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Tracer Study of Oxygen and Hydrogen Uptake by Mg Alloys in Air with Water Vapor

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Abstract

*The oxidation of pure Mg, **Mg-3Al-1Zn (AZ31B)**, and **Mg-1Zn-0.25Zr-0.5Nd (ZE10A)** was studied at 85 °C in humid air using sequential exposures with H₂¹⁸O and D₂¹⁶O for water vapor. Incorporation of ¹⁸O in the hydroxide/oxide films indicated that oxygen from water vapor participated in the reaction. Penetration of hydrogen into the underlying metal was observed, particularly for the Zr- and Nd- containing ZE10A. Isotopic tracer profiles suggested a complex mixed inward/outward film growth mechanism.*

Magnesium alloys are of great interest for the manufacture of vehicle parts, biomedical implants, and functional applications involving hydrogen storage, batteries, and fuel cells [1-3]. Understanding the high reactivity and film formation mechanism(s) associated with Mg alloys are a key to improving corrosion resistance, as well as tailoring corrosion reaction/stability

behaviors for biomedical and functional use. Both MgO and Mg(OH)₂ films are formed when Mg alloys are exposed to water [4,5].

The corrosion behavior of Mg alloys in aqueous solutions has been widely studied [e.g. 4, 5]. However, oxidation behavior studies at elevated temperatures have not been as widely pursued for Mg [6-12], but are relevant to applications such as automotive powertrain components, for example. The present authors recently demonstrated the feasibility of performing isotopic tracer studies of the film growth mechanism for the immersion of Mg in water, using sequential exposures in D₂¹⁶O and/or H₂¹⁸O water and secondary ion mass spectroscopy (SIMS) analysis [13]. The goal of the present work was to extend this experimental approach to study the oxidation film growth mechanism of Mg in hot humid air.

Ultrahigh purity Mg (UHP Mg) and two Mg alloys: AZ31B to represent the Mg-Al-Zn alloy class and Elektron® 717 (ZE10A grade, referred to as E717 for brevity), to represent the Mg-Zr-rare earth alloy class, were selected for study (Table 1). The same materials batches and sample preparation methods as described in [13] were used in the present work. Test samples ~9 mm in diameter and ~1 to 1.5mm thick were wet ground to P1200 grit finish, cleaned with acetone and deionized water, and dried with an air stream [13]. Samples were stored in a desiccator for at least 24 h prior to the tracer studies [13].

Table 1. Alloy grain size and chemical composition of UHP Mg, AZ31B, and E717 determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) [from 13, 14]. The E717 contains < 0.5 wt.% Nd, the exact level of Nd is considered proprietary.

Alloy	Grain Size (microns)	Composition weight % (wt.%)								
		Mg	Al	Zn	Zr	Mn	Nd	Fe	Cu	Ni
UHP Mg	> 1 mm	*99.98+	0.001	0.001	<0.001	<0.001	<0.001	0.002	<0.001	<0.001
AZ31B	10±5	95.64	3.03	1.06	0.001	0.25	<0.001	0.006	0.001	0.001
E717	14±10	Bal.	<0.001	1.18	0.25	0.007	<0.5	0.004	<0.001	0.001

*0.01 wt.% Pb detected in one UHP Mg sample (repeat did not show Pb)

Oxidation exposures were done at 85°C in humid air using a sealed stainless steel reaction vessel approach previously developed for geochemical hydration studies [15]. The reaction vessels (~24 cm³) contained an inner Teflon liner to which 2 ml of isotopic tracer water was added, with the

test sample suspended above the water in the vapor phase (humid air) in a Teflon mesh basket. The reaction vessels were then sealed and placed in a covered aluminum block holder inside of a convection oven at 85°C. At this temperature, these vessel and fluid volumes result in a two-phase (liquid/vapor) system with an equilibrium water vapor pressure of 0.58 bar. Duplicate sequential exposure time procedures used in the previous water immersion isotopic tracer study [13] were adopted for the present work. The test samples were exposed at 85°C for 4 h to air with water vapor derived from H₂¹⁸O, and immediately removed and relocated to a second reaction vessel that was then sealed and heated to 85°C for 20 h exposure to air with water vapor derived from D₂¹⁶O (sample relocation time ~1 minute). (For brevity, this exposure protocol will be referred to as “sequential tracer 85°C humid air oxidation” in the remainder of the text). The H₂¹⁸O water was obtained as > 98 atomic percent (at.%) ¹⁸O water from Campro Scientific, Bobinestraat 7-6 3903 KE Veenendaal, The Netherlands [13]. The D₂¹⁶O was obtained as 99.96 at.% isotope purity from Cambridge Isotope Laboratories, Inc., Andover, MA USA.

