Effectivity of fluoride treatment on hydrogen and corrosion products generation in temporal implants for different magnesium alloys

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Abstract

The increasing interest on magnesium alloys relies on their biocompatibility, bioabsorbility and especially on their mechanical properties. Due to these characteristics magnesium alloys are becoming a promising solution to be used, as temporary implants. However, magnesium alloys must overcome their poor corrosion resistance. This paper analyses the corrosion behaviour in PBS solution of three commercial magnesium alloys (AZ31B, WE43 and ZM21) as well as the influence of fluoride treatment on their corrosion behaviour. It is shown that the

corrosion rate in all the alloys is decreased by fluoride treatment. However, fluoride treatment affects differently to each alloy.

Keywords: Magnesium; Biodegradation; Corrosion; Corrosion product; Surface treatment.

1. Introduction

The corrosion resistance and the high mechanical properties of some metallic biomaterials make them very suitable to be used in long-term and load-bearing applications [1, 2]. This way, metallic alloys such as Ti alloys, Co-Cr alloys and stainless steels are commonly used materials in prosthesis, implants, plates or screws.

On the other hand, novel medical applications and novel medical requirements are demanding solutions beyond the state of the art. As an example, tissue engineering, besides bioinert ability, demands bioabsorbable and bioactive

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materials [3]. However, these properties, which were developed in ceramic and polymer materials in the decade of the 80s, have not been achieved in metallic materials yet. As a result, bioabsorbable metallic biomaterials have become an attractive group of materials to be researched in recent years. This way, several studies have been carried out with metallic bioabsorbable materials such as Mg and its alloys [1, 4-19], Fe and Fe-Mn alloys [20, 21] and W [22-24].

Among the mentioned metallic materials, magnesium is the metal that is having a greater impact on the scientific community, since it combines the property of being compatible and absorbable by the human body and the property of accelerating bone regeneration [4, 5]. In fact, most of the magnesium in the human body is in the skeleton, being an essential component for bone growth and maturation [25, 26]. Regarding biocompatibility, magnesium is a biocompatible metallic material representing the fourth most abundant cation in the body and the second most important, after potassium, in the intracellular medium [27]. And finally, regarding its ability to be bioabsorbed, the cations generated due to corrosion are efficiently regulated by the body [15].

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However, and as mentioned before, magnesium is not widely used in medical applications yet due to its rapid corrosion in the organism [1, 4, 5, 28, 29]. The corrosion of magnesium in physiological media generates hydroxides and hydrogen (eq. 1). Depending on the corrosion rate, the hydroxides could alkalinize the implant area [28] and the hydrogen generation could create subcutaneous gas bubbles that could damage the tissue adjacent to the implantation site [4, 5]. As a solution, a lower corrosion rate than the human body capacity to regulate hydroxides and hydrogen would avoid both mentioned drawbacks.

$$Mg(s) + 2\,H_2O \rightarrow Mg(OH)_2 + H_2(g) \qquad \text{(eq. 1)}$$

A strategy to solve the rapid corrosion of magnesium is the application of surface treatments [2, 14, 30-49]. One of the surface treatments most studied in literature to improve the corrosion resistance of magnesium is the fluoride treatment [30-34, 50]. Fluoride treatment is a chemical conversion that consists on the immersion of magnesium in hydrofluoric acid (HF) to form a coating of MgF_2. The MgF_2 coating

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presents a low water solubility and good biocompatibility [32, 33].

In the present work, the corrosion rate of three magnesium alloys widely used in literature is evaluated: AZ31B [19, 30, 31, 50-54], WE43 [11, 19, 55-58] and ZM21 [59, 60]. This evaluation is carried out by measuring the hydrogen generation in PBS solution. Furthermore and since a high adhesion of corrosion products on magnesium surface could avoid the tissue growth in a cell culture, the corrosion products generated during the degradation are also characterized.

2. Experimental methods

2.1. Materials

10 × 10 × 1.5 mm^3 samples of commercial AZ31B (Magnesium Elektron, nominal composition: 3 wt.% Al and 1 wt.% Zn), WE43 (Magnesium Elektron, nominal composition: 4 wt.% Y and 3 wt.% rare earths), and ZM21 (Magnesium Elektron, nominal composition: 2 wt.% Zn and 1 wt.% Mn) magnesium alloys were prepared.

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The samples were ground with SiC papers from 1000 grits to 4000 grits, ultrasonically rinsed in ethanol for 15 minutes and finally dried. 6 repetitions were prepared for each material and surface treatment.

2.2. Fluoride treatment

To improve the corrosion resistance of magnesium alloys, the samples were immersed in 48 wt.% concentration hydrofluoric acid (HF) solution for 24 hours and 72 hours under slow stirring to achieve the MgF_2 coating. MgF_2 coating was formed by the reaction of HF with Mg, according to eq. (2) [61]. The treated samples were ultrasonically rinsed in ethanol for 15 minutes and dried. The nomenclature used in this work for each sample is described in table 1.

$$2\mathrm{HF} + Mg(s) \rightarrow MgF_2 + H_2(g) \quad \text{(eq. 2)}$$

A maximum of 72 hours of immersion in HF was chosen in this work. According to literature, Yan *et al.* [50] showed that after 72 hours in HF the coating thickness on

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AZ31B alloy was not increased notoriously, neither the corrosion resistance. Yan *et al.* [50] postulate that the formed barrier film of MgF_2 on the surface after 72 hours was thick enough to terminate the reaction. Based on this previous research, and in order to achieve comparable results, a maximum of 72 hours immersion in HF is proposed for all the analysed alloys.

2.3. Immersion test

The samples were immersed in commercial PBS solution, which has been used for magnesium implants evaluation in literature [32, 51, 62-67] and is recommended in corrosion standards like ASTM F2129-08 or ASTM F746-04 for implants evaluation. Dulbecco's Phosphate-Buffered Saline (D-PBS) (200 mg l^{-1} KCl, 200 mg l^{-1} KH_2PO_4, 8000 mg l^{-1} NaCl, 1150 mg l^{-1} Na_2HPO_4), was used with a starting pH of 7.4 at 37ºC and without agitation. Approximately 40 ml of PBS per cm^2 sample surface were used in order to avoid the change in the corrosivity of the media according to ASTM G 31-72. Also the entire volume of PBS was changed every 48 hours to prevent the pH increase due to the generation of hydroxides.

