Corrosion of magnesium and its alloys

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ARTICLE INFO

Article history:
Received 16 January 2009
Accepted 28 April 2009
Available online 7 May 2009

Keywords:
A. Magnesium
B. Modeling studies
C. Electrochemical calculation

ABSTRACT

Any detailed study of the corrosion of magnesium and its alloys in aqueous environment, must consider the three important aspects: galvanic corrosion reaction between magnesium and another metal, microgalvanic corrosion reaction between magnesium and the secondary phases or impurity grains, and the negative difference effect (NDE). In this paper, we propose a mathematical model to describe microgalvanic corrosion. We also discuss the NDE based on Tafel type kinetics and explain the NDE behavior in a consistent manner.

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1. Introduction

Due to their light weight and relative strength, the number of applications of magnesium alloys is increasing every year mainly in the automotive and aircraft industries. However, the corrosion of magnesium and its alloys is still a consistent problem [1–8]. Owing to the low standard electrode potential, magnesium is the most reactive metal. It will readily form galvanic corrosion system with another metal and even a microgalvanic corrosion system with some secondary phases (such as α-phase and/or β-phase) and impurity grains [9–11] in an aqueous environment. It is thus very useful to discuss the possible galvanic corrosion current density and over-potential of microgalvanic corrosion systems. Especially, different from most other metals such as Fe and Cu, magnesium and its alloys exhibit the negative difference effect (NDE), which plays a very important role in the process of magnesium corrosion. Finding the correct cause thereof might lead to progress in magnesium corrosion research.

The galvanic corrosion rate is basically determined by the galvanic current $I_g$ and its distribution. Theoretically expressed [1,12]:

$$I_g = (\phi_c - \phi_a)/(R_a + R_c + R_s + R_m)$$

where $I_g$ is the galvanic current between the anode and the cathode, $\phi_c$ and $\phi_a$ are the open circuit potentials of the cathode and anode, $R_s$ and $R_c$ are the cathode and anode resistances, respectively, $R_s$ is resistance of the solution between the anode and cathode, and $R_m$ is the metal resistance from the anode surface to the cathode surface through a metallic path. Normally $R_m$ is negligible if the two electrode metals are in a direct electrical contact. Any factor that can affect these parameters will influence the galvanic corrosion rate. We may use the following schematics to visualize the corrosion principle as a galvanic cell shown in Fig. 1.

Many reports about research of magnesium corrosion may be found in the literature. Some have performed detailed studies experimentally, to evaluate the microstructure effect (such as α-phase and β-phase) on the corrosion behavior of Mg-alloys [11,13,14], to our knowledge none have performed detailed numerical or theoretical modeling to express the micro-process of the microgalvanic corrosion theoretically and relate them to the elemental composition of the alloy. It is known, however, that the elemental composition of the alloy influences the corrosion properties markedly [15–20]; small ratio of Fe/Ni/Cu may heavily diminish the corrosion resistance. Thus, setting up a model expressing the micro-process theoretically, is both practical and meaningful.

Experimentally, Song [13] and Atrens [8] et al. found that magnesium and its alloys show the negative difference effect in a manner which is shown in Fig. 2. Normally, for most metals such as Fe and Cu, when the potential, $E_{app}$, is higher than the corrosion potential $E_{cor}$ (to which the corresponding current is $I_0$), the current on the cathode (along $I_e$), $I_{H,e}$, should be less than $I_0$ and that on the anode (along $I_a$), $I_{H,a}$ should be greater than $I_0$. However, for magnesium, the situation is totally different. Experiment results show that, instead of decreasing to $I_{H,a}$, the hydrogen evolution reaction rate increases to $I_{H,a}$ along the dashed line $I_b$. Simultaneously, the dissolution current of the anodic magnesium increases faster (along the dashed curve $I_{H,b}$ to $I_{H,m}$) than expected (along the real line $I_a$ to $I_{H,m}$).

