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Surface Modification of Magnesium and its Alloys for Biomedical Applications

Volume 2: Modification and Coating
Techniques

Edited by

***T. S. N. Sankara Narayanan, Il-Song Park
and Min-Ho Lee***



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Fluoride conversion coatings for magnesium and its alloys for the biological environment

1

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1.1 Introduction

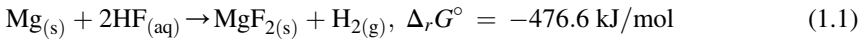
In the last few years, magnesium and its alloys have been considered as biodegradable materials for applications such as orthopedic implants and stents for vessel dilatation (Witte, 2010; Virtanen, 2011). Due to its biocompatibility (of magnesium and of its corrosion products) and good mechanical properties, magnesium-based implants may serve as load-bearing devices, contributing to the healing of the organism and then gradually degrading without causing adverse effects. Among the beneficial effects of such devices is that surgery for implant removal is not required. However, magnesium alloys have low corrosion resistance in aqueous environments containing ions such as Cl^- , like the biological environment. Therefore, magnesium implants in such mediums may undergo earlier failure, excessive hydrogen production (which forms gas cavities and inflammation), and a high pH increase in the neighborhood of the implant, causing postoperative complications (Virtanen, 2011).

The literature reports numerous surface treatments and coatings to control magnesium corrosion in biological environments (Hornberger, Virtanen, & Boccaccini, 2012). Among these, the preparation of fluoride conversion coatings has received special attention. The most studied fluoride conversion coating on magnesium is magnesium fluoride (MgF_2), which can be easily prepared by immersion of magnesium in a solution containing fluoride anions, as hydrofluoric acid (HF) solutions. Reports in the literature suggest that, besides increasing corrosion resistance, this conversion coating has antibacterial properties (Lellouche, Friedman, Lellouche, Gedanken, & Banin, 2012; Lellouche, Kahana, Elias, Gedanken, & Banin, 2009) and may induce bone healing due to beneficial effects of fluoride (Berglundh, Abrahamsson, Albouy, & Lindhe, 2007). In this chapter, the formation of MgF_2 coating on magnesium alloys is discussed. The potential of this treatment to protect magnesium from corrosion and to enhance its corrosion resistance in biological environments is considered in detail, as well as future trends and current challenges.

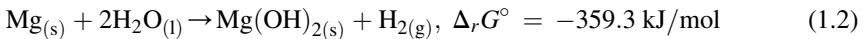
1.2 Coating formation: Mechanism and characteristics

1.2.1 Hydrofluoric acid immersion

The traditional method for preparing fluoride coating on magnesium and its alloys is to immerse the sample in an aqueous solution of hydrofluoric acid for a time period that can vary from a few minutes to days. It is generally assumed that the coating is formed by the reaction of magnesium with HF, as shown in Eqn (1.1). This reaction has a negative change in the Gibbs free energy, indicating that this is a product-favored reaction (the change in free energy was obtained using the data in chemical thermodynamic tables, in the temperature of 298.15 K, reported by Wagman et al., 1982). The literature reports different conditions for this treatment in regard to treatment time, acid concentration, and substrate pretreatment. Table 1.1 shows some characteristics of HF treatment described in the literature for different magnesium alloys. A systematic investigation on solution concentration and treatment time on the coating properties is reported in detail by Conceição, Scharnagl, Blawert, Dietzel, and Kainer (2010), Verdier, Laak, Delalande, Metson, and Dalard (2004), and Bakhsheshi-Rad, Idris, Kadir, and Daroonpavar (2013). Coating properties such as thickness, constitution, and porosity change significantly depending on these parameters.



In the studies of Conceição et al. (2010) and Verdier et al. (2004) it was shown that the coating can present a considerable amount of hydroxides and oxides, even when ground samples are used. In general, the lower the acid concentration the higher the amount of hydroxides/oxides formed on the metal surface. This observation is related to the possible formation of magnesium hydroxide during the HF treatment in aqueous solutions. Magnesium hydroxide can be formed by the reaction of the metal with water (Eqn (1.2)), which is the main reaction in the aqueous corrosion of magnesium. By comparing Eqns (1.1) and (1.2) it can be seen that both reactions have a similar thermodynamic tendency to take place. Therefore, from a thermodynamic point of view, it is expected that these reactions occur simultaneously when metallic magnesium is in contact with water and HF. The rate of each process will depend on the HF concentration.

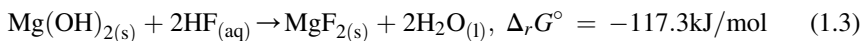


Increasing the acid concentration assures a coating constituted basically of MgF_2 with small amounts of magnesium oxide. By using a high HF concentration, magnesium hydroxide, eventually formed during the treatment, can be converted into magnesium fluoride according to the reaction shown in Eqn (1.3). This process is thermodynamically favored, and therefore it is expected to take place at high HF concentrations. In fact, studies in the literature report the preparation of MgF_2 coatings by first preparing a $\text{Mg}(\text{OH})_2$ layer and then performing the conversion shown in Eqn (1.3) (see the last entries in Table 1.1).

Table 1.1 Characteristics of MgF₂ coating reported in the literature for different alloys prepared with different parameters

Reference	Alloy	HF ^a concentration	Time/ temperature (h/°C)	Surface color	Coating thickness (μm)
Ground or as-received substrate					
Conceição et al. (2010)	AZ31	7–28 (mol/L)	1–24/R ^b	Brown and black	1.0–2.0
Verdier et al. (2004)	AM60	10 ⁻³ –10 ⁻¹ (mol/L)	—	—	—
Chiu et al. (2007)	Pure	48%	6–24/R	Golden/ brown	1.5
Mao et al. (2013)	JDBM	40%	12/R	—	1.5
Yan et al. (2010)	AZ31B	50%	3–168/30	—	0.5–2.75
Jian-Zhong et al. (2009)	AZ91D	10–70%	10 min–1/R–90	Gray-black	—
Sun et al. (2013)	Mg-3Zn-8Zr	20%	6/37	—	0.5
Xin-kuan et al. (2010)	AZ91	15%	—	—	1.6–3.2
Li, Zhong, Hu, and Kang (2008)	AZ91D	20%	20/R	—	—
Carboneras, Garcia-Alonso, and Escudero (2011)	AZ31	48%	24/R	—	—
Substrate previously treated in alkaline solutions					
Bakhsheshi-Rad et al. (2013)	Mg-05Ca	5–48%	6–24	Brown and black	4.0–12.6
Witte et al. (2010)	LAE442	40%	96	—	150–200
Ma, Li, Li, Zhang, and Huang (2013)	Mg-Li-Al-Ce	40%	12/R	—	6.0
Drynda et al. (2010)	MgCa	40%	96/R	Black	10–20
Thoman et al. (2009)	MgCa and WE34	40%	96/R	Gray-black	5–15

^aThe concentrations reported as % are weight percentage.^bRoom temperature.



According to studies in the literature, the quantity of hydroxides in the coating have considerable effect on its protective properties, and in general, the less the better (Conceição et al., 2010). Considering the discussion above, one may conclude that the higher the HF concentration, the better the protective properties of the formed coating. Nevertheless, depending on the alloy being treated, an increase in the HF concentration may result in thin coatings. For instance, for sheets of the alloy AZ31 (the AZ family of magnesium alloys is under certain controversy about its biological application due to concerns related to aluminum), the optimum treatment condition was found to be a concentration of 14 mol/L for 24 h, at room temperature (Conceição et al., 2010). In this case, a coating with $\sim 2.0 \mu\text{m}$ of thickness was built on the metal surface. Treating the same alloy with 28 mol/L in the same conditions resulted in a thinner coating (below $1.0 \mu\text{m}$) and in higher corrosion current densities in electrochemical tests ($19 \mu\text{A}/\text{cm}^2$ for 14 mol/L and $62 \mu\text{A}/\text{cm}^2$ for 28 mol/L) (Conceição et al., 2010). Similar observations were made by Bakhsheshi-Rad et al. (2013) for the alloy of pure magnesium with 0.5 wt% of Ca. In this study, it was reported that increasing the HF concentration from 40% to 48% produced a decrease in coating thickness from 12 to $9 \mu\text{m}$. These results are probably related to a higher rate of metal dissolution than of conversion coating formation as the solution pH decreases.

The thickness of the formed coating is very similar for different alloys and in different treatment conditions. For instance, in the study of Yan et al. (2010) the alloy AZ31B was treated with 50 wt% HF at 30°C for times varying from minutes to 168 h. The thicker coating was obtained with 70 h of treatment ($2.7 \mu\text{m}$) and no further thickness increase was observed until 168 h. This treatment time is among the longest reported in the literature. Nevertheless, the reached thickness is in the same range as the ones obtained in short treatments. For AZ31 alloy, for example, the literature reports MgF_2 coating with $2.0 \mu\text{m}$ of thickness formed by treating with 7 mol/L HF for 24 h, at room temperature (Conceição et al., 2010). These and the results summarized in the firsts entries of Table 1.1 show that by simply immersing the sample in an HF solution, the formed layer will have a thickness ranging from 1.0 to $2.5 \mu\text{m}$, even at treatment times as long as 168 h. This is indicative that the film growth takes place at the metal/solution interface. After the surface is completely covered by the MgF_2 layer, the conversion coating process stops. This interpretation is in accordance with the weight and thickness increase observed by different authors during HF treatment (Yan et al., 2010; Bakhsheshi-Rad et al., 2013).

However, studies in the literature have shown that thicker MgF_2 layers can be produced by a previous alkalization of the substrate. By this process, a thick $\text{Mg}(\text{OH})_2$ layer is formed on the metal surface, which is converted to MgF_2 by immersing the coated sample in an HF solution. For instance, Bakhsheshi-Rad et al. (2013) reports the development of a MgF_2 layer of $12.6 \mu\text{m}$ of thickness on the alloy of magnesium with 0.5 Ca. The alloy was previously immersed in a solution of sodium hydroxide for 2 h and then immersed in HF. This thickness was obtained with an HF concentration of 48 wt% HF for 24 h at room temperature. A study of Witte et al. (2010) reported MgF_2 layers of 150–200 μm of thickness on the alloy LEA442 by treating with 40% at room

temperature for 96 h. Prior to the immersion in HF, the alloy was placed in a boiling solution of sodium hydroxide to create a magnesium hydroxide coating, which was converted to MgF_2 by immersion in HF. A similar process was used by [Thomann et al. \(2009\)](#) and [Drynda et al. \(2010\)](#) for different alloys of magnesium with calcium (from 0.4 to 1.0 wt% of Ca). Thicknesses ranging from 5 to 20 μm were reported. In these cases, the final thickness is defined on the alkalizations step and the conversion of $\text{Mg}(\text{OH})_2$ to MgF_2 takes place from the film solution interface toward the metallic substrate.

The coating appearance also depends on the treatment conditions. A brown/gold color is generally considered as the traditional aspect for MgF_2 coating ([Chiu, Wong, Cheng, & Man, 2007](#)). Nevertheless, the literature also reports samples with a black surface. [Conceição et al. \(2010\)](#) and [Bakhsheshi-Rad et al. \(2013\)](#) report that the black surface is formed when the sample is treated with high HF concentrations, while the golden color is more common at milder treatment conditions. In both cases, the authors studied alloys instead of pure magnesium (AZ31 and Mg-0.5Ca, respectively). Gray to black surfaces on magnesium samples treated with HF are also reported by [Jian-Zhong, Jiu-gui, Yan-wen, and Chang-sheng \(2009\)](#), [Pereda et al. \(2010\)](#), and [Thomann et al. \(2009\)](#). As discussed in the prior section, lower HF concentrations enhance the formation of hydroxides. Therefore, it is suggested that the bronze color is related to the presence of hydroxides in the coating. This conclusion is further corroborated by the studies mentioned. [Jian-Zhong et al. \(2009\)](#) report EDS analysis of the prepared gray and black surfaces. They detected the presence of magnesium, aluminum, and fluoride on the surface (the alloy under investigation was AZ91D). The oxygen concentration was not reported. [Pereda et al. \(2010\)](#) report black surfaces for pure magnesium prepared by powder metallurgy and coated with MgF_2 and KMgF_3 . No hydroxides were detected on these surfaces according to X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis, although magnesium oxide could be detected. A similar result is reported by [Thomann et al. \(2009\)](#) investigating the composition of the coating in depth by energy-dispersive X-ray spectroscopy (EDX). On the other hand, in the study of [Chiu et al. \(2007\)](#), the obtained surface had a golden appearance. According to the results reported by Chiu, XPS analysis indicated the presence of small amounts of magnesium hydroxide in the coating.

[Figures 1.1 and 1.2](#) show a detailed investigation on the correlation between appearance and chemical composition. Sheets of the alloy AZ31 were treated either by 14 mol/L or 28 mol/L HF solution for different lengths of time (from 1 to 24 h). [Figures 1.1 and 1.2](#) show images of the aspect and the infrared spectra of these samples, respectively. By treating the samples for 1 h both solutions produced a gray to black surface. The infrared spectra show signals related to oxides and fluorides for the sample treated with 14 mol/L. The spectrum of the sample treated with 28 mol/L shows weak signals, indicating the dissolution of native magnesium oxide film. After 5 h the treatment with 14 mol/L produced a golden color while the sample treated with 28 mol/L is completely black. The surface of the sample treated with 14 mol/L is very heterogenic in appearance, however, and its infrared spectrum does not show the signal above 3000/cm related to hydroxides. Nevertheless, the

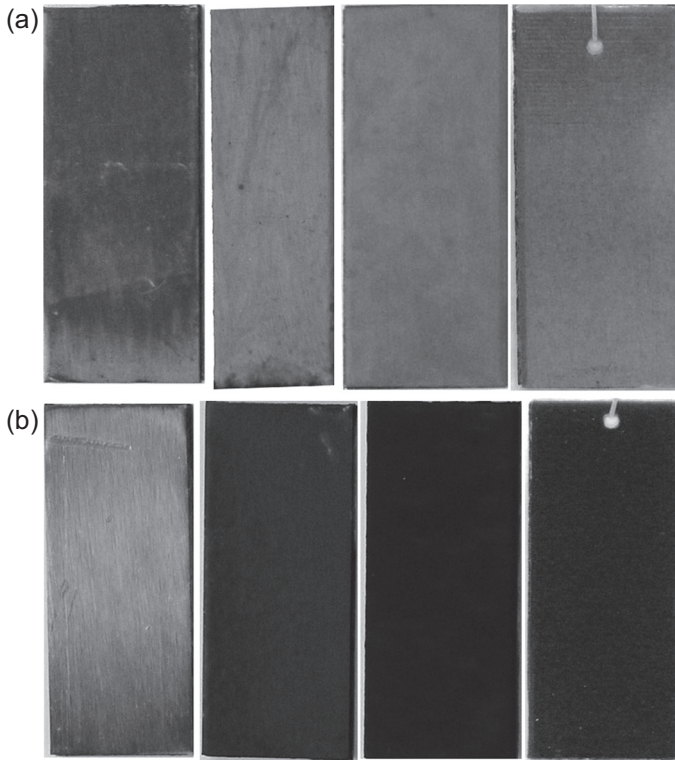


Figure 1.1 Image of AZ31 alloy sheets treated with (a) 14 mol/L HF and (b) 28 mol/L HF for 1 h, 5 h, 15 h, and 24 h (from left to right).

band related to oxides and fluorides (from 500–900/cm) became larger. In this same time, the spectrum of the sample treated with 28 mol/L showed an increase in the presence of fluoride. By increasing the treatment time with 14 mol/L the surface starts to be more homogeneous, resulting in the brown/golden color, while treatment with 28 mol/L results in a black appearance. It is clear from the infrared spectra that the presence of hydroxides in the sample treated with 14 mol/L, and the amount of hydroxides, increase with treatment time. These results further corroborate the assumption that the bronze color indicates the presence of hydroxides in the coating.

It is important to notice that hydroxides were detected after 15 h of treatment, indicating that they were formed way after magnesium fluoride. It is unlikely that magnesium fluoride was converted into magnesium hydroxide at this point of the process, since this conversion is not thermodynamically favored on the applied conditions. Nevertheless, it is possible that a compound of general formula $\text{MgF}_{2-x}(\text{OH})_x$ is formed on the surface, as shown in different studies in the literature (Booster, Sandwijk, & Reuter, 2003; Prescott, Li, Kennitz, Deutsch, & Lieske, 2005). The literature does not provide thermodynamic information about such compounds; therefore, it is not possible to conclude if this process is favored from a thermodynamic point of view. The late formation of hydroxide may also be related to a slower rate of magnesium

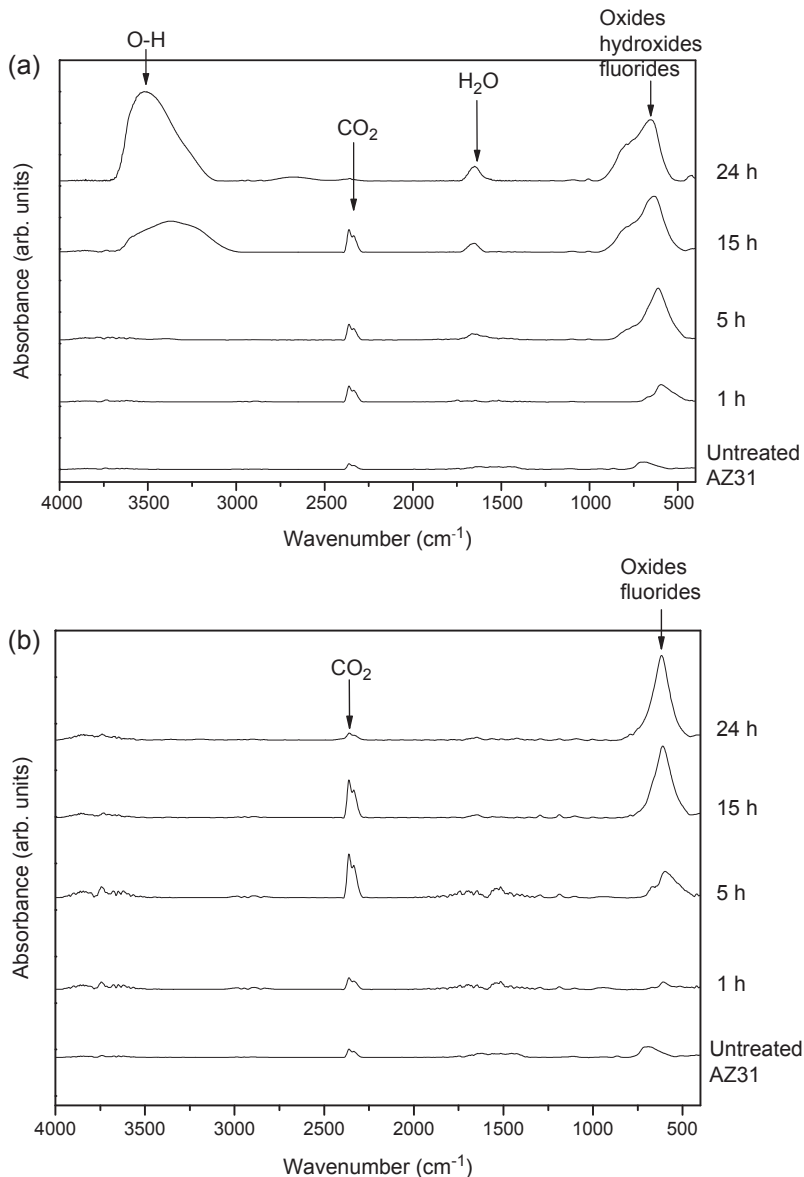


Figure 1.2 FTIR spectra of Mg AZ31 alloy sheets treated with (a) 14 mol/L HF and (b) 28 mol/L HF, at different treatment times.

Reprinted with permission from [Conceição et al. \(2010\)](#).

hydroxide formation at the beginning of immersion in HF, on the tested conditions. However, as the reaction between magnesium and HF (Eqn (1.1)) proceeds, the concentration of HF will decrease in the solution. It is possible that this concentrations falls enough to allow the reaction in Eqn (1.2) to occur at a higher rate. Nevertheless, a

complete understanding on the formation of hydroxides during the MgF_2 formation process by immersion in HF solutions needs further investigation considering thermodynamics and kinetics aspects.

1.2.2 *Alternative methods*

Due to the high toxicity of hydrofluoric acid, different alternative methods have been proposed for creating a MgF_2 conversion layer on magnesium alloys. An approach that has been considered by different authors is the immersion of magnesium alloys in solutions of fluoride salts such as NaF, KF, and NH_4F (Gulbrandsen, Tafto, & Olsen, 1993; Verdier et al., 2004). In some studies, the fluoride salt is mixed with an acid or a base to control the pH. It is shown that the corrosion current density of magnesium and its alloys is considerably reduced in the presence of fluoride salt, which is attributed to the formation of a protective film. Some studies also investigated the aid of electrochemical methods to enhance the MgF_2 formation rate on magnesium alloys exposed to KF solutions. In the study of Wu, Dong, and Ke (2013), for example, a potential difference of -1.4 V was applied on magnesium AZ31 alloy, exposed to 0.1 M KF solution. A mixed layer consisting of $\text{Mg}(\text{OH})_2$, MgF_2 , and KMgF_3 was formed with a total thickness of about $0.6\text{ }\mu\text{m}$. The corrosion protection provided by this treatment was not reported. The use of fluoride-containing salts to prepare MgF_2 layers was also investigated in micro-arc oxidation (MAO) processes. Mu and Han (2008) prepared and characterized MAO coatings on pure magnesium disks using potassium fluorozirconate as electrolyte. The authors report that the presence of fluoride enhances coating properties by the formation of MgF_2 . Nevertheless, a mixed coating is formed with tetragonal and monoclinic zirconium oxide. Liu, Shan, Song, and Han (2011) report similar improvements for this electrolyte in plasma electrolytic oxidation (PEO) coatings. In fact, the use of fluoride salts in MAO and PEO processes for magnesium alloys is well known in methods such as DOW-7 and HAE (Gray & Luan, 2002). In all cases, MgF_2 is formed among other compounds.

Recently, studies in the literature report the use of vacuum deposition techniques to deposit MgF_2 on the surface of magnesium alloy. In fact, such techniques are well known for the preparation of MgF_2 thin coatings on optical materials (see, for example, Perales, Herrero, Jaque, & Heras, 2007). In the study of Li et al. (2013), a magnesium alloy with $1\text{ wt\%}$ Ca was coated with MgF_2 by vacuum deposition. The coating had a cracked surface and a thickness of $0.95\text{ }\mu\text{m}$. The coating increased the alloy biocompatibility and provided corrosion protection to some degree. Another interesting method described by Lellouche et al. (2009) resulted in nanoparticles of MgF_2 prepared by sonochemical and microwave radiation of a mixture of magnesium acetate and 1-butyl-3-methylimidazolium tetrafluoroborate. Glass sheets were coated with these nanoparticles by dipping into the reaction medium. It was shown that these nano-sized MgF_2 particles have antibiofilm properties. Nevertheless, this method has not been applied for coating metals with corrosion protection purposes. The synthesis of magnesium fluoride from sol–gel routes is also described in the literature (Prescott et al., 2005), but the performance of the synthesized particles on corrosion protection is not

described. In general, these alternative methods tested on magnesium create mixed layers, with higher amounts of hydroxides and oxides in comparison to the traditional HF treatment. As a consequence, the corrosion protection is usually inferior, as well as the coating thickness. Therefore, more research is necessary to create protective fluoride coatings without using hydrofluoric acid.

1.3 Corrosion protection properties

1.3.1 General characteristics

The literature reports different studies about the protectiveness of MgF_2 coatings on magnesium and its alloys in corrosive environments. Table 1.2 shows a summary of the results obtained in corrosion tests for magnesium and magnesium alloys coated with MgF_2 . Direct polarization tests have shown that the conversion coating

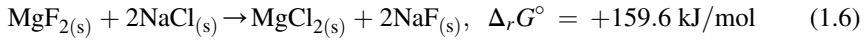
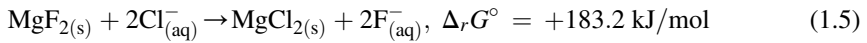
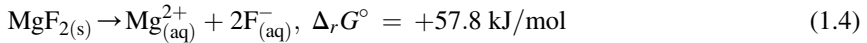
Table 1.2 Results of electrochemical polarization tests of magnesium and magnesium alloys, coated with MgF_2 , in different solutions

Reference	Alloy	MgF_2 thickness (μm)	Test solution	Lowest corrosion current density ($\mu\text{A}/\text{cm}^2$)	Highest corrosion potential (mV)
Conceição et al. (2010)	AZ31	2.0	3.5 wt% NaCl	13.0	−1445
Chiu et al. (2007)	Pure	1.5	Hank's solution	10.0	−1580
Mao et al. (2013)	JDBM	1.5	Artificial plasma	1.05	−1590
Yan et al. (2010)	AZ31B	2.7	SBF	1.14×10^{-2}	−1478
Li et al. (2008)	AZ91D	—	3.5 wt% NaCl	1.17	−1533
Li et al. (2013)	Mg-1Ca	0.9	Hank's solution	6.06	—
Bakhsheshi-Rad et al. (2013)	Mg-05Ca	12.6	Kokubo solution	6.20	−1658
Drynda et al. (2010)	MgCa	10–20	2.5% NaCl	150	—

process generally moves the corrosion potential toward more positive values, indicating a decrease in the thermodynamic tendency for oxidation. Generally, the thicker the coating the nobler the corrosion potential. Therefore, the corrosion potential tends to move toward the nobler direction by increasing the treatment time at a fixed HF concentration. For instance, [Yan et al. \(2010\)](#) show that the corrosion potential of the alloy AZ31B continuously moves toward the noble direction by increasing the treatment time with 50% HF. After 168 h of treatment, the corrosion potential was 200 mV nobler than that of the untreated metal. Similar results are reported by [Conceição et al. \(2010\)](#) for different HF concentrations. The effect of HF concentration on the corrosion potential, at a fixed time, does not follow a regular trend.

The corrosion current density does not decrease continuously with treatment time at a fixed HF concentration. In the study of [Yan et al. \(2010\)](#) the corrosion current density reached a constant value after 72 h (decreased from $12.62 \mu\text{A}/\text{cm}^2$ to $0.011 \mu\text{A}/\text{cm}^2$), and no further decrease was observed by longer treatment times. As the coating thickness reaches a constant value at this same treatment time, the result indicates that the corrosion current density is directly related to the coating thickness. This conclusion is corroborated by the results of [Conceição et al. \(2010\)](#) and by analyzing the effect of different HF concentrations, at a fixed treatment time, on the corrosion current density. When the HF treatment is applied on the as-received sample, the decrease in corrosion current density is also related to a decrease on the Fe/Mn ratio to below its critical value. The Fe/Mn ratio is an important parameter for studying magnesium corrosion, as manganese can dissolve iron particles forming a phase with lower cathodic activity, decreasing the microgalvanic corrosion ([Song & Atrens 1999](#)). The treatment of as-received AZ31 sheets with HF decrease the Fe/Mn ratio from 0.035 to 0.024, below the tolerance limit of 0.032 ([Conceição et al., 2010](#)).

Impedance tests have shown that the protectiveness of MgF_2 layers formed by HF treatment does not hold for a long time. It was shown that the impedance of AZ31 sheets coated with MgF_2 ($2.0 \mu\text{m}$ of thickness) falls by 4 decades after 20 h of exposure to a 3.5 wt% NaCl solution ([Conceição et al., 2010](#)). Such a behavior was observed for black and golden MgF_2 layers on AZ31, of similar thickness. This indicates that the corrosive solution can easily penetrate in the coating, reaching the metallic substrate in short time periods. Some studies discuss a possible instability of MgF_2 in solutions containing chloride as the reason for its short-term protection (for example, see [Cowan & Harrison, 1979](#)). It is shown in [Eqns \(1.4\)–\(1.6\)](#) that MgF_2 dissolution in water is not thermodynamically favored, as well as its reaction with chlorine. Thus, from a thermodynamic point of view, MgF_2 is rather stable in chlorine-containing solutions. The low long-term protection it provides is probably related to cracks and holes in the coating, which allow the metal underneath the coating to corrode, producing an undermining effect. Therefore, in order to improve the long-term stability, the coating defects must be either covered by another layer or suppressed by optimizing the coating process. Nevertheless, further studies are required to elucidate the influence of chlorine anions on the degradation mechanisms of MgF_2 layers.



The short-term protection provided by the HF treatment attracted the attention of some researchers to its potential as a pretreatment step instead of a final corrosion protection process. As the defects on the MgF_2 layer can be covered by a sealant, the literature reports the deposition of different coatings on an HF-treated magnesium sample. For instance, [Conceição et al. \(2010\)](#), [Conceição et al. \(2011a,b\)](#), and [Conceição, Scharnagl, Dietzel, and Kainer \(2012\)](#) have shown that polymer coatings on HF-treated magnesium substrates behave much better than on the substrates with other kinds of pretreatments. Such observation was made for different polymers such as polyetherimide (PEI), polyacrylonitrile (PAN), and polyvinylidene difluoride (PVDF). For these polymers, superior corrosion performance was observed in comparison with ground, as-received, and acid-etched samples (acetic and nitric acids) in electrochemical and immersion tests.

[Figure 1.3](#) shows images of AZ31 samples after immersion tests. The samples where PEI was coated were either pretreated with HF (14 mol/L and 20 mol/L) or ground. Both samples pretreated with HF show fewer signals of corrosion after a longer immersion time in the corrosive solution than the ground and as-received samples. It can be observed that the grinding process considerably decreased the corrosion attack on the sample surface (compare the aspect of the ground and as-received sample); however, one can observe coating delamination on the lower edge of the sample.

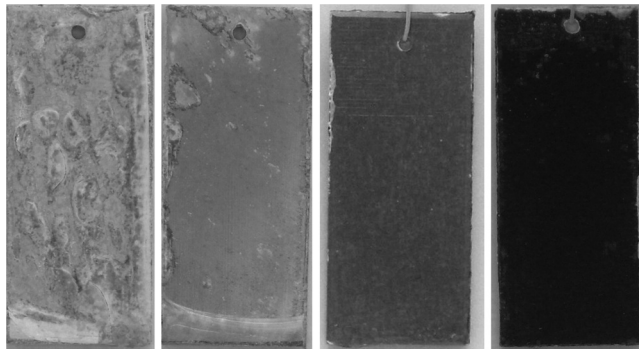


Figure 1.3 Image of AZ31 sheets coated with PEI (thickness of 15 μm), with different pretreatments, after immersion on 3.5 wt% NaCl at room temperature. From left to right: as-received (2 days of immersion), ground (2 days of immersion), 14 mol/L HF for 24 h (7 days of immersion), and 20 mol/L HF for 24 h (7 days of immersion). Reprinted with permission from [Conceição et al. \(2010\)](#).

For both coatings pretreated with HF no delamination was observed even after 7 days of immersion in the solution. These results indicate an improvement in adhesion produced by the formed MgF_2 layer.

Such adhesion improvement allows self-healing processes to take place at the interface of an HF-treated/polymer-coated sample, as confirmed by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) analysis (Conceição et al., 2010, 2011b, 2012). These self-healing processes produce impedance increases after a certain exposure time to the corrosive solution. In general, these processes were related to reactions between the corrosion product (magnesium hydroxide) and the polymer. Such reactions resulted in polar groups attached to the polymer, at the interface, and in some cases in the formation of carboxylic acid groups. This allows acid–base interactions to take place at the interface, stabilizing the system. For PVDF, PEI, and PAN coatings on AZ31 sheets pretreated with HF, a stable impedance was observed for more than 1000 h of exposure to a 3.5 wt% NaCl solution (Conceição et al., 2010, 2011a,b, 2012).

1.3.2 Corrosion in simulated body fluids and interaction with biomolecules

Different studies in the literature report the influence of MgF_2 coating on magnesium samples in simulated body fluids. These fluids simulate the ionic composition of the body, and the composition of some of these is shown in Table 1.3. The measurements are usually performed at 37 °C and at a pH of 7.4 to better mimic the conditions of the human body. Chiu et al. (2007) investigated the corrosion performance of pure magnesium ingots treated with HF in Hank's solution. It was observed that the corrosion current density was significantly decreased by the HF treatment, while the impedance increased by 1 decade. Immersion tests corroborate the better corrosion resistance for

Table 1.3 Composition of simulated body fluids (SBF) commonly reported in the literature

SBF	Composition (10^{-3} mol/L)
Hank's solution (Chiu et al., 2007)	NaCl (137), CaCl_2 (1.26), KCl (5.37), NaHCO_3 (4.17), glucose (5.56), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (0.49), $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ (0.34), KH_2PO_4 (0.44), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (0.26)
Kokubo solution (Kokubo & Takadama, 2006)	Na^+ (142.0), K^+ (5.0), Mg^{2+} (1.5), Ca^{2+} (2.5), Cl^- (147.8), HCO_3^- (4.2), HPO_4^{2-} (1.0), SO_4^{2-} (0.5)
Mao et al. (2013)	NaCl (116), CaCl_2 (1.80), KCl (5.37), MgSO_4 (0.83), NaHCO_3 (26), Na_2HPO_4 (0.89), NaH_2PO_4 (0.22)

the coated sample, in comparison to the uncoated one. [Li et al. \(2013\)](#) report the behavior of MgF_2 -coated Mg-1Ca alloy (the coating was deposited by physical vapor deposition and had a reported thickness of $0.95\ \mu\text{m}$) in Hank's solution. The protectiveness provided by the coating was evaluated by means of electrochemical techniques, hydrogen evolution, and pH evaluation. It was reported that anodic and cathodic currents were considerably decreased by the coating, and the corrosion current density fell by half. Considerable decrease in the hydrogen gas evolution and pH increase was observed in time periods from 250 to 500 h.

Hank's solution was also used by [Mao, Yuan, Niu, Zong, and Ding \(2013\)](#), who investigated the performance of the alloy JDBM coated with MgF_2 by means of immersion in HF. The corrosion rate, obtained by gravimetric analysis, falls from $0.337\ \text{mm/y}$ to $0.253\ \text{mm/y}$ by treating with 40% HF for 12 h. Electrochemical impedance spectroscopy showed the expected increase in impedance, related to the appearance of a second semicircle in the Nyquist plot, and the direct polarization confirmed the results from the gravimetric analyses, showing a lower corrosion current density for the coated sample. Similar results are reported by different authors in other simulated body fluids as Kokubo solutions (for example, [Bakhsheshi-Rad et al., 2013](#)). It is clear from the results in the literature that coating magnesium and its alloys with MgF_2 , either by immersion in HF or by other methods, improves the corrosion resistance in 3.5 wt% NaCl and simulated body fluid.

The performance of magnesium samples pretreated with HF and postcoated with polymers on SBF is scarce in the literature. In the study of [Conceição et al. \(2012\)](#) it was shown that the performance of AZ31 sheets pretreated with HF and postcoated with PAN was inferior in SBF in comparison to a 3.5 wt% NaCl solution. On the one hand, the lower chloride concentration of the SBF makes it less aggressive to the metal, but on the other hand, it produces a lower osmotic pressure. The water at the polymer/metal interface experiences a lower osmotic pressure toward the solution in SBF in comparison to 3.5 wt% NaCl solution, and therefore, the water can more easily diffuse through the coating. [Figure 1.4](#) compares these samples after

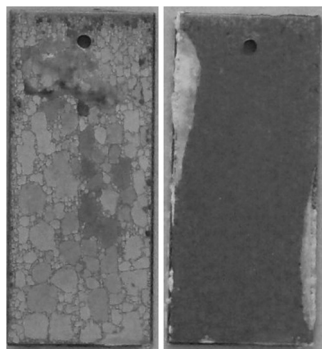


Figure 1.4 Image of AZ31 sheets coated with PAN (thickness of $8\ \mu\text{m}$), pretreated with 14 mol/L HF (room temperature and 24 h) after one week of immersion in SBF (left) and 3.5wt% NaCl. The test in SBF was performed at $37\ ^\circ\text{C}$ while in the other solution the test was performed at $25\ ^\circ\text{C}$.

immersion tests, where it can be seen that the more intense corrosion attack took place in the SBF. Besides the effect of osmotic pressure, the higher temperature of the test performed in SBF also played an important role in the sample performance.

The literature also reports the biocompatibility of MgF_2 coated magnesium samples *in vitro*. Tests of cytotoxicity, hemolysis, and antibiofilm properties are usually performed to investigate the interaction of the fluoride coating in the presence of cells and biological molecules. Experiments of cell adhesion generally show that magnesium fluoride coating significantly decreases cytotoxicity in comparison to the uncoated alloy. For instance, [Li et al. \(2013\)](#) report the adherence of human osteosarcoma cells (MG63) and of mouse osteoblast-like cells (MC3T3-E1) on Mg-1Ca alloy coated and uncoated with MgF_2 (0.9 μm of thickness) during 72 h of culture. It was observed that the coated samples had many more cells adhered to their surface than the uncoated ones. The few cells present on the uncoated sample were unhealthy, which according to the authors was related to the attack of magnesium hydroxide. As the coated sample had a lower corrosion attack in the culture medium, the cell adhesion was higher. Similar results are reported by [Drynda et al. \(2010\)](#) for smooth muscle cells on Mg-Ca alloys of different compositions. The coatings (thicknesses ranging from 0.5 to 20 μm) provide considerable decrease in corrosion on the cultivation medium, and after 240 h, the cell viability was very high (ranging from 70–90%).

For endothelial cells, however, the MgF_2 coating shows considerable toxicity. In the study of [Drynda et al. \(2010\)](#), the viability for this kind of cell was below 5% for all tested samples. In the study of [Mao et al. \(2013\)](#) on the cytotoxicity of JDBM alloys coated with MgF_2 (1.5 μm of thickness) toward endothelial cells, it was observed that the coating decreased the cell viability in comparison to uncoated samples. Nevertheless, according to the authors, the performance of both coated and uncoated samples was compatible to the requirements for cell application. In this study it is also shown that MgF_2 -coated JDBM has a high hemolysis rate on blood tests, which is a measure of how the implant reacts with blood constituents. The obtained rate is way above the maximum required for biological applications (10.1% when the required rate is 5%).

Another important requirement for a biomedical implant is its antibiofilm properties. Here, “biofilm” refers to bacterial communities on a self-made polymer matrix. According to studies in the literature, the occurrence of biofilm is responsible for many cases of infections on the implanted area ([Costerton, Stewart, & Greenberg, 1999](#); [Darouiche, 2004](#)). As these films are usually resistant to antibiotics, a coating on biomedical implants must possess good antibiofilm properties. [Lellouche et al. \(2009, 2012\)](#) report an interesting result on the effect of MgF_2 nanoparticles on *Escherichia coli* and *Staphylococcus aureus* growth. It was shown that the nanoparticles effectively hindered the bacteria proliferation on coated glass substrates. According to the authors, the bacteria-killing property was related to the ability of the nano-sized MgF_2 particles to penetrate the bacteria. In the study of [Mao et al. \(2013\)](#), it is shown that MgF_2 coatings also have good antiplatelet properties.

1.3.3 Corrosion *in vivo*

While the literature shows different studies on the corrosion performance of MgF₂-coated magnesium samples *in vitro*, only a few studies report tests *in vivo*. However, such tests are of great relevance considering the dynamic nature of biological environments, which may induce corrosion processes very distinct from those observed *in vitro*. Besides the problem of early implant failure, the corrosion of magnesium implants presents two main problems: hydrogen production and alkalization. A too high hydrogen production may cause subcutaneous cavities with potential postoperative inflammation. The surface alkalization of the implant, as mentioned above, may damage the cells neighboring the implant, causing different adverse effects (Virtanen, 2011).

Most of these studies on MgF₂-coated magnesium implants *in vivo* perform implantation in rabbit bones (femur and tibiae) with a focus on orthopedic applications. Only one study reported a subcutaneous implantation in mice, considering the potential of application as stents. All of these studies show that the coating could effectively decrease the corrosion rate without significant adverse effects. For instance, Sun et al. (2013) investigated the performance of Mg-3Zn-0.8Zr rods, coated with MgF₂ (0.5 μm of thickness), implanted in the femur of white rabbits. Uncoated samples and samples coated with calcium phosphates were used for comparison purposes. Gas cavities were not observed in any case; however, after 3 months of implantation, the sample coated with MgF₂ showed much lower corrosion attack and volume loss (see Figure 1.5). Further, the MgF₂-coated alloy had more cells adhered to it after 3 months, in comparison to the other samples. Micro-computed tomography indicated that the fluoride-coated surface enhanced new bone growth, and that the bone trabecula formed on the surface of the fluoride-coated alloy was in much better condition in comparison to the control groups. No adverse effect of alloy and MgF₂ degradation was observed.

Similar observations were made by Witte et al. (2010) and Thomann et al. (2009) for the alloys LAE442 and MgCa0.8 implanted in the femur and tibiae of white rabbits, respectively. In the study of Witte et al. (2010), no blood alterations were detected in the follow-up analysis. However, some irritation was observed and attributed to the dissolution of MgF₂. According to the authors, this might be related to the very high thickness of the applied coating (150–200 μm). The coating considerably increased the corrosion protection. In the study of Thomann et al. (2009), very similar results were obtained in regard to corrosion rate and biocompatibility. Nevertheless, the authors mentioned that the coated magnesium alloy had lower mechanical properties during the implantation time, compared to other studies in the literature. The positive influence of MgF₂ in *in vivo* tests was also reported by Drynda, Seibt, Hassel, Bach, and Peuster (2013) on the study of MgF₂-coated magnesium alloys subcutaneously implanted in mice.

These results show that the use of HF treatment is an effective way of increasing corrosion resistance of magnesium alloy implants in biological environments. In all cases, superior corrosion resistance was observed for MgF₂-coated samples with only a few adverse effects. However, more investigations are required to assure that

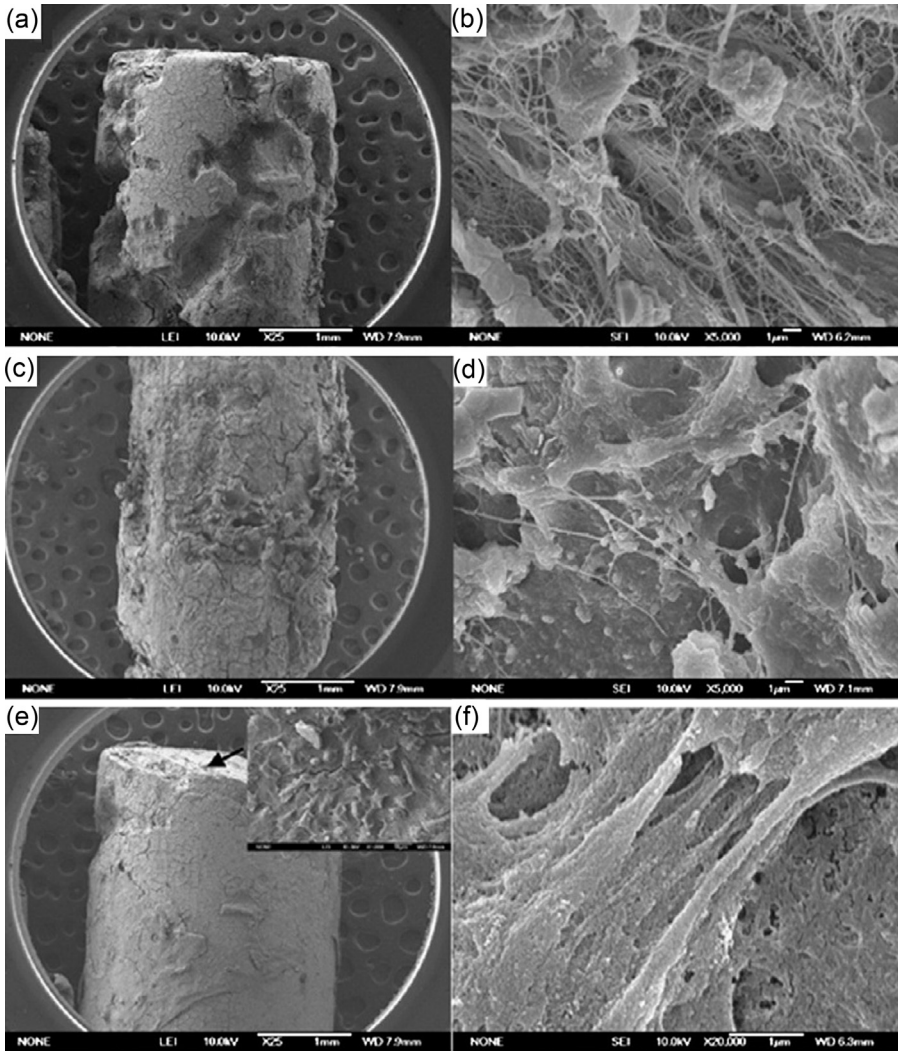


Figure 1.5 Images of untreated (a, b), phosphate coated (c, d), and MgF_2 coated (e, f) implants of the alloy Mg-3Zn-0.8Zr after 3 months of implantation in white rabbits. Reprinted with permission from [Sun et al. \(2013\)](#).

this process is safe for human application. For instance, the investigation of the behavior *in vivo* of magnesium biomedical screws and stents, coated with MgF_2 , is of particular interest, since these formats are more likely to be implanted than cylinders (most of the *in vivo* studies used cylinders for the implant). More clinical investigations are also required to further increase the understanding of host response in contact with MgF_2 -coated magnesium implants.

1.4 Conclusions and future trends

The preparation of MgF_2 coating on magnesium and magnesium alloys is an effective way of improving corrosion resistance in regular saline solutions, simulated body fluids, and *in vivo*. The most effective method for preparing thick (and consequently more protective) MgF_2 coating is by converting Mg(OH)_2 into MgF_2 by previously preparing the Mg(OH)_2 layer. This method also makes use of HF, which is a toxic chemical. The preparation of MgF_2 coating without HF needs further research to achieve similar corrosion protection properties. The synthesis of nano-sized MgF_2 particles by microwave irradiation of a mixture of magnesium acetate and 1-butyl-3-methylimidazolium tetrafluoroborate is an interesting method in this regard, but the corrosion protection it renders needs investigation. The short-term instability of the MgF_2 layer in chlorine solutions needs to be clarified in order to improve performance. Nevertheless, tests performed *in vivo* indicate that, with a proper alloy choice, the MgF_2 coating provides enough corrosion protection, inhibiting gas cavities formation and inflammation related to pH increase. Further tests *in vivo* are required to assure the safeness of the process, especially with biomedical screws and stent implants.

References

- Bakhsheshi-Rad, H., Idris, M. H., Kadir, M. R. A., & Daroonpavar, M. (2013). Effect of fluoride treatment on corrosion behavior of Mg–Ca binary alloy for implant application. *Transaction of Nonferrous Metals Society*, 23, 699–710.
- Berglundh, T., Abrahamsson, I., Albouy, J. P., & Lindhe, J. (2007). Bone healing at implants with a fluoride-modified surface: an experimental study in dogs. *Clinical Oral Implants Research*, 18, 147–152.
- Booster, J. L., Sandwijk, V., & Reuter, M. A. (2003). Conversion of magnesium fluoride to magnesium hydroxide. *Minerals Engineering*, 16, 273–281.
- Carboneras, M., Garcia-Alonso, M. C., & Escudero, M. L. (2011). Biodegradation kinetics of modified magnesium-based materials in cell culture medium. *Corrosion Science*, 53, 1433–1439.
- Chiu, K. Y., Wong, M. H., Cheng, F. T., & Man, H. C. (2007). Characterization and corrosion studies of fluoride conversion coating on degradable Mg implants. *Surface and Coatings Technology*, 202, 590–598.
- Conceição, T. F., Scharnagl, N., Blawert, C., Dietzel, W., & Kainer, K. U. (2010). Surface modification of magnesium alloy AZ31 by hydrofluoric acid treatment and its effect on the corrosion behavior. *Thin Solid Films*, 518, 5209–5218.
- Conceição, T. F., Scharnagl, N., Dietzel, W., & Kainer, K. U. (2011a). Corrosion protection of magnesium AZ31 alloy using poly(ether imide) [PEI]coatings prepared by the dip coating method: influence of solvent and substrate pre-treatment. *Corrosion Science*, 53, 338–346.
- Conceição, T. F., Scharnagl, N., Dietzel, W., & Kainer, K. U. (2012). Controlled degradation of a magnesium alloy in simulated body fluid using hydrofluoric acid treatment followed by polyacrylonitrile coating. *Corrosion Science*, 62, 83–89.

- Conceição, T. F., Scharnagl, N., Höche, D., Dietzel, W., & Kainer, K. U. (2011b). Study on the interface of PVDF coatings and HF-treated AZ31 magnesium alloy: determination of interfacial interactions and reactions with self-healing properties. *Corrosion Science*, 53, 712–719.
- Costerton, J. W., Stewart, P. S., & Greenberg, E. P. (1999). Bacterial biofilms: a common cause of persistent infections. *Science*, 284, 1318–1322.
- Cowan, K. G., & Harrison, J. A. (1979). The dissolution of magnesium in Cl^- and F^- containing aqueous solutions. *Electrochimica Acta*, 24, 301–308.
- Darouiche, R. O. (2004). Treatment of infections associated with surgical implants. *The New England Journal of Medicine*, 350, 1422–1429.
- Drynda, A., Hassel, T., Hoehn, R., Pery, A., Bach, F., & Peuster, M. (2010). Development and biocompatibility of a novel corrodible fluoride-coated magnesium-calcium alloy with improved degradation kinetics and adequate mechanical properties for cardiovascular applications. *Journal of Biomedical Materials Research Part A*, 93A, 763–775.
- Drynda, A., Seibt, J., Hassel, T., Bach, F., & Peuster, M. (2013). Biocompatibility of fluoride-coated magnesium-calcium alloys with optimized degradation kinetics in a subcutaneous mouse model. *Journal of Biomedical Materials Research Part A*, 101A, 33–43.
- Gray, J. E., & Luan, B. (2002). Protective coatings on magnesium and its alloys — a critical review. *Journal of Alloys and Compounds*, 336, 88–113.
- Gulbrandsen, E., Taftø, J., & Olsen, A. (1993). The passive behavior of Mg in alkaline fluoride solutions. Electrochemical and electron microscopical investigations. *Corrosion Science*, 9, 1423–1440.
- Hornberger, H., Virtanen, S., & Boccaccini, A. R. (2012). Biomedical coatings on magnesium alloys — a review. *Acta Biomaterialia*, 8, 2442–2455.
- Jian-Zhong, L., Jiu-gui, H., Yan-wen, T., & Chang-sheng, L. (2009). Corrosion action and passivation mechanism of magnesium alloy in fluoride solution. *Transactions of Nonferrous Metals Society*, 19, 50–54.
- Kokubo, T., & Takadama, H. (2006). How useful is SBF in predicting in vivo bone bioactivity? *Biomaterials*, 27, 2907–2915.
- Lellouche, J., Friedman, A., Lelouche, J., Gedanken, A., & Banin, E. (2012). Improved antibacterial and antibiofilm activity of magnesium fluoride nanoparticles obtained by water-based ultrasound chemistry. *Nanomedicine: Nanotechnology*, 8, 702–711.
- Lellouche, J., Kahana, E., Elias, S., Gedanken, A., & Banin, E. (2009). Antibiofilm activity of nanosized magnesium fluoride. *Biomaterials*, 30, 5969–5978.
- Li, N., Li, Y. D., Wang, Y. B., Li, M., Cheng, Y., Wu, Y. H., et al. (2013). Corrosion resistance and cytotoxicity of a MgF_2 coating on biomedical Mg–1Ca alloy via vacuum evaporation deposition method. *Surface and Interface Analysis*, 45, 1217–1222.
- Li, Q., Zhong, X., Hu, J., & Kang, W. (2008). Preparation and corrosion resistance studies of zirconia coating on fluorinated AZ91D magnesium alloy. *Progress in Organic Coatings*, 63, 222–227.
- Liu, F., Shan, D., Song, Y., & Han, E. H. (2011). Effect of additives on the properties of plasma electrolytic oxidation coatings formed on AM50 magnesium alloy in electrolytes containing K_2ZrF_6 . *Surface and Coatings Technology*, 206, 455–463.
- Ma, Y., Li, N., Li, D., Zhang, M., & Huang, X. (2013). A two-step surface treatment, combining fluoride pretreatment and anodic electrophoresis deposition of waterborne acrylic resin, for Mg–Li–Al–Ce alloy. *Materials Letters*, 90, 11–13.
- Mao, L., Yuan, G., Niu, J., Zong, Y., & Ding, W. (2013). In vitro degradation behavior and biocompatibility of Mg–Nd–Zn–Zr alloy by hydrofluoric acid treatment. *Materials Science and Engineering: C*, 33, 242–250.

- Mu, W., & Han, Y. (2008). Characterization and properties of the $\text{MgF}_2/\text{ZrO}_2$ composite coatings on magnesium prepared by micro-arc oxidation. *Surface and Coatings Technology*, 202, 4278–4284.
- Perales, F., Herrero, J. M., Jaque, D., & Heras, C. (2007). Improvement of MgF_2 thin coating films for laser applications. *Optical Materials*, 29, 783–787.
- Pereda, M. D., Alonso, C., Burgos-Asperilla, L., del Valle, J. A., Ruano, O. A., Perez, P., et al. (2010). Corrosion inhibition of powder metallurgy Mg by fluoride treatments. *Acta Biomaterialia*, 6, 1772–1782.
- Prescott, H. A., Li, Z., Kemnitz, E., Deutsch, J., & Lieske, H. (2005). New magnesium oxide fluorides with hydroxy groups as catalysts for Michael additions. *Journal of Materials Chemistry*, 2005(15), 4616–4628.
- Song, G. L., & Atrons, A. (1999). Corrosion mechanisms of magnesium alloys. *Advanced Engineering Materials*, 1, 11–33.
- Sun, J., Wang, J., Jiang, H., Chen, M., Bi, Y., & Liu, D. (2013). In vivo comparative property study of the bioactivity of coated $\text{Mg}-3\text{Zn}-0.8\text{Zr}$ alloy. *Materials Science and Engineering: C*, 33, 3263–3272.
- Thomann, M., Krause, C., Angrisani, A., Bormann, D., Hassel, T., Windhagen, H., et al. (2009). Influence of a magnesium-fluoride coating of magnesium-based implants (MgCa0.8) on degradation in a rabbit model. *Journal of Biomedical Materials Research Part A*, 93, 1609–1619.
- Verdier, S., Laak, N., Delalande, S., Metson, J., & Dalard, F. (2004). The surface reactivity of a magnesium–aluminium alloy in acidic fluoride solutions studied by electrochemical techniques and XPS. *Applied Surface Science*, 235, 513–524.
- Virtanen, S. (2011). Biodegradable Mg and Mg alloys: corrosion and biocompatibility. *Materials Science and Engineering: B*, 176, 1600–1608.
- Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., et al. (1982). The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C1 C2 organic substances in SI units. *Journal of Physical and Chemical Reference Data*, 11(Suppl. 2), 2-260–2-266.
- Witte, F. (2010). The history of biodegradable magnesium implants: a review. *Acta Biomaterialia*, 6, 1680–1692.
- Witte, F., Fischer, J., Nellesen, J., Vogt, C., Vogt, J., Donath, T., et al. (2010). In vivo corrosion and corrosion protection of magnesium alloy LAE442. *Acta Biomaterialia*, 6, 1792–1799.
- Wu, L., Dong, J., & Ke, W. (2013). Potentiostatic deposition process of fluoride conversion film on AZ31 magnesium alloy in 0.1 M KF solution. *Electrochimica Acta*, 105, 554–559.
- Xin-kuan, L., Liu, Z., Liu, P., Xiang, Y., Ku, W., & Ding, W. (2010). Properties of fluoride film and its effect on electroless nickel deposition on magnesium alloys. *Transactions of Nonferrous Metals Society*, 20, 2185–2191.
- Yan, T., Tan, L., Xiong, D., Liu, X., Zhang, B., & Yang, K. (2010). Fluoride treatment and in vitro corrosion behavior of an AZ31B magnesium alloy. *Materials Science and Engineering: C*, 30, 740–748.

Phosphate treatment of magnesium alloy implants for biomedical applications

2

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2.1 Introduction

Recently, magnesium and magnesium alloys have attracted much attention as potential biodegradable bone implant materials (Witte et al., 2006, 2005; Xu, Yu, Zhang, Pan, & Yang, 2007) and stent materials (Erbel et al., 2007) due to their biodegradability in bio-environment and their excellent mechanical properties such as high strength and an elastic modulus close to that of bone (Staiger, Pietak, Huadmai, & Dias, 2006). More details on the biodegradable magnesium and magnesium alloys have been reviewed elsewhere (Witte, 2010; Zheng, Gu, & Witte, 2014). One of the big problems for the clinical application is their fast corrosion or degradation rate in chloride-containing solutions including human body fluid or blood plasma (Song, 2007; Staiger et al., 2006).

