



An innovative specimen configuration for the study of Mg corrosion

Zhiming Shi, Andrej Atrens*

The University of Queensland, Division of Materials, Brisbane, Qld 4072, Australia

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ABSTRACT

Based on an analysis of galvanic corrosion research, the research reported herein was formulated to examine the measurement of polarisation curves for Mg to develop a methodology whereby reliable polarisation curves can be measured for Mg. Cathodic polarisation curves were measured for high purity Mg in 3.5% NaCl saturated with $\text{Mg}(\text{OH})_2$ using three specimen types: (i) mounted specimens, (ii) specimens hung by fishing line and (iii) plug-in specimens. Cathodic polarisation curves were evaluated to yield the corrosion current density i_{corr} and the corresponding corrosion rate P_i , which was compared with the corrosion rate evaluated from hydrogen evolution measurements, P_H , and the corrosion rate evaluated by weight loss measurements, P_W . Mounted specimens produced values of corrosion rate, P_i , three times larger than values of corrosion rate, P_i , for plug-in specimens, attributed to crevice corrosion in the mounted specimens. Crevice corrosion in Mg is totally unexpected from prior research. The plug-in specimen configuration was designed to have no crevice and to allow simultaneous measurement of P_H and P_i ; P_i was consistently less than P_H and indicated an apparent valence for Mg of 1.45 in support of the Mg corrosion mechanism involving the uni-positive Mg^+ ion. The plug-in specimen has advantages for the study of Mg corrosion.

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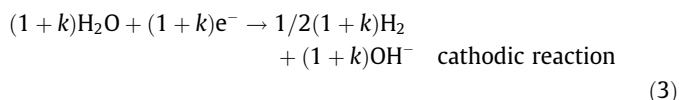
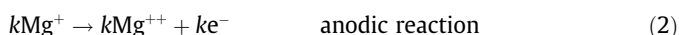
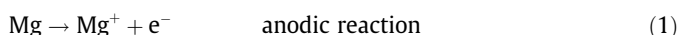
1. Introduction

1.1. Galvanic corrosion

This research is part of our effort to understand Mg corrosion, which has led to a number of reviews [1–6]. In our research on galvanic corrosion, Jia et al. [7–11] studied AZ91 (a typical Mg alloy) in contact with steel, and predicted the galvanic current by the boundary element method (BEM) model using as inputs the measured polarisation curves for AZ91D and steel. The galvanic current predicted by the BEM model was in good agreement with experimental measurements [7,8,10]. However, the experimentally measured galvanic corrosion rate was significantly higher than the galvanic corrosion rate predicted by the BEM model [11]. The excess corrosion rate corresponded to ~ 230 mm/year. The lack of agreement between the measured galvanic corrosion rate and the BEM model predictions, may be for the following reasons: (i) this may be another consequence of the uni-positive Mg^+ ion in the Mg corrosion mechanism, or (ii) this may be a consequence of the form of the corrosion (pitting, crevice corrosion, filiform corrosion, hydrogen evolution), or alternatively (iii) polarisation curves may not provide an adequate characterisation of Mg corrosion (i.e. an inappropriate input into the BEM model would lead to an inadequate BEM model prediction).

1.2. Uni-positive Mg^+ ion

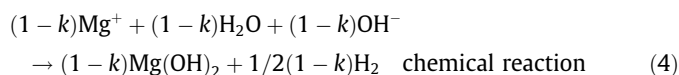
The existence of the uni-positive Mg^+ ion and its role in the Mg corrosion mechanism is still somewhat controversial. For example the existence of the uni-positive Mg^+ ion was disputed by the recent study of Swiatowska et al. [12]. Nevertheless, the following summary of the Mg corrosion mechanism [1,2,4,13–15] provides the best explanation of all the experimental data. Corrosion of Mg converts metallic Mg to the stable ion, Mg^{++} in two electrochemical steps, involving the uni-positive ion, Mg^+ , as a short-life intermediate, as given by Eqs. (1) and (2). These anodic partial reactions are balanced by the cathodic partial reaction of hydrogen evolution, Eq. (3):



The uni-positive ion, Mg^+ , is reactive and has an extremely short life (it has never been detected [2]), and can react chemically with water. Thus, a fraction, k , of the uni-positive Mg^+ , reacts electrochemically via Eq (2) to Mg^{++} , and the complement reacts chemically via Eq. (4):

* Corresponding author. Tel.: +61 7 3365 3748.

E-mail address: andrejs.atrens@uq.edu.au (A. Atrens).



The overall reaction is given by:



The corrosion of Mg is thus only partly electrochemical, and electrochemical measurements would be expected to predict a corrosion rate that is lower than the real corrosion rate as determined for example by weight loss, or hydrogen evolution. The apparent electrochemical valence is given by $(1 + k)$. Petty et al. [16] measured the apparent valence to be 1.50 in 150 g/L NaCl.

If this was the only important effect, electrochemical measurements should always under predict the actual corrosion rate by a constant fraction (which might depend on solution and Mg alloy). However, the measured corrosion rate in galvanic corrosion was not simply a constant factor greater than the galvanic corrosion rate predicted by the BEM model [11]. There must be at least one other factor.

