



Analysis of the surface film formed on Mg by exposure to water using a FIB cross-section and STEM–EDS

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ABSTRACT

The composition and structure of the surface film formed on pure Mg exposed at the corrosion potential in pure water for 48 h was investigated using a FIB cross-section and STEM–EDS. The surface film formed is duplex in nature, consisting of a thinner, more-porous, nano-crystalline MgO-rich inner layer, and a thicker, less-porous Mg(OH)₂-rich outer platelet layer. The results are consistent with the theory that a chemical breakdown (hydration) of the bulk inner MgO layer (native oxide) is a necessary precursor step to the corrosion process that leads to the significant thickening of the partially protective outer Mg(OH)₂ layer.

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1. Introduction

Mg alloys, with relatively high specific strength and stiffness, provide significant opportunities within the transportation industry to reduce mass, and, thus improve fuel efficiency. A major technological issue preventing widespread application of Mg alloys in this regard is the relatively poor corrosion resistance, which is governed by the alloy composition, microstructure and the formation of a partially protective surface film corrosion product [1–4]. Any attempt to improve the level of self-protection of Mg alloys requires knowledge of the composition, structure and protection properties of the surface film formed on unalloyed (commercially pure) Mg, and the manner in which the structure–property relations are modified through alloying [5–10]. The surface film formed on Mg has been analyzed after exposure to a range of experimental environments, including air [9–17], controlled humidity atmospheres [9–11,18–21] and pure H₂O [11,13,14,16,17,22]. However, a consistent composition and structure model of the surface film formed on Mg when in contact to H₂O with the experimental exposure condition has yet to be attained.

XPS studies consistently show that the film formed on the surface of Mg after ambient atmospheric exposure is relatively thin and is comprised of both MgO and Mg(OH)₂ [9–20]. Hydration by absorbed H₂O molecules is believed to account for the observed, albeit slow, thickening of the film with time through hydroxide formation [19,20]. The structure of the surface film formed has been discussed in the context of existing as a single layer, comprised of either a MgO/Mg(OH)₂ mixture [9,10,18–20] or a

MgO_x(OH)_y·nH₂O compound [12], or a bi-layer, comprised of an outer Mg(OH)₂-rich layer on top of an inner MgO-rich layer [11,13,15–17]. A carbonate (MgCO₃) peak also has been detected on occasion in the outer part of the surface film formed after ambient atmospheric exposure [9,10,13–17,21]. It has been estimated to be only a monolayer thick when formed under such exposure [14]. However, in the presence of CO₂ (350 ppm) and high humidity (95%), the surface film is believed to be more protective due to the formation of a thick Mg₂(OH)₂CO₃·3H₂O film [21].

The stability of the native surface film formed on Mg after exposure to H₂O, after short times, has received some attention. Yao et al. [13] found that the surface film on Mg, after aging in H₂O at E_{corr} for 60 s, remained mainly a mixture of Mg(OH)₂ and MgO, but was significantly thicker than that formed in laboratory air. Depth profiling revealed that the Mg(OH)₂ component was predominant at the top layer and decreased gradually with depth, whereas MgO exhibited the opposite behavior. In contrast, Santamaria et al. [16] reported that the surface film, formed during dry-polishing, after aging in H₂O at E_{corr} for 0–300 s maintained the original bi-layer structure, consisting of an ultra-thin MgO inner layer and a Mg(OH)₂ outer layer. A similar bi-layer structure was used to model the data collected for dry mechanically-polished Mg after aging in H₂O at E_{corr} for 0–420 s by Lui et al. [17]. In both of these studies, the Mg(OH)₂ outer layer was found to become the dominant component for exposure times greater than 30 s, and the composition and thickness of the inner (MgO) layer was found to remain unchanged. Using ToF-SIMS depth profiles, Seyeux et al. [22] reported that the surface film, formed during dry-polishing, after aging in H₂O at E_{corr} for 120 s was a mixture comprised of Mg(OH)₂, predominantly in the outer layer, MgO, predominantly in the inner layer, and small amount of MgH₂. Again, a carbonate

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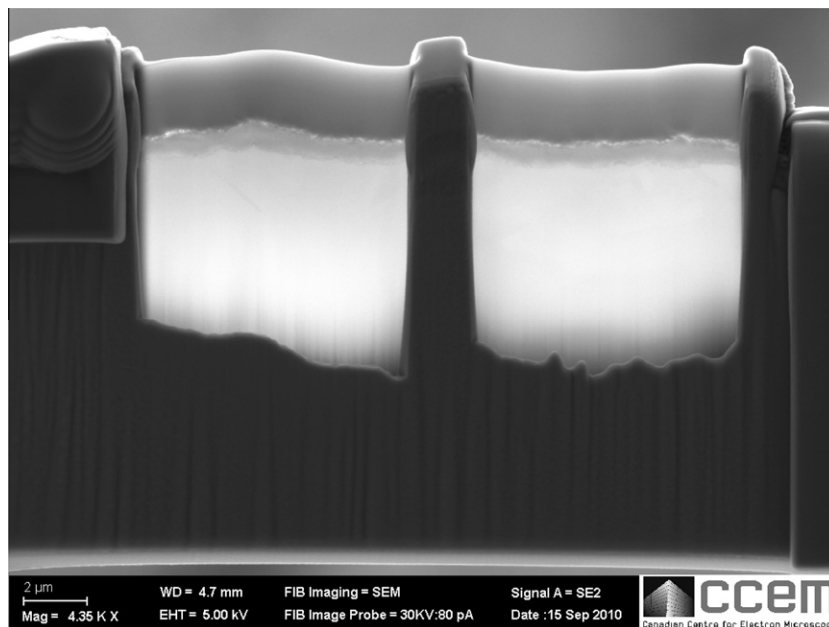