There are several methods that have the potential to reduce the degradation rate or to improve the corrosion resistance of magnesium alloy in a biological environment:

- 1. Purification of alloy.** Copper, iron, and nickel are the most harmful impurities in magnesium alloys in that they greatly reduce the corrosion resistance. It was reported that Cu element adversely affects the corrosion resistance of magnesium alloy if present in quantities exceeding 0.05 wt% (Avedesian & Baker, 1999). Iron and nickel also greatly reduce the corrosion resistance when they exceed the upper limit of 0.005 wt% (Avedesian & Baker, 1999).
- 2. Element alloying.** Manganese and zinc are two alloying elements that can improve the corrosion resistance of Mg-Al and Mg-Al-Zn alloys by removing iron and other heavy metal elements into relatively harmless intermetallic compound and overcoming the harmful corrosion effect of iron and nickel impurities, respectively (Avedesian & Baker, 1999). In the ASM system, magnesium-manganese (MA1A alloy) is the only alloy developed for corrosion resistance (Avedesian & Baker, 1999). In recent years, many alloy systems have been developed for biomedical applications. In our previous studies, Mn and Zn were selected as alloying elements to develop Mg-Mn-Zn alloys due to the good biocompatibility of Mn and Zn (Yin, Zhang, & Zeng, 2008; Zhang, Yin, Xu, Yang, & Yang, 2009). The addition of Mn and Zn improves both the mechanical properties and the corrosion resistance of magnesium alloys. It has been shown that the corrosion resistance of Mg-1.0 Mn-1.0 Zn alloy in simulated body fluid (SBF) is slightly better than that of WE43 alloy (containing 3.78 wt.% Y,

2.13 wt.% Nd, and 0.46 wt.% Zr), which is one of the best commercially available magnesium alloys (Xu, Zhang, Yin, & Yang, 2008). Zhang, Zhang, et al. (2010) developed an Mg-Zn alloy that was reported to exhibit good comprehensive properties. Calcium is another element to be chosen to produce a binary Mg-Ca alloy (Kim, Kim, Lee, & Seok, 2008; Li, Gu, Lou, & Zheng, 2008; Wan et al., 2008) and Ca-containing AZ91 magnesium alloy (AZ91Ca) (Kannan & Raman, 2008) for bone implants due to the beneficial effect of Ca ion on bone growth. It was shown that the addition of Ca increased the corrosion resistance of AZ91 alloy (Kannan & Raman, 2008). Results on binary Mg-Ca alloys indicated that an Mg-Ca binary alloy with 0.6–1.0 wt.% Ca provides good overall mechanical properties and corrosion resistance (Li et al., 2008; Wan et al., 2008). Further increase in the Ca content would lead to deterioration in the mechanical properties and corrosion resistance (Vojtech, Elova, & Volenec, 2006). However, addition of Zn in Mg-Ca alloy can significantly improve the corrosion resistance of Mg-Ca alloy (Zhang & Yang, 2008). In other research, rare earth (RE) elements were selected to develop RE-containing alloys, such as Y (Xu, Liu, Xu, & Han, 2006; Zainal Abidin, Atrens, Martin, & Atrens, 2011; Zhang, He, Du, & Yang, 2008), Nd (Mao et al., 2012; Zhang, Wang, Yuan, & Xue, 2012; Zhang, Yuan, et al., 2012; Zong et al., 2012), and Gd (Huang, Kato, Chen, Wang, & Yuan, 2012; Huang, Yuan, Chu, & Ding, 2013; Zhang et al., 2013). Although it has been reported that the corrosion resistance of magnesium alloys has been improved by element alloying to some degree, the corrosion rate is still high.

3. **Surface treatment.** Besides element alloying, another effective method for improving the corrosion resistance of magnesium and magnesium alloy is surface treatment. In commercial application, many technologies have been developed, such as chromate conversion coating. Not all of these coating technologies can be used directly for biomedical applications. For example, chromate conversion coating cannot be used due to the toxicity of chromate ion. During past years, much research has been carried out to find out a proper coating technology, including Al coating (Chiu, Chen, & Yang, 2005; Chiu et al., 2003) and Ti coating (Zhang, Xu, & Yang, 2005). Although metal coating or some ceramic coatings such as TiN, CrN, and AlN can protect magnesium substrate from fast corrosion, they cannot improve the surface bioactivity of the substrate. Bioactive coatings such as various calcium-phosphate compounds (Ca-P) are of importance for modifying the surface of implanted devices and have been successfully applied to the surface modification of Ti and its alloys in order to promote direct attachment of the surrounding hard tissue and to suppress the release of corrosion products into the human body. Therefore, phosphate coating has been widely studied worldwide due to the consideration of good biocompatibility of phosphates to bone tissue. Other surface-modification methods have also been investigated in detail for possible application in biomedical magnesium.

In this chapter, we focus on phosphating treatment of magnesium alloys for biomedical application, including the phosphating process, the anticorrosion property of the coated magnesium, the *in vitro* cell adhesion, and *in vivo* bone response.

2.2 Degradation of magnesium and magnesium alloys

Degradation of magnesium or magnesium alloys in a biological environment is actually a corrosion process of magnesium or magnesium alloys in a Cl^- -containing

aqueous solution. Magnesium is a reactive element. When magnesium contacts or is immersed in water, the following reaction will happen on the surface of magnesium:



As a result, magnesium dissolves into the solution and hydrogen gas is released from the solution. Meanwhile, the pH value of the solution is raised due to the accumulation of hydroxyl (OH^{-}) ions. Also, a reaction between Mg^{2+} ion and OH^{-} happens on the surface to form $\text{Mg}(\text{OH})_2$. $\text{Mg}(\text{OH})_2$ has relatively low solubility in aqueous solution; therefore $\text{Mg}(\text{OH})_2$ will precipitate on the surface of magnesium. This is the main reason why magnesium dissolves fast at the beginning and then more slowly with increased immersion duration.

The formation of $\text{Mg}(\text{OH})_2$ precipitate on the surface forms a covering layer. Although the covering layer is porous, the existence of this covering layer can protect magnesium alloy from fast dissolution or degradation. However, the biological environment is a Cl^{-} ion-rich solution, which contains normally 0.9 wt% NaCl. Cl^{-} has a potential to react with $\text{Mg}(\text{OH})_2$ to form MgCl_2 , which is dissolvable in aqueous solution. This reaction removes the $\text{Mg}(\text{OH})_2$ protective layer from the surface of magnesium and accelerates the degradation of magnesium. Therefore, magnesium and its alloys show a faster degradation rate in a biological environment than in a normal aqueous solution:



Magnesium alloy is designed to be an absorbable bone implant material or stent material. For bone implant application, the bone healing duration is about one year or longer. Therefore, it is desired that the bone implant provides strong support during the first 3 months and then it gradually degrades in volume and strength in the following healing process. For stent application, it is desired that the stent can give enough support to the blood vessel for up to 6 months. So far, available magnesium and magnesium alloys as well as newly developed magnesium alloys all show a high degradation rate in a biological environment.

Fast degradation of magnesium implants may result in the following problems:

- 1. Early loss of mechanical properties of magnesium implants.** This will be a serious problem for both bone implants and stents. The unexpected early loss of mechanical properties, especially strength, will cause the deformation of the fixed bone for bone implant applications. For stent applications, the early loss of the mechanical properties might result in the complete damage of the stent, which might lead to thrombus or stenosis.
- 2. Hydrogen bubbles.** In several *in vivo* studies, gas bubbles have been clearly observed at the implantation site of magnesium bone implants. It was considered to be due to the fast

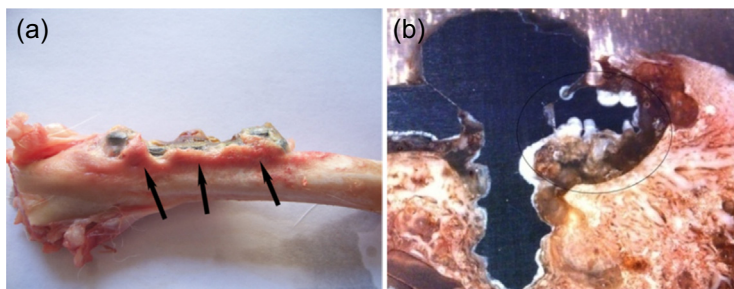


Figure 2.1 Bone absorption after 4 weeks of implantation of magnesium screw and plate. New bone tissue is observed around the magnesium implant, as indicated by the arrows in [Figure 2.1\(a\)](#). The circle in [Figure 2.1\(b\)](#) shows where bone absorption happened around the magnesium implant.

degradation of magnesium implants. Although no bad results caused by the gas bubbles have been reported so far, there is no good effect on the bone healing process. For stents, no gas bubbles were reported or detected due to the fast blood circulation.

3. **Bone absorption.** *In vitro* and *in vivo* studies have proven that magnesium and magnesium alloys actually show good bone response. It is thought that the degradation of magnesium will increase the pH value in the surrounding environment (micro-environment), which accelerates the deposition of calcium phosphate. [Figure 2.1](#) shows the appearance of a magnesium alloy plate and screws after 4 weeks of implantation. New bone tissues were clearly found around the plate, as shown in [Figure 2.1\(a\)](#), but bone absorption was also found somewhere, as shown in [Figure 2.1\(b\)](#). The bone absorption is considered to be due to increasing in pH value in the micro-environment.
4. **Hemolysis.** It has been reported that degradation of some magnesium alloys can cause serious hemolysis, for example, a hemolysis rate of 35–60% for pure magnesium ([Gao, Qiao, Li, & Wang, 2006](#)), 41.4% for AZ31, 69% for Mg-Mn-Zn alloy, and 9.27% for WE43 alloy ([Ye, Xi, Zheng, Wang, & Li, 2013](#)). All these values are much higher than the recommended value of 5% by Standard 10,992. The fast degradation of magnesium and magnesium alloy normally results in a high pH value, as high as 11, and high metal ion concentrations. Therefore, it is possible that the high hemolysis rate is caused by the high metal ion concentrations or the high pH value. In order to resolve this problem, we investigated the effects of metal ion concentration and the pH value on hemolysis rate. [Table 2.1](#) lists the hemolysis rate with different metal ion concentrations. In these experiments, pH values were adjusted to 7.4. It was assumed that up to 2000 mg/L Mg ion was released from magnesium alloys and magnesium alloys contain 9 wt% Al, 6 wt% Zn, 2 wt% Mn, 4 wt% Y, and 5 wt% Ca. It can be found that the hemolysis rates keep at a very low value, much lower than the recommended value when metal ion concentrations change in the research range. These results indicate that high metal ion release due to the degradation of magnesium alloys does not cause hemolysis in the blood system.

[Figure 2.2](#) shows the effect of pH value on the hemolysis rate. It can be found that the hemolysis rate increases with the increase of pH value. When pH value is less than a critical value, 10.3 here, the hemolysis rate is less than the recommended value of 5%. With the consideration of the influence of metal ion concentration, it can be

Table 2.1 Influence of metal ion concentration on the hemolysis rate

Ions	Concentration (mg/L)	Hemolysis (%)	Ions	Concentration (mg/L)	Hemolysis (%)
Mg ²⁺	46.4	0	Zn ²⁺	2.7	0
	66.4	0		3.9	0
	86.4	0		5.1	0
	106.4	0.81		6.3	0
	186.4	0		11.1	0.91
	2000	0.25		121.5	0
Ca ²⁺	54.6	0	Mn ²⁺	0.4	0.37
	55.6	0		0.8	0.61
	56.6	0		1.2	1.5
	57.6	0		1.6	0.24
	61.6	0		3.2	0
	153.6	0.62		40	0.86
Y ³⁺	0.8	0	Al ³⁺	1.8	0
	1.6	0		3.6	0.12
	2.4	0		5.4	0.12
	3.2	0		7.2	0
	6.4	0		14.4	0
	80	1.1		180	0

concluded that hemolysis caused by the degradation of magnesium is mainly attributed to the increase in pH rather than the increase in the metal ion concentration.

2.3 Basic requirement of surface modification

The preceding section clearly indicates that the fast degradation of magnesium implants will bring damage to the human body. So it is necessary to reduce the degradation of magnesium by some measurements. To develop new alloys by element alloying is one of the possible methods. So far, magnesium with different purity and magnesium alloys with different elements have been investigated in detail to assess the degradation rate, including commercial high-purity alloys, such as AZ91, AZ31, and WE43, and new alloys systems, such as binary magnesium alloys Mg-Mn, Mg-Zn (Gao, Wu, Qiao, & Wang, 2008; Zhang, Zhang, et al., 2010), Mg-RE and ternary magnesium alloys, Mn-Mn-Zn (He, Zhang, & Yang, 2010; Zhang et al., 2009), Mg-Zn-Ca

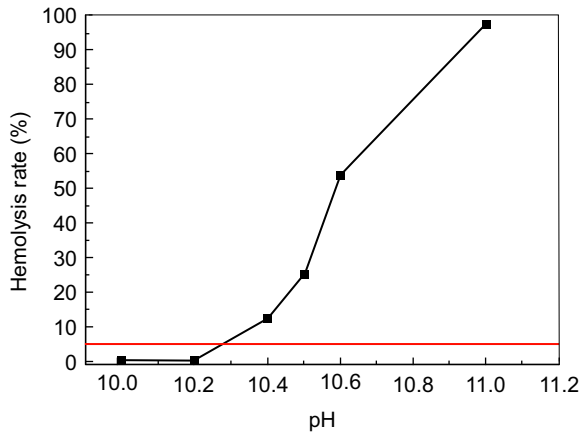


Figure 2.2 Effect of pH value on the hemolysis rate. When the pH value is larger than a critical value, 10.3 here, the hemolysis rate is larger than the recommended value of 5%, indicating that the pH value plays a main role in the hemolysis of magnesium and magnesium alloys.

(Gu et al., 2010; Li et al., 2011; Tong et al., 2009; Wang, Guan, Wang, Ren, & Wang, 2010), and Mg-Si-Zn(Ca) (Zhang, Wei, Yang, Xu, & Song, 2010). However, the research results demonstrate that high purity and element alloying cannot give enough protection against the aggressive attack of the biological environment.

An effective way to protect magnesium alloys from fast degradation or reduce the degradation rate is surface treatment. In commercial applications, many types of conversion coatings are applied to Mg alloy substrates, including chromate, phosphate/phosphate-manganese (Liu, Sun, Mao, & Wang, 2012), stannate, fluoride, RE, Mg, Al hydrotalcite, ionic liquid, molten salt, vanadium, stearic acid, etc. But each case has its own disadvantages. Chromate, fluoride, and vanadium-based coatings still have toxicity concerns, which might bring damage to the human body. The biocompatibility of the surface coating has to be considered in the selection of possible surface treatment technology. In addition, the surface treatment should reduce the degradation rate but also provide good cell and bone tissue response. From this point of view, the surface treatment is named “surface biomodification.”

For biomedical application, the surface modification of magnesium and magnesium alloys has to meet the following requirements:

- 1. To be nontoxic.** Nontoxicity is a basic requirement for the surface biomodification. Ion released from the surface coating might bring harm to the cell, surrounding tissue, blood circulation system, immune system, reproductive system, and heredity. Metal allergy is also a serious problem. For example, nickel ion causes skin disease.
- 2. To provide low degradation rate.** The main target of the surface biomodification is to adjust the degradation rate of magnesium alloy to an acceptable range, not to stop the degradation. The compatibility between the degradation of magnesium implant and the healing process is always desired. It is suggested that the biomodified or coated magnesium or magnesium alloys degrade at a very low rate at the beginning of the healing process in order to provide enough support. When the fixed tissue or the repaired tissue recovers its function, the magnesium should degrade at a relatively high rate in order to match the tissue healing process.

This process will be dependent on the biological application environment and the healing process of tissue. However, no one can give a recommended degradation rate of magnesium alloy *in vitro* and *in vivo*.

3. **To be degradable or absorbable.** Magnesium is designed as a biodegradable implant material; therefore the surface biomodification layer or coating has to be biodegradable or absorbable.
4. **To be biocompatible.** To be nontoxic is a basic requirement for surface biomodification not only for magnesium alloys but also for other biomaterials. In order to play a good biofunction, the surface layer or the surface coating of the implant should exhibit bioactivity so that the cells can easily adhere to and spread over the surface, which will speed up the healing process. By careful selection of the surface chemical composition, surface physical topology, or even surface electronic properties, the surface biomodification really can promote the tissue healing process.

Based on the above considerations, a number of surface treatments have been developed, such as hydroxyapatite (HA) coating prepared in aqueous solution (Tomoza, Hiromoto, & Harada, 2010), calcium phosphate/chitosan composite coating (Zhang, Dai, Wei, & Wen, 2012), biphasic calcium phosphate coating by micro-arc oxidation (MAO) (Pan, Chen, Wang, & Lin, 2013; Seyfoori, Mirdamadi, Seyedraoufi, Khavandi, & Aliofkhazraei, 2013), calcium phosphate by a biomimetic approach (Hu, Wang, Ren, Zhang, & Liu, 2010; Yanovska, Kuznetsov, Stanislavov, Danilchenko, & Sukhodub, 2012; Zhang & Yang, 2005) or electrodeposition (Song, Shan, & Han, 2008), magnesium hydroxide by hydrothermal technique (Gupta, Mensah-Darkwa, & Kumar, 2014), MgO/MgAl₂O₄ composite coating by plasma electrolytic oxidation (PEO) (Bala Srinivasan et al., 2010; Lv et al., 2011; Sreekanth, Rameshbabu, & Venkateswarlu, 2012), MgO/calcium phosphate composite coating by MAO followed by hydrothermal treatment (Chang, Tian, Liu, & Duan, 2013), magnesium hydroxide and magnesium phosphate compound coating by a chemical conversion and steam curing (Janning et al., 2010), and MgO coating by MAO with the help of supersonics. These coatings protect magnesium and magnesium alloy from fast degradation and also provide surface bioactivity.

2.4 Basic phosphating process

The main mineral component of human bone is calcium-deficient carbonate hydroxyapatite. Calcium phosphate coatings show an advantage in improving the biocompatibility of metallic implants and increasing bone growth at the site of implantation (Keim, Brunner, Fabry, & Virtanen, 2010).

Phosphating treatment is widely used as a pretreatment for metal painting. It can significantly reduce the corrosion rate of metal and metal alloys, including iron and aluminum alloys. Recently, magnesium alloys have been commercially used in the automobile industry and military industry. However, the fast corrosion rate of magnesium alloys resists the application. Therefore, the prevention of the corrosion of magnesium becomes a serious problem and attracts much attention worldwide. As an effective method, phosphating treatment can provide good protection against aqueous

solution corrosion (Li, Lian, Niu, Jiang, & Jiang, 2006). According to the chemical composition of the phosphating bath, the phosphating can be divided into zinc phosphate (Li et al., 2006), barium phosphate (Chen et al., 2010), etc.

Normally, a phosphating treatment is a kind of conversion coating technology, during which a substance, magnesium alloy here, is immersed in a phosphating bath that contains several phosphates and other additives if necessary. Then, several chemical reactions happen at the surface of the substance. As a result, a preset phosphate coating is deposited on the surface.

Here, we take $M_3(PO_4)_2$ as an example to describe the basic phosphating process. M represents a kind of metal ion. In a phosphating bath, dihydric phosphate is a main precursor in the phosphating bath. $M(H_2PO_4)_2$ can dissolve in water but has a potential to decompose into $MHPO_4$ and H_3PO_4 according to the reaction (2.5) depending on the bath condition, such as temperature and pH value, as well as the concentration of the chemical in the reaction (2.5). Then, $MHPO_4$ decomposes further into $M_3(PO_4)_2$ and H_3PO_4 according to the reaction (2.6). Also, $M(H_2PO_4)_2$ can decompose directly into $M_3(PO_4)_2$ and H_3PO_4 according to the reaction (2.7):



where $MHPO_4$ and $M_3(PO_4)_2$ both have low solubility in the aqueous solution or are even insoluble.

When Mg and Mg alloy are immersed into the solution, magnesium will react with H_3PO_4 according to the following reaction:



As a result, hydrogen gas bubbles will be released on the surface of magnesium sample. The reaction (2.8) consumes the reaction product H_3PO_4 (2.5–2.7), which forms more and more phosphates according to reactions (2.5–2.7), such as $MHPO_4$ and $M_3(PO_4)_2$. Thus, these phosphate products deposit on the surface of a magnesium sample as a phosphating film. In commercial application, zinc phosphate, iron phosphate, manganese phosphate, and their mixture have been widely used as the phosphating film.

From the above reactions, it can be concluded that the fast consumption of H_3PO_4 or release of H_2 will accelerate the reaction (2.8) and then accelerate the reactions (2.5–2.7), in turn speeding up the deposition of phosphating film.

All the phosphating compositions are essentially dilute phosphoric acid-based solutions containing alkali metal/heavy metal ions besides suitable accelerators (Narayanan, 2005). Based on the nature of the metal ion constituting the major component of the phosphating solution, these compositions are classified as zinc, manganese, and iron phosphating baths.

The process of phosphating involves a consistent depletion of bath constituents. In order to obtain a satisfactory phosphate coating, the following bath parameters have to be strictly controlled within the optimum limits, including (Narayanan, 2005): (1) the free acid value (FA), which refers to the free H^+ ions present in the phosphating solution; (2) total acid value (TA), which represents the total phosphate content of the phosphating solution; (3) the ratio of FA to TA, expressed as the acid coefficient; (4) accelerator content; and (5) other metallic and nonmetallic constituents present.

The reactions that happen on the surface of the magnesium sample and in the bath are very complex, and there are many factors that affect the final phosphating process. The next sections list several factors that play very important roles in the process.

2.4.1 pH value

Release of H_2 leads to increasing the pH value, which further promotes the precipitation of insoluble phosphates and thus speeds up the formation of phosphating film. It was reported that when pH value was higher than 2.5, some white sludge deposits were formed on the surface of phosphate coating (Niu, Jiang, Li, Gu, & Lian, 2006). A high pH value will result in a fast precipitation of insoluble phosphates. The imbalance between the low deposition rate and the fast precipitation rate of the phosphates will result in the formation of white sludge. Therefore, it was recommended that pH should be between 1.8 and 2.5 during the phosphating process in order to get a phosphating coating with good quality. Therefore, pH value has to be controlled in order to obtain good surface coating. In practice, some acids are used to adjust the pH value. For example, tartaric acid was used to adjust the pH value and reduce the production of sludge by combining with HPO_4^{2-} to form a soluble compound to stabilize the bath (Niu et al., 2006).

2.4.2 Anticorrosion agent

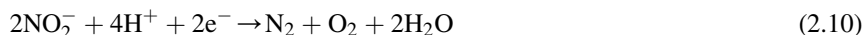
Magnesium and magnesium alloy are very reactive metal materials. Although the reaction between magnesium alloy and phosphoric acid in the bath will consume phosphoric acid and in turn accelerate the reactions (2.5–2.7) or the deposition of phosphate film according to the above reactions, no phosphating film will be formed on the surface when the reaction rate of the reaction (2.4) is faster than the depositing rates. Therefore, in practice, some agents are added into the bath to resist the reaction between magnesium substance and the solution, such as sodium fluoride, a mixture of sodium fluoride and organic amine (NaF: organic amine = 9:1 in weight) (Niu et al., 2006). For example, fluoride activation of magnesium alloy in an HF solution is generally used before phosphating treatment. The formation of MgF film on the surface can restrain the corrosion of the magnesium matrix. In some experiments, organic amine was also used with sodium fluoride to resist the corrosion of the magnesium matrix (Niu et al., 2006). Niu et al. (2006) reported the effect of the anticorrosion agent on the phosphating quality and found that the content should be at least 1.5 g/L.

2.4.3 Accelerator

In practice, phosphating reaction tends to be slow, owing to the polarization caused by the hydrogen evolved in the cathodic reaction. In order to promote the formation process, some acceleration methods have to be employed. Recently, Sankara Narayanan (Narayanan, 2005) has made an overview on the acceleration of the phosphating process. The different means of accelerating the formation of phosphate coatings can be broadly classified as (1) chemical acceleration, (2) mechanical acceleration, and (3) electrochemical acceleration. Magnetic fields were also used to promote the phosphating process (Bikulčius, Burokas, Martušlė, & Matulionis, 2003; Yanovska et al., 2012; Zhao, Li, He, Xie, & Fu, 2013). It was reported that magnetic fields can promote the generation of small hydrogen gas bubbles and accelerate their desorption (Zhao et al., 2013).

In the chemical acceleration, an oxidant, organic chemical compound, ethanolamine (Li et al., 2010), and heavy metal were used, in which oxidizing substances are the most important chemical accelerators. Oxidizing agents depolarize the cathode half-cell reaction by preventing the accumulation of hydrogen at the cathodic sites (Narayanan, 2005). The most commonly employed oxidizing accelerators are nitrites, chlorates, nitrates, peroxides, sulfate, and organic nitro-compounds either alone or in various combinations (Amini & Sarabi, 2011). Common combinations are nitrite-nitrate, nitrite-chlorate-nitrate, and chlorate-nitrobenzene sulphonic acid.

A mixture of nitrate and nitrite has been proven to be an effective accelerator. In a phosphating bath, nitrate and nitrite react with hydrogen ion. The reactions are (Niu et al., 2006):



These two reactions consume H^+ rapidly, and as a result, the local pH at the metal–solution interface can be increased quickly and facilitate the precipitation of insoluble phosphate.

Niu et al. (2006) investigated the influence of nitrite, nitrate, and a mixture of nitrite and nitrate (nitrite/nitrate = 5/1 in weight) on the phosphate formation rate. It has been found that the mixture of nitrite and nitrate accelerates the phosphating process more effectively.

2.5 The formation process of phosphate coating and microstructure evaluation

2.5.1 Formation process of phosphate coating

In order to reveal the formation process of a phosphate coating on magnesium alloy, Mg-Mn-Zn alloy was taken as an example. The phosphating bath constitutes 6–8 mL/L

phosphoric acid, 7.92 g/L $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, 1.55 g/L $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, 1–3 g/L NaNO_3 , and 2–5 g/L NaNO_2 .

Figure 2.3 shows the open current potential (OCP) curve of Mg-Mn-Zn alloy in the phosphating bath recorded by an electrochemical tester. From this OCP curve, the phosphating process can be roughly divided into four stages: (2.1) the dissolving of magnesium on the surface (from A to B in the curve), (2.2) the fast formation of a phosphating layer on the surface (from B to C), (2.3) the formation of the phosphate layer (from C to D), and (2.4) the stable growth of the phosphate (from D to E).

The First Stage (from A to B in the curve). In this stage, the potential moves suddenly to a more negative direction, corresponding to the dissolving of magnesium on the surface. When a magnesium sample is immersed into a phosphating bath, reactions immediately happen on the surface. As a result, magnesium dissolves in the phosphating solution. This stage should be controlled as short as possible by oxidant additive in the bath. Figure 2.4 shows the change in the surface morphology and the chemical composition before and after 10 s phosphating treatment. Almost no difference can be found in the surface morphology and the chemical composition before and after the phosphating, indicating the dissolving of magnesium was controlled at a very low level by the phosphating system. However, in another study on the zinc phosphating processing of AM63, this stage was not observed (Kouisni, Azzi, Dalard, & Maximovitch, 2005; Kouisni, Azzi, Zertoubi, Dalard, & Maximovitch, 2004).

The Second Stage (from B to C in the curve). In this stage, as shown in Figure 2.3, the potential rapidly moves toward a more noble direction, corresponding to a fast formation of a phosphate layer. Normally, this stage lasts several minutes to tens of minutes dependent on the phosphating system. Figure 2.5 shows the surface morphology and Energy Dispersive Spectrometer (EDS) analyses result after

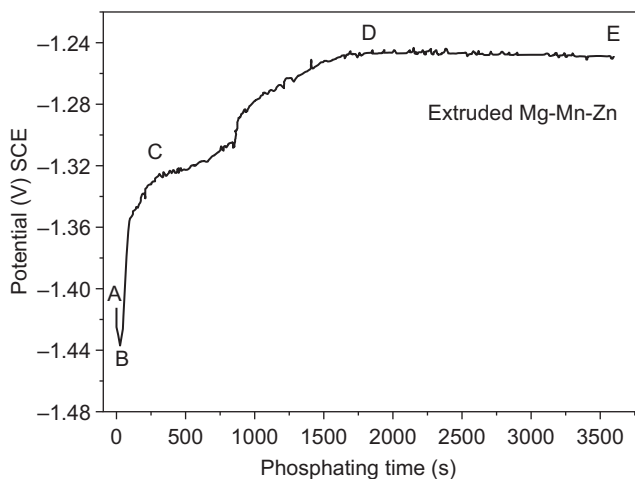


Figure 2.3 OCP curve for the phosphate conversion coating on Mg-Mn-Zn alloy recorded by an electrochemical working station. The whole phosphating process can be roughly divided into four stages. OCP, open current potential.

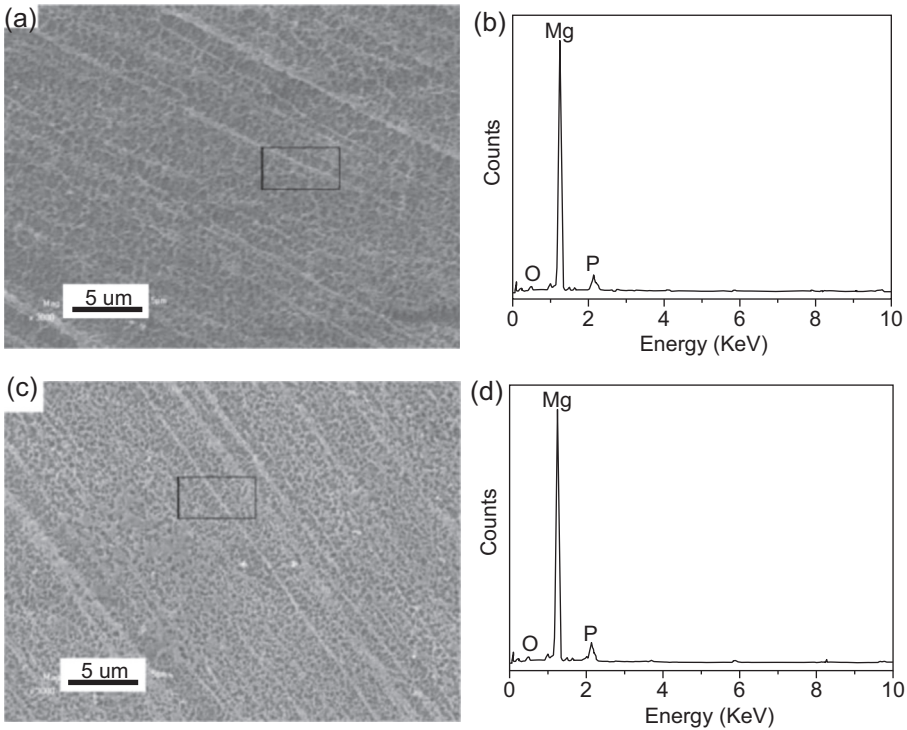


Figure 2.4 Surface morphology and EDS analysis of Mg-Mn-Zn alloy after acid washing and phosphating treated for 10 s. (a) Surface morphology after acid activation. (b) EDS spectrum of the framed area in (a). (c) Surface morphology after phosphating treatment for 10 s. (d) EDS spectrum of the framed area in (c).

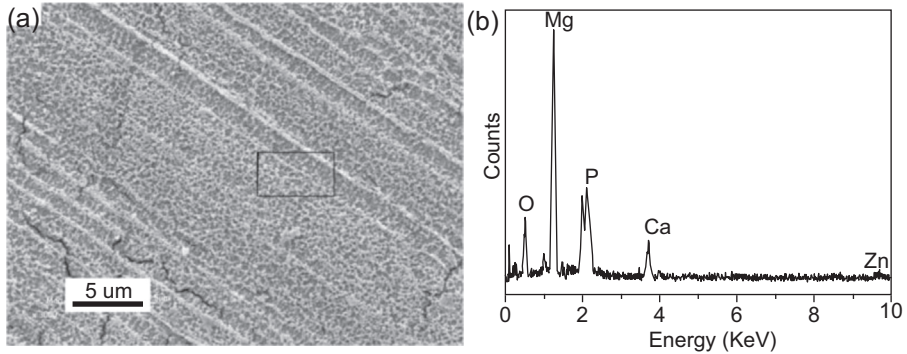


Figure 2.5 Surface morphology and EDS analysis of the extruded Mg-Mn-Zn alloy after immersion in phosphate-treating solution for 3 min. (a) Surface morphology. (b) EDS spectrum of the framed area in (a).

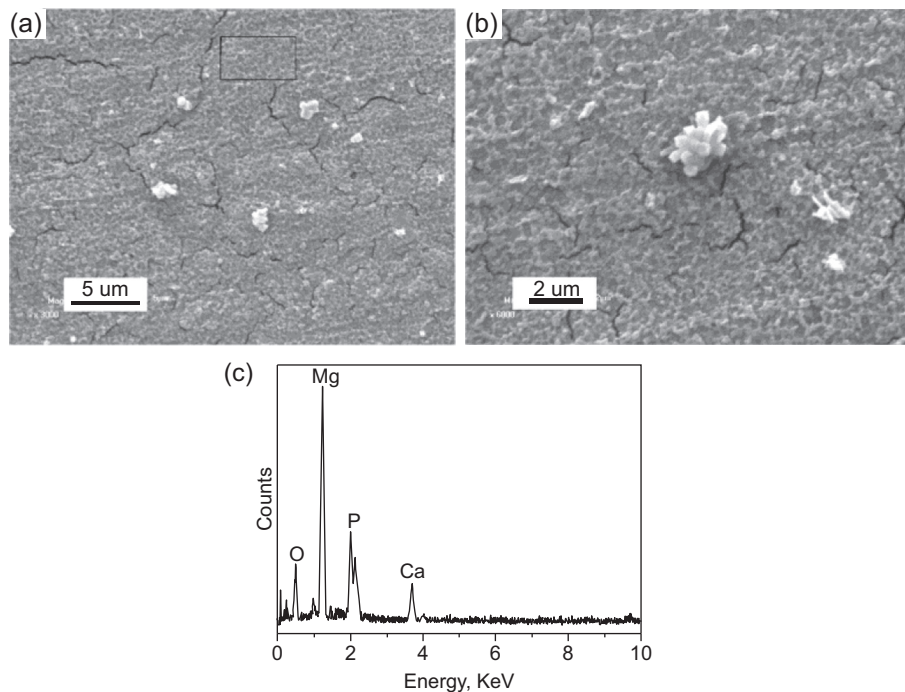


Figure 2.6 Surface morphology and EDS analysis of extruded Mg-Mn-Zn alloy after immersion in phosphate-treating solution for 5 min. (a) Surface morphology. (b) Morphology of particle. (c) EDS spectrum of the framed area in (a).

phosphating for 3 min. A fine network structure was observed on the surface. EDS results proved that a phosphate film was formed on the surface. After 5 min of treatment, the surface was covered by a relatively dense layer, as shown in Figure 2.6(a). Several small particles were found on the surface, as shown in Figure 2.6(b). EDS in Figure 2.6(c) also confirms the formation of phosphate. At the end of this stage, the magnesium sample was covered by a phosphate film. Kouisni et al. (2005) reported that two types of particles were observed, light and dark, on the surface of magnesium after 30 s immersion in a zinc phosphating bath. After 2 min only dark particles were visible, and after 5 min immersion the phosphate coating covered about 90% of the surface. The dark and compact phosphating layer was considered to be the growth site of the following crystal phosphate (Kouisni et al., 2005). In our study, only a few light particles were observed on the surface.

The Third Stage (from C to D in the curve). In this stage, the potential increases much more slowly with the increase of phosphating duration in comparison with that in the second stage. After the second stage, the magnesium sample has been completely covered by a compact phosphate layer. The reaction between magnesium substrate and the bath solution was reduced by the formation of the phosphate layer. Further deposition of phosphate has to nucleate and grow on the surface of the phosphate layer. As shown in Figure 2.7, lots of phosphate particles were found on the

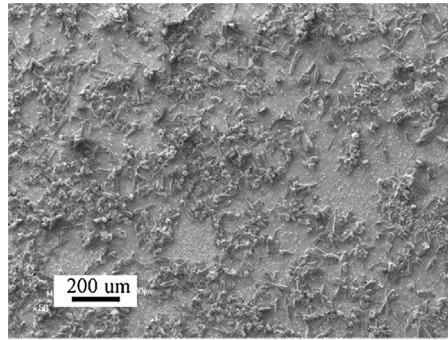


Figure 2.7 Surface morphology of the extruded Mg-Mn-Zn alloy after immersion in phosphate-treating solution for 7 min.

surface of magnesium alloy after phosphating treatment for 7 min. This stage was also reported in other studies ([Kouisni et al., 2005](#)).

The Fourth Stage (from D to E in the curve). In this stage, the potential changes very slowly with the treatment time, corresponding to a stable growth of phosphate on the substrate. [Figure 2.8](#) shows the surface morphologies of the phosphate coating after phosphating treatment for 10 min to 50 min. The magnesium sample was covered by a

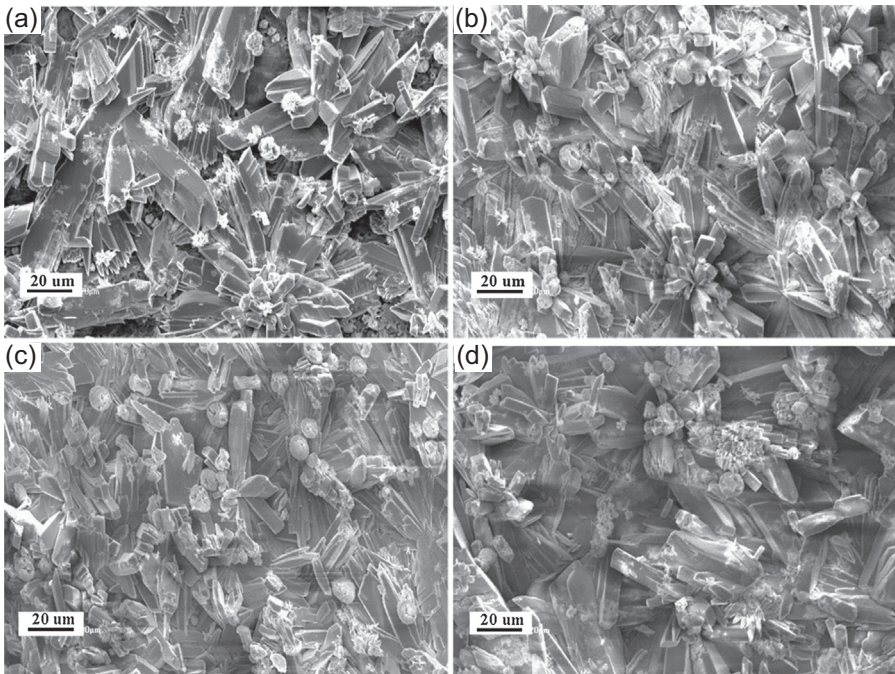


Figure 2.8 Scanning electron microscope (SEM) surface morphologies of the Mg-Mn-Zn alloy after phosphating treatment for different durations. (a) 10 min. (b) 20 min. (c) 30 min. (d) 50 min.

rough layer with a regular and prismatic shape crystal. Nearly no difference can be found in the surface morphology between the samples treated for 10–50 min, indicating that the growth rate is very low at this stage. Small-angle X-ray diffraction (SAXD) results indicate that the phosphate is brushite.

2.5.2 Surface microstructure and composition

The phosphating coating can be roughly divided into two layers depending on the processing parameters (Chen et al., 2010; Zhang, Huang, Yang, Zhang, & Ai, 2007). The lower layer is a flat and dense amorphous phosphate layer with low roughness, and the top layer is a porous large crystal layer with high roughness (Chen et al., 2010; Li et al., 2010). As shown in Figure 2.6(a), after a short immersion time, a dense and flat phosphating coating was formed on the surface and the extension of phosphating duration results in a porous and rough surface. The two-layer structure coating provides good protection to the substance. But on the other hand, the surface roughness will also influence the cell adhesion and spreading on the surface. Research on hydroxapatite (HAp) formed on magnesium and AZ31 in a solution also reported that the HAp coatings consisted of an inner dense layer and an outer coarse layer (Hiromoto & Tomozawa, 2011). The inner layer was composed of dome-shape precipitates densely packed and the outer layer was composed of rod-like crystals growing from each dome in the radial direction.

It is possible to change the surface morphology by further treatment. Kannan (2012) reported that the surface morphology of the calcium phosphate coating was changed from a loosely packed and grain-like surface structure to a flat and compact surface by using a pulse-potential method instead of constant potential. This closely packed morphology exhibited ~3 times higher polarization resistance and 65% lower corrosion current than the loosely packed structure.

The two-layer structure displays different characteristics. Besides the difference in the chemical composition and structure, the adhesive strength is also different. Chen's results on barium phosphate coating on AZ31 (Chen et al., 2010) indicated that the adhesion strength between the top layer and the lower layer (0.94 MPa) was lower than the value between the lower layer and the substrate (1.45 MPa), but the two-layer structure provided a higher corrosion resistance than the lower-layer coating.

2.6 Anticorrosion resistance

2.6.1 Electrochemical test

Nearly all available papers on phosphating coating on magnesium alloy report that the phosphating treatment improved the anticorrosion resistance of magnesium alloy not only in a biological environment (Ye et al., 2013) but also other solutions (Kouisni et al., 2005). Results indicate that the phosphating process changes the coating structure and also changes the surface morphology. The coating structure in turn might

alternate the anticorrosion resistance. Figure 2.9 shows typical Tafle curves of phosphated magnesium and magnesium substrate measured in a SBF. From the curves, it can be found that 10 min phosphate treatment moves the curve to a noble direction significantly. Further extension in the phosphate duration moves the curve to a more noble direction. Calculated electrochemical parameters from these curves are summarized in Table 2.2. From these data, it can be clearly demonstrated that the phosphating treatment increases the corrosion potential, reduces the corrosion current density, and increases the corrosion resistance. Also with the increase of the phosphating duration, the corrosion potential becomes more noble, the current density decreases, and the corrosion resistance increases. The best results were obtained after phosphating treatment for 30 min. However, the improvement in the anticorrosion resistance by the extension in the phosphate duration from 10 to 50 min is lower than the improvement caused by the phosphate treatment for 10 min.

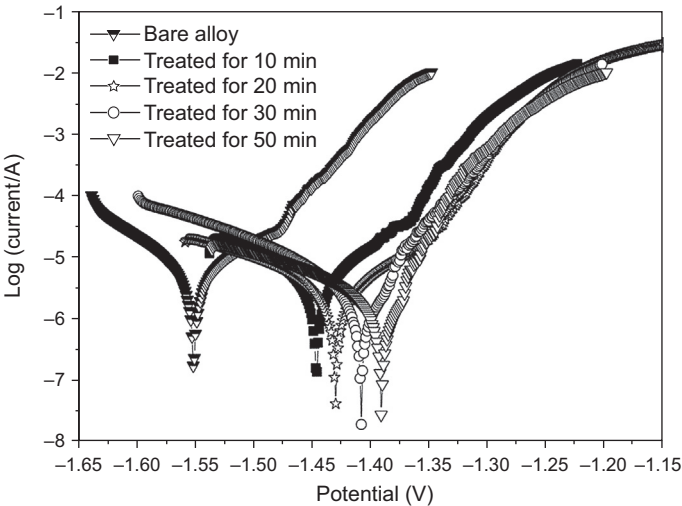


Figure 2.9 Electrochemical polarization curves in SBF solution of magnesium alloy samples with and without phosphating treatment. SBF, simulated body fluid.

Table 2.2 The parameters of the electrochemical polarization tests in SBF solution

Samples	i_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{corr} ($\text{V}_{(\text{SCE})}$)	R_p (Ω)
Bare alloy	6.666	−1.552	2665
Phosphated for 10 min	4.435	−1.446	3812
Phosphated for 20 min	2.960	−1.430	6590
Phosphated for 30 min	1.384	−1.408	7770
Phosphated for 50 min	0.914	−1.391	9975

2.6.2 Immersion test

Electrochemical tests reveal the corrosion behavior of magnesium in a short time. To assess the long-term corrosion properties, the magnesium samples before and after phosphating treatment were also immersed into SBF for several days and the pH values were recorded.

The pH values of the SBF solutions in which the bare and the phosphated magnesium samples were immersed (for 30 min) are shown in [Figure 2.10](#) against the immersion time. For both the bare samples and the phosphated samples, pH values increase with the immersion time. However, the increase of the pH value of the SBF solution containing the phosphated samples is slower than that of the solutions containing the bare samples. After 1 day of immersion, the pH value of the solutions containing the bare samples was about 8.17 while the pH value of the solution containing the phosphated samples was about 7.95. After 2 days, 4 days, and 9 days of immersion, the difference in pH between the solutions containing the phosphated samples and the bare samples was as high as 0.5 unit. The low pH value demonstrates that dissolution or the degradation of the phosphated magnesium is lower than the bare alloy.

2.6.3 Surface morphology

[Figure 2.11](#) shows the surface morphologies of the bare samples after immersion in SBF for different durations. After 1 day of immersion, the surface of the bare sample was covered by a corrosion layer with many cracks on the surface. Some white particles were also deposited on the corroded surface. With the increase of the immersion time, more and more particles were observed. EDS analysis was conducted on the

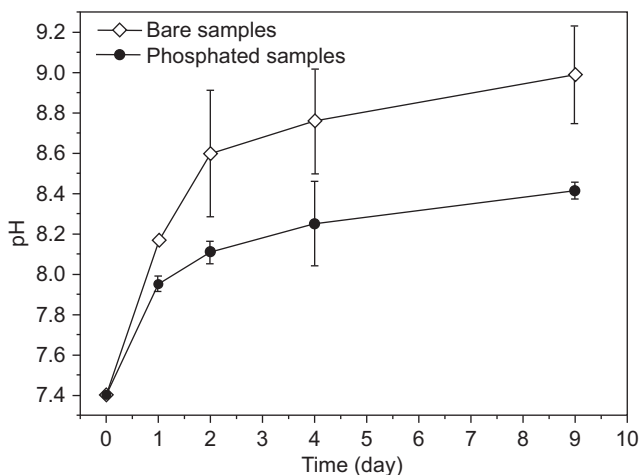


Figure 2.10 Change in the pH value of SBF solutions containing the bare samples and the phosphated samples with the immersion time (Xu, Zhang, & Yang, 2009). SBF, simulated body fluid.

corrosion layer and the particles after 9 days of immersion. The results indicate that both the corrosion product and the deposition particles are mainly composed of O, P, Mg, Ca, and a small amount of Na. The ratios of Ca to P (Ca/P) are less than 0.8, which is much lower than that of HA.

The surface morphologies of the phosphated samples after immersion in SBF solution for different durations are shown in Figure 2.12. After 1 day of immersion, partial brushite crystals lost their sharp edges and corners, as marked by the arrow in Figure 2.12(a), indicating that the brushite crystals on the surface of magnesium substrate began to dissolve in SBF. Also, some white particles were found on the surface. After 2 days of immersion, no obvious difference in the surface morphology was observed by SEM compared to that immersed for 1 day. After 4 days of immersion, more and more brushite crystals were dissolved, as shown in Figure 2.12(c). Nine days later (Figure 2.12(d)), there were cracks on the surface of the sample, displaying the brushite dissolved and became many smaller parts. Meanwhile, more particles were found on the surface. EDS analysis results on the dissolving brushite and the deposited particles disclose that the dissolving brushite layer is mainly composed of P, O, Ca, and a tiny amount of Mg, and the Ca/P ratio is 1.467, close to that of calcium phosphates. The particles deposited on the surface are mainly composed of O, P, Mg, Ca, and Na, and the Ca/P ratio is 1.292. In order to identify the phase transformation of

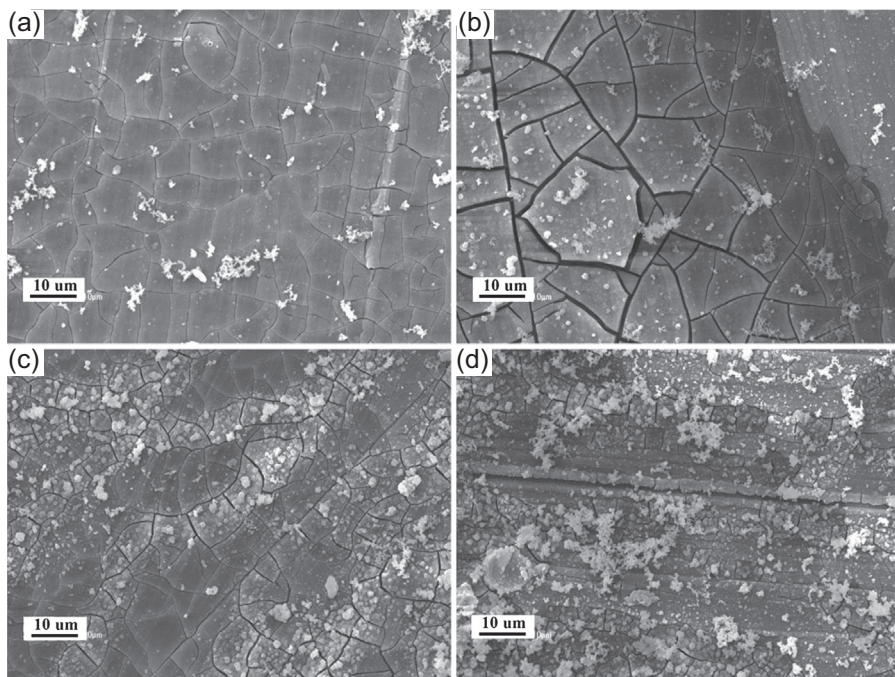


Figure 2.11 Surface morphology of the bare samples immersed in SBF solution for (a) 1 day, (b) 2 days, (c) 4 days, and (d) 9 days (Xu, Zhang, et al., 2009). SBF, simulated body fluid.

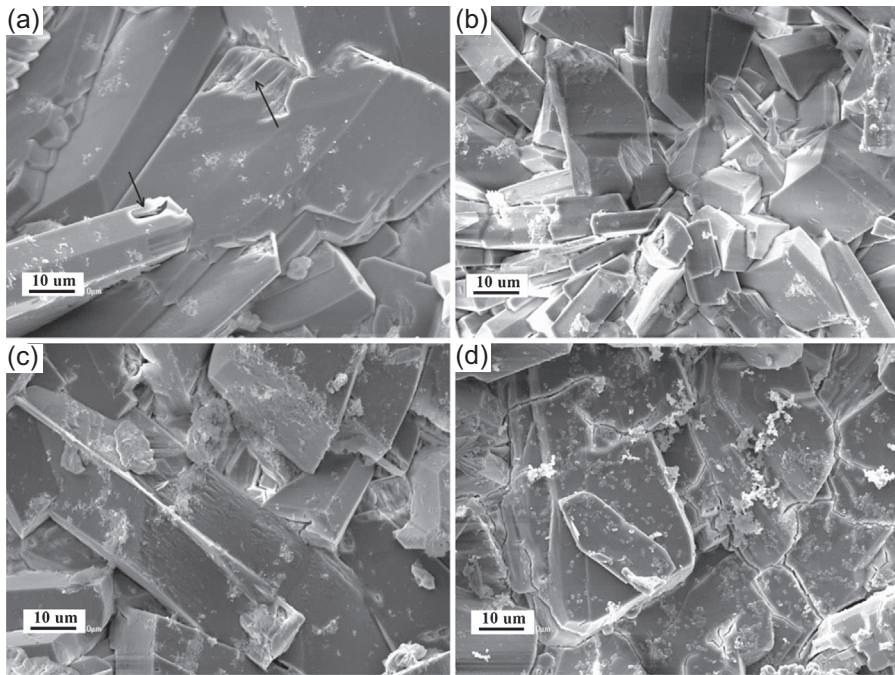


Figure 2.12 Surface morphology of the phosphated samples immersed in SBF solution for (a) 1 day, (b) 2 days, (c) 4 days, and (d) 9 days (Xu, Zhang, et al., 2009). SBF, simulated body fluid.

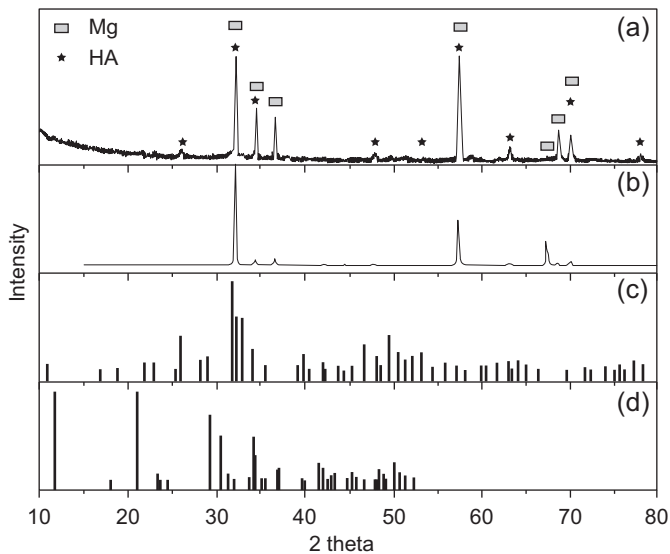


Figure 2.13 X-ray diffraction patterns of the phosphated Mg-Mn-Zn alloy immersed in SBF for 9 days. (a) The phosphated Mg alloy sample, (b) Mg-Mn-Zn substrate, (c) HA (JCPDS09-0432), and (d) brushite (JCPDS09-0077) (Xu, Zhang, et al., 2009). SBF, simulated body fluid.

the brushite layer during the immersion, XRD was conducted on the surface of the phosphate sample after immersion in SBF solution for 9 days, as shown in [Figure 2.13](#). It can be found that HA phase as well as magnesium matrix were detected, but the brushite phase completely disappeared, suggesting that the brushite was transformed to HA during the immersion.

In the research on DCPD coating on magnesium ([Wang, Wei, & Gao, 2009](#)), it was reported that after 3 days of immersion in SBF, the DCPD coating was still intact and completely covered the substrate. DCPD dissolution was observed on the third day and became noticeable on the fifth day, but it did not completely disappear until the end of the experiment. The DCPD phase was not observed by XRD from the seventh day, and no new phases were found in the entire immersion period.

In another study, it was reported that the surface morphology of DCPD changed with the hydrothermal temperature and duration. High temperature and long duration resulted in a dissolution of DCPD and disappearance of the platy structure ([Chang et al., 2013](#)).

2.7 In vitro biocompatibility

The previous section revealed that the surface morphology of the phosphated magnesium changes from a porous but flat surface with Ca and P elements to a rough brushite surface with the extension of the phosphating process. Cell adhesion is influenced by lots of surface properties of a substrate, including the chemical composition, physical topology, and whether it is hydrophilic or hydrophobic. Brushite with a long prismatic shape provides a substrate with strong anticorrosion properties but also a rough surface. However, the rough surface might resist the adhesion.

[Table 2.3](#) lists the toxicity test results by MTT assay on the bare magnesium alloy and the phosphated magnesium alloy. The L929 cell line was used to assess the cytotoxicity. The extract was prepared according to Standard ISO10993-12. Relative

Table 2.3 MTT assay of the bare Mg alloys and the phosphated Mg alloys

Materials	Incubation duration (day)	RGR (%)	Toxicity grade
Extract of bare magnesium	1	87.0	1
	2	99.7	1
	3	109.3	0
Extract of the phosphated magnesium alloy	1	89.6	1
	2	100.8	0
	3	110.4	0

growth rate (RGR) of the cells on the bare magnesium alloys ranges between 87.0 and 109.3%, responding to a toxicity Grade 1. Meanwhile, RGR on the phosphated magnesium alloy is about 89.6–110.4%, similar to that of the bare magnesium alloy. Toxicity of grade one was tested both for the bare magnesium alloy and the phosphate magnesium alloy; however, the toxicity meets the standard requirement, which means that these materials are safe to the L929 cell line.

Another study also reported that the calcium phosphate-coated WE43 alloy showed a cell (L929) viability of 83–96% up to 4 days of incubation while the cell viability on the WE43 substrate was only 25–34.8% (Ye et al., 2013).

These results demonstrate that phosphating treatment can improve the cell toxicity of magnesium alloys. However, the phosphating system has to be selected carefully to avoid side effects.

