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Materials Letters

Do phosphate ions affect the biodegradation rate of fluoride-treated Mg?

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ARTICLE INFO

ABSTRACT

Previous studies have shown that pure Mg that is reinforced by powder metallurgy (Mg(PM)) is a promising biodegradable material, because it circumvents the drawbacks of the toxic components of Mg alloy implants. However, its degradation rate is high, which can be reduced with fluoride coatings (Mg(PM)F). This protective effect is temporary, because chloride induces further biodegradation of Mg(PM) in biological media. The aim of this report was to examine the effects of phosphates on Mg(PM)F in chloride-containing medium. By surface analysis of Mg(PM)F, the aggressive activity of chlorides induced a rapid decrease in F content of the layer. However, by electrochemical impedance spectroscopy and EDX, the surface attack was hindered in the presence of phosphates that precipitated onto the regions where localized attack occurred and formed a more protective P-containing layer. Our results highlight the robust activity of phosphates, which act synergistically with fluorides, controlling the degradation of F-coating in biological media and prolonging the service period of temporary Mg(PM)F implants.

1. Introduction

Pure Mg overcomes the effects of the toxic components of magnesium alloys, but it has an excessively high degradation rate [1–6] and insufficient yield strength [7]. In this study, we examined Mg that was reinforced by powder metallurgy (Mg(PM)). Mg(PM) has a yield strength of 280 MPa — considerably higher than that of pure cast magnesium and approximating that of AZ31 Mg alloy. Many reports have demonstrated the importance of chloride ions, phosphates, and the pH and buffer capacity of solutions on the degradation of bare Mg and alloys in biological media [6,7].

Immersion of Mg(PM) in KF solution has been proposed to improve its resistance to degradation, because it is low-cost, nontoxic, simple, and amenable for biomedical applications [7]. After this treatment a conversion coating is formed [7–14].

The aim of this letter was to examine the effects of phosphate ions on the control of degradation of fluoride-treated Mg(PM) (referred to as Mg(PM)F) in chloride-containing media by electrochemical impedance spectroscopy (EIS) and EDX analysis. To mitigate the interference of other ions, simple synthetic solutions that are used frequently to simulate biological media – NaCl solution and chloride-containing phosphate-buffered solution (PBS) – were used as electrolytes.

2. Materials and methods

2.1. Materials

Magnesium powder (99.8%, 325 mesh) was supplied by Alfa Aesar. The powder was cold-pressed, and the resulting cylindrical compacts, 40 mm in diameter, were extruded in the form of bars at 420 °C at an extrusion ratio of 16:1.

Cylindrical samples (1 cm in diameter) were cut from Mg(PM) bars. The lateral surfaces were covered by epoxy resin, leaving a circular exposed area of 0.785 cm^2. The samples were ground and dry-polished with successively fine SiC paper to 1500 grit. A Philips XL30 scanning electron microscope (SEM), coupled to an EDX DE4i analyzer, was used to characterize the magnesium samples.

All solutions were prepared with ultrapure water from a Millipore Milli-Q system (18.2 MΩ^{-1}). The compositions of the solutions were: 0.1 M KF, 8 g L^{-1} NaCl, and PBS (8 g L^{-1} NaCl, 0.2 g L^{-1} KCl, 0.2 g L^{-1} KH$_2$PO$_4$, 1.15 g L^{-1} Na$_2$HPO$_4$). Analytical-grade reagents were used in all cases. Mg(PM) electrodes were used untreated or after immersion in 0.1 M KF for 1 h. To demonstrate the synergistic effect of phosphates and fluoride, we also performed experiments with electrodes that were treated with 0.1 M KF for 1 h, followed by immersion in PBS for 30 min.

