



Towards a Physical Description for the Origin of Enhanced Catalytic Activity of Corroding Magnesium Surfaces



M. Taheri^a, J.R. Kish^{a,*}, N. Birbilis^b, M. Danaie^c, E.A. McNally^a, J.R. McDermid^a

^a GM Centre for Automotive Materials and Corrosion, McMaster University, Hamilton, Ontario, L8S 4L7 Canada

^b Department of Materials Engineering, Monash University, Clayton, VIC, 3800, Australia

^c Canadian Centre for Electron Microscopy, McMaster University, Hamilton, Ontario, L8S 4L7 Canada

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ABSTRACT

The so-called “negative difference effect” (NDE) exhibited by corroding magnesium (Mg) surfaces, where the rate of hydrogen evolution increases with the extent of anodic polarization, has been well documented. Recently this behaviour has been explained by a theory involving an increase in the cathodic exchange current density that occurs during anodic polarization, rather than the popular theory involving the formation of a univalent Mg^+ ion and its subsequent chemical reaction with water to produce hydrogen. The present study reports on the results of transmission electron microscopy (TEM) conducted on focused ion beam (FIB) prepared cross-section lamellae of the dark film formed on a corroding area of a Mg surface from which hydrogen evolved. The film was found to consist of an outer columnar mixed magnesium oxide-hydroxide layer on top of a magnesium oxide-rich inner layer. X-ray energy dispersive spectroscopy (EDS) reveals iron (Fe)-rich particles embedded in the columnar outer layer. Subsequent cathodic polarization measurements showed that the corroded surface became cathodically activated relative to a non-corroded surface. These observations demonstrate that a surface film enriched in more noble metals can catalyze the cathodic process, provide physical evidence towards support of the enhanced catalytic surface theory explaining the NDE, and validate the chemistry and structure of the surface film that forms upon corroding regions during anodic polarization.

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1. Introduction

The corrosion of magnesium (Mg) and its alloys remains a practical barrier to their wider industrial application. As such, unambiguously understanding Mg corrosion is increasingly topical given the demand for product weight reduction across several industries, including automotive, consumer electronics, and aerospace. There has been both mystery and debate regarding the origin of the so-called “negative difference effect” (NDE), which involves an increase in the rate of hydrogen production with increasing applied anodic potential, for over a century [1]. This phenomenon is readily observed on Mg, where the principal cathodic reaction upon Mg is water reduction ($2H_2O + 2e^- \rightarrow H_2 + 2OH^-$). The work of Petty et al. in the 1950s [2] was amongst the first to suggest that Mg may be corroded as univalent Mg^+ ions. In the corrosion field, a popular theory that hydrogen evolution on corroding Mg surfaces arises from a secondary chemical reaction between the univalent Mg^+ ion and water to form excess hydrogen gas has been developed in recent decades [3–7]. It is prudent to note that the

study of Petty et al. did not include any experimental data, nor has any researcher isolated or confirmed the existence of univalent Mg^+ ions by spectroscopic [8,9] or any other means to date. Alternative theories put forth to explain the NDE effect include, Mg particle undermining [10–14], formation and dissolution of magnesium hydride (MgH_2) [15,16], and chemical equilibrium [17].

In a recent study by Frankel et al. [18], a mechanism to account for hydrogen evolution on Mg during anodic polarization was described in terms of enhanced catalytic (i.e. cathodic) activity on the corroding Mg surface. For example, if the ability to support water reduction is enhanced during corrosion, then the cathodic reaction may still appreciably persist at potentials anodic relative to the corrosion potential of Mg. Such a mechanism would indeed account for the so-called “negative difference effect”; however, a physical basis for the origin of such a mechanism has yet to be presented. In this vein, Williams and co-workers [19,20] have revealed via the scanning vibrating electrode technique (SVET) that corroded regions of the Mg surface are subsequently ‘cathodically activated’ and take the role of a cathode during the continued corrosion of Mg. The SVET studies are important because they demonstrate that cathodic sites on anodically polarized Mg are spatially associated with prior corrosion. It has been postulated that the sites of cathodic activity may be sites of relatively noble impurity metals [19,21],

* Corresponding author. Tel.: +905525914021492.

E-mail address: kishjr@mcmaster.ca (J.R. Kish).

based on the foundational findings of McNulty and Hanawalt [22]. Given further consideration, it may be reasonable to assume accumulation of metal impurities that are more noble than Mg (such as Fe) as they would remain cathodically polarized at potentials where Mg is anodically polarized. As such, preferential anodic corrosion of Mg could reasonably occur, akin to de-alloying, albeit that the Mg is the significant major constituent of the alloy.

To date enrichment of other metals at the surface of Mg has not been definitively shown, likely due to the combination of it not being regarded as a significant issue and that it was simply difficult to discern. For example, with respect to the latter issue, conventional scanning electron microscopy (SEM) based energy dispersive spectroscopy (EDS) is not sensitive to the near surface, and other techniques like Auger electron spectroscopy (AES) or X-ray photoelectron spectroscopy (XPS) may lack the required signal to noise ratio or spatial resolution to detect minor enrichment. It is noted that typical impurity levels in Mg are at the ppm amount (such that the sum of impurities may be ~ 200 ppm), and even a doubling or tripling of the impurity level would not be significant in terms of signal to noise ratio unless the experiment was carefully executed. However, recent work has shown that focused ion beam (FIB) prepared cross-section lamellae can be studied using transmission electron microscopy (TEM) to reveal the morphology and local composition of the surface of Mg-alloys following exposure to an electrolyte [23–26], and it was more recently revealed that localized enrichment of metallic Al could be detected in an Mg–Al alloy using this technique [27]. As such, the FIB preparation method for TEM investigation was used to survey the morphology, structure, and chemistry of the darkened surface of pure Mg following anodic polarization. The aim was to provide a physical description of the surface and reveal whether or not noble metal enrichment is present.

