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Short communication

Investigating ion release using inline ICP during in situ scratch testing of an Mg-Li(-Al-Y-Zr) alloy

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ABSTRACT

An electrochemical flow cell was constructed to permit the application of a mechanical scratch to the exposed material while monitoring the open circuit dissolution rates of the elemental alloy components. Elemental dissolution rates were determined where measured downstream using inductively coupled plasma atomic emission spectrometry (ICP-AES). The technique is demonstrated with Mg-Li(-Al-Y-Zr) alloy exposed to 0.01 M NaCl. A mechanical scratch was applied manually using a non-conductive and non-contaminating sapphire lancet without interrupting the on-line measurement. The ion dissolution rate from the newly exposed surface was significantly higher than the dissolution rate from the remaining surface area, corresponding to a high local current density. Notably, the increase in the dissolution rate from the scratched area occurred gradually after the scratch; then subsided within 200 s after the scratch, indicating that this particular Mg-alloy can repassivate by the formation of a surface film after a scratch was applied. This is the first reported use of an in situ scratch cell coupled with ICP-AES.

1. Introduction

The magnesium-lithium (Mg-Li) alloys are ductile, ultra-lightweight alloys which are promising in many critical structural applications [1–3]. By appropriate alloy design and processing, Mg-Li alloys can also achieve high specific strength, high elastic modulus, and low anisotropy [4–6]. The addition of Li has also been reported to be beneficial to the corrosion resistance of Mg alloys when Li addition exceed ~10.3 wt% to ensure the formation of a single-phase body centred cubic (bcc) matrix [7,8]. To date, the mechanisms for the improvement of corrosion resistance on the bcc Mg-Li alloys are still not yet fully elucidated. In the work of Xu et al. [7], who developed the bcc Mg-Li(-Al-Y-Zr) alloy system, the formation of a protective Li_2CO_3 surface film was proposed to be the main reason for the improvement in corrosion resistance. This surface film was suggested to be similar to a passive film which can heal quickly after damage. The subsequent work of Hou et al. [9] suggested the film on the Mg-Li(-Al-Y-Zr) alloy surface was dynamically formed, unlike a conventional passive film that is thermodynamically stable, it was suggested a Li_2CO_3 surface film forms as a result of alloy dissolution and critical surface enrichment of Li. Aside from a small number of studies, most of which have studied Mg-Li surface films developed in air [7,10,11], detailed research regarding the structure and formation process of the surface film on Mg-Li alloys is scarce; in particular, the surface dissolution and film formation following damage of the Mg-Li alloy surface has not been studied.

The measurement of current transients has been widely used to study the pitting process in passivating alloys. To study the repassivation process, fresh surfaces have been exposed using abrading techniques or scratching in situ, and the electrochemical response recorded [12–15]. However, such methods have not been applied to Mg alloys on the basis that Mg alloys do not typically passivate, and therefore, are unable to repassivate. Moreover, the measurement of current transients only provides information regarding the dissolution current, where the specific elements dissolved cannot be monitored. To solve the issue of monitoring elemental dissolution in real time, the atomic emission spectroelectrochemistry (AESEC) method was developed, consisting of a flow cell coupled downstream to inductively coupled plasma atomic emission spectrometry (ICP-AES). The AESEC method has proved to be

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very efficient in accurately determining the multi-elemental dissolution profile of alloy surfaces in real time [16,17]. The AESEC method has been successfully applied to monitor the ion release and film formation process for Mg alloys [18–23]. In the study of Hou et al. [9] the ion release from a bcc Mg-Li(-Al-Y-Zr) alloy in 0.01 M NaCl was recorded using the AESEC method (via downstream ion detection using online inductively coupled plasma – mass spectroscopy). An Mg:Li ion release ratio of ~3.2:1 from the Mg-Li(-Al-Y-Zr) surface was reported while the compositional ratio (in atomic percent) of Mg:Li is ~2:1. It was proposed that the higher Mg:Li release ratio to the compositional ratio might indicate the formation of a Li-containing surface film. However, owing to the design of the electrochemical flow cell utilised in the study by Hou et al. [9], the possible repassivation process cannot be assessed by the abrading techniques or scratching (as the flow cell was enclosed), and a deeper understanding that may arise from in situ study of dissolution ratios in response to a surface scratch and the possibility of retarding dissolution via a repassivation process could not be monitored. Herein, a modified electrochemical flow cell was designed, which enabled a mechanical scratch to be applied to the sample surface without interrupting the AESEC measurement. The re-passivation process of the exposed surface created by the scratch on a bcc Mg-Li(-Al-Y-Zr) sample was monitored. The scratched surface area was estimated and the ion release from the freshly exposed surface created by the applied scratch was determined.

