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Quantifying the Role of Transition Metal Plating in the Cathodic Activation of Corroding Magnesium

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This paper examines the effect that transition metal ions have on the corrosion behaviour of high purity magnesium. A series of experiments indicate the ability of the selected transition metal ions to accelerate corrosion through cathodic plating aiming to gain an insight on the Mg corrosion activation described in recent publications. High purity magnesium samples were used in conjunction with known additions of Fe²⁺, Cu²⁺, Zn²⁺ and Mn²⁺ cations. The results indicate that the presence of transition metal ions in the corrosive electrolyte leads to transition metal plating and to an increase of the magnesium corrosion rate. By systematically varying the transition metal ion concentration it was possible to determine the relative efficiencies of the selected metal cations. It was also observed that the metal plating process and the efficiency of the cathodic activation were limited by the formation of insoluble transition metal (hydr)oxide precipitates and the time-dependent hydrolysis.

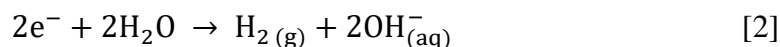
Introduction

It is evident that magnesium and magnesium alloys follow a rather anomalous corrosion behavior in which the dissolution of magnesium and its alloys is accompanied by a gradually enhanced hydrogen evolution that is then further increased analogously with the magnitude of anodic polarization (1-3). Several assumptions have been made in order to explain this phenomenon including the enrichment in metal traces, the existence of univalent magnesium, film based models, metal spalling and magnesium hydride models as reviewed in (1) as well as the cathodic activation of corroding magnesium (2-5). High interest also presents the concept that the cathodic activation of the corroding magnesium is enhanced by the presence of transition metals in the form of impurities (2, 6-11).

Overall, magnesium of commercial purity and its alloys entrap within their matrix a variety of transition metals which are either added intentionally to the bulk concentration or occur as trace impurities. Examples of such alloying elements or impurities include iron, zinc, copper and manganese. During the production of magnesium and its alloys, these elements are not homogeneously distributed within the matrix and thus they exist as distinct particles of sub-micron size either in high or low local concentrations that may as well act as local cathodes (1, 6, 7, 10, 12). The mechanism through which they contribute to the

cathodic activation of corroding magnesium is not yet fully understood with several assumptions to exist including the impurity elements being collected at the film to metal interface, plating on the surface, accumulated within the corrosion film or not being dissolved at the magnesium dissolution potential (6, 7, 12). It may also be assumed that due to the cathodic character of the impurity elements as being more noble than magnesium a micro-galvanic coupling may be formed between them that may lead to a further enhancement of the magnesium dissolution resulting in high rates of hydrogen evolution taking place closely to the anodic site (1, 10).

The present paper investigates the possible effect that the transition metal ions may have on the cathodic activation of corroding magnesium. The metal ions of interest for this study are the Fe^{2+} , Cu^{2+} , Zn^{2+} and Mn^{2+} ions as they commonly exist within the bulk composition of commercially important magnesium alloy, such as the AZ series, either intentionally as alloying elements or unintentionally as impurities. Two types of experiment have been performed. In the first, known concentrations of transition metal cations were established by dissolving an appropriate metal salt in the experimental electrolyte. In the second, known quantities of the solid metal salt were dropped directly onto the magnesium surface prior to electrolyte immersion. In all cases the rate of magnesium corrosion (equation 1) was determined by following volumetrically the accompanying evolution of hydrogen gas (equation 2).



Experimental

All of the laboratory equipment used was cleaned thoroughly using 2M of HCl followed by distilled water. Magnesium samples of commercially high purity (<80ppm Fe) were provided as a gift by Prof. A. Atrens (University of Queensland) and were shaped down to 3cm square coupons of 0.5cm thickness. The surface of each sample was then prepared using silicon carbide polishing pads (Buehler CarbiMet™) with ethanol to be used as lubricant during the process. The order followed during polishing was ascending from grit 320[P400] to grit 1000[P2500] with the samples to be rinsed with ethanol in the end of the process. The abraded magnesium samples were then covered with 90µm thick extruded PTFE 5490 tape (3M Ltd) leaving exposed a square area of 10 x 10 mm.