There are at present two approaches to the magnesium NDE [13,8] and these may be designated as (i) the unipositive Mg⁺ ion NDE mechanism and (ii) the magnesium self corrosion mechanism. Based on Mg⁺ ions the Song and Atrens [13,8] attempted to explain
Magnesium alloys are composed in addition to magnesium itself, mainly of elements Al, Mn, Si, Cu, Zn, Ni and Fe. The chemical composition is typically about: Al: 6–10%, Mn: 0.1–0.3%, Si: 0.1–0.5%, Cu: 0.01–0.35%, Zn: 0.2–1%. The concentration of Ni and Fe is usually rather small. Though they can be mixed in an atomically uniform manner, each kind of alloy elements may still form a galvanic cell in the magnesium environment. We also call it microgalvanic cell. There may be some α-phase (Mg–Al–Zn solid solution) grains, β-phase (Mg17Al12) grains, Al-grains, Zn-grains and impurities. Because the size of those is small, we collectively call them micro-grains. As magnesium concentration is about 90%, the concentration ratio of other elements is very small. Thus the possibility of forming galvanic cells between any other two alloy elements is vanishingly small. Consequently, all microgalvanic cell is formed between one kind of the alloy elements/micro-grains and magnesium. The number of microgalvanic cells should be dependent upon the specific alloy composition. Here we take AZ91-series alloys as an example. The alloy composition of Al is 9% and Zn is 1%. We can estimate the number of Al and Zn in a unit area. The number of galvanic cells should be proportional to the number of Al and Zn in a unit area. The number of Mg–Al microgalvanic cells is about 10 times the number of Mg–Zn microgalvanic cells. We may get the statistical number by experiment. Because $\phi_{Mg} = -2.37 \text{ V}$, $\phi_{Al} = -1.67 \text{ V}$, $\phi_{Zn} = -0.76 \text{ V}$. Mg is always an anode. In every microgalvanic cell, the micro-grains are small grains of metal. Because the size of them is very small, we can take the potential on the surface of the micro-grains as a constant $\phi(r)$. The structure of the surface layer is most important. In the aqueous environment, these small grains and the magnesium elements around them form some microgalvanic cells. This situation is depicted in Fig. 3.

Though the governing equation can still be expressed by the Plank–Nernst law, the boundary condition is different due to the microgalvanic cells which are formed by the micro-grains and the elements of magnesium. For a given magnesium alloy, we may estimate statistically or actually measure/determine the ratio of each kind of micro-grains and their distribution. For these microgalvanic cells, the resistance in the circuit may be very small, but the electrode overpotential may not be small, then the corrosion current may also not be small. Therefore, the microgalvanic corrosion may cause serious results/consequences in magnesium alloys.

Now let us try to calculate the current on the micro-grains. We suppose that the polarization relationship still follow the Tafel kinetics. Here we take Al-grain-Mg as an example. At every contact point of Al-grain-Mg, the potential should be the same as on the surface of the Al-grain. The overpotential on the Al-grain is $E_{Al} = \phi - \phi_{Al}$. According to the polarization relationship, for Al-grain (cathodic), the current density on the surface thereof can be expressed as:

$$i_{Al} = i_{0Al} \exp \left[ \frac{z_{Al}(1 - \gamma_{Al})F}{RT}(\phi - \phi_{Al}) \right]$$

where $\gamma_{Al}$ is the symmetry factor, $z_{Al}$ is the valence, $F$ is the Faraday’s constant, $R$ is the universal gas constant, $T$ is absolute temperature and $\phi_{Al}$ is the electrode potential. From Eq. (2), we have:

$$\phi - \phi_{Al} = -\frac{RT}{z_{Al}(1 - \gamma_{Al})} \ln(i_{Al}/i_{0Al})$$

Similarly, for magnesium (anode), the overpotential at the connecting point is $\phi - \phi_{Mg}$, thus

$$i_{Mg} = i_{0Mg} \exp \left[ \frac{z_{Mg}(1 - \gamma_{Mg})F}{RT}(\phi - \phi_{Mg}) \right]$$