After exposure, samples were characterized by SIMS profiling, x-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and surface and cross-section scanning and transmission electron microscopy (SEM, TEM). The SIMS data was obtained by sputtering with a 45 to 50 nA primary beam of Cs⁺; a 400 µm field aperture and 150 µm contrast aperture were used to select ions from the center of the rastered area, with ions effectively obtained primarily from a ~75 micron diameter region [13]. In order to optimize detection, oxygen and hydrogen isotopes were analyzed separately, i.e. different sputtering locations on the same sample [13]. The XPS analysis used a monochromated, micro-focusing, Al Kα X-ray source (1486.6 eV) with a ~400 µm X-ray spot size for maximum signal and to obtain an average surface composition over the largest possible area [14]. Depth profiling analyses were conducted with a Thermo Scientific EX06 argon ion gun operated at 1000 eV and rastered over a 2 mm x 4 mm area [14]. STEM specimens of the film and metal/film interface regions were prepared via the focus ion beam (FIB) in-situ lift-out technique [14]. Further details of the SIMS, XPS, and STEM characterization procedures are described in [13] and [14].

Cross-section TEM images of UHP Mg, E717, and AZ31B after the sequential tracer 85°C humid air oxidations are shown in Fig. 1. The film formed on the UHP Mg was the thickest of the 3 materials, with regions ranging from less than 100 nm to areas with nodule-like protrusions

extending several microns into the metal (Fig. 1a). The film formed on E717 was generally in the ~100-400 nm range. The E717 contains nanoscale second phase particles previously identified as Zn_2Zr_3 [13, 14]; these particles (bright phase in Fig 1b) were evident both within the film and the underlying alloy (Fig. 1b, d). The film formed on AZ31B in **sequential tracer 85°C humid air oxidation** (Fig. 1c) was also in the ~100-400nm range, but with layered, nodule-like outer growths overlying a Zn and Al enriched region at the film-metal interface (Fig 1 c, e). The film morphologies observed in **sequential tracer 85°C humid air oxidation** for UHP Mg and E717 were similar to those observed in the previous work [13,14] **for a sequential tracer room-temperature water immersion of 4 h in D_2^{16}O and 20 h in H_2^{18}O for UHP Mg and E717.** However, for AZ31B in the **sequential tracer room-temperature water immersion** [13,14], only a thin (~100 nm) relatively uniform film was observed, in contrast to the outward nodule-like growths observed in **sequential tracer 85°C humid air oxidation** (Fig. 1c).

Analysis by grazing incidence XRD identified substrate Mg metal peaks, with only a single small film peak consistent with the (001) of $\text{Mg}(\text{OH})_2$ also detected. Limited TEM selected area diffraction (SAD) analysis also suggested the films were primarily $\text{Mg}(\text{OH})_2$, but also contained MgO (confirmed by SAD only for E717). XPS was therefore used to better characterize the film structure (Fig. 2). The XPS analysis was based on fitting of the O1s, with $\text{Mg}(\text{OH})_2$ at ~532.4 eV, O that is associated with Ar ion sputter damage of $\text{Mg}(\text{OH})_2$ at ~529.7 eV, and O that is associated with MgO at ~531.2 eV, with further corroboration from the Mg 2p spectra. However, due to fitting complexities resulting from sputter damage of $\text{Mg}(\text{OH})_2$ during profiling, the fitted fractions of $\text{Mg}(\text{OH})_2$ and MgO (Fig 2) should be considered semi-quantitative. For **UHP Mg, E717, and AZ31B in sequential tracer 85°C humid air oxidation**, the outer films were rich in $\text{Mg}(\text{OH})_2$, particularly for UHP Mg, with increasing amounts of MgO detected on sputter profiling through the films formed on E717 (data stopped at ~1100 s sputtering due to charging) and AZ31B (Fig. 2). In contrast, the films formed on these alloys in **sequential tracer room-temperature water immersion** [13,14] were primarily MgO, with a minor amount of $\text{Mg}(\text{OH})_2$ at the outer surface. (It should be noted that the MgO formed in room-temperature water was “partially” hydrated as above background H signal was still detected throughout the MgO-base films by SIMS [13,14]).

Figures 3 a,b show SIMS profile data through the UHP Mg, E717, and AZ31B films after the **sequential tracer 85°C humid air oxidation**. Consistent with the TEM cross-sections and XPS data (Figs 1,2), the oxygen isotope depth profiles for the UHP Mg film extended deeper (thicker) than the films formed on E717 and AZ31B. The ^{18}O and ^{16}O signals decreased to $\sim \leq 10$ counts per second (c/s) and 100-1000 c/s background levels, respectively, after ~ 3000 s of sputtering for E717 and AZ31B, and ~ 6000 - 7000 c/s of sputtering for UHP Mg (background ^{16}O and ^{18}O intensities determined from as-polished surfaces [13]). ^{18}O intensities of $\sim 10,000$ c/s were observed at the film surfaces ($> 1000\times$ above background), which suggests preferential oxidation by oxygen **in the water vapor derived from the H_2^{18}O** , rather than oxygen in the air. Similar behavior consistent with preferential water vapor reaction behavior has been observed in high-temperature humid air oxidation of Fe- and Ni-base alloys [16, 17].