Cell nontoxicity is a basic requirement for biomaterials. For bone implant, it is also desired that bone cell can adhere to the surface, spread on the surface, and proliferate significantly. The cell adhesion is affected by the surface chemical composition, surface toughness, and surface hydrophilic and hydrophobic properties. Figure 2.14 shows the cell morphologies (L929 cell line) on the bare magnesium alloy, the phosphated magnesium alloy, and cp-Ti titanium as a control sample. Several cells with a nearly round shape were observed on the bare magnesium sample. On the control sample, also only several cells with a round shape were observed on the surface. On the contrary, many cells were observed on the phosphated magnesium sample, and the cells nearly covered the whole sample. In addition, the cells spread out and contacted each other, displaying good living conditions. Even after 3 and 5 days of incubation, there were still only several cells on the surface of the bare magnesium alloy, as shown in Figures 2.15 and 2.16. However, the cells covered the whole surface of the phosphated magnesium and cp-Ti samples after 3 and 5 days of incubation. It is believed that the phosphate group and Ca element on the phosphated magnesium sample greatly contributed to the good cell compatibility.

Figure 2.17 displays the cell number on the samples after 1 day to 5 days culture. At all culture periods, cells on the phosphated magnesium sample show a significantly higher proliferation rate than the bare magnesium alloy ($p < 0.05$).

2.8 *In vivo* investigation

In vivo degradation of magnesium and magnesium alloy is quite different from the *in vitro* behavior. An *in vivo* study on the corrosion resistance of the Ca-P coated AZ60 magnesium alloy indicated that severe degradation of uncoated Mg alloy was observed by micro-CT image 3 months postimplantation (Xiao et al., 2013). The calculated results displayed that the corrosion rate of the Ca-P coated Mg was only one-third of that of the uncoated Mg alloy.

Newly formed osteoid tissue was observed around both the naked Mg alloy implant and the Ca-P coated Mg alloy implant after 4 weeks implantation by fluoroscopic microscopy (Xu, Pan, et al., 2009). Compared with the naked Mg alloy implant, the newly formed osteoid tissue around the phosphated Mg alloy implant was compact

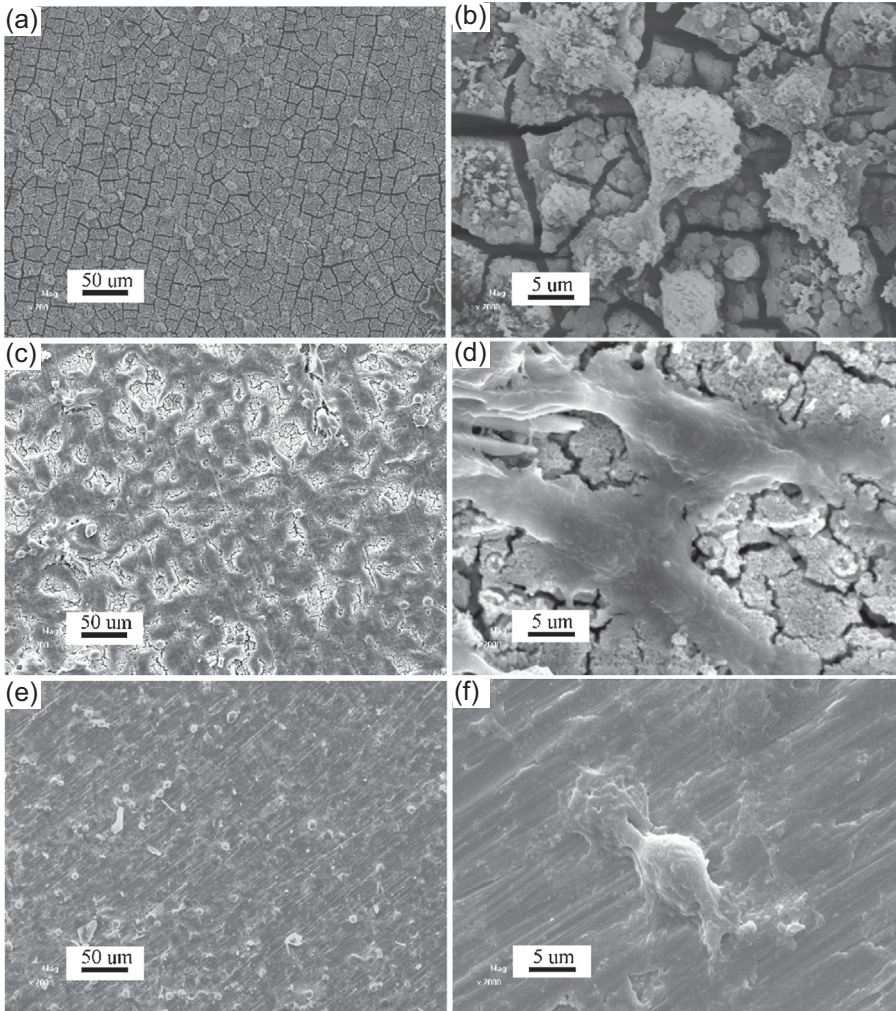


Figure 2.14 L-929 cell morphology after 1 day of incubation on different samples. (Xu, Pan, et al., 2009). (a) and (b) Naked Mg alloy. (c) and (d) Treated Mg alloy. (e) and (f) Pure Ti.

and uniform. In addition, the outline shape of the magnesium implants was slightly changed, indicating that the implants were corroded by the body fluid, or the implant degraded in the body. However, it is hard to distinguish the difference in the degradation between the naked Mg alloy implant and the phosphated Mg alloy implant after 4 weeks implantation because the duration is not long enough to evaluate the *in vivo* degradation.

Figure 2.18 shows the optical HE microstructure of the interfaces between the magnesium implants and new bone 1 to 4 weeks postimplantation. For the naked Mg alloy, lymphocytic infiltration at the interface was observed 1 week postimplantation, as indicated by “L” in Figure 2.18(a). After 2 weeks implantation, there was a

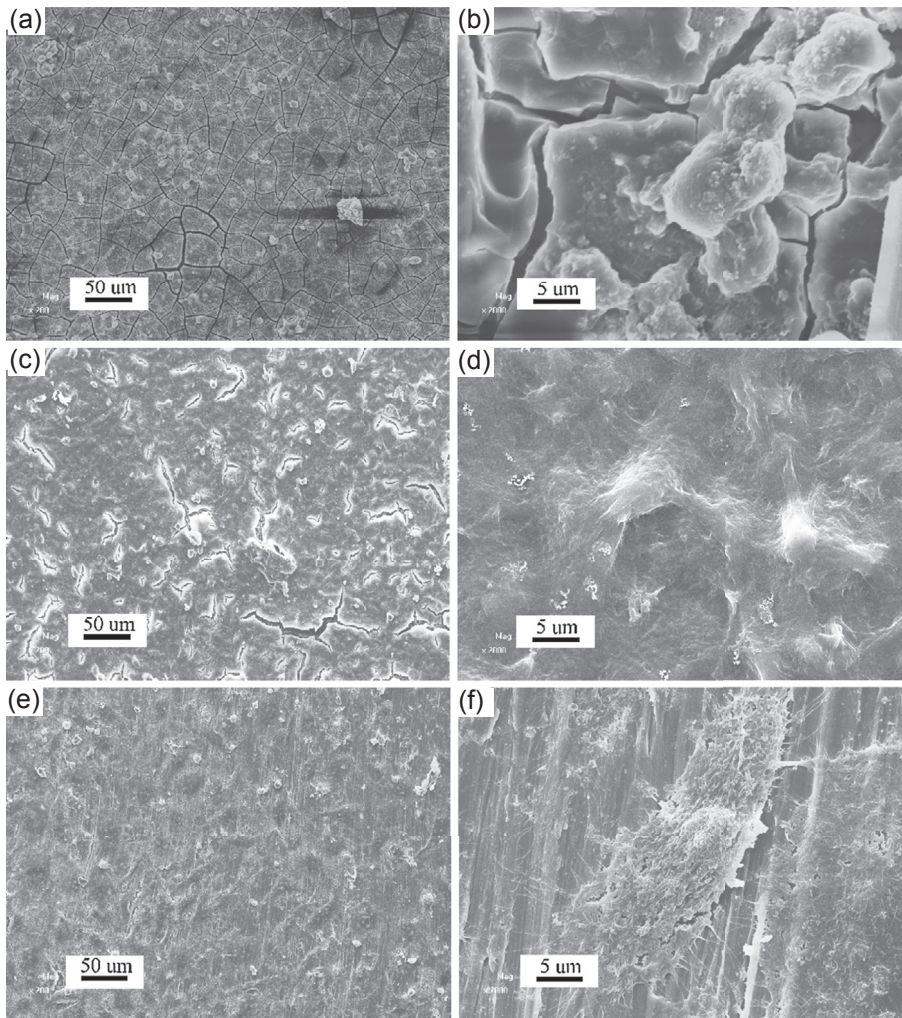


Figure 2.15 L-929 cell morphology after 3 days of incubation on different samples. (Xu, Pan, et al., 2009). (a) and (b) Naked Mg alloy. (c) and (d) Treated Mg alloy. (e) and (f) Pure Ti.

continuous fibroblast band between the implant and the bone, as indicated by “F” in Figure 2.18(b). However, lymphocytic infiltration and plasmablastic infiltration were not noted. Three weeks later, the fibroblast band became thinner, as shown by “F” in Figure 2.18(c), and a small amount of newly formed osteoid tissue was found, as indicated by “N” in Figure 2.18(c). At week 4, the surface of the implant was taken up by newborn bone and bone trabecular, as indicated by “N” in Figure 2.18(d). Crowded osteoblasts and bone matrix were observed. For the Ca-P-coated Mg alloy, connective tissue was seen at the interface 1 week postimplantation, as indicated by “C” in Figure 2.18(e), but lymphocytic infiltration and plasmablastic infiltration

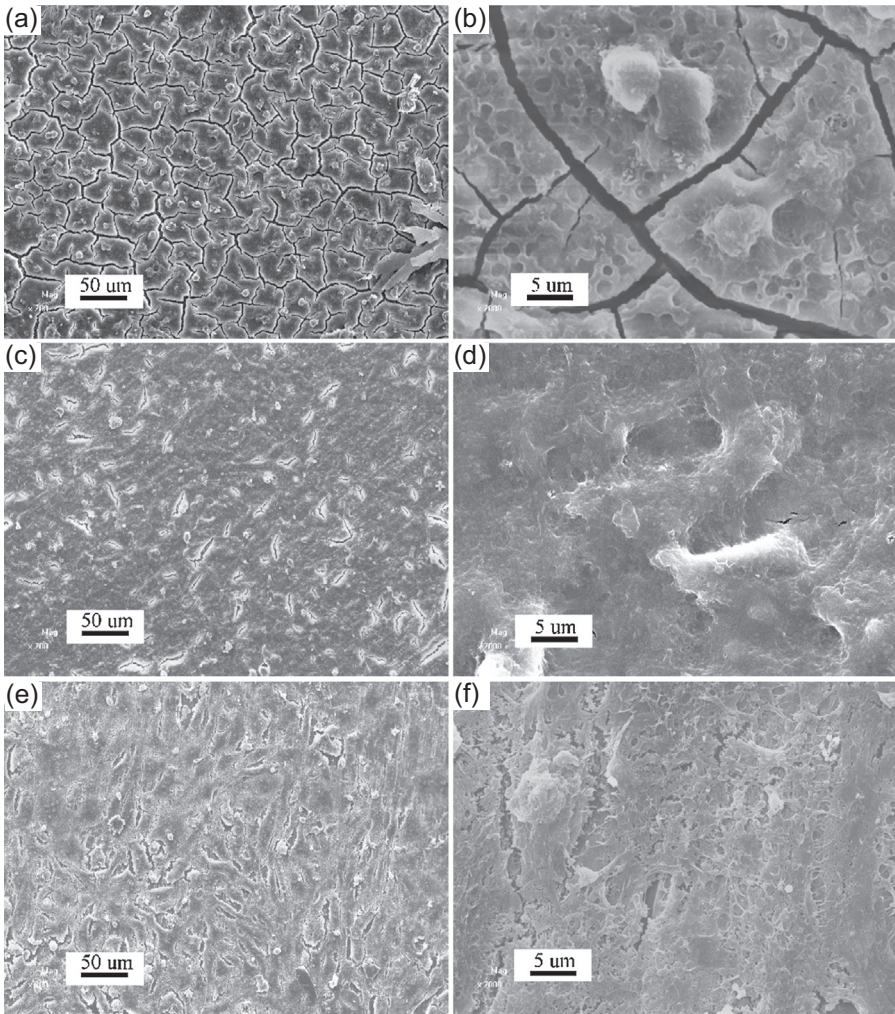


Figure 2.16 L-929 cell morphology after 5 days of incubation on different samples (Xu, Pan, et al., 2009). (a) and (b) Naked Mg alloy. (c) and (d) Treated Mg alloy. (e) and (f) Pure Ti.

were not seen. At week 2, the connective tissue became thinner, and osteoblasts and bone matrix were noted. Newly formed osteoid tissue with embedded osteocyte formed in some areas, as indicated by “N” in Figure 2.18(f). Three weeks later, the connective tissue was replaced by osteoblasts and bone matrix, as indicated by “N” in Figure 2.18(g). Bone trabeculae connected together, but the alignment of the connected bone trabeculae was disorganized.

Four weeks later, more newborn bone was observed, as indicated by “N” in Figure 2.18(h). Osteoid tissue and newborn bone trabeculae almost covered the implant surface completely. Osteoid tissues connected together, and bone trabeculae

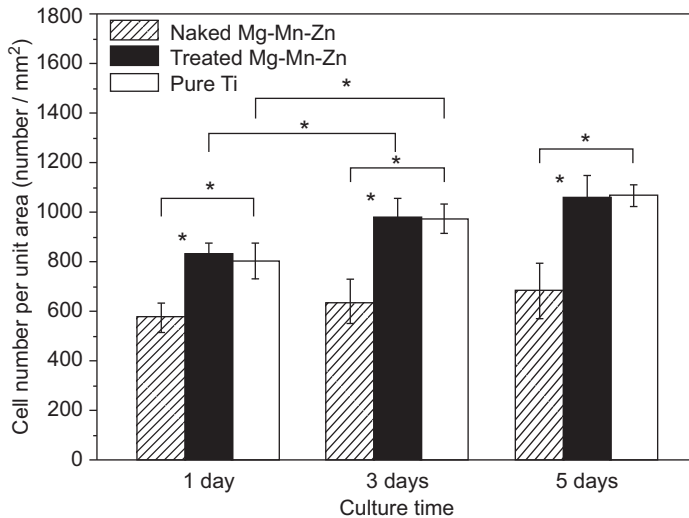


Figure 2.17 Growth of L929 cells versus culturing time. * $p < 0.05$ (Xu, Pan, et al., 2009).

aligned compactly and regularly, in which mature osteocyte was embedded. Ossification was manifest. Table 2.4 summarizes the routine pathological examination results.

Compared with the naked Mg alloy, routine pathological examination analysis results such as no lymphocytic infiltration (inflammation) at week 1, thinner connective tissue and the formation of bone matrix at week 2, more bone matrix and interconnected bone trabecular at week 3, and more newborn bones at week 4, as shown in Figure 2.18, reveal clearly that the phosphated Mg alloy exhibits better surface biocompatibility than the naked alloy during the first 4 weeks postoperation.

BMP-2 expression, TGF- β 1 expression, and PDGF expression were investigated at the implant/bone interface to reveal the effect of the phosphating coating on the bone response at the early stage (Xu, Pan, et al., 2009). As an example, Figure 2.19 shows BMP-2 staining photomicrographs at the interfaces between the implants and bones after different periods of implantation. Figure 2.20 shows the MOD values in the BMP-2 expression at the implant/bone interface after different periods of implantation. At week 1, strong positive activities were observed at the interfaces for both the naked alloy implant group and the phosphate alloy implant group. At week 2, positive activities increased and peaked. At weeks 3 and 4, osteoid tissues were clearly observed at the interface, and the BMP-2 expressions gradually reduced. At all time intervals, the phosphated Mg implant group shows a higher MOD value in the BMP-2 expression than the naked implant. A significant positive activity was found at the first 3 weeks as found for the Ca-P coated implant ($p < 0.05$). Similar results have also been observed in the TGF- β 1 expression and PDGF expression (Xu, Pan, et al., 2009).

The BMP plays crucial roles in normal skeletal development as well as bone healing, and is able to activate transcription of genes involved in cellular migration,

Table 2.4 Summary of the routine pathological examination of the implant/bone interface (Xu, Pan, et al., 2009)

Periods (weeks)	Naked Mg alloy	Ca-P coated Mg alloy
1	Lymphocytic infiltration	Connective tissue No lymphocytic infiltration No plasmablastic infiltration
2	Continuous fibroblast band No lymphocytic infiltration No plasmablastic infiltration	Thinner connective tissue Osteoblasts Newly formed bone matrix Newly formed osteoid with osteocyte
3	Thinner fibroblast band Small amount of newly formed osteoid	No connective tissue Osteoblasts Bone matrix Connecting trabecular
4	New bone Trabecular Osteoblasts	More new bones New bone trabecular aligned compactly and regularly

proliferation, and differentiation. It was reported that endogenous BMP-2 is an indispensable osteogenic stimulus for initiation of fracture healing in mice (Tsuji et al., 2006). In addition, it is believed that TGF- β 1 stimulates osteogenesis, angiogenesis, fibroblast migration, and deposition of matrix (Helm, Dayoub, & Jane, 2001) and has osteoinductive properties (Beck et al., 1993; Noda, 1989; Zhang, Ahmad, & Gronowicz, 2003). PDGF stimulates osteoblast proliferation, collagen synthesis, and may play a regulatory role in fracture repair (Helm et al., 2001). The above immunohistochemical analysis results strongly demonstrated that the phosphate-coated implant provided a high BMP-2 expression during the first 4 weeks postimplantation, and especially statistically significant differences in BMP-2 expression between the phosphate-coated Mg alloy and the naked Mg alloy after 1 week, 2 weeks, and 3 weeks postoperation. The phosphate-coated implant also exhibited a high TGF- β 1 expression during the first 4 weeks postimplantation, and statistically significant differences in the TGF- β 1 expression between the phosphate Mg alloy and the naked Mg alloy after 2 weeks, 3 weeks, and 4 weeks postoperation. Similarly, a statistically significant difference was also observed in PDGF expression between the phosphate Mg alloy and the naked Mg alloy after 1 weeks, 2 weeks, and 4 weeks postoperation. All the above *in vivo* results demonstrated significantly good osteoconductivity of the phosphate Mg alloy at the early osseous integration stage.

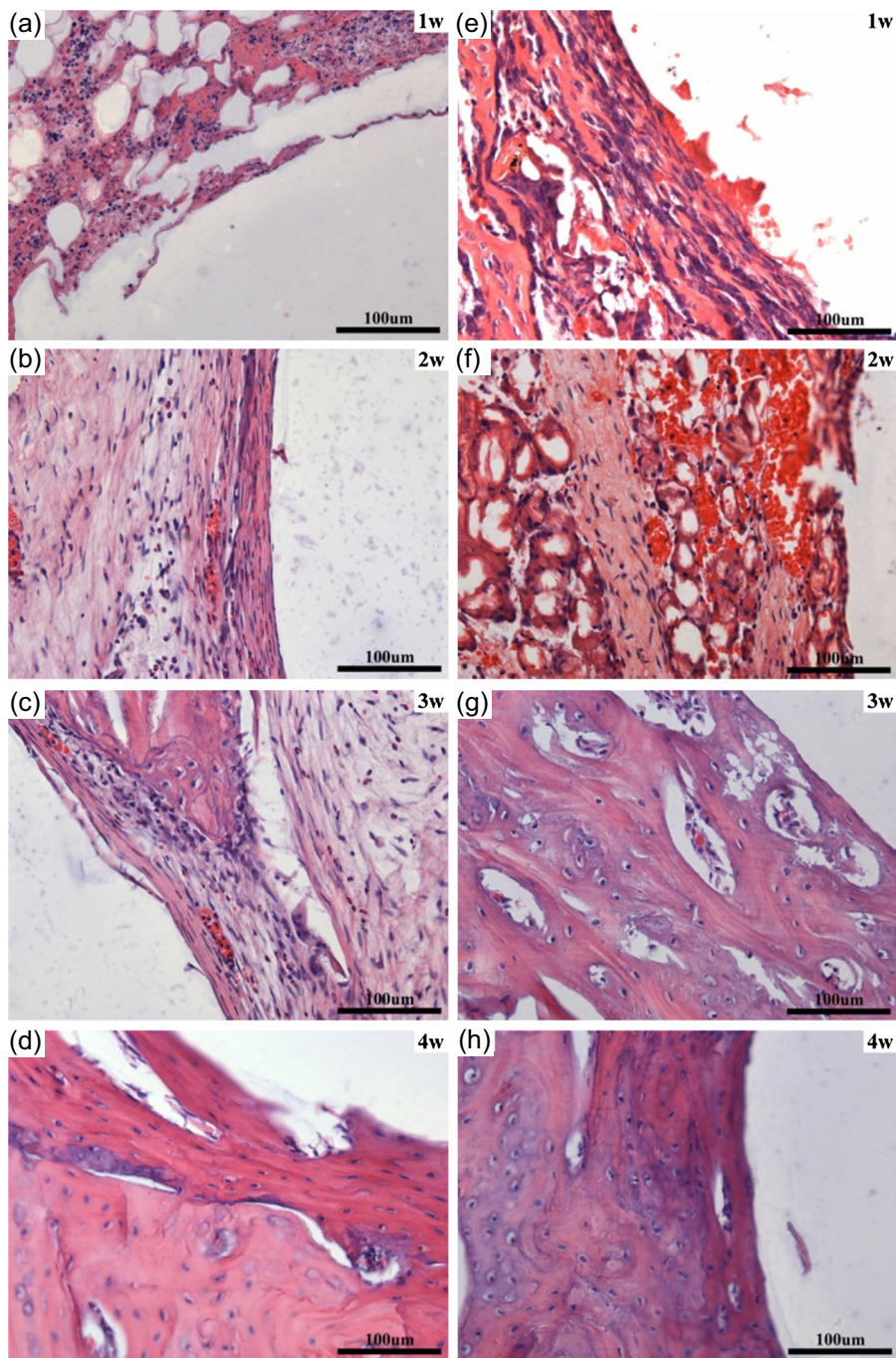


Figure 2.18 HE microstructure of the bone tissue at the interface between bone tissue and magnesium implants (Xu, Pan, et al., 2009).

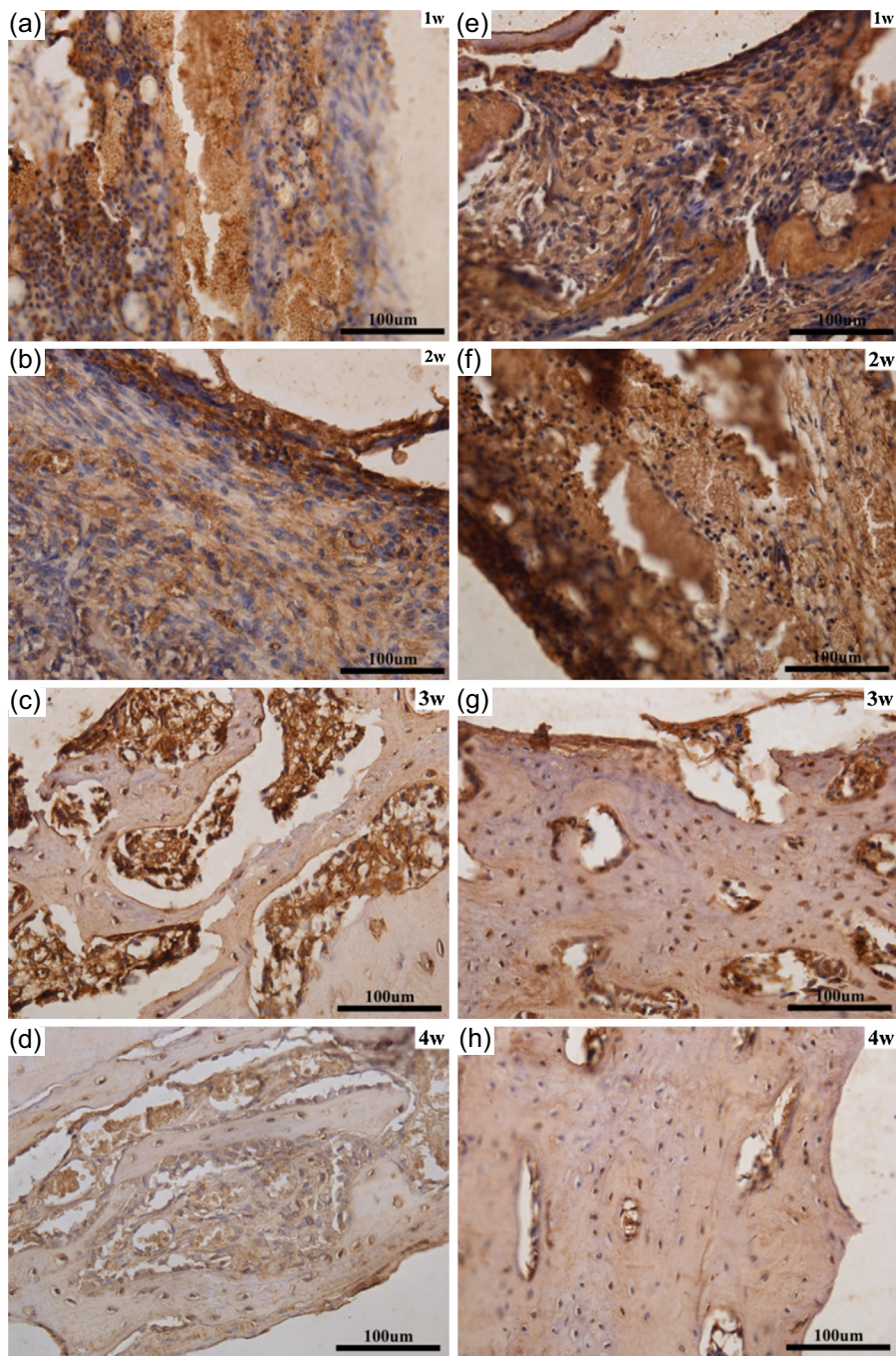


Figure 2.19 Photomicrographs of BMP-2 expression at interfaces between the implants and bones after 1, 2, 3, and 4 weeks of implantation. (a–d) Naked alloy implants. (e–h) Treated alloy implants (Xu, Pan, et al., 2009).

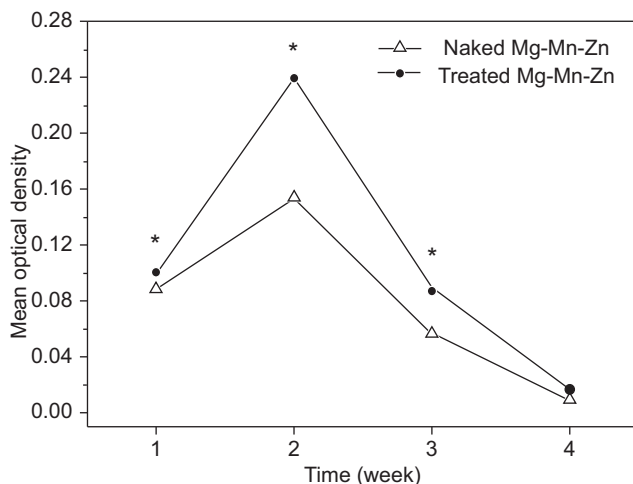


Figure 2.20 BMP-2 expression at the interface between Mg alloy implant and bone after different periods of implantation. * $p < 0.05$ (Xu, Pan, et al., 2009).

For biomaterials application, the surface bioactivity is mainly controlled by the physical properties and the chemical properties of the surface. A porous surface at the microscale or nanoscale level would contribute greatly to the faster adhesion and growth of cells, and a porous coating helps in bone cells' growth and proliferation on the surface of the implant, resulting in a significantly stronger bond to the parent tissue. After the phosphating process, a porous surface structure was successfully prepared on a magnesium sample, as stated in the previous section, which would definitely contribute to the good surface bioactivity. On the other hand, the surface chemical properties of the biomaterials also play a very important role in good surface bioactivity. Various calcium phosphate coatings including brushite, octacalcium phosphate, and HA have been successfully applied to titanium-based and other alloys (Shirkhanzadeh, 1998; Vijayaraghavan & Bensalem, 1994) because these compounds contain the same chemical composition or structure as the mineral composition of natural bone, and the release of Ca^{2+} and HPO_4^{2-} during hydrolysis can be utilized in the course of forming new bone. Furthermore, Ca^{2+} is also essential in chemical signaling with the cell. Research has shown that the osteoblast quantity and activity on the calcium-containing titanium surface are higher than those on the titanium surface with solely phosphate ions and the surface of pure Ti. And Ca^{2+} sites on the material surfaces favor protein absorption, such as fibronectin and vitronectin, which are important cell attachment-promoting proteins and have influence over cell attachment and spreading onto the surface due to positive electricity and chemical and biological function (Feng, Weng, Yang, Qu, & Zhang, 2004). Mg^{2+} and Zn^{2+} also play important roles in controlling the function of osteoblasts and increasing osteoblast adhesion and the alkaline phosphatase activity of bone cells.

2.9 Future trends

Phosphating treatment as a successful surface biomedical treatment has been used in titanium implants. Although magnesium and magnesium alloys have not been used clinically, the phosphating treatment has shown potential application as a surface modification method for reducing the degradation rate and improving the surface biocompatibility. However, it has to be pointed out that in the future, the following areas might be interesting in the development of the phosphating treatment of magnesium implants:

1. Careful selection of the phosphating system, keeping it as simple as possible. Biosafety is always the first important characteristic for an implant, especially an implant that will degrade *in vivo*.
2. Balance between the surface microstructure and the degradation rate. The phosphating treatment should provide magnesium with good protection from fast degradation but also cell biocompatibility, including cell adhesion and cell proliferation.

References

- Amini, R., & Sarabi, A. A. (2011). The corrosion properties of phosphate coating on AZ31 magnesium alloy: the effect of sodium dodecyl sulfate (SDS) as an eco-friendly accelerating agent. *Applied Surface Science*, 257, 7134–7139.
- Avedesian, M. M., & Baker, H. (1999). *ASM specialty handbook: Magnesium and magnesium alloys*. Materials Park, OH: ASM International.
- Bala Srinivasan, P., Liang, J., Balajee, R. G., Blawert, C., Stormer, M., & Dietzel, W. (2010). Effect of pulse frequency on the microstructure, phase composition and corrosion performance of a phosphate-based plasma electrolytic oxidation coated AM50 magnesium alloy. *Applied Surface Science*, 256, 3928–3935.
- Beck, L. S., Amento, E. P., Xu, Y., Deguzman, L., Lee, W. P., & Nguyen, T. (1993). TGF-beta 1 induces bone closure of skull defects: temporal dynamics of bone formation in defects exposed to rhTGF-beta 1. *Journal of Bone and Mineral Research*, 8, 753–761.
- Bikulčius, G., Burokas, V., Martušienė, A., & Matulionis, E. (2003). Effects of magnetic fields on the phosphating process. *Surface and Coatings Technology*, 172, 139–143.
- Chang, L., Tian, L., Liu, W., & Duan, X. (2013). Formation of dicalcium phosphate dihydrate on magnesium alloy by micro-arc oxidation coupled with hydrothermal treatment. *Corrosion Science*, 72, 118–124.
- Chen, Y., Luan, B. L., Song, G.-L., Yang, Q., Kingston, D. M., & Bensebaa, F. (2010). An investigation of new barium phosphate chemical conversion coating on AZ31 magnesium alloy. *Surface and Coatings Technology*, 210, 156–165.
- Chiu, L.-H., Chen, C.-C., & Yang, C.-F. (2005). Improvement of corrosion properties in an aluminum-sprayed AZ31 magnesium alloy by a post-hot pressing and anodizing treatment. *Surface and Coatings Technology*, 191, 181–187.
- Chiu, L. H., Lin, H. A., Chen, C. C., Yang, C. F., Chang, C. H., & Wu, J. C. (2003). Effect of aluminium coatings on corrosion properties of AZ31 magnesium alloy. *Materials Science Forum*, 419–422, 909–914.
- Erbel, R., Bose, D., Haude, M., Kordish, I., Churzidze, S., Malyar, N., et al. (2007). Absorbable coronary stents. New promising technology? *Herz*, 32, 308–319.

- Feng, B., Weng, J., Yang, B. C., Qu, S. X., & Zhang, X. D. (2004). Characterization of titanium surfaces with calcium and phosphate and osteoblast adhesion. *Biomaterials*, 25, 3421–3428.
- Gao, J.-C., Qiao, L.-Y., Li, L.-C., & Wang, Y. (2006). Hemolysis effect and calcium-phosphate precipitation of heat-organic-film treated magnesium. *Transactions of Nonferrous Metals Society of China*, 16, 539–544.
- Gao, J.-C., Wu, S., Qiao, L.-Y., & Wang, Y. (2008). Corrosion behavior of Mg and Mg-Zn alloys in simulated body fluid. *Transactions of Nonferrous Metals Society of China*, 18, 588–592.
- Gu, X., Zheng, Y., Zhong, S., Xi, T., Wang, J., & Wang, W. (2010). Corrosion of and cellular responses to Mg-Zn-Ca bulk metallic glasses. *Biomaterials*, 31, 1093–1103.
- Gupta, R. K., Mensah-Darkwa, K., & Kumar, D. (2014). Corrosion protective conversion coatings on magnesium disks using a hydrothermal technique. *Journal of Materials Science & Technology*, 30, 47–53.
- He, W., Zhang, E., & Yang, K. (2010). Effect of Y on the bio-corrosion behavior of extruded Mg–Zn–Mn alloy in Hank's solution. *Materials Science and Engineering: C*, 30, 167–174.
- Helm, G. A., Dayoub, H., & Jane, J. A. (2001). Gene-based therapies for the induction of spinal fusion. *Neurosurgical Focus*, 10, Article 5.
- Hiromoto, S., & Tomozawa, M. (2011). Hydroxyapatite coating of AZ31 magnesium alloy by a solution treatment and its corrosion behavior in NaCl solution. *Surface and Coatings Technology*, 205, 4711–4719.
- Hu, J., Wang, C., Ren, W. C., Zhang, S., & Liu, F. (2010). Microstructure evolution and corrosion mechanism of dicalcium phosphate dihydrate coating on magnesium alloy in simulated body fluid. *Materials Chemistry and Physics*, 119, 294–298.
- Huang, H., Kato, H., Chen, C., Wang, Z., & Yuan, G. (2012). The effect of nanoquasicrystals on mechanical properties of as-extruded Mg–Zn–Gd alloy. *Materials Letters*, 79, 281–283.
- Huang, H., Yuan, G., Chu, Z., & Ding, W. (2013). Microstructure and mechanical properties of double continuously extruded Mg–Zn–Gd-based magnesium alloys. *Materials Science and Engineering: A*, 560, 241–248.
- Janning, C., Willbold, E., Vogt, C., Nellesen, J., Meyer-Lindenberg, A., Windhagen, H., et al. (2010). Magnesium hydroxide temporarily enhancing osteoblast activity and decreasing the osteoclast number in peri-implant bone remodelling. *Acta Biomaterialia*, 6, 1861–1868.
- Kannan, M. B. (2012). Enhancing the performance of calcium phosphate coating on a magnesium alloy for bioimplant applications. *Materials Letters*, 76, 109–112.
- Kannan, M. B., & Raman, R. K. S. (2008). In vitro degradation and mechanical integrity of calcium-containing magnesium alloys in modified-simulated body fluid. *Biomaterials*, 29, 2306–2314.
- Keim, S., Brunner, J. G., Fabry, B., & Virtanen, S. (2010). Control of magnesium corrosion and biocompatibility with biomimetic coatings. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, 96B, 84–90.
- Kim, W.-C., Kim, J.-G., Lee, J.-Y., & Seok, H.-K. (2008). Influence of Ca on the corrosion properties of magnesium for biomaterials. *Materials Letters*, 62, 4146–4148.
- Kouisni, L., Azzi, M., Dalard, F., & Maximovitch, S. (2005). Phosphate coating on magnesium alloy AM60 part 2: electrochemical behavior in borate buffer solution. *Surface & Coating Technology*, 239–246.
- Kouisni, L., Azzi, M., Zertoubi, M., Dalard, F., & Maximovitch, S. (2004). Phosphate coatings on magnesium alloy AM60 part 1: study of the formation and the growth of zinc phosphate films. *Surface & Coating Technology*, 185, 58–67.

- Li, G. Y., Lian, J. S., Niu, L. Y., Jiang, Z. H., & Jiang, Q. (2006). Growth of zinc phosphate coatings on AZ91D magnesium alloy. *Surface and Coatings Technology*, 201, 1814–1820.
- Li, Q., Xu, S., Hu, J., Zhang, S., Zhong, X., & Yang, X. (2010). The effects to the structure and electrochemical behavior of zinc phosphate conversion coatings with ethanolamine on magnesium alloy AZ91D. *Electrochimica Acta*, 55, 887–894.
- Li, W., Guan, S., Chen, J., Hu, J., Chen, S., Wang, L., et al. (2011). Preparation and in vitro degradation of the composite coating with high adhesion strength on biodegradable Mg–Zn–Ca alloy. *Materials Characterization*, 62, 1158–1165.
- Li, Z., Gu, X., Lou, S., & Zheng, Y. (2008). The development of binary Mg–Ca alloys for use as biodegradable materials within bone. *Biomaterials*, 29, 1329–1344.
- Liu, Z.-X., Sun, R.-N., Mao, Z.-P., & Wang, P.-C. (2012). Effects of phosphate pretreatment and hot-humid environmental exposure on static strength of adhesive-bonded magnesium AZ31 sheets. *Surface and Coatings Technology*, 206, 3517–3525.
- Lv, G.-H., Chen, H., Wang, X.-Q., Pang, H., Zhang, G.-L., Zou, B., et al. (2011). Effect of additives on structure and corrosion resistance of plasma electrolytic oxidation coatings on AZ91D magnesium alloy in phosphate based electrolyte. *Surface and Coatings Technology*, 205, S36–S40.
- Mao, L., Yuan, G., Wang, S., Niu, J., Wu, G., & Ding, W. (2012). A novel biodegradable Mg–Nd–Zn–Zr alloy with uniform corrosion behavior in artificial plasma. *Materials Letters*, 88, 1–4.
- Narayanan, T. S. N. S. (2005). Surface pretreatment by phosphate conversion coatings- A Review. *Reviews on Advanced Materials Science*, 9, 130–177.
- Niu, L. Y., Jiang, Z. H., Li, G. Y., Gu, C. D., & Lian, J. S. (2006). A study and application of zinc phosphate coating on AZ91D magnesium alloy. *Surface and Coating Technology*, 200, 3021–3026.
- Noda, M. (1989). In vivo stimulation of bone formation by transforming growth factorbeta. *Endocrinology*, 124, 2991–2994.
- Pan, Y. K., Chen, C. Z., Wang, D. G., & Lin, Z. Q. (2013). Preparation and bioactivity of micro-arc oxidized calcium phosphate coatings. *Materials Chemistry and Physics*, 141, 842–849.
- Seyfoori, A., Mirdamadi, S., Seyedraoufi, Z. S., Khavandi, A., & Aliofkhazraei, M. (2013). Synthesis of biphasic calcium phosphate containing nanostructured films by micro arc oxidation on magnesium alloy. *Materials Chemistry and Physics*, 142, 87–94.
- Shirkhanzadeh, M. (1998). Direct formation of nanophase hydroxyapatite on cathodically polarized electrodes. *Journal of Materials Science: Materials in Medicine*, 9, 67–72.
- Song, G. L. (2007). Control of degradation of biocompatible magnesium in a pseudo-physiological environment by a ceramic like anodized coating. *Advanced Materials and Processing*, 29–30, 95–98.
- Song, Y. W., Shan, D. Y., & Han, E. H. (2008). Electrodeposition of hydroxyapatite coating on AZ91D magnesium alloy for biomaterial application. *Materials Letters*, 62, 3276–3279.
- Sreekanth, D., Rameshbabu, N., & Venkateswarlu, K. (2012). Effect of various additives on morphology and corrosion behavior of ceramic coatings developed on AZ31 magnesium alloy by plasma electrolytic oxidation. *Ceramics International*, 38, 4607–4615.
- Staiger, M. P., Pietak, A. M., Huadmai, J., & Dias, G. (2006). Magnesium and its alloys as orthopedic biomaterials: a review. *Biomaterials*, 27, 1728–1734.
- Tomozawa, M., Hiromoto, S., & Harada, Y. (2010). Microstructure of hydroxyapatite-coated magnesium prepared in aqueous solution. *Surface and Coatings Technology*, 204, 3243–3247.

- Tong, L. B., Zheng, M. Y., Chang, H., Hu, X. S., Wu, K., Xu, S. W., et al. (2009). Micro-structure and mechanical properties of Mg-Zn-Ca alloy processed by equal channel angular pressing. *Materials Science and Engineering: A*, 523, 289–294.
- Tsuji, K., Bandyopadhyay, A., Harfe, B. D., Cox, K., Kakar, S., & Gerstenfeld, L. (2006). BMP2 activity, although dispensable for bone formation, is required for the initiation of fracture healing. *Nature Genetics*, 38, 1424–1429.
- Vijayaraghavan, T. V., & Bensalem, A. (1994). Electrodeposition of apatite coating on pure titanium and titanium alloys. *Journal of Materials Science Letters*, 13, 1782–1785.
- Vojtich, D., Elova, H., & Volenec, K. (2006). Investigation of magnesium-based alloys for biomedical applications. *Kovove Materialy-Metallic Materials*, 44, 206–219.
- Wan, Y., Xiong, G., Luo, H., He, F., Huang, Y., & Zhou, X. (2008). Preparation and characterization of a new biomedical magnesium-calcium alloy. *Materials & Design*, 29, 2034–2037.
- Wang, H. X., Guan, S. K., Wang, X., Ren, C. X., & Wang, L. G. (2010). In vitro degradation and mechanical integrity of Mg-Zn-Ca alloy coated with Ca-deficient hydroxyapatite by the pulse electrodeposition process. *Acta Biomaterialia*, 6, 1743–1748.
- Wang, Y., Wei, M., & Gao, J. (2009). Improve corrosion resistance of magnesium in simulated body fluid by dicalcium phosphate dihydrate coating. *Materials Science and Engineering: C*, 29, 1311–1316.
- Witte, F. (2010). The history of biodegradable magnesium implants: a review. *Acta Biomaterialia*, 6, 1680–1692.
- Witte, F., Fischer, J., Nellesen, J., Crostack, H.-A., Kaese, V., Pisch, A., et al. (2006). In vitro and in vivo corrosion measurements of magnesium alloys. *Biomaterials*, 27, 1013–1018.
- Witte, F., Kaese, V., Haferkamp, H., Switzer, E., Meyer-Lindenberg, A., Wirth, C. J., et al. (2005). In vivo corrosion of four magnesium alloys and the associated bone response. *Biomaterials*, 26, 3557–3563.
- Xiao, X., Yu, H., Zhu, Q., Li, G., Qu, Y., & Gu, R. (2013). In vivo corrosion resistance of Ca-p coating on AZ60 magnesium Alloy. *Journal of Bionic Engineering*, 10, 156–161.
- Xu, D. K., Liu, L., Xu, Y. B., & Han, E. H. (2006). The influence of element Y on the mechanical properties of the as-extruded Mg-Zn-Y-Zr alloys. *Journal of Alloys and Compounds*, 426, 155–161.
- Xu, L., Pan, F., Yu, G., Yang, L., Zhang, E., & Yang, K. (2009). In vitro and in vivo evaluation of the surface bioactivity of a calcium phosphate coated magnesium alloy. *Biomaterials*, 30, 1512–1523.
- Xu, L. P., Yu, G. N., Zhang, E., Pan, F., & Yang, K. (2007). In vivo corrosion behavior of Mg-Mn-Zn alloy for bone implant application. *Journal of Biomedical Materials Research Part A*, 83A, 703–711.
- Xu, L. P., Zhang, E. L., & Yang, K. (2009). Phosphating treatment and corrosion properties of Mg-Mn-Zn alloy for biomedical application. *Journal of Materials Science: Materials in Medicine*, 20, 859–867.
- Xu, L. P., Zhang, E. L., Yin, D. S., & Yang, K. (2008). In vitro corrosion behaviour of Mg alloys in a phosphate buffered solution for bone implant application. *Journal of Materials Science. Materials in Medicine*, 19, 1017–1025.
- Yanovska, A. A., Kuznetsov, V., Stanislavov, A., Danilchenko, S., & Sukhodub, L. (2012). Calcium-phosphate coatings obtained biomimetically on magnesium substrates under low magnetic field. *Applied Surface Science*, 258, 8577–8584.

- Ye, C.-H., Xi, T.-F., Zheng, Y.-F., Wang, S.-Q., & Li, Y.-D. (2013). In vitro corrosion and biocompatibility of phosphating modified WE43 magnesium alloy. *Transactions of Nonferrous Metals Society of China*, 23, 996–1001.
- Yin, D.-S., Zhang, E.-L., & Zeng, S.-Y. (2008). Effect of Zn on mechanical property and corrosion property of extruded Mg-Zn-Mn alloy. *Transactions of Nonferrous Metals Society of China*, 18, 763–768.
- Zainal Abidin, N. I., Atrens, A. D., Martin, D., & Atrens, A. (2011). Corrosion of high purity Mg, Mg₂Zn_{0.2}Mn, ZE41 and AZ91 in Hank's solution at 37C. *Corrosion Science*, 53, 3542–3556.
- Zhang, E., He, W., Du, H., & Yang, K. (2008). Microstructure, mechanical properties and corrosion properties of Mg-Zn-Y alloys with low Zn content. *Materials Science and Engineering: A*, 488, 102–111.
- Zhang, E., Wei, X., Yang, L., Xu, J., & Song, C. (2010). Effect of Zn on the microstructure and mechanical properties of Mg-Si alloy. *Materials Science and Engineering: A*, 527, 3195–3199.
- Zhang, E., Xu, L., & Yang, K. (2005). Formation by ion plating of Ti-coating on pure Mg for biomedical applications. *Scripta Materialia*, 53, 523–527.
- Zhang, E., & Yang, K. (2005). Biomimetic coating of calcium phosphate on Biometallic materials. *Transaction of Non-ferrous Metal Society China*, 15, 1199–1205.
- Zhang, E., & Yang, L. (2008). Microstructure, mechanical properties and bio-corrosion properties of Mg-Zn-Mn-Ca alloy for biomedical application. *Materials Science and Engineering: A*, 497, 111–118.
- Zhang, E., Yin, D., Xu, L., Yang, L., & Yang, K. (2009). Microstructure, mechanical and corrosion properties and biocompatibility of Mg-Zn-Mn alloys for biomedical application. *Materials Science and Engineering: C*, 29, 987–993.
- Zhang, G. D., Huang, J. J., Yang, K., Zhang, B. C., & Ai, H. J. (2007). Experimental study of in vivo implantation of a magnesium alloy at early stage. *Acta Metallurgica Sinica*, 43, 1186–1190.
- Zhang, H., Ahmad, M., & Gronowicz, G. (2003). Effects of transforming growth factor-beta 1(TGF-1) on in vitro mineralization of human osteoblasts on implant materials. *Biomaterials*, 24, 2013–2020.
- Zhang, J., Dai, C.-S., Wei, J., & Wen, Z.-H. (2012). Study on the bonding strength between calcium phosphate/chitosan composite coatings and a Mg alloy substrate. *Applied Surface Science*, 261, 276–286.
- Zhang, S., Liu, W., Gu, X., Lu, C., Yuan, G., & Ding, W. (2013). Effect of solid solution and aging treatments on the microstructures evolution and mechanical properties of Mg-14Gd-3Y-1.8Zn-0.5Zr alloy. *Journal of Alloys and Compounds*, 557, 91–97.
- Zhang, S. X., Zhang, X. N., Zhao, C., Li, J. N., Song, Y., Xie, C., et al. (2010). Research on an Mg-Zn alloy as a degradable biomaterial. *Acta Biomaterialia*, 6, 626–640.
- Zhang, X., Wang, Z., Yuan, G., & Xue, Y. (2012). Improvement of mechanical properties and corrosion resistance of biodegradable Mg-Nd-Zn-Zr alloys by double extrusion. *Materials Science and Engineering: B*, 177, 1113–1119.
- Zhang, X., Yuan, G., Mao, L., Niu, J., Fu, P., & Ding, W. (2012). Effects of extrusion and heat treatment on the mechanical properties and biocorrosion behaviors of a Mg-Nd-Zn-Zr alloy. *Journal of the Mechanical Behavior of Biomedical Materials*, 7, 77–86.
- Zhao, M., Li, J., He, G., Xie, H., & Fu, Y. (2013). An investigation of the effect of a magnetic field on the phosphate conversion coating formed on magnesium alloy. *Applied Surface Science*, 282, 499–505.

-
- Zheng, Y. F., Gu, X. N., & Witte, F. (2014). Biodegradable metals. *Materials Science and Engineering: R: Reports*, 77, 1–34.
- Zong, Y., Yuan, G., Zhang, X., Mao, L., Niu, J., & Ding, W. (2012). Comparison of biodegradable behaviors of AZ31 and Mg–Nd–Zn–Zr alloys in Hank’s physiological solution. *Materials Science and Engineering: B*, 177, 395–401.

Chemical solution deposition of hydroxyapatite and octacalcium phosphate coatings for magnesium and its alloys to improve biocompatibility

3

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3.1 Introduction

Improvement and control of corrosion resistance are an essential issue for the practical application of bioabsorbable Mg/Mg alloys to biomedical devices. Here, the control of corrosion resistance implies the retardation of corrosion initiation and/or reduction of the corrosion rate; the former and the latter correspond to the retention of original strength until the initiation of corrosion and the gradual degradation of strength, respectively. Implant materials should show good biocompatibility, depending on the implantation sites. Surface coating is an effective method to improve both corrosion resistance and biocompatibility of metallic materials; other methods include the alloying and control of microstructure.

In the case of conventional orthopaedic and dental metallic biomaterials such as Ti alloys, calcium phosphate compounds, especially hydroxyapatite (HAp), are often coated on the surface to improve biocompatibility, mainly bone conductivity, because HAp is a main component of bones (Kasuga, 2010; Leon & Jansen, 2009). The bone conductivity of HAp coatings depends on the crystallinity and how different the composition is from the stoichiometric composition (Layrolle & Daculsi, 2009). As an artificial bone, β -tricalcium phosphate (β -TCP) and octacalcium phosphate (OCP), in addition to HAp, are examined to control the dissolution rate and bone conduction behaviours, since β -TCP and OCP are soluble in physiological environments in which stoichiometric HAp is stable, and OCP is a precursor of HAp (Ioku, 1996; Layrolle & Daculsi, 2009). Additionally, the prior study revealed that the deposition of calcium phosphate on pure Mg improves the corrosion resistance in a simulated body fluid (Kuwahara, Al-Abdullat, Mazaki, Tsutsumi, & Aizawa, 2001). Therefore, calcium phosphate compounds, such as HAp, β -TCP and OCP, are promising coating materials for bioabsorbable Mg/Mg alloys to retard corrosion initiation and control corrosion rate thereafter.

It is important to develop a coating method that can control the coating thickness and the crystal structure, crystallinity and composition of the calcium phosphate compounds on the surface of Mg/Mg alloys. Preferably, the coating method would be

simple and applicable to any shape of device. The chemical solution deposition (CSD) method satisfies these requirements. However, the HAp formation on Mg/Mg alloys in aqueous solutions is difficult because Mg/Mg alloys easily corrode under such conditions, and dissolved Mg ions prevent the crystallisation of HAp (Bigi et al., 1993). In some cases, amorphous calcium phosphate or a precursor of HAp such as dicalcium phosphate anhydrous, dicalcium phosphate dihydrate or β -TCP, is electrochemically deposited in the first step; subsequently, they are crystallised or transformed to HAp in an alkaline solution in the second step (Song, Shan, & Han, 2008; Song, Zhang, Li, Zhao, & Zhang, 2010). In other cases, dissolution of Mg ions, i.e. corrosion of a Mg substrate, is prevented with the addition of a fluoride (NaF, HF, etc.) in the pre-treatment solution or the calcium phosphate solution (Bakhsheshi-Rad, Idris, & Abdul-Kadir, 2013; Jo et al., 2011; Song et al., 2010; Wen et al., 2009). Then HAp and/or other calcium phosphate compounds including fluoridated hydroxyapatite are electrochemically deposited concurrently or in the second step. Since fluorides are not environmentally friendly, a fluoride-free process is preferable.

We developed a novel CSD method for the single-step formation of HAp and OCP coatings on Mg/Mg alloys (Hiromoto, 2009; Hiromoto & Tomozawa, 2010; Hiromoto & Tomozawa, 2011; Tomozawa, Hiromoto, & Harada, 2010; Tomozawa & Hiromoto, 2011a, 2011b). Formation of HAp and OCP can be controlled with the pH of the treatment solution and the treatment period (Hiromoto & Tomozawa, 2011; Tomozawa & Hiromoto, 2011b). The thickness of HAp and OCP coatings can be controlled with the treatment period (Tomozawa & Hiromoto, 2011a, 2011c). The formation mechanism and chemical and mechanical properties of an OCP- and HAp-coated Mg/Mg alloy will be introduced in this chapter.

3.2 Hydroxyapatite and octacalcium phosphate coatings formed by a chemical solution deposition technique

3.2.1 Chemical solution deposition

CSD is a coating method in which the coating is formed with the reaction between the substrate surface and components of the solution (Yoshimura, 2009). This method is named following the name ‘chemical vapour deposition’. CSD is a kind of soft solution-processing performed using a simple experimental setup under atmospheric pressure and a temperature below 373 K. While the CSD reaction can be accelerated (activated) with hydrothermal and electrochemical reactions, the simple CSD process without extreme heating or electrochemical power is more beneficial for industries. The simple CSD can be applied to low heat-resistant materials, complicated shape substrates and porous materials. Therefore, CSD attracts attention as a low-cost and environmentally friendly coating process. On the other hand, CSD is not often employed in industries because it is difficult to form a coating with CSD in many cases. Dots or islands, rather than a coating, are easily formed on the substrate due to the preferential growth of the nuclei over the formation of new nuclei. To form a uniform coating, precise control of the deposition conditions is necessary.

The biomimetic coating method (a kind of CSD) is used for the calcium phosphate coating of conventional metallic biomaterials (Kokubo, 1996; Liu & Hunziker, 2009) because the biomimetically formed coating is expected to show better biocompatibility than coatings formed under extreme conditions, such as high temperature. In a typical biomimetic process to form bone-like hydroxyapatite, pre-treated substrate metals and alloys are immersed in a Kokubo's simulated body fluid (SBF) or Hank's solution supersaturated with calcium phosphate under physiological conditions of 310 K and pH 7.4. When the biomimetic method is applied to an Mg/Mg alloy, HAp coatings with very low crystallinity are formed (Al-Abdullat et al., 2001; Keim, Brunner, Fabry, & Virtanen, 2011; Kuwahara et al., 2001). This is because the SBF and Hank's solution contain chloride ions, which cause the severe corrosion of Mg/Mg alloys; in addition, the dissolved Mg ions prevent the crystallisation of HAp (Bigi et al., 1993).

Therefore, a new simple CSD method is needed for Mg/Mg alloys to form a coating consisting of well-crystallised HAp and OCP. The treatment solution should not contain chloride ions or environmentally hazardous or biologically toxic substances. The treatment temperature should be below 373 K. It was supposed that the prevention of HAp crystallisation by Mg ions can be overcome by rapid formation of a coating to stop the corrosion of Mg/Mg alloys as soon as possible. An increase in the concentration of Ca and phosphate ions is one way to achieve that goal; however, the solubility of inorganic Ca salts, except for CaCl_2 , is not sufficiently high. Ethylenediaminetetraacetic acid calcium disodium salt hydrate (Ca-EDTA: $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8\text{Na}_2\text{Ca}$), a Ca-chelate compound, was then employed because its solubility in aqueous solution is higher than that of inorganic Ca salts. Additionally, it has been used for the synthesis of HAp on titanium, aluminium, copper and iron substrates (Fujishiro, Sato, & Okuwaki, 1995; Fujishiro, Yabuki, Kawamura, Sato, & Okuwaki, 1993). Ca-EDTA showed a wide pH range for the formation of OCP and HAp coatings comparable to other calcium chelate compounds such as *N*-(2-Hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic acid calcium salt (Ca-EDTA-OH: $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_7\text{Ca}$), calcium gluconate ($\text{C}_{12}\text{H}_{18}\text{CaO}_{14}$) and calcium lactate ($\text{C}_6\text{H}_{10}\text{CaO}_6$).