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The hydrogen evolution, as an indicator of the corrosion rate, was measured in a eudiometer tube with a resolution of 0.1 ml. The procedure to measure the corrosion is described by Song *et al.* [68].

2.4. Characterisation of the fluoride coating and surface corrosion

A scanning electron microscope was used for analysing the final morphology of the samples. The energy dispersive X-ray (EDX) was used to analyse the coating and the composition of depositions and corrosion products.

3. Results

3.1. Fluoride treatment

After fluoride treatment a stable film was formed on all the samples (figure 1). The thickness of the coating increased with the immersion time for all the alloys. AZ31B

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alloy presented a uniform film of 1.5 μm after 24 hours immersed in HF (figure 1a) and grow to 2.5 μm after 72 hours immersed in HF (figure 1b). However, the protected layer on the WE43 alloy was barely perceptible after 24 hours of immersion. After 72 hour the film was not homogeneous and was clearly concentrated in the intermetallics (figure 1d). In this thin film no cracks were detected. Finally, the film on ZM21 alloy grows up to 2.8 μm in the first 24 hours (figure 1e) and to 5 μm after 72 hours (figure 1f). Some cracks on the layer were found.

Figure 1g shows the composition of the layer on the sample AZ31BHF72h after the immersion. As it was expected the layer was rich in Mg and F indicating MgF_2 generation.

3.2. Immersion test

All magnesium alloys degraded during the immersion tests. In figure 2 hydrogen evolution of the alloys during the immersion test is shown and it is also shown its

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corrosion rate in order to get a better evaluation of the corrosion behaviour due to pH changes. All the bare alloys revealed higher hydrogen generation during the first 24 hours of the test with a decreasing and stabilizing corrosion rate over increasing immersion time (figure 2). ZM21 bare alloy had the higher hydrogen generation (0.0155 ml/mm^2 after 96 hours in PBS), followed by AZ31B (0.0109 ml/mm^2 after 96 hours in PBS) and WE43 (0.0093 ml/mm^2 after 96 hours in PBS).

Higher corrosion resistance was achieved for all the alloys after fluoride treatment. However, fluoride treatment had a different influence in each magnesium alloy. This way, and compared to bare alloys, the immersion of the samples in HF during 24 hours increased the corrosion resistance by 25% for AZ31B, 34% for ZM21 and 37% for WE43. Furthermore, the immersion of the samples in HF during 72 hours increased the corrosion resistance by 50% for WE43, 52% for AZ31B and 75% for ZM21. ZM21HF72h sample showed the lowest hydrogen generation (0.0039 ml/mm^2 after 96 hours in PBS) of all the samples. The corrosion rate evolution for all the bare alloys is shown in figure 2.

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In contrast to bare alloys, coated alloys started with a low corrosion rate and it increased slightly over immersion time due to magnesium fluoride film dissolution (figure 2). It was also observed that fluoride treatment made the alloys to show less dispersion in the results from sample to sample (figure 2).

There were not significant pH variations (table 2). However, the corrosion rate in the samples did show small changes due to these pH changes (figure 2).

3.3. Characterisation of the surface corrosion

The morphological features of the samples after an immersion in PBS for 72 hours are shown in figure 3. The highest adhesion of precipitates was observed on AZ31B (figure 3a) alloy. WE43 (figure 3d) and ZM21 (figure 3g) alloys presented less activity. In all cases, the fluoride treatment decreased the adhesion of crystals to the surface (figure 3).

Furthermore, in figure 3c and figure 3g some small black depositions were

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detected. As shown in figure 4, these particles are rich in C, Mg and O.

Regarding the beginning of the corrosion, figure 5 shows the start of a corrosion point on AZ31B alloy. The distribution maps showed the presence of O, P, and Ca. Also the influence of Cl was detected on the surface. Longer immersion test in PBS of bare alloys give as a result the presence of several formations. After 7 days of immersion, needle like depositions rich in Mg, K, P, Na, K and O (figure 6) and sponge-like depositions rich in Mg, P, Ca, Na, K and O (figure 7) were adhered on AZ31B sample surface. In ZM21 samples depositions rich in Mg, P and O were also adhered but in more localized areas (figure 8). In the case of WE43 bare alloy no significant adhesions were found.

Regarding the beginning of the corrosion in coated alloys, figure 9 shows the start of the corrosion on AZ31B alloy with a fluoride treatment of 24 hours. After MgF_2 dissolution, corrosion point becomes richer in O, P, Na and Ca. For AZ31BHF72h and for coated WE43 and ZM21 alloys no significant formations were found.

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4. Discussion

The corrosion of three different magnesium alloys under the same conditions has been compared in the present work. The results are compared with literature in table 3. The first conclusion when analysing the literature is the high dispersion of the results achieved by different authors. There may be many reasons for this dispersion but the most important one is the lack of standardisation [65] and, in the cases when potentiodynamic polarisation is used, the inability of Tafel extrapolation to estimate the corrosion rate reliably [6, 7, 68]. Nevertheless, the results achieved in the present research work fit with the results achieved by other authors as shown next.

First, a comparison of the bare alloys is carried out. In the case of AZ31B magnesium alloy, the corrosion rate measured by other authors moves between 0.25 and 2 mm $year^{-1}$. The corrosion rate for AZ31B measured in this work, 0.56 mm $year^{-1}$, is between literature values and close to the results measured *in vivo*, 0.672 mm $year^{-1}$ [70]. In the case of WE43 magnesium alloy, the corrosion rate

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measured by other authors moves between 0.3 and 1.5 mm year^{-1}. As happened with the previous mentioned alloy, the corrosion rate of WE43 measured at the present research work, 0.47 mm year^{-1}, is between literature values. However, in the case of WE43 magnesium alloy, the *in vivo* corrosion rate measured by other authors is greater, 0.704 mm year^{-1} [56], 0.896 mm year-1 [70], 1.44 mm year^{-1} [56]. Finally, not many works with ZM21 magnesium alloy were found in literature. However, and as shown in table 3, the most common measured corrosion rate for ZM21 is around 0.9 mm year^{-1} and the corrosion rate measured at the present research work is 0.79 mm year^{-1}, close to the literature values.

