Electrochimica Acta 121 (2014) 394–406

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Accurate Electrochemical Measurement of Magnesium Corrosion Rates; a Combined Impedance, Mass-Loss and Hydrogen Collection Study

A.D. King[a,*], N. Birbilis[a,b], J.R. Scully[a]

[a] Department of Materials Science and Engineering, University of Virginia, Charlottesville, VA, 22904. USA
[b] Department of Materials Engineering, Monash University, Clayton, VIC. 3800. Australia

ARTICLE INFO

Article history:
Received 23 September 2013
Received in revised form
20 December 2013
Accepted 23 December 2013
Available online 4 January 2014

Keywords:
Magnesium
Corrosion
Monitoring
Polarization
Hydrogen Collection
EIS.

ABSTRACT

Experiments were conducted to enable the simultaneous measurement of electrochemical impedance and collection of hydrogen gas during the corrosion of pure magnesium in NaCl solutions. These results were then assessed along with the attendant specimen mass loss, providing three unique measures of magnesium corrosion for the same specimen. It was determined that analysis of impedance data, while accounting for a physically justified inductive response at low frequencies, enabled the determination of the polarization resistance, R_P at the zero frequency limit. The determination of R_P, as evaluated herein from electrochemical testing, provided excellent correlation to the mass loss and volume of hydrogen collected. This finding is elaborated in a broader discussion that critically addresses previous studies which have utilized the impedance behavior of magnesium and which claim electrochemical tests may underestimate Mg corrosion when attempting to use a charge transfer resistance at intermediate frequencies.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The accurate determination of corrosion rates for magnesium (Mg) and its alloys is a technologically important issue, given the increasing usage of Mg in science and engineering applications [1]. Corrosion is a particularly important consideration for Mg, on the basis of its high reactivity. Therefore, assessing corrosion rate is critical for ensuring structural Mg alloys do not corrode at excessively rapid rates, to ensure that Mg in biomedical applications corrodes at specific rates [2], and to also evaluate the efficacy of corrosion protection strategies [3–10].

There are many reports of the determination of corrosion rate for high purity Mg and for most commercial Mg-alloys [11–20]. Tests can be classified as short term (such as potentiodynamic polarization or one-time electrochemical impedance spectroscopy, EIS), or as longer term (such as mass loss or hydrogen gas collection). Such methods have been applied to many metal systems for several decades, and the relative merits and demerits of the methods are well-established [21]. Perhaps the most obvious issue is that short-term experiments may not be indicative of long-term corrosion, and that long-term corrosion tests may require untenable test durations with respect to maintenance of constant test conditions. As such, there is a paucity of reports with correlation between short and long term testing–even for full immersion conditions. However in the case of Mg corrosion, the rapid corrosion rates nominally observed, allow for mass loss testing within relatively short time frames (often hours to days). Moreover, the fact that the electrode corrosion potential (« -1.0 V vs. SHE) is very electronegative with respect to the hydrogen evolution reaction also permits the collection of hydrogen for the assessment of the primary cathodic partial reaction.

There are further considerations that have been identified as important for the accurate determination of corrosion rate for Mg, and these factors vary from test to test, as noted by Kirkland [21]. Rather than review all the information in the relevant papers, the key points are mentioned here for context and motive for the current study. There can be no doubt that potentiodynamic polarization offers significant kinetic information, and is the only method which can reveal the relative anodic and cathodic contributions (and how these may vary from alloy to alloy) that lead to an instantaneous corrosion rate. The method, however, is short-term and destructive in nature. As such, whilst potentiodynamic polarization is indispensable in understanding the mechanistic origins of corrosion rate, it may not serve as a good index to long-term corrosion rates. Cao and Qiao [19,22] have claimed that potentiodynamic polarization is unsuited to Mg on the basis that the near

---

[*] Corresponding author. Tel.: +1 434 982 5465; fax: +1 434 982 5799.
E-mail address: adk3m@virginia.edu (A.D. King).

0013-4686/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.12.124

surface electrolyte and corroding surface itself is (very) dynamic in the case of Mg. During dissolution, the near surface pH can rise to alkaline levels (pH >10) for Mg, and the surface of Mg also displays enhanced catalytic activity (i.e. ability to support the cathodic reaction) as shown by independent works [23,24]. Therefore comparing an instant test to a long-term test is not valid as the electrolyte and relative rates of reaction have altered with time.

Many Mg corrosion studies employ the collection of gaseous hydrogen (H_2) on the basis that the primary cathodic reaction ($2H_2O + 2e^- \rightarrow 2OH^- + H_2$) is an index to the rate of anodic dissolution (where at open circuit, $I_{anodic} = I_{cathodic}$). As a standalone method, however, hydrogen collection is not without its shortcomings, given that (i) hydrogen collection may be inefficient in cases where experiment design is not ideal, (ii) the solubility of hydrogen in water varies significantly relative to sea level and temperature, and (iii) studies rarely pre-saturate the electrolyte with hydrogen. This latter point is imposed on essentially all the Mg corrosion studies reporting hydrogen collection to date [19,22]. Hydrogen collection alone has also been shown to be problematic on the basis that Mg dissolution also occurs in the 'cathodic regime' of Mg (below open circuit), and that hydrogen evolution persists in the 'anodic regime' of Mg (above open circuit). The latter effect has often been termed the negative difference effect (NDE), where an increase in anodic polarization of the metal results in an increase in H_2 gas production [25–28]. Despite a commonly postulated theory for this based on the purported existence of Mg^+, recent data eliminates the mechanism [23–25,29,30].