Deposition of calcium phosphate compounds on Mg/Mg alloys is suggested to initiate from the corrosion of the Mg/Mg alloy substrate, as illustrated in Figure 3.1 (Hiromoto, 2009). Generation of OH^- ions in the cathode reaction raises the surface pH, leading to the nucleation of calcium phosphate compounds on the surface. The pH increase is limited to the surface, which is the key to forming a uniform coating rather than dots and islands.

3.2.2 Influence of deposition conditions

According to the proposed deposition mechanism shown in Figure 3.1, temperature, pH and concentration of Ca-EDTA and $\text{H}_x\text{PO}_4^{3-}$ ions influence the calcium phosphate coating behaviour. The influence of these factors on the coating behaviour was then examined.

Treatment temperature needs to be higher than a certain level to dissociate Ca-EDTA and to initiate the calcium phosphate deposition reaction. The calcium phosphate compound did not deposit at a temperature below 313 K (Figure 3.2). At a temperature

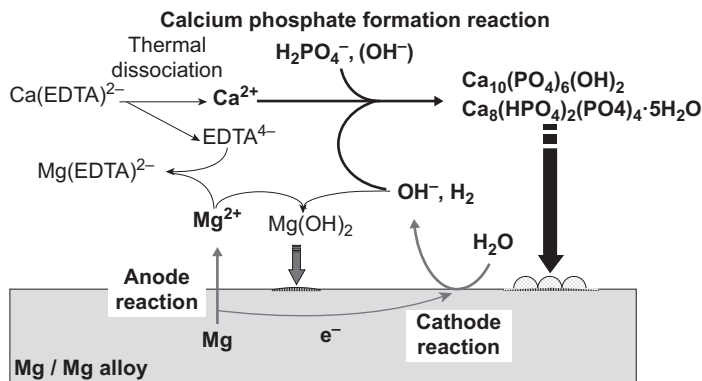


Figure 3.1 The proposed mechanism of calcium phosphate deposition on Mg/Mg alloys using Ca-EDTA by chemical solution deposition method.

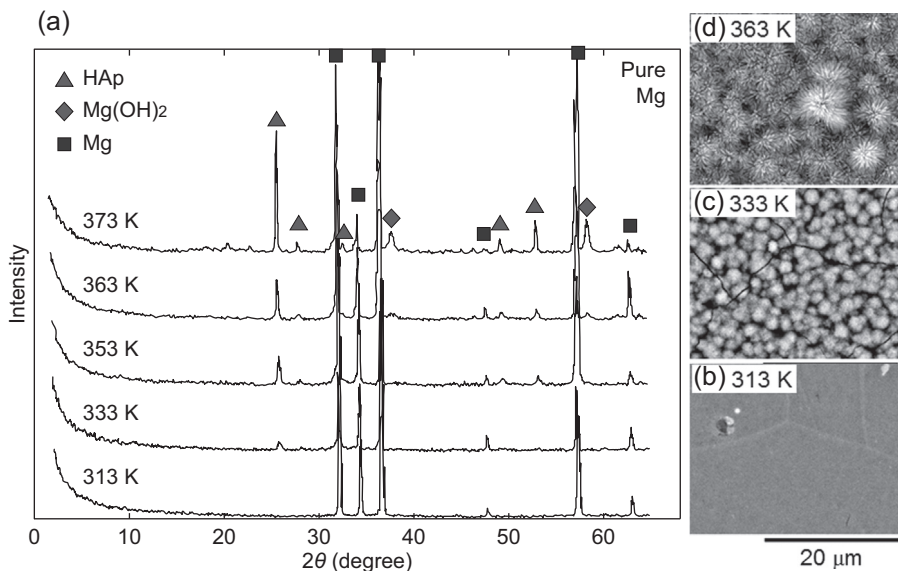


Figure 3.2 (a) X-ray diffraction (XRD) patterns of pure Mg treated with 50 mmol/L of Ca-EDTA and KH_2PO_4 at pH 8.9 and various treatment temperatures for 8 h. Scanning electron microscopy (SEM) images of pure Mg treated at (b) 313 K, (c) 333 K and (d) 363 K. From Tomozawa et al. (2010), with permission.

above 313 K, deposition of HAp could be observed. The amount of deposition and crystallinity of HAp increased with an increase in temperature, as evidenced by the increase in intensity and sharpness of the diffraction peaks originating from HAp (Figure 3.2) (Tomozawa et al., 2010). The HAp deposition was also enhanced by an increase in Ca-EDTA concentration (Figure 3.3) (Tomozawa et al., 2010). Concurrently, micro-pitting (localised corrosion) of substrate Mg/Mg alloys was accelerated with an increase

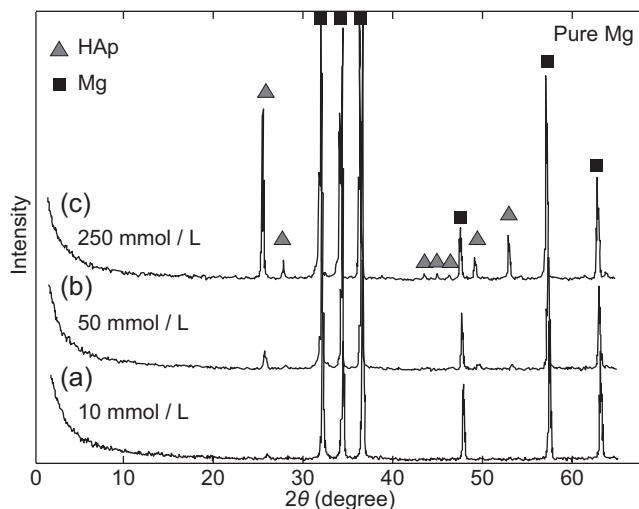


Figure 3.3 X-ray diffraction (XRD) patterns of pure Mg treated at pH 8.9 and 363 K for 2 h with (a) 10 mmol/L, (b) 50 mmol/L and (c) 250 mmol/L of Ca-EDTA and KH_2PO_4 . From Tomozawa et al. (2010), with permission.

in temperature and Ca-EDTA concentration. The pitting density of the substrate Mg alloy treated at 363 K was higher than that at 333 K (Figure 3.4). Since fatigue behaviour of Mg/Mg alloys is sensitive to micro-pits, as mentioned later (Hiromoto, Tomozawa, & Maruyama, 2013; Khan, Miyashita, Mutoh, & Koike, 2008), the treatment temperature and concentration of Ca-EDTA should be decided to achieve a balance between the coating speed and the magnitude of substrate pitting.

The crystal structure of calcium phosphate compounds varied with the pH of the treatment solution. OCP and HAp were formed roughly below and above pH 7, respectively, on pure Mg and AZ31 alloy (Figure 3.5) (Tomozawa et al., 2010). At a pH below 6, monetite ($\text{CaPO}_3(\text{OH})$) and CaHPO_4 was apt to be formed over the OCP layer as a by-product (Hiromoto, Inoue, Taguchi, Yamane, & Ohtsu, in press). In the pH range from neutral to weak alkaline, OCP transformed to HAp with an increase in treatment period, and a mixture of OCP and HAp can be formed. Depending on the kind of Mg alloy, β -TCP was deposited at a relatively low pH, while β -TCP did not form a uniform coating (Figure 3.6). The deposition of β -TCP at 363 K was surprising because β -TCP is formed only at more than 1073 K according to thermodynamic stability (Layrolle & Daculsi, 2009). In this case, it is suggested that the Mg alloy released a large amount of Mg ions that were incorporated into the deposited calcium phosphate compound and caused the formation of β -TCP.

3.2.3 Influence of Mg/Mg alloy substrate

The morphology and structure of calcium phosphate coatings depends on the composition and microstructure of Mg alloys, since the corrosion behaviour of Mg/Mg alloys depends on these factors (Shaw, 2003; Song, 2011). Pure Mg, AZ31, AZ61, AZ91 and

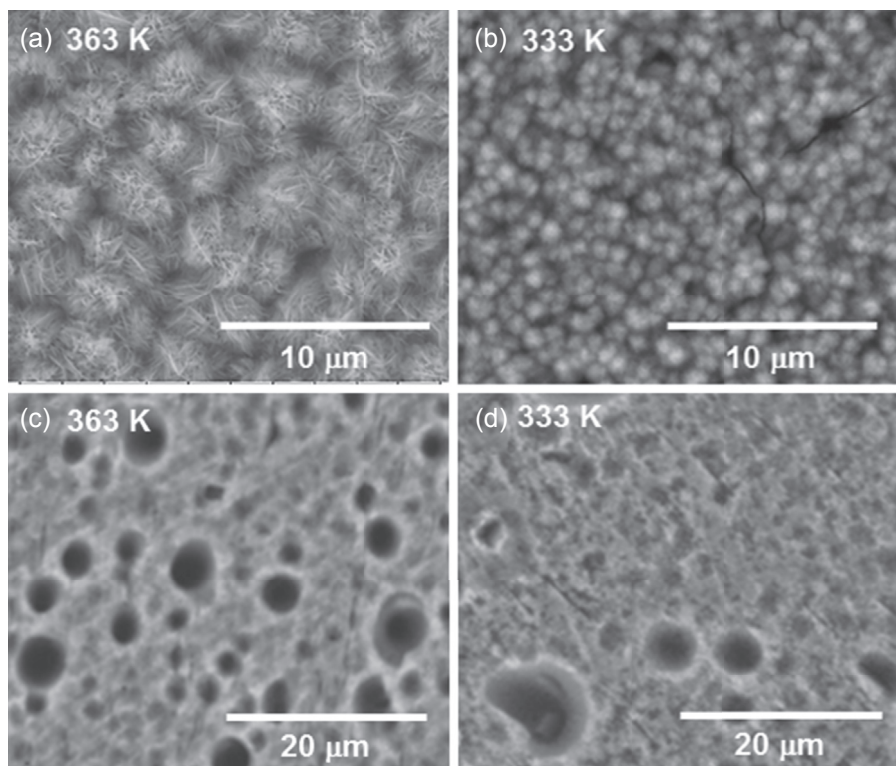


Figure 3.4 Scanning electron microscopy (SEM) images of WE43 treated with 250 mmol/L of Ca-EDTA and KH_2PO_4 at pH 8.3 and (a) 363 K and (b) 333 K for 1 h. SEM images of the substrate WE43 treated at (c) 363 K and (d) 333 K after chemically removing the hydroxyapatite (HAp) coatings.

WE43 alloys were treated under the same condition as that for HAp coating. The amount of HAp deposited varied depending on Mg and Mg alloys, as indicated by the intensity of the X-ray diffraction (XRD) peak at around 26 degrees from HAp (Figure 3.7(a)). The amount of HAp deposited on pure Mg was larger than that on AZ series alloys. This fact is attributed to the lower corrosion resistance of pure Mg compared to that of the AZ alloys. The low corrosion resistance causes a rapid increase in the surface pH, leading to an enhanced nucleation of HAp. The amount of HAp deposited increased with an increase of Al content because of the enhancement of micro-galvanic corrosion between the matrix and β -phase (second phase), which is apt to precipitate with an increase of Al content of AZ alloys. In the case of WE43, Y preferentially precipitated in grain boundaries, and an Mg-Y intermetallic compound sometimes precipitated inside grains as a second phase (Sato, 2007). Micro-galvanic coupling between matrix and Mg-Y intermetallic compound might accelerate the corrosion in the treatment solution, leading to the deposition of a relatively large amount of HAp on WE43. The acceleration of corrosion on WE43 compared to the AZ alloys and pure Mg was indicated by the deposition of β -TCP only on WE43 under

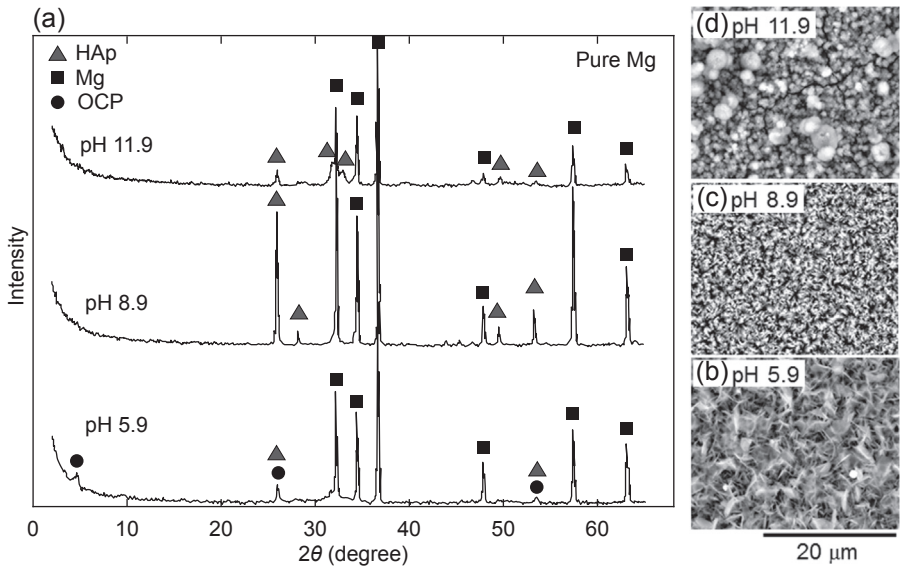


Figure 3.5 (a) X-ray diffraction (XRD) patterns of pure Mg treated at pH 5.9, 8.9 and 11.9 with 250 mmol/L Ca-EDTA and KH_2PO_4 at 363 K for 2 h. Scanning electron microscopy (SEM) images of pure Mg treated at (b) pH 5.9, (c) pH 8.9 and (d) pH 11.9.

From Tomozawa and Hiromoto (2011b), with permission.

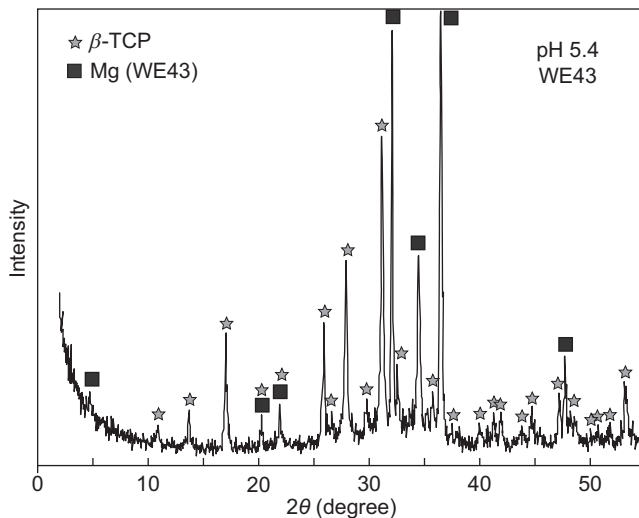


Figure 3.6 X-ray diffraction (XRD) pattern of WE43 treated at pH 5.4 and 363 K for 1 h.

the OCP formation condition for pure Mg and AZ31. β -TCP is formed with the substitution of Mg ions in the calcium phosphate deposits under a moderate temperature. In other words, composition and microstructure of the Mg alloy influence the crystal structure of deposited calcium phosphate compounds.

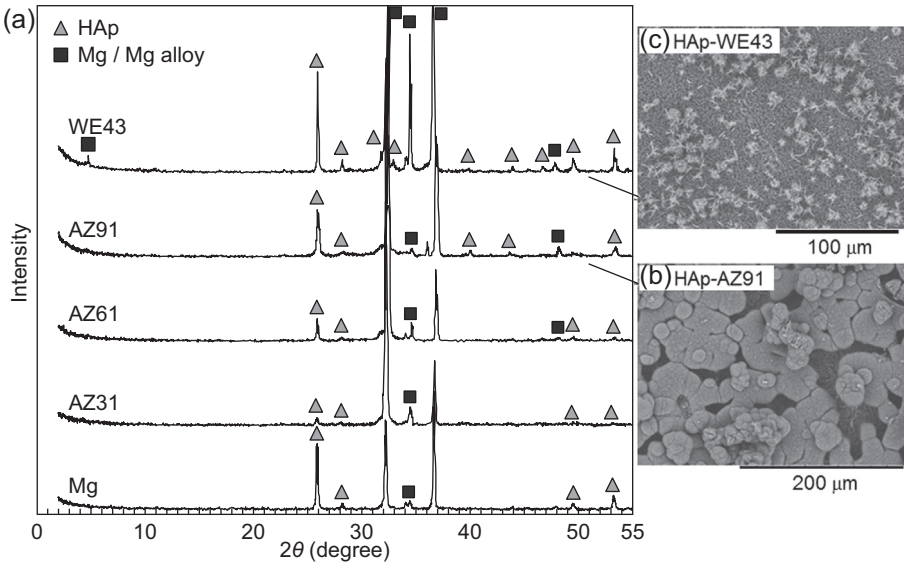


Figure 3.7 (a) X-ray diffraction (XRD) patterns of various Mg/Mg alloys treated with 250 mmol/L of Ca-EDTA and KH_2PO_4 at pH 8.9 and 363 K for 2 h. Scanning electron microscopy (SEM) images of treated (b) AZ91 and (c) WE43.

The microstructure of Mg alloys influenced the coating morphology. When the second phase was large, similar to β -phases on AZ91, HAp deposited, avoiding the second phases (Figure 3.7(b)). Because the size of Mg-Y precipitates was smaller than the β -phase in AZ91, the WE43 surface was uniformly coated with HAp, as shown in Figure 3.7(c). To form a uniform calcium phosphate compound coating on multiphase alloys, a pre-treatment may be necessary to uniformly form nuclei.

On all the XRD patterns of HAp and OCP coatings formed under the conditions mentioned above, the intensity of $(002)_{\text{HAp}}$ and $(002)_{\text{OCP}}$ peaks at around 26 degrees was higher than that of the other diffraction peaks from HAp and OCP, respectively. These results indicate that $(002)_{\text{HAp}}$ and $(002)_{\text{OCP}}$ planes were oriented parallel to the substrate surface.

3.2.4 Formation and growth mechanism of HAp and OCP coatings

As mentioned above, the corrosion of substrate Mg/Mg alloys initiates the calcium phosphate compound deposition, as shown in Figure 3.1. To examine the formation and growth mechanism of the OCP and HAp coatings, treatment time was varied from 10 min to 8 h using pure Mg. In both cases of OCP and HAp coating, at the very initial stage, the surface was almost covered with a layer of dome-shape deposits consisting of a dense inner core and outer fine needles (HAp coating) or fine plates (OCP coating) (Figure 3.8(a)–(d)) (Tomozawa & Hiromoto, 2011a, 2011c). With an increase in treatment period, both inner and outer parts grew simultaneously and

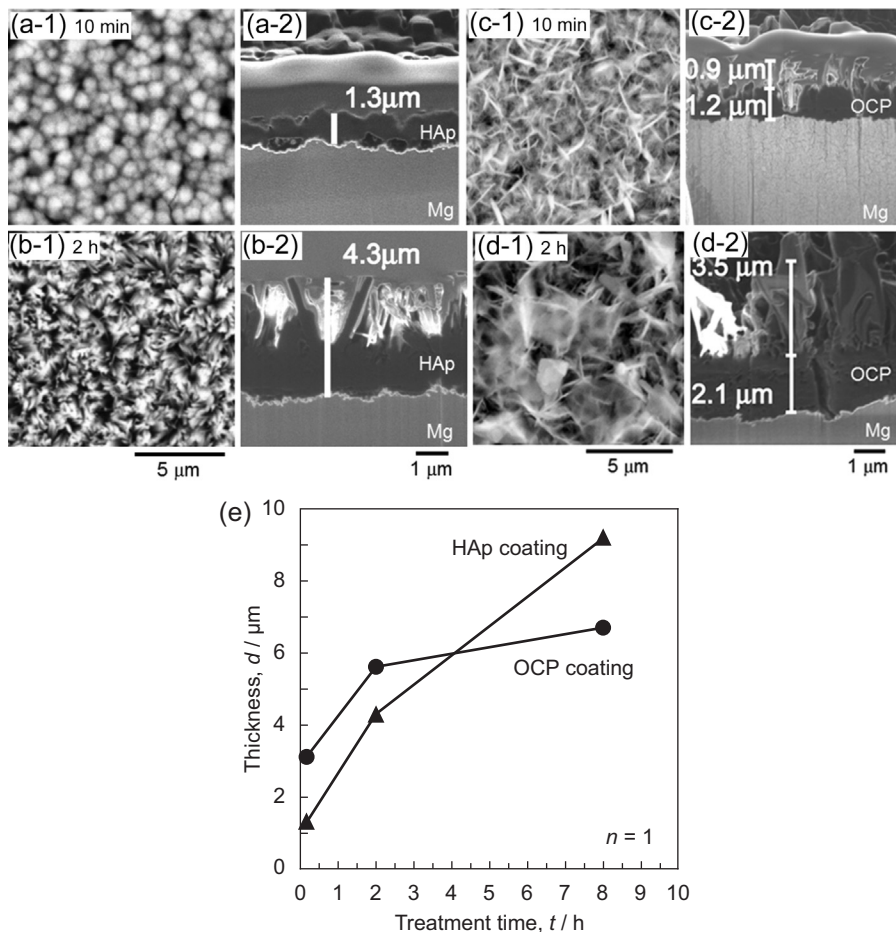


Figure 3.8 Surface and cross-section secondary electron microscopy (SEM) images of pure Mg treated at pH 8.9 for (a) 10 min and (b) 2 h and at pH 5.9 for (c) 10 min and (d) 2 h. (e) Growth curves of hydroxyapatite (HAp) and octacalcium phosphate (OCP) coatings formed on pure Mg.

From Tomozawa and Hiromoto (2011a), with permission.

became a continuous dense layer and a porous layer consisting of rod-like (HAp coating) or plate-like (OCP coating) crystals. The OCP coating was formed faster than the HAp coating, as indicated by the greater thickness of the initial OCP coating than that of the initial HAp coating (Figure 3.8(e)). The proposed growth mechanism is illustrated in Figure 3.9. On the other hand, the thickness of the HAp coating increased linearly for 8 h, while that of the OCP coating was saturated between 2 and 8 h. Because the OCP coating was formed in a weak acid solution in which the corrosion rate of substrate pure Mg is relatively high, the OCP coating was initially rapidly formed. However, because the OCP is soluble in a weak acid solution (Kanazawa & Monma, 1995), the growth and dissolution of OCP are balanced thereafter. The

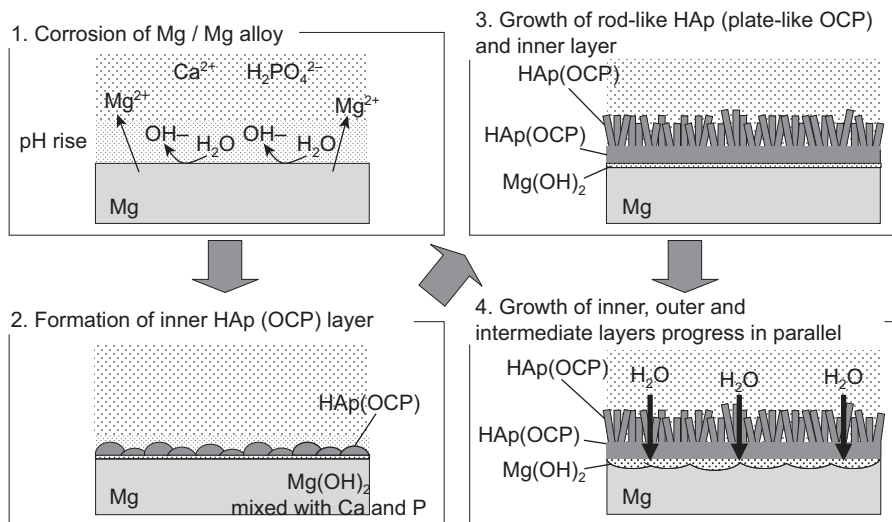


Figure 3.9 Schematic illustration of the proposed growth mechanism of hydroxyapatite (HAp) and octacalcium phosphate (OCP) coatings.

HAp coating was formed in a neutral solution in which the corrosion rate of pure Mg was relatively low and HAp was not soluble; therefore, the initial HAp formation was slower than that of the OCP coating, although the HAp coating can grow with an increase in treatment time. At all events, it was revealed that the thickness of OCP and HAp coating can be controlled with the treatment period.

3.3 Morphology, crystal structure and composition of HAp and OCP coatings

The coating morphology and crystal structure were precisely characterised using Field emission-secondary electron microscopy (FE-SEM), Transmission electron microscopy-selected area diffraction pattern (TEM-SADP) and XRD. Plate-like OCP and rod-like HAp crystals grew from a continuous inner layer and formed a porous outer layer (Figure 3.10(a) and (b)). SADP analysis revealed that the growth direction of plate-like OCP and rod-like HAp crystals was (002) axis (Figure 3.10(c) and (d)); therefore, the intensity of diffraction peaks from (002) and (004) planes of OCP and HAp was relatively higher than the others and increased with an increase in treatment time (Figure 3.2, 3.3, 3.5–3.7).

The continuous inner layer of the OCP coating showed nano-pores, while that of the HAp coating was microscopically dense under FE-SEM observation (Figure 3.11). At the initial stage of OCP coating, a significant amount of H_2 gas bubbles generated in the relatively low pH treatment solution, which presumably causes the formation of nano-pores in the inner layer. In the case of the HAp coating procedure, the amount of H_2 gas bubbles generated was much smaller than that for OCP coating.

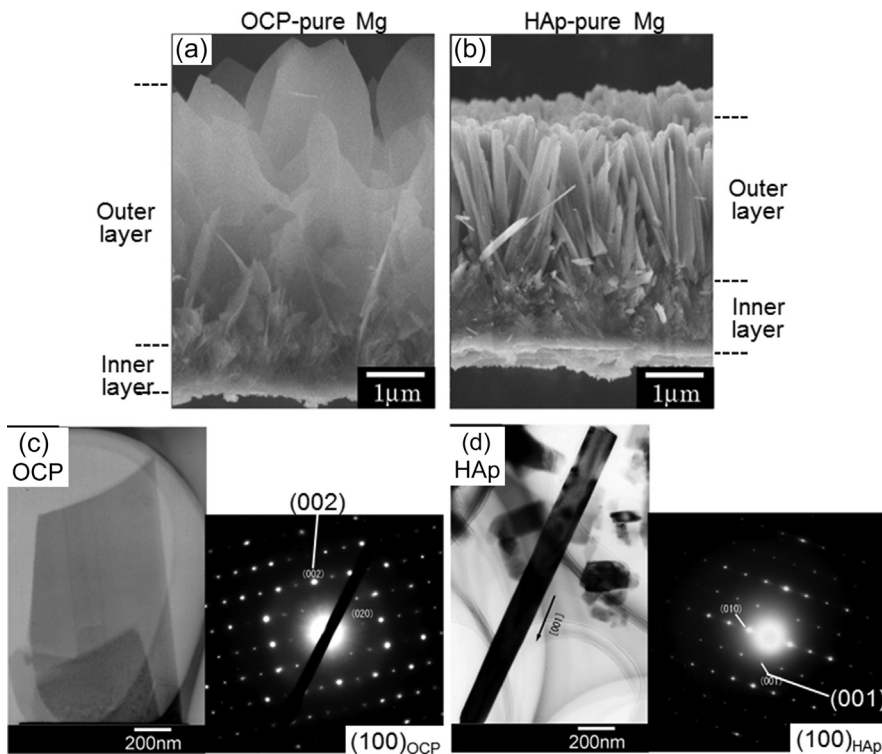


Figure 3.10 Side view field emission-secondary electron microscopy (FE-SEM) images of (a) Octacalcium phosphate (OCP) and (b) Hydroxyapatite (HAp) coatings scraped off from the substrate pure Mg. Transmission electron microscopy (TEM) images and the corresponding selected area diffraction pattern (SADP) of (c) plate-like OCP and (d) rod-like HAp crystals in the outer layer of the coatings formed on pure Mg. The OCP and HAp coatings were formed with 250 mmol/L of Ca-EDTA and KH_2PO_4 at 363 K and pH 5.9 (a, c) and 8.9 (b, d), respectively, for 2 h.

From Tomozawa and Hiromoto (2011b), with permission.

The boundary between the OCP and HAp coatings and the substrate was precisely observed with TEM, and it was revealed that a thin intermediate $\text{Mg}(\text{OH})_2/\text{MgO}$ layer was formed from the very beginning and grew with an increase in treatment time (Figure 3.12). Since the $\text{Mg}(\text{OH})_2/\text{MgO}$ layer contained a slight amount of Ca and P, the mixing with $\text{Mg}(\text{OH})_2/\text{MgO}$ and calcium phosphate at the boundary is a reason for good adhesiveness of the coatings to the substrate, as mentioned later.

The composition of OCP and HAp coatings formed on pure Mg was precisely characterised by X-ray photoelectron spectroscopy (XPS) (Ohtsu, Hiromoto, Yamane, Satoh, & Tomozawa, 2013) and Fourier transform-infrared spectroscopy (FT-IR). A slight amount of Na^+ and CO_3^{2-} was detected with XPS and FT-IR, respectively (Figure 3.13). No Na-containing compound was detected with high-resolution XRD. These results revealed that HAp and OCP crystals contained a slight amount of Na^+ and CO_3^{2-} in their crystal structure by substituting Ca^{2+} and PO_4^{3-} , respectively.

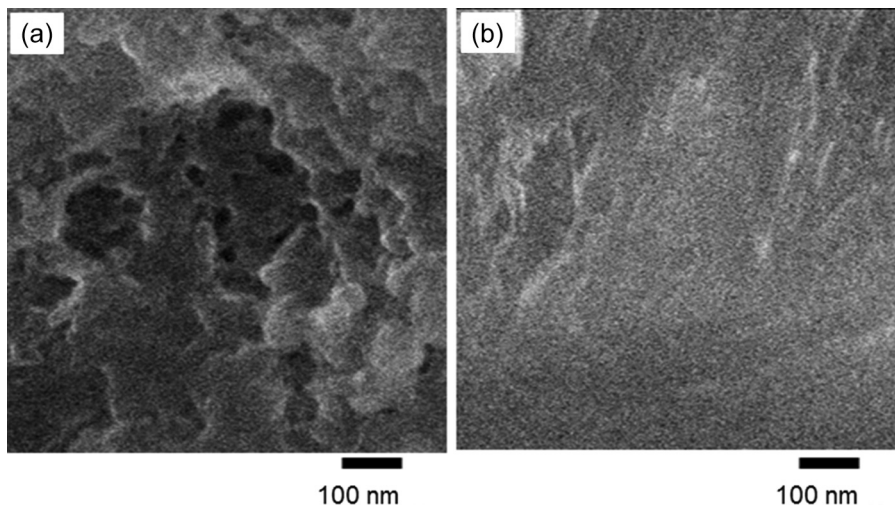


Figure 3.11 Cross-section field emission-secondary electron microscopy (FE-SEM) images of the inner layer of (a) Octacalcium phosphate (OCP) and (b) Hydroxyapatite (HAp) coatings formed on pure Mg.

From [Tomozawa and Hiromoto \(2011b\)](#), with permission.

3.4 Long-term corrosion behaviour of OCP- and HAp-coated Mg alloy in a cell culture medium

3.4.1 Magnesium ion release behaviour

The effect of the OCP and HAp coatings on the corrosion behaviour of Mg/Mg alloys was examined by a one-year immersion test of the coated AZ31 alloy (OCP-AZ31 and HAp-AZ31) in Eagle's minimum essential medium supplemented with 10 vol.% fetal bovine serum and buffered with HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid). Chemically polished AZ31 (Cpol-AZ31) was also immersed under similar conditions for comparison. Magnesium ion concentration in the medium was quantitatively monitored using an aliquot of the medium by colorimetric measurement. Here, it was estimated that about 60% of the dissolved Mg ions were detected by analysing the Mg ion concentration ([Hiromoto et al., in press](#)). [Figure 3.14\(a\)](#) shows the Mg ion release curve of OCP-, HAp- and Cpol-AZ31 in the medium up to 12 weeks ([Hiromoto, 2012](#)). The Mg ion release increased almost linearly after 12 weeks. Both HAp and OCP coatings retarded the apparent initial Mg ion release for about 4 days, while Cpol-AZ31 showed obvious Mg ion release soon after the immersion. The retardation of corrosion initiation is a beneficial property to maintain the strength of the substrate Mg alloy. After the initiation of Mg ion release, the coatings reduced the Mg ion release rate by 4–6 times. The Mg ion release rate from HAp-AZ31 was about one-half that from OCP-AZ31. The higher protective-ness of the HAp coating is attributed to the microscopic dense structure of the inner

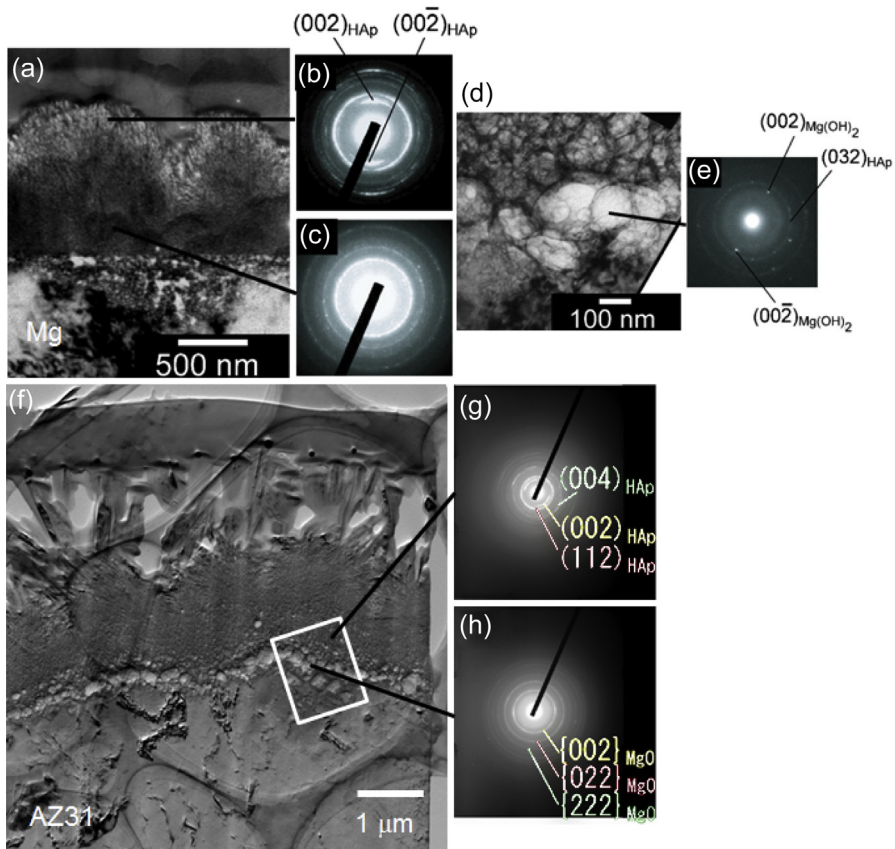


Figure 3.12 Cross-section transmission electron microscopy (TEM) images and the corresponding selected area diffraction pattern (SADP) of hydroxyapatite (HAp) coatings formed on (a)–(e) pure Mg and (f)–(h) AZ31. The coating treatment period was 10 min and 2 h for pure Mg and AZ31, respectively.

From Tomozawa and Hiromoto (2011a); Hiromoto et al. (2013), with permission.

layer, and the lower protectiveness of the OCP coating is attributed to the nano-porous structure of the inner layer (Tomozawa & Hiromoto, 2011b).

3.4.2 Corrosion morphology of the substrate Mg alloy

The medium-immersed AZ31 showed visible filiform corrosion regardless of the coatings. The filiform corrosion broke the coatings on the pits. The OCP and HAp coatings reduced the filiform corrosion area (Figure 3.14(b) and (c)). The surface outside of the corrosion area was observed with SEM and analysed with XRD, revealing that OCP and HAp coatings remained almost in their original morphology after the immersion and a part of the OCP coating transformed to HAp.

After immersion for 52 weeks, the coatings and corrosion products outside of the filiform corrosion area were chemically removed, and profiles of the substrate were

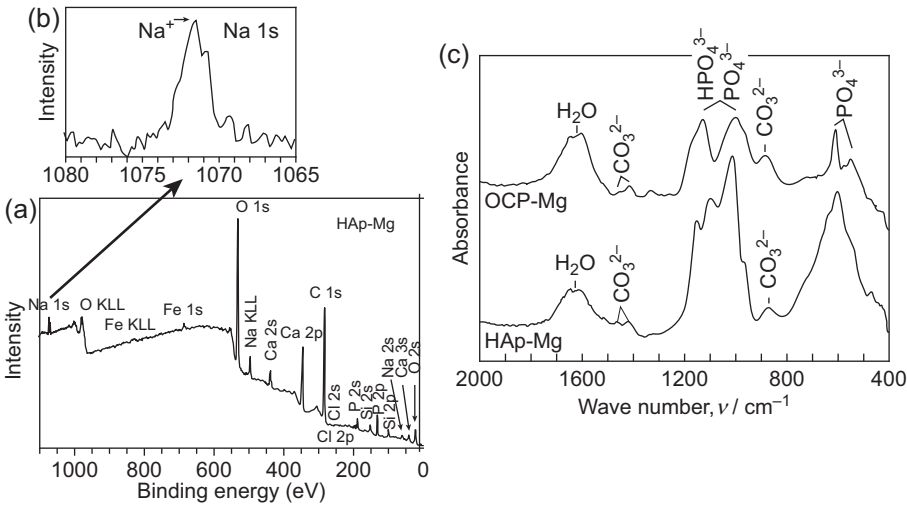


Figure 3.13 X-ray photoelectron spectroscopy (XPS) (a) survey spectrum and (b) narrow spectrum of Na 1s region of HAp-coated pure Mg, and (c) Fourier transform-infrared spectroscopy (FT-IR) spectra of OCP- and HAp-coated pure Mg. From [Ohtsu et al. \(2013\)](#), with permission.

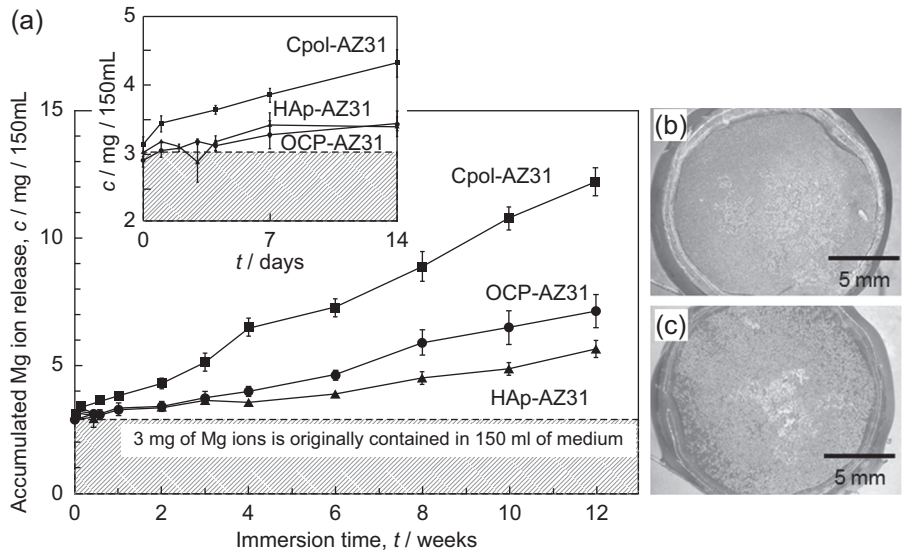


Figure 3.14 Magnesium ion release curves of Cpol-, OCP- and HAp-AZ31 in a cell culture medium for (a) 12 weeks and appearances of (b) Cpol- and (c) HAp-AZ31 immersed for 14 weeks and 52 weeks, respectively. Cpol-AZ31, chemically polished-AZ31; HAp-AZ31, HAp-coated AZ31.

measured using a laser microscope. Figure 3.15 shows laser reflectivity images and the corresponding profiles of Cpol-, OCP- and HAp-AZ31 as prepared and immersed in the medium. The substrate underneath the as-prepared OCP and HAp coatings showed micro-pits with a depth of about a few tens of μm , revealing that the substrate AZ31 was corroded during the coating treatment (Figure 3.15(a)–(c)). The number and size of the micro-pits underneath the as-prepared OCP coating were larger than those underneath the as-prepared HAp coating (Figure 3.15(b) and (c)). After immersion, the number of micro-pits and the roughness of the substrate increased, while the depth of the micro-pits appeared to decrease slightly (Figure 3.15(d) and (e)). These results indicate that micro-pits were formed in addition to the previously existing micro-pits and that, concurrently, almost uniform corrosion occurred underneath the coatings in the medium. It is suggested that some micro-pits that grew faster than the others broke the coatings, grew in a lateral direction and formed visual filiform pits on the coated surface. Simultaneously, the corrosion proceeded underneath the coatings, which allowed the solution permeation.

3.4.3 Structure of the coatings after immersion

The OCP and HAp coatings after immersion for 52 weeks were observed with SEM. OCP plate-like and HAp rod-like crystals were thickened on the OCP and HAp

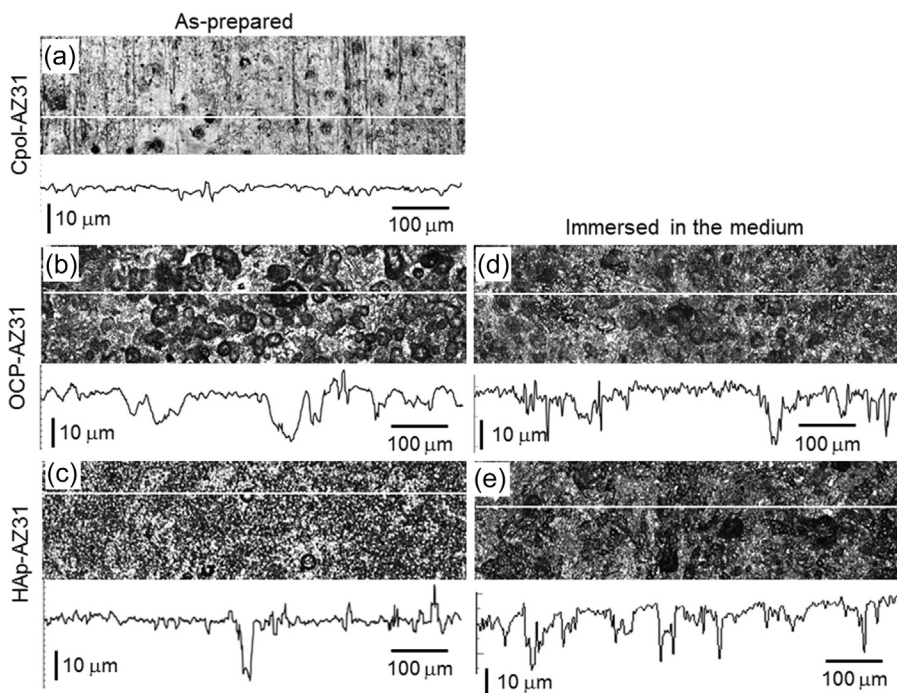


Figure 3.15 Laser reflectivity images and the corresponding profiles of (a) Cpol-, (b, d) OCP- and (c, e) HAp-AZ31 as-prepared (a)–(c) and immersed in the medium (d, e).

coatings, respectively. The two-layer structure remained after long-term immersion in the medium. Amorphous-like corrosion products deposited on Cpol-AZ31. According to XRD measurement before and after immersion, HAp deposited on OCP- and HAp-AZ31, while amorphous calcium phosphate deposited on Cpol-AZ31 and a part of OCP transformed to HAp. The remainder of the almost-original morphology of OCP and HAp coatings in the medium indicates that the coatings may remain for a long time also *in vivo*. The influence of the remaining OCP and HAp coatings on the surrounding tissues should be investigated *in vivo*. The influence of the surrounding tissues on the degradation of OCP and HAp coatings should also be investigated *in vivo*.

3.5 Short-term cell culture test on HAp-coated Mg alloy

Human osteosarcoma cells MG-63 were cultured on the pure Mg and AZ31 with and without HAp coating to evaluate the short-term biocompatibility (cell adhesion behaviour) (Hiromoto, 2013). Cell adhesiveness of pure Mg and AZ31 was not significantly improved with HAp coating (Figure 3.16(a)), while the ratio of dead cells to living cells decreased with HAp coating. The decrease in the ratio of dead cells is attributed to the remarkable suppression of the generation of H_2 gas bubbles with HAp coating. On the other hand, the low cell adhesion on HAp-coated surfaces is not attributed to the corrosion suppression of the magnesium substrate. Cells might adhere to the tip of rod-like HAp crystals in the outer layer because cells made focal adhesion on the edges of vertically oriented TiO_2 nanotubes (Park, Bauer, Von Der Mark, & Schumuki, 2007). On the TiO_2 nanotubes, the intervals (diameter of nanotubes) played an important role in cell adhesion and proliferation. Then, possibly because the tip of rod-like HAp crystals was too small and/or the distance between rod-like crystals was too large, the cells hardly made focal adhesion on the tips of rod-like HAp crystals. For the same reason, good cell adhesiveness cannot be expected on the OCP-coated surfaces since

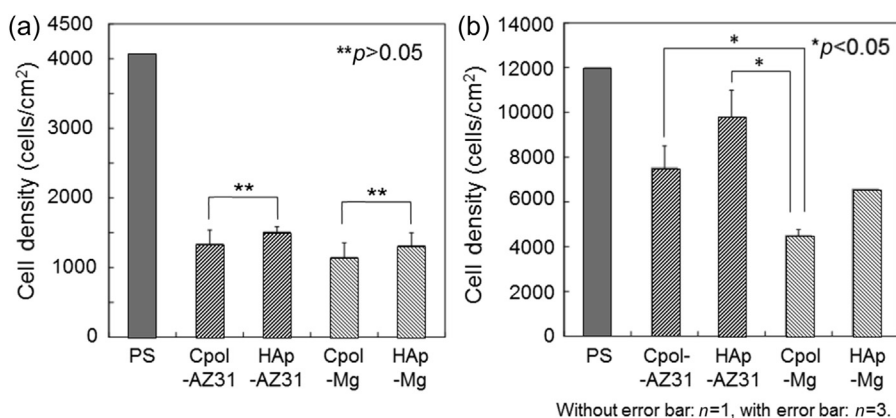


Figure 3.16 Density of human osteosarcoma MG-63 cells cultured on AZ31 and pure Mg with and without hydroxyapatite (HAp) coating for (a) 4 h and (b) 24 h. (PS, polystyrene).

the outer layer of OCP coating consists of plate-like OCP crystals, which expose the plate rims to the outside. Further adhesion behaviour of cells should be investigated to understand the low cell adhesiveness on HAp-coated surfaces.

After 24 h of incubation, cell density on HAp-Mg and AZ31 became higher than that on Cpol-Mg and AZ31, respectively, although the difference was not significant (Figure 3.16(b)). The ratio of spreading cells to round cells increased with HAp coating. These results indicate that the biocompatibility of Mg/Mg alloys can be improved with HAp coating. The cell density on HAp-AZ31 was higher than that on HAp-pure Mg, although the difference was not significant. This difference is attributed to the higher corrosion resistance of AZ31 than that of pure Mg. These facts suggest that the biocompatibility of HAp-coated Mg/Mg alloys is affected by the coating morphology and the corrosion of substrate Mg/Mg alloys.

3.6 Adhesiveness of the HAp coating under tensile load

Orthopaedic devices such as bone plates and wires are deformed to adjust the shape to that of the affected part of the patient during surgery. Therefore, good adhesiveness is required for the coating under the substrate deformation. HAp-AZ31 was deformed by a tensile load, and the fracture and detachment behaviour of the HAp coating to the substrate was evaluated (Hiromoto et al., 2013). The tensile test specimen was deformed by 5% and 12% of elongation (1.5% and 7.5% of residual strain, respectively; Figure 3.17(a)), the tensile load was removed and then the surface was observed with SEM. On the specimen surface with 5% elongation, neither crack nor detachment of the HAp coating was observed (Figure 3.17(b)). With 12% elongation, cracks were formed perpendicular to the tensile direction, and fragments of the coating became detached (Figure 3.17(c)). The lack of damage to the coating under 5% elongation (1.5% residual strain) demonstrated the good adhesiveness of the HAp coating to the substrate with plastic deformation under static loading. In the coating-detached area on the 12% elongated HAp-AZ31, the coating fracture occurred inside the boundary layer consisting of $\text{Mg}(\text{OH})_2$ and calcium phosphates. This indicates that the coating adhesiveness can be improved by reducing the boundary $\text{Mg}(\text{OH})_2$ layer. Reducing the coating treatment period may be one way to accomplish this.

3.7 Fatigue behaviour of HAp-coated Mg alloy

3.7.1 Fatigue behaviour in air

Many medical devices are used under a fatigue load during walking and pulsation. Therefore, influence of the coating on fatigue strength of the substrate Mg alloy should be understood. A fatigue test of HAp-AZ31 and as-polished AZ31 (Mpol-AZ31) (surface was polished with SiC paper) was performed in air, and stress amplitude—cycles to failure curves (S—N curves) are shown in Figure 3.18 (Hiromoto et al., 2013). Fatigue life in a low-cycle region slightly decreased, and fatigue strength at 10^7 cycles

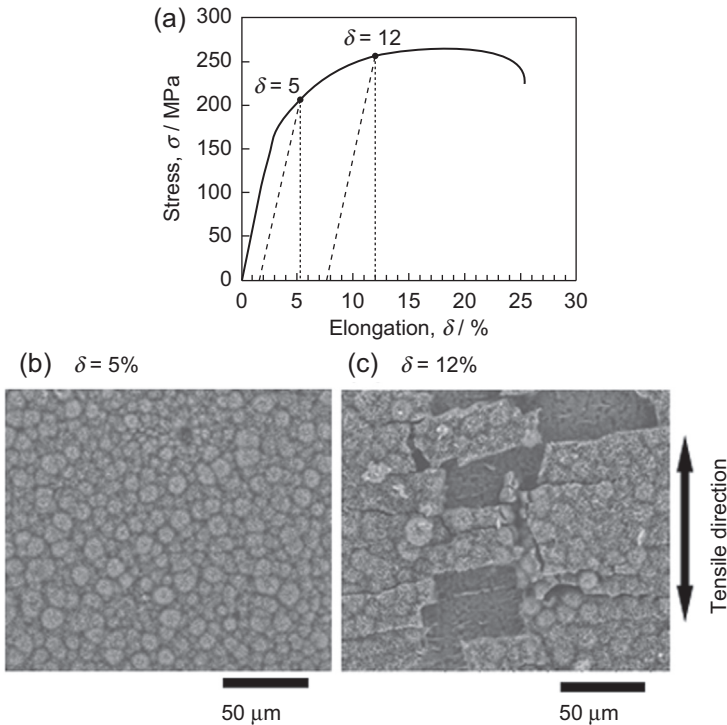


Figure 3.17 (a) Stress-elongation curve of HAp-AZ31. Scanning electron microscopy (SEM) images of the tensile test specimen surface after elongation by (b) 5% and (c) 12%.

From [Hiromoto et al. \(2013\)](#), with permission.

decreased by about 10% with the HAp coating. Since micro-pits were formed on the substrate AZ31 during the HAp coating treatment, as shown in [Figure 3.15](#), the decrease in fatigue strength was attributed to the micro-pits, which accelerate the crack initiation. Formation of micro-pits could be reduced with a dilution of the treatment solution (Ca-EDTA– KH_2PO_4 solution) and a decrease in treatment temperature ([Figure 3.4](#)). With a decrease in treatment temperature from 363 K to 333 K, the micro-pit density decreased on WE43 ([Figure 3.4](#)). Since the micro-pit density did not remarkably increase with an increase in treatment period, the coating can be thickened to obtain sufficient corrosion resistance by increasing the treatment period. It is thus expected that the fatigue strength of Mg/Mg alloys can be maintained after coating by improving the treatment condition.

3.7.2 Adhesiveness of the HAp coating under cyclic loading

The HAp coating of the test specimen that did not fracture over 10^7 cycles of loading showed neither crack nor detachment under SEM observation ([Figure 3.18\(b\)](#)). The fatigue strength at 10^7 cycles was about 80 MPa, which corresponds to 178 MPa of

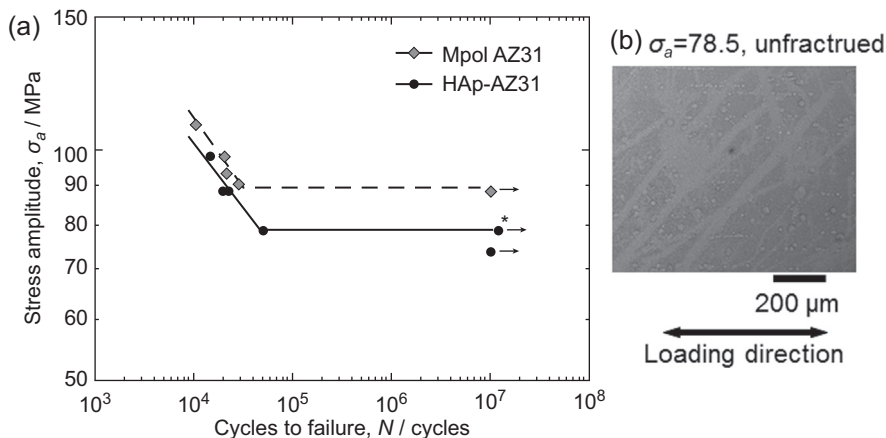


Figure 3.18 (a) Stress amplitude—cycles to failure (S–N) curves of AZ31 with and without hydroxyapatite (HAp) coating. (b) Scanning electron microscopy (SEM) image of surface of the test specimen unfactured over 10^7 cycles of loading. (*The surface of this specimen is shown in (b)) (Mpol, polished with #1200 SiC paper).

From [Hiromoto et al. \(2013\)](#), with permission.

the maximum stress in the fatigue test. According to the S–S curve of HAp-AZ31 ([Figure 3.17\(a\)](#)), the maximum stress of 178 MPa was slightly over the yield strength of 173 MPa, indicating that the first stroke of fatigue load was in the elastic region. Generally, Young's modulus (elastic modulus) of ceramics coating is higher than that of the metal substrate, and such a difference in Young's modulus causes detachment of the coating under the deformation of the substrate. No detachment of the HAp coating suggests that Young's modulus of the coating may not be so high.

Materials are generally used under stress below their fatigue strength. Therefore, the obtained results revealed that the HAp coating shows excellent adhesiveness that is sufficient for practical use. The excellent adhesiveness of the HAp coating is presumably attributed to the reaction between the substrate and coating treatment solution and the relatively low Young's modulus of the coating.

3.8 Summary and future perspectives

Well-crystallised OCP and HAp coatings were formed on Mg/Mg alloys by a novel chemical solution deposition method. A relatively high concentration of calcium chelate compound allows an initial rapid formation of a calcium phosphate coating, which further prevents the release of Mg ions from the substrate, leading to the formation of well-crystallised OCP and HAp on a Mg/Mg alloy substrate. The coatings showed a two-layer structure with a very thin intermediate layer between the coatings and the substrate. The continuous inner layer, which is responsible for corrosion protection, consisted of nano-crystals. The inner layer showed nano-pores when the pH of the treatment solution was low.

The OCP and HAp coatings could effectively improve and control the corrosion resistance of a Mg alloy. In the cell culture medium, the initiation of corrosion was retarded and the corrosion rate was reduced by about 50% with OCP and HAp coatings. The protective effect of the HAp coating was $\sim 20\%$ higher than that of the OCP coating. Filiform pits of a visible size were formed, and concurrently, quasi-uniform corrosion proceeded underneath the coating. While the original morphology of the HAp and OCP coatings outside of the visible filiform pits remained for 1 year in the medium, OCP crystals were partially transformed to HAp. The difference in degradation behaviour between HAp and OCP coatings would be useful for appropriate bone conductivity, depending on the implanted sites. To enhance this usefulness, influence of crystallinity and composition of OCP and HAp coatings on the bone conductivity should be examined.

The HAp coating showed excellent adhesiveness under static deformation of the substrate and under cyclic loading around the fatigue limit. The fatigue strength of the Mg alloy was not remarkably damaged by the HAp coating. These results indicate that the HAp coating shows sufficient adhesiveness for practical use, whereas the decrease in fatigue strength with the coatings should be reduced.

Controllability of corrosion behaviour, improvement of biocompatibility and good adhesiveness indicate that the OCP and HAp coatings developed have high potential for bioabsorbable magnesium alloys. To promote the practical use of the coatings, further *in vivo* and *in vitro* degradation behaviour and biocompatibility (including toxicity of corrosion products and the remnant coatings) should be examined as well as fatigue behaviour and wear and fretting wear behaviour in physiological environments.