Fig. 1. SEM image showing the thinned foil cross-section windows extracted from the Mg sample, using the FIB technique, after aging in pure H₂O at room temperature for 48 h.

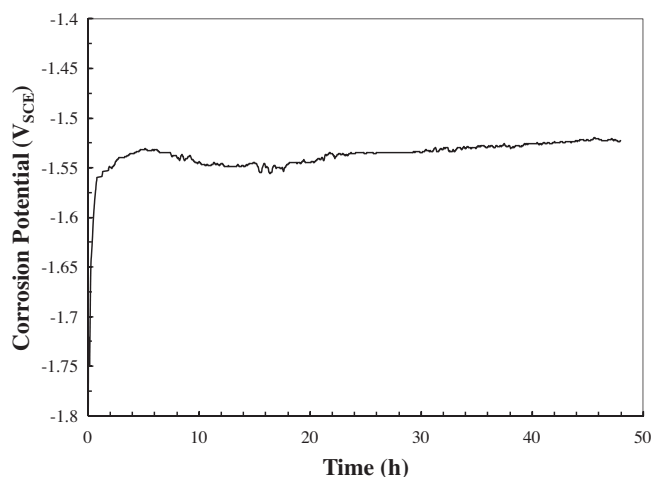


Fig. 2. Plot showing the E_{corr} of the Mg sample aged in pure H₂O at room temperature, as a function of time for the 48 h exposure period.

(MgCO₃) peak was also detected on occasion in the outer part of the surface film formed [14,16,17,22].

In all of these studies, the structure of the surface film has been discussed in the absence of direct imaging of the surface film in cross-section. Nordlien et al. [11] used ultramicrotomed cross-sections and TEM-EDS, and limited plan view sections and XPS, to investigate the morphology, composition and structure of the surface films formed naturally on Mg by exposure to humid air and distilled water. The initial surface film formed just after exposing fresh surface, by scratching, in low-humidity (35–55%) air for 0.25–1 h was found to be a thin, amorphous mixture of MgO and Mg(OH)₂. In high-humidity (65%) air, the exposure after 168 h was found to form a hydrated amorphous layer between the Mg metal and the initial layer, which was attributed to water ingress and subsequent oxidation at the metal surface. This amorphous, hydrated inner layer was found to dehydrate and crystallize to MgO with sustained irradiation under the electron beam. The

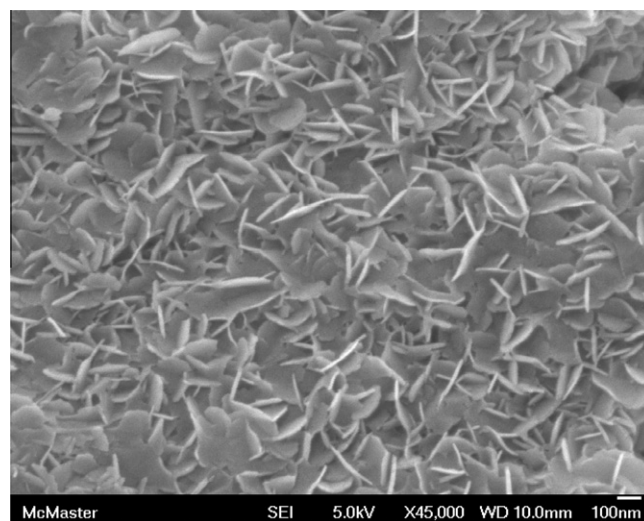


Fig. 3. SEM image showing the plate-like morphology of the film surface formed on the Mg sample after aging in pure H₂O at room temperature for 48 h.

surface film formed in H₂O at E_{corr} after 48 h was found to contain an additional top layer of crystalline MgO embedded in an amorphous Mg(OH)₂ matrix with an overall plate-like morphology. The formation of this third layer was attributed to the redeposition of sparingly soluble Mg, which migrates outwards also through the initial layer. The observation of a surface film with a plate-like morphology is consistent with that reported for Mg exposed in H₂O for 1.67 h by Vermilyea and Kirk [23] using plan view sections and electron microscopy. However, Vermilyea and Kirk concluded that the platelets were crystalline Mg(OH)₂ based on infrared spectroscopy experiments.

In addition to the uncertainty regarding the number of layers present, the role played by carbonate and the degree of crystallinity within the surface film formed on Mg upon exposure to water, there is also an apparent uncertainty regarding the thickness of the surface film formed, particularly for exposure to ambient

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