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Reducing the corrosion rate of magnesium alloys using ethylene glycol for advanced electrochemical imaging

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ABSTRACT

The corrosion of an AM50 Mg alloy was studied in ethylene glycol using electrochemical and electron microscopy techniques. Switching from H_2O to ethylene glycol, it was shown that the corrosion of the AM50 alloy was significantly suppressed thereby slowing H_2 evolution. The corrosion of the AM50 alloy was mapped using scanning electrochemical microscopy in the feedback mode. Ferrocenemethanol can be used to expose the reactive anodic areas on the Mg alloy. These studies confirmed that studies in ethylene glycol can be used to elucidate reaction features obscured by rapid corrosion in H_2O without significantly altering the mechanism and damage morphology.

1. Introduction

Mg alloys possess several desirable properties for use in the automotive and aerospace industries, such as their high strength to weight ratio and good castability [1]. A deterrent to their application is their high corrosion rates in aqueous media. Driving the corrosion of Mg alloys is the microgalvanic coupling between the α-Mg matrix and the secondary microstructural constituents, such as β-phase and intermetallic particles [2] with the cathodic reactivity of the latter increased if it contains contaminant elements such as Fe [3]. Understanding the behavior of these microstructural features during corrosion is essential if alloys with improved corrosion properties are to be developed. Separating the responses of individual microstructural components acting as cathodes is inherently difficult using standard electrochemical measurements.

Scanning probe techniques provide valuable insights on a microscale with high spatial resolution. Such techniques have been applied to study the corrosion of Mg alloys including localized electrochemical impedance spectroscopy (LEIS) [4,5], scanning Kelvin probe force microscopy (SKPFM) [6,7], the scanning vibrating electrode (SVET) technique [8–12], and different modes of scanning electrochemical microscopy (SECM) [13–17]. Monitoring corrosion processes above Mg alloys in an aqueous environment with these techniques is challenging because of large H_2 fluxes evolving as corrosion progresses which can interfere with mediator detection at the microelectrode tip and create a convective medium at the corroding surface [18]. Recently, these fluxes of H_2 have been used to monitor the corrosion process on Mg alloys [19,20].

To overcome this issue we have focused on controlling the corrosion rate, and hence, the amount of H_2 produced, using ethylene glycol as the corrosion medium since it limits the availability of H_2O, the primary cathodic reagent during corrosion. The corrosion of Mg alloys in ethylene glycol solutions has previously been investigated with a primary focus on their behavior as potential engine block materials which use ethylene glycol-based coolants [21–23]. In these studies increasing the ratio of ethylene glycol to H_2O was found to decrease the corrosion rate of the Mg alloys, although little detail was paid to pure ethylene glycol or to this solvent containing only small percentages of H_2O. Corrosion was also not investigated on the microscale.

Here, we present a study of the corrosion of the AM50 Mg alloy in ethylene glycol using a range of electrochemical techniques, including SECM, to compare the corrosion behavior to that observed in aqueous solution. Scanning electron microscopy (SEM) and energy dispersive X-ray analyses (XEDS) were used to locate and elementally analyze the alloy microstructure, and to locate and correlate surface microstructural features with an *in-situ* SECM map. Confocal scanning laser microscopy (CLSM) was used to observe the locations of corrosion damage.

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2. Experimental procedures

2.1. Materials

Bulk AM50 sand cast and graphite cast Mg alloy rods were received from General Motors Canada and machined into 1 cm × 1 cm × 0.7 cm size samples. For SECM measurements the AM50 sand cast alloy was machined into 4 mm × 4 mm × 0.5 cm samples. All samples were threaded on the backside to allow connection to external circuitry, and Struers EpoFix epoxy resin was used to seal the samples allowing only the exposure of a single face to the aqueous solution. Solutions were prepared with ethylene glycol (ACP), reagent grade NaCl (Caledon), ferrocenemethanol (FcMeOH) (97% Sigma Aldrich Canada), and NanoPure® (18.2 MΩ cm) H_2O.

2.2. Sample preparation

The mounted AM50 samples were ground successively with 800, 1200, 2400 grit SiC paper with a 50:50 ethanol/isopropanol solution as a lubricant, and subsequently polished with a Struers DP-Dur cloth saturated in 3 μm Struers DP-Suspension A for 5–10 min with the ethanol/propanol mixture once again used as a lubricant. A final 2–3 min polish was performed on a Struers OP-Chem cloth using an equal volume mixture of Struers OP-S Suspension and ethylene glycol, as an abrasive. The polished sample was then rinsed and sonicated in anhydrous ethanol for 2 min, Ar dried, and stored in a desiccator.

2.3. Electrochemical measurements

Electrochemical measurements were carried out in a standard three electrode cell with a Pt-mesh counter electrode and a saturated calomel reference electrode (SCE) (with a Luggin capillary placed 2 mm from the working electrode) in aerated solutions at ~22 °C. Electrochemical responses were measured with a Solartron® 1287 potentiostat coupled to a Solartron® 1255B frequency response analyzer for electrochemical impedance spectroscopy (EIS) measurements.

