The negative difference effect of magnesium and of the AZ91 alloy in chloride and stannate-containing solutions

Department of Metallurgy, Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, Brazil

A R T I C L E   I N F O

Article history:
Received 27 August 2009
Accepted 11 March 2010
Available online 15 March 2010

Keywords:
A. Magnesium
C. Pitting corrosion

A B S T R A C T

The negative difference effect of pure magnesium and of the alloy AZ91 was investigated by volumetric tests in NaCl with and without addition of Na2SnO3. Hydrogen comes from two sources: H2 which accompanies localized magnesium dissolution inside the pits and H2 from H2O reduction at the passive surface outside the pits. By separating the two parts it could be shown that the rate of hydrogen evolution inside the pits is quantitatively consistent with a two-step EC-mechanism of magnesium dissolution with hydrogen evolution coupled to the second dissolution step. Addition of Na2SnO3 does not influence the second step.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Magnesium and its alloys undergo pitting corrosion in chloride containing solutions. The massive attack by this type of localized corrosion usually begins above a pronounced threshold potential, called pitting potential. Above this threshold the current density rises by several orders of magnitude within a small potential range [1–3]. Pitting corrosion of magnesium and its alloys in chloride solutions is accompanied by hydrogen evolution. This is not a unique feature of magnesium, but it is reported for other metals like aluminium [4–6], aluminium alloys [7] and ferrous materials [8].

The curious effect that the rate of hydrogen evolution increases with the anodic polarization of the electrode is known in the literature as the negative difference effect. Under these conditions the difference between the current density of hydrogen evolution at the corrosion potential \( I_{H,corr} \) and that under anodic polarization \( I_{H,pol} \) becomes negative:

\[
I = |I_{H,corr}| - |I_{H,pol}| < 0
\]  

Several models were presented in order to explain this phenomenon [2,9–14]. The main proposals, published about the negative difference effect of magnesium [1,2,9,15–17], are based on the breakdown of a protective film, the formation of magnesium hydride, mechanical disintegration of the electrode and dissolution of magnesium involving monovalent ions. Despite of the different ways to explain the negative difference effect there is strong evidence that the effect is correlated with localized anodic dissolution of the metal since the effect is typically known from systems where the metal undergoes pitting corrosion. This applies, for example, to aluminium in chloride, bromide and iodide solutions [4,7]. The generation of hydrogen bubbles inside pits was confirmed by in situ optical microscopy by different authors [7,18–21] and the convection of the pit electrolyte by bubble generation was part of the discussion about transport and dissolution kinetics during pitting [21]. Drazic and Popic [19] examined the negative difference effect of aluminium with a rotating ring-disc electrode and stated that there is no negative difference effect without pitting.

More recently, the interaction of magnesium alloys with hydrogen has gained attention due to the search for new hydride forming lightweight alloys with high hydrogen storage capacity. Moreover, it was observed that charging with hydrogen can improve the corrosion resistance of magnesium alloys [22–24]. Bakkar and Neubert [22] attributed the beneficial effect to the formation of a stable and electrically isolating hydride. Zhang et al. [23] observed a decrease of the negative difference effect after a cathodic pretreatment of magnesium specimens. They explained the effect by the modification of the semiconductive properties of the passive layer due to H-absorption and resulting lower charge carrier density.

The pitting potentials of magnesium and its alloys in chloride solutions are strongly negative: \(-1.2 \to -1.4 \text{ V(SHE)}\) [25]. At these potentials the direct reduction of hydrogen from water molecules by

\[
2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2
\]  

cannot be neglected. The production of OH\(^-\) and the subsequent alkalinization of the surface might be an important factor for the stability of the passive film of magnesium. For the examination of the negative difference effect, however, the hydrogen evolution at the passive surface means that the hydrogen collected during a
volumetric test comes from two different sources: First from a reaction which is associated with the localized dissolution of magnesium and takes place inside the pits and second from the decomposition of H2O on the oxide covered surface outside the pits. Most reports, published about this issue, even more recent ones [23], do not consider that hydrogen is generated by at least two different reactions. Thus, a more complete model, considering all involved reactions and related current values, was previously formulated [25]. In the present work this model was tested in chloride solutions with Na2SnO3 additions.