The source of metal cations were salts of analytical-grade chemicals, CuSO_4 , FeCl_2 , ZnSO_4 and MnCl_2 , (Aldrich Chemical Co.) dissolved to 0.86 M NaCl aqueous solution. For the initial volumetric measurements, the metal salts were diluted within the main electrolyte with their concentrations to be ranged gradually from 10^{-6}M to $8 \cdot 10^{-3}\text{M}$. Further volumetric measurements were performed where the metal salts would be injected in powder form at a weight range of 5mg to 50mg to the immediate proximity of the sample's exposed area and 0.86 M aqueous NaCl would then be introduced to the system.

Following the preparation of the magnesium sample, further PTFE tape was used in order to secure the sample on a petri dish. A 10 ml \pm 0.02 ml conically ended burette was then placed on top of the sample at a minimal distance so that the exposed area was fully covered by the conical end of the burette, thus limiting the possibility of the evolved

hydrogen gas escaping the burette tube. Freshly prepared electrolyte of 250 ml was then poured into the petri dish. Via the use of a syringe the electrolyte was pulled upwards through the burette tube to its maximum point. The burette valve was then closed and recordings were made every 10min for 3hrs.

Results and Discussion

At lower electrolyte concentrations and/or when higher purities of magnesium are of concern, the pattern of localized attack changes to a filiform-like corrosion (2) as opposed to when lower purities of magnesium are used (3). Figure 1 shows a typical appearance of the sample after immersion for 180 min in the absence of any added transition metal cation.

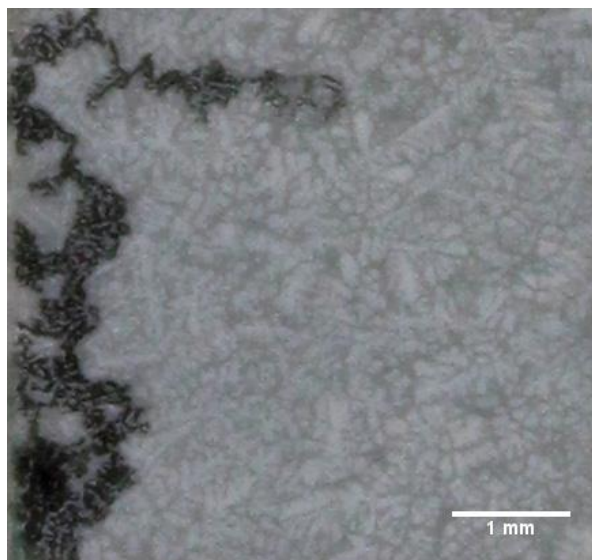


Figure 1. Filiform-like corrosion on high purity magnesium (<80ppm Fe) after 180 min of immersion in 0.86 M aqueous NaCl.

The time-dependent hydrogen volumes recorded for each type of metal salt and concentration are analytically illustrated in Figure 2. In all cases they present a relatively linear behaviour except for the case of 10^{-8} M FeCl_2 concentration in which a curvature is observed that could be attributed to the competed reaction of metal cation hydrolysis. Nonetheless, the approximate linearity observed in all of the graphs indicates that: a) the presence of transition metal cation accelerates the rate of magnesium corrosion and hydrogen evolution, b) the accelerating effect in cation concentration increasing as the cation concentration increase, c) the accelerating effect is ‘non-accumulative’, that is to say it does not increase with time and d) the magnitude of the effect is dependent on the identity of the cation increasing in the order $\text{Mn}^{2+} < \text{Zn}^{2+} \approx \text{Fe}^{2+} < \text{Cu}^{2+}$ (Figure 3).

