Nuclear Microprobe Analysis for Determination of Element Enrichment Following Magnesium Dissolution

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Surface enrichment of parts-per-million-level impurity elements during magnesium dissolution is of interest in the context of structural materials and battery electrodes. Particle induced X-ray emission (PIXE) measurements were performed on pure magnesium using a nuclear microprobe instrument with high sensitivity for trace elements. PIXE was capable of performing trace analysis, revealing surface enrichment of Fe, Cu, Mn, Pb, As and Zn, indicating that magnesium displays incongruent dissolution accompanied by impurity enrichment as a result of dissolution. The concentration of surface impurities was shown to appreciably increase after modest anodic dissolution corresponding to only 1.2 C/cm². It was revealed however, that the enrichment efficiency was low, at < 1%.

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With significant increases in the production and utility of magnesium (Mg) in the past decade, Mg-alloys remain an attractive material for weight reduction in several industries,1 in addition to substantial exploration as electrode materials in primary and secondary batteries.2,3 In such cases, the unambiguous determination of factors that play a role in corrosion/electrochemistry of Mg are of critical importance.

The influence of impurities on the corrosion of Mg has been well documented since the early 20th century,4 with tolerance limits for a number of elements in Mg proposed.5 In particular, the influence of deliberate alloying additions of low levels of transition metals (iron, manganese and zirconium) on corrosion of Mg have been documented by systematic studies.6 Furthermore, the comparison of the electrochemistry of pure Mg specimens with low (at commercial levels of ∼40 ppmw) and ultra low levels (< 1 ppmw) of Fe were also recently presented.7 Such studies add to the evidence that impurity elements, nominally of low solubility,8–10 influence the corrosion electrochemistry of Mg. In spite of this, at least two key aspects with respect to the in-service performance of Mg remain under researched. The first of these includes the detection and analysis of impurity elements on the Mg surface, and the study of possible enrichment of impurity elements on Mg during dissolution; both aspects are worthy of elaboration.

Regarding the analysis of impurity elements on Mg surfaces, this is a particularly challenging task for the common methods nominally used in corrosion related works. Nominally, impurity concentrations are in the parts per million range. For example, commercial purity Mg will nominally contain < 100 ppmw Fe, which is below < 0.01% on the basis of weight %, and even lower on the basis of atom %.

The analysis of such low levels of Fe with accuracy is not readily possible by methods such as X-ray photoelectron spectroscopy or Auger electron spectroscopy, which require concentrations approaching 1% (which is ∼100 times larger than the typical Fe impurity content) for accurate detection. Similarly, the signal to noise ratio, and large interaction volume, from energy dispersive X-ray spectroscopy are also prohibitive. In fact, even imaging of, and evidence of, impurity Fe (which is known to be present from ICP analysis of chemically dissolved metals) using Field Emission Gun-Scanning Electron Microscopy (FEG-SEM) is elusive. Site-specific Transmission Electron Microscopy (TEM) specimens as prepared by focused ion beam milling have indicated that it is potentially possible to observe impurities visually, on the fine nanoscale.11 However, the area of surface surveyed by such a method remains very small and not representative of the overall surface evolution which regulates electrochemical behavior. Most recently however, it was shown by Rutherford Backscattering Spectroscopy (RBS), that impurity elements could be detected on the Mg surface,12 with high (parts per million) sensitivity. In this vein, it is clear that specialized methods are essential for the requisite analysis of the Mg surface (or near surface) chemistry. Herein, a specific analysis method that also (like RBS) employs the nuclear microprobe, known as particle induced X-ray emission (PIXE), was explored. In particular, the PIXE method was used for its ability to quantitatively analyse and distinguish transition elements from each other, which includes a large number of elements of interest, including analysis at the trace level (i.e. ppm level).13 This was a potential shortcoming in the RBS study since transition elements of similar atomic mass may be difficult to distinguish depending on kinematic factors.12 A major advantage of ion induced X-ray analysis is reduced background relative to that of electrons; further, the ability to exploit the sensitivity of PIXE is sought in this application in order to determine the possible enrichment of impurity elements in the vicinity of the Mg surface, arising from anodic dissolution.