Regarding the coating treatment, the corrosion resistance of all magnesium alloys was increased by fluoride treatment. Longer fluoride treatment resulted in lower hydrogen generation. Therefore, a positive influence of the fluoride treatment on the magnesium corrosion was observed as stated previously [30-34, 50]. Cracks were found on ZM21HF24h and ZM21HF72h samples, and also sporadically on AZ31BHF72h sample, where thicker layers were generated during the fluoride treatment. On the other hand, no cracks were found in the others samples where

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thinner layers were created. The cracks may have appeared due to the brittleness of the coating [75] in samples with a thick layer.

The increase of the corrosion resistance by fluoride treatment depends on the morphology of the coating generated for each alloy (figure 1). In the case of the AZ31B and ZM21 magnesium alloys this dependency is clearer. For both alloys, the greater the coating thickness is, the greater the corrosion protection it offers. AZ31BHF24h, with a coating thickness of 1.5 μm, shows a corrosion rate 25% smaller than the untreated AZ31B magnesium alloy. AZ31BHF72h, with a coating thickness of 2.5 μm, shows a corrosion rate 52% smaller than the untreated AZ31B magnesium alloy. In the case of ZM21 magnesium alloy, the ZM21HF24h with a coating thickness of 2.8 μm shows a corrosion rate 34% smaller than the untreated ZM21 magnesium alloy and the ZM21HF72h with a coating thickness of 5 μm shows a corrosion rate 75% smaller than the untreated ZM21 magnesium alloy. The tendency towards greater protection when the fluoride treatment is longer is also proved for the WE43 magnesium alloy. WE43HF24h shows a corrosion rate 37% smaller than the untreated alloy and the WE43HF72h shows a corrosion rate

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50% smaller than the untreated alloy. However, unlike AZ31B and ZM21 alloys, there is no a direct relation between the corrosion rate decrement and the coating thickness for WE43 magnesium alloy: the coating on WE43HF24h was barely perceptible and WE43HF72h presented a non-uniform coating.

Despite WE43 alloy did not present a homogeneous coating it achieved the highest reduction in corrosion rate (37%) after 24 hours of immersion in HF. The explanation for this may be that micro-galvanic corrosion occurs in magnesium alloys with rare earth [76]. As mentioned before, the coating concentrated around the intermetallics, leaving α-Mg almost without protection. Therefore this encapsulation could have eliminated the micro-galvanic couples between α-Mg and the intermetallics thereby increasing the corrosion resistance of the alloy.

In order to analyse the possibility of form a thicker coating on α-Mg of WE43 alloy, samples were immersed in HF during 168 hours. The coating on these samples was also non uniform and barely appreciable in some areas (figure 10). This figure also shows that the coating concentrates around the intermetallics. This effect

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could disappear dissolving the intermetallics in a heat treatment before fluoride treatment.

After 72 hours of immersion in PBS, MgF_2 coating was still present on the all sample surface, especially in ZM21 alloy. Regarding the adhesion of corrosion products to the surface, WE43 alloy was the one that showed the lowest adhesion. Nevertheless, the adhesion in the other magnesium alloys is decreased with fluoride treatment. In the case of AZ31, as shown in figure 3, the adhesion of crystals decreased dramatically after fluoride treatment.

The elemental analysis suggests that, at the beginning of the corrosion, a mixture of $MgCl_2$ and $Mg(OH)_2$ could be the predominant species in the corrosion of bare alloys. The formed $Mg(OH)_2$ could be dissolved in aqueous medium and transformed into soluble $MgCl_2$ by chloride ions [66]. As corrosion progresses, the elemental analysis suggests that different phosphates $(PO_4)^{3-}$ with Mg, Ca, K or Na were deposited on the surface. Depositions or corrosion products containing $(PO_4)^{3-}$ are also detected in others works [51, 77, 78]. Finally, some $(CO_3)^{2-}$

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particles (figure 4) were also detected. The presence of carbonates are common after the immersion of magnesium in physiological medium [54, 59, 77], however, in this work there were no many of carbonate because PBS does not contain any. Nevertheless the presence of some could be explained due to the reaction of distilled water with the CO_2 of the atmosphere. In the same way, although PBS does not contain Ca, elemental analysis detected small amounts of Ca. In this case, it may be found as an impurity in PBS.

5. Conclusions

(i) Immersion tests in PBS showed an improved corrosion rate, ranging from 25% for AZ31B alloy after 24 hours in HF to 75% for ZM21 alloy after 72 hours in HF, and a reduced corrosion products and crystals adhesion for the coated alloys compared to the bare alloys.

(ii) For all the alloys it was stated that the corrosion rate depends on the immersion time in HF, higher immersion times offer lower corrosion rates.

(iii) Morphology and formed MgF2 thickness depend on alloy microstructure. In

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the case of WE43, MgF2 was concentrated on intermetallics and coating was not homogeneous. On the other hand, for AZ31B and ZM21 alloy the coating thickness was proportional to the fluoride treatment time.

(iv) There is not a direct relation between the coating thickness and the corrosion protection achieved in all the alloys. In the case of the ZM21 and AZ31B alloys this direct relation has been found. However, in the case of the WE43 alloy even very thin protection layers generates high corrosion protection.