Stannate is of interest in this context for two reasons:

1. Tin is a metal with a high overvoltage for hydrogen evolution. When migrating into pits, stannate might be reduced at the very negative pitting potential of magnesium and might inhibit hydrogen evolution in chloride solutions.

2. Stannate has been used as a component in electrolytes for anodizing [26] and for conversion coatings [27,28] to improve the resistance to localized corrosion. It is therefore of interest to study the behaviour of stannate in the case of pitting.

2. Model of the localized corrosion of magnesium and development of equations

The partial reactions occurring inside a pit during the localized corrosion of magnesium are:

\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \]  
\[ 2H^+ + 2e^- \rightarrow H_2 \]  
\[ 2H^+ + 2e^- \rightarrow H_2 \]  

The cathodic reaction outside the pits, due to the strongly negative pitting potential of magnesium and might inhibit hydrogen evolution in chloride solutions.

As a consequence, the volume of hydrogen gas, evolved during magnesium corrosion in chloride containing solutions, is given by the sum of the reactions (2) and (4). Assuming that the reduction of oxygen is also a possible reaction, the partial currents during a galvanostatic test with an applied current density \( i_{app} \) can be described as follows:

\[ i_{Mg} = |i_{HP}| + |i_{HO}| + |i_O| + i_{app} \]  

with \( i_{Mg} \) is the current density of Mg-dissolution under galvanostatic anodic polarization; \( i_{app} \) is the current density of hydrogen reduction inside pits under galvanostatic anodic polarization; \( i_{HO} \) is the current density of hydrogen reduction outside the pits; Definition: "outside" means \( H_2 \) evolution at a surface which at that moment does not undergo active metal dissolution by pitting. This can be an unattacked passive surface as well as a repassivated surface inside a pit; \( i_O \) is the current density of oxygen reduction; and \( i_{app} \) is the anodic current density applied to a galvanostatic test.

The current density of oxygen reduction \( i_O \) can be considered small [29,30] and can therefore be neglected in comparison with the current density of hydrogen reduction. It should be mentioned that this is not a necessary condition for our model since \( i_O \) will be eliminated from the equations in the following steps.

In a volumetric test under galvanostatic polarization the following equation is valid:

\[ i_{HO} + i_{HP} = i_{HV} \]  

where \( i_{HV} \) is the current density determined by volumetric measurement.

The assumption implied in Eq. (7) is supported by the experimental results of different authors [7,19], who studied the negative difference effect of aluminum. Due to the much higher pit- 
ential potential of aluminium, the hydrogen evolution in this case must be correlated with the localized aluminium dissolution inside the pits. Hydrogen evolution on aluminium in nearly neutral electrolyte is negligible at this potential without pitting corrosion. Moreover, Tunnold et al. [1] found proportionality between the rate of hydrogen evolution and the applied current density for pure magnesium and for the alloy AZ63 at low applied current densities and low chloride concentrations.

Applying Eqs. (7) to (5) and (6), one obtains:

\[ i_{Mg}(1-k) - |i_{HO}| = |i_O| = i_{app} \]  
\[ |i_{HO}| + ki_{Mg} = |i_{HV}| \]  

The equations show that the constant \( k \) can be determined from volumetric measurements with different applied current densities:

\[ k = \frac{|i_{HV,1}| - |i_{HV,2}|}{|i_{HV,1}| - |i_{HV,2}| + i_{app,1} - i_{app,2}} \]  

After calculating \( k \), \( i_{HO} \) can also be determined from Eq. (9). The current density \( i_{HO} \) can be considered as constant when the polarization is small, i.e. when the electrode potential \( E(i_{app,1}) \approx E(i_{app,2}) \).

Since

\[ i_{Mg} = |i_{HV}| + i_{app} \]  

Eq. (10) can also be written as:

\[ k = \frac{\Delta i_{HV}}{\Delta i_{HV} + \Delta i_{app}} = \frac{\Delta i_{HV}}{\Delta i_{Mg}} \]  

or written as gradient:

\[ k = \frac{di_{HV}}{di_{Mg}} \]  

The integration gives:

\[ |i_{HV}| = ki_{Mg} + C \]  

Since

\[ i_{HO} + i_{HP} = i_{HV} \]  

the integration constant is

\[ C = |i_{HO}| \]  

Consequently, the constant \( k \) and the current density of hydrogen evolution outside the pits \( i_{HO} \) can be determined from the slope and the abscissa, respectively, of a \( i_{HV} \) vs \( i_{Mg} \) diagram.

