

# Magnesium Corrosion Mechanisms

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This paper provides an overview of the corrosion mechanisms of magnesium alloys based on our recent research and the literature. Magnesium is a very reactive metal. Thus galvanic corrosion is very important. Galvanic corrosion is associated with (1) impurities, particularly Fe, Ni & Cu (2) second phases, eg  $\beta$ , and (3) coupling with a less active metal. Magnesium alloys exposed without galvanic coupling have a corrosion resistance that, in general, is not as good as that of aluminium alloys. When magnesium is passive, then the corrosion rates are low. But the range of environmental conditions for passivity for magnesium is less than for aluminium; ie passive films are not very stable. Corrosion is typically important as localised corrosion such as pitting & SCC. There is the expectation that SCC failures will increase with increased use of Mg alloys in load bearing applications. Corrosion of AZ91 is by "pitting" in 1N NaCl. The corrosion potential,  $E_{\text{corr}}$  is above the "pitting" potential. Corrosion of cast AZ91 has the following morphologies, (1) preferential attack of primary  $\alpha$ , (2) preferential attack of eutectic  $\alpha$  & undermining of  $\beta$ . The  $\beta$  phase is more stable than  $\alpha$ , and  $\beta$  is a better cathode. There is corrosion protection and low corrosion rates if there is a significant fraction of finely divided continuous  $\beta$ . Otherwise  $\beta$  accelerates corrosion. Corrosion acceleration is significant if there are large blocks of interconnected  $\beta$ . Corrosion acceleration may be small if  $\beta$  is small and finely divided.

**Keywords** : magnesium alloys, corrosion mechanism, galvanic corrosion, passivity, AZ91

## 1. Introduction

This paper provides an overview of the corrosion mechanisms of magnesium alloys based on our recent research<sup>1-6)</sup> and on the literature. Magnesium usage is currently growing rapidly, albeit from a small base. The overall growth of magnesium metal usage is 5%, whereas the die-casting usage is growing much more rapidly at 18%pa. The total metal usage was 420,000 tonnes in 2000. The rapid increase is due to the light-weight and consequently the favourable strength-to-weight ratio of magnesium alloys, which provides considerable weight saving potential in automobile and transport industries. Its good processing capabilities, particularly its ability to be die cast into large thin sections can also lead to considerable economic savings.

However, magnesium is a very reactive metal and consequently corrosion protection is an issue of great importance. Overall it can be said that magnesium alloys have a corrosion resistance that, in general, is not as good as that of aluminium alloys. This comes about because the surface films that form on the surface of magnesium

alloys are not as stable as those that form on aluminium alloys. This has restricted the application of unprotected magnesium alloys to fairly benign exposure conditions like indoor (and outdoor) atmospheric exposures. Typical examples are automobile seats, instrument panels, computer cases etc. Magnesium alloys are also being considered for various auto under-bonnet applications, including engine blocks and heads etc. Although the range of environmental conditions wherein magnesium alloys can be used unprotected is not as wide as that for aluminium alloys, it should nevertheless be emphasised that for these appropriate environmental conditions, modern magnesium alloys have corrosion rates lower than those of comparable aluminium alloys, and much lower corrosion rates than shown by carbon steel. For example Hillis and Reincheck<sup>7</sup> showed that AZ91 containing low levels of impurities had corrosion rates lower than the cast aluminium alloy 380 and steel for salt spray testing and for atmospheric exposures at the Brazos River Site on the Texas Gulf Coast.

The active nature of magnesium means that galvanic effects are always an issue. Some typical values of the corrosion potential  $E_{\text{corr}}$  are given in Table 1. It is clear

**Table 1. Typical corrosion potentials for common engineering alloys**

Metal	$E_{\text{corr}}, V_{\text{SCE}}$
Mg	-1.65
Zn	-1.02
Al-7075	-0.88
Al-1xxx	-0.73
Fe	-0.50
Cu	-0.12
Ni	+0.01

**Fig. 1.** (a) External galvanic corrosion; (b) Internal galvanic corrosion

that magnesium is more active than all the common engineering alloys, and consequently magnesium is the anode and corrodes preferentially in any galvanic couple.

Thus galvanic corrosion is very important and considerable attention needs to be paid to protecting against galvanic corrosion in any engineering application using magnesium alloys. Forms of galvanic corrosion, as illustrated in Figure 1, include galvanic corrosion associated with

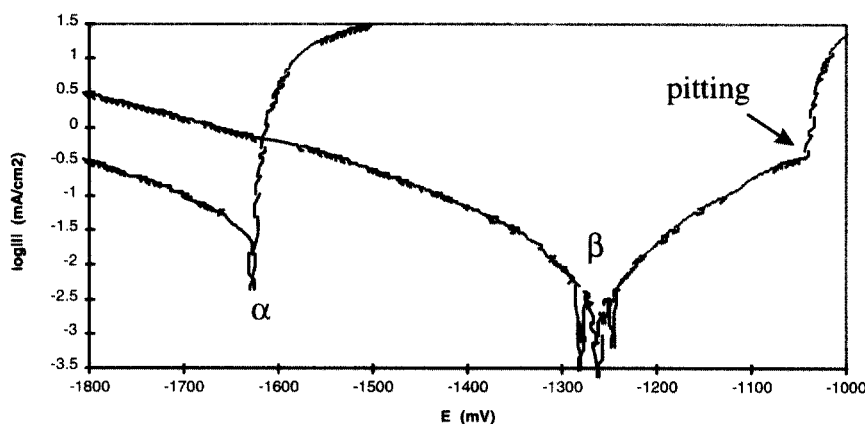
(1) impurities, particularly Fe, Ni & Cu, (2) second phases, eg  $\beta$ , and (3) coupling with a less active metal. Design considerations for reducing galvanic corrosion of magnesium have been considered by Hawke *et al.*<sup>8)</sup> and are detailed in Uhlig's Corrosion Handbook<sup>9)</sup>.

