



The influence of arsenic alloying on the localised corrosion behaviour of magnesium



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ABSTRACT

An in-situ scanning vibrating electrode technique is used to investigate the effect of alloyed arsenic on magnesium immersed in chloride containing aqueous solution, both in freely corroding and anodically polarised conditions. Arsenic is shown to strongly suppress cathodic activation of the corroding Mg even under circumstances where breakdown has occurred and subsequent propagation of dark filiform-like tracks is observed. Under galvanostatic anodic polarisation, rates of hydrogen evolution are significantly mitigated compared to pure Mg and no time-dependent evolution of local cathodic sites is detected. The findings support the theory that cathodic activation of the dark corroded Mg surface is associated with accumulated transition metal impurity, which in turn become poisoned towards cathodic hydrogen evolution by the presence of As. In addition, these preliminary studies suggest that alloying with a strong cathodic poison may provide a means of producing a more-charge effective anode material for primary sea-water activated Mg batteries.

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1. Introduction

The poor corrosion resistance of magnesium (Mg) and its alloys currently presents a significant obstacle to its mainstream use as a lightweight structural material [1,2]. Of the approaches used to reduce corrosion rates, one of the most attractive routes is by alloying with an element which imparts intrinsic corrosion resistance [3]. This precludes the need to rely on protection by surface treatments and coatings which form a physical barrier, isolating the underlying Mg from a potentially corrosive environment, but invariably add extra cost to any Mg-based product. A significant breakthrough in producing an intrinsically corrosion resistant form of Mg, by alloying with a low level of an Arsenic (As) addition was recently reported by Birbilis et al. [4]. Alloy design was influenced by a previous investigation on the influence of dissolved arsenate salts in a sodium chloride test solution, which produced a profound inhibition of corrosion rates observed for commercially pure Mg [5]. In both studies it was proposed that elemental As acted as a strong cathodic poison which deactivated iron-containing impurity phases towards cathodic hydrogen evolution [4,5].

The dependence of corrosion rate on iron (Fe) impurity level has been known since the publication of seminal works by Boyer [6] and Hanawalt [7], who proposed that iron-rich second-phase particles comprise the principal sites of cathodic hydrogen evolution. A tolerance limit of approximately 170 ppm Fe was demonstrated, above which corrosion rates increased dramatically and explained on the basis that the threshold represents a situation where iron containing second-phase particles become too large to be covered over by a protective surface film. Recent investigations have thrown more light on the role of iron impurity by demonstrating considerable cathodic activation of the previously anodically attacked Mg surface, either after undergoing corrosion at open circuit conditions [8–10], or following prior anodic polarisation [11,12]. The extent of cathodic activation has also recently been shown, by means of scanning vibrating electrode (SVET) studies, to be strongly dependent upon the iron impurity content of the Mg [13]. The origin of this cathodic activation has been the subject of much contemporary research in the field of Mg corrosion science [14–17]. High resolution microscopic analysis of the corroded, cathodically active regions on pure Mg has revealed evidence of sub-micron iron particles within the surface oxide layer [18], while a Rutherford Backscatter Spectroscopic (RBS) investigation demonstrated Fe impurity enrichment at the Mg-oxide interface [19] following anodic dissolution. Based on this evidence, Lysne et al. [20] proposed a model of cathodic activation

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based on iron-rich impurity accumulation based on phases remaining electrically connected to the Mg matrix during anodic dissolution. Others have recently presented a new theory of iron impurity enrichment, based on iron rich phases becoming detached from the matrix and undergoing rapid self-corrosion followed by re-plating on the newly corroded Mg surface [21]. It would therefore seem plausible therefore, that the presence of a strong cathodic poison, such as As [22] as an alloying addition, should act to limit hydrogen evolution on accumulated iron-rich impurity deposits.

The principal aim of the investigation reported herein is to expand on the preliminary work, recently published in a previous short communication on the origin of the corrosion resistance of As-alloyed Mg [4]. In this work an in-situ SVET is employed to visualise time-dependent localised corrosion pattern changes for both freely corroding Mg-As and pure Mg to fully describe the mode(s) by which alloyed As acts to significantly retard the rate of corrosion. Conditions are employed which produce breakdown in the Mg-As alloy, along with subsequent evolution of a dark, film covered surface, which in the absence of As has previously been demonstrated to act as a site of enhanced cathodic activity when compared with the original uncorroded Mg [8,9]. A second aim is therefore to ascertain whether the presence of As significantly influences cathodic current density values on the cathodically activated, corroded Mg surface. In addition, we have also sought to use SVET analysis to compare and contrast localised corrosion patterns obtained under galvanostatic anodic polarisation for both Mg and Mg-As. Previous studies using pure Mg have demonstrated that progressively higher rates of hydrogen evolution are observed as the specimen potential is increased above its free corrosion potential. A further aim of this work is to determine whether or not alloyed As influences hydrogen evolution rates under imposed anodic polarisation and to identify whether the Mg-As alloy demonstrates promise as a self-discharge resistant primary battery anode.

