Electrochemical behaviour of chromium-implanted magnesium in hydroxide, chloride and sulphate solutions

M. Vilarigues\textsuperscript{a,b}, J.C.S. Fernandes\textsuperscript{c,*}, L.C. Alves\textsuperscript{a,b}, R.C. da Silva\textsuperscript{a,b}

\textsuperscript{a} LFI/Dep. Física, ITN, Sacavém, Portugal
\textsuperscript{b} Centro de Física Nuclear da Univ. de Lisboa, Lisboa, Portugal
\textsuperscript{c} ICEMS/DEQB, Instituto Superior Técnico, TULisbon, Lisboa, Portugal

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Abstract

Despite the development and subsequent improvement of new Mg-based alloys, their vulnerability to oxidation and corrosion continues to pose a major obstacle to their more generalized use. The possibility of blocking high diffusivity paths, such as grain boundaries, by ion implantation may help to improve their oxidation and corrosion resistance, because mass transport through these short circuiting paths is reduced.

Electrochemical techniques were used to investigate the effect of Cr ion implantation in the electrochemical behaviour of Mg in aqueous solutions. In particular ion implanted fluences of $5 \times 10^{16}$ and $5 \times 10^{17}$ at./cm$^2$ have been evaluated in solutions of NaCl, NaOH and Na$_2$SO$_4$.

The corroded surfaces and products were analysed by ion beam analysis, scanning electron microscopy and X-ray diffraction. A model of the corrosion mechanism is proposed to explain the obtained results.

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1. Introduction

Magnesium and its alloys are promising materials able to compete, substitute and/or combine or complement with aluminium alloys in structural applications in several industrial fields. With just one quarter the density of steel and two thirds that of aluminium, and having superior mechanical strength by weight, magnesium is a base material adequate for the formation of light alloys with the necessary high mechanical resistance. However its vulnerability to corrosion on marine and oxidant environments is a limiting factor to the more widespread utilization of Mg and its alloys [1].

Ion implantation has been successfully used in the last decades to introduce a wide range of elements in the surface layers of metals. The corrosion of metals is a surface phenomenon and is consequently suitable for investigation using implanted surface layers. Moreover, by using this technique an element can be introduced in the surface of a solid material in concentrations far above its solid solubility limit, allowing for the production of metastable phases and amorphous alloys that are generally unattainable by conventional alloying techniques [2,3].

In this work, the effect of ion implantation of chromium into magnesium substrates was studied. According to the basics of corrosion, the addition of chromium could be deleterious to the...
performance of the material if galvanic couples Cr/Mg are formed, as expected if the alloy is produced by conventional metallurgy. However, this could not be the case if chromium is incorporated in a solid solution through the ion implantation process, similarly to what has been observed with ion implantation in aluminium substrates. Thus, surfaces of commercial Mg were implanted with Cr ions and submitted to electrochemical tests in 0.5 M aqueous solutions of NaOH, NaCl and Na2SO4, with the aim of studying the effect of Cr implantation in the electrochemical behaviour of Mg in different aggressive media.

2. Experimental details

140 keV Cr+ ions were implanted into commercial polycrystalline magnesium samples (Goodfellow, 99.9% pure) with fluences of $5 \times 10^{16}$ and $5 \times 10^{17}$/at./cm².

Prior to implantation, the Mg surfaces were submitted to a sequence of mechanical polishing stages, the final one with 4 μm diamond paste. Petrol was used as a lubricant in order to minimise oxidation.

Electrochemical tests were performed in 0.5 M NaOH, 0.5 M NaCl and 0.5 M Na2SO4 solutions, previously deaerated with nitrogen. Open circuit potential vs. time curves were recorded until a steady state value was attained for each case. Anodic polarization curves were obtained at a sweep rate of 2 mV/s, starting 50 mV below the free corrosion potential. The potentials were measured against the saturated calomel electrode (SCE).

The Cr and O profiles were measured by Rutherford Backscattering Spectrometry (RBS) and information about H content and depth profiles was obtained by Elastic Recoil Detection (ERD), in the as-implanted state and after the corrosion tests. All the RBS and ERD analyses were performed using 1.6, 2.0 or 2.4 MeV He+ beams from a Hitachi S/2400 Scanning Electron Microscope (SEM).