2.2. Electrochemical impedance spectroscopy measurements

EIS measurements were made with an Autolab PGSTAT 30 potentiostat from Eco-Chemie. A sinusoidal potential modulation, ± 10 mV

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in amplitude in the 10^5 Hz–10^{-2} Hz frequency range, spaced logarithmically (120 per 8 decades), was superimposed onto the open circuit potential of the Mg(PM)F in 8 g L^{-1} NaCl or PBS.

3. Results and discussion

3.1. Electrochemical results

We compared the electrochemical behavior of untreated and KF-treated samples (Mg(PM)F) in NaCl-sol and PBS. The EIS results on the Mg(PM) samples under the open circuit potential condition are shown in Fig. 1. The Nyquist diagrams show a semicircle that corresponds to the limiting of charge transfer resistance (R_{CT}), related to the F$^-$-containing coating/electrolyte or Mg(PM)/electrolyte interfaces. At low frequency, we observed an inductive behavior, usually associated with ion adsorption–desorption during dissolution (Fig. 1a).

The impedance modulus Bode diagrams (Fig. 1b) revealed a plateau at high frequencies. The impedance value in this region, with $\varphi = 0$, yields electrolyte resistance ($R_e \sim 108$ Ω) for each case. At decreasing frequencies (10^3 Hz–10 Hz), the slope can be attributed to one capacitor in parallel with resistance, corresponding to the F$^-$-containing coating/electrolyte interface. In the lower frequency range (1–10^{-2} Hz), the phase angle is close to 0°, corresponding to a plateau in the impedance modulus-versus-frequency plot. From this region, it is possible to obtain the total resistance of the system ($R_{TC} + R_e$).
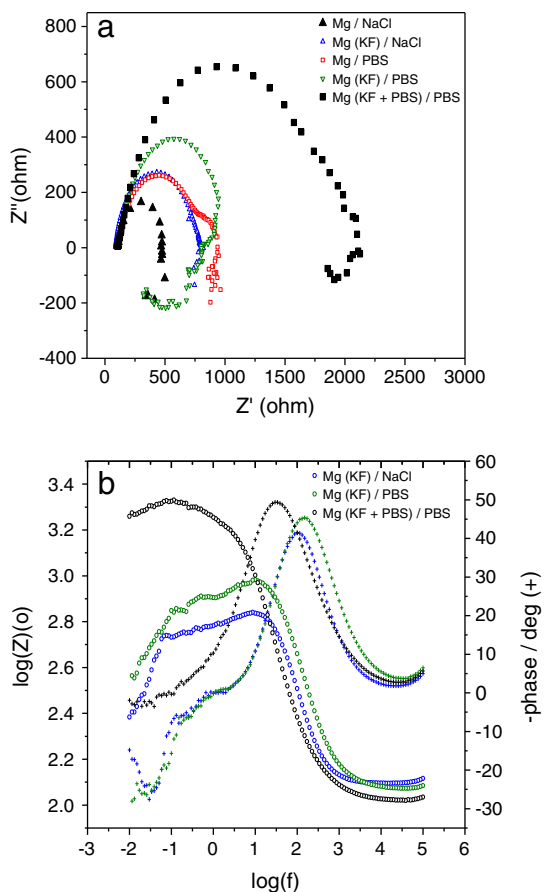
Table 1
Electrochemical parameters obtained from EIS measurements.

Test number[a]	Electrode (treatment)/ solution	R_{TC} Ω cm^2	C F·cm^{-2}	b |Z| vs. logf	Θ°
1	Mg/NaCl	319	8.94 E-6	0.46	−34
2	Mg/PBS	537	1.25 E-5	0.50	−39
3	Mg (KF)/NaCl	586	6.99 E-6	0.52	−42
4	Mg (KF)/PBS	754	5.03 E-6	0.57	−45
5	Mg (KF + PBS)/PBS	1445	1.63 E-6	0.62	−49

[a] Mg(PM) without treatment in NaCl (1) and in PBS (2) electrolyte solutions. Mg(PM) with 1 h treatment with KF using NaCl or PBS electrolytes (3, 4 respectively) and (5) Mg(PM) with 1h treatment with KF followed by 30 min immersion in PBS, using PBS as electrolyte solution.