For magnesium alloys exposed without galvanic coupling, corrosion typically takes the form of localised corrosion.<sup>3),4)</sup> This is because the free corrosion potential is more positive than the pitting potential, as illustrated in Figure 2 for AZ21( $\alpha$ ) in 1N NaCl. The corrosion form of magnesium is called localised corrosion<sup>3),4)</sup> to distinguish it from the auto-catalytic pitting observed in stainless steels. Localised corrosion in magnesium initiates as irregular pits, which spread laterally and cover the whole surface. There does not seem to be much tendency for deep pitting. There is the expectation that environment assisted cracking (EAC) (including stress corrosion cracking (SCC) and hydrogen embrittlement (HE)) failures will increase with increased use of Mg alloys in load bearing applications. EAC is reviewed later.

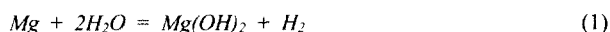
## 2. Corrosion of pure magnesium

### 2.1 Reactiron Sequence

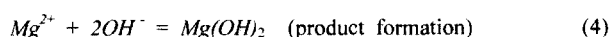
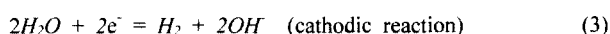
The corrosivity of a magnesium alloys is governed by the corrosion reactions of the individual constituent phases of the alloy. If there are some components in an alloy that are reactive with the environment, then the alloy has low corrosion resistance in that environment. The reactions on pure magnesium are of the particular interest. They provide the base for understanding corrosion of magnesium alloys. Magnesium dissolution in aqueous environments generally proceeds by an electrochemical reaction with water to produce magnesium hydroxide and hydrogen gas, so magnesium corrosion is relatively insensitive to the

**Fig. 2.** Polarization curves for the  $\alpha$  phase and the  $\beta$  phase in 1N NaCl at pH 11.

oxygen concentration,<sup>10</sup> although the oxygen concentration is an important factor in atmospheric corrosion. The corrosion attack in aqueous environments often involves microgalvanic coupling between cathodic and anodic areas. The overall reaction for the corrosion of Mg is:



The net reaction may be expressed as the sum of the following partial reactions:



The anodic reaction (2) described above probably involves some intermediate steps which may produce the monovalent magnesium ion ( $Mg^+$ ) which has a short lifetime.<sup>10</sup> The reduction process of hydrogen ions and the hydrogen overvoltage of the cathodic phase play an important role in the corrosion of Mg. Low overvoltage cathodes facilitate hydrogen evolution, causing a substantial corrosion rate.

The overall corrosion reactions of magnesium alloys have not yet received systematic study. It is however reasonable to believe that the corrosion reactions on magnesium alloys should be similar to those on pure magnesium. According to the investigation carried out by Song et al,<sup>5,6</sup> during the anodic dissolution of Mg-Al-Zn alloys, Mg was still the main component dissolved into solution; a small amount of Al was also dissolved but almost no dissolved Zn was found in solution. This suggested that even for the magnesium alloys, the above 4 overall reactions might still be responsible for the corrosion processes. Certainly, it could not be excluded that the alloying elements, eg. Al and Zn. etc, might play a critical role in the reactions.

At 25°C magnesium ( $Mg^{2+}/Mg$ ) has a standard electrode potential of -2.37Vnhe, assuming that bare metal is in contact with its divalent ion containing solution. However the actual potential of Mg is usually about -1.7 Vnhe in dilute aqueous solutions. Magnesium forms a magnesium hydroxide film which can provide some protection over a wide pH range. Assuming that the protective film on Mg is  $Mg(OH)_2$  (not proven but most probably correct), the thermodynamics that govern the formation of this film are described by the Pourbaix diagram.

### 2.2 Negative Difference Effect (NDE)

Magnesium has a very strange phenomenon, known as the negative difference effect (NDE). From an electrochemical

approach, all corrosion reactions can be classified into anodic and cathodic processes. Normally, the anodic reaction rate increases and the cathodic reaction rate decreases with increasing potential. For most metals like iron, steels and copper, when the potential is increased, the anodic dissolution rates increase and the cathodic hydrogen evolution rates decrease. However, on magnesium, the hydrogen evolution behaviour is quite different from those on iron and steels. On first examination such behaviour seems contrary to the very basics of electrochemical theory.

Figure 3 presents the experimental manifestation of the NDE and compares the NDE with normal polarization curves. The normal anodic partial reaction and the cathodic partial reaction are shown by the solid lines marked Ia and Ic respectively; these are both assumed to obey Tafel kinetics. The rates of these two reactions are equal to  $I_0$  at the corrosion potential,  $E_{corr}$ . When the potential is changed to a more positive value  $E_{appl}$ , the rate of the normal anodic partial reaction would be expected to increase along the curve marked Ia to the value  $I_{Mg,e}$  and simultaneously the normal cathodic reaction would be expected to decrease along curve Ic to the value  $I_{H,e}$ . This is the case of normal electrochemical polarization behaviour exhibited by most metals, typically like iron and steels.

However, for magnesium, it is found experimentally that the hydrogen evolution reaction (HER) rate increases rather than decreases with increasing potential, as showed as dashed line marked IH. Thus for an applied potential  $E_{appl}$ , the actual rate corresponds to the value  $I_{H,m}$  (which represents a HER current significantly greater than the expected current corresponding to  $I_{H,e}$ ). A second experimental observation is that the anodic magnesium dissolution current can increase faster than expected from

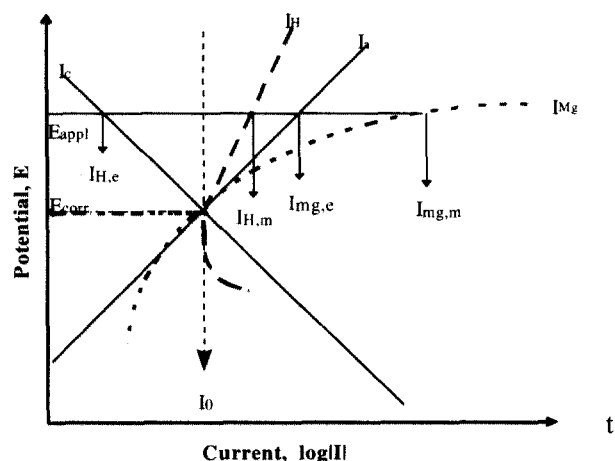
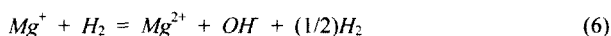