3. Results

3.1. Cr-implanted Mg

The characterisation of the systems obtained after implantation of Cr with fluences of $5 \times 10^{16}$/at./cm² and $5 \times 10^{17}$/at./cm² was performed by RBS, ERD and GIXRD, and presented in a previous work [9]. The effect of the implantation in the Mg surface was clearly visible in the RBS spectra related to the implantation of the higher fluence but not in the spectra of the lower fluence implantation. The analytical calculation of the retained fluences has revealed that they are identical to the nominal fluences. This is surprising considering that Mg sputtering coefficient is very high (∼3) [10]. As it is known, this coefficient expresses the number of atoms ejected from the target per incoming beam ion. The continued action of sputtering leads to a receding surface along with loss of material, resulting in altered implantation profiles, and prevents attaining the nominal implantation fluence (i.e. the intended value).

For implantation of $5 \times 10^{17}$/cm² Cr+ ions of 140 keV energy into Mg, a sputtering coefficient of 3 would lead to a maximum attainable fluence of $1.42 \times 10^{17}$/cm², i.e. 45% of the nominal value, and a concentration of 25 at.% at the flat top of the profile. Lower sputtering coefficients, e.g. 1, lead to Gaussian-like profiles, only slightly truncated at the surface, with maximum concentrations of 43 at.% and fluences corresponding to 95% of the nominal implantation values. Zero sputtering corresponds to Gaussian-like implantation profiles with maximum concentration of 50 at.% and full implantation fluence (equal to the nominal value). So, the fact that retained fluences are, in the present case, identical to the nominal fluences may indicate the presence of an oxide layer in the surface of Mg during implantation since it is well known that metallic oxides have lower sputtering coefficients [10]. The results are in agreement with the fact that O and H content and distribution are independent of the implanted fluence.

The high fluence implantation results in a maximum concentration of Cr of 50 at.% at 200 nm depth in Mg. For the low fluence implantation the maximum concentration is approximately 6 at.% at the same depth.

GIXRD spectra of the samples implanted with $5 \times 10^{17}$/at./cm² reveal the existence of a mixed Mg–Cr oxide, MgCrO₄, along with hydrated forms of this compound. There are also diffraction lines that can be attributed to Mg(OH)₂.

3.2. Tests in NaOH solutions

Typical potential vs. time and potentiodynamic polarization curves obtained in 0.5 M NaOH solution (pH=12.8) for unimplanted and implanted Mg are shown in Fig. 1. The free corrosion potential for the samples implanted with $5 \times 10^{17}$/at./cm² is approximately 500 mV higher than that observed for pure magnesium (Fig. 1 a). The anodic polarization curves (Fig. 1b) show a passive behaviour, above approximately
−1000 mV, for the unimplanted samples. This result is in accordance with the expected behaviour for pure magnesium at solutions with pH above 9 [11]. A 10 fold increase can be observed in the corrosion current density from unimplanted samples to implanted samples with measured $i_{corr}$ of $\sim 0.035 \, \mu A/cm^2$ and $0.3 \, \mu A/cm^2$ respectively. These current densities correspond to corrosion rates of $\sim 1 \times 10^{11}$ at./cm$^2$·s and $\sim 9.5 \times 10^{11}$ at./cm$^2$·s, respectively. Meanwhile, Tafel slopes, $b_a$ and $b_c$, present identical values, $\sim 20$ mV and $\sim 27$ mV for both unimplanted and implanted samples.

### 3.3. Tests in NaCl solutions

The second set of tests was performed in 0.5 M NaCl solutions (pH = 5.5). The effect of Cr implantation can be noticed in the free corrosion potential and polarization curves of Fig. 2.

The corrosion potential has increased as a function of the implanted fluence: $E_{corr}$ is approximately $-1686$ mV for the unimplanted Mg, $-1584$ mV for samples implanted with $5 \times 10^{16}$ at./cm$^2$ and $-1530$ mV for the samples implanted with $5 \times 10^{17}$ at./cm$^2$. The current density has also increased as a function of the implanted fluence: $i_{corr}(Mg)=25 \, \mu A/cm^2$, $i_{corr}(5 \times 10^{16} \, \text{at./cm}^2)=260 \, \mu A/cm^2$ and $i_{corr}(5 \times 10^{17} \, \text{at./cm}^2)=1194 \, \mu A/cm^2$. The corresponding corrosion rates are $0.08 \times 10^{15}$ at./cm$^2$·s, $0.8 \times 10^{15}$ at./cm$^2$·s and $3.7 \times 10^{15}$ at./cm$^2$·s, respectively. Like in the previous tests, $b_a$ and $b_c$ do not exhibit any change correlated with the variation of the implanted fluence.

At approximately $-1450$ mV the curves overlap, expressing a similar electrochemical behaviour of the different surfaces, which is the one found for pure magnesium. This can be explained by a very fast and intense attack that leads to the removal of the implanted material. Once Cr is almost totally removed, the systems become identical and a similar behaviour is expected as observed.