1.3. Form of corrosion

We have carried out extensive studies of the corrosion of typical two-phase Mg alloys [17–29] because most Mg alloys contain two or more phases. This research can be summarised as showing that corrosion of a typical two-phase Mg alloy, in a typical environment like 3% NaCl, is characterised by heterogeneous corrosion. Corrosion typically initiates in the alpha-Mg phase next to an intermetallic particle, and corrosion of the alpha-Mg phase is accelerated by micro-galvanic coupling with the second phase particle acting as an efficient cathode and accelerating the corrosion of the alpha-Mg matrix.

Filiform corrosion has been observed on (un-coated) Mg [30,31], Mg–Al [32–34], Mg–Li [35], Mg–6Zn–1Y–0.6Zr [36], Mg–Zn–Y [37], Mg–Al–RE–Mn [38] and Mg–Y [20] in NaCl solutions.

The fact that the corrosion is heterogeneous should not invalidate an electrochemical measurement. The electrochemical rate measurement is a corrosion current density, which measures the number of electrons generated by a corroding surface per apparent unit area. This formally relates directly to the mass loss per unit area (i.e. number of Mg atoms leaving the metal surface), and to hydrogen generated per unit area (i.e. number of hydrogen atoms formed in the corrosion reaction, Eq. (5)). Each of these measurements typically provides an average over the whole apparent surface area and they should be formally equivalent. So the form of corrosion as heterogeneous corrosion is unlikely to be of fundamental concern and should not invalidate an electrochemical measurement.

However, an important factor may be the hydrogen evolved during the corrosion of Mg alloys as part of the cathodic reaction. Recent research [20], directly observing the corrosion of Mg–Y alloys, indicated that the evolved hydrogen could collect on the surface of the Mg alloy and appeared to be stuck on the surface. There was the appearance that such hydrogen bubbles would insulate the surface, however, the continued growth of these hydrogen bubbles indicated that corrosion continued beneath the bubbles.

Another factor may be the local electrochemical behaviour. The fundamental issue is the electrochemical behaviour driving the corrosion behaviour of the alpha-Mg matrix in a two-phase Mg alloy. Under free corrosion conditions, the second phase accelerates the corrosion of the alpha-Mg phase by micro-galvanic corrosion, and there is typically a driving force of about 300 mV driving the corrosion as measured by Song et al. [18] as the difference in corrosion potential of the alpha and beta phases in AZ91D. Is this electrochemical behaviour adequately captured in an electrochemical measurement? Can the applied potential over-ride the local poten-

tial, or is the local effect of the second phase overwhelming, so that the second phase causes self corrosion independent of an applied potential (or applied current)? It is indeed conceivable that, for a Mg sheet with a steel insert as studied by Jia et al. [11], the galvanic electrochemical potential imposed by the steel on the Mg becomes increasingly weak with increasing distance from the steel–Mg interface, and that at some distance away from the steel, the galvanic potential from the steel is so weak that it can no longer suppress the local corrosion processes and that there self corrosion becomes more important than galvanic corrosion.

In other words, self-corrosion may be particularly significant because of the micro-galvanic corrosion of two-phase Mg alloys, and the galvanic modelling may provide a significant underestimation for the corrosion of two-phase alloys particularly at some distance from the anode. If this is the important effect, how can it be taken into account in a BEM model? Maybe a deeper understanding of the electrochemical corrosion mechanism for two-phase Mg alloys would indeed be useful.

1.4. Polarisation curves

Polarisation curves may not provide an adequate characterisation of Mg corrosion. Their quality can be evaluated by their ability to correctly predict the corrosion rate by Tafel extrapolation. Shi et al. [39] examined the measurement of corrosion rates using Tafel extrapolation in the recent literature. The literature shows that, for Mg alloys, corrosion rates evaluated by Tafel extrapolation from polarisation curves have not agreed with corrosion rates evaluated from weight loss and hydrogen evolution. Typical deviations have been ~50% to 90%. These were much larger than the precision of the measurement methods and indicate a need for careful examination of the use of Tafel extrapolation for Mg. For research that nevertheless does use Tafel extrapolation to elucidate Mg corrosion associated with service conditions, it was strongly recommended that these corrosion rate measurements be complemented by the use of at least two of the three other simple corrosion rate measurement methods: (i) weight loss rate, (ii) hydrogen evolution rate and (iii) rate of Mg^{++} leaving the metal surface. There is much better insight for little additional effort.

A key finding by Shi et al. [39] was that there is a need for careful examination of the use of Tafel extrapolation for Mg. This implies that polarisation curves may not provide an adequate characterisation of Mg corrosion. Their use as inputs in a BEM model may lead to incorrect results. This is clearly important for numerical modelling of galvanic corrosion. It means that it is unclear what should be the inputs to the modelling or how the inputs should be measured.

1.5. Research aim and approach

The aim of the research reported herein was to examine the measurement of polarisation curves for Mg with a view to developing a methodology whereby reliable polarisation curves can be measured for Mg. The quality of a polarisation curve was evaluated by the ability of the polarisation curve to correctly predict the corrosion rate as measured by for example Tafel extrapolation. High purity (HP) Mg in 3.5% NaCl saturated with $\text{Mg}(\text{OH})_2$ was chosen as a model system to be studied. HP Mg is the simplest Mg alloy. 3.5% NaCl is typical of the solutions used to study the corrosion of Mg alloys for use in applications like automobile construction where it is important to consider corrosion by road salt and marine environments. The overall corrosion reaction, Eq. (5) leads to solution alkalinisation, and the surface of the corroding Mg alloy is thought to be in contact with a solution saturated with $\text{Mg}(\text{OH})_2$ [2].

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