Acknowledgements

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References

- Al-Abdullat, Y., Tsutsumi, S., Nakajima, N., Ohta, M., Kuwahara, H., & Ikeuchi, K. (2001). Surface modification of magnesium by NaHCO_3 and corrosion behavior in Hank's solution for new biomaterial applications. *Materials Transactions*, 42, 4.
- Bakhsheshi-Rad, H. R., Idris, M. H., & Abdul-Kadir, M. R. (2013). Synthesis and in vitro degradation evaluation of the nano-HA/ MgF_2 and DCPD/ MgF_2 composite coating on biodegradable Mg-Ca-Zn alloy. *Surface & Coatings Technology*, 222, 79.
- Bigi, A., Falini, G., Foresti, E., Gazzano, M., Ripamonti, A., & Roveri, N. (1993). Magnesium influence on hydroxyapatite crystallization. *Journal of Inorganic Biochemistry*, 49, 69–78.

- Fujishiro, Y., Sato, T., & Okuwaki, A. (1995). Coating of hydroxyapatite on metal plates using thermal-dissociation of calcium-EDTA chelate in phosphate solutions under hydrothermal conditions. *Journal of Materials Science-Materials in Medicine*, 6, 172–176.
- Fujishiro, Y., Yabuki, H., Kawamura, K., Sato, T., & Okuwaki, A. (1993). Preparation of needle-like hydroxyapatite by homogeneous precipitation under hydrothermal conditions. *Journal of Chemical Technology and Biotechnology*, 57, 349–353.
- Hiromoto, S. (2009). High corrosion resistance of magnesium coated with hydroxyapatite directly synthesized in an aqueous solution. *Electrochimica Acta*, 54, 7085–7093.
- Hiromoto, S. (2012). Biodegradable materials, present and prospects -Surface coatings for corrosion control of bioabsorbable magnesium-. *Materia Japan*, 51, 319–322.
- Hiromoto, S. (2013). Calcium phosphate coatings for bioabsorbable Mg alloys. *Journal of the Japan Society of Colour Material*, 86, 295–300.
- Hiromoto, S., Inoue, M., Taguchi, T., Yamane, M., & Ohtsu, N. In vitro and in vivo biocompatibility and corrosion behaviour of a bioabsorbable magnesium alloy coated with octacalcium phosphate and hydroxyapatite. *Acta Biomaterialia*. (in press).
- Hiromoto, S., & Tomozawa, M. (2010). Corrosion behavior of magnesium with hydroxyapatite coatings formed by hydrothermal treatment. *Materials Transactions*, 51, 2080–2087.
- Hiromoto, S., & Tomozawa, M. (2011). Hydroxyapatite coating of AZ31 magnesium alloy by a solution treatment and its corrosion behavior in NaCl solution. *Surface & Coatings Technology*, 205, 4711–4719.
- Hiromoto, S., Tomozawa, M., & Maruyama, N. (2013). Fatigue property of a bioabsorbable magnesium alloy with a hydroxyapatite coating formed by a chemical solution deposition. *Journal of the Mechanical Behavior of Biomedical Materials*, 25, 1–10.
- Ioku, K. (1996). Hydroxyapatite and related calcium phosphates as ceramic biomaterials. *Inorganic Materials*, 3, 412–418.
- Jo, J. H., Kang, B. G., Shin, K. S., Kim, H. E., Hahn, B. D., Park, D. S., et al. (2011). Hydroxyapatite coating on magnesium with MgF_2 interlayer for enhanced corrosion resistance and biocompatibility. *Journal of Materials Science Materials in Medicine*, 22, 2437–2447.
- Kanazawa, K., & Monma, H. (1995). Bioceramics -especially calcium phosphates biomaterials. *Shigen-to-Sozai*, 111, 199–204.
- Kasuga, T. (2010). Coatings for metallic biomaterials. In M. Niinomi (Ed.), *Metals for biomedical devices* (pp. 260–282). Cambridge, UK: Woodhead Publishing Limited.
- Keim, S., Brunner, J. G., Fabry, B., & Virtanen, S. (2011). Control of magnesium corrosion and biocompatibility with biomimetic coatings. *Journal of Biomedical Materials Research Part B-Applied Biomaterials*, 96B, 84–90.
- Khan, S. A., Miyashita, Y., Mutoh, Y., & Koike, T. (2008). Effect of anodized layer thickness on fatigue behavior of magnesium alloy. *Materials Science & Engineering A*, 474, 261–269.
- Kokubo, T. (1996). Formation of biologically active bone-like apatite on metals and polymers by a biomimetic process. *Thermochimica Acta*, 280, 479–490.
- Kuwahara, H., Al-Abdullat, Y., Mazaki, N., Tsutsumi, S., & Aizawa, T. (2001). Precipitation of magnesium apatite on pure magnesium surface during immersing in Hank's solution. *Materials Transactions*, 42, 1317–1321.
- Layrolle, P., & Daculsi, G. (2009). Physiocochemistry of apatite and its related calcium phosphates. In B. Leon, & J. A. Jansen (Eds.), *Thin calcium phosphate coatings for medical implants* (pp. 9–24). New York, NY: Springer.
- Leon, B., & Jansen, J. A. (Eds.). (2009). *Thin calcium phosphate coatings for medical implants*. New York, NY: Springer.

- Liu, Y. L., & Hunziker, E. B. (2009). Biomimetic coatings and their biological functionalization. In B. Leon, & J. A. Jansen (Eds.), *Thin calcium phosphate coatings for medical implants* (pp. 301–314). New York, NY: Springer.
- Ohtsu, N., Hiromoto, S., Yamane, M., Satoh, K., & Tomozawa, M. (2013). Chemical and crystallographic characterizations of hydroxyapatite- and octacalcium phosphate-coatings on magnesium synthesized by chemical solution deposition using XPS and XRD. *Surface & Coatings Technology*, 218, 114–118.
- Park, J., Bauer, S., Von Der Mark, K., & Schumuki, P. (2007). Nanosize and vitality: TiO₂ nanotube diameter directs cell fate. *Nano Letters*, 7, 1686–1691.
- Sato, E. (2007). General statement of magnesium alloy. In Y. Kojima (Ed.), *Handbook of advanced magnesium technology* (pp. 71–104). Tokyo: Kallos Publishing.
- Shaw, B. A. (2003). Corrosion resistance of magnesium alloys. In S. D. Cramer, & B. S. Covino, Jr. (Eds.), *ASM handbook, volume 13A corrosion: Fundamentals, testing, and protection*. Novelty, OH: ASM International.
- Song, G. L. (2011). *Corrosion of magnesium alloys*. Cambridge, UK: Woodhead Publishing Limited.
- Song, Y. W., Shan, D. Y., & Han, E. H. (2008). Electrodeposition of hydroxyapatite coating on AZ91D magnesium alloy for biomaterial application. *Materials Letters*, 62, 4.
- Song, Y., Zhang, S. X., Li, J. A., Zhao, C. L., & Zhang, X. N. (2010). Electrodeposition of Ca-P coatings on biodegradable Mg alloy: in vitro biomineralization behavior. *Acta Biomaterialia*, 6, 1736–1742.
- Tomozawa, M., & Hiromoto, S. (2011a). Growth mechanism of hydroxyapatite-coatings formed on pure magnesium and corrosion behavior of the coated magnesium. *Applied Surface Science*, 257, 8253–8257.
- Tomozawa, M., & Hiromoto, S. (2011b). Microstructure of hydroxyapatite- and octacalcium phosphate-coatings formed on magnesium by a hydrothermal treatment at various pH values. *Acta Materialia*, 59, 355–363.
- Tomozawa, M., & Hiromoto, S. (2011c). Microstructure, corrosion resistance and adhesive strength of calcium phosphate coatings formed on pure magnesium by a simple immersion method. *ECS Transactions*, 33, 31–37.
- Tomozawa, M., Hiromoto, S., & Harada, Y. (2010). Microstructure of hydroxyapatite-coated magnesium prepared in aqueous solution. *Surface & Coatings Technology*, 204, 3243–3247.
- Wen, C. L., Guan, S. K., Peng, L., Ren, C. X., Wang, X., & Hu, Z. H. (2009). Characterization and degradation behavior of AZ31 alloy surface modified by bone-like hydroxyapatite for implant applications. *Applied Surface Science*, 255, 6433–6438.
- Yoshimura, M. (2009). Feature and importance of solution processings for ceramics - nanoparticles, thin films, thick films, patterns and bulks. *Journal of Mining and Materials Processing Institute of Japan*, 125, 381–388.

Physical vapour deposition on Mg alloys for biomedical applications

4

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4.1 Introduction

The term ‘physical vapour deposition (PVD)’ was first laid on paper by C.F. Powell, J.H. Oxley and J.M. Blocher Jr. in their 1966 book *Vapour Deposition*. However, the PVD process is much older. Perhaps the earliest modern-day origin of this process can be attributed to Thomas Alva Edison, as the tungsten filament inside the original light bulbs evaporated at ‘low temperatures’ rendering the glass of static bulbs gradually opaque. Since those early days, this technology has come a long way, but still there are a number of limitations that need to be addressed if this process is to be used successfully at low deposition temperatures.

The most important characteristic of PVD processes is that deposition is conducted at substrate temperatures substantially lower than the melting temperature of the coating material (adatoms). Low-temperature deposition is usually an important advantage, as this makes the coating relatively insensitive to thermodynamic phenomena (Morton, 1992) and greatly extends the applicability of this technology. Apart from the increased flexibility in terms of attainable structures and chemical composition, the ability to coat at low to moderate substrate temperatures is particularly attractive if the coating is to be deposited on temperature-sensitive materials such as magnesium and its alloys. This advantage, however, comes at great costs, and a lot of effort has gone into the development of useful low-temperature PVD technologies. To understand the problems associated with coating at low substrate temperature, one must delve into the mechanics of this deposition process. In this chapter I will try to briefly convey the principles of this technology and the workarounds required for its applicability to Mg alloys, without going into elaborate analytical investigations. I will include various references where needed for those who want a deeper understanding of this complex subject.

4.2 The physical vapour deposition process and its limitations

In its most basic form, physical vapour deposition involves the evaporation of a condensable material and its subsequent condensation on a substrate surface. The coating material, often referred to as condensable material, is vaporised from a source (slug or

target). The source material is situated a short distance away from the object to be coated, known as the substrate. The vapour is obtained by exposing the source (solid or liquid) to very high temperatures/kinetic energy (Mahan, 2013; Mattox, 1998). The condensable material enters the vapour state and travels in vacuum in straight lines (flux) until it collides with a cold surface. As soon as the condensable vapour reaches a cool surface, the small agglomerate of atoms/single atoms start to hop on the surface and rapidly lose their kinetic energy, a process known as lateral mobility or surface diffusion. These eventually cool and condense on the surface to form a solid film. The lateral mobility of adatoms on the surface has an enormous influence on the structure, adhesion and mechanical properties of the resulting coating (Anders, 2006). Depending on the condensable material deposited, for a reasonably dense coating a deposition temperature ranging from 380–550 °C or even higher is needed. Plasma-enhanced processes can achieve good results at lower temperatures, as in these processes the thermal energy is augmented by the impact of the energetic ions on the surface. This process is carried on until sufficient atomic layers (coating thickness) are deposited on the substrate surface to satisfy the particular requirements of the intended application.

If the substrate material is sensitive to heat, it is still possible to deposit material at lower temperatures, even at room temperature. At low substrate temperatures, however, the ability of the adatoms/agglomerates to hop around on the substrate surface in search of an active site on the surface (atomic ledge or point defect) is greatly reduced. The inability to diffuse on the surface makes the condensable material pack loosely, not unlike flocculates of snow on a very cold day (Itoh, 1989). As the first mounds of atoms form on the surface, these obstruct the path of the rest of the straight-moving flux, resulting in shadowing of a large number of spots on the substrate surface. The combined effect is a type of growth known as columnar growth, often resulting in a loosely bound and open fibrous surface. The diameter of the growing columns often shrinks, with coating thickness yielding tapering columns. At moderate substrate temperatures and if adequate mechanical support is provided by a clean substrate, this intrinsically porous film generally provides reasonably good wear resistance but is unable to protect the substrate from corrosion, and in some cases the coating material actively accelerates corrosion by exchanging electrons with the environment (Hoche, Scheerer, Probst, Broszeit, & Berger, 2003).

The inability of atoms to diffuse on the surface of the substrate results in yet another serious problem. This is a direct result of the nature of the metallic bond that makes metal surfaces have a significantly higher free energy state than that of the bulk material. This is true for all solids and liquids, but the difference in metals is usually perceptibly bigger (Vitos, Ruban, & Skriver, 1998). The high surface energy results in physically absorbed (physisorbed) contaminants on metallic substrate surfaces as soon as these are exposed to the environment. The film is usually composed of polar and electrophilic molecules such as water and oxygen. The latter, due to its highly electronegative nature, eventually strip electrons from the metallic surface and forms chemical bonds, becoming chemisorbed.

When coating at low temperature, the movement of the adatoms through the physisorbed film is very sluggish if there is any movement at all. This usually results

in a loosely bound film with lots of impurities and defects (Busk, 1987). This is because as the adatom flux reaches such a contaminated surface at low temperature, the vapour cools very fast and it is unable to displace the loosely bound molecules on the surface. The adatoms are pinned in place, resulting in a very fine texture and often weakly bound coatings, possibly even in a fall off (coating flaking off the surface spontaneously on cooling). In some cases, the coating adheres to the oxide layer on the surface; in such cases, the weak oxide film is not able to provide adequate support to the coating on top and will give rise to adhesion problems. This problem is greatly exaggerated at low temperatures and medium to high vacuum, where the desorption rate of the physisorbed gases is several orders of magnitude lower than their arrival rate and their sticking coefficient onto the exposed metal is very high (Abela, 2007). In modern PVD deposition techniques like magnetron sputtering techniques, the condensable material has much higher energies; this helps condensable material to mitigate those problems. However, even in those cases and when depositing at room temperatures, the high arrival rate and sticking coefficient of contaminants can result in a lot of contamination, grain boundary pining and extensive porosity. The end result is a 'spongy' soft coating with generally better corrosion protection characteristics but comparatively weak mechanical properties. This effect is noticeable even at chamber pressures as low as 1×10^{-7} mbars. In order to mitigate this problem as much as possible, this process has to be conducted at very low pressures.

In ultra-high vacuum, the vapour flux suffers little collisions (scattering) on its way to the substrate and the surface takes a long time to be contaminated, allowing the successful deposition of dense coatings even at room temperature. The corrosion protection provided by such coatings is, however, limited by the line-of-sight (LOS) problem. This LOS problem becomes chronic in UHV. This complication limits the complexity of the components that can be successfully coated and requires the use of elaborate gigging and substrate manipulation during processing (Mahan, 2013).

To complicate matters even further, Mg, Al and some Ti alloy substrates are too soft to provide adequate support for the hard coating, giving rise to the thin-ice effect. This means that for adequate tribological performance, thicker or multi-layer coatings must be deposited. These problems on their own make it very difficult to successfully apply PVD coatings directly on top of magnesium substrates; however, there are ways and means to mitigate these problems and create hard and dense coatings for various applications.

4.3 Physical vapour deposition at low temperatures to suit magnesium alloys

Metallic magnesium can play an essential role as biomedical application materials for bone and for dental or vascular implants (Niinomi, 2002). Compared with ceramics or polymeric materials, metals are more suitable for load-bearing application due to their attractive combination of high mechanical strength and fracture toughness. The general requirements for biomaterials besides non-toxicity include biocompatibility, mechanical properties, ease of manufacturing, reproducibility and stability.

Much effort is focusing on the design, synthesis and fabrication of the biomaterials and devices to ensure that they have the appropriate set of properties and functionality (Yang, Cui, Lee, & Wang, 2010), properties in which magnesium and its alloys excel. The only problem with this metal is its poor corrosion resistance, especially in chloride ion-containing environments (Antunes & de Oliveira, 2012; Mandl & Rauschenbach, 2000). Surface engineering of this metal would make it a suitable candidate as a biomaterial. Plasma surface modification techniques combining the advantages of conventional plasma and ion beam technologies are effective methods for medical implants with complex shapes (Mandl & Rauschenbach, 2000; Sodhi, 1996).

The low melting temperature of magnesium metal poses serious limitations on the applicable surface engineering processing techniques. The stability of the structure and exterior dimensions during processing cannot be guaranteed if magnesium and its alloys are exposed to temperatures in excess of 250 °C (Avedesian & Barker, 2007; Polmear, 1995). In most cases, the optimal deposition temperature to prevent solid-state reactions inside magnesium alloy substrates is even lower (Meshinchi, 2011). This makes the PVD coating of magnesium alloys for any application challenging to say the least. The biggest challenges in PVD coating of Mg substrates are the control of the deposition temperature and then the good adhesion under the low-temperature conditions. In this application, because the substrate cannot be heated to enhance surface diffusion, the only PVD processes that can be used are those in which the energy required for lateral mobility is mostly supplied by the plasma or high-energy flux (condensable flux, ion beam). These include plasma-enhanced PVD (PEPVD), sputter deposition, ion beam sputter deposition (IBSD), ion plating, ion beam-assisted deposition (IBAD), reactive ion beam-assisted deposition (RIBAD) and plasma immersed ion implantation and deposition (PIIID). IBAD, RIBAD and PIIID actually represent an evolution of the more traditional PVD processes, where PIIID is the current pinnacle of this evolution. These innovative processes are designed to supply the bulk of the energy required for coating densification through the ion beam and condensable material eliminating the need to heat the substrate altogether. In fact, in these processes, it is often required to cool the substrate to keep the temperature from rising uncontrollably.

In the past few decades, plasma processing of materials has matured at an incredible rate. Since the first international conference on plasma surface engineering, held on the 19–23 September 1988, in Garmisch-Partenkirchen, the current state of technology has made unprecedented strides. As early as 1989, low-temperature ion-assisted film growth processes were already predominantly forcing their way into the fabrication of microelectronic devices.

Ion beam-assisted deposition (IBAD), also referred to by some scientists as ion beam-enhanced deposition (IBED), is a combination of two surface treatment processes, namely, physical vapour deposition (PVD) and ion implantation (Anders, 2006; Deutchman & Partyka, 2002; Itoh, 1989; Klingenberg, Arps, Wei, Demaree, & Hirvonen, 2002). The deposition process is usually accountable for the material build-up, while the ion flux imparts the kinetic energy required to achieve adhesion and the required coating properties (Deutchman & Partyka, 2002). The kinetic energy imparted by the ion beam activates a number of processes on the surface of the growing film. Surface atoms are displaced, enhancing migration of atoms along the

surface and thereby increasing the coating density even at low deposition temperature. The ion beam also provides the required stitching (ion beam mixing) of the coating to the substrate at a low temperature (Itoh, 1989, pp. 170–179). This enables this process to be applied to a wider range of materials. Furthermore, accurate tuning of the ion to condensable flux ratio enables the control of coating stoichiometry, structure and residual stresses (Anders, 2006, pp. 177–209).

The main difference between IBAD, RIBAD and PIID deposition techniques and other ion-assisted deposition processes is that, in the former, the energetic ion source and the condensable material flux source are separated into two distinct devices. Thus these processes allow better control over these parameters independently. In comparison, in other plasma-based deposition techniques such as DC and RF magnetron sputtering and the PEPVD techniques, the condensable material and ion fluxes are extracted from the same plasma source. This feature gives the ion beam-assisted processes more control over the deposition parameters, as compared to other deposition processes, resulting in better coating properties (Emmerich, Enders, & Ensinger, 1992).

Another important difference is the operating pressure. Plasma-assisted coatings usually operate between 1×10^{-2} to 13 mbar, which is the pressure required to sustain a plasma. In contrast, IBAD techniques usually operate in high vacuum, between 2×10^{-6} and 2×10^{-10} mbar. This is mainly due to physical limitations of the hardware and mean free path restrictions (Mändl, Brutscher, Günzel, & Höller, 1996). As IBAD techniques operate in the collision-free pressure regime, the evaporate and the ion beam travel in straight lines (line-of-sight) to the substrate. This is a serious limitation of the IBAD process, which restricts the complexity of the parts that can be treated. This serious limitation is tackled in the PIID process, which is an evolution of the IBAD process. In this process the substrate is immersed in cold plasma and high-voltage pulses are applied. However, in PIID the chamber pressure is usually a bit higher.

Conventional plasma-assisted deposition techniques allow for the deposition of coatings with thickness ranging in the tens of microns. However, the interface between the coating and the substrate is often very thin (Mahan, 2013), especially when the process is conducted at low temperatures. Frequently, this results in poor coating adhesion, particularly for coatings thicker than 3 microns. Ion beam mixing can potentially solve this problem. In this process, the substrate is coated up to a thickness that is shallower than the penetration depth of the ions. This thickness is dependent on the maximum available ion energy. The newly formed surface is subsequently ion implanted such that the original interface is broadened by the ballistic effect of the ion beam, as shown in Figure 4.1 (Hopf, Jacob, & von Keudell, 2005; Emmenrich et al., 1992).

The resulting coating is very shallow, in the range of 0.2–0.5 μm , but the physical properties are vastly superior to those produced by traditional methods. This shallow coating provides an excellent foundation for additional coatings. By combining ion irradiation and deposition, IBAD allows for the deposition of relatively thick coatings (sometimes more than 100 μm) with excellent adhesion. In addition, it provides a means to control the residual stresses, as well as the texture of the coating produced.

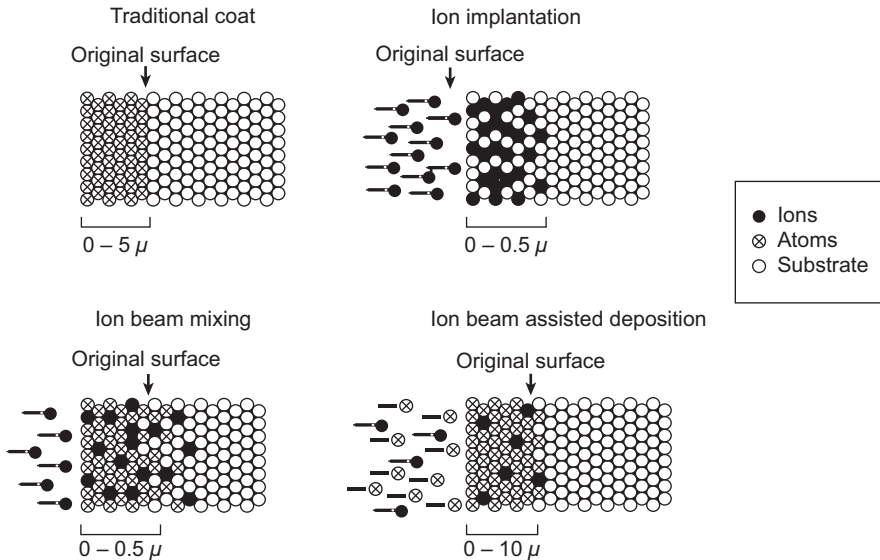


Figure 4.1 Ion beam deposition processes.

From Enders, Emmerich, and Ensinger (2000).

There are two principal ways to carry out IBAD process. The coating can be deposited under simultaneous or alternating ion bombardment. In the first case, low-energy ion sources with no mass separation are used, such as the broad-beam Kaufman type. In the second case, a higher energy is required, depending on the thickness deposited between each irradiation interval. The increment in thickness on each successive pass is usually a few tenths of a nanometre. In both cases, the typical energy range used for IBAD/RIBAD is 100 eV to 30 KeV. When higher energies are used, decomposition of the deposited compounds occurs and the coating structure is damaged, often resulting in the disruption of the crystalline structure. This is particularly the case in the RIBAD process (Möller, Fukaren, Lange, von Keudell, & Jakob, 1995).

These plasma-enhanced processes offer numerous other advantages when it comes to depositing coatings at low temperature, foremost of which are more tolerance to substrate contamination, better control of film chemistry and morphology, very good adhesion, conformal and pinhole-free films and very dense coatings yielding excellent permeation barriers with a low level of leachables; the extremely energy-rich deposition environment yields sterile components upon preparation (Ratner, Chilkoti, & Lopez, 1990).

An alternative deposition method at low temperature is the sputtering of condensable material from a target, which is situated in front of the substrate. This can be accomplished either by magnetron sputtering or ion beam sputter deposition (IBSD). Sputtering methods usually result in low deposition rates and require ultra-high vacuum to limit coating contamination from the residual gas and the loss of kinetic energy of the adatoms due to collisions with the residual gas molecules in the deposition chamber and on the substrate surface. The high kinetic energies of the adatoms (in the range of

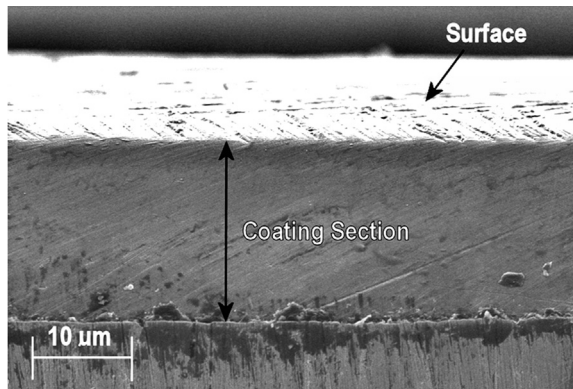


Figure 4.2 A sectioned IBSD Al_2O_3 coating, deposited on AM50 magnesium alloy at room temperature, by sputtering Al with O_2 for 432 h, showing a ‘thick’ and uniform coating. From [Abela, 2007](#).

100 eV) impart excellent adhesion and coating densification, resulting in superior wear and corrosion protection ([Valvoda, 1996](#)). It is because of this high adatom kinetic energy that sputter deposition can be conducted at lower temperatures than other traditional physical deposition process ([Wasa & Hayakawa, 1992](#), pp. 65–78). The high adatom kinetic energy results in self-sputtering of the growing film and permits the deposition of stress-free thick coatings at low temperature ([Figure 4.2](#)).

The choice of a suitable method/process would be based on many factors, including the substrate material, component design and geometry, cost and the end applications. These usually translate to parameters such as coating thickness and process temperature, which often narrow down the choice to a specific process ([Yang et al., 2010](#)).

4.4 Film structure

The early growth of thin films is a result of the interaction of adatoms with the substrate surface and with each other. Other kinetic effects such as nucleation, surface diffusion and atomic interactions with surface imperfections such as dislocations, ledges and kinks ([Venables, 2000](#) pp. 108–141) are also important. There are three main categories of models for the early growth of thin films. The Frank-van der Merwe (F-M) model represents a layer-by-layer growth. In this model, a continuous monolayer covers the substrate surface, and this is covered by additional layers as the coating grows. In the Volmer-Weber (V-W) or island growth model, deposition processes occur in which the atoms tend to aggregate into islands on the surface. These islands can be several atomic layers high before the substrate surface is completely covered.

The mode of growth in the early stages of film formation is very important, as this influences subsequent film formation in the stationary growth phase. It controls whether the coating will be porous or columnar, as described by the V-W growth model, or epitaxial, as in the F-M growth model. It is not uncommon, however, that during film growth in the F-M model, the growth switches to the V-W model after

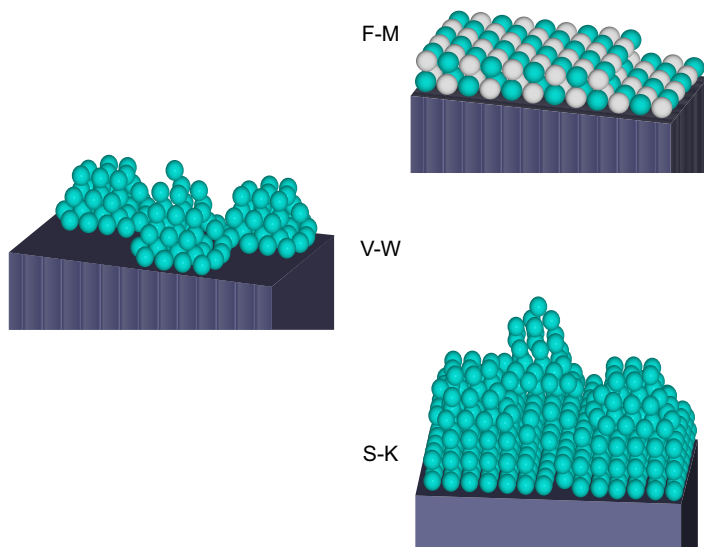


Figure 4.3 Early film growth models.

a few monolayers have formed. This is believed to happen because of the progressive build-up of internal stresses. When processes display a combination of these two extreme behaviours, the Stranski-Krastanov (S-K) models are used. These three growth models are illustrated in [Figure 4.3](#).

Ion bombardment is known to influence the mode of growth ([Mattox, 1998](#)). The most obvious effect is the creation of surface defects, as a direct consequence of the ballistic effect. These defects may behave in two different ways depending on the substrate temperature. If the temperature is high enough, then the additional strain energy provided by the surface defects may result in enhanced surface diffusion (lateral mobility). This situation tends to favour the V-W type of growth. At lower temperatures, the defects created by the ion beam reside on the surface for a long time, providing a very large number of nucleation sites. This, in turn, favours the F-M growth model. However, if the stress induced by the ion beam in the growing film is too high, the growth mode changes from F-M to S-K with subsequent deposition. Also, high-energy ion bombardment may completely dissolve the small grains nucleating on the surface, leading to amorphous layers or significant lateral coarsening of islands ([Anders, 2006](#), pp. 182–183). [Figure 4.4](#) summarises the various effects of ion bombardment on the growing film. Surface defects such as adatoms (A) or vacancies (V) may be generated, onto which nucleation takes place. Atomic collisions enhance mobility ([Inoue, Kawamura, Matsushita, Hayashi, & Koike, 2001](#)) (M) or dissolve smaller, less stable islands (D).

Two additional outcomes, which are not included in [Figure 4.4](#), are the atomic mixing effect, which is more pronounced at high ion beam energies (100 KeV), and the chemical activation effect ([Smith, 1995](#), p. 406). The latter feature is very important in the synthesis of nitrides using this process, where nitrogen molecular ions are used to irradiate the growing film. Upon collision, the N_2^+ molecular bond breaks,

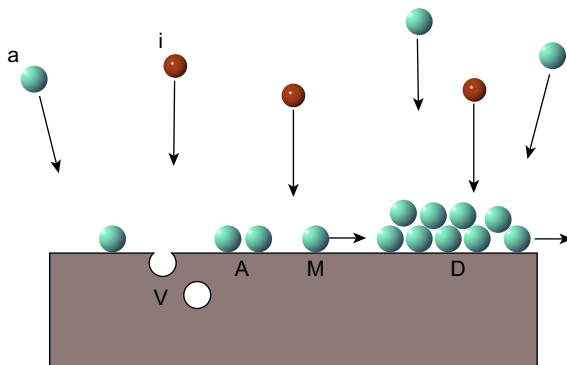


Figure 4.4 Ion bombardment effects in ion beam-assisted deposition processes.

forming two monatomic reactive radicals, available for nitride formation. In this case, the diatomic molecule behaves as two monatomic particles each having, roughly, half the energy of the original molecule less half the energy required to break the molecular bond (European Material Research Society, 1995, pp. 1–11).

The ion beam will also activate adsorbed contaminants from the residual gas. Consequently, from a chemical point of view, these processes are more sensitive to contamination than thermal-activated processes, as at low temperature contaminants tend to reside longer on the substrate surface. The final outcome of these conflicting effects is strongly dependent on the individual film–substrate combination. Some process parameters also have a significant influence on the morphology of the film produced, the most influential of which are described next.

An increase in substrate temperature favours growth to nucleation, driving the process towards the V-W mode and generally resulting in film coarsening.

The effect of ion energy is somewhat difficult to predict, as it changes drastically in different energy regimes. The ion energy required to generate a superficial Frenkel defect is just about half of that required to produce a bulk defect. Hence, it is possible to create the required surface defects without damaging the bulk structure of the coating. This operating window is very important for the deposition of epitaxial layers, where the integrity of the bulk of the coating material is important.

Last, but not least, in importance is the ion beam to condensable flux ratio, which controls the energy input to the growing film. This parameter is normally used to control the stoichiometry of the growing film. However, numerous researchers have demonstrated that this parameter has a strong influence on the texture of the coatings produced.

The bulk film structure and properties will be influenced by the seeding process, during early film formation. The microstructure of metal films can be schematically depicted using a structural-zone diagram. When the processing temperature is low, compared to the melting temperature (T/T_m), low surface mobility results. The resulting film is consequently fine grained, partly porous and has a relatively rough surface (zone 1). In zone 2, growth is initially by the V-W mode, but due to surface recentralisation caused by thermal energy, it subsequently changes to a columnar structure. In zone 3, the high temperatures involved result in bulk diffusion, grain boundary migration and the formation of large grains (Mattox, 1998 pp. 470–487).

Increasing ion bombardment intensity has the effect of extending the T zone to lower temperatures. This is due to the increased surface mobility, induced by the ballistic effect of the ion beam. It is worth noticing that the effect of ion bombardment on zones 2 and 3 in particular is barely noticeable. This is because the long-range mobility imparted to the adatoms in zone 2 by thermal activation, and to the bulk structure in zone 3, is far more influential than the short-range motion imparted by the knocking effect of high-energy ions on the surface. In other words, the effect of ion bombardment is only important where there is not enough thermal energy to drive surface and bulk diffusion (Anders, 2006, pp. 185–187).

Surface features as small as 10 nm have an influence on the adhesion of cells to the surface (Dalby, Riehle, Johnstone, Affrossman, & Curtis, 2004). When a biomaterial comes into contact with a biological system, for example by implantation in the human body, proteins spontaneously adsorb onto the surface. The resulting surface-bound protein layer is influenced by the surface properties of the biomaterial (Kasemo, 2000). The geometrical and chemical properties of biomaterial surfaces direct cellular functions such as cell migration and proliferation, modulate phenotypic differentiation and alter the responsiveness to extracellular signals. This phenomenon is a direct consequence of the different physical and chemical properties of surfaces that are often dependent on the grain orientation of crystalline solids. C. (Rungsiyakull, Li, Sun, Li, & Swain (2010)) looked for a relationship between the surface morphology-induced micromechanics and bone remodeling responses to a solid bead-coated porous implant in order to develop an objective optimisation framework for the coating design of biomaterials. In this study it was concluded that the optimal design parameters of particle diameter and volume fraction are 100 micron and 35%, and 38 micron and 17.5%, for the cortical and cancellous bones, respectively. These findings agreed well with clinical data. In their publication, these researchers recommend specific surface coating designs for particular locations in order to maximise the implant/bone interfacial stability. Lorda, Fossb, and Besenbacherb (2010) published an excellent review of different methods to synthesise and fabricate surfaces with well-defined nanoscale topography. They also explored the way in which these nanostructured surfaces can be used as model systems in protein and cellular assays.

The scientific knowledge in this area is growing at a fast rate and the author is not going to try to give an in-depth review of this topic as it is outside the area of his expertise. What the author wants to point out is that we have the knowledge and the means to control the surface morphology of coatings. If the deposition chamber is equipped with the necessary hardware, it is possible to create deposited surfaces designed to be better compatible with particular types of cells.

4.5 Controlling material degradation through intelligent design of PVD coating

The role of PVD processes in Mg surface finishing can be divided into two sections: the deposition of extrinsic wear and corrosion protection coatings and the creation of new high-purity Mg alloy surfaces with improved corrosion resistance (Yamamoto,

Watanabe, Sugahara, Tsubakino, & Fukumoto, 2001; Yang et al., 2010). For the PVD coating of Mg substrate, the major challenge is to control the deposition temperature while ensuring good adhesion at low temperature. Numerous researchers have shown that the deposition temperature can be significantly reduced by applying a pulsed bias voltage or by the concurrent bombardment with energetic ions during deposition (Ensinger et al., 1992; Jin et al., 2006).

Besides the most obvious process parameters, there are a number of important choices when designing a coating process that can have a significant impact on the coating properties. Substrate surface roughness, in situ substrate cleaning, chamber pressure and source of condensable material are all important parameters that are often overlooked.

4.5.1 *In situ cleaning*

The very first step in a surface engineering process is the preparation of the substrate surface. When dealing with thin coatings the surface roughness needs to be controlled as it can affect the coating integrity deleteriously. This is particularly so for PVD processes due to the shadowing effect of the hills on a rough surface, which would seriously compromise adhesion and the fatigue performance of a coating. When dealing with low-strength alloys such as magnesium alloys, fatigue is a very prominent issue. Chao and López (2007) reported that nearly 90% of the surface fractures of cement-less hip prostheses manufactured with Ti–6Al–4V alloy were due to fatigue mechanisms.

Surface cleanliness is even more important, as it has a more profound effect on coating adhesion. When coating magnesium and its alloys, the weakly adherent natural magnesium oxide must be cleaned from the surface of the substrate. This step is required in order to enhance the adhesion of the coatings, prior to commencement of the deposition process. Magnesium oxide present on the substrate is a weak link in the coating system and is thought to be responsible for poor coating adhesion. R.S. Busk (1987) describes this oxide as unstable, due to a misfit between the lattices of the cubic oxide and that of the hexagonal metal, resulting in a Pilling-Bedworth factor less than 1. In addition, when exposed to humid atmosphere, magnesium oxide reacts to form hydroxide, further compromising coating adhesion. While investigating plasma surface treatment of magnesium alloys, Hoche et al. (2003) have shown that the presence of magnesium oxide at the interface of a hard coating is detrimental for the coating hardness and adhesion. They suggest that the weak bond of the MgO with the parent metal inhibits the formation of compressive stresses in hard coatings deposited on top of the MgO, resulting in lower hardness and adhesion.

In order to enhance the adhesion of the IBAD and RIBAD coatings, it is necessary to clean the substrate from the weakly adherent magnesium oxide; the author conducted an investigation to establish the effect of substrate cleaning on coating performance. In an attempt to establish the optimum pre-sputtered time, the substrates were first irradiated for an increasing period of time. The samples were pre-sputtered and then coated with TiN. This coating was built by successive deposition layers of Ti (100 nm), which were post-implanted using nitrogen ions, prior to depositing the next Ti layer.

The effect of pre-sputtering time on coating properties was investigated using the pin-on-disc tribo-test. The test criterion was the time required for the pin to expose the substrate. The obtained results show that as the sputtering time is increased from zero to approximately 10 minutes, there is a very rapid increase in coating endurance, from about 20 s up to 156 s. This effect is believed to be due to the sputter cleaning of the weak oxide film and the generation of a large number of point defects on the specimen's surface that later act as nucleation sites supporting film growth. A further increase in pre-sputtering time to 20 minutes leads to a marked reduction in scatter of results, even though the average coating endurance remains constant. Pre-sputtering beyond 20 minutes, however, results in a rapid reduction in the endurance of the film and reaches a minimum at approximately 75 min. [Yongquin, Xiaodong, et al. \(1997\)](#) and [Yongquin, Zhu, et al. \(1997\)](#) investigated the IBSD of TiN on Si substrates. In their case, pure ion beam sputter deposition yielded the poorest adhesion. Pre-implanting the substrate surface for 1 h with the N⁺ beam yielded better results, yet they found that even better adhesion was achieved when the pre-sputtered time of 30 min was used.

The loss in coating performance due to prolonged pre-sputtering is believed to be due to the preferential sputtering resulting in induced surface roughness. Various micrographs of sectioned specimens reveal the presence of deep cracks just below the coating/surface interface, as shown in [Figures 4.5–4.7](#). It was observed that the material at the grain boundaries sputtered preferentially, leaving relatively deep cracks in the substrate surface.

[John A. Thornton and Joseph E. Greene \(1994, pp.292–295\)](#) also described the roughening of magnetron sputtering compound targets by the preferential sputtering of certain elements or phases. These investigators refer to this process as 'cone formation', due to the presence of patches on the surface, which have lower sputtering yield than the rest.

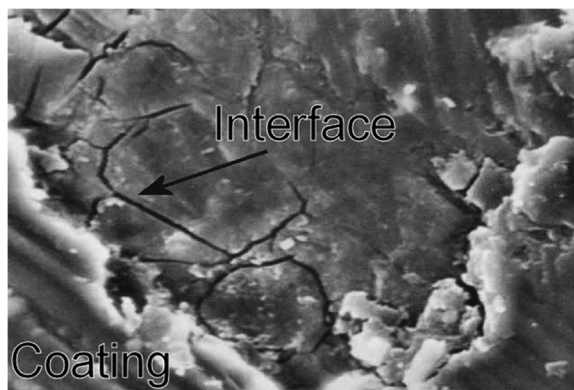


Figure 4.5 SEM micrograph of a TiO₂ coating on an AM50 substrate, pre-implanted for 90 min with O₂. The specimen is sectioned at 3° to the surface, to reveal loose grains just beneath the coating. (X5K.)

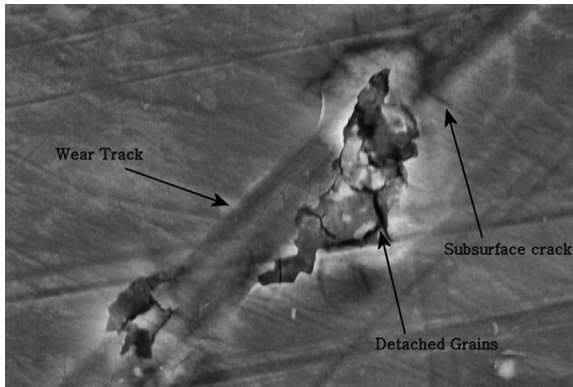


Figure 4.6 SEM micrograph showing a wear track on Al_2O_3 coating deposited on AM50 substrate pre-implanted for 90 min with O_2^+ , showing a dislodged portion of the coating exposing cracks in the underlying substrate. (X5K.)

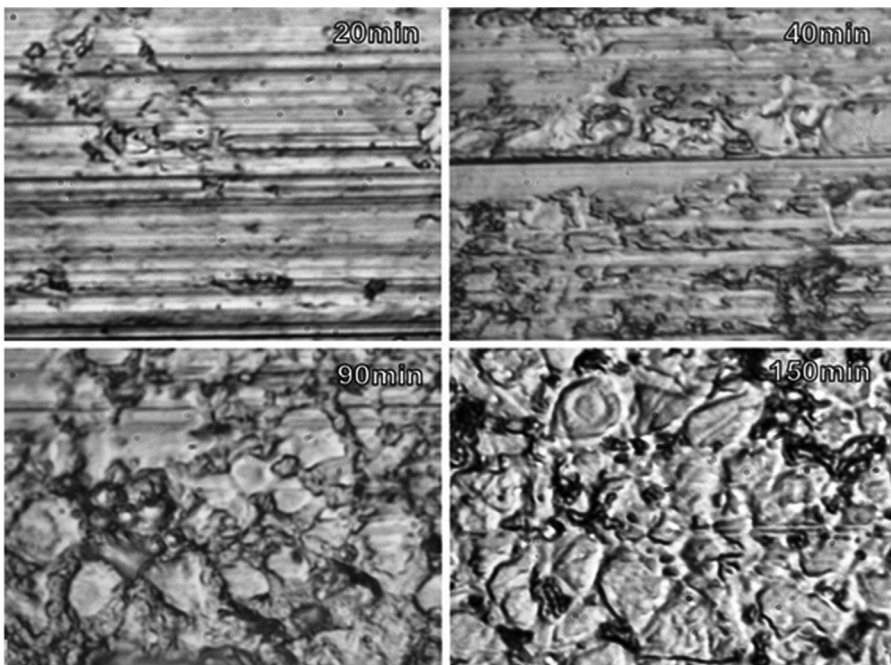


Figure 4.7 500X optical micrographs of shallow ($0.5\ \mu\text{m}$) Al_2O_3 -coated substrates pre-implanted for periods varying between 20 and 150 min. (X1K.)

The mechanisms leading to the formation of surface roughness were investigated by Andreas Friedrich and Herbert M. Urbassek (2003), who used a series of molecular dynamic simulations to investigate the effect of the presence of ledges and interfacial defects on the sputtering yield. Amongst their findings, these investigators found that

at room temperature, the sputtering yield of metals irradiated with particles having energies in the KeV range, and impinging at sharp angles, is significantly higher in the vicinity of interfacial defects, further increasing the surface roughness. This phenomenon is independent of the type of coating deposited on the surface.

To understand the reason why the material at the grain boundaries is being sputtered at a much faster rate than the material in the central region of the grain, one has to consider the structural and chemical differences between these two regions. The most obvious difference is that at the grain boundary there are more atomic vacant sites, resulting in a less ordered crystal structure and weaker bonding. The difference in chemical composition between the core and the grain boundaries is even more important. This is brought about by the preferential growth of the Mg-Al-Fe along the grain boundary. Research conducted at Hydro Magnesium ([Hydro Magnesium headquarters, 2005](#), pp. 1–12) reported that in the case of AM50 as well as other Mg-Al-Zn alloys, corrosion starts at the Mg-rich areas, which are at the centre of the grains, and then it propagates to the grain boundaries in the form of pits where it is stopped by the Al-rich phase, situated along the grain boundaries. Data published by the above-mentioned company shows that in AM50 alloys, these precipitates contain Fe and Mn atoms, in the form of complex aluminates at the grain boundaries. These intermetallic compounds, AlMn_xFe_y , have a cubic structure and contain 15–35% Fe (55.84 amu) and 15–35% Mn (54.94). The presence of such a high concentration of heavy elements in a light metal matrix gives rise to a process known as yield amplification during sputtering. Accelerated sputtering only takes place in regions rich in Fe and Mn, which have a higher-impact cross-section, resulting in the roughening of the surface. The loss of Al and Mg leads to precipitates containing more Fe and Mn, rendering the substrate more susceptible to galvanic corrosion. [Berg & Katardjiev \(1999\)](#) explain how a small percentage of impurity content of atoms, which are significantly heavier than those of the host, leads to an increase in sputtering rate up to two orders of magnitude higher than that of the pure substance.

In order to investigate further this sputtering effect on the substrate surface, a number of experiments were conducted, in which the substrates were pre-sputtered for increasing durations. Immediately following the pre-sputtering, and before breaking the vacuum, the specimens were coated with transparent IBAD alumina. This served to protect the substrate surface from the atmosphere and hence preserve the sputter-generated morphology on the substrate surface. Precipitates rich in Fe and Mn made the sputtered surface particularly susceptible to galvanic corrosion; thus, protecting it from the surrounding atmosphere was especially relevant. The morphology of the substrates produced in this series of experiments is illustrated in [Figure 4.7](#). This shows significant preferential sputtering at the grain boundaries leading to surface roughening, as described by Thornton and Joseph E. Greene. In these experiments, the substrates were pre-sputtered for 20, 40, 90 and 150 min and subsequently coated with 0.5- μm transparent alumina, so that the resulting surface could be analysed with the aid of an optical microscope. In [Figure 4.5](#), it can be seen that following pre-implantation for 150 min, most of the Mn-Fe precipitates on the surface protrude out of the coating, with much of the surface in their vicinity heavily eroded.

Also, the microstructure of the surface is clearly visible, with the grain boundary regions preferentially sputtered. The Fe- and Mn-rich phase, AlMn_xFe_y , appears as dark coagulates on the surface. The sputtered Al and Mg generate sharp voids. Excessive surface in situ cleaning by sputtering can lead to the surface roughening, which in turn has a negative effect on the mechanical properties of the coated surface and the corrosion resistance of the substrates. However, in situ surface cleaning by pre-sputtering is an indispensable prerequisite for good coating adhesion. If conducted with moderation, pre-sputtering yields improved adhesion with no marked deterioration in surface roughness and corrosion resistance.

In contrast, work conducted by [Stippich et al. \(1998\)](#) has shown that magnesium oxide can be grown, under controlled conditions, to form a protective layer. In their work, they explain that IBAD deposited MgO , using 5–15 KeV Ar^+ and an I/C of 0.2, can generate a range of useful crystal structures that can offer moderate corrosion protection on their own but more importantly can be used to provide support for more protective surface layers. In this way, the affinity for oxygen of magnesium can be used to produce the first corrosion barrier of a multi-coat system.

4.5.2 Chamber base pressure

The base pressure of the deposition chamber is a very important parameter. Unfortunately, increasing the quality of the vacuum inside the chamber is a very expensive endeavour in terms of capital expenditure and running costs. High residual pressure in a deposition chamber results in a continuous build-up of physisorbed gas molecules on the substrate surface even before the coating process commences. These molecules hinder coalescence of a growing coating island, resulting in a high concentration of voids inside the coating. This phenomenon has been put to good use by [Gao, Malmhall, and Chen \(1997\)](#). In their experiment, the chamber pressure was intentionally increased to decrease adatom mobility and deposit films with nanometric grains containing nano-voids, thus enhancing their magnetic properties. A large number of voids 10–15 Å in diameter were also reported by J. R. Lloyd and S. Nakahara (1977) who reported findings of the investigation of the morphology of sputter-deposited gold films. In these experiments they experienced gas incorporation in the films as a result of adsorbed gas on the surface of the growing film. They attributed the high void concentration to the low deposition temperature and high residual gas pressure in the deposition chamber. They also discovered that the defect concentration was much more sensitive to changes in temperature than to changes in base pressure. Nonetheless, it has to be mentioned that the best base pressure attained by J. R. Lloyd and S. Nakahara was 2×10^{-6} mbar, which is still rather poor compared to today's standard. [Iriarte, Engelmark, Ottosson, and Katardjiev \(2003\)](#), in a separate investigation, reported the tendency of AlN deposited at low deposition rate to develop high compressive stresses that result in the premature failure of electronic devices. This phenomenon was attributed to the absorption of residual gases such as oxygen and water.

These researchers also linked this phenomenon to the low deposition rates and temperatures used.

G. Konczos, I. Bársony, and P. Deák (1998, chapter 5), in their discussion of the effect of residual gas pressure in deposition system, mention the effects of adsorbed gases on the growing film surface. They affirm that at room temperature, residual reactive gases occupy the reactive sites of the substrate surface and ‘act as a source of mechanical stresses to pin grain boundaries and vacancies’. In turn, this results in poorly adherent films, which are either amorphous or have very small grains. At higher temperature, according to G. Konczos et al., the incorporated gases give rise to mechanical stresses in the coatings and significantly modify both their electrical and optical properties. They also describe that the presence of these adsorbed gases can change the deposition mode from epitaxial to polycrystalline or amorphous, depending on the extent of contamination. According to G. Konczos et al., the continuous formation of residual gas molecular film on the surface is responsible for atomic shadowing. This eventually leads to the formation of nano-trenches in the surface, which when covered would give rise to the voids. This phenomenon is identical to the one described by J. R. Lloyd, S. Nakahara and Chum Gao et al.

Ignatenko, Klyakhina, & Badekin (2005) reported findings regarding reactive ion beam sputter deposition (RIBSD) of TiN coatings on various refractory metals. In this work, the residual gas pressure used was almost identical to that reported by J. R. Lloyd and S. Nakahara, while the deposition rate was almost twice as much. In their paper, significant XRD peak broadening was reported. This has been imputed to the high oxygen content, which according to the authors reduced adatom mobility and promoted nucleation rate, even if a high deposition temperature was used. In addition, P. I. Ignatenko et al. noted the presence of a considerable amount of dispersed titanium oxides. This is in accord with the statements reported by G. Konczos et al. and J. R. Lloyd et al.

Despite the high residual gas pressure and the low deposition rate, the coating adhesion and wear resistance reported by P. I. Ignatenko et al. are significantly better than those of RIBAD TiN deposited by J. R. Lloyd et al. on the same substrates. At first sight, this appears to be a contradiction; however, this difference originates mainly from the difference in operating parameters used. In fact, J. R. Lloyd et al. did not allow the substrate temperature to exceed 100 °C and no substrate bias was used, whilst P. I. Ignatenko et al. applied a deposition temperature of 500 °C and a substrate bias of –200 V. This is believed to be responsible for the considerable improvement of both the coating hardness and adhesion to such an extent that it actually outperformed RIBAD TiN deposited in the same study.

Petrov, Brana, Hultman, and Greene (2003) also showed that low-density coatings result when metal films are deposited with an impurity arrival rate much higher than that of the metal itself. They also stated that, for alumina deposited under these conditions, adequate mechanical properties cannot be achieved at deposition temperatures lower than 500 °C in case of ion beam bombardment and 800 °C when no ion beam irradiation is applied. The findings of this investigation concur with the findings of Petrov et al., whose conclusions are based on experimental data gathered from work carried out by a number of researchers over several decades.

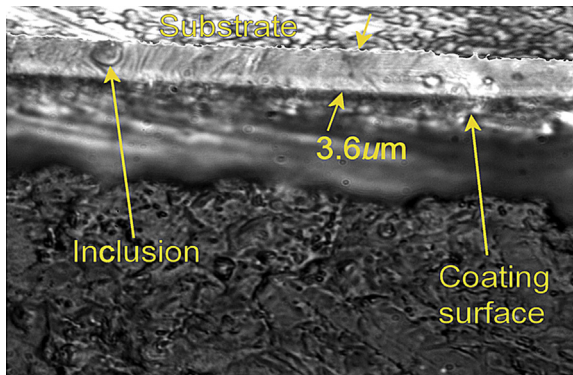


Figure 4.8 An optical micrograph of a sectioned IBAD Al_2O_3 coating deposited with an I/C ratio of 0.3, showing a relatively large inclusion. From Abela, 2007.

These investigators have shown the complex interrelation between the residual chamber pressure, deposition temperature and deposition rate as well as a number of other parameters. The adhesion of the coating and its structure as well as its density can be controlled by simply controlling these three important parameters. In particular, for the PVD deposition of wear and corrosion protective coatings on magnesium substrates, the low deposition temperature prerequisite demands a very low chamber base pressure (1×10^{-10} mbar) preferably combined with the highest possible deposition rates, such that the impurity arrival rate would be a low fraction of the incoming flux on the substrate during deposition (Abela, 2007).

4.5.3 Vapour source

The vaporising medium of condensable material can also contribute substantially to the quality of the coating. In this regard, sputtering techniques by far outperform electric arc and electron beam sources, though the deposition rate of the former tends to be at least an order of magnitude lower than the latter two. Sputtering techniques do not generate large agglomerates, which can result in large inclusions in the protective film (Figure 4.8). The presence of these pores on the surface renders the coating ineffective

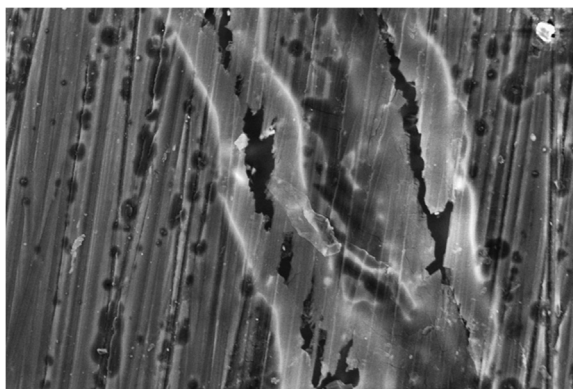


Figure 4.9 Filiform corrosion acting on $0.76 \mu\text{m}$ RIBAD Ti_2O_3 deposited on AM50 alloy and subjected to potentiodynamic testing in 5% NaCl solution at 20°C . (X5K.) From Abela, 2007.

in protecting the substrate from corrosion (Figure 4.9). Thermal evaporation techniques also generate significant radiant heat, which needs to be dissipated in order to keep the substrate temperature under control.

As can be seen from this brief chapter, the successful deposition of a PVD coat is only possible if the complex interaction of the many parameters is understood, the preparation and required procedures are carried out meticulously and the processing setup is designed appropriately for the coating requirements. If those three steps are not mastered, it is not possible to produce PVD coatings reliable enough to be suitable for the biomedical sector.