3. Experimental

Tests were performed with pure magnesium and with an AZ91 alloy. The composition of these materials is listed in Table 1. The pure metal has been acquired in the form of cylinders with a diameter of 6 mm. One-millimetre thick discs were cut from these cylinders. The AZ91 alloy was available in the form of an ingot and was cut into discs with 1200-grit SiC-paper. For the electrical contact the specimens were squeezed between two platinum tips and the contact was isolated from the electrolyte with a lacquer. A burette with a funnel-shaped opening was turned upon the specimens in order to collect the hydrogen gas. The counter-electrode was positioned outside this opening to avoid the entrance of gas evolved at this electrode. The burette had a 0.02 mL scale and was filled with
electrolyte up to the zero-millilitre-level before the beginning of the tests. The volume of the solution used in the volumetric tests was always 350 mL. The surface area of the specimen of pure magnesium was always about 0.5 cm² and that of the AZ91 alloy was always about 2 cm². All tests were performed in an open cell, i.e. in air-saturated solutions. The solutions were prepared from p.a. grade chemicals and distilled water. The molar H₂ volume was corrected for the temperature of the test (25 °C), the height of the electrolyte column in the burette and the vapour pressure of the electrolyte. The following equation was applied:

\[ V_{\text{mol}} = V_{\text{mol}}^0 \frac{T}{T_0} \left[ \frac{p^0 - p_{\text{H₂O}}}{\gamma g h_{\text{sol}} + p_{\text{H₂O}}} \right] \]

with \( p^0 \), \( T^0 \), \( V_{\text{mol}}^0 \) is the pressure, absolute temperature, molecular volume at standard condition; \( T \) is the absolute temperature at test conditions (298 K); \( \gamma \) and \( g \) is the density of the test solution; \( h_{\text{sol}} \) is the average height of the electrolyte column in the burette during the test; and \( p_{\text{H₂O}} \) is the vapour pressure in equilibrium with the test solution.

Potentiodynamic tests were performed with a scan rate of 3 mV/min using a Pine Instrument Bipotentiostat with a modified scan generator.

When potential measurements were necessary, an Ag/AgCl electrode in 3.5 M KCl was used as reference electrode. All potentials mentioned in this work refer to the standard hydrogen scale (SHE).

4. Results

4.1. Volumetric tests in 1 M NaCl solution

4.1.1. H₂-Volume vs time curves in galvanostatic tests

Typical curves of the hydrogen gas volume \( V_H \) vs time during galvanostatic tests with the AZ91 alloy are shown in Fig. 1. The curves start with an initially lower rate of hydrogen evolution. The rate rises after some time and in the following the rate stabilizes at a constant rate. This effect disappears at applied current densities higher than about 4 mA/cm². The reproducibility of tests with these s-shaped curves was generally worse than under conditions where this effect did not appear.

4.2. Hydrogen evolution as a function of the anodic current density

4.2.1. The negative difference effect

The results of the volumetric tests with pure magnesium and with the AZ91 alloy in 1 M NaCl solution showed the main characteristics of the negative difference effect, i.e. the increase of the rate of hydrogen evolution with the increase of the anodic polarization (Fig. 3). In the case of pure magnesium, there was a considerable scattering of the results, especially, when the applied anodic current density was lower than about 4 mA/cm² (Fig. 3). This scattering was much less in the case of the AZ91 alloy.

In Fig. 4, \( I_{\text{HV}} \) is plotted vs the current density of magnesium dissolution \( I_{\text{Mg}} \), which can be calculated by

\[ I_{\text{Mg}} = I_{\text{HV}} + I_{\text{app}} \]  

For the curve of pure magnesium, the averaged values of Fig. 3 were used. As predicted by the model presented in the model-and-equations paragraph (Eq. (14)), a linear relation between \( I_{\text{Mg}} \) and \( I_{\text{HV}} \) can be observed.

