Direct observation of hydrogen in the early stages of oxidation of a magnesium alloy

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Abstract

The early stage oxidation of germanium-doped magnesium alloys was investigated via atom probe tomography. A catalytic reaction cell attached to a local electrode atom probe was used for controlled exposure of electropolished specimens to oxygen gas. Hydrogen was detected in certain samples, thought to be introduced during electropolishing. A preferential interaction/reaction between oxygen and hydrogen was found in samples containing hydrogen-rich regions prior to oxidation. These results suggest that hydrogen plays an important role as a catalyst to oxidation, where the increase in the H evolution rate experienced when oxidising Mg alloys, may be directly related to the presence of H within the material prior to oxidation. Results revealed the ability of this unique experimental set-up to provide new information about surface/sub-surface hydrogen and its effects on magnesium oxidation.

Main Text

The natural abundance of magnesium (Mg) and desirable strength to weight ratios make lightweight Mg alloys appealing candidates for application within the transport industry. However, their wider application as structural components is hindered by poor corrosion resistance [1, 2] and a susceptibility to hydrogen embrittlement [3-5]. Hydrogen (H) is absorbed into engineering alloys on contact with gaseous molecular hydrogen (H₂), or by a parasitic partial reaction that accompanies the hydrogen evolution reaction (HER) during metal corrosion [6]. Atomic H typically either permeates or diffuses through metal lattice interstices and may become trapped at defects such as vacancies, grain boundaries, or dislocations [6, 7]. It may also form hydrides with suitable metals [8].

The diffusible H concentration ($C_{H, Diff}$) represents the resident, mobile H atoms within alloys that can readily diffuse towards regions of tri-axial stress resulting in H-assisted cracking or H embrittlement

[7]. Pundt et al. [9] proposed that metal surfaces have several trap sites, and at these sites the H concentration at the surface/sub-surface might be significantly higher than $C_{H, \text{Diff}}$. High-resolution analytical techniques are required to detect and quantify H atoms within the first few mono-layers of the metal surface, however, experimental verification of surface and sub-surface H is difficult due to the tendency of H to spontaneously exit the metal during oxidation or out-gassing at room temperature.

Atom probe tomography (APT) provides both high resolution and high chemical sensitivity [10] and has been used in recent years to study both H absorption and H embrittlement [11-14]. Through the direct observation of H within materials such as ferritic steels [15] and zirconium alloys [16], APT has provided experimental validation to theories of proposed mechanisms to tackle H embrittlement. Here we have used APT to better understand the corrosion processes of Mg alloys, observing the relationship between H and oxygen (O) in the early stages of Mg oxidation after controlled exposure to molecular oxygen gas (O_2). To ensure the controlled oxidation of an atomically clean Mg alloy surface, an atom probe connected by vacuum transfer to a catalytic reaction cell, was used. This custom-designed system is known as a ‘catalytic atom probe’ [17]. The combined APT and catalytic cell is unique in its ability to provide information about the material composition, including the surface composition, prior to and after oxidation [18]. Through the use of the catalytic atom probe, it is possible to observe H and O atoms at the surface of an atomically clean Mg surface or absorbed into the bulk of the Mg alloy.

This study focuses on the early stage oxidation of a Mg alloy containing 880 parts per million (ppm), or 0.03 at. %, germanium (Ge). The composition of the material, as measured by inductively coupled plasma-atomic emission spectroscopy, ICP-AES (Spectrometer Services, Vic. Australia) is provided in Table 1. The Ge-doped Mg alloy was chosen for its increased resistance to corrosion compared to other Mg alloys [19, 20]. The reduced corrosion rate of the Mg alloy helped to minimise oxidation during sample preparation, and ensured that the initial stages of oxidation could be captured within the scope of the study. The alloy was prepared by adding master alloys to pure Mg in a resistance furnace. Melts were poured into graphite-coated cast iron moulds and allowed to cool in air.

Table 1: Mg alloy composition in at. %, as determined by ICP-AES.

Sample	Mg	Ge	Fe	Mn	Al	Zn	Cu	Si	Ca
Mg-880Ge	Bal.	0.030	<0.001	0.011	0.009	<0.004	<0.001	<0.017	0.006

Atom probe tips were prepared by electropolishing small matchstick-like samples, approximately 0.4 x 0.4 x 15 mm, into a needle shape with a final diameter of less than 200 nm (see Figure 1). Two electropolishing steps were used: ‘rough-polishing’ was conducted in 25 % perchloric acid in glacial acetic acid, and ‘fine-polishing’ in 2 % perchloric acid in butoxyethanol. The lower concentration of acid in the fine-polishing step enables a slower polishing process and control of the final needle shape and size. In the context of the current study, the process of electropolishing is an accelerated analogue to anodic dissolution (such as the dissolution that occurs during aqueous corrosion). As a result, oxides are often observed at the tip of the electropolished samples in the initial stages of APT analyses.