In the context of analysis of impurity enrichment and its evolution with Mg dissolution, it is important to elucidate if Mg undergoes incongruent dissolution. In fact, incongruent dissolution may be rationally expected on the basis that the potential of Mg when polarized to currents up to hundreds of mA/cm², remains ≪ −1V\textsubscript{SHE}.14 Such a potential is well below the oxidation potential of the impurity elements anticipated to populate Mg (including Fe), unlike enrichment in Al alloys, complexion and surface curvature effects cannot be used to rationalize oxidation at otherwise large underpotentials and therefore such elements may accumulate on the Mg surface.

Recently it was proposed by Frankel et al.15 that the exchange current density for the hydrogen evolution reaction, HER, increases as the rate of dissolution increases for pure Mg. This would result from increased catalytic activity on the Mg anode, which has now been well documented by various independent tests.15,16 The physical origins of such enhanced catalytic activity have not been fully elucidated as yet, although factors that may contribute to catalytic activity would include the surface enrichment of impurities or incongruent dissolution allowing noble metal accumulation, if the enrichment does indeed occur.
Experimental

Materials and sample preparation.— High purity Mg used in this investigation (AmaC alloys, Croydon South, VIC, Australia). From independent ICP analysis (Spectrometer Services, Coburg, VIC, Australia), the impurity Fe concentration was determined to be approximately 5 ppm, where ppm refers to ppm atoms. For all descriptions and discussions in the remainder of this work, ppm refers to ppm atoms. The Mg samples were successively ground to a 4000 grit SiC finish using ethanol as lubricant. Sample surfaces were cleaned with ethanol and dried using compressed air after each grinding step.

Electrochemical methods.— Anodic electrochemical dissolution was performed using a three electrode flat cell (Princeton Applied Research) with a platinum mesh counter electrode and saturated calomel reference electrode (SCE). The cell provided an exposed area of 1 cm², and a Biologic VMP3 potentiostat was used to apply a galvanostatic signal for 2 minutes (at current densities as specified in Table I). The electrolyte was 0.1 M NaCl prepared using 18.2 MΩ deionized water at 25°C; the initial pH of the electrolyte was adjusted to pH 3 using HCl. The reason for this was to avoid the generation of thick surface films (such as magnesium hydroxide, Mg(OH)₂). By employing an acidified electrolyte, surface films were largely soluble for the period of anodization, and the specimen surfaces were analyzed without the need for cleaning post dissolution.

Nuclear microprobe analysis.— The as-prepared and electrochemically dissolved pure Mg samples were loaded into the CSIRO Nuclear Microprobe (NMP) chamber and exposed to a focused 3.0 MeV proton beam from the University of Melbourne Pelletron accelerator. Micro-PIXE induced X-ray emission measurements were performed over a 200 × 200 μm area, employing a 2 μm beam spot with a current ranging between 0.3 to 0.5 nA. The charge applied in each scan was 10 μC. A 250 μm Be filter placed on the face of a Canberra Hyper-pure germanium (Ge) X-ray detector mounted at 45 degrees to the incident beam was used to limit the high count rate from the Mg host. For all analyses, the MicrolabQ system was used to collect dead-time corrected image data. Post data collection analysis was performed using the GeoPIXE software suite, the complex details of which are reported elsewhere by Ryan et al.

Results and Discussion

The utility of PIXE has been previously exploited in several studies to quantify the near surface composition of alloys, which includes the composition of the surface and a volume incorporating a relevant subsurface depth. For example, Boag et al. successfully employed PIXE to investigate the corrosion process and pitting in the aerospace alloy AA2024-T3 and its relationship to the presence of inter-metallic inclusions. For the Mg alloy examined here, the need for a trace level detection limit or Minimum Detection Limit (MDL) of the order of a part per million (ppm) across the scan area and reacted depth requires reducing the Mg X-ray count rate, so as to not saturate detector electronics. This allows the detector time to detect x-rays from minor and trace levels which is an advantage over RBS. As with previous reports of PIXE experiments, a Be filter was employed to limit counts from the light host whilst achieving an excellent detection limit for elements heavier than Mg. The raw data showing the PIXE spectra collected from all three samples investigated here are given in Figure 1.