The constant \( k = dI_{\text{HV}}/dI_{\text{Mg}} \) and the current density of hydrogen evolution outside the pits \( I_{\text{HO}} \) can be determined from the slope and the abscissa, respectively, of the least square fits in Fig. 4.

Table 1
Composition of Mg and of the AZ91 alloy.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>Zn</th>
<th>Cu</th>
<th>Ni</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.002</td>
<td>0.0015</td>
<td>0.0015</td>
<td>0.0015</td>
<td>0.0015</td>
<td>0.0004</td>
<td>–</td>
<td>Rest</td>
</tr>
<tr>
<td>AZ91</td>
<td>8.0–9.5</td>
<td>&lt;0.006</td>
<td>0.10–0.40</td>
<td>&lt;0.06</td>
<td>0.30–1.0</td>
<td>&lt;0.015</td>
<td>&lt;0.001</td>
<td>Rest</td>
</tr>
</tbody>
</table>

![Fig. 1](image1.png) Volumetric measurement of hydrogen evolution vs time during galvanostatic tests with AZ91 in 1 M NaCl for applied current densities between 0 and 16 mA/cm².

![Fig. 2](image2.png) Volumetric measurement of hydrogen evolution vs time during galvanostatic tests with pure magnesium in 1 M NaCl for applied current densities between 0 and 16 mA/cm².
One obtains: $k = \frac{dI_{HP}}{dI_{Mg}} = 0.51$ and $|I_{HO}| = 2.6 \text{ mA/cm}^2$ for pure magnesium and $k = 0.31$ and $|I_{HO}| = 0.13 \text{ mA/cm}^2$ for the AZ91 alloy.

Because of the scattering of the data at low current densities, $I_{HO}$ was also determined by a second way: $I_{HO}$ can be determined from the graph $I_{HV}/I_{Mg}$ vs $I_{Mg}$ in Fig. 5. Here, $k$ appears as the limit of $I_{HV}/I_{Mg}$ at high current densities since then $|I_{HO}|$ is much smaller than $|I_{HV}|$ and therefore $I_{HV} \approx I_{HR}$. The current density of hydrogen reduction outside the pits can be deduced from the part of Fig. 5 where $I_{HV}/I_{Mg}$ begins to rise. This rise comes from the growing part of $I_{HO}$ included in $I_{HV}$ at lower current densities $I_{Mg}$. With values of $I_{HV}$ and of $k$ from Fig. 4, Eq. (9) can be used to calculate $I_{HO}$. The results, plotted in Fig. 6, confirm the tendency of the values obtained from Fig. 4: For pure magnesium, $|I_{HO}|$ is between 1.0 and 3.5 mA/cm² i.e. much higher than the value for the alloy AZ91 which is between 0.05 and 0.18 mA/cm². As observed in the other measurements, the scattering of $I_{HO}$ for pure magnesium was stronger than for the alloy. The values of $I_{HO}$ do not show a pronounced dependence from the applied current density. Consequently, the assumption $I_{HO} = \text{constant}$, made in the previous section, can be considered as correct.

### 4.3. Volumetric tests in stannate-containing solution

Fig. 7 shows the influence of stannate on the hydrogen evolution reaction for pure magnesium and for the AZ91 alloy. For the sake of comparison, the results in NaCl solution without stannate are included as dashed lines. In the case of pure magnesium, the current density of hydrogen evolution is generally lower than in the pure 1 M NaCl solution. The least square fit of the data in stannate-containing solution gives a straight line with: $|I_{HV}| = 0.84 \text{ mA/cm}^2 + 0.48 \cdot I_{Mg}$. This shows a reduction of the current density of hydrogen evolution outside the pits from about 2 mA/cm² to 0.84 mA/cm² without stannate and with stannate, respectively (Fig. 7). The influence of stannate on the $H_2$ evolution inside the pits is expressed by the factor $k = \frac{dI_{HV}}{dI_{Mg}}$. With $k = 0.51$ in pure 1 M NaCl and $k = 0.48$ in stannate-containing solution, this influence is rather small.

In the case of the AZ91 alloy, the influence of Na$_2$SnO$_3$ on the hydrogen evolution is very small. The $H_2$ evolution outside the pits (abscissa) and the constant $k = \frac{dI_{HV}}{dI_{Mg}}$ (gradient of the curve) and thus the hydrogen evolution inside the pits remains nearly unchanged within the experimental error.