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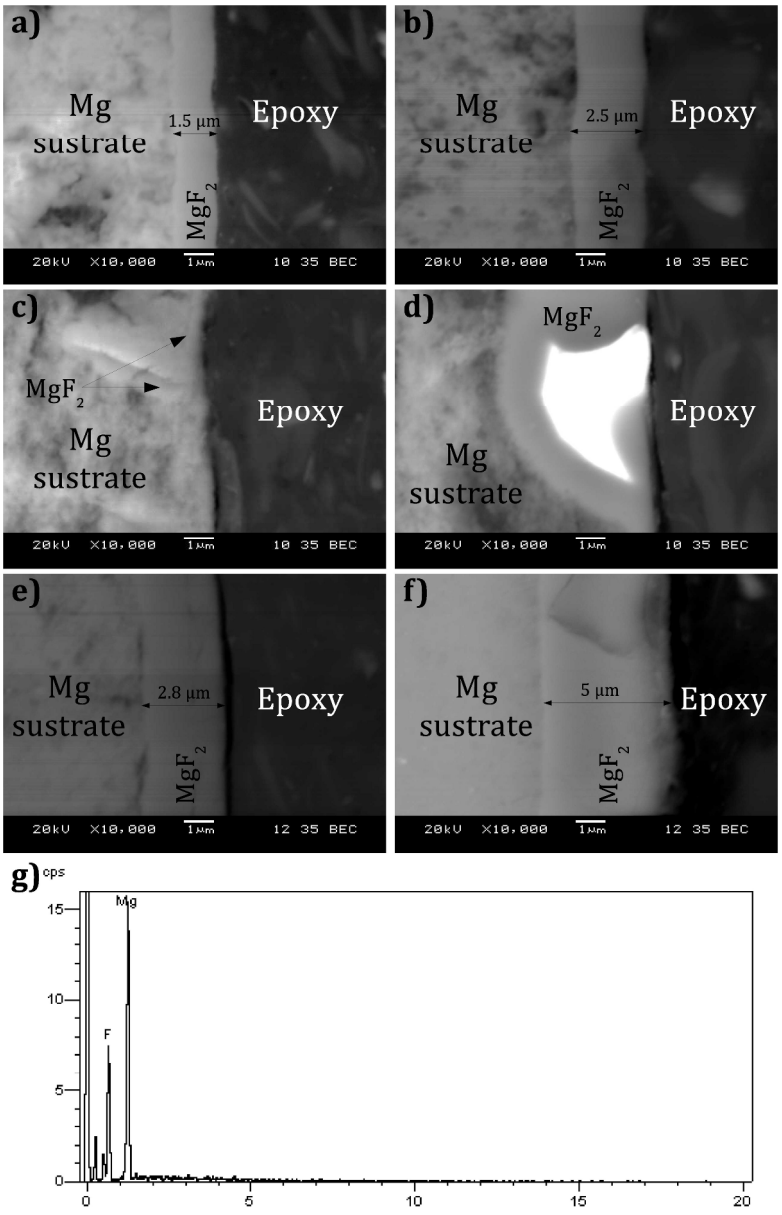

Figure 1: Detail of the thickness of the different coatings. a) AZ31BHF24h b) AZ31BHF72h c) WE43HF24h d) WE43HF72h e) ZM21HF24h f) ZM21HF72h g) Elemental analysis on the formed layer of AZ31B72h
253x392mm (300 x 300 DPI)