From Eq. (4), we have:

$$\phi - \phi_{Mg} = \frac{RT}{z_{Mg}(1 - \gamma_{Mg})} \ln(i_{Mg}/i_{0Mg})$$

Now, electron currents always flow out from an anode and flow into a cathode. The direction of the current density vector on the anode
and that on the cathode are reverse, so the current density at the contact point is zero. Then

\[ i_{Al} + i_{Mg} = i_{oAl} \exp \left( \frac{-z_{Al}(1 - \gamma_{Al})F}{RT} (\phi - \phi_{Al}) \right) + i_{oMg} \exp \left( \frac{z_{Mg}^2 \gamma_{Mg}F}{RT} (\phi - \phi_{Mg}) \right) = 0 \]  

(6)

This way, we can get the potential and the current density on the surface of the Al-grain.

\[ \phi = -\frac{RT}{F} \ln \left[ \frac{i_{oAl}}{i_{oMg}} \frac{z_{Mg}^2 \gamma_{Mg} + z_{Al}(1 - \gamma_{Al})}{z_{Al} + z_{Mg}(1 - \gamma_{Al})} \right] \]

(7)

\[ i_{Al} = i_{oAl} \exp \left[ -\frac{z_{Al}(1 - \gamma_{Al})}{RT} \ln \left( \frac{i_{oAl}}{i_{oMg}} \right) \right] \frac{z_{Mg}^2 \gamma_{Mg}(\phi - \phi_{Al})}{z_{Mg} + z_{Al}(1 - \gamma_{Al})} \]

(8)

Similarly for the Zn-grain-Mg microgalvanic cell. For \( \alpha \)-phase or \( \beta \)-phase micro-grains, the situation is a little bit different. They may have some Mg-micro-grains as well as Al-micro-grains in both \( \alpha \)-phase and \( \beta \)-phase grains. We may have to view however these; \( \alpha \)- and \( \beta \)-phase grains as composed of smaller micro-grains. When a Mg-micro-grain and a Al-micro-grain connect, they form a microgalvanic cell in the aqueous environment. We may then use similar method, as we used above, for the Al-grain-Mg microgalvanic cell.

Now, the current on the surface of a Mg-micro-grain can also be taken as constant (\( i_{Mg} = i_{oMg} \)) and Eqs. (6)–(8) still apply. When small size anodes exist, that is not really sufficient for corrosion protection. In other words, when the size of anodic electrode is small but the current may not be small, that may cause serious corrosion problems. This may explain why \( \alpha \)-phase or \( \beta \)-phase microstructure leads to localized microgalvanic corrosion.

From the discussion above we know that the boundary conditions should include the effect of the micro-grains when microgalvanic systems exist, which may cause serious corrosion consequences.

3. Negative difference effect of magnesium and discussion

In a normal situation, when we use the Butler–Volmer equation to express the corrosion system, the polarization is:

\[ i_{net} = i_0 \left\{ \exp \left( \frac{\gamma_{Mg}^2 F}{RT} (\phi - \phi_{MgCorr}) \right) - \exp \left[ \frac{- \gamma_{Mg}^2 F}{RT} (\phi - \phi_{MgCorr}) \right] \right\} \]

(9)

As in Ref. [13], we assume \( \phi_{MgCorr} = -1.7 \) V, then

\[ i_{net} = i_0 \left\{ \exp \left[ \frac{\gamma_{Mg}^2 F}{RT} (\phi + 1.7) \right] - \exp \left[ \frac{- \gamma_{Mg}^2 F}{RT} (\phi + 1.7) \right] \right\} \]

(10)

We can separate it into anodic reaction part and cathodic reaction part:

\[ i_a = i_0 \exp \left( \frac{2 \gamma_{Mg}^2 F}{RT} (\phi + 1.7) \right) \]

(11)

\[ i_c = i_0 \exp \left( \frac{-2 \gamma_{Mg}^2 F}{RT} (\phi + 1.7) \right) \]

(12)

In short, there are two aspects for the negative difference effect:

(1) The difference \( \Delta \) between the spontaneous rate of hydrogen evolution reaction (HER) on the Mg surface at free corrosion potential and the one which corresponds to the measured HER rate for the applied galvanostatic current \( i_{appl} \) is negative. That is, \( \Delta = i_{corr} - i_{appl} < 0 \), which is different from most metals such as Fe and Zn [8].

