Short communication

Poisoning the corrosion of magnesium

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N. Birbilis [a,*], G. Williams [b], K. Gusieva [a], A. Samaniego [a,c], M.A. Gibson [a,d], H.N. McMurray [b]

[a] Department of Materials Engineering, Monash University, VIC, Australia
[b] Materials Research Centre, Swansea University, Swansea, UK
[c] Department of Materials Engineering, CENIM, Madrid, Spain
[d] CSIRO Division of Process Science and Engineering, VIC, Australia

ABSTRACT

Despite possessing excellent specific properties, rapid corrosion of magnesium is a significant barrier in its widespread use. Alloying Mg to enhance mechanical properties nominally increases susceptibility to corrosion from microstructural heterogeneity. Furthermore, alloying Mg nominally accelerates cathodic kinetics and hence also accelerates corrosion. To date, no alloying additions to Mg suggest that a reduction in corrosion rate can be imparted, however we reveal for the first time that alloying additions of arsenic can impart significant corrosion resistance to Mg via retarding the cathodic reaction.

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1. Introduction

The specific strength of Mg, coupled with other favourable properties, has seen technologies such as consumer electronics adopt Mg alloys in low corrosivity environments due to their lightweight and mass production capability. There is major interest in the utility of Mg deployment in many more forms, such as automotive sheet, powertrains, laptop casings, and anywhere that significant energy reductions can be realised. From a corrosion perspective, Mg is highly reactive in aqueous environments. This is due in part to the highly negative potential of Mg ($\sim -2.38V_{NHE}$) [1], and also because the attendant cathodic reaction is the reduction of water ($2H_2O + 2e^- \rightarrow H_2 + 2OH^-$) – with no rate limitation from the requirement of oxygen, allowing corrosion to freely occur in the whole pH range below about 11 [2].

The susceptibility to corrosion of Mg has been documented for nearly a century [3], and to date, alloying additions and impurities have increased the corrosion of Mg [4–7]. The principal reasons include the formation of second phases that serve as intense local cathodes, driving anodic dissolution. In spite of the high reactivity of Mg, one salient feature of Mg is that it is an inherently poor cathode, with one of the lowest exchange current densities of all metals [8,9]. As such, even in the pure form, Mg is fortunate that its sluggish cathodic ability limits what could be significantly more rapid corrosion (which is indeed what occurs when Mg is alloyed or when impurities elements such as Cu, Fe and Ni exist). Limited solubility of most elements in Mg [10,11] makes it difficult to reach a critical alloying content to impart a stainless character

such as that in stainless steels, whereby the native oxide is replaced by that of a passive oxide (such as one based on Cr). Of the elements with a thermodynamic tendency to form oxides in preference to Mg, such elements are even more reactive and have equally wide pH windows of instability (such as Ca and Y) [12,13].

Recent work studying the corrosion of Mg in electrolytes containing soluble As species (arsenate) indicates an inhibition character capable of slowing the rate of Mg corrosion [14]. This was related to the ability of arsenate to serve as a poison for the cathodic reaction by inhibiting hydrogen atom recombination through the electrodeposition of elemental arsenic, As(0) at cathodic sites. This, in turn, retarded the dissolution of Mg significantly. Remarkably, the efficiency of arsenate was greatest at low pH, consistent with conditions favouring the deposition of As (0), while under neutral conditions, a mechanism of inhibition involving the formation of insoluble Mg-arsenate compounds predominated. Overall however, the remarkable corrosion inhibition from dissolved As was clear.

To date, the influence of metallic As upon the electrochemical and corrosion response of Mg remains unstudied. The work herein was designed to explore the ability of metallic As to impart corrosion protection to Mg similar to that of the case of As-species in solution.

2. Materials and methods

Pure metals were sourced from Alfa-Aeser (USA). The composition of the pure Mg and the Mg–As alloy were independently analysed using ICP-AES (Spectrometer Services, Australia).

The Mg–As alloy was produced by encapsulating Mg and As in a quartz tube. The tube was backfilled with high purity argon to avoid

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* Corresponding author. Tel.: +61 3 9905 4941; fax: +61 3 9905 4940.
E-mail address: nick.birbilis@monash.edu (N. Birbilis).

any reaction of the Mg with the atmosphere. As an extra precaution, to avoid reaction of any molten metal with the quartz itself, the tube was internally coated with graphite. The charge was held molten at 700 °C for 3 min, and periodically agitated to ensure mixing. The alloy was then left to cool in air, removed from the encapsulation, and tested in this condition.

Electrochemical testing was conducted using a Bio-logic VMP potentiostat. A three-electrode setup was employed using a PAR Flat Cell incorporating a saturated calomel reference electrode and Pt-mesh counter electrode. In all cases, the electrolyte was 0.1 M NaCl (pH 6). Potentiodynamic polarisation was carried out at a scan rate of 0.5 mV/s. Hydrogen collection was executed via an inverted funnel and burette assembly above the mass loss specimens. Nuances related to this method were outlined by Kirkland [15]. All reported tests were repeated a minimum of six times. SEM was conducted using a JEOL 7001 F.

3. Results and Discussion

The custom Mg–As alloy preparation methodology resulted in the successful formation of an Mg-0.37 wt.% As alloy (Fig. 1a). The alloy microstructure was comprised of the α-Mg matrix, and the presence of the Mg_3As_2 phase. This phase is the only intermetallic that forms between Mg and As for levels of As up to ~65 wt.% [10], and confirmed via EDX analysis.