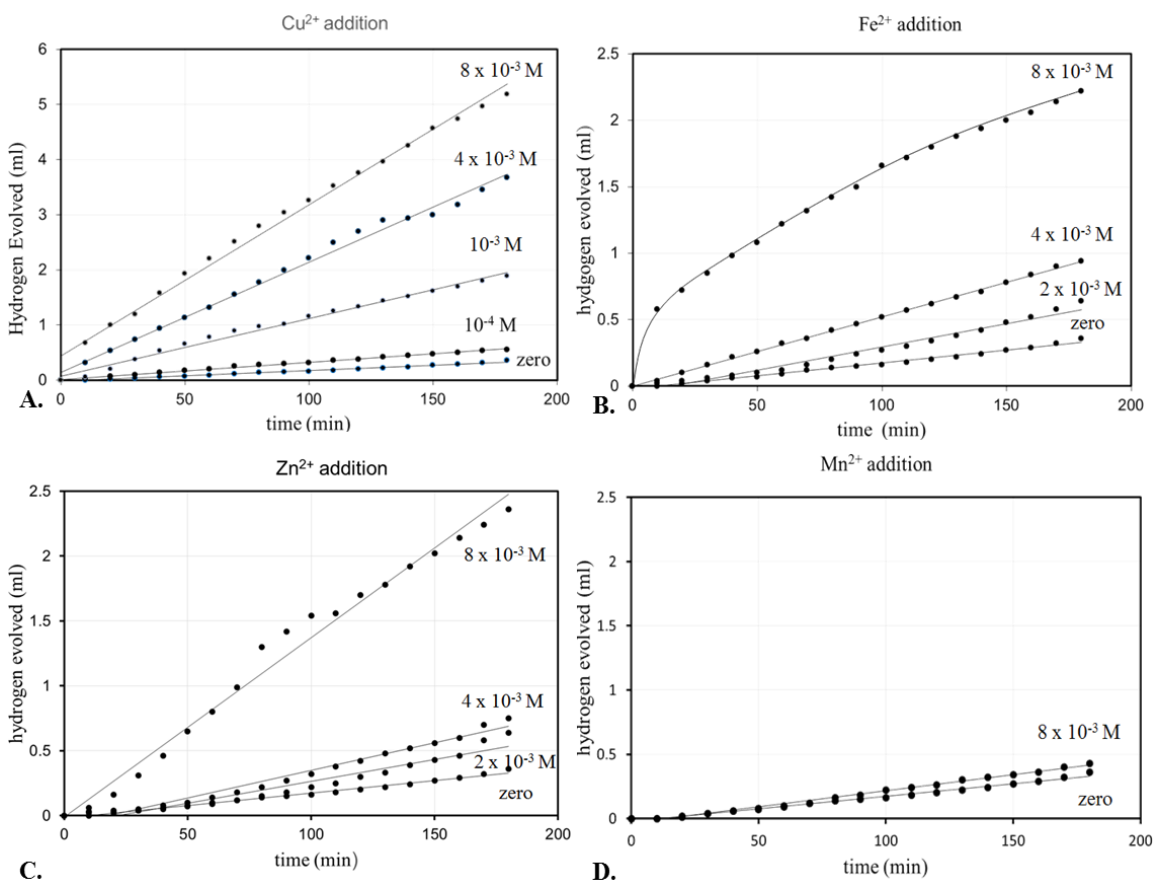


Figure 2. Volumetric recordings and rates of hydrogen evolution for when the metal salts are diluted within 0.86 M aqueous NaCl (A) CuSO₄ (B) FeCl₂ (C) ZnSO₄ (D) MnCl₂. The curve labels indicate transition metal cation concentration.