2. Experimental

2.1. Materials

All experiments were carried out using 99.99% high purity Mg, with the principal impurity elements being Fe (40 ppm), Ni (10 ppm) and Cu (20 ppm). An Mg-As alloy was produced by initially encapsulating quantities of the Mg and As (sourced from Alfa-Aesar, USA) in a quartz tube. This was backfilled with high purity argon to avoid any reaction of the Mg with the atmosphere and to contain any molten As. To avoid reaction of any molten metal with the quartz itself, the inside of the tube was coated with graphite prior to encapsulation. The charge was held in the molten state at 700 °C for 3 minutes, and periodically agitated to ensure mixing. The alloy was then left to cool in air, removed from encapsulation by breaking the quartz, and tested in this condition. The chemical composition of both pure Mg and the Mg-As alloy were independently analysed using ICP-OES (Spectrometer Services, Coburg, Victoria, Australia). The alloy preparation route described above resulted in the successful formation of an Mg-0.37 wt.% As alloy. The alloy microstructure has been reported elsewhere [4], showing that the majority of the alloyed As is present as an Mg₃As₂ precipitate within an α -Mg matrix, with only a small amount (<0.01%) existing in solid solution.

2.2. Methods

SVET investigation of Mg and Mg-As alloy specimens was carried out in both unpolarised (i.e. freely corroding) conditions and under anodic polarisation. The SVET instrument employed a

probe consisting of a platinum wire (125 μm , Goodfellow metals Ltd) sealed in a glass sheath so that vibrating electrode comprised a 125 μm diameter Pt micro-disc electrode. Full details of SVET instrument design and calibration procedure are given in previous publications [8,23]. After making electrical connection to Mg and Mg-As alloys specimens, they were cold mounted in two-part epoxy resin so that a minimum area of ca 30 mm² was showing. The exposed surfaces were abraded using silicon carbide paper and polished using an aqueous slurry of 5 μm polishing alumina, washed with aqueous surfactant and rinsed with distilled water followed by ethanol. Sample surfaces were completely immersed in an electrolyte bath containing aqueous sodium chloride electrolyte at concentrations in the range 0.1–2 mol dm⁻³ at pH 6.5 and a temperature of 20 °C. The SVET probe was held vertically and scanned at a constant height of 100 μm above the exposed surface. For anodically polarised specimens, current densities values in the range 0.4 to 1.0 mA cm⁻² were applied by means of micro-galvanostat of in-house construction, employing a Pt gauze counter electrode. SVET scans were carried out immediately following the start of polarisation and at 4 min intervals thereafter for periods of up to 3 h. The matrix of SVET-derived peak-to-peak voltage values comprising each scan was converted to values of current flux density along the axis of probe vibration (j_z), by applying a calibration factor determined by galvanostatically checking the calibration using a two-compartment cell containing the relevant NaCl (aq) electrolyte, as described previously [8]. In the concentrated electrolytes of 0.1 mol dm⁻³ NaCl (aq) and above used here, the assumption is made that any local conductivity increases at anode and cathode sites will be negligible in comparison with the high bulk electrolyte conductivity. In addition, the fact that the probe tip is scanned at a height of 100 μm above the corroding surface also mitigates the likelihood of interference of surface accumulation of ionic species on the accuracy of the SVET measurement.

Bulk hydrogen evolution rates were determined using volumetric measurements, employing an arrangement consisting of an upturned, electrolyte filled burette and glass funnel [24]. Potentiodynamic experiments in electrolytes containing varying sodium chloride concentration were carried out using a Solartron 1280B workstation in conjunction with a conventional 3 cell arrangement. This consisted of a Pt gauze counter electrode and saturated calomel (SCE) reference electrode using a Luggin capillary to minimize any ohmic drops possible when using dilute chloride concentrations.

3. Results and Discussion

3.1. Characterisation of localised corrosion under freely corroding conditions

Previously published results, using a combination of mass loss and volumetric hydrogen capture to compare the bulk corrosion rates of pure Mg in the presence and absence of alloyed As, showed that significantly higher corrosion resistance was observed for the latter upon immersion in 0.1 mol dm⁻³ NaCl (aq) [4]. Furthermore, potentiodynamic experiments carried out in the same electrolyte suggested that a marked retardation of cathode kinetics was primarily responsible for the significantly lower corrosion rate determined for the Mg-As alloy. To further elucidate the role of As, we have employed in-situ SVET to compare and contrast the same Mg-As alloy with pure Mg, in terms of time-dependent changes in current density distributions observed over their surfaces when immersed under freely corroding conditions in 0.1 mol dm⁻³ NaCl (aq). The localised corrosion behaviour of pure Mg (40 ppm Fe impurity) is discussed at length elsewhere [8] and will only be briefly re-capped here.

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