References

- Abela, S. (2007). *The development of hard and protective coatings for magnesium alloys*, A PhD. dissertation submitted at the University of Malta.
- Anders, A. (2006). *Handbook of plasma immersion ion implantation and deposition*. (1st ed., 672 pp.). Wiley-interscience, ISBN: 0-471-24698-0.
- Antunes, R. A., & de Oliveira, M. C. L. (2012). Corrosion fatigue of biomedical metallic alloys: mechanisms and mitigation. *Acta Biomaterialia*, 8, 937–962.
- Avedesian, M. M., & Barker, H. (2007). *Magnesium and magnesium alloys*, ASM specialty handbook published by the materials information society, ASM ISBN: 0-87170-657-1. <https://books.google.com.mt/books?id=0wFMfJg57YMC&pg=PA322&lpg=PA322&dq=ISBN:+0-87170-657-1&source=bl&ots=WDK56TdWF2&sig=RCvhN99Mp0E5Xdulfm aGDYwjvcU&hl=en&sa=X&ei=tgeNVNL-EKXTygPavoLYCg&ved=0CB8Q6AEwA A#v=onepage&q=ISBN%3A%200-87170-657-1&f=false>.
- Berg, S., & Katardjiev, I. V. (1999). *Journal of Vacuum Science & Technology A, Vacuum, Surfaces, and Films*, 17(4), 1916–1925.
- Busk, R. S. (1987). *Magnesium Association*, S497–S499.
- Chao, J., & López, V. (2007). Failure analysis of a Ti6Al4V cementless HIP prosthesis. *Engineering Failure Analysis*, 14, 822–830.
- Dalby, M. J., Riehle, M. O., Johnstone, H. J. H., Affrossman, S., & Curtis, A. (2004). *Cell Biology International*, 28, 229.
- Deutchman A. H., & Partyka R. J. (October 7–10, 2002). Ion beam enhanced deposited (IBED) tribological coatings for non-Ferrous alloys. In: *Proceedings from the first international surface engineering Congress and the 13th IFHTSE Congress*. Columbus, Ohio.
- Emmerich, R. Enders, B., & Ensinger, W. (November 1992). Ion beam assisted deposition of thin films and coatings: Part 3. In: *Proceedings of the Sixth international conference on surface modification technologies held in Chicago*, ISBN: 0873392175.
- Emmerich, R., Enders, B., & Ensinger, W. (November 2–5, 1992). Ion beam assisted deposition of thin films and coatings: Part 1. In: *Surface modification technologies*, VI, ISBN 0-87339-217-5.
- Enders, B., Emmerich, R., & Ensinger, W. (2000). *Surface and Coatings Technology*, 128–129, 303–307.
- Enginger, W., Enders, B., & Emmerich, R. (November 2–5, 1992). Ion beam assisted deposition of thin films and coatings: Part III. In F. Czerwinski (Ed.), *Surface modification technologies*, VI (344 pp.). InTech, ISBN: 0-87339-217-5.

- European Material Research Society (1995). Ion beam processing of materials and deposition processes of protective coatings. Symposia proceeding 53, North Holland.
- Friedrich, A., & Urbassek, H. M. (2003). *Journal of Surface Science*, 547, 315–323.
- Gao, C., Malmhall, R., & Chen, Ga-L. (1997). *IEEE Transactions on Magnetics*, 33(5), 3013–3015.
- Hoche, H., Scheerer, H., Probst, D., Broszeit, E., & Berger, C. (2003). *Surface and Coating Technology*, 174–175, 1018–1023.
- Hopf, C., Jacob, W., & von Keudell, A. (2005). *Journal of Applied Physics*, 97(9), 094904 s2005d.
- Hydro Magnesium headquarters, Avenue Marcel Thiry 83, B-1200. (September 2005). *Corrosion and finishing of magnesium alloys*. Belgium: Brussels.
- Ignatenko, P. I., Klyakhina, N. A., & Badekin, M. Y. (2005). *Journal of Inorganic Materials*, 41(2), 148–151. Translated from *Neorganicheskie Materialy* 2005, 41(2), 193–196.
- Inoue, A., Kawamura, Y., Matsushita, M., Hayashi, K., & Koike, J. (2001). *Material Research Society*, 16(7), 1894–1900.
- Iriarte, G. F., Engelmark, F., Ottosson, M., & Katardjiev, I. V. (2003). *Materials Research Society*, 18(2).
- Itoh, T. (1989). *Ion beam assisted film growth. Beam modification of materials*. North Holland: Elsevier. ISBN 444872809. <http://researchbooks.org/0444872809>
- Jin, F. Y., Chu, P. K., Xu, G. D., Zhao, J., Tang, D. L., & Tong, H. H. (2006). Materials science and engineering. A, structural materials: properties. *Microstructure and Processing*, 435–436, 123–126.
- Kasemo, B. (2000). *Surface Science*, 500, 656.
- Klingenberg, M., Arps, J., Wei, R., Demaree, J., & Hirvonen, J. (2002). *Surface and Coatings Technology*, 158–159, 164–169.
- Konczos, G., Bársony, I., & Deák, P., (1998) with the support of the Tempus Sjepp 09614–95. *Introduction to materials science and technology*. A textbook of the technical university of Budapest. For the Ph.D. students in physics. www.omikk.bme.hu.
- Lloyd, J. R., & Nakahara, S. (1977). *Journal of Vacuum Science and Technology*, 14(1), 655–659.
- Lorda, M. S., Fossb, M., & Besenbacher, F. (2010). *Nano Today*, 5(1), 66–78.
- Mahan, J. E. (2013). *Physical vapor deposition of thin films*. Wiley-interscience, ISBN: 0-471-33001. <http://eu.wiley.com/WileyCDA/WileyTitle/productCd-0471330019.html>.
- Mändl, S., Brutscher, J., Günzel, R., & Höller, W. (1996). *Nuclear Instruments and Methods in Physics Research B*, 112, 252–254.
- Mandl, S., & Rauschenbach, B. (2000). *Biomedical Technik*, 45(7/8), 193.
- Mattox, D. M. (1998). *Journal of Vacuum Science and Technology*, A7, 1105–1114.
- Mattox, D. M. (1998). *Handbook of physical vapor deposition (PVD) processing. Film formation, adhesion, surface preparation and contamination control*. Noyes Publications, ISBN:0-8155-1422-0. <http://www.sciencedirect.com/science/book/9780815514220>.
- Meshinchi, K. (January 14, 2011). Improving the properties of magnesium alloys for high temperature applications Asl School of Materials Science and Engineering, Clemson University, Clemson USA. In F. Czerwinski (Ed.), *Magnesium Alloys - Design, Processing and Properties*. InTech, ISBN 978-953-307-520-4.
- Möller, W., Fukaren, W., Lange, K., von Keudell, A., & Jakob, W. (1995). *Journal of Applied Physics*, 34, 2163–2171.
- Morton, P. H. (1992). *Surface engineering and heat treatment, past, present, and future* (364 pp.). Maney Pub, ISBN 0901716014 <http://www.openisbn.com/isbn/0901716014/>.

- Niinomi, M. (2002). *Metallurgical and Materials Transactions A*, 33, 477.
- Petrov, I., Brana, P. B., Hultman, H., & Greene, J. E. (2003). *Journal of Vacuum Science and Technology A*, 21(5).
- Polmear, J. (1995). *Light alloys, metallurgy of light metals* (3rd ed.). In I. Polmear (Ed.), *Metallurgy and materials science series*. Butterworth-Heinemann, ISBN: 0-340-63207-0.
- Ratner, B. D., Chilkoti, A., & Lopez, G. P. (1990). In R. d'Agostino (Ed.), *Plasma deposition, treatment and etching of polymers* (p. 463). New York: Academic Press.
- Rungsiyakull, C., Li, Q., Sun, G., Li, W., & Swain, M. V. (2010). Surface morphology optimization for osseointegration of coated implants. *Biomaterials*, 31(27), 7196–7204.
- Smith, D. L. (1995). *Thin-film deposition principles and practice*. New York, NY: McGraw-Hill, ISBN: 0-07-058502-4.
- Sodhi, R. N. S. (1996). *Journal of Electron Microscopy and Related Phenomena*, 81, 269.
- Stippich, F., Vera, E., Wolf, G. K., Berg, G., & Friedrich, Chr (1998). *Surface and Coatings Technology*, 103–104, 29–35.
- Thornton, J. A., & Greene, J. E. (1994). In R. F. Bunshah (Ed.), *Handbook of deposition technologies for films and coatings* (2nd ed.). Noyes Publications, ISBN 0-8155-1337-2.
- Valvoda, B. (1996). *Surface and Coatings Technology*, 80(1–2), 61–65.
- Venables, J. A. (2000). *Introduction to surface and thin film processes*. Cambridge University Press, ISBN: 0-521-78500-6.
- Vitos, L., Ruban, A. V., & Skriver, H. L. (1998). *J. Kollár Surface Science*, 411, 186–202.
- Wasa, K., & Hayakawa, S. (1992). *Handbook of sputter deposition technology principles, technology and applications. Materials science and process technology series*. (392 pp.) Noyes Publications, ISBN 0-8155-1280-5. <http://www.gettextbooks.com/search/?isbn=HANDBOOK+OF+THIN+FILM+DEPOSITION+Krishna+Seshan>.
- Yamamoto, A., Watanabe, A., Sugahara, K., Tsubakino, H., & Fukumoto, S. (2001). *Scripta Materialia*, 44, 1039.
- Yang, J., Cui, Fu-zhai, In Seop. Lee, & Wang, X. (2010). *Surface and Coatings Technology*, 205, S182–S187.
- Yongquin, F., Xiaodong, Z., Kewei, X., Jiawen, H., & Batchelor, A. W. (1997). Ion bombardment on mechanical properties of IBAD TiN films, part: 2. In T. S. Sudarshan, K. A. Khor, & M. Jeandin (Eds.), *Surface modification technologies X, proceedings of the 10th international conference on surface modification technologies singapore 1996*. London: Verlag, ISBN 1861250223.
- Yongquin, F., Zhu, X., Xu, K., & He, J. (1997). Ion bombardment on the mechanical properties of IBAD TiN films, Part 1. In T. S. Sudarshan, K. A. Khor, & M. Jeandin (Eds.), *Surface modification technologies (Vol. X)*. David Brown Book Co., ISBN 1861250223

Cryogenic machining and burnishing of magnesium alloys to improve *in vivo* corrosion resistance

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5.1 Introduction

Magnesium alloys are emerging as a novel biodegradable material in which the relatively fast corrosion phenomenon is used as a unique advantage for temporary fixation implants (Witte, 2010). No systematic reactions and only little inflammation were observed in human trials of such implants. A marked stimulatory effect for bone healing was reported (Mcbride, 1938). However, the premature failure of magnesium-based implants due to the poor corrosion resistance in physiological environments and gas bubbles generated due to the high corrosion rate impeded further investigation until recently.

Despite their attractive features, little progress has been achieved in controlling the biodegradation rate of magnesium alloys. Alloying and coating are two major approaches widely studied (Hornberger, Virtanen, & Boccaccini, 2012; Song & Song, 2007). However, alloying may introduce elements that lead to adverse biological reactions. Stability of the coating under cyclic loading in physiological conditions is a great challenge, while the complexity of coating techniques may significantly increase the cost of implants.

Mechanical processing of magnesium alloys provides an alternative approach to controlling the biodegradation rate through the modification of the surface integrity, including grain size, residual stresses, and crystallographic orientations. A literature review on how these surface integrity changes influence the corrosion resistance will be presented in the next section. Two novel mechanical processing methods, cryogenic machining and cryogenic burnishing, will be discussed with respect to their ability to modify the corrosion rate of AZ31B Mg alloy samples. Experimental results on their influence on surface integrity, as well as corrosion resistance, will be presented. A finite element model that can be used to predict the grain size after cryogenic machining is also briefly introduced.

5.2 Literature concerning surface integrity and corrosion resistance of Mg alloys

5.2.1 Grain size

The grain size of magnesium alloys has a remarkable influence on their corrosion resistance (Wang, Estrin, Fu, Song, & Zuberova, 2007). Grain refinement from 25.7 μm to 4.5 μm induced by equal channel angular pressing (ECAP) led to better corrosion performance for AZ31 Mg alloy when placed in simulated body fluid (SBF) (Alvarez-Lopez et al., 2010). It was also reported on pure magnesium that grain refinement from 125 μm to 2.6 μm by ECAP enhanced its corrosion resistance in 0.1 mol/L NaCl solution (Birbilis, Ralston, Virtanen, Fraser, & Davies, 2010). A clear relationship between the corrosion current and the grain size exists in pure magnesium (Birbilis et al., 2010); smaller grains lead to reduced corrosion current (improved corrosion resistance). The grain boundary of AZ31B Mg alloy was claimed to be physical corrosion barriers, and smaller grain size led to better corrosion resistance in 3.5 weight percent (wt%) NaCl solution (Aung & Zhou, 2010). The critical influence of grain size on corrosion resistance was also reported on other materials, such as titanium (Balakrishnan, Lee, Kim, & Panigrahi, 2008) and stainless steel (Wang & Li, 2002). This relationship was claimed to be analogous to the classic Hall–Petch relationship, which describes the dependence of hardness on grain size (Birbilis, Ralston, & Davies, 2010). It was reported that grain refinement also improves the atmospheric corrosion resistance of AZ31B alloy (Liao, Hotta, Motoda, & Shinohara, 2013).

In addition to improved corrosion performance, the beneficial effects of grain refinement were reported on the fatigue life of AZ31 Mg alloy (Wang et al., 2007), as well as many other materials, such as titanium, Al alloys, and copper (Mughrabi & Hoppel, 2010). Compared with coarse-grained annealed copper, copper with a nanocrystalline surface layer obtained by using surface mechanical attrition treatment (SMAT) exhibited remarkably better wear resistance (Zhang, Han, Wang, & Lu, 2006).

5.2.2 Crystallographic orientation

The importance of crystallographic orientations on corrosion resistance was reported for both pure Mg (Liu, Qiu, Zhao, Song, & Atrens, 2008) and Mg alloys (Song, Mishra, & Xu, 2010). It was found both experimentally and theoretically that the (0001) basal plane of AZ31 Mg alloy is more corrosion resistant than the other planes due to its higher atomic coordination and thus lower surface energy (Song et al., 2010).

Xin et al. prepared AZ31 Mg samples with different crystallographic orientations by cutting the sample at different angles of 0°, 30°, 60°, and 90° from the rolled sheet, as shown in Figure 5.1(a) (Xin, Li, Li, & Liu, 2011). A rolled sheet of Mg alloys was reported frequently to have a strong basal texture on the rolled surface (Chang, Wang, O, & Lee, 2003). Therefore, the intensity of the basal texture on the Mg samples decreased with the larger angles, as shown in Figure 5.1 (b).

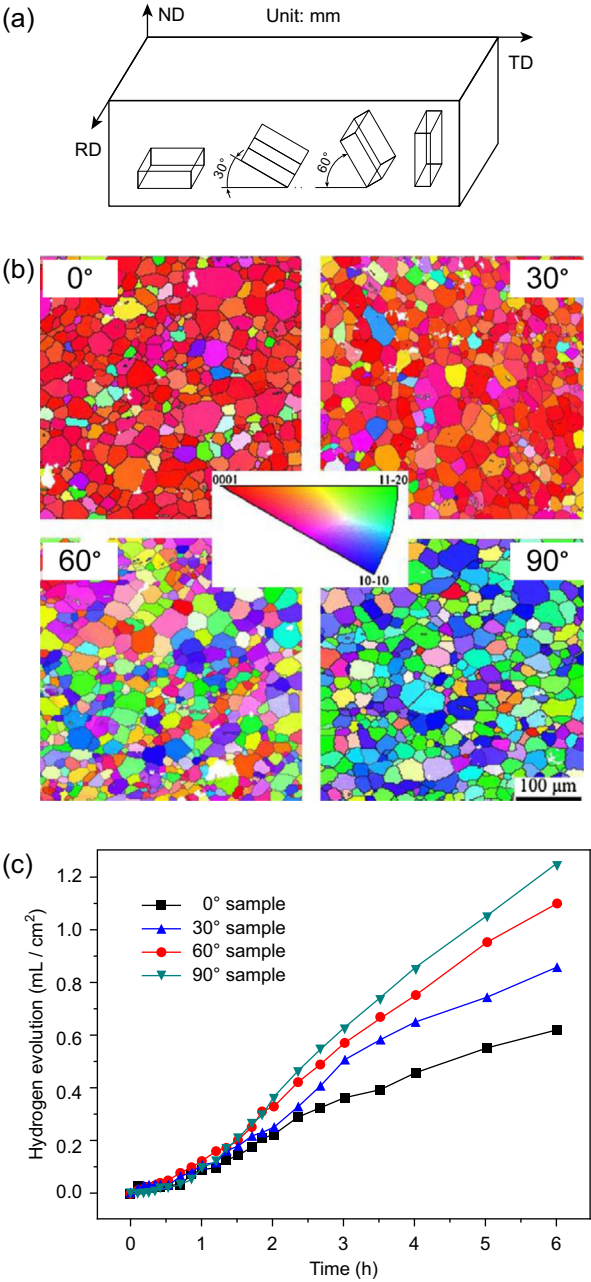


Figure 5.1 (a) Schematic illustration of sample preparation. (b) Inverse pole figure maps of 0°, 30°, 60°, and 90° samples. (c) Hydrogen evolution rates of the AZ31 Mg samples immersed in 3.5 wt% NaCl (Xin et al., 2011).

The hydrogen evolution method (Song, Atrens, & St. John, 2001) was used to evaluate the corrosion resistance of the Mg alloy samples with different crystallographic orientations (smaller hydrogen volume, better corrosion resistance). As shown in Figure 5.1(c), a clear relationship between the corrosion resistance and the crystallographic orientation exists, and this agreed with earlier data from the literature that the corrosion resistance of Mg alloys increases with increased intensity of basal texture. The effects of crystallographic orientations on corrosion resistance were also reported to outweigh those of grain size in pure titanium after ECAP (Hoseini, Shahryari, Omanovic, & Szpunar, 2009). The difference in corrosion resistance between the crystallographic basal plane dominated rolling surface of AZ31 Mg alloy and the prismatic plane dominated cross-section surface was reduced after heat treatment (Song & Xu, 2012). The authors claimed that the growth of intermetallic particles deteriorated the corrosion performance after heat treatment and its influence outperformed the influence of crystallographic orientations.

5.2.3 Residual stresses

The influence of residual stresses on fatigue life of manufactured components has been reported, while the influence on corrosion resistance was, until recently, less well known. The pitting corrosion resistance of American Iron and Steel Institute (AISI) 316L stainless steel was improved after inducing near-surface compressive residual stresses by sand blasting and wire brushing (Ben Rhouma, Braham, Fitzpatrick, Ledion, & Sidhom, 2001). The high compressive residual stress generated in the sub-surface via a deep rolling process was also claimed to reduce the corrosion rate of a biphasic magnesium-calcium alloy by a factor of approximately 100 (Denkena & Lucas, 2007). The corrosion performance of 7475-T7351 aluminum alloy was significantly improved by inducing large compressive residual stresses near the surface through low plasticity burnishing (LPB) (Scheel, Prev  y, & Hornbach, 2010). It was also reported that large residual stresses would reduce the corrosion resistance of magnesium alloys, although the grain size of the alloys became smaller (Ralston & Birbilis, 2010). The influence of different machining and grinding procedures on stress corrosion cracking of AISI 304 stainless steel was recently investigated, and high tensile stresses induced by grinding were also found to cause more severe pitting corrosion (Turnbull et al., 2011).

In addition to affecting corrosion resistance, the residual stress has a critical influence on fatigue life, which is also an important factor in biomedical implants. Leverant et al. studied the fatigue life of machined Ti-6Al-4V alloy and showed that the surface residual stresses played a dominant role in the determination of fatigue micro-crack growth rates and consequently the total fatigue life (Leverant, Langer, Yuen, & Hopkins, 1979). Matsumoto et al. conducted the rolling contact fatigue tests on AISI 52100 steel after hard turning and grinding and also measured the residual stresses after processing (Matsumoto, Hashimoto, & Lahoti, 1999). They found that longer fatigue life was achieved by hard turning than grinding, which was attributed to the larger penetration depth of compressive residual stresses created by turning. The significantly enhanced fatigue performance was also reported on various

materials processed by LPB for critical applications, including Ti-6Al-4V (Hornbach, Prevey, & Loftus, 2006) used in femoral hip stems and the stainless steels Alloy 450 and 17-4 PH used in steam turbines (Prevéy, Jayaraman, & Ravindranath, 2010). These improvements were all attributed to the large compressive surface residual stresses induced by LPB.

5.3 Surface integrity in the cryogenic machining and burnishing of AZ31 Mg alloy

Machining and burnishing are severe plastic deformation (SPD) processes that involve large strains, high strain rates, and large temperature changes (up to more than 1000 °C). Significant grain refinement was reported on the machined surface of various materials due to dynamic recrystallization (DRX), including AISI 52100 steel (Ramesh, Melkote, Allard, Riester, & Watkins, 2005; Umbrello et al., 2011) and nickel-based superalloy IN100 (Wusatowska-Sarnek et al., 2011). These processes also lead to substantial changes of residual stress (Brinksmeier et al., 1982) and crystallographic orientations on the workpiece surfaces (Pu et al., 2012a; To, Lee, & Cheung, 2003). All these changes have the potential to improve the corrosion performance of Mg alloys after machining processes.

Cryogenic machining and burnishing, where liquid nitrogen is used to significantly reduce the temperature in the processing zone, are discussed in this chapter in order to investigate their influence on three key surface integrity factors that are critical to the corrosion performance of Mg alloys: grain size, residual stresses, and crystallographic orientations. Results from immersion corrosion tests of these processed samples are also presented.

The work material studied was the commercial AZ31B-O Mg alloy. The work material was received in the form of a 3.22-mm thick sheet. Disc specimens of 130-mm diameter were cut from the sheet by vertical milling in the machine shop and subsequently subjected to machining/burnishing.

As shown in Figure 5.2(a), a Mazak Quick Turn-10 Turning Center, equipped with an Air Products ICEFLY[®] liquid nitrogen delivery system, was used to conduct orthogonal turning and burnishing. Figure 5.2(b) and (c) shows the method of liquid nitrogen being sprayed to the workpiece surface using a nozzle at a flow rate of 0.6 kg/min during cryogenic machining/burnishing. The tool materials used in machining and burnishing were uncoated carbide and high-speed steel, respectively.

Metallurgical samples were cut from the machined discs. After cold mounting, grinding, and polishing, acetic picric solution was used as the etchant to reveal the grain structure. Optical microscopy and scanning electron microscopy (SEM) were used to observe the microstructure of the AZ31B Mg discs. The crystallographic orientations on the circumferential surfaces before and after machining were analyzed using a Bruker D8 Discover X-ray diffractometer. The radiation used was Cu-K α at 20 kV and 5 mA. The residual stress state in machined AZ31B Mg samples was analyzed by X-ray diffraction technique using the $\sin^2\psi$ method (Noyan & Cohen, 1987). The equipment used was iXRD from PROTO[®].

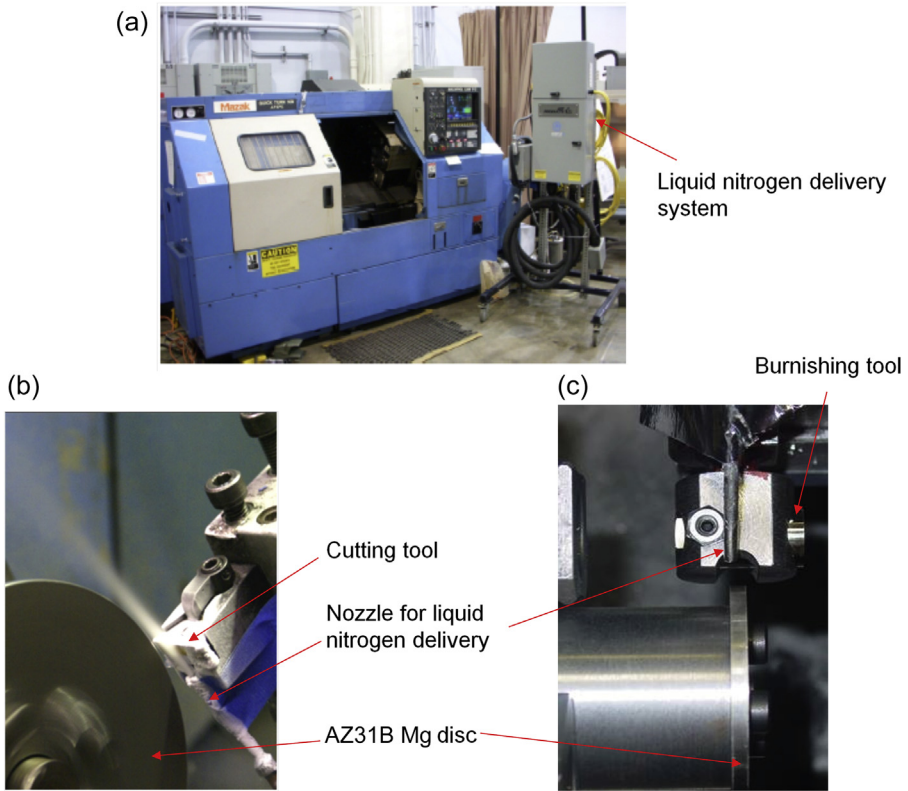


Figure 5.2 (a) Mazak Quick Turn-10 Turning Center equipped with a liquid nitrogen delivery system. Orthogonal turning (b) and burnishing (c) of AZ31B Mg disc with application of liquid nitrogen (Pu et al., 2012a).

5.3.1 Surface integrity in cryogenic machining

The machining conditions used are shown in Table 5.1. The cutting speed and feed rate were kept constant. The cutting edge radius has a strong influence on the plowing forces and therefore is important for surface integrity studies (Nasr, Ng, & Elbestawi, 2007).

The microstructure near the surface before machining is shown in Figure 5.3. The grain boundaries were clearly visible near the surface. There were some deformation twins in the region, presumably resulting from the vertical milling process used to cut the disc specimens from the sheet.

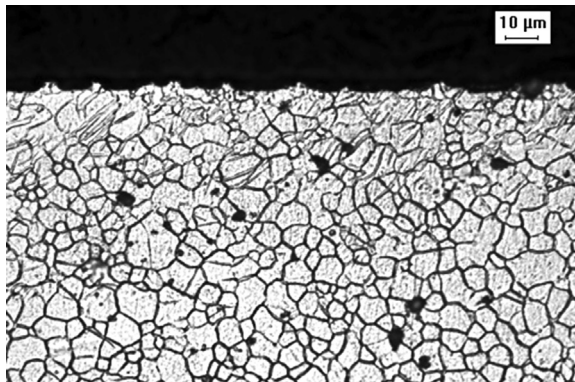
Figure 5.4 shows the microstructures of the machined surface created using different conditions. The microstructure of the machined surface, using a 30- μm edge radius tool under dry conditions, is similar to the initial microstructure shown in Figure 5.3, and the grain boundaries are still visible. However, using the same edge radius tool under cryogenic conditions, a “featureless” surface layer in which grain boundaries were no longer visible at this magnification (Figure 5.4(b)) was formed; this deformed layer was about

Table 5.1 Experiment matrix for machining under different edge radii and cooling methods

No.	Tool edge radius, r_n [μm]	Cooling method	Cutting speed, V [m/min]	Feed rate, f [mm/rev]
1	30	Dry	100	0.1
2	70	Dry	100	0.1
3	30	Cryogenic	100	0.1
4	70	Cryogenic	100	0.1

8 μm thick. The thickness of this layer increased to 15 μm with a 70- μm edge radius tool under cryogenic conditions (Figure 5.4(d)). With the same edge radius of 70 μm , a featureless layer with a darker appearance of approximately 20 μm formed under dry conditions. Using large edge radius tools while machining will induce effects similar to burnishing and will change the microstructures of the machined surface to greater depths, which may improve the corrosion resistance.

The appearance of the featureless layers formed under cryogenic machining (Figure 5.4(b) and (d)) was similar to the “white layers” in the machined surfaces of AISI 52100 steel (Ramesh et al., 2005) and nickel-based superalloy IN-100 (Wusatowska-Sarnek et al., 2011), where significant grain refinement to the nanocrystalline level was found due to DRX. To find the possible structures and properties of the featureless layer on the machined surface of AZ31B Mg alloy, the samples machined with 70- μm edge radius tools under cryogenic condition (Figure 5.4(d)) were further studied using SEM and atomic force microscope (AFM). The SEM picture of the machined surface is shown in Figure 5.5(a). Although the grain boundaries

**Figure 5.3** Microstructure near the surface before machining experiments (Pu et al., 2012a).

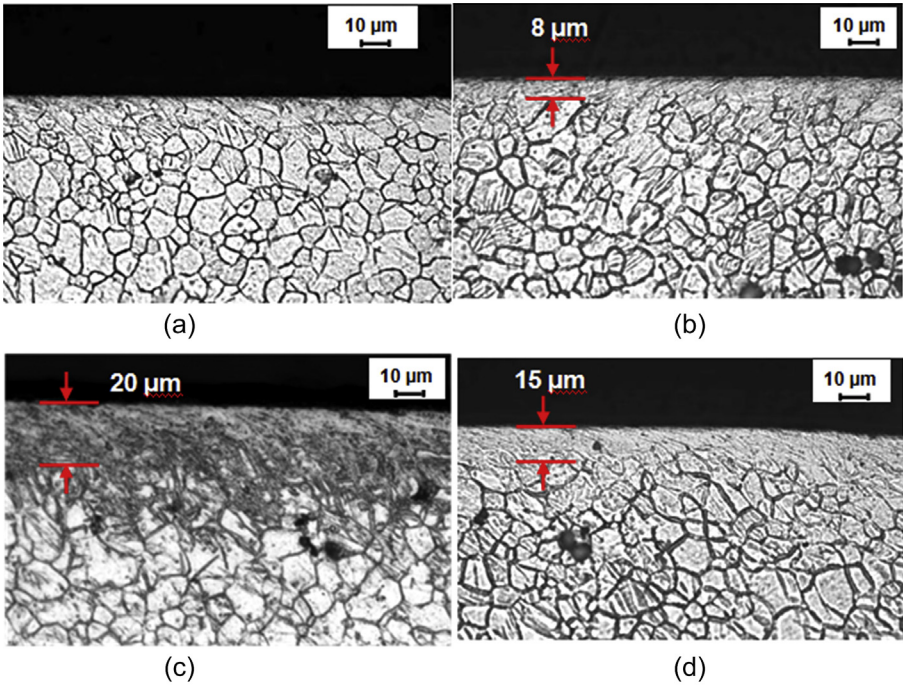


Figure 5.4 Microstructure of the machined surface and chips after machining under different conditions: (a) dry machining, $r_n = 30 \mu\text{m}$; (b) cryogenic machining, $r_n = 30 \mu\text{m}$; (c) dry machining, $r_n = 70 \mu\text{m}$; and (d) cryogenic machining, $r_n = 70 \mu\text{m}$. $V = 100 \text{ m/min}$; $f = 0.1 \text{ mm/rev}$ (Pu et al., 2012a).

are clearly visible below the featureless layer, no features can be found within the layer at this magnification. The AFM image (Figure 5.5(b)) shows that there were nanocrystalline grains, about 30 nm, in the featureless layer. This agrees with other studies that significant grain refinement could be achieved on Mg alloys through strain-induced DRX in various processes, such as SMAT (Shi, Sun, Zhang, & Lu, 2007) and cryogenic burnishing (Pu et al., 2011).

The featureless layer produced by dry machining using a 70- μm edge radius tool (Figure 5.4(c)) has a darker appearance than those under cryogenic conditions. Figure 5.6 shows the SEM pictures of the machined surface under this condition at different magnifications. Compared with the SEM picture of the machined surface after cryogenic machining using the same edge radius tools (Figure 5.5(a)) under the same magnification, a clear transition from the initial microstructure to the featureless layer on the top was shown in Figure 5.6(a), while the changes were abrupt under cryogenic conditions. Severe shear deformation started at about 20 μm below the machined surface. The grains were first elongated and then the grain boundaries disappeared near the surface. This process was very clear at a higher magnification, as shown in Figure 5.6(b), where grain elongation was evident from 10 to 20 μm below the machined surface. No grain boundaries were visible in the top 10- μm layer. A significant grain

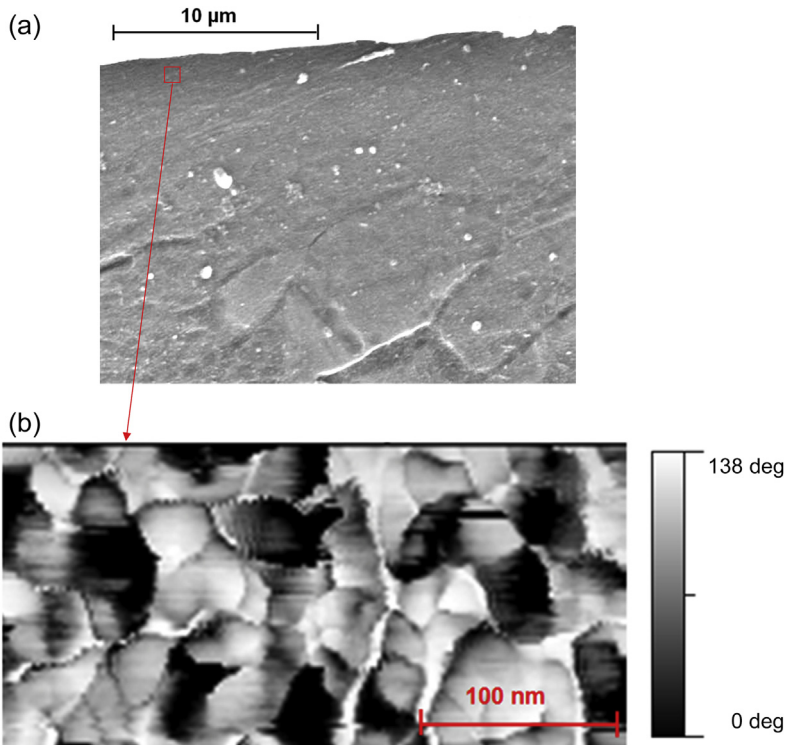


Figure 5.5 (a) Scanning electron microscopy (SEM) pictures of the machined surface using a 70- μm edge radius tool under cryogenic conditions ($V = 100 \text{ m/min}$, $f = 0.1 \text{ mm/rev}$). (b) Atomic force microscope (AFM) tapping mode phase image of the small area in (a) (Pu et al., 2012a).

refinement is expected in this layer due to the large plastic strains at high strain rates imposed by machining with a large edge radius tool. The recrystallized grain size achieved should be larger than those found after cryogenic machining due to higher temperatures, according to the following empirical relationship (Watanabe et al., 2001):

$$\frac{d_{\text{rec}}}{d_{\text{init}}} = 10^3 \times Z^{-1/3} \quad (5.1)$$

Here, d_{rec} is the fully recrystallized grain size; d_{init} is the initial grain size; and Z is the Zener-Hollomon parameter, defined as:

$$Z = \dot{\epsilon} \times \exp\left(\frac{Q}{RT}\right) \quad (5.2)$$

where $\dot{\epsilon}$ is the strain-rate; Q is the activation energy; R is the gas constant; and T is the temperature.

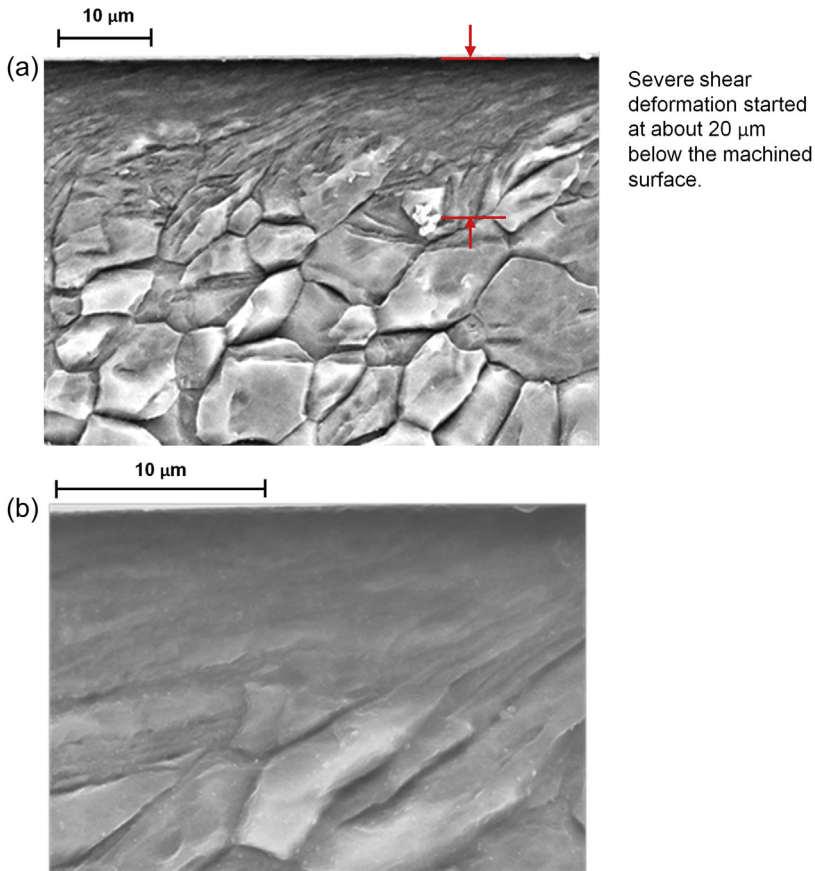


Figure 5.6 Scanning electron microscopy (SEM) pictures of the machined surface using a 70- μm edge radius tool under cryogenic conditions: (a) $\times 2000$ and (b) $\times 5000$ magnification (Pu et al., 2012).

Using the same edge radius tool, the influence of dry machining on microstructure extended to greater depth than the influence of cryogenic machining. Similar differences in microstructures near the machined surface between dry and cryogenic conditions were reported on nickel-based superalloy Inconel 718 (Kenda, Pusavec, & Kopac, 2011).

Figure 5.7 shows the evolution of crystallographic orientations on the machined surface before and after machining under different conditions. The relative height of the peak corresponding to the basal plane (0002) increased significantly, especially after cryogenic machining using a 70- μm edge radius tool. The relative intensity of the basal peak, which was calculated by dividing its absolute intensity by the absolute intensity of the most intense peak ($10\bar{1}1$), was used to quantitatively evaluate the texture changes using different machining conditions. As shown in Figure 5.7(b), machining with larger edge radius tools led to stronger intensity of the basal peak under both dry

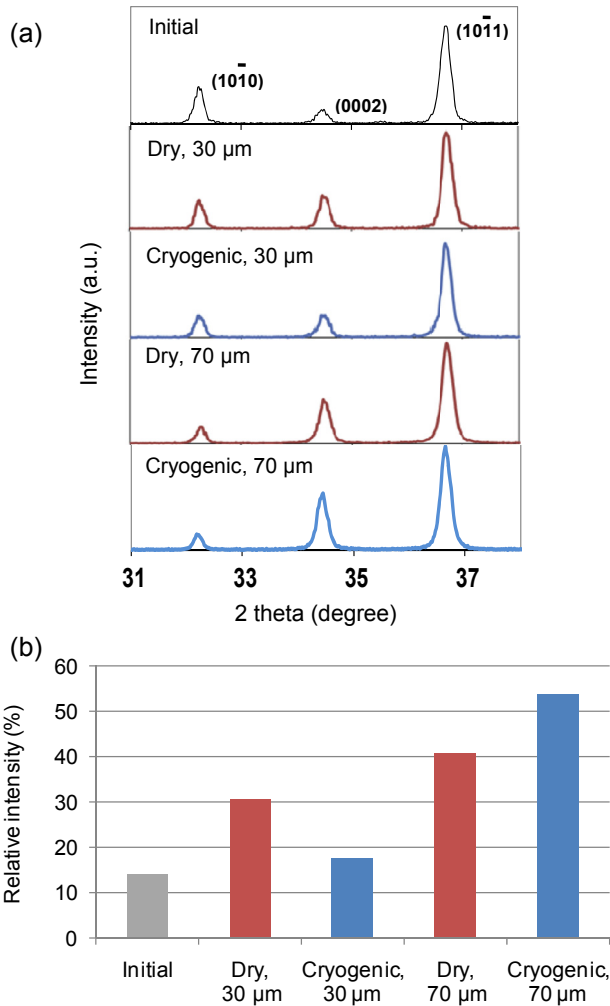


Figure 5.7 (a) Evolution of crystallographic orientations and (b) relative intensity of basal peak (0002) on the machined surface before and after machining under different conditions ($V = 100$ m/min, $f = 0.1$ mm/rev) (Pu et al., 2012a).

and cryogenic conditions. The formation of strong basal texture was reported on Mg alloys after cryogenic burnishing (Pu et al., 2011). Machining with a large edge radius tool induces greater plowing effects on the workpiece surface and is closer to the burnishing process, which leads to the higher intensity of the basal planes appearing on the machined surface.

With the edge radius of 30 μm , dry machining led to a larger increase in the basal peak intensity than it did in cryogenic machining. With higher temperatures, the local adhesion of the material and the flank side of the rounded cutting edge could be increased, which led to more severe shear deformation of the material near the

workpiece. This was supported by a finding where less shear deformation occurred on the machined surface under cryogenic cooling conditions compared with dry machining (Kenda et al., 2011). However, this trend was reversed when the edge radius was increased to 70 μm , where cryogenic machining led to the stronger basal texture. Larger deformation tends to occur within the basal plane when the temperature is near the room temperature because the critical resolved shear stress for basal plane slip in Mg is the smallest at room temperature (Reedhill & Robertson, 1957). Dry machining using 70- μm edge radius tools induced more SPD on the machined surface than machining using 30- μm edge radius tools; it also generated much higher surface temperatures than 125 $^{\circ}\text{C}$, which was the measured temperature during dry machining using 30- μm edge radius tools (Pu et al., 2012a). The higher temperature activated more nonbasal slip systems, and this led to weaker basal textures compared with cryogenic machining.

Figure 5.8 shows the measured residual stresses in the circumferential and axial directions after machining using cutting tools with two different edge radii under

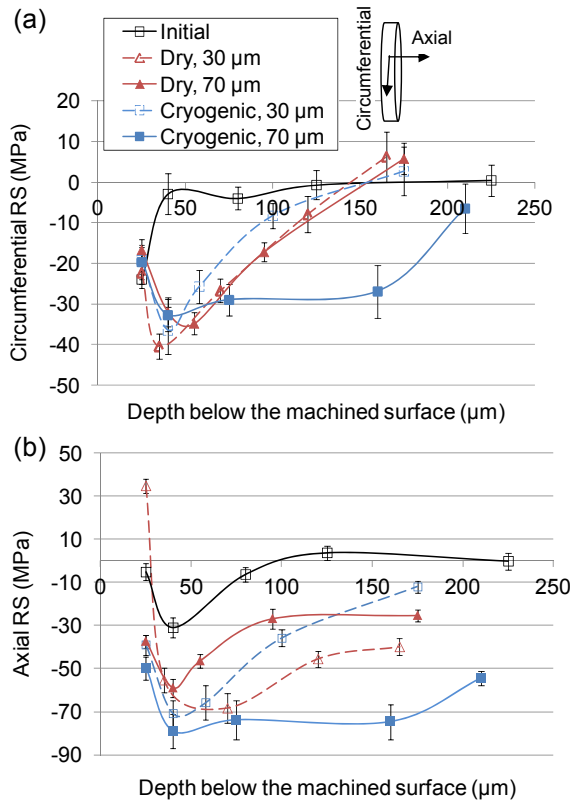


Figure 5.8 Residual stresses after machining using cutting tools with different edge radii and cooling conditions in (a) circumferential and (b) axial directions ($V = 100 \text{ m/min}$, $f = 0.1 \text{ mm/rev}$) (Pu et al., 2012a).

both dry and cryogenic conditions. The initial residual stresses in both directions were close to zero when the distance from the surface reached approximately 70 μm . With a 30- μm edge radius tool, compressive residual stresses were induced under both dry and cryogenic conditions up to 140 μm below the machined surface in the circumferential direction. The peak compressive stress for dry machining was approximately -40 MPa at a depth of 30 μm below the surface. These two parameters were almost the same when cryogenic cooling was used. Much larger differences were found in the axial direction between dry and cryogenic machining with the same edge radius of 30 μm . Tensile residual stress of 37 MPa was generated in the axial direction, while cryogenic machining led to compressive residual stress of -39 MPa in that direction.

When the cutting edge radius was increased to 70 μm , the penetration depth of the compressive residual stresses was extended to approximately 200 μm in the circumferential direction under cryogenic conditions compared with 150 μm under dry conditions—a 54% increase. The residual stresses in the axial direction were also more compressive and extended to greater depths during cryogenic machining than those created during dry machining. For dry machining, the peak compressive stresses in both directions were reduced by approximately 16% when the cutting edge radius was increased from 30 to 70 μm , which was due to the increased temperature resulting from more severe plowing effects. For cryogenic machining, the peak compressive residual stress was reduced slightly in the circumferential direction and increased by 12% in the axial direction.

5.3.2 Surface integrity in cryogenic burnishing

The previous section showed that the maximum depth of the featureless layer obtained through cryogenic machining is smaller than 20 μm . The major objective of this section is to investigate and determine whether cryogenic burnishing has the ability to create a thicker featureless layer and how it changes residual stresses and crystallographic orientations.

As shown in Figure 5.2(c), a burnishing tool made of high-speed tool steel was pushed against the Mg discs at a constant feed rate of 0.01 mm/rev. The diameter of the burnishing roller used is 14.3 mm. The burnishing speed (i.e., the linear speed at the contact point between the fixed roller and the rotating disc) was set to 100 m/min. The burnishing process was stopped when the final diameter had been reduced to 126 mm from 128 mm. Two burnishing tests were conducted—one under dry conditions and the other under cryogenic condition.

The microstructures near the surface before and after burnishing under dry and cryogenic conditions are shown in Figure 5.9. Some deformation twins are seen in the microstructure before burnishing, which is likely induced by the vertical milling process used in removing the disc samples from the sheet. It is evident from Figure 5.9(b) that the grain size is significantly reduced by dry burnishing. Under the same magnification, the grain boundaries near the surface after cryogenic burnishing are not discernible, as shown in Figure 5.9(c). Figure 5.9(d) shows that a majority of the grains near the burnished surface are smaller than 1 μm . The average

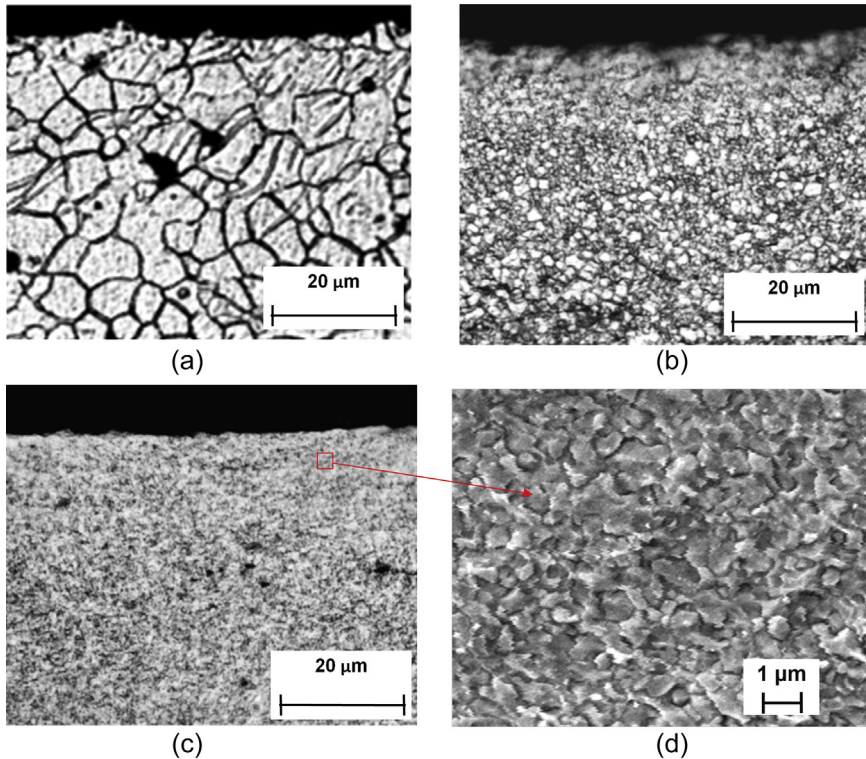


Figure 5.9 Microstructures near the surface (a) before burnishing, (b) after dry burnishing, and (c) after cryogenic burnishing. (d) Scanning electron microscopy (SEM) picture of the highlighted area in (c) (Pu et al., 2012b).

longitudinal axis grain size after cryogenic burnishing is 523 ± 131 nm. A comparison of the longitudinal axis grain size distribution before and after burnishing is shown in Figure 5.10. The average grain size before burnishing was $11.9 \mu\text{m}$ and the scatter of the grain size was large. Although not as significant as in cryogenic burnishing, grain refinement also occurred under dry burnishing and the average grain size was reduced to $1.4 \mu\text{m}$. The larger recrystallized grain size obtained under dry conditions agrees with Eqn (5.1) because the temperature was much higher when compared with cryogenic burnishing.

Figure 5.11 shows the evolution of textures caused by burnishing. The relative heights of the peaks corresponding to the basal plane (0002) increased significantly after both dry and cryogenic burnishing. This became the strongest peak, which indicates that strong basal textures were created by the process used. As discussed in Section 5.2.2, this has recently been shown to improve the corrosion resistance of AZ31B Mg alloy. The application of liquid nitrogen during burnishing does not have a significant influence on the crystallographic orientations. This suggests that the mechanical deformation induced by burnishing is the major cause for the texture changes. It was

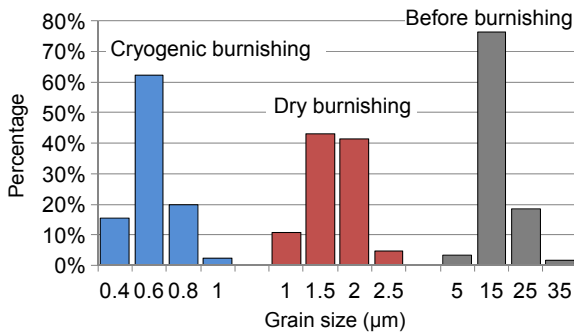


Figure 5.10 Distribution of average longitudinal axis grain size before and after burnishing under dry and cryogenic conditions (Pu et al., 2012b).

reported in Section 5.3.1 that the increased plowing effects induced by large edge radius cutting tools resulted in the remarkable increase in the intensity of the basal plane. The deformation of the workpiece induced by the plowing effects in machining and by burnishing is somewhat similar to what occurs in rolling. It has been reported frequently that the rolled surfaces of AZ31 Mg alloy often exhibit strong basal textures (Chang et al., 2003; Sakai, Hashimoto, Hamada, & Utsunomiya, 2011). Therefore, it is expected that a burnished surface would become more basal textured, which should then result in better corrosion resistance (Song et al., 2010).

Figure 5.12 shows residual stresses generated on the ground and burnished AZ31B Mg surfaces at a depth of 25 μm from the surface (the smallest achievable depth due to limits in the penetration depth of X-ray in this material). The

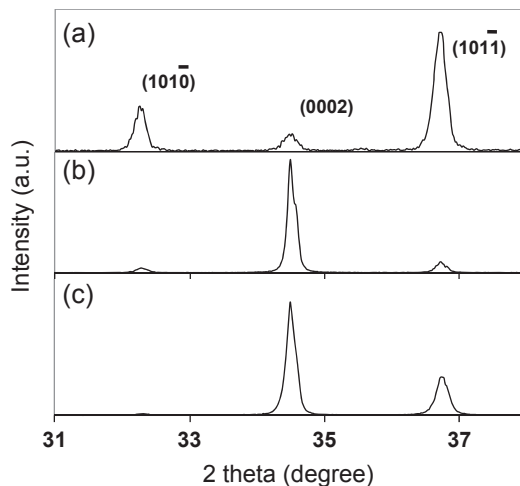


Figure 5.11 Evolution of crystallographic orientations: (a) before burnishing and (b) after dry and (c) cryogenic burnishing (Pu et al., 2012b).

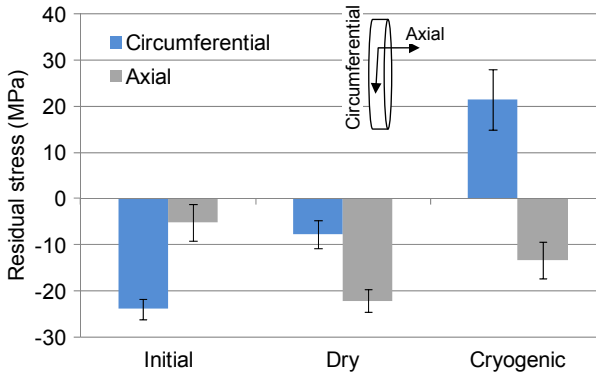


Figure 5.12 Residual stress at 25 μm from the surface of AZ31B Mg disc before burnishing and after burnishing under dry and cryogenic conditions (Pu et al., 2012b).

circumferential residual stresses were claimed to be more critical than the axial ones for in-service performance of a disc (Umbrello, Outeiro, M'saoubi, Jayal, & Jawahir, 2010). Although the axial residual stresses in the burnished samples are more compressive than in the ground sample, the circumferential residual stresses become less compressive or more tensile after burnishing compared with their state before burnishing. This is different from what has been reported in most literature reports, where burnishing normally induces more compressive residual stresses (Denkena & Lucas, 2007; Salahshoor & Guo, 2011; Scheel et al., 2010; Zinn & Scholtes, 1999). The contradictory findings from this study and the literature data may be caused by the different roller settings. The roller used in this study was fixed, while in most literature examples it was allowed to rotate.

5.4 Corrosion performance of machined and burnished samples

It was shown in the previous section that the surface integrity of AZ31B Mg alloy was remarkably changed after cryogenic machining and burnishing. These changes may improve or reduce the corrosion resistance of the processed materials.

To evaluate the corrosion performance, the processed samples were immersed in two different solutions. One solution was 5 wt% NaCl solution and the corrosion test was conducted at room temperature. The other solution used was SBF, whose composition is shown in Table 5.2 (Song & Song, 2007). The pH value of the SBF was adjusted to 7.4. The solution was held in an incubator to maintain the temperature at $37 \pm 1^\circ\text{C}$.

The immersion time was 85 h for the test in 5 wt% NaCl solution and 10 days for the test in the SBF. After immersion, the samples were taken out of the solutions and the corrosion products were removed by chromic acid (200 g/L CrO_3 and 10 g/L AgNO_3). After washing with distilled water and drying, photos were taken by a camera

Table 5.2 Composition of simulated body fluid (SBF)

Name	Concentration [g/L]
NaCl	8
KCl	0.4
CaCl ₂	0.14
NaHCO ₃	0.35
C ₆ H ₁₂ O ₆	1
MgSO ₄ ·7H ₂ O	0.2
KH ₂ PO ₄ ·H ₂ O	0.1
Na ₂ HPO ₄ ·7H ₂ O	0.06

to show the overview of the corroded surface. A Zygo NewView 7300 measurement system was used to measure the corrosion depth. A 2 mm × 2 mm three-dimensional (3D) topographic picture of the severely corroded area was recorded for each condition; the depth of the deepest pits was obtained by the corresponding line profiles.

5.4.1 Corrosion performance of machined samples

Figure 5.13 shows the photos of AZ31B Mg samples, machined under different cooling conditions and cutting edge radii after the corrosion test in 5 wt% NaCl for 85 h (Pu, 2012). Differences in corrosion performance were found between specimens made using different machining conditions. The white or light gray portions on the photos in Figure 5.13 represent the original surface, while the dark portions are the places where large amounts of Mg were lost due to corrosion. It is obvious that dry machining using a 30-μm edge radius tool led to the worst corrosion performance. With the same edge radius, the application of liquid nitrogen during machining significantly improved the corrosion performance. However, when the cutting edge radius was increased to 70 μm, the differences of the corroded surface were limited between the dry and cryogenic conditions. Under the same dry cutting conditions, increasing the cutting edge radius from 30 μm to 70 μm remarkably improved the corrosion resistance of the AZ31B Mg alloy.

The differences in corrosion performance correlate well with the thickness of the “featureless layer” shown in Figure 5.4. The sample machined using a 30-μm tool under dry condition, which exhibited the worst corrosion, has no featureless layer. All other samples have the featureless layer of different thickness (8–15 μm). It could be concluded that the featureless layer, which consisted of nanocrystalline grain structures, promoted the formation of a passive film and improved the corrosion resistance of AZ31B Mg alloy. This result agrees with the finding that grain refinement improves the corrosion resistance of Mg alloys (Alvarez-Lopez et al., 2010; Birbilis et al., 2010; Wang et al., 2007).