2. Experimental

2.1. Materials

A bcc Mg-Li(-Al-Y-Zr) alloy with the composition of Mg - 30.3% Li - 2.34% Al - 0.128% Y and 0.039% Zr (at.%) was used in this study. The alloy was prepared by casting, extrusion, cold rolling and solution heat treating at 380 °C for 5 min, as described elsewhere [7]. The solution treated samples were quenched then aged at 70 °C for 3 h and then cold rolled into sheet with a final thickness of 1 mm. The rolled sheets were stored at room temperature in a desiccator for 12 months then cut into smaller test samples with the size of 30 mm × 20 mm × 1 mm. The test samples were mechanically ground to a 2000 grit finishing using silicon carbide (SiC) paper under ethanol.

2.2. In situ scratch - AESEC method

The schematic of the electrochemical flow cell system is shown in Fig. 1.

The test solution was driven through an electrochemical flow cell with an opening to allow manual scratching of the specimen surface. The total exposed surface area was about 0.52 cm^2 defined by the O-ring (Fig. 2). Two peristaltic pumps were carefully calibrated before the test to make sure the flow rate difference was balanced so that no excessive accumulation or depletion of test solution would occur in the open cell during the AESEC test period. A sapphire lancet (deliberately non-metallic and non-conducting) was inserted into the 8 mm × 1 mm open slot to perform an in situ scratch on the test sample (working electrode) surface. Such a scratching procedure nominally lasted for a duration of ~1 s. The reference electrode was placed in a salt bridge downstream from the working electrode compartment (Fig. 2). The salt bridge consists of an upper part where the Ag/AgCl reference electrode was located and a lower part where the test solution passed through. The upper part and lower part of the salt bridge were separated by a cellulose dialysis membrane (Zellu Trans/Roth).

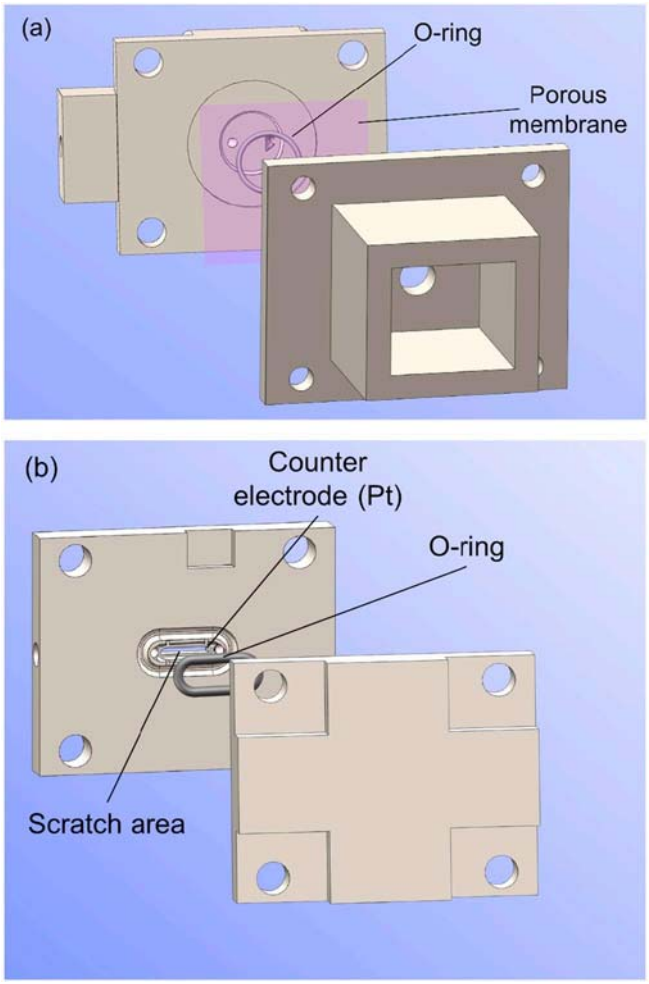

Fig. 2. Schematic representation of (a) the salt bridge and (b) the scratch cell used for the in situ scratch - AESEC test.