There are several key features in the PIXE spectra. As with the better-known Energy Dispersive X-ray (EDX) spectroscopy technique on an electron probe, we see that this form of spectroscopy results in unique elemental signature peaks with high signal-to-noise ratios (SNR) for the elements of interest, which includes transition metals other than Mg. These high SNR’s once quantified result in sub ppm Minimum Detection Limits (MDL) and less than 10 ppm MDL’s for a bulk and enriched surface layered sample, respectively. These figures of merit are orders of magnitude better than EDX, due to the much lower contributions to background, revealing PIXE to be ideal for the task at hand. The data herein were analyzed using the GeoPIXE software suite developed at CSIRO for the quantitative fitting of PIXE spectra.

The GeoPIXE analysis of the three spectra displayed in Figure 1 results in the tabulated data shown in Table I.
The data contributing to Table I were analyzed on the basis that the volume of material being investigated was that of the spatial probe (in the x-y dimensions) and an inward zone incorporating the surface and a penetration of 2 μm in thickness. The analysis of 2 μm was selected on the basis of SEM analysis that revealed surface disruption from the electrochemical dissolution was confined to this thickness, which also includes a thin oxide/hydroxide and surface roughening. Dissolution was also localized, so analysis of a volume which leads to an average near surface composition was considered most relevant to the task at hand. As such, the value of 2 μm was utilized in the PIXE yield model to calculate an average elemental concentration within that zone, assuming a near zero contribution to trace level concentrations from below it (i.e., a homogeneous substrate). With this assumption, data analysis provides the quantified results that are presented in Figure 2.

Analysis reveals that the ‘as prepared’ near-surface (denoted as 0 mA/cm², i.e. unpolarized) displays an average Fe content of 4.1 ppm (which is equivalent to 0.0004 at.%), concomitant with what is defined as high purity Mg and very similar to the bulk value determined from ICP analysis. We also note that ready detection of Mn at ~27 ppm and Zn at ~20 ppm, indicating both of these to be present in the vicinity of the near surface (as also labelled on Figure 1). Traces were detected of Cu (0.7 ppm), Pb (2.1 ppm) and As (0.3 ppm).

Following anodic treatment at 2 mA/cm² for 2 mins (providing a total anodic charge of 0.24 C/cm²), we observe an increase in all of the impurity elements detected, signifying an impurity increase. The change in the measured surface impurity content for all of Fe, Mn and Zn, was increased by a factor of approximately 20 (Table I), with this increase and its uniformity across the elements being statistically relevant.

We also note that, due to the anodic treatment, the presence of trace levels of Cu, Pb and As have emerged to be significant. It appears that the anodic treatment resulted in enrichment of such elements, namely Pb and As, revealing that elements not previously considered as near surface impurities may indeed become present at the near-surface due to incongruent Mg dissolution.

Prior to discussing the characteristics of impurity enrichment, we will also present the near-surface composition following anodic treatment at 10 mA/cm² for 2 mins (which corresponds to an anodic charge of 1.20 C/cm²). In the case of the impurity levels measured following the higher current 10 mA/cm² two treatment, impurities were increased by approximately 50% further than the values determined from comparison to the 2 mA/cm² treatment. Analysis suggests that the measured impurity increase may not necessarily be monotonic with applied charge, and this is indicated in Figure 2 (which we elaborate further below).

In the case of the higher current treatment (1.20 C/cm²) we also note that the Pb and Cu levels (which have notably emerged following dissolution) also increased, which supports that their presence is indeed real, and significant. Also, in a similar vein to the emergence of Pb and Cu following dissolution, we now see that impurity As is readily detected at the Mg surface. Again, the dissolution was able to enrich elements that were originally at low levels (viz. below 1 ppm million atoms), to concentrations a factor of 20 greater. It also merits comment that, whilst not reported in Table I, we detected that CI was present upon the Mg surface at a concentration of 0 ppm for the ‘as prepared’ surface, and ~1080 and ~1510 ppm after the 2mA/cm² and 10mA/cm² treatments, respectively.