For corrosion potential (E_{CORR}) measurements the samples were placed in solution, face down for selected durations. Potentiodynamic polarization (PDP) scans were performed following a 2 h exposure to solution by scanning (at 0.167 mV/s) from −200 mV below E_{CORR} to either −800 mV (vs. SCE), or until a current density of 0.05 mA/cm^2 was measured to limit the extent of surface damage to the sample. EIS measurements were performed by potentiostatically fixing the potential and applying a sinusoidal potential perturbation of ±10 mV vs. E_{CORR}. The current response was recorded over the frequency range, 10^5 Hz to 10^{-3} Hz, and a one point per decade reverse scan was recorded from 10^{-2} to 10^5 Hz to ensure steady-state was maintained throughout the measurement.

2.4. Electron microscopy

Scanning electron microscopy (SEM) images were collected in secondary electron (SE) and back scattered electron (BSE) modes on either a LEO 440, Hitachi 3400-N Variable Pressure SEM, LEO 1540 XB SEM, or a Hitachi SU6600 Field Emission SEM. X-ray energy dispersive spectroscopy (XEDS) maps were collected using a Quartz XOne XEDS system. Confocal laser scanning microscopy (CLSM) was performed by measuring the reflected light intensity from a Zeiss 510 confocal with a HeNe 633 nm laser.

2.5. Scanning electrochemical microscopy (SECM)

Prior to SECM measurements, a montage image of a polished 4 mm × 4 mm area on an AM50 sand cast alloy sample was collected at 150× magnification using a Hitachi SU6600 Field Emission SEM. A complete map of the surface was produced by stitching the images using Image-Pro Plus 7.0®. SECM characterization was performed using an ElProScan 1 system (HEKA, Germany; bipotentiostat model PG340) by positioning a 25 μm Pt microelectrode over the alloy surface immersed in 1 mM FcMeOH solution (Sigma Aldrich) in ethylene glycol (Fisher Scientific). An approach curve was performed using feedback current from the FcMeOH mediator at an approach speed of 1 μm/s in order to position the microelectrode at a known distance of 10 μm from the surface. The microelectrode tip was polarized to 500 mV (vs. Ag/AgCl) and rastered at 5 μm/s over an area of interest (AOI). A 0.5 mm diameter (as drawn) Pt counter electrode (99.99%, Goodfellow Cambridge Limited, Huntingdon, England) and a Ag|AgCl quasi-reference wire electrode (fabricated as reported elsewhere [24] using a Ag wire of 1.0 mm diameter, annealed 99.99% from Goodfellow) were employed to record electrochemical data.

3. Results

3.1. AM50 alloy microstructure

The main microstructural constituents of the AM50 alloy are shown in the SEM micrograph in Fig. 1a, in which one of the many β-phase particles ($Mg_{17}Al_{12}$) is marked with a green arrow and an AlMn intermetallic with a red arrow. The compositions of individual phases were confirmed in the XEDS maps for Mg, Fig. 1b, which show the general distribution of Mg throughout the alloy matrix. The Al was present in both the β-phase and the intermetallic, Fig. 1c, with some enrichment in the network running between the β-phases corresponding to eutectic α-Mg. The Mn was present within the ten AlMn intermetallic particles in the imaged region, Fig. 1d.

3.2. Electrochemical behavior

The electrochemical behavior of the AM50 sand cast alloy was investigated in 3 mM NaCl in both NanoPure® H_2O and ethylene glycol. The chloride was added to enhance solution conductivity. Fig. 2 shows the E_{CORR} measured in 3 mM NaCl + H_2O (black) and 3 mM NaCl + ethylene glycol (red). In H_2O, E_{CORR} initially rose over the first 2 h of immersion from −1.56 V (vs. SCE) to −1.50 V (vs. SCE), and then increased slowly over the 24 h to −1.49 V (vs. SCE) accompanied by a number of small fluctuations. This final value was in the range expected for AM50 in aqueous chloride solutions [25]. In ethylene glycol E_{CORR} initially decreased from −1.05 V (vs. SCE) to −1.4 V (vs. SCE) over the first 2 h of immersion before increasing to a final steady-state value of ~−1.26 V (vs. SCE) after 24 h.

The PDP behavior of the alloy in both solutions is shown in Fig. 3. As expected the cathodic current at potentials less than E_{CORR} was considerably higher in H_2O than in ethylene glycol. In H_2O (black), once the net current became anodic at −1.45 V (vs. SCE) it increased (region I). For higher potentials the current increased sharply (region II). These features were typical of the behavior observed on this alloy [25] with an attempt to grow a partially protective film in region I followed by film breakdown and the onset of rapid dissolution in region II. In ethylene glycol (red), a similar initial event was observed with region I persisting to a potential of −1.10 V (vs. SCE). The subsequent increase in reactivity was minor, currents <1 μA/cm^2 being maintained before final film breakdown