Fig. 3. The negative difference effect.

he polarisation curve. This is shown by the dashed curve marked IMg which is to the right of the solid curve marked Ia. Thus for an applied potential  $E_{appl}$ , the actual dissolution rate corresponds to the value  $IM_{g,m}$  (which represents a corrosion current significantly greater than the expected current corresponding to  $IM_{g,e}$ ). Furthermore, for anodic dissolution of magnesium alloys under an applied current,  $I_{appl}$ , the experimentally measured weight loss (which corresponds to  $IM_{g,m}$ ) can be greater than that calculated from the applied current,  $I_{appl}$ , using Faraday's Law. For decades, investigators have been trying to explain the NDE phenomenon by means of electrochemical reaction mechanisms and four different mechanisms have been proposed for pure magnesium and magnesium alloys. All the four mechanisms succeed in explaining some phenomena, and fail to deal with other aspects.

After careful analysis of the experimental data and predictions based on the above models, Song et al.<sup>(2,11)</sup> proposed a new electrochemical mechanism for the negative difference effect as illustrated in figure 4. This model proposes that there is an increase in the area free of surface film with increasing applied potential. These film free areas are crucial to the NDE behaviour. In the film free areas, magnesium corrosion occurs with the production of univalent magnesium ion and the subsequent generation of hydrogen.



When the applied potential is highly negative, the surface film is intact and there is no film free area. Anodic dissolution of magnesium is very low. Cathodic hydrogen production can still proceed on the surface film at such a negative potential, but the evolution rate increases with increasing potential until the pitting potential is reached. At the pitting potential the surface film begins to break

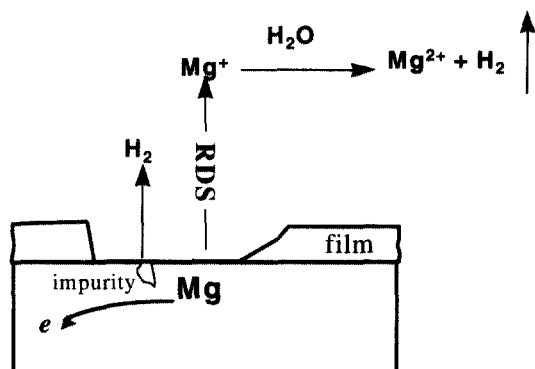


Fig. 4. Mechanism of the NDE.

down, and both hydrogen evolution and magnesium dissolution become much easier on the film free area. With increasing potential, the film free area increases, so there is more hydrogen evolution. Also the rates of reactions (5) and (6) increase causing more hydrogen to be produced at higher potentials. In the anodic dissolution, reaction (5), there is only one electron involved, ie half the number of electrons expected. This means that at the same current density more magnesium is dissolved than expected.

The Negative Difference Effect (NDE) is very common in the corrosion of magnesium. Magnesium alloys also exhibit NDE phenomena. Song et al.<sup>(3,5,6)</sup> found that  $\alpha$ ,  $\beta$ , and AZ91 diecast alloys all had similar NDE behaviour. Furthermore, the NDE was closely related to the corrosion performance - a strong NDE was observed for alloys with low corrosion resistance. The NDE phenomenon always starts at the same time and the same potential as localized corrosion for magnesium and magnesium alloys. NDE is usually associated with accelerated corrosion of the metal. These conditions should be avoided in practice. In this, magnesium has the same shortcoming as aluminium whereas steels do not suffer from such an extra corrosion. Because aluminium alloys can form a stable surface film, NDE can often be prevented. This also indicates that if the surface film on magnesium alloys could be improved, then the NDE phenomenon could be prevented, and the corrosion rate would be reduced.

### 3. Corrosion of alloys

#### 3.1 Elements in solid solution in the $\alpha$ -phase

The corrosion of magnesium alloys depends on their metallurgy and the environment of exposure. The former includes alloying and contamination elements, phase components and corresponding micro-structures. Metallurgical techniques are an effective way to improve the corrosion resistance of magnesium alloys and there has been much progress in recent decades. Different elements have different influences on the corrosion resistance of magnesium alloys. Some elements are beneficial to the enhancement of corrosion resistance. Also there are some elements whose effects on corrosion processes of magnesium alloys are not significant or still uncertain. However, some elements have been found to be extremely detrimental to the corrosion performance of magnesium alloys.

Hanawalt et al.<sup>(12)</sup> found that of 14 elements studied in binary magnesium alloys, four (Fe, Ni, Cu, and Co) had a very profound accelerating effect on the salt water corrosion rate at contents of less than 0.2%, three (Ag, Ca, Zn) had more modest effects at concentrations of 0.5 to 5%, while the remainder (Al, Sn, Cd, Mn, Si, and Na)

had little, if any, effect at concentrations up to 5%. Subsequent studies have confirmed that a critical factor is the purity of the base metal. Corrosion rates were accelerated 10-100 fold when the level of the critical contaminants Fe, Ni and Cu were increased.<sup>13)</sup> Iron, nickel and copper have extremely deleterious effects because of their low solid-solubility limits and their abilities to serve as active cathodic sites.<sup>14)</sup> At the same concentration, the detrimental effect of these elements decreases in the order : Ni > Fe > Cu. For each of these elements a tolerance limit can be defined as illustrated in figure 5. When the impurity content exceeds the "tolerance limit", the corrosion rate is greatly accelerated, whereas, when the impurity content is lower than the "tolerance limit" the corrosion rate remains low.