2.3. ICP-AES

The emission intensities of Mg (279.55 nm), Li (670.78 nm), Y and Al were monitored as a function of time with a data acquisition rate of 1 point per second. The instantaneous elemental concentrations, C_M, were calculated from the emission intensities using standard ICP-AES calibration techniques. The potential of the test sample monitored by a Gamry Reference 600 potentiostat simultaneously. Dissolution rates of

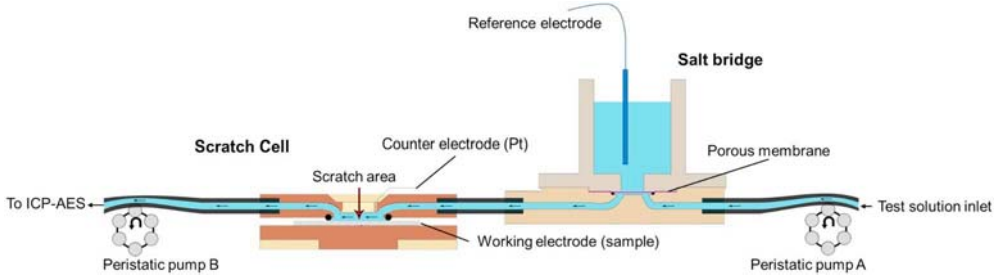

Fig. 1. Experimental setup for the in situ scratch - AESEC test. The electrochemical flow cell system includes an open cell for scratching the sample and a salt bridge to house the reference electrode. This setup is capable of performing polarisation testing. However, in the present study, only open circuit exposure was performed, and the counter electrode was not used.

metal ν_M were calculated from the downstream concentration as:

$$\nu_M = \not{f}\, C_M \quad (1)$$

where $\not{f}$ is the flow rate of the electrolyte through the cell. The dissolution rates may also be expressed as equivalent current and current densities by application of Faraday's law to Eq. (1).

A test solution of 0.01 M NaCl with pH 6.8 passed through the cell with a flow rate of 3 ml/min. The sample was exposed in the test solution for 30 min. After about 750 s of immersion, a scratch was applied to the sample surface using a sapphire lancet. The release rate of Mg and Li was recorded by ICP-AES during the entire exposure.

In a separate calibration experiment, the residence time distribution (RTD) for the flow cell system was obtained by measuring the Cu dissolution rate as a function of time following application of a 1 mA, 1 s anodic pulse to a 99.9% Cu electrode in 1 M HCl. The methodology has been described in previous publications [17,24]. The RTD revealed a broad maximum between 47 and 62 s with a 95% elution at 124 s.

3. Results and discussion

The typical dissolution profile for a scratch experiment is presented in Fig. 3.

This figure shows the open circuit potential, the Mg:Li ratio, the total ICP determined dissolution current $i_{total,\ ICP}$ and the Mg and Li dissolution rates as a function of time. No measurable dissolution of the minor alloying additions Y or Al was detected. From these results, it can be observed that Li was actively dissolved when the sample was first in contact with the test solution. The dissolution of Li however decreased rather significantly, reaching a relatively stable rate after about 250 s of immersion. The dissolution of Mg increased slightly during the first 100 s of contact with the test solution, then decreased steadily.