Potentidynamic polarisation results contrasting pure Mg and Mg–As alloy reveal significant features that are atypical from all other reported polarisation data from Mg-alloys compared with pure Mg (Fig. 2). There are two significant features to note from the Fig. 2. The first is that cathodic reaction kinetics for Mg–As are lower than those of pure Mg. This feature is remarkable given that Mg is already a sluggish cathode, however the presence of alloyed As was able to effectively reduce the cathodic reaction rates. The corrosion potential of the Mg–As alloy is ~150 mV less noble than that of pure Mg, owing to the reduction in
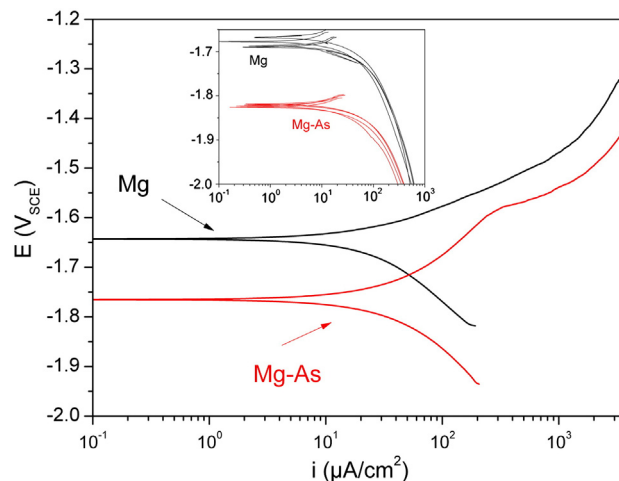

Fig. 2. Potentiodynamic polarisation curves for Mg and Mg-0.37 wt.% As (inset: replicate cathodic polarisation curves).

the rate of the cathodic reaction. To ensure that this finding was highly reproducible, a significant number of duplicate cathodic polarisation tests were conducted and shown in the inset of Fig. 2. It is therefore revealed that metallic As has a significant influence on the electrochemical response of Mg. The other feature of note in Fig. 2 is that the Mg–As alloy reveals somewhat of an inflexion in the current density at potential values of about $-1.65V_{SCE}$. This inflexion appears to be of the form of what is typically termed a breakdown potential, however such breakdown is usually reserved for passive system signalling the passive to active transition. In the case of Mg, any surface films are nominally only partially protective. In the case of Mg–As where the corrosion potential of the alloy has been suppressed, the revelation of a breakdown in the
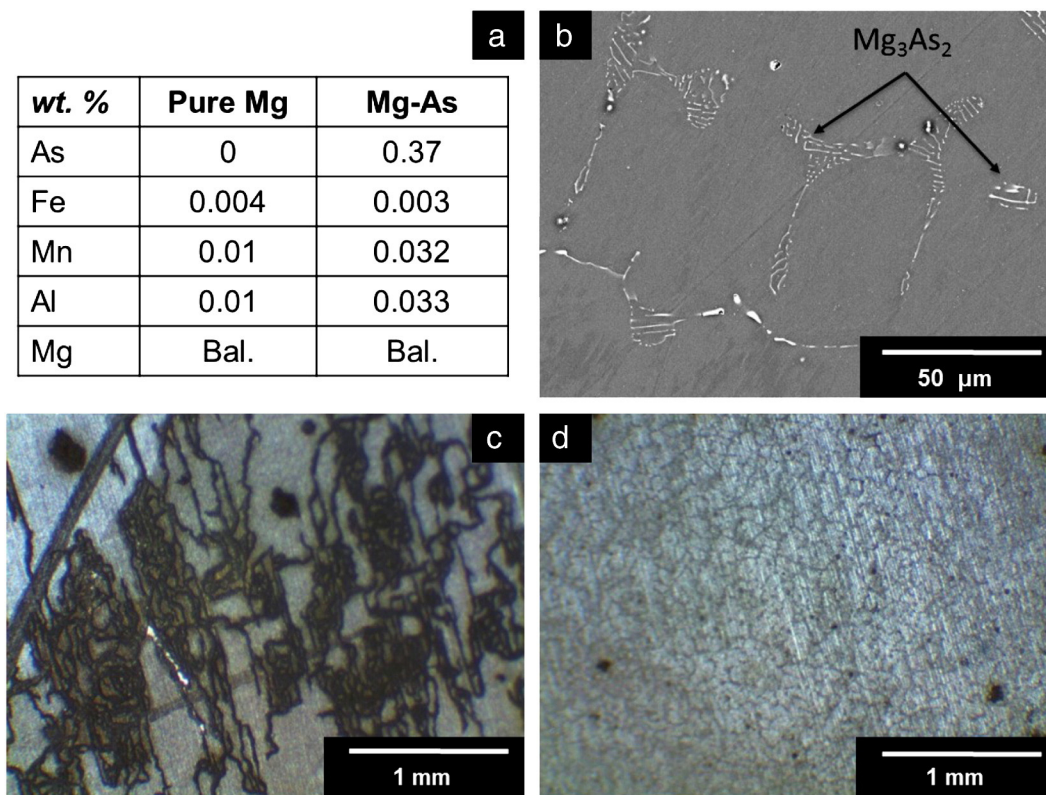

Fig. 1. a) Composition of alloys tested herein as measured using ICP-AES. b) Backscattered SEM image of Mg-0.37 wt.% As. c) Optical micrograph of pure Mg following 24 h immersion in 0.1 M NaCl. Filiform-like corrosion morphology is observed. d) Optical micrograph of Mg- 0.37 wt.% As following 24 h immersion in 0.1 M NaCl. Discrete corrosion sites observed with a substantial portion of the surface left un-attacked.

wt. %	Pure Mg	Mg-As
As	0	0.37
Fe	0.004	0.003
Mn	0.01	0.032
Al	0.01	0.033
Mg	Bal.	Bal.