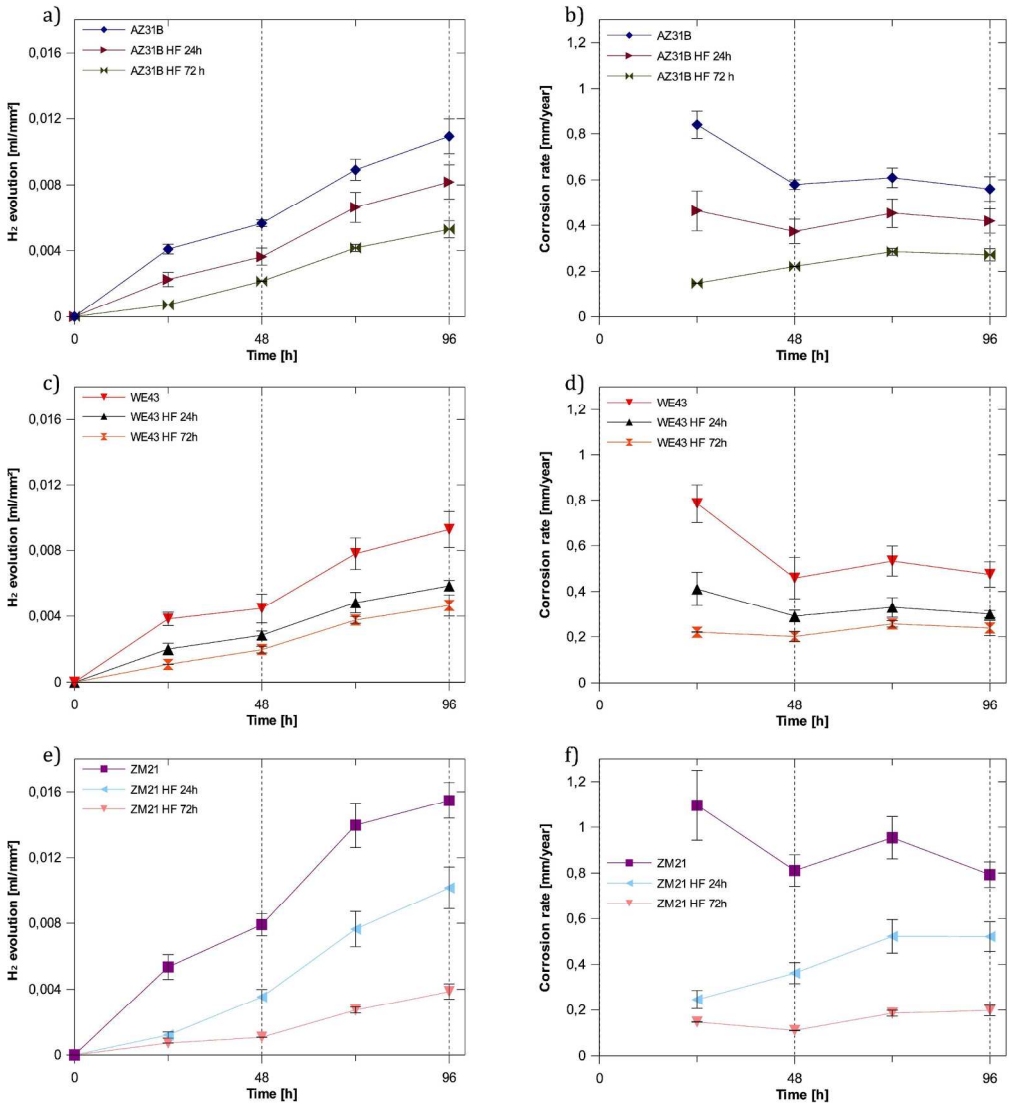

Figure 2: Hydrogen evolution and corrosion rate of, a) b) AZ31B, c) d) WE43 and, e) f) ZM21
197x216mm (300 x 300 DPI)

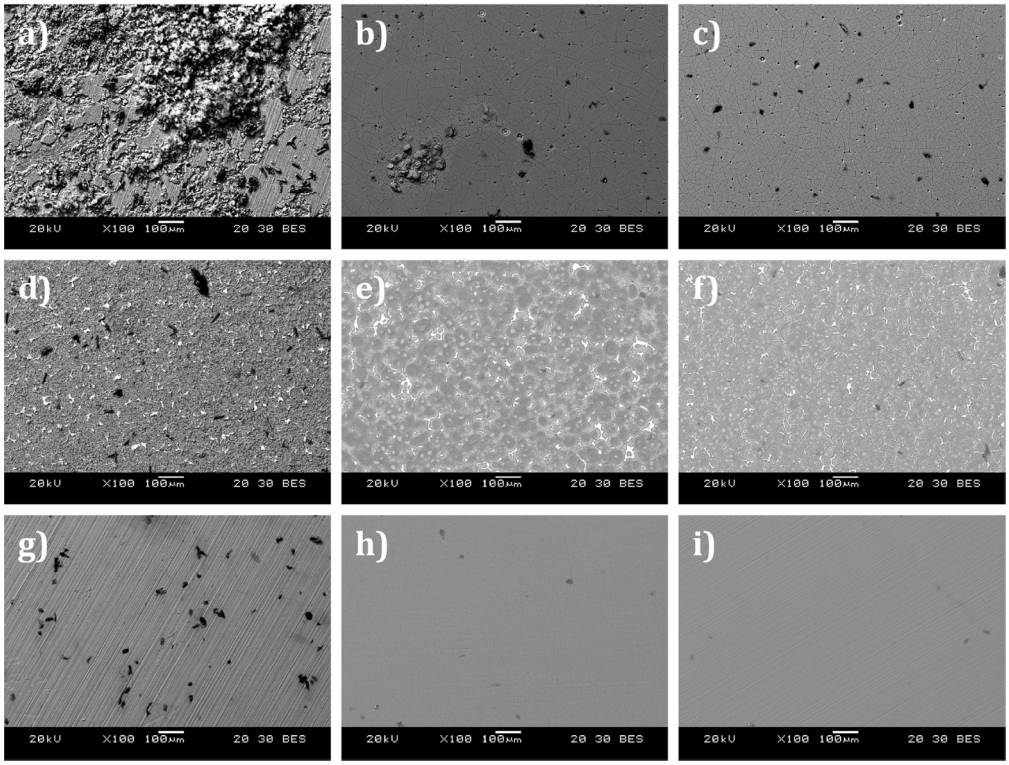

Figure 3: Surface of the samples after 72 h in PBS a) AZ31B b) AZ31BHF24h c) AZ31BHF72h d) WE43 e) WE43HF24h f) WE43HF72h g) ZM21 h) ZM21HF24h i) ZM21HF72h
139x105mm (300 x 300 DPI)

eview

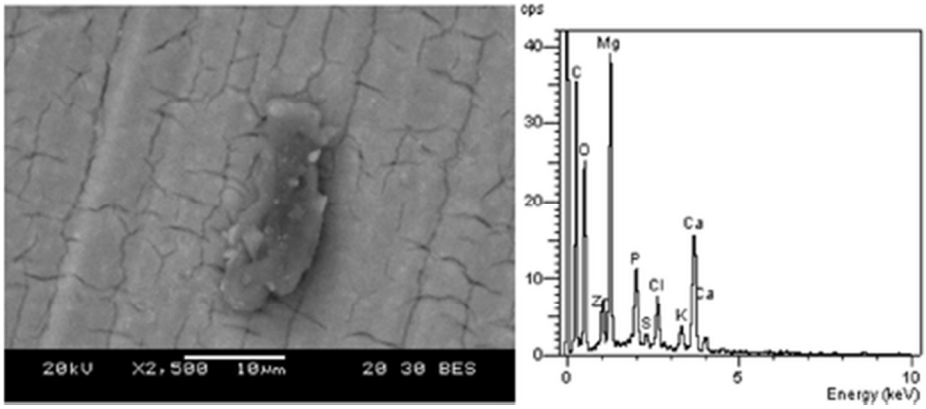

Figure 4: Deposition on ZM21 alloy after 72 hours in PBS
39x16mm (300 x 300 DPI)