2. Experimental

Square samples (10 mm \times 10 mm) were prepared from 2 mm thick polycrystalline cold-rolled Mg sheet (99.99% nominal purity with 50 ppm Fe). The samples were annealed for 350 °C for 0.5 h in air and quenched in water to obtain a recrystallized grain structure. Each working electrode was prepared by attaching a coated copper (Cu) wire to the rear of the Mg sample and then cold mounted in epoxy resin. The working surface was mechanically abraded using silicon carbide (SiC) paper up to a 4000 grit surface finish, using absolute ethanol as a lubricant, rinsed using absolute ethanol, then dried using a stream of warm air.

The 0.01 M NaCl test solution was prepared by adding reagent grade NaCl to high purity (HPLC-grade) water. The 0.01 M concentration was chosen specifically to provide a mildly aggressive solution so as to prevent widespread localized corrosion from occurring during the open-circuit exposure. All experiments were conducted at room temperature in a 1000 mL electrochemical cell. A fresh solution was used for each test with no attempt to deaerate or aerate the solution. The electrochemical measurements were made using a Gamry Reference 600TM potentiostat coupled with the Gamry FrameworkTM software package. Graphite rods were used as the counter electrode along with a saturated calomel reference electrode (SCE). Two types of Mg working electrodes were prepared by conditioning at the open-circuit potential for 24 h, one type was left in this condition, and the other was additionally treated by applying potentiostatic anodic polarization at $-1.0 V_{SCE}$ for 0.5 h. The rationale behind the 24 h open-circuit exposure was to allow sufficient time for the surface film to establish and maintain a quasi-steady state in terms of the film formation and dissolution processes that are believed to occur in the absence of any localized corrosion [23]. The applied potential of $-1.0 V_{SCE}$ was

100 mV more positive than the observed breakdown potential of $-1.1 V_{SCE}$ exhibited in the anodic polarization recorded after the 24 h exposure. The 30 minute polarization time was chosen as comprise between being long enough to initiate and sustain localized corrosion, yet short enough to limit corrosion product formation. The latter was important from a TEM sample preparation perspective since the goal was to include both the film and substrate in the FIB-prepared cross-section lamella. No attempt was made to capture the hydrogen evolved and cross-correlate this with mass lost or charge passed. The potentiodynamic cathodic polarization measurements were initiated from a potential 20 mV more positive than the open circuit potential and swept in the cathodic direction at a scan rate of 1 mV/s on both types of samples.

FIB-prepared cross-section lamellae were extracted from a working surface that had been conditioned at the open-circuit potential for 24 h and then anodically polarized at $-1.0 V_{SCE}$ for 0.5 h. Once removed from the test solution, the working surface was rinsed with absolute ethanol and dried in a stream of warm air before the sample was extracted from the cold mount and transferred into the chamber of a dual beam SEM/FIB (Zeiss NVision 40) equipped with an EDS detector (Oxford Inca with a silicon (Si) drift detector). The specific site for FIB milling was selected based on secondary electron imaging and EDS analysis of the corroded surface regions on which hydrogen had evolved. The site of interest was coated with a protective tungsten (W) film and subsequently milled to produce an approximately 70 nm thick lamella with a depth of nearly 3 μm from the W-coated surface, via the standard in-situ lift-out TEM sample preparation routine. The FIB gallium (Ga) ion beam accelerating voltage was initially set at 30 kV and then gradually reduced to 1 kV during thinning of the FIB lamella. The microstructure analysis was performed using a FEI Titan TEM operated at 300 kV equipped with EDS [Oxford Inca, Si(Li)] detector. The FIB lamella was held in a cryogenic holder capable of maintaining the lamella temperature at -178°C to reduce damage caused by the electron beam. Selected area diffraction (SAD) patterns were acquired without the use of an area-selective aperture in parallel “nanobeam” TEM operation mode. The parallel electron beam illumination used for diffraction measured about 150 nm in diameter and was centred on various locations within the film. SAD simulations were carried out using the JEMS software package and the published crystallographic data for Mg [28], magnesium oxide (MgO) [29] and magnesium hydroxide [Mg(OH)₂] [30].

3. Results and Discussion

3.1. Composition and Structure of Corroded Surface

An image of the macroscopic visual appearance of the Mg electrode surface after conditioning at the open circuit-potential for 24 h is shown before [Figure 1(a)], during [Figure 1(b)] and after [Figure 1(c)] anodic polarization at $-1.0 V_{SCE}$ for 0.5 h. Anodic polarization was observed to initiate and sustain dark regions of localized corrosion on the Mg surface, upon which hydrogen gas evolved. Away from the edges, these dark corroded regions were radial-like in appearance, which is similar to what has been reported for pure Mg exposed in the more aggressive 5 wt.% NaCl solution under open-circuit conditions [19].

Figure 2 shows the current density transient recorded during the anodic polarization at $-1.0 V_{SCE}$ for 0.5 h (1800 s). The transient consists of two stages. The first stage occurred within the initial 200 s of polarization, in which the current density increased only marginally with time. This stage coincided with the initiation of localized corrosion. The second stage essentially involved the remainder of the polarization, in which the current density increased significantly with increasing time; albeit a decreasing

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