Specifically, the role of EIS used as a means for rationalizing the existence of Mg^+ is further critiqued below. EIS provides a means to determine the polarization resistance, R_P[31]. The corrosion rate of freely corroding metal in absence of coverage effects is inversely proportional to polarization resistance as described by the Stern-Geary relationship [31,32]:

$$j_{corr} = \frac{B}{R_p} = \frac{\beta_a \beta_c}{2.303 R_p \left(\beta_a + \beta_c\right)} \qquad (1)$$

Where β_a and β_c are the anodic and cathodic Tafel slopes (as described and qualified further below) [27,33,34]. The form of the Stern-Geary equation expressed in Equation 1 is not strictly correct in the case of voltage dependent coverage effects which affect the values of the term B in Equation 1, represented by the added terms in Equation 2 [31,35,36]. However, j_{corr} still depends strongly on R_p^{-1} and weakly on B (in brackets in Equation 2). R_p incorporates effects of coverage as expressed in Equation 2 at low frequency where coverage near E_{corr} can adjust to potential.

$$\frac{1}{R_P} = \frac{\partial I_{app}}{\partial E} = 2.303 I_{corr} \left[\left(\frac{1}{\beta_{a\theta(a)corr}} + \frac{1}{\beta_{c\theta(c)corr}} \right) + \left(\frac{1}{\theta_a}\frac{\partial \theta_a}{\partial E} - \frac{1}{\theta_c}\frac{\partial \theta_c}{\partial E} \right) \right] \qquad (2)$$

where θ_a and θ_c are the coverage of anodic and cathodic intermediates, respectively and $\beta_{a\theta(a)corr}$ is the Tafel slope at the coverage present at E_{corr}. R_P can be replaced by R_t when the coverage is frozen and the second term in the brackets on the right of Equation 2 is zero. The anodic charge consumed can then be estimated by integrating the EIS-estimated corrosion rate over the time of exposure, with knowledge of appropriate Tafel slopes with Equation 3 assuming the second term on the right of Equation 2 is negligible and β is evaluated near E_{corr}:

$$Q_a^{EIS} = \int j_{corr} \cdot A \cdot dt = \int \frac{\beta_a \beta_c A}{2.303 R_P (\beta_a + \beta_c)} dt \qquad (3)$$

Table 1
Composition of high purity Mg Rod (Alfa Aesar). All compositions reported in wt. %. Compositions provided by QUANT (Quality Analysis and Testing Corporation).

Element	Al	Fe	Cu	Zn	Mn	Ni	Zr	Mg
wt. %	0.02	0.008	0.003	0.03	<0.01	<0.001	<0.01	Bal.

The effective use of Equations 1, 2 and 3 implies that appropriate Tafel slopes of Mg[1] are used, with the values for Mg nominally within a rather well defined window on the basis that Mg is non-polarizable (anodically) resulting in low β_a values ($\leq$150 mV/decade), and that reports of β_c are nominally in the vicinity of ~ 200-300 mV/decade [19,22,24,25,37] (the anodic and cathodic Tafel slopes assumed in this study are listed in Table 4). As a result, the key variable of attention in Equations 1 and 2, for which the accurate determination is required, is R_P. In this regard, the issue of R_P determination merits comment in the context of Mg corrosion, since electrochemically determined values of corrosion rate based on EIS determined R_t using a charge transfer resistance at intermediate frequencies are regularly quoted as underestimating the corrosion rate [22,37]. Furthermore, on the basis of EIS determined R_t underestimating the corrosion rate as determined from other methods (mass loss or hydrogen collection), authors have previously used this as a means for rationalizing the purported existence of Mg^+[19,22]. In determining R_P, the use of an equivalent circuit to represent the impedance response is required. A survey of essentially every readily accessible report of EIS data for Mg (too many to individually cite) indicates that the electrochemical response usually displays inductive behavior with decreasing frequency [22,33,37–45]. In spite of many such papers showing the inductive response on Mg, a very small portion of papers actually acknowledge or attempt to explain the inductive response. The principal reasoning for the inductive response provided by the few papers which discuss it is adsorption of species [43,44], with no further comment or description of the precise species themselves. Interestingly, one recent study suggests interpretation of inductance seems to be rather complicated and is immaterial in studies of electrochemical corrosion, in which the kinetics information are estimated from the capacitive arc [46] (which we subsequently reveal to not be sound). Exceptions to this include a study from Baril [40], which ascribes the inductance to a process involving Mg^+. However, the paper itself has no validation or spectroscopic evidence for the existence of Mg^+, and refers back to the hypothesis of Song [33], which also presents no firm evidence for Mg^+. In light of the recent aforementioned works, a description on the basis of unipositive Mg cannot be supported.

The extraction of a meaningful R_P from EIS data mandates the inclusion of an inductor in any equivalent circuit as a prerequisite due to the inductive response observed on Mg. Many papers that report R_P for Mg or its alloys do not present the relevant or associated equivalent circuit, which makes the veracity of the data difficult to gauge; which should be borne in mind when the EIS determined corrosion rate is asserted to underestimate the true corrosion rate [22,37]. In fact, many such papers use R_t at intermediate frequencies while extraction of R_P requires the inclusion of the inductive data. The determination of R_P from systems displaying inductive behavior was previously given considerable attention in the Fe in acid system, which also indicated some of the foundations for the assessment of impedance data [47–50]. Of those works, the corresponding mass loss was determined using either atomic adsorption or gravimetric methods to unequivocally relate the actual corrosion with the EIS determined corrosion rate [48].

---

[1] Coverage complicates determination of β_a and β_c but R_P is determined at the low frequency limit.

Download English Version:

https://daneshyari.com/en/article/186576

Download Persian Version:

https://daneshyari.com/article/186576

Daneshyari.com