(2) The dissolution current \( i_{Mg} \) of the anodic magnesium increases faster than expected.

Now let us approach the NDE behavior numerically from Butler–Volmer/Tafel equation. 50 years ago, Petty et al. [21] found that when electrolysis of an aqueous solution of any one of several salts is carried out between magnesium electrodes in a divided cell, the metal dissolves anodically with an initial mean valence number appreciably lower than two. Also, they found that the measured hydrogen evolution volume was always slightly greater than that calculated when sodium sulfate solution is used as the electrolyte. These results, it is believed, point strongly toward the conclusion that the primary reactions at a magnesium anode consist of the oxidation of the metal to both the unipositive (Mg\(^+\)) and the dipositive (Mg\(^{2+}\)) state. They indicated that the low initial valence numbers obtained by the oxidation of a magnesium anode might be due to some sort of anodic activation. However, it remains ambiguous as to what the meaning of “the some sort of anodic activation” is. We do adopt the proposal and suppose that there are two kinds of anodic reactions for magnesium loss: one produces univalent magnesium ions (Mg\(^+\)) and the other produces bivalent magnesium ions (Mg\(^{2+}\)). Now, assume the number of Mg\(^+\) is \( N_1 \) per mole and the number of Mg\(^{2+}\) is \( N_2 \) per mole. Then the effective/average valence of anode reaction is

\[ z = \frac{N_1 + 2N_2}{N_1 + N_2} \]

(13)

where, \( 1 \leq z \leq 2 \). The polarization of the anode is expressed as:

\[ i_{Mg} = i_0 \exp \left( \frac{\gamma_{Mg}^2 F}{RT} (E_{appl} - E_{corr}) \right) \]

(14)

We recognize three cases:

(1) When the over potential \( E_{appl} - E_{corr} \) is low, the anodic reaction for magnesium loss is mostly:

\[ 2 \text{Mg} \rightarrow 2 \text{Mg}^{2+} + 2\text{e}^- \] (anodic partial reaction).
And then, \(2 \text{Mg}^+ + 2\text{H}_2\text{O} \rightarrow 2\text{Mg}^{2+} + 2\text{OH}^- + \text{H}_2\), is just a relatively slow chemical reaction [13].

The cathodic partial reaction is: \(2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2\)

There are mostly univalent magnesium ions \((\text{Mg}^+)\) for magnesium dissolution reaction and \(z \approx 1\). Therefore,

\[
\tilde{i}_{\text{Mg}} \approx \tilde{i}_0 \exp \left[ \frac{\gamma F}{RT} (E_{\text{appl}} - E_{\text{corr}}) \right]
\]

However, in the low overpotential region, the dissolution rate of magnesium is low, so the total number of \(\text{Mg}^+\) is not large.

(2) When the over potential \(E_{\text{appl}} - E_{\text{corr}}\) is high, mostly the anodic reaction for magnesium loss is:

\[
\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e} \quad \text{(anodic partial reaction)}
\]

Still, the cathodic partial reaction is: \(2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2\)

There are mostly bivalent magnesium ions \((\text{Mg}^{2+})\) for magnesium dissolution reaction and \(z \approx 2\).

Therefore,

\[
\tilde{i}_{\text{Mg}} \approx \tilde{i}_0 \exp \left[ \frac{2\gamma F}{RT} (E_{\text{appl}} - E_{\text{corr}}) \right]
\]

In the high overpotential region, the dissolution rate of magnesium is high, so the total number of both \(\text{Mg}^+\) and \(\text{Mg}^{2+}\) is large even though \(N_1 \gg N_2\).

(3) In the middle region, both anodic partial reactions exist (in fact, even for high over potential situation, there still exist some low over potential areas).