For the oxidation experiments, atomically clean samples are required prior to gas exposure. To achieve suitably clean surfaces, oxides were removed from the atom probe tip via high-field evaporation, as

carried out during a brief APT experiment, Figure 1. Real-time mass spectrum data was used to analyse the composition of the tip as material was removed. Once it had been ascertained that oxides were no longer present within the analysis volume, the atom probe run was stopped and the tip transferred through a series of interconnected vacuum chambers to the reaction cell. As it will later be seen, the process of electropolishing introduced varying levels of hydrogen into the samples, and this had a dramatic effect on the subsequent oxidation.

After cleaning, the catalytic chamber could be used to expose the samples to any desired gas; in the current experiments samples were exposed to O₂ at 200 mbar and at room temperature for one hour. Gas was pumped out of the chamber and the samples were immediately returned via vacuum transfer to the atom probe analysis chamber, where further data was collected to observe any reactions that had occurred on the clean metal surface as a result of O₂ exposure. A LEAP 3000 HR with a green laser (532 nm wavelength) was used to collect pre- and post-exposure data. APT experiments were run at 30 K using a laser energy of 0.4 nJ, a pulse frequency of 200 kHz, and a 1 % detection rate. In the current study twenty samples were transferred to the gas reaction cell. Of these, ten were successfully re-run in the atom probe, providing a 50 % success rate for samples after successfully collecting the initial atom probe data.”

Figure 1: Schematic of the atom probe cleaning process, the red dotted lines indicate the region detected by APT (~ 45 % of the tip). a) initial tip after electropolishing, b) detectable (blue dots) and non-detectable (red dots) oxide removed during the APT high-field cleaning process, c) final tip surface after APT high-field cleaning; oxide remains on the shank of the tip only (yellow dots).

Figure 2 reveals results from a successfully cleaned tip, where no oxides from electropolishing remain on the tip prior to oxidation. In Figure 2a, Mg and MgOH⁺¹ ions from the final 20 nm of the tip are shown in an atom map, with the respective mass spectrum shown to the right. The areas relating to MgOH_x⁺, Mg₂O⁺, and OH_x⁺, the most abundant ions evaporating from the oxide region of the Mg tips, are highlighted in the mass spectrum. The smaller peaks not highlighted relate to a variety of O, H and Mg combinations as well as some nitrogen (N), which was used to purge the gas chamber before removing the sample. The atom probe map and the associated mass spectrum demonstrate that there is no oxide present after high-field cleaning, with only Mg peaks present. Underneath the image of the cleaned tip is an atom probe map from the same sample after exposure to O₂ (Figure 2b). Again, Mg

and MgOH^+ ions are shown. It is evident from Figure 2b that a single monolayer layer containing O and H is present at the surface after exposure to O_2 gas. No further oxidation of the sample was observed below this. The measured concentration of O and H in both tips is shown in Table 2. The Mg alloy in the electropolished and cleaned tip contained 0.9 at.% H, consistent with what might be expected as a result of hydrogen present in the atom probe chamber [21, 22]. The level of H detected in the Mg alloy in the oxidised sample is similar (1.0 at.%). The surface layer contained 66.3 at.% H and 33.7 at.% O, which is consistent with the composition of H_2O .

Figure 2: a) Final 20 nm of the field evaporated tip after electropolishing, associated mass spectrum is shown to the right of the atom probe map. b) Atom probe data from the same tip after exposure to O_2 , associated mass spectrum is shown to the right of the atom probe map.

Table 2: Concentration of Mg, H, and O within distinguishable regions of the pre- and post- O_2 exposed atom probe tip.