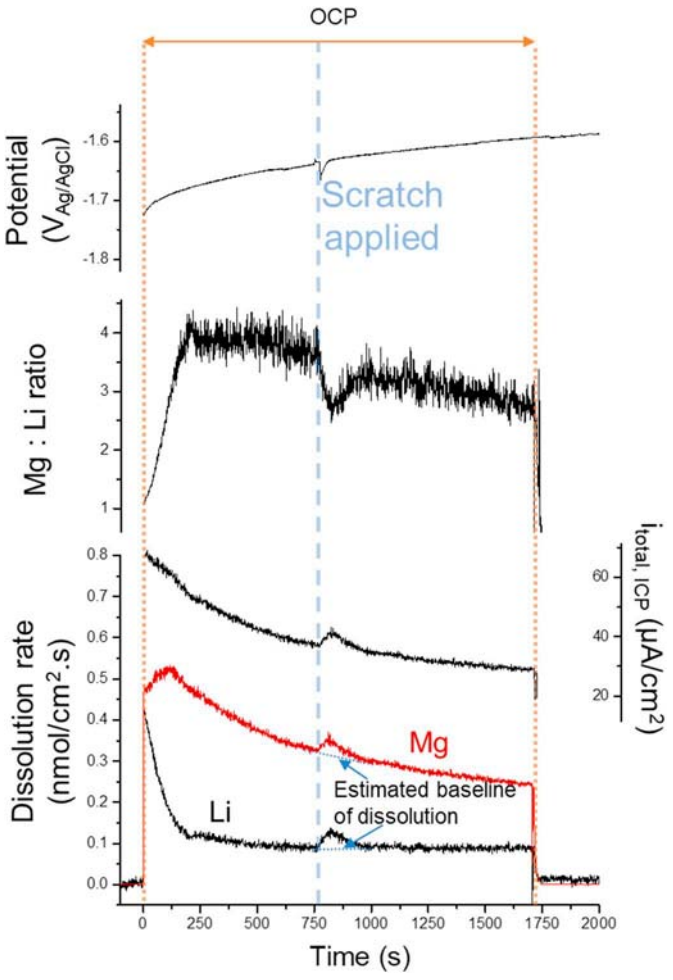

Fig. 3. The ion dissolution rate, total ICP determined dissolution current $i_{total,\ ICP}$, Mg:Li ratio and measured potential of an Mg-Li(-Al-Y-Zr) sample during an in situ scratch - AESEC test in 0.01 M NaCl (pH 6.7) at 25 °C.

The equivalent dissolution current density was calculated from the sum of the Mg and Li dissolution rates shown in Fig. 3 normalised to the geometrical surface area. A relatively high dissolution current density $i_{total,\ ICP}$ of about 65 μA/cm^2 was observed at the beginning of immersion. However, the $i_{total,\ ICP}$ decreased during the test and reached about 30 μA/cm^2 after 1700 s of immersion and continued to slowly decrease. Unlike the increasing dissolution rate in other Mg alloys [18], the decrease in the dissolution rate in the Mg-Li(-Al-Y-Zr) alloy indicates a difference in the controlling mechanisms of the corrosion process.

A mechanical scratch was applied in situ to the sample surface after about ~750 s of immersion to locally expose the bare alloy surface. After the scratch, the dissolution rates of Mg and Li increased significantly and then returned to the original pre-scratch value. The dissolution transients correlated with a similar transient drop in E_{oc} followed by a slow return to the original value. The E_{OC} decreased sharply after the scratch then recovered to the original level in about 50 s. In about 20 s after the potential recovered to the original level, the dissolution current started to decrease. The overall behaviour was consistent with an immediate reaction of the exposed surface followed by repassivation.

The dissolution transient was small as compared to the background dissolution rate in Fig. 3, due to the small surface area exposed by the scratch. The approximate area was estimated at 0.66 mm^2 determined from optical images of the sample surface after immersion (Fig. 4a) and assuming a semicircular profile (Fig. 4b) with $S = d\pi L/2 \approx 0.66$ mm^2 where the width (d) and the length (L) are defined in the respective figure.

To determine the dissolution created by the scratched area, a baseline of the open circuit dissolution from the unperturbed surface was estimated as shown in Fig. 3. The scratch was applied after about 750 s of immersion and the excessive ion release event subsided after about 950 s of immersion. Therefore, the baseline was obtained by drawing a line between the starting point and the ending point of the ion release event, assuming a steady decrease of ion release throughout the small interval. The starting point and ending point were obtained by getting the average value of ion dissolution from 700 s to 750 s of immersion and from 950 s to 1000 s of immersion respectively. In this way the scratch induced dissolution rate and dissolution current density was extracted from the dissolution profile of Fig. 3 as shown in Fig. 5. A large current density increase occurred at the scratch site and the ion dissolutions per unit area were much greater than the ion dissolution from the other area of the surface. The maximum dissolution current density at the scratch site reached about 600 μA/cm^2, about 10 times higher than the maximum rate observed shortly after the electrolyte contacted the sample. Further, the freshly exposed material also displayed selective dissolution of Li with a Mg:Li of 1:1 as was observed in the early stages of the experiment – consistent with excess Li dissolution relative to the alloy stoichiometry.

The residence time distribution (RTD) is shown superimposed on the kinetic data in Fig. 5 as a dashed curve. The similarity of the scratch results and the RTD demonstrate that the form of the dissolution profile is indistinguishable from that of a single pulse of dissolution, that is to say that the true scratch induced Mg dissolution rate transient is below the time resolution of the system. Therefore, the initial rate of dissolution may be much more intense than estimated above, and the repassivation time much more rapid.