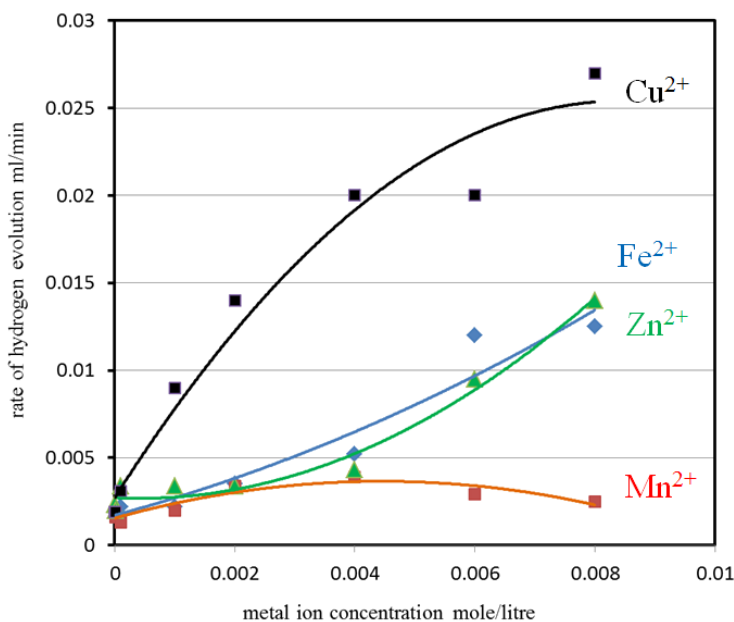


Figure 3. Rate of hydrogen evolution versus the metal salt concentration within the bulk electrolyte. Each point at graph represents the gradient of the hydrogen evolved for each corresponding metal cation concentration except for the case of $8 \cdot 10^{-3}$ M FeCl₂ for which the average over time has been taken.

During the experimental process, it was observed by eye that insoluble coloured transition metal (hydr)oxides were forming thus the time-dependent hydrolysis might be an important negative factor to the overall observation of the kinetics of the magnesium corrosion. Therefore, a second set of volumetric measurements took place in which the metal salts were injected directly onto the exposed area of the magnesium sample. Such an action would minimize the effect of metal cation hydrolysis as the metal cations would be directly introduced to the magnesium metal surface based on the assumption that both the diffusion path length and the hydrolysis initiation time would be shorter. It should be noted that for the needs of this experiment the use of FeCl_2 as a source of Fe^{2+} ions was substituted by $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ as during the experiment the use of FeCl_2 led to high hydrogen gas evolution that was not possible to be recorded accurately.

From Figure 4 it is evident that there exist two phases. The first one would be attributed to the hydration of the metal cations, whereas the second one would correspond to the initiation and immediate effect of hydrolysis and precipitation of the metal (hydr)oxides. During the first phase, the metal cations are hydrated from the electrolyte and because they are at close proximity with the exposed magnesium surface their contribution towards the cathodic activation is immediate. This explanation arises from the assumption that during the hydration of the solid particles found on the area of interest the diffusion path length for the metal cations is much shorter as compared to when there are diluted within the electrolyte, thus leading to higher hydrogen gas evolution rates. The time period before hydrolysis commences is most probably depended on the affinity of the metal cations to hydrolysis. During the second phase, where it is assumed that hydrolysis plays an immediate role to the efficiency of the metal cations on the cathodic activation, the rate of the hydrogen gas evolution presents a decrease. This outcome inherently proves that the effect of hydrolysis and hence precipitation of the metal (hydr)oxides is not a negligible one but contrary has a very direct role on the process of magnesium cathodic activation via limiting the attribution of the metal cations. Overall, though, the kinetics still maintain linearity. Overall, dropping the metal salt directly on the magnesium surface significantly accelerates the rate of magnesium corrosion and hydrogen evolution, the accelerating effect increases together with the metal salt concentration and the magnitude of the effect depends on the identity of the metal cation in the order of $\text{Mn}^{2+} < \text{Zn}^{2+} \approx \text{Fe}^{2+} < \text{Cu}^{2+}$ (Figure 5).