	Magnesium (at. %)	Hydrogen (at. %)	Oxygen (at. %)	Potential Phases
Electropolished				
Mg alloy	99.1	0.9	0.0	Mg
O_2 Exposed				
Surface layer	--	66.3	33.7	$\text{Mg}^*\text{H} + \text{Mg}^*\text{OH}$ [23]
Mg alloy	99.0	1.0	0.0	Mg

As no H or H_2O was intentionally introduced during the oxidation process, it is necessary to identify the source of the H_2O . It is well established that H penetrates the steel walls and exists within the atom probe chamber, and H is routinely observed within atom probe mass spectra in small quantities

[21, 22], such as observed in the bulk alloy (Table 2). It is therefore possible that pre-existing H from the atom probe chamber is the source of the H in the H₂O observed on the atom probe tip. To test whether this was the case, a sample was first cleaned by running it in the atom probe, transferred to the buffer chamber, and then transferred back to the analysis chamber and re-analysed. A small amount of Nitrogen (N) was detected on the tip surface, which is thought to have migrated to the surface from the specimen shank in the buffer chamber, but a layer of H₂O was not present. This indicates that the presence of O and H on the tip surface resulted from the gas exposure and not from adsorbed species from within the atom probe chamber.

The H in the surface layer is therefore thought to originate from the reaction cell. As for the atom probe chamber, H₂ is also present within the reaction cell chamber. Results from a residual gas analyser, prior to filling the reaction cell with O₂, confirmed the presence of H₂ and H₂O in the reaction cell prior to and after exposure, Figure 3. The addition of O₂ into the chamber may result in the production of additional H₂O that may be adsorbed at the specimen surface (Reaction 1). To understand the exact state of the H₂O layer, we refer to a recent first-principles study of surface reaction kinetics for the adsorption of water molecules on Mg surfaces by Taylor [23]. Taylor suggests that adsorbed water dissociates on the surface of the Mg alloy via Reaction 2. This dissociation alone would be consistent with the 2:1 H:O ratio that is experimentally observed here (Table 2). However, it is known that the H can recombine on the surface to form H₂ (reaction 3) and that other reactions (4 and 5) lead to the formation of OH⁻ and Mg²⁺. The fresh Mg sites that result from these later reactions would allow further adsorption (and dissociation) of H₂O, which still supports our finding that the ratio of H to O on the tip surface is consistent with H₂O.

Figure 3: Residual gas analysis of the reaction cell chamber both pre- and post- O₂ exposure.

The data presented in Figure 2 shows a sample that contained very little residual H after electropolishing. In this case, the presence of H₂ and H₂O in the reaction cell during O₂ exposure resulted in the presence of H and O at the surface of the clean Mg tip, and no further oxidation of the Mg sample was observed. Although there was no intentional difference in the sample preparation, some samples contained significant residual hydrogen and these samples displayed markedly different oxidation behaviour, Figure 4. The initial high-field cleaning for the sample presented in Figure 4 was again stopped after it was observed that there were no longer any oxides present within the sample. Post experimental data analysis revealed that, although all O atoms were removed from the tip apex, a significant number of H atoms remained.

To illustrate the distribution of H within the tip, a 3D atom map is shown in Figure 4a, together with 2D contour plots of MgH₃⁺ and total O from the final 20 nm of the cleaned tip. The section of the dataset from which the contour plots are taken is separated from the rest of the dataset in the image. MgH₃⁺ has been chosen for identifying the location of H because it does not overlap with any of the Mg⁺ peaks, providing a clear indication of the location of H. The 2D contour plot shows a locally enriched region of H within the tip. The total concentration of H in the H-rich region is approximately 16 at. % (Table 3). An analysis of the O concentration within the H-rich region prior to O₂ exposure, revealed that the H-rich region was completely free of O. It is assumed that the H was absorbed into the tip during electropolishing [24], with the most likely pathway for H diffusion being along dislocations [25]. However, it is not impossible that the H was trapped in the tip during the production

of the Mg alloy [26]. Given the significant quantity of H observed however, and the profile of the H (more towards the edges and the surface of the tips), the source of hydrogen is ascribed to electropolishing.

Table 3: Concentration of Mg, H, and O within distinguishable regions of the pre and post O₂ exposed atom probe tip.