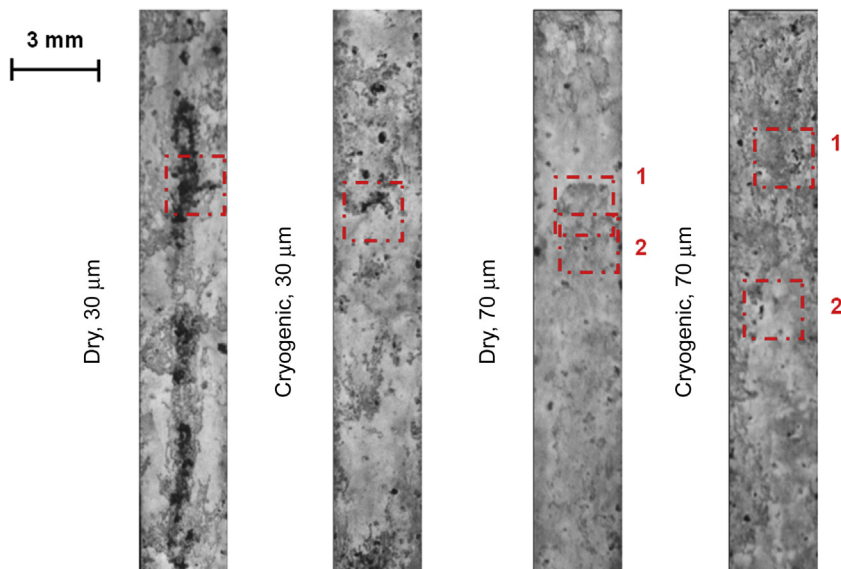


Figure 5.13 Photos of machined AZ31B Mg samples under different cooling conditions and cutting edge radii after corrosion test in 5 wt% NaCl for 85 h ($V = 100$ m/min, $f = 0.1$ mm/rev) (Pu, 2012).

Figures 5.14 and 5.15 show the 3D topographic pictures of the severely corroded area, as marked by a red square in Figure 5.13, and the corresponding line profiles. While the total corroded area is much smaller on the sample machined under cryogenic condition (Figure 5.13) using the 30- μ m edge radius tools, the difference of maximum depths of the corrosion pits are very small: 175 and 198 μ m for cryogenic and dry conditions, respectively (Figure 5.14). As shown in Figure 5.15, the application of liquid nitrogen does not lead to notable differences in the total corroded area. However, cryogenic machining results in about 183% increase in the maximum depth of the corrosion pits (130 μ m vs 71 μ m).

The results obtained when using both 30- μ m and 70- μ m edge radius tools show that the application of liquid nitrogen does not lead to a notable reduction in the maximum corrosion pit depth, and it even increases significantly when the large edge radius tool is used. This could be explained by the microstructures of the machined samples in Figure 5.4; large amounts of deformation twins, which were reported to increase the corrosion rate of AZ31B Mg alloy (Aung & Zhou, 2010), formed below the featureless layers when liquid nitrogen was used. Therefore, after the 5 wt% NaCl solution penetrates the featureless layer, the twinning areas in the samples after cryogenic machining are more easily corroded the initial microstructure with no twinning, and this leads to deeper corrosion pits.

Figure 5.16 shows the photos of AZ31B Mg samples machined under different cooling conditions and cutting edge radii after corrosion test in SBF for 10 days. Similar to the corrosion performance in 5 wt% NaCl, dry machining using the 30- μ m cutting edge radius tool led to the poorest corrosion resistance. This finding further proves that the

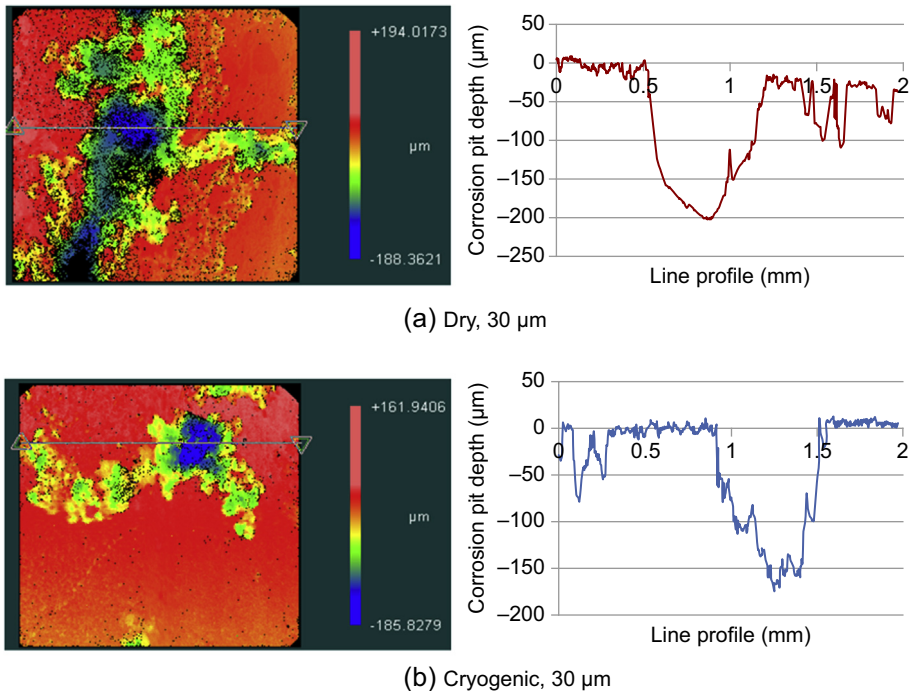


Figure 5.14 Zygo three-dimensional (3D) topographic pictures of the corroded area as marked by a red square in Figure 5.13 and corresponding line profiles under different cutting conditions: a) dry, 30 μm and b) cryogenic, 30 μm ($V = 100$ m/min, $f = 0.1$ mm/rev) (Pu, 2012).

featureless layers formed on the other three samples shown in Figure 5.4 acted as protective coatings and prevented the matrix from further corrosion.

When using 30- μm edge radius tools, the maximum depth of the corrosion pits on the machined samples under cryogenic cooling was reduced significantly from 167 μm to 73 μm when compared with dry machined specimens shown in Figure 5.17. This finding is different from the results obtained in 5 wt% NaCl solution, which suggests that the deformation twins might not reduce the corrosion resistance of AZ31B Mg alloy in SBF. Even greater reductions in the maximum depth of corrosion pits were found on samples machined using 70- μm edge radius tools. Almost no corrosion damage can be found on the sample machined using cryogenic conditions with the large edge radius tool. This finding agrees with the expectation because the surface integrity induced by cryogenic machining with the 70- μm edge radius tool was the best in terms of nanograin structures, strongest basal texture, and large and deep compressive residual stresses.

5.4.2 Corrosion performance of burnished samples

As shown in Figure 5.18, dramatic differences in surface morphologies can be found between the ground and burnished surfaces after the immersion test of 200 h in 5 wt% NaCl; the differences between burnished samples produced using dry and cryogenic

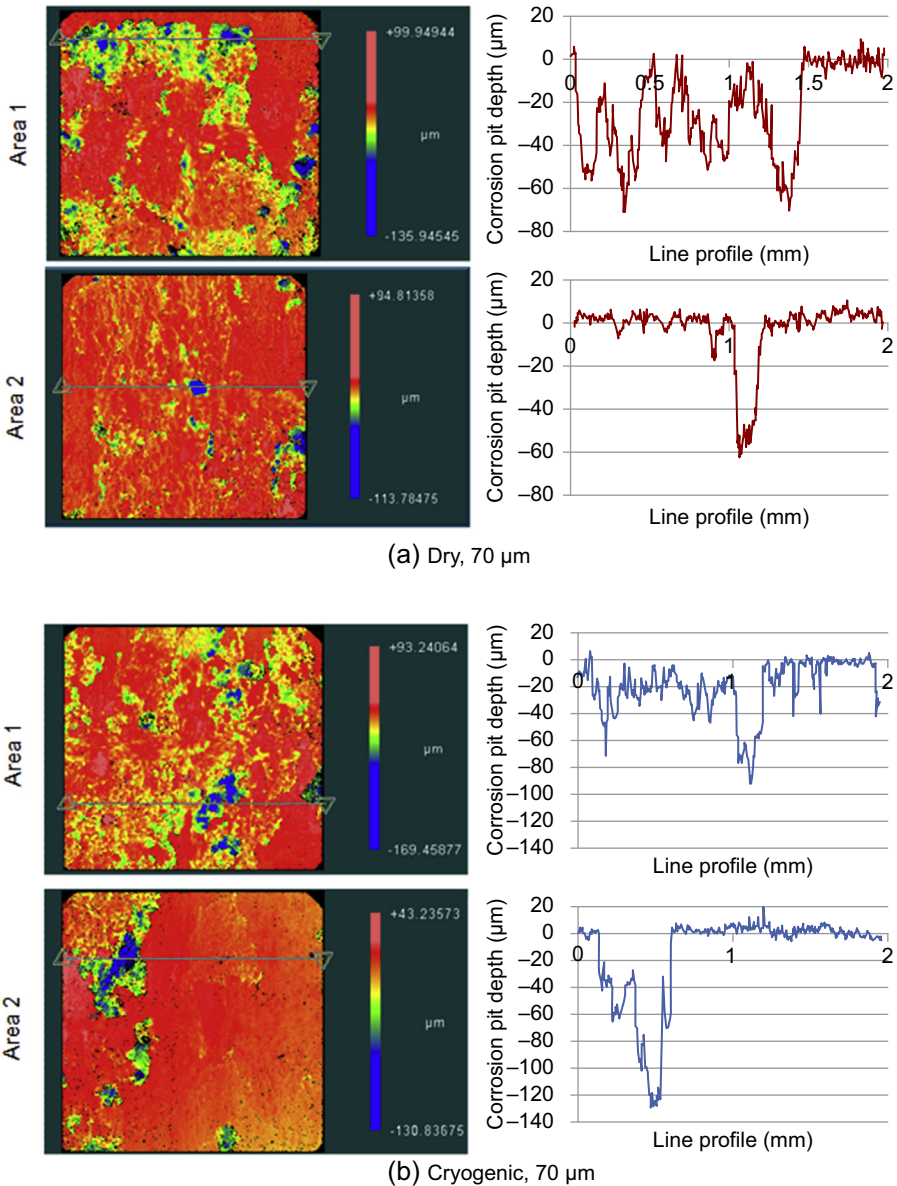


Figure 5.15 Zygo three-dimensional (3D) topographic pictures of the corroded area as marked by a red square in Figure 5.13 and corresponding line profiles under different cutting conditions: a) dry, 70 μm and b) cryogenic, 70 μm ($V = 100$ m/min, $f = 0.1$ mm/rev) (Pu, 2012).

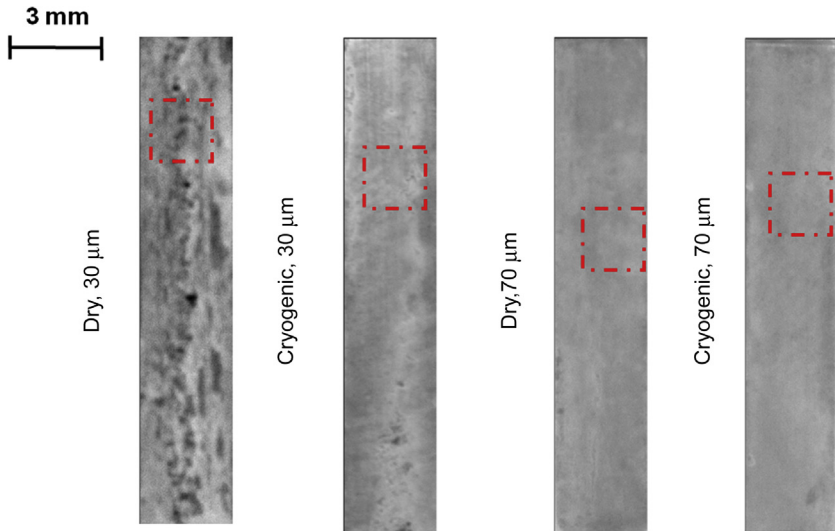


Figure 5.16 Photos of machined AZ31B Mg samples under different cooling conditions and cutting edge radii after corrosion test in simulated body fluid (SBF) for 10 days ($V = 100$ m/min, $f = 0.1$ mm/rev) (Pu, 2012).

conditions are much smaller for the same test duration than the difference between ground and burnished surfaces. The preburnished ground samples were successively ground using up to 4000 grit SiC paper in order to have similar surface roughness as the burnished samples. This eliminates the possible influence of surface roughness on corrosion resistance (Song & Xu, 2010).

The ground surface after the immersion test is very rough; large and deep pits are visible over the entire surface. On the dry and cryogenic-burnished surfaces, there are only some small pits in the surfaces and the corroded areas of the burnished samples are smaller than those in the ground samples. This suggests that much less Mg was corroded from the burnished surfaces than from the ground ones.

To investigate the depth of the corrosion pits, topographic maps of the severely corroded portion of each surface (marked as square boxes in Figure 5.18) were obtained using the Zygo NewView 6000 measurement system, as shown in Figure 5.19 (a–c). The depth profiles along the dotted lines shown in Figure 5.19 (a–c) are presented in Figure 5.19 (d). The profiles show that the corrosion pits on the ground samples are very deep; the maximum measured depth is $512\ \mu\text{m}$ while the pits on the burnished surfaces are less than $200\ \mu\text{m}$ deep. Figure 5.19 also shows that the corrosion on the burnished samples is more uniform than that on the ground samples.

Typical cross-sectional microstructures of ground and cryogenic-burnished samples after a 30-h immersion test are shown in Figure 5.20. There are significant differences in corrosion morphology between the samples prepared by grinding and those made by cryogenic burnishing. Wide and deep corrosion pits are present on the ground sample. The grain boundaries are clearly visible and do not show any barrier effects to corrosion development. The surface after cryogenic burnishing is much smoother and corrosion

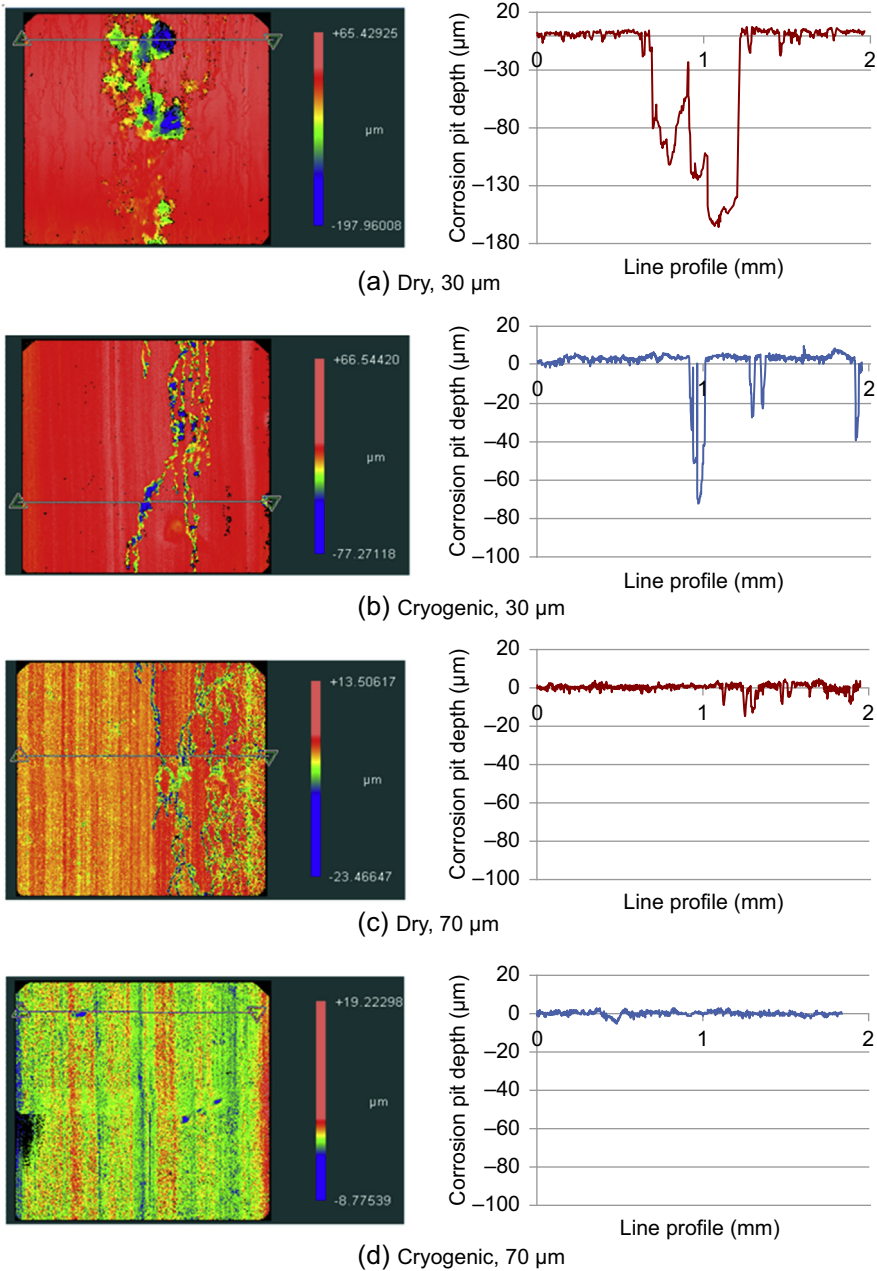


Figure 5.17 Zygo three-dimensional (3D) topographic pictures of the corroded area as marked by a red square in Figure 5.16 and corresponding line profiles under different cutting conditions: a) dry, 30 μm , b) cryogenic, 30 μm , c) dry, 70 μm , and d) cryogenic, 70 μm ($V = 100$ m/min, $f = 0.1$ mm/rev) (Pu, 2012).

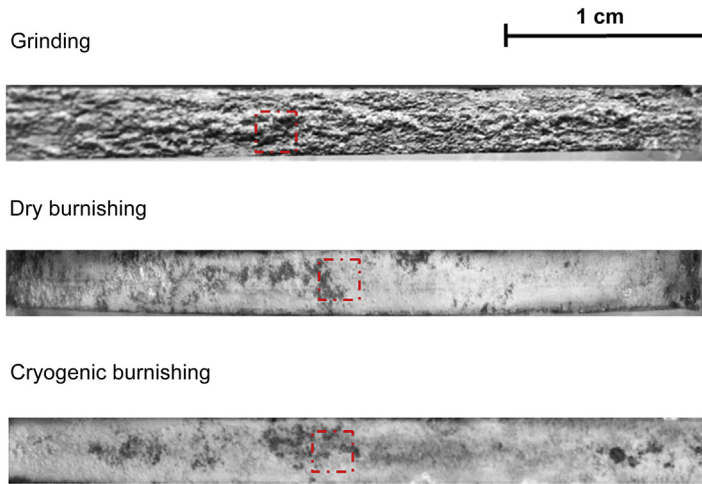


Figure 5.18 Surface morphology of AZ31B Mg samples processed by different treatments after immersion in 5 wt% NaCl solution for 200 h (details in the square boxes are shown in Figure 5.19) (Pu et al., 2012b).

occurred more uniformly, creating small and shallow pits. The grain boundaries are not visible at this scale, and the microstructure is similar to the one shown in Figure 5.9(c), which suggests that corrosion occurred within the grain refined layer after 30 h of immersion. The uniformity in corrosion may be due to the similarity in grain size and the electrochemical homogenization (Orlov, Ralston, Birbilis, & Estrin, 2011) induced by the burnishing process. Different from the ground sample, a layer of corrosion products adhered to the cryogenically burnished surface, as shown in Figure 5.20 (b). Apparently, the uniform corrosion products better protect the substrate from corrosion. This finding is directly supported by the literature showing that a higher density of grain boundaries promoted better mechanical adhesion through an oxide pegging mechanism (Balakrishnan, Lee, Kim, & Panigrahi, 2008; Tao & Li, 2006).

A corrosion test of the burnished samples in SBF will be conducted in the future. Based on the similar trend of machined samples subjected to immersion tests in 5 wt% NaCl solution and SBF, it is expected that the burnished samples will exhibit improved corrosion resistance than the unburnished ones.

5.5 Finite element modeling of grain size changes in cryogenic machining

It was shown in the previous section that both cryogenic machining and cryogenic burnishing significantly changed the surface integrity of the AZ31B Mg alloy, which led to remarkable changes in its corrosion resistance. To achieve the desired biodegradation rate (which is controllable and predictable) on the Mg-based implants, it is important to use the correct processing conditions. Instead of extensive trial-and-

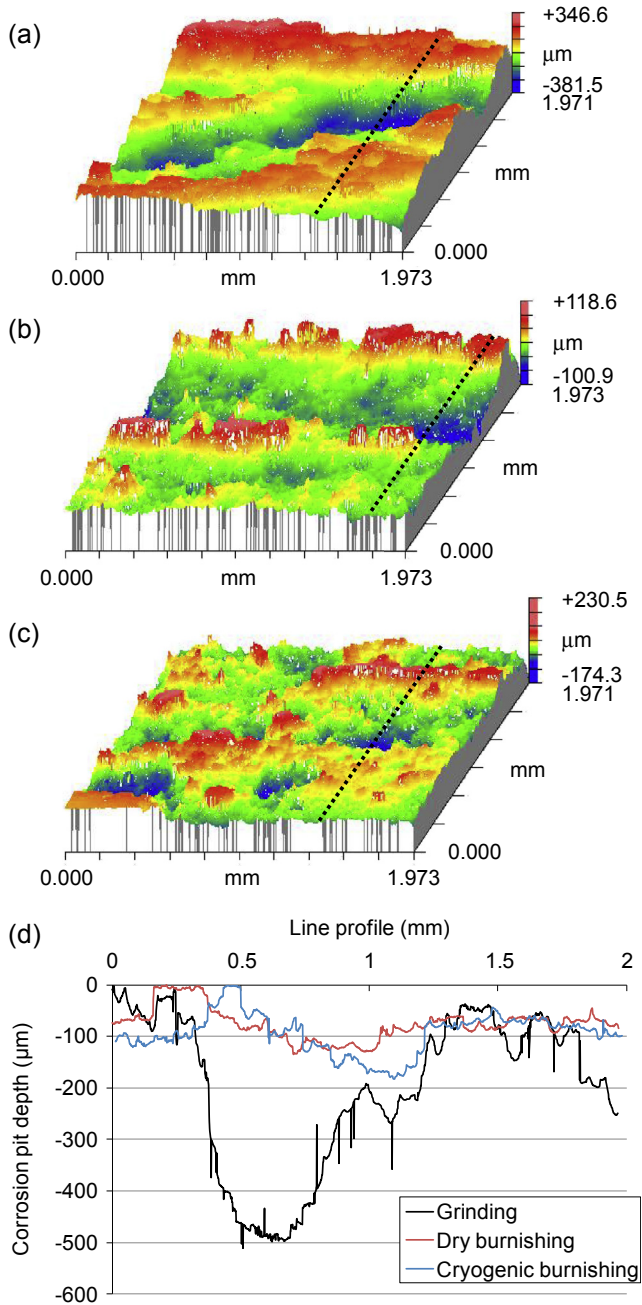


Figure 5.19 Topographic maps of the square boxes in [Figure 5.18](#) obtained by Zygo: (a) ground; (b) dry- and (c) cryogenic-burnished samples; and (d) corrosion pit depth profiles along the dotted lines ([Pu et al., 2012b](#)).

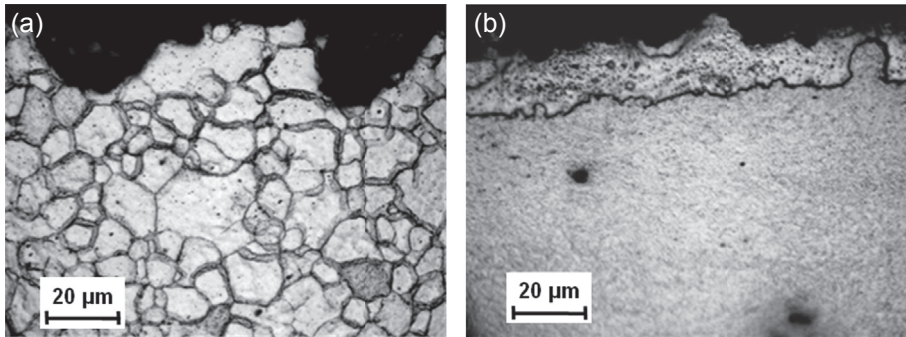


Figure 5.20 Typical cross-sectional microstructures of (a) ground and (b) cryogenic-burnished samples after immersion in 5 wt% NaCl solution for 30 h (Pu et al., 2012b).

error tests, predictive models can greatly reduce the time and cost to find suitable processing conditions. Obviously, some mixture of modeling and experimental tests is needed for more complete understanding.

Grain size is one of the most important factors for corrosion resistance, according to the literature review and the current study. However, very limited research has been conducted to predict grain size changes created by machining. A subroutine based on an empirical relationship between grain size and the Zener-Hollomon parameter (Yanagimoto, Karhausen, Brand, & Kopp, 1998) during DRX was developed and implemented in DEFORM 2D to simulate the grain size changes in the machining of AISI 52100 (Caruso et al., 2011) and AA7075-T561 Alloy (Rotella, Dillon, Umbrello, Settineri, & Jawahir, 2013). Dislocation density-based material models were developed to model grain size refinement and grain misorientation during orthogonal machining of commercially pure Ti (Ding & Shin, 2011).

In this study, a user subroutine based on the empirical relationship between grain size and the Zener-Hollomon parameter was developed by the authors and implemented in DEFORM 2D software to predict the grain size changes on the machined surface of AZ31B Mg alloy under both dry and cryogenic conditions (Pu et al., 2014). An iterative procedure was used to evaluate the constants employed in the subroutine using the experimental data, as shown in Figure 5.21. The results from numerical studies using the calibrated model (Figures 5.22 and 5.23) agree well with the experimental data (Figure 5.4).

5.6 Summary and future trends

This chapter demonstrates that cryogenic machining and burnishing processes can be used as effective mechanical processing methods to change and control the corrosion rate and other surface integrity parameters of magnesium alloys and therefore modify

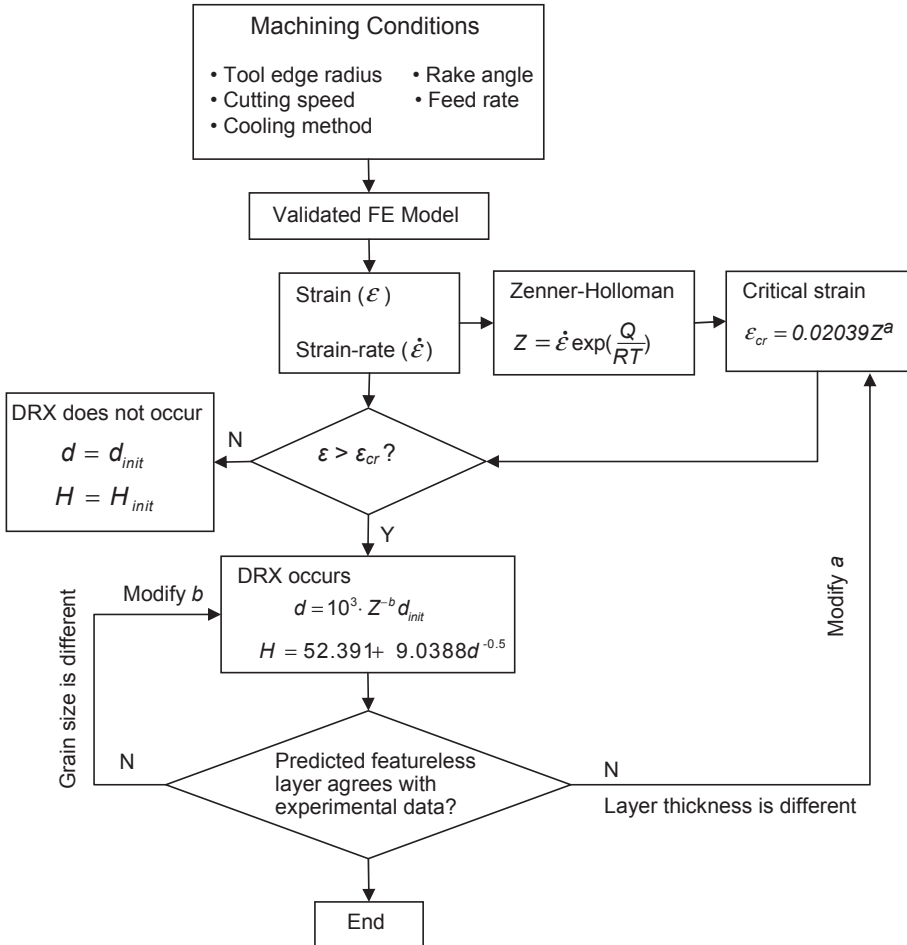


Figure 5.21 Flow chart for the calibration of the user subroutine to predict the featureless layer on the machined surface (Pu et al., 2014).

their biodegradation rate without changing the chemical composition. Major findings from this study are as follows:

- Cryogenic machining using the large honed cutting tool led to enhanced surface integrity in terms of significant grain refinement from 12 μm to 31 nm in the featureless surface layer, preferred orientation of the (0002) basal plane on the machined surface, and compressive residual stresses. Cryogenic machining also resulted in the best corrosion resistance in the machined samples tested in both 5% NaCl solution and SBF.
- A strong correlation between grain size and corrosion resistance was found for both the machined and burnished samples. The grain refinement layer promotes the formation of a passive film and improves the corrosion resistance in the both 5% NaCl solution and SBF.
- Under dry conditions, the surface machined with a 70- μm edge radius tool is more corrosion resistant than the one machined with a 30- μm edge radius tool in both the 5 wt% NaCl solution and the SBF.

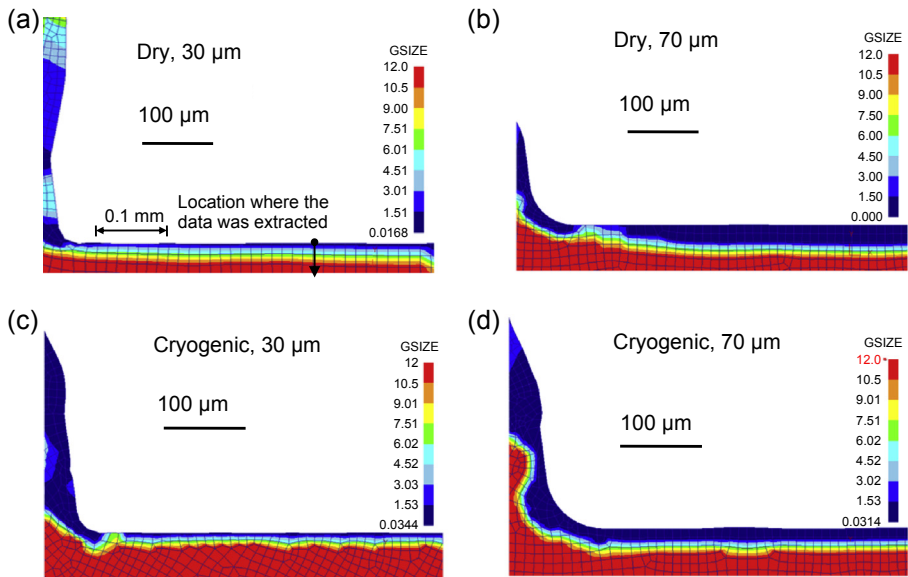


Figure 5.22 Predicted grain size distribution after machining using different cooling methods and tools with various edge radii: a) dry, 30 μm , b) dry, 70 μm , c) cryogenic, 30 μm , and d) cryogenic, 70 μm ($V = 100 \text{ m/min}$, $f = 0.1 \text{ mm/rev}$) (Pu et al., 2014).

- Burnishing remarkably increased the grain refinement layer thickness compared with machining and also created a much stronger basal texture. The total process-influence layer where significant microstructural changes occurred is up to 3.4 mm. The application of liquid nitrogen during burnishing resulted in a greater reduction in grain size on the burnished surface than dry burnishing (0.5 μm vs 1.4 μm , initial grain size is 12 μm). The corrosion resistance of burnished samples is much higher than the reference sample. The difference in corrosion resistance between dry and cryogenic conditions is small.
- Although in its infancy, finite element modeling can be used to predict grain size resulting from cryogenic machining, and this can remarkably reduce the time and cost needed for extensive experimental studies.

One of the most significant implications of this study is that, by proper selection of processing parameters, cryogenic machining and cryogenic burnishing are simple and cost-effective manufacturing processes that could offer a unique opportunity to modify the biodegradation rate of Mg-based implants by tailoring their microstructures, crystallographic orientations, and residual stresses on the surface and subsurface. However, to achieve this goal, more research is needed, including the following:

- The influence of other important processing parameters on surface integrity needs to be studied, such as rake angle, cutting speed, feed rate, tool materials, etc.
- Other manufacturing processes frequently used in biomedical implant manufacturing, such as milling, drilling, and tapping, need to be investigated.
- More comprehensive *in vitro* corrosion tests need to be conducted, such as tests that can simulate the effects of cyclic loading of implants during service.

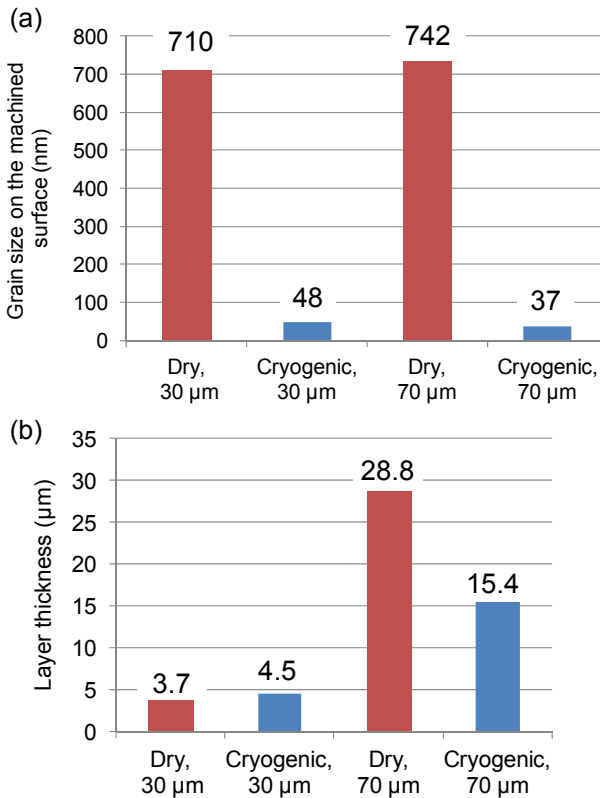


Figure 5.23 (a) Predicted grain size on the machined surface and (b) thickness of the featureless layers under different machining conditions ($V = 100$ m/min, $f = 0.1$ mm/rev) (Pu et al., 2014).

- *In vivo* tests are needed to study the corrosion performance of processed samples in actual biological environments.
- Fatigue tests are also needed to evaluate the influence of these processing methods. It is expected that the fatigue life is improved due to the induced compressive residual stresses.
- Predictive models need to be developed for both cryogenic machining and cryogenic burnishing to predict not only the grain size after processing but also other important surface integrity parameters, such as residual stresses and crystallographic orientation.

References

- Alvarez-Lopez, M., Pereda, M. D., Del Valle, J. A., Fernandez-Lorenzo, M., Garcia-Alonso, M. C., Ruano, O. A., et al. (2010). Corrosion behaviour of AZ31 magnesium alloy with different grain sizes in simulated biological fluids. *Acta Biomaterialia*, 6, 1763–1771.
- Aung, N. N., & Zhou, W. (2010). Effect of grain size and twins on corrosion behaviour of AZ31B magnesium alloy. *Corrosion Science*, 52, 589–594.

- Balakrishnan, A., Lee, B. C., Kim, T. N., & Panigrahi, B. B. (2008). Corrosion behaviour of ultra Fine grained titanium in simulated body fluid for implant application. *Trends in Biomaterials and Artificial Organs*, 22, 54–60.
- Ben Rhouma, A., Braham, C., Fitzpatrick, M. E., Ledion, J., & Sidhom, H. (2001). Effects of surface preparation on pitting resistance, residual stress, and stress corrosion cracking in austenitic stainless steels. *Journal of Materials Engineering and Performance*, 10, 507–514.
- Birbilis, N., Ralston, K. D., & Davies, C. H. J. (2010). Revealing the relationship between grain size and corrosion rate of metals. *Scripta Materialia*, 63, 1201–1204.
- Birbilis, N., Ralston, K. D., Virtanen, S., Fraser, H. L., & Davies, C. H. J. (2010). Grain character influences on corrosion of ECAPed pure magnesium. *Corrosion Engineering Science and Technology*, 45, 224–230.
- Brinksmeier, E., Cammett, J. T., König, W., Leskovaar, P., Peters, J., & Tönshoff, H. K. (1982). Residual stresses—Measurement and causes in machining processes. *CIRP Annals-Manufacturing Technology*, 31, 491–510.
- Caruso, S., Renzo, S., Umbrello, D., Jayal, A. D., Dillon, O. W., & Jawahir, I. S. (2011). Finite element modeling of microstructural changes in hard turning. *Advanced Materials Research*, 223, 960–968.
- Chang, T.-C., Wang, J.-Y., O, C.-M., & Lee, S. (2003). Grain refining of magnesium alloy AZ31 by rolling. *Journal of Materials Processing Technology*, 140, 588–591.
- Denkena, B., & Lucas, A. (2007). Biocompatible magnesium alloys as absorbable implant materials – adjusted surface and subsurface properties by machining processes. *CIRP Annals - Manufacturing Technology*, 56, 113–116.
- Ding, H., & Shin, Y. C. (2011). Dislocation density-based grain refinement modeling of orthogonal cutting of commercially pure titanium. *ASME Conference Proceedings*, 2011, 89–98.
- Hornbach, D., Prevey, P., & Loftus, E. (2006). Application of low plasticity burnishing (LPB) to improve the fatigue performance of Ti-6Al-4V femoral hip stems. *Journal of ASTM International*, 3.
- Hornberger, H., Virtanen, S., & Boccaccini, A. R. (2012). Biomedical coatings on magnesium alloys – a review. *Acta Biomaterialia*, 8, 2442–2455.
- Hoseini, M., Shahryari, A., Omanovic, S., & Szpunar, J. A. (2009). Comparative effect of grain size and texture on the corrosion behaviour of commercially pure titanium processed by equal channel angular pressing. *Corrosion Science*, 51, 3064–3067.
- Kenda, J., Pusavec, F., & Kopac, J. (2011). Analysis of residual stresses in sustainable cryogenic machining of nickel based alloy-Inconel 718. *Journal of Manufacturing Science and Engineering*, 133, 041009.
- Leverant, G., Langer, B., Yuen, A., & Hopkins, S. (1979). Surface residual stresses, surface topography and the fatigue behavior of Ti-6Al-4V. *Metallurgical and Materials Transactions A*, 10, 251–257.
- Liao, J., Hotta, M., Motoda, S.-I., & Shinohara, T. (2013). Atmospheric corrosion of two field-exposed AZ31B magnesium alloys with different grain size. *Corrosion Science*, 71, 53–61.
- Liu, M., Qiu, D., Zhao, M. C., Song, G., & Atrens, A. (2008). The effect of crystallographic orientation on the active corrosion of pure magnesium. *Scripta Materialia*, 58, 421–424.
- Matsumoto, Y., Hashimoto, F., & Lahoti, G. (1999). Surface integrity generated by precision hard turning. *CIRP Annals - Manufacturing Technology*, 48, 59–62.
- Mcbride, E. D. (1938). Absorbable metal in bone surgery. *Journal of the American Medical Association*, 111, 2464–2467.
- Mughrabi, H., & Hoppel, H. W. (2010). Cyclic deformation and fatigue properties of very fine-grained metals and alloys. *International Journal of Fatigue*, 32, 1413–1427.

- Nasr, M. N. A., Ng, E. G., & Elbestawi, M. A. (2007). Modeling the effects of tool-edge radius on residual stresses when orthogonal cutting AISI 316L. *International Journal of Machine Tools & Manufacture*, 47, 401–411.
- Noyan, I. C., & Cohen, J. B. (1987). *Residual stress: Measurement by diffraction and interpretation*. New York, NY: Springer.
- Orlov, D., Ralston, K. D., Birbilis, N., & Estrin, Y. (2011). Enhanced corrosion resistance of Mg alloy ZK60 after processing by integrated extrusion and equal channel angular pressing. *Acta Materialia*, 59, 6176–6186.
- Prevéy, P. S., Jayaraman, N., & Ravindranath, R. (2010). Fatigue life extension of steam turbine alloys using low plasticity burnishing (LPB). *ASME Conference Proceedings*, 2010, 2277–2287.
- Pu, Z. (2012). *Cryogenic machining and burnishing of AZ31B magnesium alloy for enhanced surface integrity and functional performance*. PhD. University of Kentucky. http://works.bepress.com/zhengwen_pu/1/.
- Pu, Z., Outeiro, J. C., Batista, A. C., Dillon, O. W., Jr., Puleo, D. A., & Jawahir, I. S. (2012a). Enhanced surface integrity of AZ31B Mg alloy by cryogenic machining towards improved functional performance of machined components. *International Journal of Machine Tools and Manufacture*, 56, 17–27.
- Pu, Z., Song, G. L., Yang, S., Outeiro, J. C., Dillon, O. W., Jr., Puleo, D. A., et al. (2012b). Grain refined and basal textured surface produced by burnishing for improved corrosion performance of AZ31B Mg alloy. *Corrosion Science*, 57, 192–201.
- Pu, Z., Umbrello, D., Dillon, O. W., Jr., Lu, T., Puleo, D. A., & Jawahir, I. S. (2014). Finite element modeling of microstructural changes in dry and cryogenic machining of AZ31B magnesium alloy. *Journal of Manufacturing Processes*, 16(2), 335–343.
- Pu, Z., Yang, S., Song, G. L., Dillon, O. W., Jr., Puleo, D. A., & Jawahir, I. S. (2011). Ultrafine-grained surface layer on Mg-Al-Zn alloy produced by cryogenic burnishing for enhanced corrosion resistance. *Scripta Materialia*, 65, 520–523.
- Ralston, K. D., & Birbilis, N. (2010). Effect of grain size on corrosion: a review. *Corrosion*, 66.
- Ramesh, A., Melkote, S. N., Allard, L. F., Riester, L., & Watkins, T. R. (2005). Analysis of white layers formed in hard turning of AISI 52100 steel. *Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing*, 390, 88–97.
- Reedhill, R. E., & Robertson, W. D. (1957). The crystallographic characteristics of fracture in magnesium single crystals. *Acta Metallurgica*, 5, 728–737.
- Rotella, G., Dillon, O. W., Jr., Umbrello, D., Settineri, L., & Jawahir, I. S. (2013). Finite element modeling of microstructural changes in turning of AA7075-T651 alloy. *Journal of Manufacturing Processes*, 15, 87–95.
- Sakai, T., Hashimoto, A., Hamada, G., & Utsunomiya, H. (2011). *Deformation and evolution of microstructure and texture during high speed heavy rolling of AZ31 magnesium Alloy sheet. Magnesium technology 2011*. Hoboken, NJ: John Wiley & Sons, Inc.
- Salahshoor, M., & Guo, Y. B. (2011). Surface integrity of biodegradable magnesium-calcium orthopedic implant by burnishing. *Journal of the Mechanical Behavior Biomedical Materials*, 4, 1888–1904.
- Scheel, J. E., Prevéy, P. S., III, & Hornbach, D. J. (2010). *The effect of surface enhancement on the corrosion properties, fatigue strength, and degradation of aircraft aluminum*. Corrosion 2010, March 14–18, San Antonio, TX.
- Shi, Y. N., Sun, H. Q., Zhang, M. A., & Lu, K. (2007). Plastic strain-induced grain refinement in the nanometer scale in a Mg alloy. *Acta Materialia*, 55, 975–982.

- Song, G., Atrens, A., & St. John, D. (2001). *An hydrogen evolution method for the estimation of the corrosion rate of magnesium alloys*. New Orleans, LA: Magnesium Technology 2001.
- Song, G. L., Mishra, R., & Xu, Z. Q. (2010). Crystallographic orientation and electrochemical activity of AZ31 Mg alloy. *Electrochemistry Communications*, 12, 1009–1012.
- Song, G. L., & Song, S. Z. (2007). A possible biodegradable magnesium implant material. *Advanced Engineering Materials*, 9, 298–302.
- Song, G. L., & Xu, Z. Q. (2010). The surface, microstructure and corrosion of magnesium alloy AZ31 sheet. *Electrochimica Acta*, 55, 4148–4161.
- Song, G. L., & Xu, Z. (2012). Effect of microstructure evolution on corrosion of different crystal surfaces of AZ31 Mg alloy in a chloride containing solution. *Corrosion Science*, 54, 97–105.
- Tao, S., & Li, D. Y. (2006). Tribological, mechanical and electrochemical properties of nanocrystalline copper deposits produced by pulse electrodeposition. *Nanotechnology*, 17, 65–78.
- To, S., Lee, W. B., & Cheung, C. F. (2003). Orientation changes of aluminium single crystals in ultra-precision diamond turning. *Journal of Materials Processing Technology*, 140, 346–351.
- Turnbull, A., Mingard, K., Lord, J. D., Roebuck, B., Tice, D. R., Mottershead, K. J., et al. (2011). Sensitivity of stress corrosion cracking of stainless steel to surface machining and grinding procedure. *Corrosion Science*, 53, 3398–3415.
- Umbrello, D., Outeiro, J. C., M'saoubi, R., Jayal, A. D., & Jawahir, I. S. (2010). A numerical model incorporating the microstructure alteration for predicting residual stresses in hard machining of AISI 52100 steel. *Cirp Annals-Manufacturing Technology*, 59, 113–116.
- Umbrello, D., Pu, Z., Caruso, S., Outeiro, J. C., Jayal, A. D., Dillon, O. W., et al. (2011). The effects of cryogenic cooling on surface integrity in hard machining. *Procedia Engineering*, 19, 371–376.
- Wang, H., Estrin, Y., Fu, H., Song, G., & Zuberova, Z. (2007). The effect of pre-processing and grain structure on the bio-corrosion and fatigue resistance of magnesium alloy AZ31. *Advanced Engineering Materials*, 9, 967–972.
- Wang, X. Y., & Li, D. Y. (2002). Mechanical and electrochemical behavior of nanocrystalline surface of 304 stainless steel. *Electrochimica Acta*, 47, 3939–3947.
- Watanabe, H., Tsutsui, H., Mukai, T., Ishikawa, K., Okanda, Y., Kohzu, M., et al. (2001). Grain size control of commercial wrought Mg-Al-Zn alloys utilizing dynamic recrystallization. *Materials Transactions (Japan)*, 42, 1200–1205.
- Witte, F. (2010). The history of biodegradable magnesium implants: a review. *Acta Biomaterialia*, 6, 1680–1692.
- Wusatowska-Sarnek, A., Dubiel, B., Czyrska-Filemonowicz, A., Bhowal, P., Ben Salah, N., & Klemberg-Sapieha, J. (2011). Microstructural characterization of the White etching layer in nickel-based superalloy. *Metallurgical and Materials Transactions A*, 1–13.
- Xin, R., Li, B., Li, L., & Liu, Q. (2011). Influence of texture on corrosion rate of AZ31 Mg alloy in 3.5 wt.% NaCl. *Materials & Design*, 32, 4548–4552.
- Yanagimoto, J., Karhausen, K., Brand, A. J., & Kopp, R. (1998). Incremental formulation for the prediction of flow stress and microstructural change in hot forming. *Journal of Manufacturing Science and Engineering-Transactions of the ASME*, 120, 316–322.
- Zhang, Y. S., Han, Z., Wang, K., & Lu, K. (2006). Friction and wear behaviors of nanocrystalline surface layer of pure copper. *Wear*, 260, 942–948.
- Zinn, W., & Scholtes, B. (1999). Mechanical surface treatments of lightweight materials - effects on fatigue strength and near-surface microstructures. *Journal of Materials Engineering and Performance*, 8, 145–151.

Anodic electrodeposition of MgO coatings to improve corrosion resistance *in vivo*

6

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6.1 Introduction

Magnesium and its alloys have attracted great attention as orthopedic biodegradable implant materials due to their close mechanical properties to natural bone and perfect biocompatibility (Staiger, Pietak, Huadmai, & Dias, 2006). However, the currently developed magnesium alloys are extremely susceptible to galvanic corrosion and thus degrade earlier than the actual period of the bone healing process, which is primarily attributed to the high chemical activity of magnesium and the lack of a protective passive oxide film (Makar & Kruger, 1993). This disadvantage has restricted their widespread application, especially in aggressive environments (Song & Atrens, 2003).

There is a high demand to design magnesium alloys with controllable corrosion rates and suitable mechanical properties. To improve the corrosion resistance of magnesium alloys, it is necessary to employ proper surface treatments to produce anticorrosion protection films on the substrate. In the past several decades, many surface modification techniques have been developed for the protection of magnesium alloys, including electrochemical plating, conversion coatings, anodizing, laser surface alloying, and organic coatings (Gray & Luan, 2002). Among these techniques, anodizing is one of the most popular methods to provide protection to magnesium alloys (Shi, Song, & Atrens, 2006; Blawert, Dietzel, Ghali, & Song, 2006; Khaselev, Weiss, & Yahalom, 2001). Plasma anodizing, namely micro-arc oxidation (MAO) (Wang, Wang, Xu, Zhao, Ouyang, 2009) or plasma electrolytic oxidation (PEO) (Gupta, Tenhundfeld, Daigle, & Ryabkov, 2007) treatment, is a relatively new anodizing process to provide protection to magnesium alloys. In this anodizing process, an oxide film is formed at the magnesium or magnesium alloy surface at high voltage using an electricity source in an alkaline electrolyte containing phosphate, silicate, borate, and organic substances. The MAO and PEO coatings were found to be mainly composed of magnesium oxide, with some other electrolyte-borne elements (Mg_2SiO_4 , $\text{Mg}_3(\text{PO}_4)_2$ or MgAl_2O_4 , etc.) (Arrabal, Matykina, Skeldon, Thompson, & Pardo, 2008; Barchiche, Rocca, Juers, Hazan, & Steinmetz, 2007; Cai, Wang, Wei, & Liu, 2006). However, these complex coatings are not favorable for application as biomaterials from the biocompatibility point of view. Secondary, cracks and micro-pores are generally produced in MAO or PEO coating films due to the sparking

phenomenon at high voltage in the anodizing process — the presence of which is detrimental to the corrosion resistance of oxide films.

It is well known that the passivation of magnesium in an alkaline solution commences easily, resulting in magnesium oxide (MgO) film formation on the Mg surface, which has no protective properties and leads to a heavy corrosion (Nordlien, Ono, Masuko, & Nisancioglu, 1997; Ruggeri & Roue, 2003; Lavrenko, Skorokhod, Shvets, & Khomko, 2003). Some fundamental studies about the anodic behavior of Mg in alkaline solution have been demonstrated by Huber (1953) and by Khaselev and Yahalom (1998). Stippich, Vera, Wolf, Berg, and Friedrich (1998) reported the enhanced corrosion protection of MgO coatings on magnesium deposited by ion beam-assisted evaporation. MgO coatings on Mg-Ca alloy by an alkali heat treatment also showed positive evidence of a reduction in the corrosion rate (Gu, Zheng, Cheng, & Zheng, 2009). Recently, the formation of MgO coating films on magnesium by an anodic electrodeposition process in KOH solution was also reported (Cai, Lu, Li, Liang, & Zhou, 2009). However, there is little information on the microstructure and surface morphology of the as-grown MgO passive film.

The development of new surface treatments on Mg alloy has been a challenge in biomaterials research. In this chapter, we introduce the anodic electrodeposition of MgO for biomedical applications. A simple alternative to the plasma anodizing process is proposed to produce an MgO coating film on the Mg alloy by an anodic electrodeposition process in various concentrations of KOH alkaline solution, followed by annealing treatment. The morphology and composition of the as-grown MgO coating film are discussed on the basis of observations made using scanning electron microscopy (SEM), electron dispersion X-ray spectroscopy (EDX), and X-ray diffraction (XRD). A potentiodynamic polarization test in a corrosive 3.5-wt% NaCl solution and long-term immersing test in simulated body fluid (SBF) are employed to evaluate the anticorrosion properties of the anodic MgO films. Biodegradable polymer polylactic acid (PLA) is introduced to prepare MgO/PLA composite film by dipping the Mg alloy with MgO coating into PLA solution. Further improvement in corrosion resistance is discussed.

6.2 Preparation and characterization of MgO coating on Mg alloy

6.2.1 Anodic polarization behavior

Die-cast homemade Mg-Zn-Ca alloy slices (13 mm in diameter) are used as working electrodes by sealing in a Teflon jacket with an exposed geometric area of 1 cm^2 . The anodic oxidation process of magnesium alloy in an alkaline solution was studied by a linear potential sweep, which showed different polarization characteristics in 6 and 10 M KOH solution, as shown in Figure 6.1. The anodic oxidation curve in 6 M KOH solution shows that the Mg alloy experienced four processes: active dissolution (region A), passivation (region B), secondary oxidation (region C), and transpassive processes (region D), which is in good agreement with Cai et al. (2009).

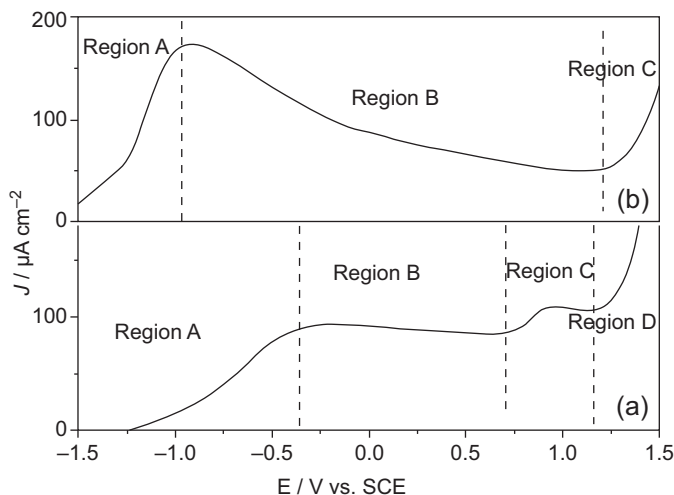


Figure 6.1 Anodic polarization curve of Mg-Zn-Ca alloy in (a) 6 M and (b) 10 M KOH solution at a scan rate of 3 mV/s.

On the contrary, only active dissolution, passivation, and transpassive processes were observed for the anodic polarization curve in 10 M KOH solution. Region A was ascribed to the anodic dissolution of magnesium, leading to the formation of Mg^{2+} (Song & Son, 2006, Udhayan & Prakash, 1996):



Therefore, when the potential applied was more positive than the open circuit potential (E_{ocp}), the Mg alloy behaved with active dissolution and the anodic oxidation product of magnesium at region A was Mg^{2+} . When the concentration of Mg^{2+} on the electrode surface reached its saturation, $\text{Mg}(\text{OH})_2$ was formed and deposited on the electrode surface, which thickened with anodization time and progressively hindered the oxidation rate; thus, the magnesium became passivated. Accordingly, the anodic oxidation of magnesium in the passive region B led to the formation of magnesium hydroxide by the reaction of dissolved Mg^{2+} with hydroxyl ions in solution:



The oxidation of magnesium in the secondary oxidation region C is confirmed to form MgO (Cai et al., 2009):



The transpassive process was ascribed to oxygen evolution, which was confirmed by the observation of a large amount of bubbles on the Mg electrode surface. Consequently, when potential was controlled at the secondary oxidation region in

6 M KOH solution for anodic oxidation of Mg alloy, the formation of MgO coating was anticipated. On the other hand, when the potential was controlled in the passivation region, $\text{Mg}(\text{OH})_2$ coating was produced.