The mechanism for the tolerance limit is sometimes related to the solubility of the impurities in the magnesium alloy matrix. When the concentrations of Fe, Ni, and Cu exceed their tolerance limits, they segregate and serve as active catalysts for electrochemical attack.<sup>15)</sup> However, in their study of tolerance limits, Hanawalt<sup>12)</sup> failed to find any correspondence between the magnitude of the tolerance limit and the solubility of the added element in solid or liquid magnesium. They only found that attack began at discrete centers, and supposed that the elements showing tolerance limit phenomena were dispersed in the alloy as fine particles. However, Bushrod<sup>16)</sup> disagreed with Hanawalt because there was no real evidence that the centres observed under the microscope were in fact cathodic particles.

So far there is no model that can perfectly explain the "tolerance limit". Most studies<sup>17,18)</sup> have shown that dramatic improvements of corrosion resistance can be realized through the control of the contaminants in the base metal. The critical contaminants<sup>19)</sup> for commercial alloys were recently defined and applied to the production specifications for AZ91 and AM60. Dow recommended that

the following specific contaminate limits should be used to ensure optimum salt water corrosion performance in AZ91: Fe < 50ppm, Ni < 5ppm, Cu < 300ppm. This actually provides an effective way to produce highly corrosion resistant magnesium alloys and is of great significance from a practical point of view. Iron, nickel, copper and cobalt are the four main elements so far found to have significant detrimental effect on corrosion resistance of magnesium alloys. They have different "tolerance limit" values. However, it is not sure yet whether they have similar mechanisms in the acceleration of corrosion processes of magnesium alloys.

### 3.2 Role of second phases

Second phases have a pronounced influence on the corrosion of Mg, because most elements only affect the corrosion resistance of magnesium alloys after the formation of second phases. For example, a high Al content alloy like AZ91 has an appreciable amount of  $\beta$  Mg<sub>17</sub>Al<sub>12</sub> along the grain boundaries. figure 6 shows the microstructure of die cast AZ91D. Mg<sub>17</sub>Al<sub>12</sub> is cathodic with respect to the matrix and exhibits a passive behaviour over a wider pH range than either of its components Al and Mg.<sup>20)</sup> Mg<sub>17</sub>Al<sub>12</sub> was found to be inert in chloride solutions in comparison with the surrounding Mg matrix and could act as a corrosion barrier<sup>21)</sup> so that its distribution determined the corrosion resistance of the Mg-Al alloys.<sup>21)</sup> The high resistance of the Mg<sub>17</sub>Al<sub>12</sub> to corrosion is due to the presence of a thin passive film on its surface. However there is also an opposite opinion that Mg<sub>17</sub>Al<sub>12</sub> is detrimental to the Mg matrix. It was suggested<sup>22)</sup> that the absence of the Mg<sub>17</sub>Al<sub>12</sub> could enhance the corrosion resistance of Al-rich Mg base alloys by eliminating the

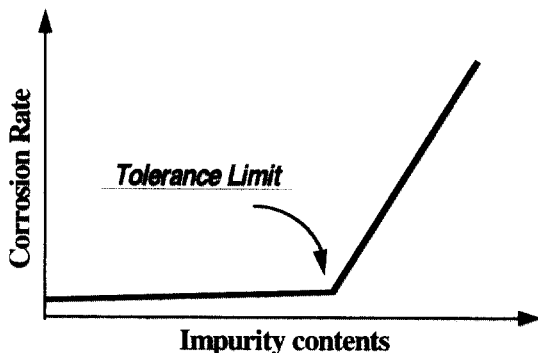


Fig. 5. Generalised curve for the influence of the impurity elements Fe, Ni, Co and Cu.

Fig. 6. Microstructure of die cast AZ91.

micro-galvanic effects. The Mg-Al based alloy was reported to corrode predominantly by galvanic action between the magnesium matrix and  $Mg_{17}Al_{12}$  phase.<sup>23)</sup>

Song et al.<sup>5,6)</sup> measured the polarisation curves for the  $\alpha$  and  $\beta$  phases as shown in figure 2. The  $\alpha$  phase was found to have a pitting potential about 15 mV more negative than its free corrosion potential, consistent with observations of pitting corrosion for the  $\beta$  phase exposed to 1M NaCl solution at its free corrosion potential. It was found that the  $\alpha$  phase had a higher cathodic activity than the  $\beta$  phase, but its anodic dissolution rate was much lower, below its pitting potential, than that of the  $\alpha$  phase. At their corrosion potentials the corrosion current density of the  $\beta$  phase was much lower than that of the  $\alpha$  phase. These findings led to the conclusion that the  $\beta$  phase was very stable in NaCl and was inert to corrosion; the  $\beta$  phase was itself, however, an effective cathode. Consequently, the  $\beta$  phase has two influences on corrosion, as a barrier and as a galvanic cathode, depending on the volume fraction of  $\beta$  in  $\alpha$  matrix. The  $\beta$  phase mainly served as a galvanic cathode and accelerated the corrosion process of the  $\alpha$  matrix if the volume fraction of  $\beta$  phase was small. However for a high volume fraction, the  $\beta$  phase might act as an anodic barrier to inhibit the overall corrosion of the alloy.

In addition to the  $\beta$ -phase, the most potent cathodes in Mg-Al alloys are iron-rich phases, probably the iron-aluminium intermetallic FeAl. It is one of the most detrimental cathodic phases present in Mg-Al alloys on the basis of its potential and its low hydrogen over-voltage<sup>24)</sup>. AlMn<sup>20,25)</sup> is also detrimental, and  $Mg_2Si$ <sup>25)</sup> seems to have no influence, while  $Mg_2Pb$  facilitates pitting and leads to a negative difference effect.

The matrix  $\alpha$  phase in Mg alloys is normally anodic to the second phases and usually is preferentially corroded. Song et al.<sup>5,6)</sup> have suggested that the primary  $\alpha$  and eutectic  $\alpha$  phases, which have different aluminium contents, have different electrochemical behaviour. Both the primary and eutectic  $\alpha$  can form galvanic corrosion cells with the  $\beta$  phase, as is illustrated in figure 7 There are therefore two kinds of corrosion morphology:

- \* The primary  $\alpha$  grain is preferentially dissolved; and
- \* The  $\beta$  phase is undermined because of the dissolution of the eutectic  $\alpha$ .