The electrochemical parameters are summarized in Table 1, in which 5 types of tests are compared. The EIS spectra that were obtained with Mg(PM) with and without KF treatment in NaCl-sol and PBS differed significantly. The R_{CT} value of the untreated electrodes that were immersed in PBS solution (Test 1) was 218 Ω higher than that in NaCl solution (Test 2) (i.e., the phosphate effect).

After KF treatment (Tests 3, 4), the R_{CT} values were higher than those of Tests 1 and 2 (without treatment) ($R_{CT3} − R_{CT1} = 267$ $R_{CT4} − R_{CT2} = 217$ Ω (KF effect)). Notably, we observed a synergistic effect between the inhibition by phosphate and fluoride when the sample was immersed in PBS for 30 min after treatment with KF. Thus, the difference between R_{CT} values between Tests 4 and 5 is 691 Ω higher than the sum of the phosphate and fluoride effects. Conversely, the phase angles (φ) and Z-log f slopes are consistent with an increase in the capacity of the interface (Table 1).

Fig. 1. (a). Nyquist EIS spectra plots of Mg(PM) immersed in 8 g L^{-1} NaCl or PBS. Experiments made without KF treatment in NaCl (▲) and PBS (□) electrolyte solutions. Experiments made with KF treatment in NaCl (△) and PBS (▽) solutions and with KF treatment + 30 min immersion in PBS before EIS measurements in PBS (■). (b). Bode EIS spectra plots of Mg(PM) immersed in 8 g L^{-1} NaCl or PBS. Experiments made with KF treatment in NaCl (○) and PBS (○) solutions and with KF treatment + 30 min immersion in PBS before EIS measurements in PBS (○).
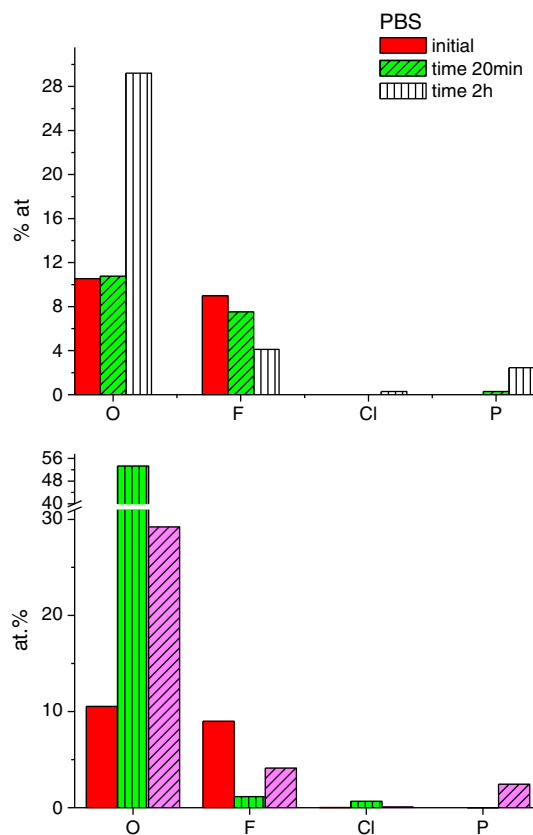

Fig. 2. (a) Influence of immersion time of Mg(PM)F in PBS-sol on degradation of F$^-$-conversion coating. EDX analysis of the surface composition of Mg(PM)F (0.1 M KF pretreatment for 1 h) after immersion in PBS-sol (□) before immersion, (///) after 20 min of immersion, and (lll) after 2 h of immersion. (b) Influence of composition of solution on degradation of F$^-$-conversion coating. EDX analysis of surface composition of Mg(PM)F (0.1 M KF solution pretreatment for 1 h) (□) before and after 2 h of immersion in (lll) NaCl-sol and (///) PBS.