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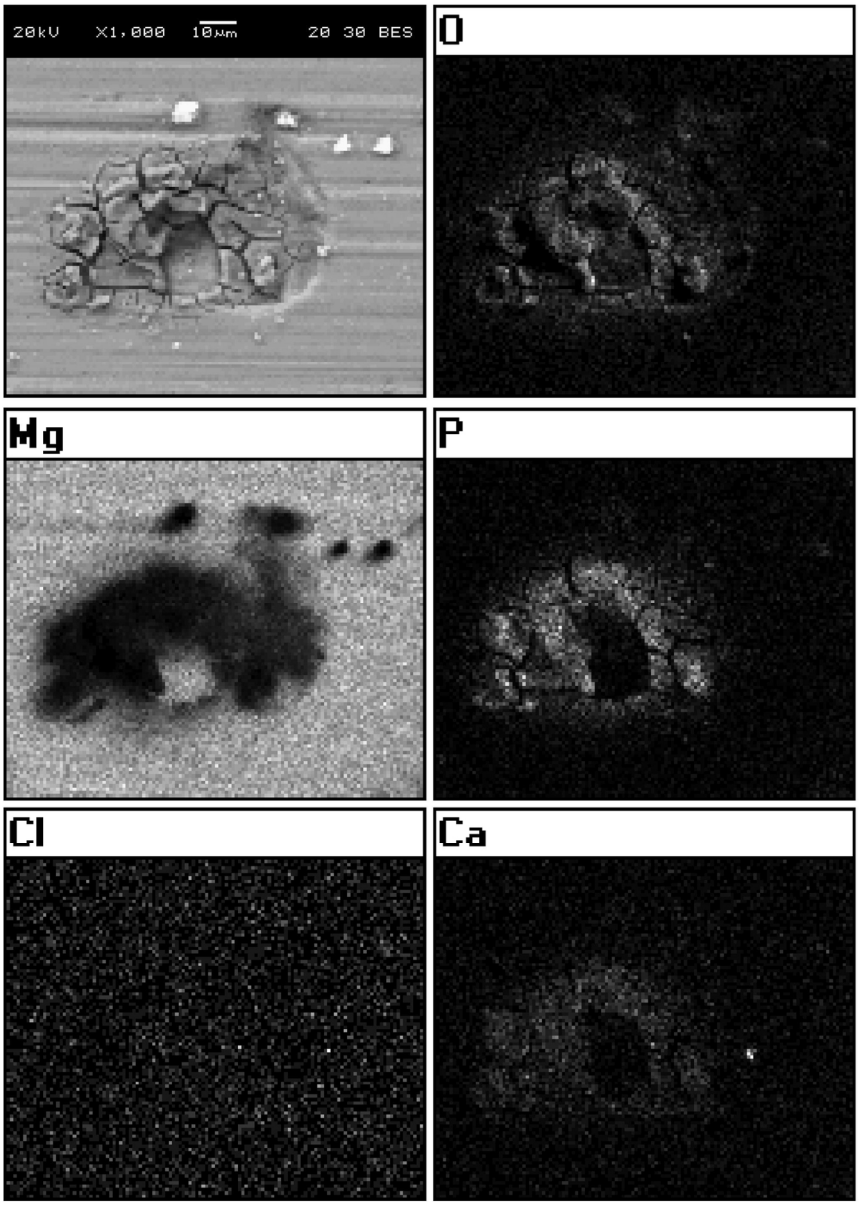

Figure 5: Element mapping of O, Mg, P, Cl and Ca on AZ31B sample after 24 hours in PBS
119x166mm (300 x 300 DPI)

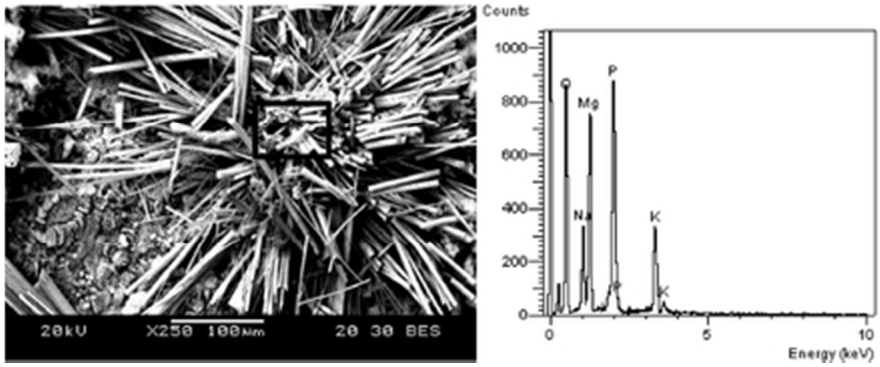

Figure 6: Needle-like depositions on AZ31B alloy after 7 days in PBS
36x15mm (300 x 300 DPI)

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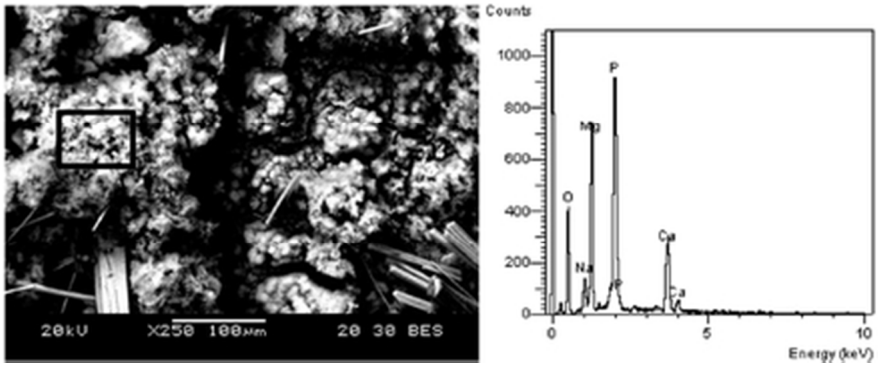

Figure 7: Sponge-like depositions on AZ31B alloy after 7 days in PBS
36x15mm (300 x 300 DPI)

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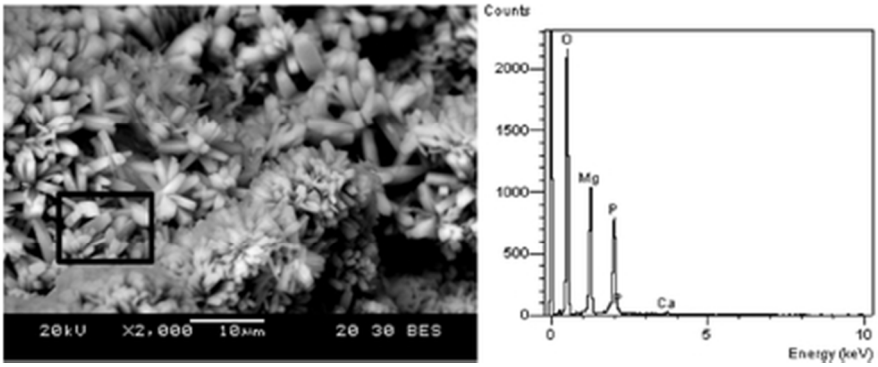