Actual exposure of die cast AZ91D in NaCl illustrates both kinds of corrosion morphology, figure 8 Furthermore, Song et al.<sup>6)</sup> found that the casting method strongly influences the corrosion performance through microstructural differences. The skin of diecast AZ91D showed a corrosion resistance significantly better (by nearly a factor of ten) than its interior, Table 2 This could be attributed

Fig. 7. Schematic representation of the galvanic corrosion between the  $\beta$  phase and the  $\alpha$  phases.

Fig. 8. Typical corrosion morphology of die cast AZ91 after a few minutes in NaCl solution.

to a higher volume fraction of  $\beta$ , and more continuous  $\beta$  around finer  $\alpha$ -grains. If the  $\alpha$ -grains are very fine and the  $\beta$  fraction is not too low, then the  $\alpha$  phase is nearly continuous like a net over the  $\alpha$  matrix, and the  $\beta$  phase particles do not easily fall out by undermining. Instead, in this case the  $\alpha$ -matrix is much more easily corroded. Also if the  $\alpha$  grains are fine, the gaps between  $\beta$  particles are narrow and the  $\beta$  phase is nearly continuous. The corrosion of the  $\beta$  phase is then quite easily obstructed by corrosion products on its surface, and so the corrosion is greatly retarded. figure 9 schematically illustrates this case. On the other hand, if the  $\alpha$  grain size is large, the  $\beta$  phase is agglomerated and the distance between the  $\beta$  phase is large, then the corrosion of the  $\alpha$  phase is not effectively

Fig. 9. Schematic representation of  $\beta$  phase protection.Table 2. Corrosion rates under open circuit conditions in 1N NaCl.<sup>6)</sup>

Sample	Rate, mm/y	Mechanism
LP Mg (240 ppm Fe)	53	Impurity accelerated corrosion
HP AZ91 sand cast	12	$\beta$ accelerates corrosion
AZ91D - die cast (interior)	5.7	$\beta$ accelerates corrosion
High purity Mg	1.1	
AZ91D - die cast (surface)	0.66	$\beta$ Phase
$\beta$ protects	0.30	

blocked either by the  $\beta$  phase or by corrosion products, and the  $\beta$  phase accelerates the corrosion of the  $\alpha$  phase.

The possible types of behaviour are summarised by the corrosion rate data given in Table 2 for magnesium and magnesium alloys corroding at their free corrosion potentials in 1N NaCl at pH11. High purity magnesium showed a corrosion rate of 1.1 mm/y. A higher corrosion rate was shown by the interior of die cast AZ91D and by the high purity sand cast AZ91. The  $\beta$  phase accelerated the corrosion. In contrast, the surface of die cast AZ91D had a corrosion rate lower than that of high purity magnesium. The  $\beta$  phase provided protection as is clear from the still lower corrosion rate shown by pure  $\beta$ .

#### 4. Environmental influences

No material can be highly corrosion resistant in all environments. The high corrosion resistance of a material always refers to some particular environment. A particular material could have a high corrosion resistance in a certain environments but a low corrosion resistance in another.

Therefore it is important to understand the various environmental influences.<sup>1),2)</sup>

Aqueous solutions bring about attack of magnesium which varies not only with the solute but with the volume, movement and temperature. Attack by cold pure water of low conductivity is very slow. A continuous film of such water can provide protection against the "mosphere" and give rise to higher fatigue endurance limits than are obtained in ordinary air. Reaction with water produces a film of sparingly soluble  $Mg(OH)_2$ .<sup>26)</sup> Dissolved oxygen does not appear to play a major role in the corrosion of magnesium and its alloys in chloride solutions. Salt solutions, or even distilled water saturated with  $CO_2$  are corrosive.

Magnesium is very resistant to corrosion by alkalis if the pH exceeds 10.5 which corresponds to the pH of saturated  $Mg(OH)_2$ ; a  $Mg(OH)_2$  film is formed on the magnesium surface. Dilute alkali solutions show negligible attack at temperatures up to the boiling point. Consequently, a 10% caustic solution is commonly used for cleaning at temperature up to the boiling point.

Sodium chloride solutions containing appreciable quantities of alkali attack magnesium and its alloys at a very low rate. With increasing pH above 10.2 at which  $Mg(OH)_2$  is formed, the effect of both impurities in the metal and in the corroding media is apparently overshadowed by the greater tendency for film formation. Chloride ions promote rapid attack of magnesium in neutral aqueous solutions. The corrosion rate increases rapidly with increasing Cl-ion concentration. Small amounts of dissolved salts in water, particularly chloride or heavy-metal salts, break down the protective film locally and lead to pitting corrosion. In chloride solutions such as sea-water, attack usually results in pitting corrosion.

Neutral or alkaline fluorides form insoluble  $MgF_2$  and are not appreciably corrosive. Fluorides are chemically inert. It is well known that the fluoride ion is a good corrosion inhibitor for Mg and its alloys.<sup>27),28)</sup> The protection is due to the formation of a  $MgF_2$  film on the surface of the metal. Magnesium fluoride is very insoluble in hydrofluoric acid and as a consequence magnesium does not dissolve in this acid. However in dilute aqueous hydrofluoric acid, attack may take place, and if so it will be of a pitting type.<sup>29)</sup>

Magnesium sulphate is readily soluble in dilute sulphuric acid, and no protective film is formed in this acid, so the attack is rapid. But magnesium sulphate is only slightly soluble in concentrated sulphuric acid. Therefore, when magnesium is immersed in strong sulphuric acid, the initial attack produces a film of magnesium sulphate which quickly saturates the acid at the interface, and the reaction

is reduced to a vanishingly low rate.