4. Conclusion

The repassivation process of an Mg-Li(-Al-Y-Zr) alloy was monitored in 0.01 M NaCl using AESEC with a unique electrochemical flow cell

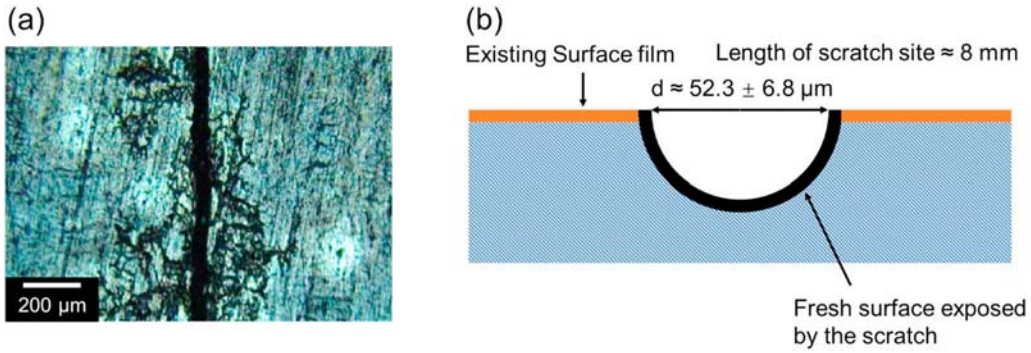

Fig. 4. (a) The optical image of the scratch site after immersion; (b) the schematic that shows the estimated size of the scratch site.

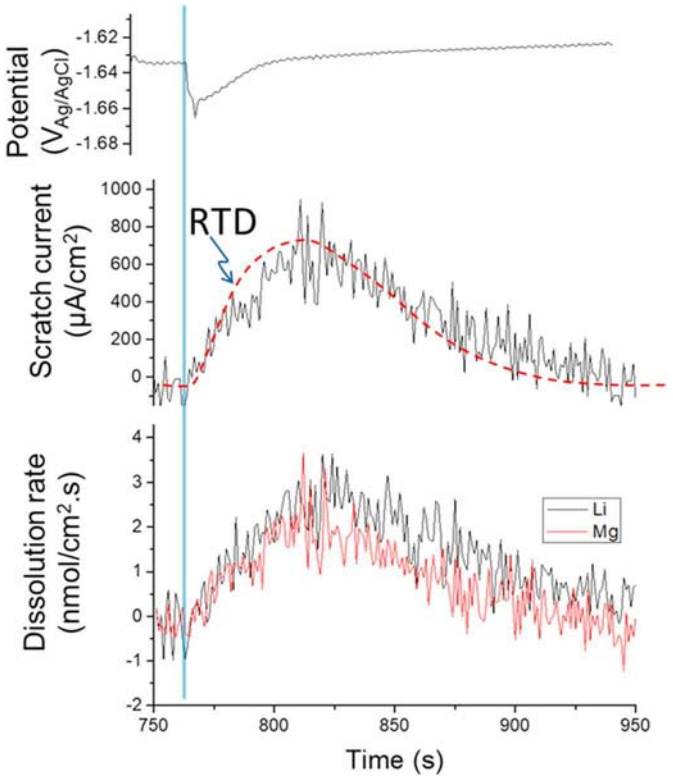

Fig. 5. Potential, calculated scratch current and calculated ion dissolution from the freshly exposed surface created by the in situ scratch. RTD is shown as the dashed curve in red. The scratch current was calculated according to the calculated ion dissolutions which were obtained by extracting the estimated baseline from the dissolution rate in Fig. 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

that permitted in situ scratching. It was shown that active dissolution occurred at the scratch site, consistent with selective Li dissolution as evidenced by an Mg:Li ratio of ~1:1, obtained for the scratch dissolution transient – as opposed to an Mg:Li ratio of ~2:1 for the alloy stoichiometry. The excessive (active) dissolution from the scratch site subsided within ~200 s, indicating repassivation. This study is the first to characterise the in situ repassivation process using AESEC, noting that such processes are able to be studied in the absence of an applied polarisation, and in real time. These results confirm that surface dissolution can be suppressed quickly after damage which is consistent with the notion that a so-called self-healing, protective film can form on Mg-Li alloys in aqueous solution.

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