\(2\text{Mg} \rightarrow 2\text{Mg}^{2+} + 2\text{e}\)

\((N_1, \text{Mg}^{2+}\) produced from this anodic partial reaction\)

\(2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2\)

\((I_{\text{H}_1}, \text{produced from this anodic partial reaction})\)

\(2\text{Mg}^{2+} + 2\text{H}_2\text{O} \rightarrow 2\text{Mg}^{2+} + 2\text{OH}^- + \text{H}_2\)

\((I_{\text{H}_2} - N_1/2\text{H}_2, \text{produced from this chemical reaction})\)

This reaction may occur slowly and \(\text{Mg}^+\) can exist a sufficient long time for some minutes in aqueous solution [8] when the overpotential is very low. With the increase of the overpotential, this reaction may occur faster.

\(\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}\)

\((N_2, \text{Mg}^{2+}\) produced from this anodic partial reaction\)

\(2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2\)

\((I_{\text{H}_2}, \text{produced from this anodic partial reaction})\)

\[
z = \frac{I_{\text{H}_2} - N_1}{I_{\text{H}_1} - N_2}, \text{the current density is expressed by Eq. (14)}.
\]

In fact, as we have already seen the local potential between the electrode and the electrolyte distributes spatially differently along the electrode surface. This makes the over potential distribution different along the electrode surface. Theoretically, if we know the critical value of the over potential for producing univalent magnesium ions \((\text{Mg}^+)\) and bivalent magnesium ions \((\text{Mg}^{2+})\), we can calculate the rate of \(N_1/N_2\) and then we may know the value of \(z\). Here, we only give a qualitative discussion. The number \(N_2\) of bivalent magnesium ions \((\text{Mg}^{2+})\) increases with the increase of the over potential \(E_{\text{appl}} - E_{\text{corr}}\) so the anodic current density increases faster than expected because of the increase of \(z\) with the over potential going up. Eq. (14) may qualitatively explain the experiment result. The situation is shown in Fig. 4 (In this figure, we assume \(\tilde{i}_0 \approx 1.0 \times 10^{-2} \text{A/m}^2\). We can try curve fitting to get \(z\) by adjusting the symmetry factor \(\gamma\) and comparing with Eq. (13)).

On the other hand, the symmetry factor or the transfer coefficient is a very important parameter of the polarization for electrode reactions. It is related to the gradients of the potential energy–distance profile for the representative points of reactant and products [23]. If the slope of the relation near the intersection points is \(z\) for the product and \(\beta\) for the reactant [24,25], then the symmetry factor can be expressed as:

\[
\gamma = \frac{\tan \alpha}{\tan \alpha + \tan \beta}
\]

According to Bockris and Matthews [26], the symmetry factor \(\gamma\) is a coefficient controlling the transfer of electrical to chemical energy, it is also called transfer coefficient. To date, only very rudimentary attempts to calculate values of \(\gamma\) have been made. In practice, the symmetry factor \(\gamma\) is a coefficient determined by experiment. Based on the Tafel Eq. (11) for anode, we have:

\[
\gamma = \frac{RT}{zF} \left( \frac{d(\ln i)}{d\phi} \right)
\]

where \(d(\ln i)/d\phi\) is the slope of curve \(\ln i - \phi\). Bauer [27] studied the history and basic concept of the symmetry factor and indicated that anodic symmetry factor/transfer coefficient plus the cathodic symmetry factor/transfer coefficient is not necessary to be “unity” 1. Also, there is no adequate justification for a \textit{a priori} introduction of the transfer coefficient \(\gamma\) as an implicitly potential-independent parameter. Savéant and Tessier [28] found that the electrochemical transfer coefficient is variation with potential for organic molecules.

\[
\gamma = 0.5 + \frac{F}{4\tilde{i}_0} (E - E' - \phi)
\]

where \(\tilde{i}_0\) is the reorganization factor. Eq. (22) shows that the coefficient \(\gamma\) decreases with the increase of over potential. Thus this effect may not apply to the NDE behavior.