Nitrates, phosphates and sulphates attack magnesium, but not to the same extent as chlorides. Silicate, fluoride, phosphate, dichromate solutions are less corrosive than  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ . In pure water, as well as alkaline and alkaline earth-hydroxide, silicate, fluoride and carbonate solutions, the corrosion rate is rather insignificant and polarisation occurs easily with small anodic currents. In solutions containing anions such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$ , the corrosion rate is fairly high, and the potential shifts very little with current density.<sup>30)</sup>

Oxidising salts, especially containing chlorine or sulphur atoms, are more corrosive than non-oxidising salts, but chromates, vanadates, phosphates, and many others are film-forming and tend to retard corrosion. Chromic acid attacks magnesium and its alloys at a very low rate. So a boiling solution of 20%  $\text{H}_2\text{CrO}_3$  in water is widely used to remove corrosion products from magnesium alloys without attacking the base metal.

Magnesium is readily attacked by all mineral acids except chromic and hydrofluoric acids. But traces of chloride ion markedly increase the corrosion rate. Some organic acids appreciably attack magnesium and its alloys, especially those which contain reactive polar groups. The stronger acids such as acetic and tartaric are often used at about 10% to pickle cast and wrought products. Many organic liquids are quite inert to magnesium at room temperatures, such as ethyl alcohol, methylated spirits, oils and degreasing agents.

In general, atmospheric attack in damp conditions is largely superficial. If the atmosphere is clean but not dry and the humidity approaches 100%, a scattered pattern of corrosion spots appears after a period, but considerable areas of unaffected surface remain for a very long time. However if the surface has been contaminated by corrosive dust or cathodic particles, then the whole surface rapidly becomes covered with a greyish layer of corrosion product. A clean, unprotected magnesium alloy surface exposed to indoor or outdoor atmospheres free from salt spray develops a gray film that protects the metal from corrosion. Magnesium alloys show inherently different corrosion rates and corrosion resistances depending upon the alloy content and the particular alloying elements.

Humidity plays a major part in the corrosion of magnesium and its alloys. Water vapour in air increases corrosion. The rate of attack is negligible at low humidity, but increases considerably above about 90% R.H.<sup>31)</sup> At relative humidities up to 90%, corrosion is very minor, resulting from the formation of a nearly invisible film of amorphous  $\text{Mg}(\text{OH})_2$ . As the humidity increases beyond this level, heavier tarnish films develop, and the principal corrosion

product is crystalline  $\text{Mg}(\text{OH})_2$ .

Dry chlorine, iodine, bromine, and fluorine cause no corrosion at ambient temperatures, even when they contain 0.02%  $\text{H}_2\text{O}$ . But wet chlorine, iodine, and bromine below the dew point cause severe attack.

Salt solutions are corrosive but dry salt particles are almost without effect. Unpainted magnesium items exposed near the sea coast invariably exhibit a dull, slightly rough surface, with no corrosion product evident.<sup>32)</sup>

$\text{SO}_2$  as either the vapour or the liquid phase causes no corrosion, but wet  $\text{SO}_2$  is severely corrosive due to formation of sulfurous and sulfuric acid. But  $\text{SO}_2$  is very effective in reducing the high temperature oxidation of Mg. Natural gas does not attack magnesium, but the presence of water vapour may lead to very slight corrosion.

Magnesium is quite resistant to corrosion in soil. The presence of calcium and magnesium salts in most soils tend to inhibit corrosion, but the corrosivity is different in different kinds of soil.

Usually, a higher temperature leads to a higher corrosion rate. The increasing rate of corrosion, with increase in temperature of the ternary alloys is relatively high compared to the relatively static rate of pure magnesium. This may be due to the presence of small amounts of impurities in the former that become active at higher temperatures. It appears that the onset of pitting corrosion in a given alloy depends on the temperature. There is probably a "critical pitting temperature" below which only uniform corrosion is encountered. The corrosion of AZ31 in magnesium perchlorate increased gradually with increasing temperature.<sup>33)</sup>

The velocity of the flowing aqueous solution is critical when it is sufficiently high to affect the protective hydroxide film. Agitation or any other means of destroying or preventing the formation of a protective film leads to increased corrosion. The higher rates of attack in flowing water are interesting in that the flowing water may mechanically dislodge some of the soft bulky hydroxide surface film and may also prevent local increases in pH in the neighborhood of the specimens.

## 5. Environment assisted cracking

There is the expectation that environment assisted cracking (EAC) (including stress corrosion cracking (SCC) and hydrogen embrittlement (HE)) failures will increase with increased use of Mg alloys in load bearing applications. Magnesium alloys are known to be susceptible to EAC. For example, the authoritative ASM Handbook,<sup>34)</sup> Vol 13, "Corrosion" on SCC of magnesium alloys can be summarised as follows. Magnesium alloys containing



more than 1.5% Al are susceptible to SCC. Wrought alloys appear more susceptible than cast alloys. While there is little documentation of service SCC of castings, laboratory tests can cause SCC at tensile loads less than 50% of yield stress in environments causing negligible corrosion. The low incidence of service SCC failures can be attributable to low actual stresses<sup>34)</sup> in service in the past.

However, the incidence of EAC is expected to increase because the service conditions for Mg alloys are changing rapidly, particularly in the automobile industry where magnesium components are being increasingly used in structural load-bearing applications. Automobile examples include: engine blocks, transmission housings, engine oil pans, magnesium wheels, and structural body castings such as doorframes, body connectors and cross-members. Furthermore, increased loading on these magnesium components is a natural progression as designers increase the loads and decrease the section sizes of components as part of the environment imperative to decrease weight. Moreover, the magnesium components in the load bearing applications are increasing in complexity, and this increasing complexity increases the probability of high loads in some parts of such components.

A similar trend of increased loading on components was carried out by aerospace designers in the period 1961 through 1969 (to increase load carrying capacity of aircraft), which led to a threefold increase in EAC of high-strength steels, Al alloys, Mg alloys and Ti alloys in these aerospace applications.<sup>35)</sup> Consequently, past experience leads to the expectation of increased incidence of EAC service failures due to the increasing use of magnesium components of increasing complexity in structural load-bearing applications.