The simplest means to interpret the dissolution related impurity enrichment is via the graphical presentation in Figure 2. Across all elements, an enrichment trend is observed. However, enrichment is clear and unambiguously shown by PIXE, which reveals that Mg dissolves incongruently from analysis of a near surface volume; the extent of enrichment relative to the applied charge was perhaps not as expected. Very recently, Thomas and Lynse considered theoretical levels of Fe impurity enrichment during Mg dissolution.21 The theoretical calculation was not however benchmarked by experiments such as those herein. We note that for the conditions of anodizing herein, the potential realized due to anodic galvanostatic polarization remained in the vicinity of ~1.45 V_{SCE} to ~1.5 V_{SCE}, without accounting for ohmic drop (such that the actual surface potential is thus even lower). The Thomas-Lynse model made a reasonable assumption that during Mg dissolution, if a monolayer of Mg atoms consists of X ppm Fe, then once enough anodic charge has been passed to dissolve the monolayer and expose the underlying monolayer, then the ‘new’ impurity concentration, if full enrichment efficiency is observed, is 2 × X ppm Fe (and so on, with the number of monolayers scaling with applied anodic charge). If full efficiency was therefore observed, the expected impurity concentration one may expect to measure is depicted in Table I, corresponding to the thousands of ppm range. Clearly, therefore, 100% enrichment efficiency was not observed herein. The comparison between the actual (PIXE determined) and theoretical enrichment indicates a practical enrichment of ~5.5% (for the 2 mA/cm² polarization), which evolved to of ~1.5%.
(for the 10 mA/cm² polarization). This ultimately translates to approximately 1.5 per 1000 impurity atoms accumulating or enriching. The independent ‘electrochemical’ analysis by Lysne et al., which employed comparing the theoretical enrichment with Mg-Fe alloys of known (cast-in) Fe content, suggested that the enrichment efficiency was in the range of ~0.2%, which is low, and consistent with the work herein. The Fe enrichment efficiency values from Lysne et al. are in fact lower than those herein, which may be a result of the larger anodic charge realized in that work (where we may speculate from the work herein that enrichment efficiency decreases with increasing anodic charge passed, albeit with the data presented herein is limited). Such low enrichment efficiency is also concomitant with calculations from the work of Cain et al. studied Mg surfaces using RBS. The Cain work when analyzed by the impurity enrichment efficiency calculation method put forth by Lysne et al. revealed an enrichment efficiency of only ~0.2%. The work herein is unable to indicate the fate of the Fe not detected at the near-surface, however it should be noted that an assumption of the model used to calculate enrichment efficiency is that all Fe is available for accumulation. Factors that may influence this assumption include that Fe is not present as unique atoms, but perhaps as discrete Fe ‘particles’, with such Fe-particles requiring the need for a critical level of dissolution to expose them, or if such particles are exposed, the possibility of being dislodged.

The work herein presents key physical information regarding the evolution of the near-surface composition, and is significant in terms of understanding the dissolution of Mg in the context of either an anode (sacrificial, or battery) or a corroding metal. To this end PIXE has been shown to be of significant utility for such analysis of Mg. The revelations herein have ramifications in the utility of Mg, and also in the clarification of factors contributing to the enhanced catalytic response of Mg, where it can be stated that enrichment does occur, but in the clarification of factors contributing to the enhanced catalytic activity herein have ramifications in the utility of Mg, and also of understanding the dissolution of Mg under anodic polarization. The implications of this are general, as for example the pursuit of ultra high purity Mg may only be suitable for prolonging, but not eliminating, the detrimental effects of impurity enrichment.

Conclusions

The present study is the first to utilize particle induced X-ray emission, PIXE, in surface analysis as relevant to Mg dissolution. The findings of the present work are as follows:

1. It was revealed that PIXE has the ability to readily analyze and quantify the presence of several impurity elements at magnesium surfaces.
2. A number of trace (parts per million) level elements were detected, including Fe, Mn, Zn, Pb and Cu.
3. It was revealed that, as a result of anodic dissolution, there is enrichment of impurity elements at the Mg surface. This is concomitant with incongruent dissolution.
4. The efficiency of impurity enrichment when compared with a model that assumes impurities will not be oxidized under Mg dissolution conditions indicates that actual (observed) impurity enrichment is of low efficiency.
5. The surface concentration of impurity Fe was shown to approximately double with an applied anodic charge of 1.2 C/cm², indicating that in spite of low enrichment efficiency, the Mg surface can significantly enrich with impurities due to progressive dissolution. Under open circuit conditions, appreciable enrichment may therefore occur, even for initially highly pure Mg over long term exposures.

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