If we accept that the fast increasing of anodic current is just because of the increase of the effect valence \(z\), then for the hydrogen evolution reaction rate, the dashed line \(I_{\text{H}_1}\) (Fig. 2) implies that the cathodic current density,

\[
I_{\text{H}} = I_{\tilde{i}_0} \exp \left[ \frac{1 - (1 - \gamma)\tilde{F}}{RT} (E_{\text{appl}} - E_{\text{corr}}) \right],
\]

should decrease faster than expected, which conflicts with the experiment results. However, we always measure the amount of hydrogen evolution which reflects the cathodic current density. As we discussed above, the hydrogen evolution is composed of three parts

\[
I_{\text{H}} = I_{\text{H}_1} + I_{\text{H}_2} + I_{\text{H}_t}
\]

![Fig. 4](image-url)  
Calculated variation of current density (\(\gamma\)-axis A/m²) of magnesium corrosion with NDE situation \((\gamma = 0.5, T = 300 K, z\) as defined in Eq. (13)).
From Eq. (23), we can see that the change of $z$ is not the unique main contribution to the NDE behavior. It implies that the symmetry factor $\gamma$ is also a parameter to influence the NDE behavior. There are three possible cases:

1. If there are no Mg$^+$ produced in the process of magnesium dissolution, $z = 2$, and $i_{NDE} = 0$, $i_{NDE} = 0$, only when $\gamma \rightarrow 1$, $1 - \gamma \approx 0$, the $i_{NDE}$ will not change much, namely, $i_{NDE} \rightarrow i_0$. Therefore, in this case, the hydrogen evolution cannot increase. This also indicates that Mg$^+$-ions must exist in the process of magnesium dissolution.

2. When there are no Mg$^{2+}$ produced in the process of magnesium dissolution, $z = 1$, and $i_{NDE} = 0$. The maximum hydrogen evolution on the cathode will be the same as the hydrogen evolution on the anode which is produced by the chemical reaction in Eq. (18). Therefore, even with $\gamma \rightarrow 0$, $1 - \gamma \approx 1$, the third part $i_{NDE}$, which comes from the reaction of Eq. (18), can make sure that the hydrogen evolution increases.

3. When there are partially Mg$^+$ and Mg$^{2+}$, only when the value of the symmetry factor $\gamma$ is greater than a specific value $\gamma_0$, can the hydrogen evolution be expected to increase. For example, assuming $N_1 = N_2 = N$ at overpotential $E_{appl} - E_{corr}$, then $z = 1.5$. The maximum hydrogen evolution on the cathode is $N_1/2 + N_2 = 3N/2$. Correspondingly, the variation of the charge of electrons is $3N$. The hydrogen evolution on the anode is $N_1/2 + N_2$, which is $1/3$ of that on the cathode. Correspondingly, the variation of the charge of electrons is $N$, which is $1/3$ of that on the cathode. It means that if the hydrogen evolution on the cathode decreases less than $1/3$, the total hydrogen evolution still increases. Therefore,

$$i_{NDE} = i_0 \exp \left[ - \frac{1.5(1 - \frac{\gamma}{\gamma_0})F(E_{appl} - E_{corr})}{RT} \right] > \frac{2}{3} i_0$$

(25)

or:

$$\gamma_0 > 1 - \frac{0.405RT}{1.5F(E_{appl} - E_{corr})}$$

(26)

The inequality here makes sure that the total hydrogen evolution increase.

Note: it is important to understand that the dissolution rate of magnesium increases with increasing of overpotential, both $N_1$ and $N_2$ increase even though $N_2$ increases faster than $N_1$. This means that $i_{NDE}$ in Eq. (24) increases because of the number of Mg$^+$ increase when the overpotential increases.

This way, we may explain the NDE behavior consistently. But still as to how to determine directly the rate of $N_1/N_2$ is an outstanding problem.

4. Conclusion

In this paper, we find that it is possible to express quantitatively the microgalvanic corrosion, especially the negative difference effect of magnesium and its alloys. Though Petty [21], Garreau and Bonora [22], Song and Atrens [13,8] attempted to explain the negative difference effect of magnesium by proposing the unipositive $M^+$ ion mechanism, they did not do so quantitatively. Based on Tafel kinetics, by supposing that both Mg$^+$ ions and Mg$^{2+}$ ions are produced and the amount changes with the variation of the overpotential in the progress of the magnesium dissolution, we can explain the negative difference effect behavior in a meaningful manner.

References