Tin was detected by EDS inside and outside the pits on corroded specimens. Generally, the tin concentrations found inside the pits were slightly higher.
4.4. Pitting potentials of magnesium and AZ91

Galvanostatic measurements of the pitting potentials are shown in Fig. 8. In 1 M NaCl solution, the pitting potential of the alloy AZ91 is about 50 mV higher than the pitting potential of the pure magnesium. The very steep rise of the current density curve for both the alloy and the pure metal justifies the assumption, used in the present work, that the hydrogen reduction outside can be regarded as nearly constant within a not too high range of applied anodic current densities.

The addition of 0.1 M Na2SnO3 shifts the pitting potential of pure magnesium by about 20 mV. The current density–potential curve remains nearly as steep as in the tests without Na2SnO3.

In the case of the AZ91 alloy, the shift by Na2SnO3 addition is higher and the pitting potential in the solution with Na2SnO3 is less stable. The difference between the solution with and without stannate is 70–110 mV.

4.5. Potentiodynamic curves

Potentiodynamic measurements started at a potential of −1.7 V(SHE) and the potential was increased until the onset of pitting corrosion (Fig. 9a and b). The scan direction was reversed when the anodic current density surpassed 2 mA/cm² and the reverse scan continued until reaching −1.7 V(SHE) again. Despite of the relatively slow scan rate of 3 mV/min, a considerable hysteresis i.e. a delay of the nucleation of pitting during the forward scan was observed in all cases. This delay was greater in the case of the AZ91 alloy than in the case of the pure magnesium. It is remarkable that the pitting potentials determined from the reverse scans are all in very good agreement with the stationary values from the galvanostatic tests. This applies to the pure 1 M NaCl solution as well as to the solution with 0.1 M Na2SnO3 in which a shift of the pitting potential is observed. The results demonstrate that for magnesium and for AZ91 the threshold potential above which heavy pitting begins and the repassivation potential for growing pits is the same.

The cathodic curve in the case of the AZ91 alloy in 1 M NaCl (Fig. 9a) has a Tafel slope of about −130 mV per decade. The cathodic curve of the reverse scan is slightly higher than that of the forward scan. The current density of hydrogen reduction outside the pits can be determined from the extrapolation to the stationary pitting potential of the cathodic curve of the forward scan. One obtains \( I_{H2/C0} = 0.15 \text{ mA/cm}^2 \) for AZ91 which is in reasonable agreement with the values determined from the volumetric tests (0.05–0.18 mA/cm²).

Some remarkable differences are observed in the cathodic curves of the pure magnesium (Fig. 9b). The curves are much less steep and the current density during the reverse scan is extremely increased when compared with the forward scan.

The extrapolation of the forward scan to the stationary pitting potential gives \( I_{H2/C0} = 0.30 \text{ mA/cm}^2 \). This is much lower than the value of about 2.6 mA/cm² measured in the volumetric tests. It is striking, however, that the extrapolation of the reverse scan gives \( I_{H2/C0} = 3 \text{ mA/cm}^2 \) which agrees with the volumetric tests. The difference between the cathodic curve of the forward scan and that of the reverse scan indicates differences between hydrogen evolution at an unattacked surface and at a pitted and repassivated surface, respectively.

The cathodic currents measured in the stannate-containing solution do not allow quantitative interpretations since they contain hydrogen evolution as well as reactions involving stannate ions. Qualitatively, the cathodic currents of pure magnesium in NaCl with stannate are clearly lower than in NaCl without stannate. This agrees with the inhibiting effect on the hydrogen evolution outside the pits, observed in the volumetric tests. For pure magnesium as well as for the AZ91 alloy the addition of stannate caused a change in the slope of the cathodic curves, indicating obviously a change of the mechanism of hydrogen reduction. In the case of the alloy, the pitting potential is shifted about 100 mV in the positive direction by stannate. However, as the volumetric tests revealed, this shift has little influence on hydrogen evolution during pitting. In order to study the inhibiting effect of stannate on hydrogen evolution at unattacked surfaces, specimens were pre-treated potentiostatically for 30 min at −1.49 V(SHE) i.e. below the pitting potential in 1 M NaCl + 0.1 M Na2SnO3 solution. Afterwards, voltammetric curves were measured in stannate-free 1 M NaCl solution. The comparison of specimens with and without stannate-pre-treatment (Fig. 10a and b) reveals the inhibiting effect of stannate.