Figure 8: Formations on ZM21 alloys after 7 days in PBS
36x15mm (300 x 300 DPI)

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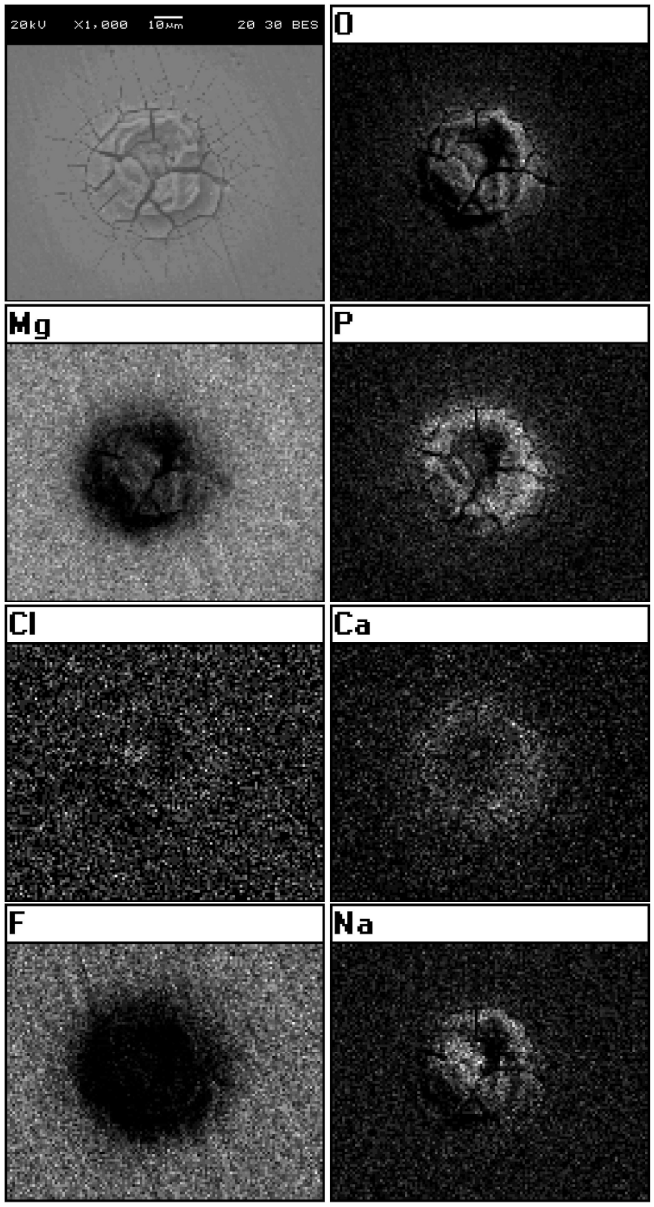

Figure 9: Element mapping of O, Mg, P, Cl, Ca, F and Na on AZ31BHF24h sample after 24 hours in PBS
157x292mm (300 x 300 DPI)

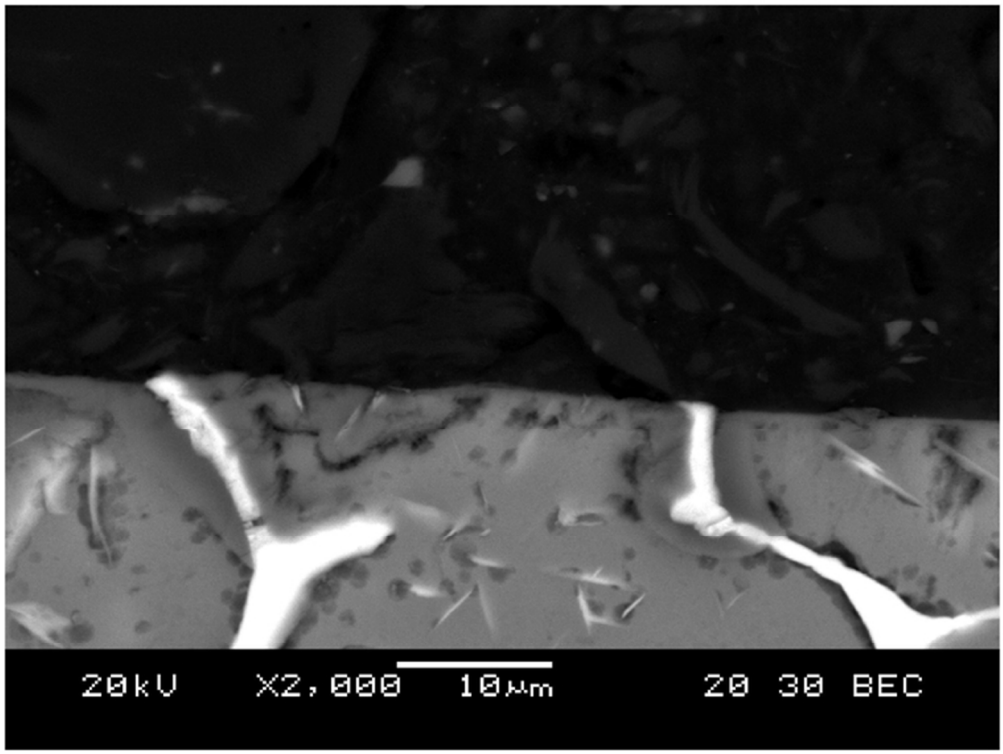

Figure 10: Detail of the MgF_2 around the intermetallics in the WE43 alloy
64x48mm (300 x 300 DPI)