Film surface D intensities for all 3 materials reached $\sim 500,000$ c/s, and leveled out to ~ 2500 - 3000 c/s for E717 and ~ 150 - 300 c/s for UHP Mg and AZ31B (Fig. 3b); whereas background D signal intensity levels in as-polished control surfaces were < 10 c/s [13]. **Significant (above background) D intensities were evident at sputtering depths beyond where the O species had decreased to background levels (Figs 3 a,b).** This indicates penetration of D beyond the $\text{Mg}(\text{OH})_2$ - MgO films and into the underlying metal on **sequential tracer 85°C humid air oxidation**, particularly for the Zr- and Nd- containing E717. Similar D penetration through the film and into underlying metal was also observed in **sequential tracer room-temperature water immersion**, again particularly for E717 [13].

Figures 3 c, d show ^{18}O and D fraction plots for the UHP Mg, E717, and AZ31B films after **sequential tracer 85°C humid air oxidation**, and comparison data [13] from **sequential tracer room-temperature water immersion**. In the **room temperature** water immersion data (**“W” in plots**), the ^{18}O fraction was highest at the outer film surface for UHP Mg, E717, and AZ31B (~ 0.2 - 0.4), with a rapid decrease with sputtering depth, consistent with inward dominated film growth (Fig. 3c) [13]. However, much different shaped profiles were observed in the **sequential tracer 85°C humid air oxidation** (Fig. 3d). The ^{18}O fractions were highest in the inner film region near the film-metal interface for AZ31B (~ 0.05 to 0.1), suggesting a strong component of

outward film growth for the 20 h water vapor derived from D₂¹⁶O step. The ¹⁸O fraction profile for UHP Mg peaked at 0.3 in the middle of the film, suggesting mixed inward/outward growth. Mixed inward/outward film growth was also evident in the ¹⁸O fraction profile data for E717, with peak values of ~0.15-0.2 observed both at the outer film surface and in the inner film region near the film-metal interface (Fig. 3c).

Much higher peak D fractions (~0.5 to 0.6) were observed in 85°C humid air oxidation data than room-temperature water immersion (~0.05 to 0.25) for UHP Mg, E717, and AZ31B (Fig 3d). The sequential tracer 85°C humid air oxidation D fraction profiles were of similar shape for all 3 materials, with a rapid increase to peak values after ~500-1000 s of sputtering for E717 and AZ31B, and ~2000-3000 s for UHP Mg. These humid air profiles are different in shape than those observed in room-temperature water, which monotonically decreased from the surface inward for UHP Mg and AZ31B, but peaked near the film-metal interface for E717 (Fig. 3d), suggesting inward lattice D diffusion in room-temperature water for UHP Mg and AZ31B, and short-circuit inward diffusion for E717 [13].

The sequential tracer 85°C humid air oxidation D fraction profiles are complex to interpret, but suggest a strong component of inward film growth for UHP Mg, E717 and AZ31B; as near-peak D fraction values occur in the outer regions of the films, although not at the film surface (Fig. 3d). This D uptake mechanism is in partial contrast to the sequential tracer 85°C humid air oxidation ¹⁸O fraction data (Fig. 3c), which suggested a strong component of outward growth for AZ31B and mixed inward/outward film growth for UHP Mg and E717. It is also not readily reconciled with morphological features observed in the film cross-section TEM images (Fig. 1). Outward nodule-like film formation was observed for AZ31B (Fig 1c), but local extensive nodular inward penetrations were observed in UHP Mg (Fig 1a), and the incorporation of Zn₂Zr₃ particles into the film formed on E717 (Fig. 1b), both of which indicate a strong component of inward growth behavior. One possible interpretation is the initial formation of MgO by mixed outward/inward growth in 85°C humid air oxidation, followed by extensive inward hydration and further oxidation of the initially-formed MgO to Mg(OH)₂. Determination of how the film phase makeup and morphology initially establishes and then evolves with time will be needed to further delineate the complex Mg film growth mechanism in hot humid air.

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Figure Captions

Fig. 1- Cross-section TEM images and maps after sequential tracer 85°C humid air oxidation (0.58 bar): a) UHP Mg; b, d) E717, and c, e) AZ31B

Fig. 2- Fitted XPS data after sequential tracer 85°C humid air oxidation (0.58 bar). AZ = AZ31B, E7 = E717, Mg = UHP Mg

Fig. 3- SIMS data after sequential tracer 85°C humid air oxidation (0.58 bar): a) ^{18}O and ^{16}O profiles; b) D and H profiles; c) Fraction $^{18}\text{O}/(^{18}\text{O}+^{16}\text{O})$; d) Fraction D/(D+H). Data marked “W” is for sequential tracer room-temperature water immersion data from [13]. AZ = AZ31B, E7 = E717, Mg = UHP Mg

Figure(s)

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