In the case of pure magnesium, stannate lowers the exchange current density, while the Tafel slope remains constant. Consequently, the curves reflect the decrease of hydrogen reduction outside the pits found in the volumetric tests.
In the case of the AZ91 alloy the curve with stannate pre-treatment also differs from that without pre-treatment. However, the behaviour is more complicated. It can be seen that the polarization to cathodic potentials has an influence on the electrode behaviour i.e. differences between forward and reverse scan can be observed. It was recently discussed that cathodic polarization changes the charge carrier concentration of films on magnesium [9,10,31,32] and this might be one reason for the effect observed here. Moreover, the Tafel slope changes between forward and reverse scan and between curves with and without pre-treatment, respectively. It seems that the superposition of various effects makes the difference in hydrogen reduction rate disappear. Hence the volumetric tests did not show an influence of stannate on the hydrogen reduction outside the pits.

Data about the corrosion of magnesium and of AZ91, obtained from the analysis of the volumetric and the voltammetric tests, are summarized in Table 2.

5. Microscopic observations

Some clear differences can be observed between the morphology of the pitting attack on pure magnesium and that on the AZ91 alloy. In the case of pure magnesium, a few pits are formed on the surface at the beginning of the test. These pits are shallow and grow laterally (Fig. 11a). In this way they spread all over the surface after some time. Inside, the pits are generally covered by a thick corrosion product layer. At the few sites where the attacked metal surface can be seen (Fig. 11b) parallel crevices are visible. According to Tunold [1] this morphology leads to exfoliation after long corrosion experiments. The AZ91 alloy consists of Mg-rich α-phase and of the intermetallic β-phase (Mg17Al12). The β-phase can be present in the lamellar eutectic phase or in the divorced eutectic with massive β-phase and islands of α-phase (Fig. 12a). It is known that the lamellar phase in Mg–Al alloys can also be formed by cellular precipitation of the β-phase out of α-grains [25]. Pits formed in the AZ91 alloy are smaller, but more numerous (Fig. 12b). Obviously, these pits are deeper and do not grow so much laterally. As a consequence, pitting on pure magnesium leads to a larger attacked area than pitting on the AZ91 alloy. The attacked surface on the AZ91 alloy is generally hidden by a thick corrosion product layer which makes it difficult to identify the phase which was attacked. However, former studies have shown that pitting attack occurs preferentially at the α-phase [15,25].

6. Discussion

In several former works a linear relation between the applied anodic current density \(I_{app}\) and the rate of hydrogen evolution in volumetric tests \(I_{HO}\) has been reported [1,33]. Values of the constant \(k\), incompatible with a supposed mechanism of magnesium dissolution via Mg\(^+\) ions, were reported in some cases:

\[
\text{Mg} \rightarrow \text{Mg}^+ + \text{e}^- \quad (19) \\
\text{Mg}^+ + \text{H}^+ \rightarrow \text{Mg}^2+ + 1/2\text{H}_2 \quad (20)
\]

According to the EC-mechanism (Eqs. (19) and (20)) with metal dissolution occurring completely via Mg\(^+\), the rate of the hydrogen evolution reaction is expected to be proportional to the current density of magnesium dissolution \(I_{Mg}\), not to the applied current density \(I_{app}\). The deduction in the introduction of this work has shown that \(k\) has to be calculated by:

\[
k = \frac{\frac{dl_{HO}}{dl_{Mg}}}{\frac{dl_{app}}{dl_{app}}} = \text{const.}
\]

(21) With this definition, a value of \(k\) = 0.5 is expected for the EC-mechanism (since \(I_{Mg}\) stands for the oxidation of Mg to Mg\(^{2+}\) where the charge for the oxidation of Mg\(^+\) to Mg\(^{2+}\) is delivered by the hydrogen). Therefore, the measured value for pure magnesium, \(k\) = 0.51, agrees well with the supposed mechanism. The lower value of 0.31 for AZ91 shows obviously an influence of the dissolution of the alloying elements, especially of aluminium, since the \(k\)-value of aluminium and its alloys is around 0.15 [10].