### 3.4. Tests in Na$_2$SO$_4$ solutions

The results of free corrosion potential and anodic polarization scans generated in 0.5 M Na$_2$SO$_4$ solutions (pH = 5.6) are presented in Fig. 3.

As can be seen in the $E_{corr}$ vs. time diagram, the free corrosion potential increases in respect with the implanted fluences, like it was observed in the previous cases presented. The difference between the corrosion potential measured for pure Mg and Mg implanted with $5 \times 10^{17}$ at./cm$^2$ is higher than 400 mV. The current density increases: $i_{corr}(Mg)=29 \, \mu A/cm^2$, $i_{corr}(5 \times 10^{16} \, \text{at./cm}^2)=260 \, \mu A/cm^2$ and $i_{corr}(5 \times 10^{17} \, \text{at./cm}^2)=1194 \, \mu A/cm^2$. The corresponding corrosion rates are $0.08 \times 10^{15}$ at./cm$^2$·s, $0.8 \times 10^{15}$ at./cm$^2$·s and $3.7 \times 10^{15}$ at./cm$^2$·s, respectively. Like in the previous tests, $b_a$ and $b_c$ do not exhibit any change correlated with the variation of the implanted fluence.

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i_{corr}(5 \times 10^{16} \text{ at./cm}^2) = 111 \mu \text{A/cm}^2 \text{ and } i_{corr}(5 \times 10^{17} \text{ at./cm}^2) = 216 \mu \text{A/cm}^2. \text{ The corrosion rates that correspond to these current densities are } 0.09 \times 10^{15} \text{ at./cm}^2 \text{s, } 0.35 \times 10^{15} \text{ at./cm}^2 \text{s and } 0.67 \times 10^{15} \text{ at./cm}^2 \text{s, respectively. The values of } b_a \text{ and } b_c \text{ are once again equal and independent of the implanted fluence.}

3.5. Corroded surface characterization

The RBS spectra obtained before and after electrochemical tests performed are presented in Fig. 4.

For 0.5 M NaOH solutions there was a significant loss, ~20%, of implanted material and an increase in O content after the electrochemical tests, as can be seen in Fig. 4a). Moreover, ERD analyses have shown an increase of H content, which occurs for all tests in the different solutions. This indicates the formation of Mg(OH)$_2$ or of a higher amount of Mg and Cr oxides and/or hydroxides.

After the electrochemical tests performed in 0.5 M NaCl and 0.5 M Na$_2$SO$_4$ solutions no Cr signal is detected by RBS (Fig. 4b and c). However traces of Cr were detected by PIXE analysis in the samples implanted with the lowest fluences, as this technique is much more sensitive than RBS.

GIXRD spectra for both implanted samples and for all tests exhibit diffraction lines that can be attributed to MgCrO$_4$ and hydrated forms of this compound. GIXRD spectra also show the presence of Mg(OH)$_2$, as can be seen in Fig. 5.

The morphology of the surfaces implanted with $5 \times 10^{17}$ at./cm$^2$, after the electrochemical polarization tests performed in 0.5 M NaOH and in 0.5 M NaCl and presented in Figs. 1 and 2, was assessed by SEM and the micrographs obtained for the different samples can be seen in Fig. 6. This morphology proved to be independent of the implanted fluence but differs for each test solution. In particular, EDS analyses after the tests in 0.5 M NaOH have shown that in the lighter regions the Cr content is very low, making possible to assume that these structures are Mg(OH)$_2$, since this is the only compound identified in the GIXRD analysis. In the case of samples exposed to NaCl solution, there is no evidence of pitting corrosion. In fact, at those pH’s Mg is expected to be in a corrosion domain, suffering generalized corrosion instead of pitting. Moreover, the structures like those shown in Fig. 6b) have already been observed in other works and have been identified as a mineral form of Mg(OH)$_2$, brucite [12], in agreement with the GIXRD spectra presented. All the samples present this type of morphology irrespective to the implanted fluence.

4. Discussion

The most relevant numeric values, i.e., the values for the most important electrochemical parameters, extracted from the data obtained from the tests are resumed in Table 1.

For each solution the values of $E_{corr}$, $i_{corr}$, $b_a$ and $b_c$ were obtained by Tafel analysis using the software Voltamaster 4. Corrosion rates values in at./cm$^2$ s were obtained taking into account that

$$N_{\text{ion/cm}^2 \text{s}} = \frac{6.25 \times 10^{15}}{n} \cdot i(\text{mA/cm}^2)$$

based on the Faraday equation, where $n$ is the valence of the ion. The calculations were performed considering the ion as Mg$^{2+}$.