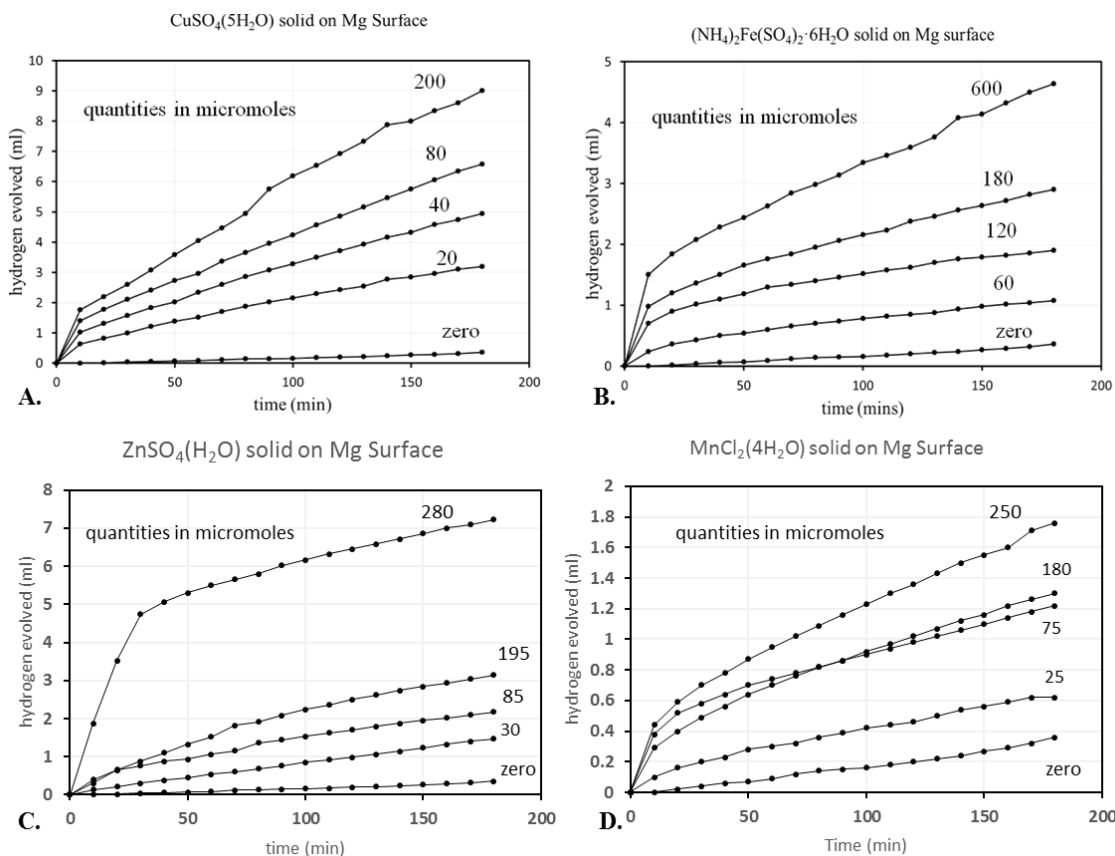


Figure 4. Volumetric recordings and rates of hydrogen evolution for when the metal salts are dropped directly onto the exposed magnesium surface prior to immersion in 0.86 M aqueous NaCl (A) CuSO₄ (B) FeCl₂ (C) ZnSO₄ (D) MnCl₂. The curve labels indicate the metal salt concentration in micromoles.

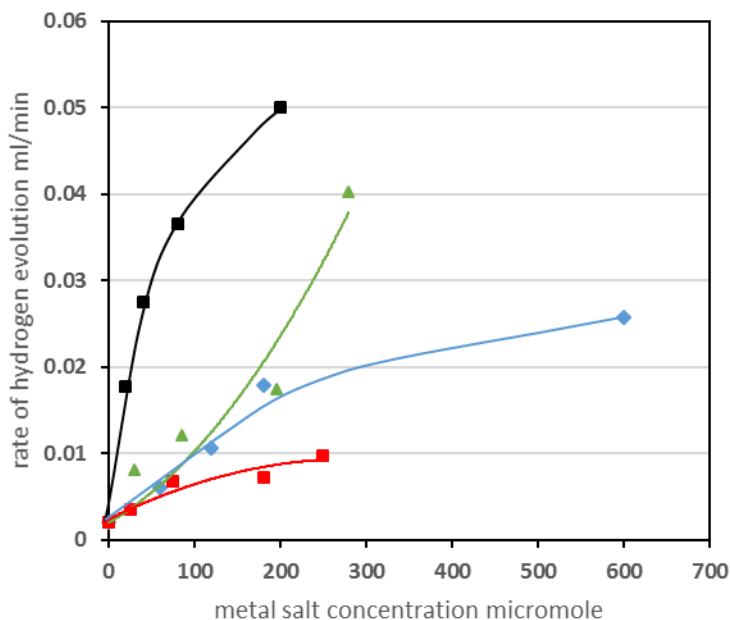


Figure 5. Rate of hydrogen evolution versus the metal salt concentration dropped on the surface of magnesium. Each point at graph represents the average over time.