Thus, while the EAC susceptibility of AZ type Mg alloys is accepted in the aerospace industry, there is little information on newer Zr refined Mg alloy systems, which are already used in aerospace applications.<sup>36)</sup> Thus there is an urgent need to understand EAC of cast automobile alloys like AZxx, AMxx, ASxx and the new engine block alloy and the sand-cast Zr containing aerospace alloys like WExx. Investigation, understanding and development of EAC related design criteria would be invaluable to the automobile and aerospace industries. Our discussion deals in turn with (1) mechanical and metallurgical aspects, (2) solution / environmental aspects and (3) mechanisms.

### 5.1 Mechanical and metallurgical aspects

There seems to be almost no published EAC research on cast magnesium alloys.<sup>2),10)</sup> This is in contrast to the considerable research on the EAC of wrought magnesium alloys during the 60s, 70s and 80s<sup>37-41)</sup> and on rapidly

solidified magnesium alloys in the early 90s<sup>42)</sup> which was prompted by the needs of the aerospace and defence industries. Early reviews<sup>37-38)</sup> in 1966 reported that alloying additions such as Al and Zn promoted EAC; thus AZxx alloys were susceptible to EAC for intermittent exposure to 0.01% NaCl and to the Weather (ie humid air with intermittent wetting and drying) whereas M1 and (the then existing) Zr containing alloys were in practice free of EAC. Subsequent studies<sup>39-44)</sup> all have concentrated on pure Mg or Mg-Al alloys. Lynch and Trevena<sup>39)</sup> showed that SCC of pure magnesium was transgranular, with significant plasticity shown on crystallographic facets. They advocated a crystallographic adsorption decohesion mechanism for the SCC of pure magnesium in 3.3% NaCl + 2% K<sub>2</sub>CrO<sub>4</sub> solution. Ebtehaj et al<sup>40)</sup> studied the EAC of Mg-7Al in NaCl + K<sub>2</sub>CrO<sub>4</sub> solutions. They found that the EAC thresholds were as low as 80 MPa or 6 MPa(m, compared with a 0.2% proof stress of 270 MPa and a K<sub>1C</sub> of 33 MPa(m. Thresholds were lowest at intermediate strain rates. This was interpreted in terms of the film rupture model of EAC. At fast strain rates ductile failure occurred because there was insufficient time for EAC. At slow strain rates, repassivation was thought to be sufficiently fast so that there was always a surface film on the alloy surface which prevented hydrogen ingress and embrittlement. At intermediate strain rates, corrosion at the bare crack tip generated hydrogen by the accompanying cathodic reaction, the hydrogen causing the actual crack advance. Stampella et al<sup>41)</sup> also concluded that hydrogen was involved in the crack advance for pure magnesium in Na<sub>2</sub>SO<sub>4</sub> solution, with the strain breaking the crack tip film and thereby allowing corrosion and concomitant hydrogen liberation. Makar et al<sup>42)</sup> studied the EAC of rapidly solidified magnesium aluminium alloys (1% and 9% Al) in 0.35 %NaCl + 0.4% K<sub>2</sub>CrO<sub>4</sub> solutions and attributed the mechanism to a brittle hydride forming ahead of the crack tip.

This prior work<sup>39-42)</sup> on pure magnesium and simple binary Mg-Al wrought alloys showed that EAC of pure Mg and simple binary Mg-Al alloys is a significant issue, and that EAC can occur for a load condition equivalent to 30% of the yield stress.<sup>40)</sup> If pure Mg and Mg-Al alloys show EAC, it would indeed be extremely surprising if M1, AMxx and Zr based alloys were free of EAC, particularly since eg the mechanical, deformation and corrosion properties of AZxx and AMxx alloys are quite similar. Indeed it was not possible to find any confirmation in the open literature of the early work,<sup>37),38)</sup> and unpublished work by MEL and confidential industrial reports from the USA indicate some EAC for Zr containing alloys.<sup>36)</sup> Clearly this early work<sup>37-38)</sup> needs to be checked, particularly for

modern cast alloys. Furthermore, the prior works<sup>37,38-39</sup> with the exception of<sup>40</sup> did not measure thresholds so it is difficult to use such results for component design. There is a need to understand how the initiation stress for EAC relates to the yield stress in commercial cast alloys. There is also the obvious question as to the influence of the additional alloying elements (Zn, Mn and Si) in the popular AZxx, AMxx, and ASxx series, as well as the influence of the other major alloying elements (Zn, Zr, Y, RE [rare earth elements]) in the other commercial alloys. Furthermore, cast alloys have significant metallurgical differences to wrought alloys. Their influence is unknown at this stage.

## 5.2 Solution/environment aspects and electrochemistry

There are significant discrepancies in the literature regarding environment conditions leading to EAC of magnesium alloys. Popular for testing are solutions containing both NaCl + K<sub>2</sub>CrO<sub>4</sub><sup>39,40,42</sup> because of the relevance to the service conditions of a chromate passivated magnesium surface being attacked by a chloride containing solution. EAC is associated with pitting<sup>40</sup> in these chloride plus chromate solutions and also in the sulphate solution without chromate oxidizer.<sup>42</sup> However, magnesium and magnesium alloys are known to pit in chloride solutions containing no chromate<sup>2</sup> but Ebtehaj et al<sup>40</sup> found no EAC in their chloride solutions containing no chromate. Other workers however have reported EAC in chloride only solutions, exposure to the atmosphere<sup>37</sup> and even in distilled water.