The evolution of $i_{corr}$ and $E_{corr}$ for each solution vs. the implanted fluence is presented in Fig. 7, allowing to assess the effect of the implanted fluence on the increase of the corrosion potential and current density. This effect is more pronounced on the rise of $i_{corr}$ than $E_{corr}$ and may be understood considering that the corrosion potential is mainly sensitive to the value of the pH of the solutions and not so much to the other aggressive ions present in it: $E_{corr}$ is a reflex of the balance between electrons exchange in the electrolyte/surface interface. On the contrary, corrosion current densities depend also on other aggressive ions: it is clearly visible the difference in the corrosion current densities between NaCl and Na$_2$SO$_4$ solutions, both with approximately the same pH value.

A similar behaviour was observed in all systems:

a) increase of the corrosion potential proportional to the implanted fluence;
b) increase of the corrosion current density proportional to the implanted fluence;
c) after the tests no Cr is retained or just a small amount is present in the samples as detected by PIXE analysis;
d) increase in H and O content and formation of Mg(OH)$_2$;
e) existence of MgCrO$_4$ and hydrated forms of this compound;
f) the values of Tafel slopes, $b_a$ and $b_c$, are independent of the fluence.

These results suggest that the presence of Cr promotes the cathodic reaction, according to the mechanism proposed in Fig. 8, that could be explained as follows. The corrosion rate of a metal is determined by the balance between the anodic and the cathodic processes taking place on its surface. For a pure Mg surface at the open circuit potential $E_{corr}(Mg)$, the current produced in the Mg oxidation, $i_{corr}(Mg)$, should be consumed in the cathodic process of water reduction with H$_2$ evolution, according to the following partial reactions:

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

Moreover, film formation may occur by chemical precipitation:

\[
\text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 
\]

The overall reaction rate is then dependent both on the tendency of Mg to oxidise and on the kinetics of the cathodic process.
reaction, which is known to be hindered when the Mg surface becomes covered by an oxide layer.

The surface of the implanted specimens is expected to present a rather high concentration of chromium. If Mg and Cr are coupled, the oxidation of Mg will continue to be the anodic process, whereas the cathodic reaction of hydrogen evolution will take place both on the Cr and on the Mg surface. Thus, the reduction rate will be equal to the sum of the rates of this reaction on each metal. As the current density associated to $H^+$ reduction is expected to be much higher on the Cr surface than on the Mg surface, the total rate of reduction will increase when compared to a pure Mg surface. The corrosion potential $E_{\text{corr}}$ of the Cr-implanted Mg will then present a value $E_{\text{corr}}(\text{Mg})$, corresponding to a higher corrosion rate. Moreover, the fact that for each one of the solutions the value of Tafel slopes, $b_a$ and $b_c$, do not present significant changes with the increase of the implanted fluence is in agreement with the proposed corrosion mechanism, as the presence of Cr is mainly expected to change the value of $i_0$ and not the slope.

Data relative to exchange current densities ($i_0$) of the hydrogen evolution reaction (HER) on Cr and Mg, that might confirm this mechanism, are scarce in the literature. Bélanger [13] presents a value of $i_{0,\text{HER}} = 5 \times 10^{-8} \text{ A cm}^{-2}$ for chromium, but no comparing values were found for magnesium. However, it is commonly accepted by several authors [14] that $i_{0,\text{HER}}$ should be considerably low for Mg and, from the plot of log $i_{0,\text{HER}}$ for various metals in acidic solution, presented by Kita [15], it is evident that $i_{0,\text{HER}}$ may be at least one order of magnitude higher on chromium than on magnesium. Moreover, according to Jakšić [16], the combination of metals from different regions of the periodic table may arise a pronounced synergic effect in the electrocatalysis of the HER reaction, which may be explained by the Brewer–Engel Valence-Bond theory. In this case, the hydrogen evolution in the Mg–Cr surface alloy could be even faster than expected for the chromium alone. Once again, there are no enough supporting data for Mg and Cr that could validate this assumption.