When the definition

\[
k = \frac{dl_{HO}}{dl_{app}}
\]

(22)
is used, the value expected for the EC-mechanism via Mg\(^+\) ions is \(k = 1\), since then
\[
k = \frac{dI_{HV}}{dI_{app}} = \frac{dI_{HV}}{d(I_{Mg} - I_{HV})} \quad \text{with} \quad I_{HV} = 0.5I_{Mg}.
\]  

It must be guaranteed that \(I_{HO}\) is constant in order to fall out by the differentiation of \(I_{HV}\). In the work of Tunold [4], \(k = 1.4\) was found for magnesium in a 100 ppm NaCl solution. Although the magnesium electrode is described as nearly unpolarizable, there rests some uncertainty about this aspect. Measurements, that we made in solutions of 0.1 and 0.01 M NaCl solution showed a much stronger polarization [25], so that we considered these conditions as unsuitable for an analysis in the above-described manner.

With the knowledge of the constant \(k\), the corrosion current density of magnesium can theoretically be determined from voltammetric tests by the extrapolation of the cathodic curve, which should represent nothing else than \(I_{HO}\). Actually, the situation is more complex. The cathodic curve depends on the history of the electrode. The rate of the hydrogen evolution reaction is higher at an electrode which has already undergone localized corrosion. Obviously, the surface is modified by the localized attack in such a manner that the rate of the hydrogen evolution reaction increases. Indeed can be observed in potentiodynamic tests with magnesium during the reverse scan that hydrogen bubbles are preferentially formed at the area of the specimen which had been attacked by localized corrosion. The effect is more pronounced in the case of pure magnesium, probably because the attack is shallower and hence a larger area is attacked than in the case of AZ91. The comparison with \(I_{HO}\), determined from volumetric tests, has shown that the extrapolation of the cathodic current density – potential curve can lead to totally erroneous results. In the case of pure magnesium in NaCl, the extrapolation of the cathodic curve from the reverse scan agrees with the volumetric data. The extrapolation of the forward scans, however, leads to an underestimation of the corrosion current by a factor of 10.

The higher rate of hydrogen evolution at pitted and repassivated surfaces explains also the s-shaped curves of the volumetric tests with pure magnesium (Fig. 2). At the beginning, the pitted and repassivated area increases constantly, increasing in this way the rate of hydrogen evolution outside the pits. At a later stage of the test, most of the surface is already attacked. Then further pitting occurs mostly at already attacked and repassivated surfaces and thus the rate of hydrogen evolution remains constant. The effect appears only at the corrosion potential and at low applied current densities since only under these conditions a considerable part of the hydrogen comes from outside the pits.

The scattering of the results in the tests with pure magnesium at low applied current densities probably reflects a statistical scattering of pit nucleation since, generally, only a few shallow pits are formed on the specimen. The fact that scattering of the data is strong as long as the applied current density is not much higher than \(I_{HO}\) and that scattering is stronger for pure magnesium, which has a higher \(I_{HO}\), shows that scattering must be related with the current density outside the pits.

Mg(OH)\(_2\) (brucite) was identified by X-ray diffraction as the main corrosion product. Infrared spectra showed peaks in the OH-stretching region. However, the spectra for pure magnesium
and for the AZ91 alloy were very similar. Therefore, these results as well as the results of Raman spectroscopy of corroded surfaces [25] did not allow a conclusion why the current densities of hydrogen evolution are different at the two materials.

From the analysis of the volumetric tests in the above-described manner, one can conclude that the higher corrosion resistance of the AZ91 alloy in neutral NaCl can be attributed to two facts:

1. The lower cathodic current density outside the pits which is about one order of magnitude lower than in the case of pure magnesium.

2. The lower constant k which is 0.51 for pure magnesium but only 0.31 for the alloy. This means that in the case of the onset of localized corrosion 51% of the anodic charge is compensated inside the pits of pure magnesium, but only 31% inside the pits of the alloy.

The constant k is of practical interest since it describes the behaviour in the case of galvanic corrosion which is an important aspect for the application of magnesium and its alloys. It is also of interest for the use as sacrificial anodes.