Furthermore, there are at present no studies concerning the EAC propensity of proposed magnesium alloys in possible automobile engine coolants. Also there appears to be no application of advanced electrochemical techniques (electrochemical transient measurements, electrochemical impedance spectroscopy, electrochemical noise-measurements) to sort out the details of the corrosion chemistry relevant to the EAC of magnesium alloys, and corrosion enhancement of localised plasticity at the crack tip<sup>46-48</sup> and the localised enhancement of corrosion due to hydrogen adsorption and the influence of surface mobility of EAC crack advance.<sup>49,50</sup>

## 5.3 EAC mechanisms

Prior studies have come to conflicting conclusions as to the EAC mechanism. Lynch and Trevena<sup>39</sup> advocated a crystallographic adsorption decohesion mechanism at the crack tip. Ebtehaj et al<sup>40</sup> and Stampella et al<sup>41</sup> both advocated a mechanism involving strain induced film rupture leading to corrosion and hydrogen production, with crack advance due to hydrogen decohesion ahead of the crack

tip. Makar et al<sup>42</sup> however attributed the EAC mechanism to a brittle hydride forming ahead of the crack tip; they also indicated that the diffusion coefficient for hydrogen in magnesium has not been measured. Pickering and Swan<sup>43</sup> advocated a mechanism involving corrosion tunnels, whereas Pugh and coworkers<sup>44</sup> advocated a mechanism of a rupture of a brittle surface film. Since these studies, there have been significant developments in the mechanistic understanding of EAC. A particularly interesting comparison of experimental data and existing EAC models was carried out by Vogt and Speidel<sup>45</sup> for two commercial aluminium alloys. Particularly interesting also are the recent ideas of Magnin and coworkers<sup>46-48</sup> regarding the interactions between anodic dissolution, hydrogen, plasticity, dislocation motion, and brittle crystallographic fracture; these were developed on FCC alloys. Also of great interest are the recent developments in the surface mobility mechanism<sup>49-50</sup> which the authors and also Vogt and Speidel<sup>45</sup> claim to be able to explain many cases of stress corrosion cracking of Al alloys (FCC crystal structure) and steels (BCC). Thus there is a significant opportunity to use the study of EAC of magnesium alloys which have a HCP crystal structure, to extend mechanistic understanding of EAC. The work of Magnin and coworkers<sup>46-48</sup> in particular illustrate the power of experiments on single crystals to elucidate the mechanisms of EAC.

## 5.4 EAC framework

Staehele<sup>51</sup> proposed the development of corrosion mode diagrams to help organise and collate the enormous amount of information needed to specify the behaviour of an alloy class with respect to EAC. For example, if a designer wants reasonable assurance concerning EAC for say cast AZxx alloys, information is needed (ie is not yet available) and must also be presented (when it becomes available) in a readily useable format regarding:

1) alloy influences such as (1) alloy chemistry (including influence of the major alloying element Al, (2) the minor alloying element Zn, (3) trace elements like Fe, Ni, Cu, (4) microstructural features such as volume fraction, distribution and electrochemical properties of second phases, particularly continuous eutectic phases, and (5) slip type in the matrix phase, at the isolated second phase particles and at the eutectic microconstituent.

2) loading influences such as (1) load, (2) loading rate, and (3) prior history, and

3) environment influences such as (1) potential, (2) pH, (3) concentration and type of dissolved inert species like Cl<sup>-</sup> or SO<sub>4</sub><sup>=</sup>, (4) presence and concentration of reducible species like Cr<sup>6+</sup>, (5) presence of inhibitors, and (6)

presence of film forming reagents like F.

This enumeration of the known factors influencing EAC also emphasises how many factors there need to be considered in understanding EAC and representing the EAC influences. It also indicates that it is impossible to test all the influence of all factors known to be important. Staehle points out that a modified E-pH diagram (Pourbaix diag) is one form of condensed presentation of environmental conditions leading to EAC.

The approach can be very powerful in the study of the influence of the known major factors (1) alloy chemistry and microstructure, and (2) environment, whilst simultaneously carrying out mechanistic studies that provide insights about the influence of the major variables. For example, a major correlation of environmental influences becomes possible if there is a correlation between EAC and pitting as is expected from the literature<sup>2),40-41)</sup> or between EAC and some characteristic of anodic dissolution or cathodic hydrogen evolution. If there is a correlation, many tests can be carried out to survey conditions leading to pitting corrosion, (such tests are relatively quick so that it is possible to carry out many such test), and a few well chosen EAC tests can then lead to the understanding of EAC under many environmental conditions. Similarly, the metallurgy of transgranular EAC may be related to the relative ease of basal and prismatic slip and twinning.

### Unanswered issues

- \* Are modern AMxx and Zr containing magnesium casting alloys in practice free of EAC as suggested by the early (uncorroborated) reviews<sup>37-38)</sup> in 1966?
- \* Design allowables for safe service of magnesium alloys, and how these are controlled by the alloy and by mechanical and environment loading conditions. Relationship to (corrosion) fatigue as the largest individual failure mechanism would be of immense interest.<sup>36)</sup>
- \* Mechanical and metallurgical conditions leading to EAC for commercial cast magnesium alloys. Specifically how the conditions for EAC (initiation stress, initiation stress intensity factor, crack velocity) depend on (1) alloy chemistry variables (major alloying components such as Al, Zn, Y, RE); and (2) minor additions such as Zr, Zn, Mn, Si, RE in AZxx, AMxx, ASxx, ZExx and WExx alloys, (3) microstructural features such as volume fraction, distribution and electrochemical properties of second phases, particularly continuous eutectic phases, and (4) slip type in the matrix phase, at the isolated second phase particles and at the eutectic.
- \* Environmental/solution/temperature conditions leading to

EAC for commercial cast magnesium alloys. Specifically how the conditions for EAC depend on environment influences such as (1) potential, (2) pH, (3) concentration and type of dissolved electrochemically inert species like Cl<sup>-</sup>, (4) presence and concentration of reducible species like Cr<sup>6+</sup>, (5) presence of inhibitors, (6) film forming species like F-etc.

- \* Framework for presenting and collating EAC conditions for Mg alloys, including relationship to yield stress, slip type and pitting corrosion, plotting E-pH diagrams etc.
- \* Mechanism for EAC for commercial cast magnesium alloys, and how mechanistic knowledge provides guidance as to the influence of the mechanical, metallurgical and environmental variables and provides guidance regarding EAC mitigation strategies.

### Concluding

Magnesium is a very reactive metal so galvanic corrosion is always an issue in the use of magnesium alloys in engineering applications. The corrosion of magnesium alloys is controlled by surface films and the distribution and electrochemical activity of the phases in their microstructure. The surface films on magnesium are not generally as stable as those on aluminium and therefore magnesium alloys find application in a narrower range of environments.

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