Review

Table 1: Nomenclature of the samples

sample	alloy	coating treatment
AZ31B	AZ31B	-
AZ31BHF24h	AZ31B	24 h immersed in HF
AZ31BHF72h	AZ31B	72 h immersed in HF
WE43	WE43	-
WE43HF24h	WE43	24 h immersed in HF
WE43HF72h	WE43	72 h immersed in HF
ZM21	ZM21	-
ZM21HF24h	ZM21	24 h immersed in HF
ZM21HF72h	ZM21	72 h immersed in HF

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Table 2: pH variation in the immersion test

Sample	0 h	24 h	48 h	medium change	72 h	96 h
AZ31B	**7.4**	7.6	7.8	**7.4**	7.6	7.8
AZ31BHF24h	**7.4**	7.7	7.8	**7.4**	7.78	7.9
AZ31BHF72h	**7.4**	7.6	7.7	**7.4**	7.8	7.85
WE43	**7.4**	7.6	7.9	**7.4**	7.58	7.78
WE43HF24h	**7.4**	7.6	7.64	**7.4**	7.6	7.8
WE43HF72h	**7.4**	7.63	7.84	**7.4**	7.64	7.8
ZM21	**7.4**	7.72	7.96	**7.4**	7.78	7.93
ZM21HF24h	**7.4**	7.72	7.82	**7.4**	7.74	7.8
ZM21HF72h	**7.4**	7.6	7.6	**7.4**	7.68	7.8

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Table 3. Comparison of the corrosion rates of the present work with the literature

	r_{corr} [mm year^{-1}]	Electrolyte	Characterization test	Ref.
AZ31B	0.56	PBS	Immersion test	Present work
	12.52	PBS	Potentiodynamic polarisation	[69]
	1.425	SBF	Potentiodynamic polarisation	[38]
	8.965	SBF	Potentiodynamic polarisation	[60]
	0.711	Hank's solution	Potentiodynamic polarisation	[70]
	0.323	Hank's solution	Immersion test	[70]
	0.672	-	*In vivo*	[70]
	0.3	Hank's solution	Immersion test	[71]
	0.709	0 mol NaCl l^{-1}	Potentiodynamic polarisation	[54]
	294	10^{-5} mol NaCl l^{-1}	Potentiodynamic polarisation	[54]
	0.505	10^{-4} mol NaCl l^{-1}	Potentiodynamic polarisation	[54]
	0.914	10^{-3} mol NaCl l^{-1}	Potentiodynamic polarisation	[54]
	1.395	10^{-2} mol NaCl l^{-1}	Potentiodynamic polarisation	[54]
	1.740	10^{-1} mol NaCl l^{-1}	Potentiodynamic polarisation	[54]
	0.284	SBF	Potentiodynamic polarisation	[50]
	1.152	0 mol NaCl l^{-1} satured with CO_2	Potentiodynamic polarisation	[54]
	1.079	10^{-5} mol NaCl l^{-1} satured with CO_2	Potentiodynamic polarisation	[54]
	1.547	10^{-4} mol NaCl l^{-1} satured with CO_2	Potentiodynamic polarisation	[54]
	3.778	10^{-3} mol NaCl l^{-1} satured with CO_2	Potentiodynamic polarisation	[54]
	5.178	10^{-2} mol NaCl l^{-1} satured with CO_2	Potentiodynamic polarisation	[54]
	8.096	10^{-1} mol NaCl l^{-1} satured with CO_2	Potentiodynamic polarisation	[54]
	6.597	Hank's solution	Potentiodynamic polarisation	[72]
	0.25	Hank's solution	Immersion test	[73]
	0.098	Hank's solution	Potentiodynamic polarisation	[73]
	0.737	m-SBF	Potentiodynamic polarisation	[74]
	0.522	m-SBF	Potentiodynamic polarisation	[74]
	8.29	m-SBF	Immersion test	[74]
	1.997	m-SBF	Immersion test	[74]
WE43	0.47	PBS	Immersion test	Present work
	1.2	SBF	Potentiodynamic polarisation	[60]

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	0.704	-	*In vivo*	[56]
	1.44	-	*In vivo*	[56]
	0.361	SBF	Potentiodynamic polarisation	[58]
	4.467	SBF	Immersion test	[58]
	0.035	SBF	Immersion test	[64]
	4.221	SBF	Immersion test	[70]
	0.896	-	*In vivo*	[70]
ZM21	0.79	PBS	Immersion test	Present work
	0.919	SBF	Potentiodynamic polarisation	[60]
	0.939	Ringer solution	Potentiodynamic polarisation	[59]
	0.004	Ringer solution	Potentiodynamic polarisation	[59]

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List of changes

The changes made to the reference JEIM1468 are listed below:

- The abstract has been reduced to 100 words.
- The organization of the paper has been improved.
- The use of the Piiper et al model has been dismissed to evaluate the hydrogen evolution.
- Reviews and more recent papers on the measurement of Mg corrosion has been included.

Experimental methods

- The conversion coating process has been explained in more detail.

Results

- Figure 1 has been presented at higher magnifications to observe the layer in more detail.
- The MgF_2 conversion layer grown on each alloy has been described. The thickness reached on each alloy and time of treatment has been indicated.

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- The composition of the MgF_2 layer has been analysed by EDX in order to demonstrate the composition of the layer.
- Symbols of the Figure 2 have been enlarged.
- A better explanation of Figure 2 has been made. The reason of supply the corrosion rate graphs in addition to the hydrogen evolution was also justified.
- The depositions and the corrosion products analysis have been improved. More studies at higher magnifications with mapping and elemental analysis have been made in order to understand the corrosion of the magnesium alloys and the protection of the coating.

Discussion

- A comparison has been made with the data of the table III and with the results of the present work.
- The summary figure about the corrosion of the samples has been removed.
- To explain the increase of the corrosion resistance in WE43 despite having a non-uniform and barely perceptible coating a possible explanation has been exposed.

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- The possible composition of the depositions and corrosion products has been discussed.

Conclusions

- Conclusions have been numbered as a list of short conclusions.

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