From the experimental data obtained in the electrochemical tests we may then conclude that in the Mg–Cr system attained

### Table 1

<table>
<thead>
<tr>
<th>Solution</th>
<th>Mg Fluence (at./cm$^2$)</th>
<th>Electrochemical Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH (0.5 M)</td>
<td>5×10$^{17}$</td>
<td>$E_{\text{corr}}$ (mV) $-1494$ $-1123$</td>
</tr>
<tr>
<td></td>
<td>5×10$^{17}$</td>
<td>$i_{\text{corr}}$ (mA/cm$^2$) 0.35</td>
</tr>
<tr>
<td></td>
<td>5×10$^{17}$</td>
<td>$b_c$ (mV) 26</td>
</tr>
<tr>
<td>NaCl (0.5 M)</td>
<td>5×10$^{16}$</td>
<td>$E_{\text{corr}}$ (mV) $-1686$ $-1530$</td>
</tr>
<tr>
<td></td>
<td>5×10$^{17}$</td>
<td>$i_{\text{corr}}$ (mA/cm$^2$) 25.6 259.4 1194</td>
</tr>
<tr>
<td></td>
<td>5×10$^{17}$</td>
<td>$b_c$ (mV) 36.5 36.3 37</td>
</tr>
<tr>
<td>Na$_2$SO$_4$ (0.5 M)</td>
<td>5×10$^{16}$</td>
<td>$E_{\text{corr}}$ (mV) $-1771$ $-1368$</td>
</tr>
<tr>
<td></td>
<td>5×10$^{17}$</td>
<td>$i_{\text{corr}}$ (mA/cm$^2$) 29 111 216</td>
</tr>
<tr>
<td></td>
<td>5×10$^{17}$</td>
<td>$b_c$ (mV) 36 39 32</td>
</tr>
</tbody>
</table>
by ion implantation a galvanic couple is formed. In this case Mg acts like an anode and Cr as a cathode, since Cr is a more noble metal, and no Cr oxides or Mg–Cr oxides capable of effective protection were formed by ion implantation. As the anodic polarization effect is not sufficient to drive the corrosion potential of Mg to a zone where its passivation could occur, it becomes deleterious to the overall behaviour of the material. So, contrary to what was expected for a surface alloy produced by ion implantation, the behaviour of the implanted layer is not far from the one obtained by traditional metallurgy.

These results are also quite different from those obtained by ion implantation of chromium in both iron and aluminium, but this fact may be explained by the completely different corrosion behaviour of magnesium and, in particular, to the stability domain of its species. In fact, the work of Ashworth et al. \[4\] has shown that chromium implantation into iron results in a surface alloy that has improved corrosion resistance when compared to unimplanted iron, although being similar to that attained by conventional bulk Fe–Cr alloys. Ion implantation is, in this case, just an alternative method to introduce Cr in the alloy, as the benefits of this element in the passivity of iron are already obtained by conventional alloying and additional benefits or extension of the solubility of the alloying element are expected in this case by using ion implantation. Regarding ion implantation of chromium into aluminium, as reported by Natishan \[6\] or by Leitão \[7\], it is very important to stress that the resulting surface alloys were tested in neutral or slightly alkaline media containing chlorides. In these cases, the surface of both unimplanted and implanted aluminium is covered by a natural-formed aluminium oxide that confers passivity to the metal, which is only expected to suffer corrosion by pitting. Thus, both authors refer the beneficial effect of the chromium implantation on the pitting potential, although Cr concentrations above 8 at.% are reported as being deleterious to pit repassivation. Natishan \[6\] explains the observed enhanced pitting resistance on the basis of the lower pH of zero charge of the implanted species. At the pH of zero charge, pH\textsubscript{pzc}, the surface of the oxide has no net charge. Only at pH values below pH\textsubscript{pzc} the surface becomes positively charged, allowing anions
such as the chloride ion to be electrostatically attracted to the interface and causing film disruption and loss of passivity. Such an effect on pitting may not be expected in the case of chromium implantation into magnesium, as it has been shown that the pH of the chloride-containing solution lies in the general corrosion domain for magnesium.

5. Conclusions

From the ion implantation of Cr in Mg the formation of mixed oxides Mg–Cr and Mg hydroxide is found.

In all electrochemical tests the values of $E_{corr}$ and $i_{corr}$ are found to increase in the presence of implanted chromium when compared with the unimplanted samples. Moreover, $E_{corr}$ and $i_{corr}$ increase with the chromium-implanted fluence.

The following model is proposed to explain the observations: the presence of Cr promotes the cathodic reaction by formation of microgalvanic couples. With the introduction of Cr in Mg the active area for the cathodic reaction of formation of molecular hydrogen increases, and this increase is more pronounced for higher implanted fluences. The corrosion potential increases and the same happens with the corrosion current, thus, the corrosion rate of the system Mg–Cr will be higher when compared with Mg.

The presence of chromium in the implanted surface layer is then found to be deleterious to the corrosion performance of magnesium, as it happens with alloys produced by traditional metallurgy.

**References**