	Magnesium (at. %)	Hydrogen (at. %)	Oxygen (at. %)	Potential Phases
Electropolished				
Hydrogen-rich	83.7	16.2	0.0	Mg + H
Mg alloy	98.8	1.1	0.1	Mg
O₂ Exposed				
Surface layer	--	64.2	35.8	Mg*H + Mg*OH
Hydroxide	53.3	26.1	20.4	Mg(OH) _x + H
Hydrogen-rich	52.8	44.7	1.5	Mg + H
Mg alloy	98.8	1.1	0.1	Mg

Following exposure to O₂, there is a considerable change to the distribution and the overall concentration of both O and H. As for the previously described tip, a layer of H and O is detected at the tip surface, Table 3 (O₂ Exposed). Figure 4b reveals an atom map of Mg and MgH₃⁺ ions, and concentration profiles for MgH₃⁺ and total O a 20 nm thick slice of the tip. To avoid influence from the surface layer on the 2D concentration plot, a volume slightly below this layer was chosen for analysis. The 2D concentration plots show that the peak concentration of the MgH₃⁺ in Figure 4b is more than double that observed in the electropolished tip, Figure 4a,, this increase in concentration suggests that the relatively dispersed H, observed in the electropolished tip, has now accumulated within a more localised region of the sample. The second key finding is that the tip now contains a reasonably high concentration of O. The O is closer to the specimen surface than the H-rich region and extends into the sample only up to the edge of the H-rich region. Note that MgH₃⁺ ions only evaporate from the H-rich region and not from the hydroxide region. In the hydroxide region the most common H-containing species is MgOH₍₀₋₃₎. Figure 4b shows the MgH₃⁺ profile only and is provided merely to show the trend in H concentration. Table 3 contains the precise measurements of the concentration of Mg, O and H within various regions observed within the tip. The base Mg alloy contains 1.1 at. % H (thought to be an artefact) and very little O. The “hydrogen rich” regions, adjacent to the Mg base alloy contain 44.7 at. % hydrogen, and the regions that contain both H and O, contain an average of 26.1 at. % H and 20.4 at. % O.

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initiation of filiform-like corrosion, initiated by the presence of hydrides. The results from Binns et al. [28] would support the hypothesis that metastable MgH_2 catalyses hydrogen evolution when reacted with H_2O .

The chemical state of the H within the sample shown in Figure 4 cannot be determined from atom probe data. The compositions presented in Table 3 suggest that the H has not bonded with Mg to form magnesium hydride (MgH_2). However, it is clear that the H is present, locally within the sample, in significant quantities. A schematic, Figure 4c, illustrates how the presence of H may affect the oxidation of this Ge-doped Mg alloy. Reactions 1-5 remain the same for both the atomically clean sample and the H-free regions on the sample containing localised H enrichment. However, above the H-rich region, the interaction of the water molecules and the sample changes and the H-rich Mg begins to oxidise. It is hypothesised that an increase in H ions reduces the local pH of the thin film of H_2O on the tip surface, inducing oxidation in the form of Reaction 6 [29, 30].

The $\text{Mg}(\text{OH})_2$ layer developed on Mg alloys is known to be porous [2], providing a pathway for H_2O to reach the H-rich Mg layer, which continues to act as a cathode to the oxidation processes. Two H^+ ions evolve from the oxide surface as a by-product of the reaction between the Mg alloy and H_2O . However, the H that initially existed within the material is driven further into the sample, concentrating at the oxidation front, as previously observed by Melia et al. [31]. A final pathway for the H to be removed from the system is along the boundary between the metal and the oxide [28, 31].

This study was conducted on a Ge-doped Mg alloy. It is possible that there is some difference between these results and those that would be expected for pure Mg. For example, some literature suggests that group IV and V alloying additions increase corrosion resistance by poisoning cathodic hydrogen evolution, by stopping or slowing hydrogen atom recombination [32]. If this is the case for Ge, then more atomic hydrogen might enter the Ge-doped Mg alloy than would be the case for the pure metal.

Additional information might also be gleaned by repeating these experiments using heavy water for electropolishing. This would confirm that the hydrogen originates from the electropolishing step, and would eliminate any contributions from ambient hydrogen in the atom probe chamber.

In this study a new method has been demonstrated to study the early stage oxidation of Mg alloys at the nanometer scale using a unique reaction cell coupled to an atom probe. Using this method, it has been revealed that the oxidation behaviour of a Ge-doped Mg alloy is heavily dependent on the presence or absence of H within the sample. Upon short term exposure to O, water molecules are adsorbed at the tip of H-free specimens and disassociate to form Mg^*OH and Mg^*H , but the sample is otherwise unaffected. A tip containing H-rich regions is oxidised, with $\text{Mg}(\text{OH})_x$ forming within the H-rich region.

It is therefore proposed that the oxidation behaviour of Mg alloys is affected by the presence of H within the material prior to oxidation. This would indicate that control of the oxidation of Mg alloys may be intrinsically linked to control of the H diffusion properties.

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Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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