concentrations of $^{18}\text{O}$ fraction were not observed in the middle of the UHP Mg film, Fig. 5e, as is characteristic of Fig. 9f. Further, the decrease of $^{18}\text{O}$ fraction in the UHP Mg film data after the initial decrease/increase/dip is likely representative of the transition from film to alloy, and not an absence of $^{18}\text{O}$ in the inner film as would be the case for mixed film growth along similar paths, Fig. 9f). In contrast, the $^{18}\text{O}$ fraction data for E717 is more difficult to interpret, and could conceivably match both Fig. 9a for outward metal film growth and Fig. 9d for inward oxygen lattice transport. The retention of peak $^{18}\text{O}$ fraction levels at the film surface in the 4 h $^{18}\text{O}$ water + 20 h $^2\text{H}_2\text{O}$ data shown in Fig. 8a, as well as the incorporation of $\text{Zn}_2\text{Zr}_3$ precipitates from the underlying alloy into the growing film (Fig. 1d) indicate that film growth on E717 is more complicated than that for the E717 $^{18}\text{O}$ fraction profile (Fig. 5e). This profile in E717 contains nanoparticles of $\text{Zn}_2\text{Zr}_3$. It is speculated that the extensive and preferential inward short circuit transport of hydrogen in the film formed on E717 is related to preferential transport at the film-oxide/particle interfaces, particularly given the high affinity of Zr for hydrogen, although the Nd rare earth addition may also certainly play a role. Such penetration of hydrogen may have implications not only for Mg corrosion, including stress corrosion cracking and embrittlement mechanisms, but also for Mg in hydrogen storage or production applications.

Compared to the UHP Mg, the tracer data for the AZ31B and E717 alloys indicated more inward oxygen and hydrogen dominated growth rather than mixed growth also involving outward metal transport. This finding suggests that one effect of alloying additions to Mg is to alter the film growth mechanism in water to more inward growing. As discussed in reference 31, $\text{Zn}$ segregation to the film-metal interface outward transport along different paths, although Fig. 9f for mixed growth along similar paths is also a possibility. In addition, the D fraction for AZ31B shows a decrease with sputtering time consistent with the theoretical profile shown in Fig. 9d for inward hydrogen transport. However, the D fraction profile for E717 (Fig. 5f) has a different shape than that for the E717 $^{18}\text{O}$ fraction profile (Fig. 5e). This D fraction profile for E717 shows an increase with sputtering time (film depth) followed by a decrease. The point at which the D fraction begins to decrease occurs after ~4000–5000 s of sputtering, consistent with the estimated location of the film-metal interface, and the subsequent decrease is likely associated with D penetration into the underlying metal. Therefore, the pattern of D fraction profile in E717 (Fig. 5f), where the signal increases with sputter time in the film region best matches Fig. 9c hydrogen inward growth by short-circuit paths. As shown in Fig. 1d, the film formed on E717 contains nanoparticles of $\text{Zn}_2\text{Zr}_3$. It is speculated that the extensive and preferential inward short circuit transport of hydrogen in the film formed on E717 is related to preferential transport at the film-$\text{Zn}_2\text{Zr}_3$ particle interfaces, particularly given the high affinity of Zr for hydrogen, although the Nd rare earth addition may also certainly play a role. Such penetration of hydrogen may have implications not only for Mg corrosion, including stress corrosion cracking and embrittlement mechanisms, but also for Mg in hydrogen storage or production applications.

Compared to the UHP Mg, the tracer data for the AZ31B and E717 alloys indicated more inward oxygen and hydrogen dominated growth rather than mixed growth also involving outward metal transport. This finding suggests that one effect of alloying additions to Mg is to alter the film growth mechanism in water to more inward growing. As discussed in reference 31, $\text{Zn}$ segregation to the film-metal interface
Figure 8. Fraction $^{18}$O/$^{16}$O (a) and Fraction D/(D + H) (b) master plots for E717. Conditions include: as-polished (AP, red), 4 h D$_2$O (purple), 4 h $^{18}$O water (orange), 4 h D$_2$O + 20 h $^{18}$O water (black), and 4 h $^{18}$O water + 20 h D$_2$O. Zero sputtering time corresponds to the film surface.

Conclusions

1) SIMS-isotopic tracer studies can be successfully performed for films formed by Mg alloys exposed to pure water. Interpretation of the data is complicated by the undulating, non-uniform nature of film formation on Mg, but obtaining data over relatively large surface regions (effectively ~75 microns diameter) yielded datasets that were reasonably consistent among the exposure conditions studied (4 h D$_2$O, 4 h $^{18}$O water, 4 h D$_2$O + 20 h $^{18}$O water, 4 h $^{18}$O water + 20 h D$_2$O) for the UHP Mg, AZ31B, and E717 materials.

2) The SIMS-isotopic tracer data indicated that film growth for UHP Mg in water likely involved aspects of both oxygen and hydrogen inward and metal outward transport. In contrast, the data for the Mg-Al-Zn AZ31B and the Mg-Zn-Zr-Nd E717 alloys indicated an inward film growth mechanism for both oxygen and hydrogen. In the case of AZ31B, the data was most consistent with inward lattice transport for oxygen and hydrogen. The film growth mechanism for E717 was more complicated. The data suggested inward lattice transport for oxygen but inward short-circuit transport for hydrogen. It was speculated that the short-circuit transport of hydrogen in E717 may have resulted from nanoscale Zn$_2$Zr$_3$ precipitates in the film and underlying alloy. Similar precipitate-film structures were not observed for AZ31B or UHP Mg.

3) The data suggested extensive hydrogen penetration through the film and into the underlying metal during corrosion of Mg in water. Such hydrogen penetration was particularly extensive for the E717 alloy, and was observed both in 4 h and 20 h + 4 h (24 h total) water exposures. In contrast, the oxygen and hydrogen profiles after 4 h water exposures alone for UHP Mg and AZ31B reduced to near baseline values after similar sputtering times, indicating little to no preferential hydrogen penetration beyond the film. However, the 4 h + 20 h water exposures for UHP Mg and AZ31B suggest penetration of hydrogen beyond the film depth into the underlying alloy, with hydrogen species persisting to greater sputtering depths than oxygen species, although to a lesser extent than in E717. Such phenomena may have significant implications not only for Mg corrosion, including stress corrosion cracking and embrittlement mechanisms, but also for Mg in hydrogen storage or production applications.

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Appendix

A duplicate sample of the E717 alloy was exposed for 4 h in D2O, and a second duplicate was exposed for 4 h in 18O water. SIMS data obtained on these duplicate samples was compared with the original SIMS data for these exposure conditions as a check on the consistency and repeatability of the results. Figures (A1) and (A2) show that similar profiles were obtained for the original and duplicate samples, suggesting that the experimental protocol adopted in this work was sufficient to obtain reasonably repeatable data despite the non-uniform nature of film formation by Mg in water.

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