Comparing Figure 2 and Figure 4, it is possible to argue that diluting the metal salts to the bulk electrolyte is not as efficient. In addition, the linear kinetics observed would imply that no accumulation of impurities occurs on the surface of the corroding magnesium, which is a scenario that is not true (10). Therefore, to physically explain the linear kinetics of hydrogen evolution a magnesium filiform mechanism is proposed in Figure 6.

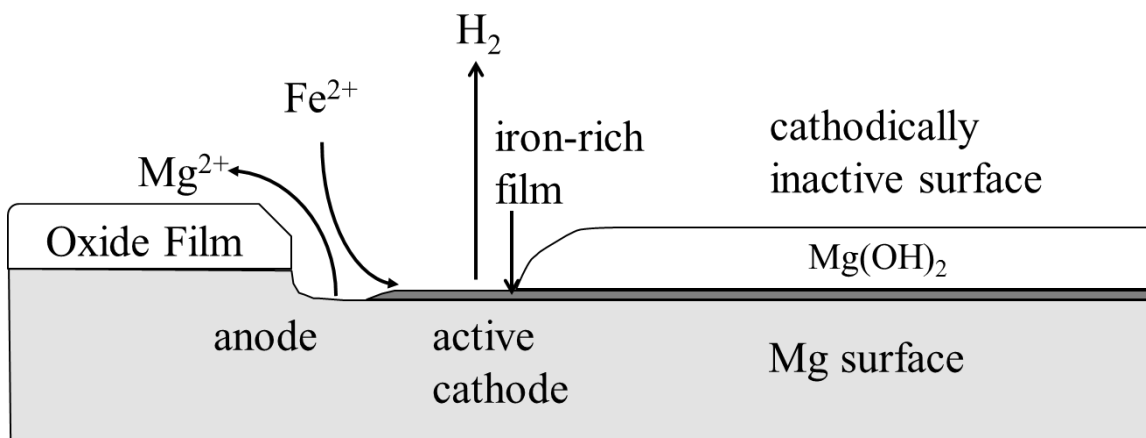


Figure 6. Schematic of magnesium filiform cathodic activation.

Figure 6 illustrates a schematic of magnesium filiform cathodic activation in which the anodic and the cathodic sites are at close proximity to each other. From the anode site pure magnesium is being dissolved into Mg^{2+} ions while at the cathode site the impurities are being re-plated back to the corroding magnesium and hydrogen gas evolves. Through the dissolution of pure magnesium, the local pH increases to be alkali due to the pK_a of the Mg^{2+} ion under which conditions the precipitation of magnesium hydroxide is favourable leading to the formation of a film in the cathodic site covering the re-plated impurities (9, 13, 14). Assuming that the rate at which the cathodic site is formed equals the rate at which it is hindered the overall cathodic area would remain constant at all time thus giving rise to the linear kinetics observed in Figure 2 and Figure 4.

Conclusion

The volumetric measurements have shown that adding Cu^{2+} , Fe^{2+} and Zn^{2+} ions to the bulk electrolyte has a significant effect on the cathodic activation of the corroding magnesium in contrast to the addition of Mn^{2+} ions that had a minimal role to the activation of the corrosion rates of pure magnesium. The overall activation is transient with linear hydrogen gas evolution kinetics to be obtained. This linearity has been attributed to the cathodic area remaining constant as the filiform-like track progresses. Finally, the cathodic activation was not as efficient for when the transition metals were added to the bulk solution due to the competing process of hydrolysis, while activation from local surface sources is significantly more efficient.

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