The fact that stannate does not influence the constant k can have different reasons. There are, so far, no data available about the migration of stannate in the case of pitting. There might be little transport of stannate ions into the pits. However, the behaviour of stannate agrees also with the EC-model of magnesium dissolution. This means that stannate does not influence the hydrogen evolution coupled with the oxidation of Mg to Mg²⁺ since this is a homogeneous reaction taking place in the electrolyte. On the other hand, the hydrogen evolution outside the pits is a heterogeneous reaction which is easily influenced by the deposition or adsorption of other species.

Chen et al. [34] attributed hydrogen evolution under anodic potentials to the contribution of magnesium hydride decomposition, a partially protective film, dissolution via Mg⁺ ions as well as particle underming, while Song et al. [2] considered a partially protective film as the most important aspect of the negative difference effect.

Our tests have shown that the negative difference effect of pure magnesium can be entirely explained by the EC-mechanism via Mg⁺ during pitting. It is clear that the described mechanism involves a “partially protective film” in the sense that during pitting corrosion a protective passive film coexists with actively dissolving areas of pits. The variation of the active area is a commonly accepted explanation for the unpolarizability of some valve metals undergoing pitting corrosion. Song et al. [2] described this mathematically with the help of a potential dependent “unprotected area fraction φ”.

The possible formation of magnesium hydride was recently discussed in some works, although this is a cathodic reaction and therefore can hardly explain the increase of hydrogen evolution with anodic polarization. According to Chen [34], MgH₂ can form at cathodic potentials in the whole pH range. MgH₂ is unstable in contact with water and decomposes to Mg(OH)₂ and H₂. This intermediate hydride formation outside the pits does not interfere with our considerations about the negative difference effect. The only assumption was that the cathodic reaction rate outside the pits remains constant during galvanostatic polarization, no matter which is the mechanism of the reaction.

Hydrogen formation from hydride decomposition at the areas undergoing pitting can be ruled out because of the typically high true current densities during pitting. Experiments with magnesium made by Beck and Chan [35] with artificial one-dimensional pits in MgCl₂ solution revealed true current densities inside pits of over 1 A/cm². This means that the retraction of the metal/electrolyte interface by magnesium dissolution is so fast that accumulation of hydrogen in the metal phase up to a critical value necessary for hydride formation can be excluded at anodic potentials on a surface undergoing pitting.

### 7. Conclusions

1. As outlined in this paper, in the case of Mg-dissolution via EC-mechanism the constant k has to be calculated by

   \[ k = \frac{dI_{HP}}{dI_{Mg}} \]

   This means that experimental conditions have to be used which allow to determine \( I_{HP} \) from the volumetrically measured \( I_{Mg} \). It was shown that the constant k determined under this condition is not in conflict with the model of metal dissolution via Mg⁺ ions. Volumetric measurements which do not allow the separation of \( I_{HP} \) and \( I_{Mg} \) are not appropriate to verify the EC-mechanism via Mg⁺.

2. The constant k for pure magnesium is within the experimental error identical with the value predicted for the EC dissolution mechanism via Mg⁺ ions.

3. The lower constant k for the AZ91 alloy has probably to do with the simultaneous dissolution of the alloying elements.

4. Na₂SnO₃ has an inhibiting effect only on the hydrogen evolution outside the pits. This agrees with the idea that the hydrogen evolution inside the pits is not a heterogeneous reaction, and therefore cannot be influenced by the deposition or adsorption of other species.

5. For the same reason the shift of the pitting potential by Na₂SnO₃ has no influence on the constant k since the hydrogen evolution inside the pits is a homogeneous reaction. It depends, therefore, only on the Mg⁺ concentration provided by pitting, but not on the electrode potential.

6. The better corrosion resistance of the AZ91 alloy in 1 M NaCl has to do with both a lower rate of hydrogen evolution at the passive surface (about one order of magnitude lower than for pure magnesium) and a lower constant k (0.51 for magnesium, 0.31 for AZ91).

7. The determination of the corrosion current density of magnesium and its alloys by the extrapolation of the cathodic curve can lead to erroneous results, since the cathodic curve is influenced by the onset of pitting corrosion. The hydrogen reduction at surfaces repassivated after pitting is much faster than at unattacked surfaces.

### References