Based on the anodic oxidation process of magnesium alloy in 6 and 10 M KOH alkaline solution, MgO or $\text{Mg}(\text{OH})_2$ coating on Mg alloy is prepared by anodic electrodeposition at a constant potential of 1.0 V (vs. saturated calomel electrode) for 2 h. The $\text{Mg}(\text{OH})_2$ coating is then converted to MgO by subsequent calcination treatment in air at 400–450 °C (Hahn, Brunner, Kunze, Schmuki, & Virtanen, 2008; Latha, Li, Charles, Roger, & Wang, 2009)

6.2.2 Characterization of oxide coatings on Mg alloy

X-ray diffraction was employed to identify and investigate the phase composition of the oxide coatings formed by anodic oxidation of magnesium in different KOH solutions. Figure 6.2 shows the X-ray diffraction spectra of the as-grown and annealed samples. The XRD patterns, as shown in Figure 6.2a and b, indicate that the oxide coating formed in 6 M KOH solution, either at room temperature or after annealing treatment, consists mainly of MgO, which is confirmed by the specific peak at $2\theta = 42.9^\circ$ (Joint Committee on Powder Diffraction Standards card 86–0441) besides the peaks of α -Mg. This fact means that MgO coating films can be obtained by simple anodic oxidation of magnesium alloy in 6 M KOH

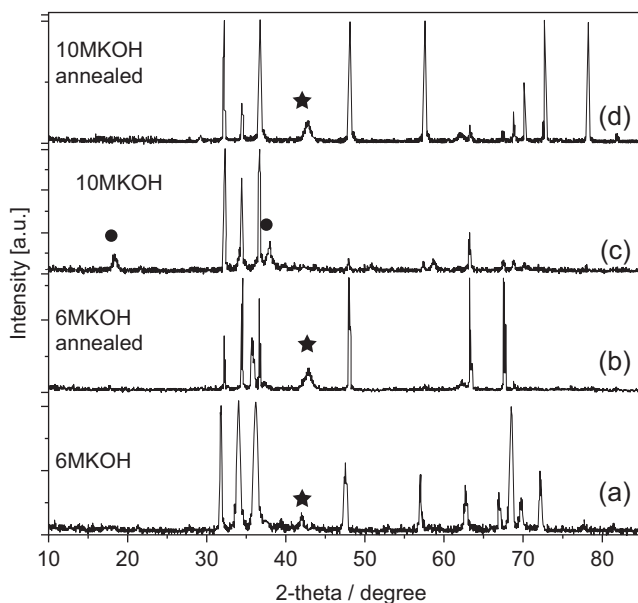


Figure 6.2 X-ray diffraction spectra of as-grown and annealed samples (at 450 °C) for (a) anodizing in 6 M KOH at room temperature and (b) after annealing, as well as (c) anodizing in 10 M KOH at room temperature and (d) after annealing.

solution. In contrast, the XRD patterns of the magnesium oxidized in 10 M KOH solution, as shown in Figure 6.2c, reveal two peaks at $2\theta = 18.3^\circ$ and 38° , respectively, corresponding to $\text{Mg}(\text{OH})_2$ crystal structure. After annealing treatment, these two peaks disappeared; instead, a peak corresponding to MgO at $2\theta = 42.9^\circ$ emerged, as shown in Figure 6.2d, indicative of crystalline MgO formation.

Figure 6.3 shows the SEM surface morphologies of the oxide coatings formed at room temperature and 50°C . Anodic oxidation of magnesium alloy in 6 M KOH

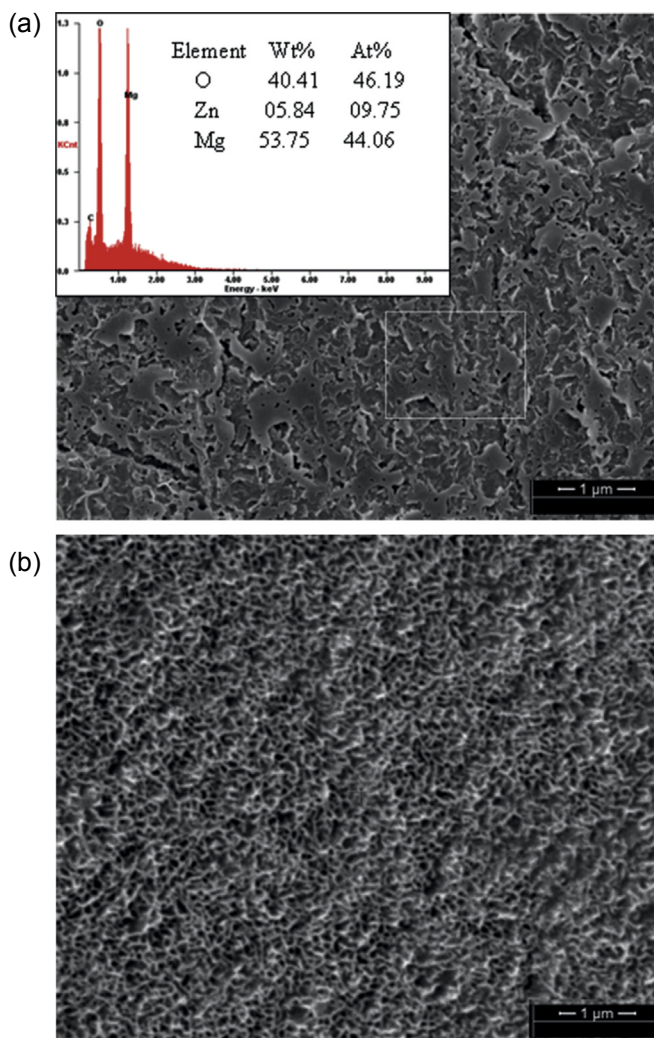


Figure 6.3 Surface morphology of MgO coatings produced by anodic oxidation in 6 M KOH (a) at room temperature (the inset is EDX analysis corresponding to the assigned area), (b) at 50°C , and (c) annealed at 450°C for 2 h in air (the inset is a cross-section micrograph).

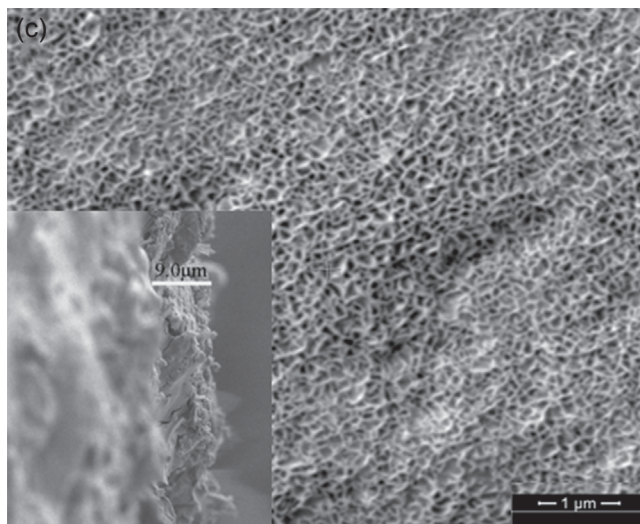


Figure 6.3 (Continued)

solution at 1.0 V (vs. SCE) for 2 h at room temperature resulted in lamellar-like oxide coatings, as observed in [Figure 6.3a](#). EDX analysis indicated that the oxide coating consists mainly of Mg and O, and the atomic ratio between Mg and O is approximately 1:1, implying that the oxide coatings consist of MgO, as evident by the inset in [Figure 6.3a](#). When the anodic oxidation temperature was raised up to 50 °C while keeping other conditions unchanged, platelet-like MgO coatings were produced, as shown by [Figure 6.3b](#). [Figure 6.3c](#) depicts the SEM micrograph of the as-formed MgO coatings after annealing treatment at 450 °C for 6 h in air. It was found that the platelet-like morphology remains unchanged without any loss of structural morphology, indicating the as-prepared platelet-like MgO coatings were thermally stable. The cross-section micrograph, shown in the inset image in [Figure 6.3c](#), disclosed that the thickness of adherent MgO coating on the Mg alloy surface is approximately 9.0 μm.

Anodic oxidation of magnesium alloy in 10 M KOH solution at 1.0 V (vs. SCE) for 2 h at room temperature results in compact oxide coatings, as observed in [Figure 6.4a](#). EDX analysis indicates the oxide coating consists mainly of Mg and O, and the atomic ratio between Mg and O is approximately 1:2; evidence of Mg(OH)₂ formation is shown in the inset of [Figure 6.4a](#). Dense oxide coatings were formed by annealing treatment at 450 °C for 6 h in air, as shown by [Figure 6.4b](#). The top left inset, showing the EDX investigation for the assigned area in [Figure 6.4b](#), revealed that the atomic ratio between Mg and O is approximately 1:1, indicating a change in chemistry of the oxide coatings from Mg(OH)₂ to MgO due to dehydration of Mg(OH)₂. The EDX analyses are in good agreement with the XRD results in [Figure 6.2](#). The lower left inset image shows the cross-section micrograph, indicative of a thickness of approximately 7.5 μm MgO coating on the surface of the Mg alloy.

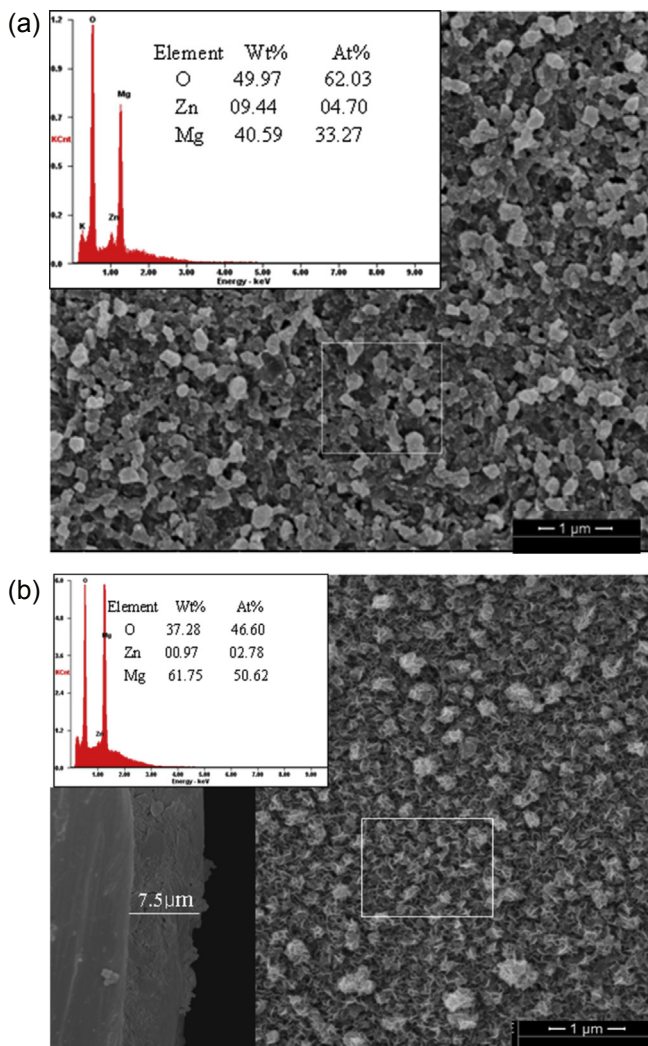


Figure 6.4 Surface morphology of oxide coatings produced by anodic oxidation in 10 M KOH (a) at room temperature (the inset is EDX analysis corresponding to the assigned area), and (b) annealed at 450 °C for 2 h in air (the top left inset is EDX analysis corresponding to the assigned area and the lower left inset is a cross-section micrograph).

6.2.3 Corrosion resistance of the as-grown MgO coatings

The corrosion resistance of the MgO coating-modified Mg alloy was determined in a 3.5-wt% NaCl solution after 45 min of immersion time using a potentiodynamic polarization test, as shown in Figure 6.5. To avoid the presence of some degree of nonlinearity in the Tafel slope region of the obtained polarization curves, the Tafel

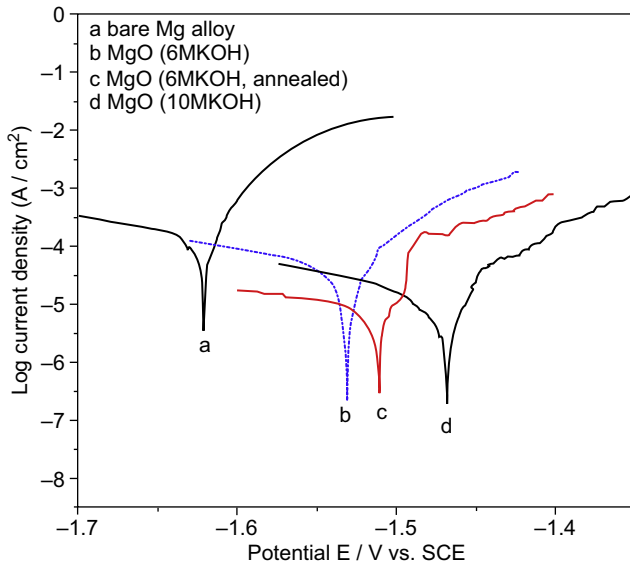


Figure 6.5 Potentiodynamic polarization curves of as-grown and annealed samples in 3.5-wt% NaCl solution.

constants were calculated as the slope of the points after the corrosion potential (E_{corr}) by 60 mV. The E_{corr} and corrosion current density (i_{corr}), and anodic/cathodic Tafel slopes (b_a and b_c), were derived directly from the polarization curves by Tafel region extrapolation. In general, the cathodic polarization curve is attributed to hydrogen evolution reaction due to the reduction of water, while the anodic polarization curve is associated with the dissolution of Mg, leading to the formation of Mg^{2+} (Ambat, Aung, & Zhou, 2000). The polarization resistance (R_p) values were determined from the Stern–Geary equation (Stern & Geary, 1957):

$$R_p = \frac{b_a b_c}{2.303 i_{\text{corr}} (b_a + b_c)} \quad (6.4)$$

These results of potentiodynamic polarization are summarized in Table 6.1. It was found that the polarization curve for annealed MgO coating formed in 6 M KOH showed a more positive shift than untreated MgO film, likely due to the consolidation and higher crystallization of MgO coating after thermal treatment. Moreover, compared with the bare Mg alloy, the E_{corr} of annealed MgO coatings, formed in either 6 or 10 M KOH, positively shifted approximately 100 and 260 mV, respectively, and the i_{corr} lowered more than 10 to 100 times, while the corrosion resistances increased by three and four orders. The positive shift of corrosion potentials accompanied by a decrease of corrosion currents and increase of polarization resistances indicate a decreased tendency to corrosion of MgO-coated samples. The polarization test

Table 6.1 Corrosion parameters of bare and MgO coatings modified Mg alloy in 3.5-wt% NaCl

Samples	$E_{\text{corr}}(\text{V})$	$i_{\text{corr}}(\text{A}/\text{cm}^2)$	$R_p (\Omega \text{ cm}^2)$
Bare Mg alloy	-1.62	1.25×10^{-4}	4.27×10^2
MgO (6 M KOH)	-1.53	2.16×10^{-5}	1.68×10^4
MgO (6 M KOH, annealed)	-1.51	6.30×10^{-6}	1.35×10^5
MgO (10 M KOH)	-1.46	6.02×10^{-6}	2.84×10^5

results lead directly to the conclusion that MgO coating film could significantly improve overall corrosion protection of Mg alloy in NaCl solution.

The different polarization behaviors of the MgO coatings on magnesium alloy are mainly due to their different structure and compact state. When the bare Mg alloy substrate was immersed in NaCl solution, loose and porous $\text{Mg}(\text{OH})_2$ formed quickly on Mg alloy surface. With increasing anodic potential during polarization, corrosive intermediate (Cl^-) was rapidly transferred through the outer porous layer and reached the inner Mg alloy matrix, which then resulted in increasing polarization current. At the same time, the chloride ions can transform $\text{Mg}(\text{OH})_2$ to more soluble MgCl_2 . High Cl^- concentration will accelerate the transform reaction of $\text{Mg}(\text{OH})_2$ to MgCl_2 and promote the dissolution of magnesium alloy (Altun & Sen, 2004). Therefore, the bare Mg alloy showed rapid corrosion rate. As evidenced by SEM, EDX, and XRD analysis, lamellar-like MgO coatings were produced on Mg alloy surface in 6 M KOH. After annealing treatment, the surface coating film was fused and consolidated to a thick layer, while the MgO coatings formed in 10 M KOH following annealing treatment were densely compact with a thickness of 7.5 μm . Thus, the as-grown MgO coating on Mg alloy surface may serve as a barrier, which could prevent the Mg matrix from direct contact with the corrosive medium as well as block the transportation of water and Cl^- needed for the corrosion reaction into the underlying Mg alloy matrix.

It was reported that the protection afforded by the coating is proportional to the coating thickness (Gray & Luan, 2002). Accordingly, the MgO coating film could protect substrate from corrosion attack by acting as a physical shield between metal and medium, and thus the corrosion process slows down by a double effect of a decrease of charge transfer rate and the decrease of diffusion flux across the surface layer (Barchiche, Rocca, Juers, Hazan, & Steinmetz, 2007). Moreover, annealed MgO coating formed in 10 M KOH showed superior corrosion resistance to that produced in 6 M KOH without performing thermal treatment, likely because there existed more micropores in the lamellar-like MgO film than in densely compact MgO film. Apparently, the corrosion properties of the MgO coating are strongly dependent on their morphology, thickness, agglomeration state, and preparation process.

6.2.4 Immersion behavior of MgO-coated Mg alloy in SBF

Regarding the immersion test, annealed MgO coating formed in 10 M KOH is discussed. Figure 6.6 shows the variation of the pH value of SBF as a function of immersion time. It can be seen that the pH values of the solutions corresponding to MgO-coated and bare Mg alloy specimens increased rapidly, from 7.2 to 8.6 in the initial 8 h of immersion. After that, the pH value of the solution for MgO-coated Mg alloy increased slowly with immersion time and became placid at 8.8, whereas the pH value of the solution for bare Mg specimens kept increasing and reached to 9.5 after 72 h of immersion.

It is well known that magnesium is an active metal element with a low potential of -2.34 V against normal hydrogen electrode. When a magnesium alloy is exposed to corrosive electrolyte, the main reaction is the anodic Mg dissolution and cathodic hydrogen evolution, which can be described as follows (Song, Andrej, & St. John, 2001):



In the case of MgO-coated Mg alloy, the MgO coatings function as a barrier, which could prevent the Mg matrix from direct contact with corrosive media as well as block the penetration of electrolytes. Accordingly, at the initial immersion stage, the corrosion attack is limited at the MgO coating layer. Thermodynamic calculations indicate that MgO and $\text{Mg}(\text{OH})_2$ could stably exist in pH domains higher than 13.83 and 11.46, respectively (Zhang, Yan, Wang, & Li, 2005). As a result, MgO coating film will be subjected to progressive chemical dissolution in neutral aqueous solutions, according to following equations (Ambat et al., 2000):

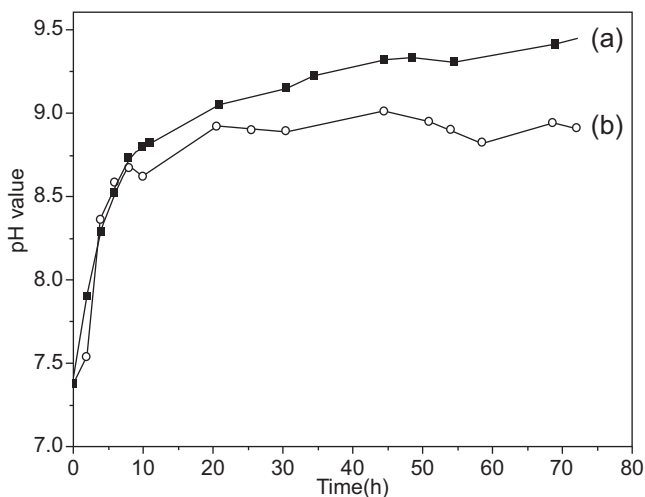


Figure 6.6 The pH value of SBF as a function of immersion time for (a) the bare and (b) MgO-coated Mg alloy specimens.



As a result of the OH^- ion formation, the pH at the specimen surface rises quickly in the initial immersion stage. The slow increase of pH value of the solution for a specimen with MgO coating indicates a relatively slow chemical dissolution and an improvement of the corrosion resistance of MgO coatings.

The corrosion behavior of MgO-coated Mg alloy specimens was also evaluated by immersion tests in SBF. At the beginning of immersion, large numbers of hydrogen bubbles are evidently observed arising from the surface of the bare Mg alloy substrate due to the reaction of substrate with the corrosive electrolyte, while almost no hydrogen evolution is found on the surface of MgO-coated Mg alloy in the 72-h immersion period, which indicates that the MgO coatings effectively retard the hydrogen gas evolution. After a few hours, the bare Mg samples were covered with white corrosion products. As the immersion time increased, the amount of corrosion products formed on the untreated specimen increased and detached corrosion products were observed on the bottom of the beaker. On the other hand, the appearance of MgO-coated Mg alloy specimens had no significant changes.

Surface morphologies after immersion in SBF for 72 h were examined to compare the corrosion resistance of Mg alloy with and without MgO coatings. The surface appearance of the samples after the immersion tests are shown in Figure 6.7, which reveals large differences in the degree of corrosion attack during the immersion period. The micrograph depicted in Figure 6.7a shows that the bare Mg alloy surface was totally covered with corrosion products with a big concave pit after 72 h of immersion in SBF, implying that locally severe corrosion occurred on the surface and the corrosion products in pits were detached away into solution. On the other hand, after the total immersion tests, a small amount of corrosion products were observed on the surface of the MgO-coated specimens, as shown by Figure 6.7b, but there were no detached corrosion products throughout the immersion test, indicating a much milder corrosion.

To get better insight on the corroded surface appearance of Mg alloy with and without MgO coatings after immersion tests, the corrosion products and MgO coatings were removed by chromic acid. Figure 6.8 shows the SEM surface morphologies of the as-cleaned Mg alloy specimens. As can be seen in Figure 6.8a, there are deep pits (indicated by arrows) on the bare Mg alloy surface, implying that the untreated Mg alloy suffered from localized severe corrosion attack. It is well known that the presence of pits is detrimental to the overall corrosion resistance, and the destruction of Mg alloy will proceed by means of pitting corrosion from one or more of them (Zhang et al., 2005). On the other hand, there is no obvious corrosion site area visible on the MgO-coated Mg alloy surface after the removal of MgO coatings, as shown in Figure 6.8b. Zooming in, only slightly corrosion-attacked spots exist on the as-cleaned Mg alloy substrate, as shown by the inset in Figure 6.8b. This is likely due to the penetration of water and electrolytes into the underlying Mg alloy matrix through the micropores existing in the MgO

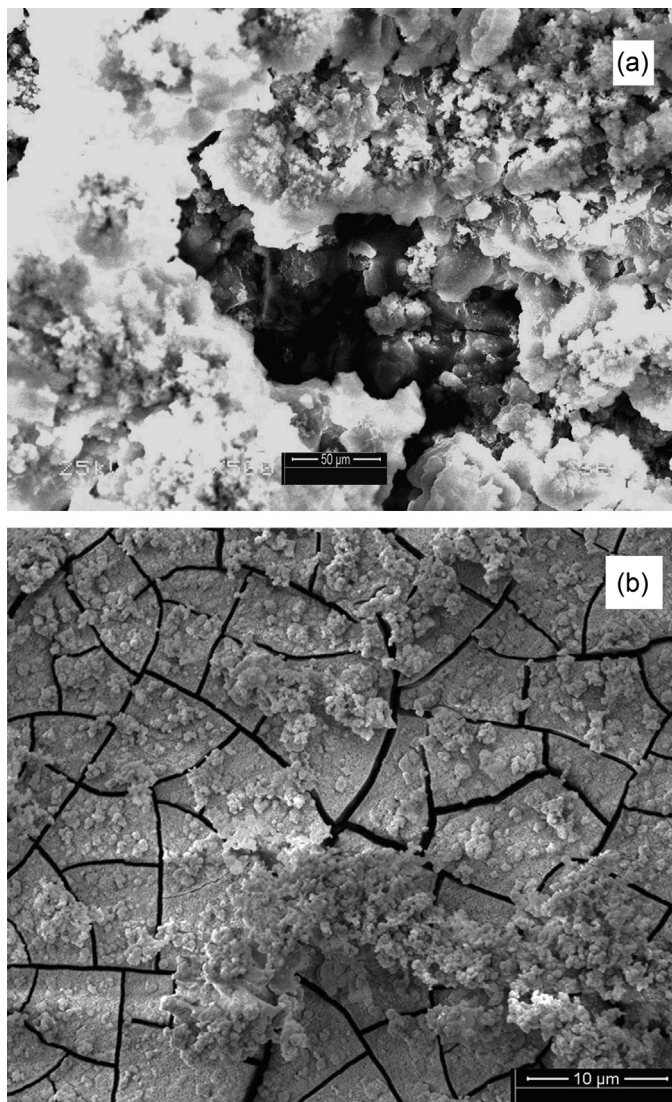


Figure 6.7 Surface morphologies after immersion in SBF for 72 h for (a) the bare and (b) MgO-coated Mg alloy specimens.

coatings, resulting in the corrosion attack. However, this decreased corrosion reaction reveals that the MgO coating film on Mg alloy could effectively protect the substrate from corrosion attacks during the immersion tests by acting as a barrier against corrosive electrolyte ingress into the underlying Mg alloy matrix. Consequently, the immersion tests indicate a much milder and more uniform corrosion attack for the MgO-coated Mg alloy specimens, consistent with the electrochemical

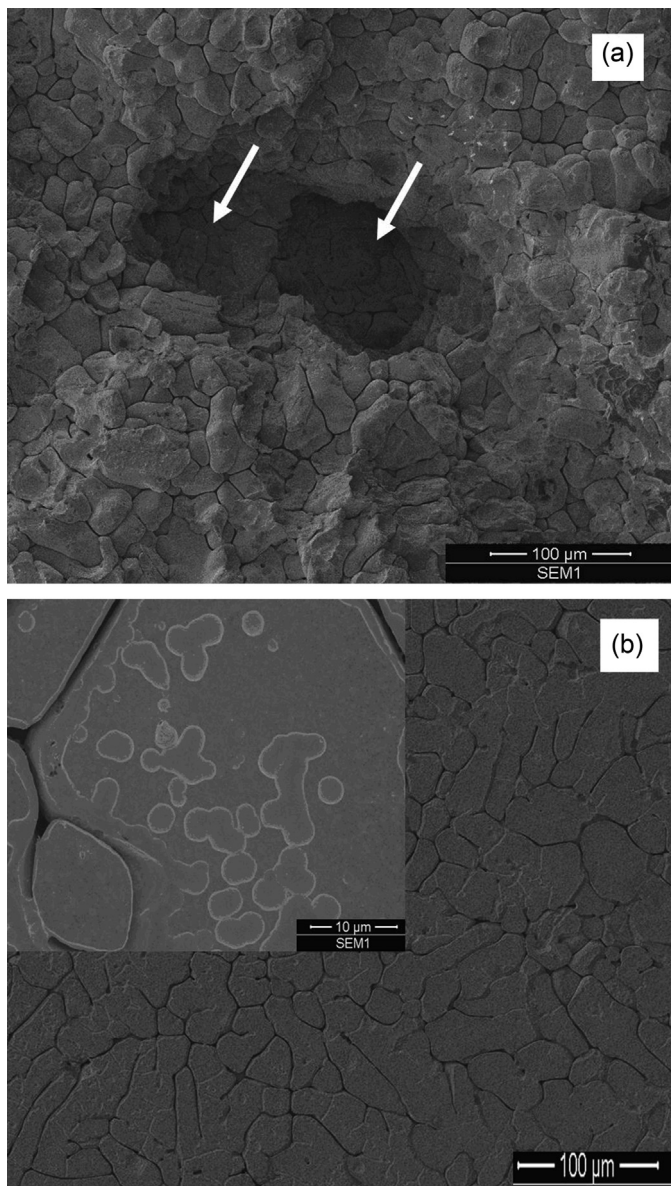


Figure 6.8 After 72 h of immersion in SBF. (a) The locally severe attacked surface morphology of the bare Mg alloy after the removal of corrosion products. (b) Slightly corroded surface morphology of Mg alloy after removal of the corrosion products and MgO coating layer. Inset is an enlarged image.

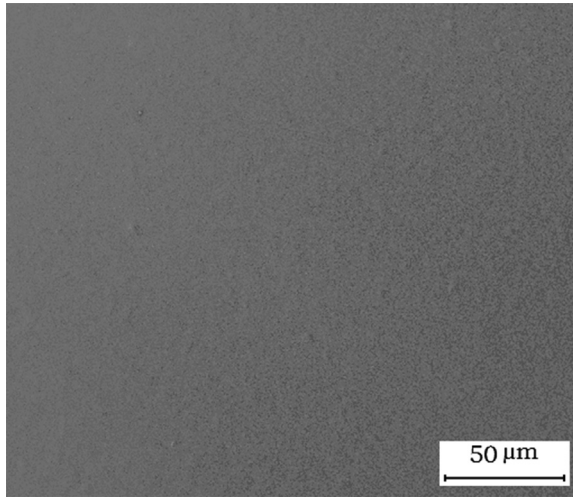


Figure 6.9 Surface morphology of MgO/PLA composite coating film.

measurements. Additionally, it might be stated that the anticorrosion performance of Mg alloy with MgO coatings is greatly enhanced as compared with bare Mg alloy.

6.2.5 MgO/PLA composite coating film on Mg alloy

PLA is a biodegradable polymer with good biocompatibility. An MgO/PLA composite film is prepared by dipping the Mg alloy with MgO coating into PLA solution, which shows a dense complex coating, as depicted in Figure 6.9. The corrosion resistance of MgO/PLA composite film was further evaluated in SBF

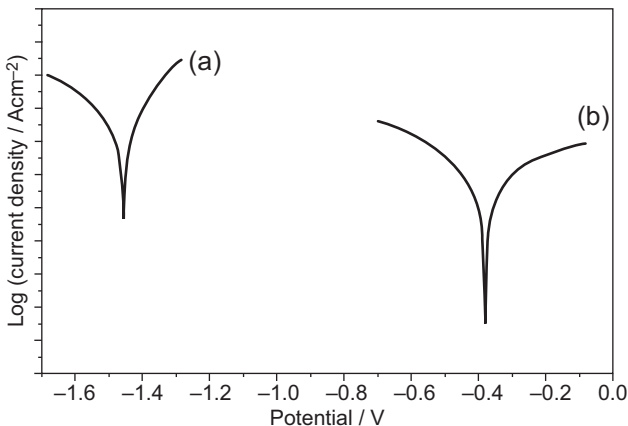


Figure 6.10 Potentiodynamic polarization curve of Mg alloy with (a) MgO coating and (b) MgO/PLA composite coating in SBF.

by a potentiodynamic polarization test, as shown in Figure 6.10. As compared to a single MgO coating, a significant shift of corrosion potential toward the noble direction and a decrease in the corrosion current density for MgO/PLA composite film are observed, indicating that MgO/PLA composite coating film exhibits superior corrosion resistance to pure MgO coatings. The enhanced corrosion resistance is attributed to the formation of a new PLA polymer cover over the MgO surface and the function of PLA macromolecules as a sealant to fill in micropores that likely exist in MgO coating film.

6.3 Conclusion

MgO coating is prepared on the Mg alloy surface simply by anodic electrodeposition in 6 M KOH solution, whereas Mg(OH)₂ coating is produced by anodization in 10 M KOH solution, which could be converted to MgO by subsequent thermal treatment. The as-grown MgO protective coatings could suppress the corrosion process by preventing the corrosive ions from transferring or diffusing to the magnesium alloy substrate, thus improving the corrosion resistance. The anodic electrodeposition might be an alternative method to PEO to produce layers that could provide better corrosion protection to magnesium alloys. An MgO/PLA composite film on the Mg alloy surface may be more effective in improving its corrosion resistance.

References

- Altun, H., & Sen, S. (2004). The effect of PVD coatings on the corrosion behaviour of AZ63 magnesium alloy. *Materials & Design*, 25, 637–646.
- Ambat, R., Aung, N. N., & Zhou, W. (2000). Evaluation of microstructural effects on corrosion behaviour of AZ91D magnesium alloy. *Corrosion Science*, 42, 1433.
- Arrabal, R., Matykina, E., Skeldon, P., Thompson, G. E., & Pardo, A. (2008). Transport of species during plasma electrolytic oxidation of WE43-T6 magnesium alloy. *Journal of the Electrochemical Society*, 155, C101–11.
- Barchiche, C. E., Rocca, E., Juers, C., Hazan, J., & Steinmetz, J. (2007). Corrosion resistance of plasma-anodized AZ91D magnesium alloy by electrochemical methods. *Journal of Electrochimica Acta*, 53, 417–425.
- Blawert, C., Dietzel, W., Ghali, E., & Song, G. (2006). Anodizing treatments for magnesium alloys and their effect on corrosion resistance in various environments. *Advanced Engineering Materials*, 8, 511–533.
- Cai, Q., Wang, L., Wei, B., & Liu, Q. (2006). Electrochemical performance of microarc oxidation films formed on AZ91D magnesium alloy in silicate and phosphate electrolytes. *Surface and Coating Technology*, 200, 3727.
- Cai, Z. P., Lu, D. S., Li, W. S., Liang, Y., & Zhou, H. B. (2009). Study on anodic oxidation of magnesium in 6 M KOH solution by alternative current impedance. *The International Journal of Hydrogen Energy*, 34, 467–472.
- Gray, J. E., & Luan, B. (2002). Protective coatings on magnesium and its alloys— a critical review. *Journal of Alloys and Compounds*, 336, 88–113.

- Gu, X. N., Zheng, W., Cheng, Y., & Zheng, Y. F. (2009). A study on alkaline heat-treated Mg-Ca alloy for the control of the biocorrosion rate. *Acta Biomaterials*, 5, 2790.
- Gupta, P., Tenhundfeld, G., Daigle, E. O., & Ryabkov, D. (2007). Electrolytic plasma technology: Science and engineering—an overview. *Surface and Coating Technology*, 201, 8746.
- Hahn, R., Brunner, J. G., Kunze, J., Schmuki, P., & Virtanen, S. (2008). A novel approach for the formation of Mg(OH)₂/MgO nanowhiskers on magnesium: rapid anodization in chloride containing solutions. *Electrochemistry Communications*, 10, 288–292.
- Huber, K. (1953). Anodic formation of coatings on magnesium, Zinc, and cadmium. *Journal of the Electrochemistry Society*, 100, 376.
- Khaselev, O., Weiss, D., & Yahalom, J. (2001). Structure and composition of anodic films formed on binary Mg-Al alloys in KOH-aluminate solutions under continuous sparking. *Corrosion Science*, 43, 1295–1307.
- Khaselev, O., & Yahalom, J. (1998). The anodic behavior of binary Mg-Al alloys in KOH-aluminate solutions. *Corrosion Science*, 40, 1149–1160.
- Latha, K., Li, W. Z., Charles, H. V., Roger, M. L., & Wang, D. Z. (2009). Synthesis, characterization and optical properties of Mg(OH)₂ micro-/nanostructure and its conversion to MgO. *Ceramics International*, 35, 3355–3364.
- Lavrenko, V. A., Skorokhod, V. V., Shvets, V. A., & Khomko, T. V. (2003). Electrochemical properties of intermetallic compounds Mg₂Ni, MgNi₂, and the hydride Mg₂NiH₄ in 30% KOH solution. *Powder Metallurgy and Metal Ceramics*, 42, 523–529.
- Makar, G. L., & Kruger, J. (1993). Corrosion of magnesium. *International Materials Reviews*, 38(3), 138–153.
- Nordlien, J. H., Ono, S., Masuko, N., & Nisancioglu, K. (1997). A TEM investigation of naturally formed oxide films on pure magnesium. *Corrosion Science*, 39, 1397.
- Ruggeri, S., & Roue, L. (2003). Correlation between charge input and cycle life of MgNi electrode for Ni–MH batteries. *Journal of Power Sources*, 117, 260–266.
- Shi, Z., Song, G., & Atrens, A. (2006). The corrosion performance of anodised magnesium alloys. *Corrosion Science*, 48, 3531.
- Song, G. L., Andrej, A., & St. John, D. (2001). Magnesium technology 2001. In Hryn (Ed.), *TMS (The minerals, metals and materials society)*, 255.
- Song, G. L., & Atrens, A. (2003). Understanding magnesium Corrosion—A framework for improved Alloy performance. *Advanced Engineering Materials*, 5, 837–858.
- Song, G. L., & Son, S. Z. (2006). Corrosion behaviour of pure magnesium in a simulated body fluid. *Acta Physico-Chimica Sinica*, 22, 1222.
- Staiger, M. P., Pietak, A. M., Huadmai, J., & Dias, G. (2006). Magnesium and its alloys as orthopedic biomaterials: a review. *Biomaterials*, 27, 1728–1734.
- Stern, M., & Geary, A. L. (1957). Electrochemical polarization I. A theoretical analysis of the shape of polarization curves. *Journal of Electrochemistry Society*, 104, 56–63.
- Stippich, F., Vera, E., Wolf, G. K., Berg, G., & Friedrich, C. (1998). Enhanced corrosion protection of magnesium oxide coatings on magnesium deposited by ion beam-assisted evaporation. *Surface and Coating Technology*, 103-104, 29–35.
- Udhayan, R., & Prakash, B. D. (1996). On the corrosion behavior of magnesium and its alloys using electrochemical techniques. *Journal of Power Sources*, 63, 103–107.
- Wang, Y. M., Wang, F. H., Xu, M. J., Zhao, B., & Ouyang, J. H. (2009). Microstructure and corrosion behavior of coated AZ91 alloy by microarc oxidation for biomedical application. *Applied Surface Science*, 255, 9124–9131.
- Zhang, Y. J., Yan, C. N., Wang, F. H., & Li, W. F. (2005). Electrochemical behavior of anodized Mg alloy AZ91D in chloride containing aqueous solution. *Corrosion Science*, 47, 2816–2831.

Surface modification of magnesium and its biodegradable alloys by calcium orthophosphate coatings to improve corrosion resistance and biocompatibility

7

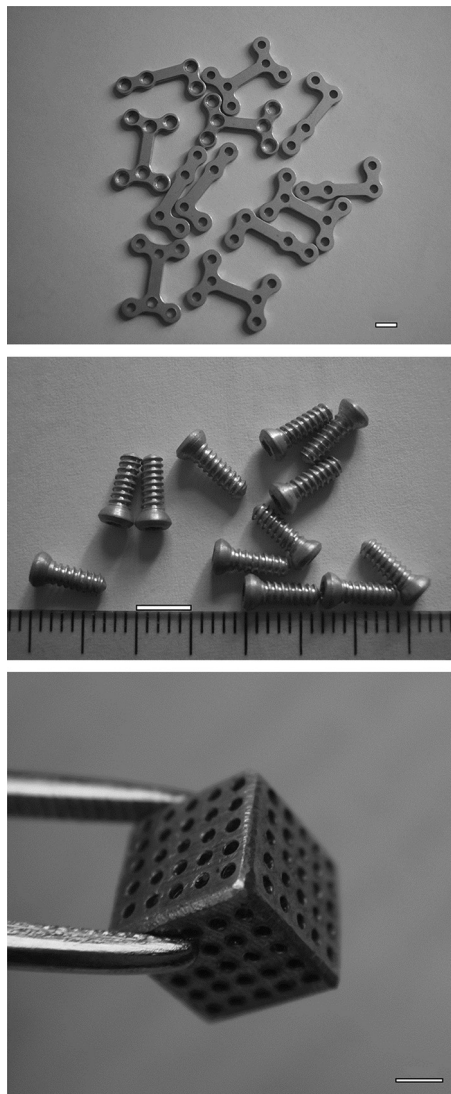
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7.1 Introduction

Metals and their alloys play an essential role as biomaterials to assist in the repair or replacement of load-bearing bones that have become diseased or damaged (Niinomi, 2002). Due to their physical nature, the majority of metals have a high strength and a long service life, combined with a low elastic module and a small plasticity at the body temperature. Considering their chemical properties (corrosion resistance) and biological compatibility (lack of toxicity), the range of applicable implantable metals is restricted to stainless steels, titanium and its alloys (e.g., Ti6Al4V, Ti6Al7Nb, shape memory Ti–Ni alloys), tantalum, cobalt-chromium-based alloys, as well as some noble metals and their alloys (the latter are used mainly for dental restoratives). Limitations of these metallic implants comprise a possible release of toxic ions and/or particles through corrosion or wear processes. Furthermore, being xenogenic, any metals evoke a physiological response to form a fibrous capsule, thus isolating the implants from the body (Jacobs, Gilbert, & Urban, 1998; Lhotka, Szekeres, Steffan, Zhuher, & Zweymüller, 2003). In addition, the mechanical properties of the aforementioned metals and alloys are not well matched with those of bones, resulting in stress shielding effects that can lead to reduced stimulation of new bone growth and remodeling, which decreases implant stability (Nagels, Stokdijk, & Rozing, 2003). Finally, those metals and alloys are essentially neutral *in vivo* and remain as permanent fixtures. Therefore, if plates, screws, and pins made of those metals and alloys are used to secure any bone fractures, after healing they will have to be removed by a second surgical procedure (Niinomi, 2010). Fortunately, there is a small group of biodegradable (also called bioresorbable or bioabsorbable) metals, which are able to degrade safely within the body. The primary metals in this category are magnesium-based and iron-based alloys, although recently zinc has also been investigated. Among them, magnesium (Mg) and its biodegradable alloys (e.g., AZ91, WE43, AM50, LAE442) appear to be the most promising. They can degrade naturally in the physiological environment by corrosion; thus, they appear to be suitable candidates to construct temporary hard

Figure 7.1 Biodegradable orthopedic devices prepared from Mg and its alloys: bone plates (top), screws for orthopedic fixation (middle), and a porous scaffold for bone void filling (bottom). Scale bar = 10 mm.

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tissue implants (Czerwinski, 2011; Kraus et al., 2012; Staiger, Pietak, Huadmai, & Dias, 2006; Virtanen, 2011; Witte, Ulrich, Rudert, & Willbold, 2007; Witte et al., 2008; Zeng, Dietzel, Witte, Hort, & Blawert, 2008). A few examples of such Mg implants are shown in Figure 7.1 (Yang & Tan, 2013).

Artificial implants made from biodegradable metals, such as Mg and its alloys, possess some novel biomedical features. Namely, after being implanted, they will slowly degrade, thus eliminating the necessity for the second removal surgeries and

thereby accelerating the entire healing process with a simultaneous decrease of health risks, costs, and scarring (Li et al., 2010). Nevertheless, to avoid various complications and undesired effects (Figure 7.2(a) and (b)), suitable degradation kinetics appear to be critical (Figure 7.2(c)). Namely, any biodegradable implant must perform its functions until the damaged tissues have been sufficiently recovered or healed (Witte et al., 2005). Additionally, the degradation (corrosion) products of such implants must be well tolerated by both the surrounding tissues and the entire organisms. Luckily, Mg^{2+} ions appear to be the fourth most abundant cation in the human body and are largely stored mainly in bones. They are vital to the metabolism processes, a cofactor in many enzymes, and a key component of the ribosomal machinery that translates the genetic information encoded by mRNA into polypeptide structures (Vormann, 2003). Therefore, contrary to other implantable metals, the wear or corrosion products of which can be potentially toxic or otherwise harmful to patients, those of Mg might be potentially beneficial (Touyz, 2004).

As seen from the aforementioned, Mg, its biodegradable alloys, and their corrosion products are well tolerated by the human body. However, in the vast majority of the cases, the *in vivo* corrosion kinetics of Mg and its alloys exceeds that of bone healing (Figure 7.2(a) and (b)); therefore, it must be slowed down. From the results of numerous investigations, one can conclude that both the properties and functional activity of any implantable biomaterials can be influenced by surface modifications, such as polishing, oxidation, passivation, coating deposition, and ion implantation (Hanawa, 1999; Roach, Eglin, Rohde, & Perry, 2007). Among them, application of synthetic calcium orthophosphate coatings appears to be the most effective surface modification, which additionally improves biocompatibility and osteointegration of the metallic implants.

7.2 Brief description of two major constituents

7.2.1 Magnesium and its alloys

Mg was named after the small regional unit Magnesia (Greek: Μαγνησία), located in Greece. It is the eighth most abundant element on the surface of our planet, making up $\sim 1.93\%$ by mass of the earth's crust and $\sim 0.13\%$ by mass of the oceans. Due to its chemical properties, Mg belongs to the alkaline earth elements, which are located in the second group of the periodic table. All alkaline earth elements possess a very high chemical reactivity and form the compounds with an oxidation number of +2. Therefore, they are not found free in nature. The first isolation of elemental Mg was performed by Sir Humphry Davy (1778–1829) in 1808 (Davy, 1808a, 1808b). In 1852, Robert Bunsen (1811–1899) realized the commercial production of Mg by electrolysis. After that, Mg started to be produced in small quantities in America and Europe, initially for pyrotechnical use and as igniting bands or wires for flashlights in the up-and-coming photographic industry (Kammer, 2000, p. 784).

From the physical and mechanical points of view, Mg and its biodegradable alloys are light in weight and low in density (1.738 g/cm^3 for pure Mg and within

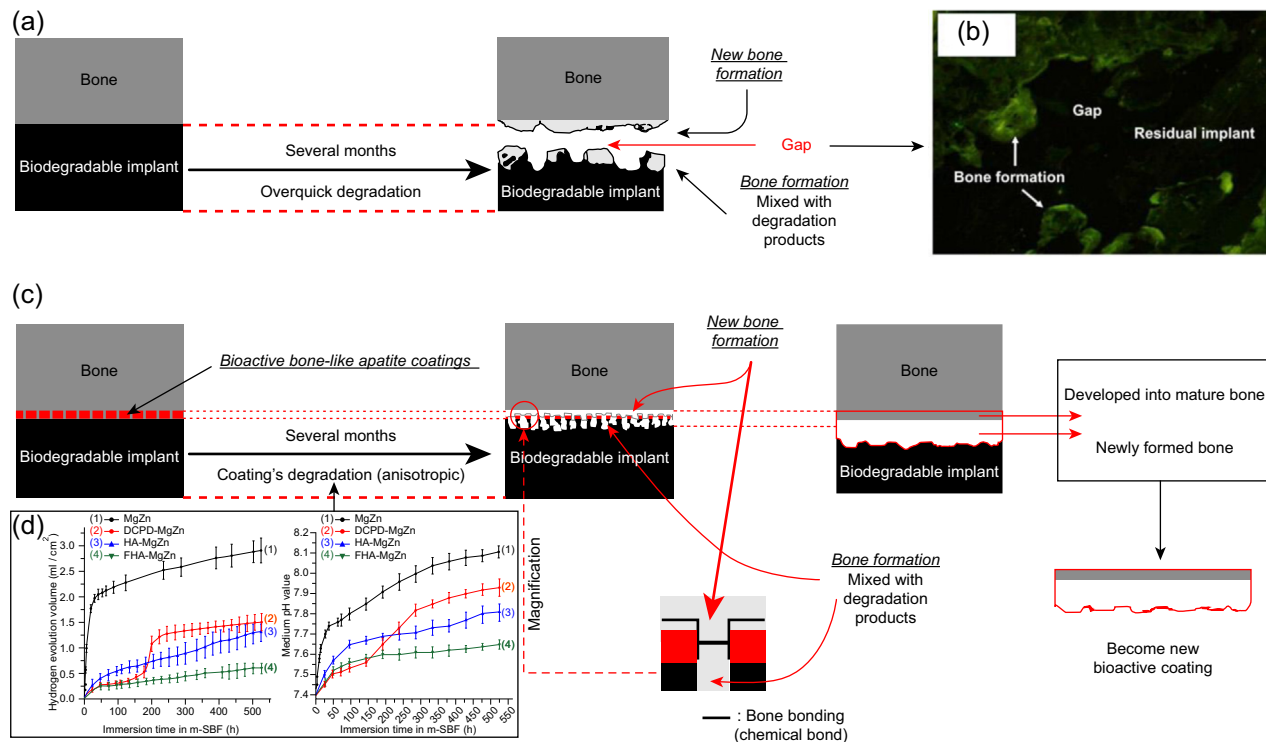


Figure 7.2 A model explaining the improvements due to the presence of bioactive calcium orthophosphate coatings on Mg and its alloys.

(a) A relatively rapid degradation rate of Mg might possibly lead to formation of gaps at the interface. (b) A typical tetracycline label taken 14 weeks postoperation. (c) Protective calcium orthophosphate coatings can reduce the degradation rate and simultaneity to ameliorate biocompatibility. (d) Corrosion protective effects of calcium orthophosphate coatings obtained by testing the H₂ release rate and the pH value changes.

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1.7–2.0 g/cm³ for the alloys), which is close to the density of bones (1.8–2.1 g/cm³). Due to a relatively low melting point (650 °C), Mg is a fusible metal. The elastic modulus of Mg is ~45 GPa (Mordike & Ebert, 2001), which is far closer to that of bones (trabecular/cancellous bones: 3–14.8 GPa, cortical bones: 18.6–27 GPa; Hamed, Jasiuk, Yoo, Lee, & Liszka, 2012; Hamed, Novitskaya, et al., 2012), if compared to the similar values of other implantable metals: Ti alloys, 110–117 GPa; stainless steels, 189–205 GPa; Co-Cr alloys, ~230 GPa. In addition, the numerical values of the compressive yield strength of bones and Mg are 130–180 MPa and 65–100 MPa, respectively, while those of fracture toughness are 3–6 MPa/m² and 15–40 MPa/m², respectively. Hence, by using Mg and its alloys for bone grafting, the stress shielding effect can be mitigated (Staiger et al., 2006; Zeng et al., 2008). In addition, some antibacterial properties of Mg have been reported (Robinson, Griffith, Shechtman, Evans, & Conzemius, 2010).

From the chemical point of view, a high reactivity (the standard electrode potential of $\text{Mg}_{(\text{aq})}^{2+} + 2\text{e}^- \leftrightarrow \text{Mg}_{(\text{s})}$ is -2.37 V, that of $\text{Mg}_{(\text{aq})}^+ + \text{e}^- \leftrightarrow \text{Mg}_{(\text{s})}$ is -2.70 V, and that of $\text{Mg}(\text{OH})_{2(\text{s})} + 2\text{e}^- \leftrightarrow \text{Mg}_{(\text{s})} + 2\text{OH}^-$ is -2.69 V; Haynes, 2013) makes Mg dissolvable in body fluids, which is the primary reason for its *in vivo* biodegradability. Therefore, when Mg is exposed to aqueous solutions, the following oxidation reaction takes place on its surface (Mueller, Nascimento, & de Mele, 2010; Song & Atrens, 2003):



This provides a possibility to measure the corrosion kinetics of Mg and its biodegradable alloys by the release kinetics of hydrogen (Figure 7.3; Zhang, Zeng, Liu, & Gao, 2010). Unfortunately, the oxidized surface layers consisting of hydrated forms of MgO and/or Mg(OH)₂ are loose in nature and cannot provide sufficient protection to resist the corrosion encountered in the physiological environment, which contains a large amount (~104 mM) of chloride ions. Therefore, the corrosion kinetics of Mg are strongly accelerated in the presence of dissolved chloride ions, which are able to convert the insoluble MgO + Mg(OH)₂ coatings into a soluble MgCl₂, while simultaneously decreasing the protected area and promoting further dissolution of Mg (Mueller et al., 2010; Song & Atrens, 2003). Because further details on the corrosion process of both Mg and its biodegradable alloys are beyond the scope of this review, the readers interested in this topic are forwarded to the relevant literature (Czerwinski, 2011; Kraus et al., 2012; Mueller et al., 2010; Song, 2011, 2013; Song & Atrens, 2003; Zhang, Zeng, et al., 2010) (in addition, the same sources summarize the information on the available Mg alloys). Here, it is just important to recognize that, to be feasible for the orthopedic applications, the corrosion kinetics of Mg and its biodegradable alloys must be reduced. Ideally, it should be slowed down to allow the mechanical integrity of the metal to remain intact during bone healing. This would also minimize hydrogen production, which was observed as a disadvantageous byproduct when using Mg (Virtanen, 2011; Zberg, Uggowitzer, & Löffler, 2009).

There are a number of ways to improve the corrosion resistance of pure Mg (Czerwinski, 2011; Gray & Luan, 2002; Song, 2011, 2013). Briefly, they comprise

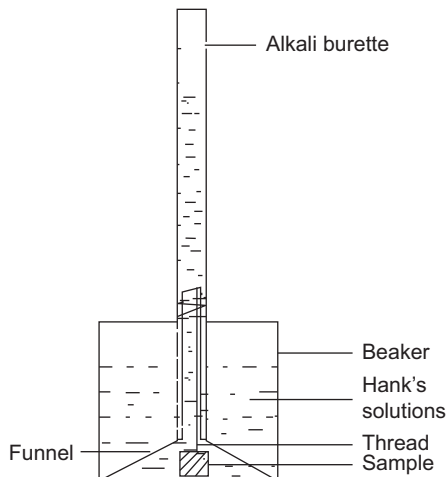


Figure 7.3 A schematic drawing of a hydrogen evolution collection set-up to follow the corrosion kinetics of Mg and its alloys.

Reprinted from [Zhang, Zeng, et al. \(2010\)](#), with permission.

the following approaches: microstructure tailoring including both grain sizes ([Hoog, Birbilis, Zhang, & Estrin, 2008](#); [Wang, Estrin, & Zúberová, 2008](#)) and texture ([Xin, Wang, Gao, Liu, & Liu, 2009](#)), alloying ([Chen, Kirkland, et al., 2012](#); [Hort et al., 2010](#); [Kraus et al., 2012](#); [Song, 2007](#); [Witte et al., 2006](#); [Xin, Hub, & Chu, 2011](#)), preparation of biocomposites ([Fathi et al., 2011](#); [Mensah-Darkwa et al., 2013](#); [Razavi et al., 2010](#); [Witte, Feyerabend, et al., 2007](#)), surface treatment ([Gu et al., 2011](#); [Guan, Zhou, & Zheng, 2009](#); [Liang, Srinivasan, Blawert, & Dietzel, 2010](#); [Majumdar, Bhattacharyya, Biswas, & Manna, 2008](#); [Xue, Yun, Schulz, & Shanov, 2011](#); [Zhang, Zhao, Wu, Wang, & Wu, 2007](#)), and deposition of protective coatings ([Chen, Kirkland, et al., 2012](#); [Hiromoto, 2012](#); [Hiromoto & Yamamoto, 2009](#); [Keim, Brunner, Fabry, & Virtanen, 2011](#); [Mensah-Darkwa et al., 2013](#); [Gray-Munro, Seguin, & Strong, 2009](#); [Nassif & Ghayad, 2013](#); [Rojaee, Fathi, & Raeissi, 2013b](#); [Shadanbaz & Dias, 2012](#); [Wang, Gao, Zhang, Zhou, & Wu, 2007](#); [Wang et al., 2012](#); [Wang, Wei, & Gao, 2009](#); [Waterman et al., 2011](#); [Xiao, Yu, et al., 2013](#)). Disregarding other topics, let us consider the protective calcium orthophosphate coatings on Mg and its biodegradable alloys. One should stress that, to improve the corrosion resistance, the surface of Mg and its alloys might be coated by both calcium orthophosphates only (the vast majority of the cited publications in this review) and calcium orthophosphate-based biocomposites ([Abdal-hay, Barakat, & Lim, 2013](#); [Du et al., 2011](#); [Hahn et al., 2011](#); [Johnson, Akari, & Liu, 2013](#); [Song, Shan, & Han, 2013](#); [Sreekanth & Rameshbabu, 2012](#); [Tang, Xin, & Wang, 2013](#); [Wang, Yan, Wan, & Yang, 2013](#); [Wu, Wen, Dai, Lu, & Yang, 2010](#); [Zhang, Dai, Wei, & Wen, 2012](#); [Zhang, Dai, et al., 2013](#); [Zhang, Li, et al., 2012](#)). Taking into consideration that the modern history of implantable calcium orthophosphates started in 1920 ([Dorozhkin, 2012a, 2013](#)), while that of calcium orthophosphate-based biocomposites and hybrid biomaterials started only in 1981

(Dorozhkin, 2011a), one can conclude that the latter subject is just at the initial stage and many more publications are expected in the near future. To finalize this topic, it should be mentioned that Mg and its biodegradable alloys might also be coated by calcium phosphate glass-ceramics (Ren et al., 2013; Wang et al., 2014); however, that is another story.

7.2.2 Calcium orthophosphates

Calcium orthophosphates were discovered in 1769 and have been investigated since then (Dorozhkin, 2012a, 2013). The main driving force behind the use of calcium orthophosphates as bone substitute materials is their chemical similarity to the mineral component of mammalian bones and teeth (Dorozhkin, 2011b; Lowenstam & Weiner, 1989 p. 324; Weiner & Wagner, 1998). As a result, in addition to being nontoxic, they are biocompatible, not recognized as foreign materials in the body, and, most importantly, both exhibit bioactive behavior and integrate into living tissue by the same processes active in remodeling healthy bone. This leads to an intimate physicochemical bond between the implants and bone, termed osteointegration (Ong & Chan, 1999). More to the point, calcium orthophosphates are also known to support osteoblast adhesion and proliferation (Anselme, 2000; Davies, 1996). Even so, the major limitations in the use of calcium orthophosphates as load-bearing biomaterials are their mechanical properties; namely, they are brittle with a poor fatigue resistance (Hench, 1998; Suchanek & Yoshimura, 1998). That is why, in biomedical applications, calcium orthophosphates are used primarily as fillers and coatings (Dorozhkin, 2011b, 2012b; Ong & Chan, 1999).

The complete list of known calcium orthophosphates, including their standard abbreviations and major properties, is given in Table 7.1. Detailed information on calcium orthophosphates, their synthesis, structure, chemistry, other properties, and biomedical application have been comprehensively reviewed elsewhere (Dorozhkin, 2011b). Even more thorough information on calcium orthophosphates might be found in special books and monographs (Amjad, 1997; Brown & Constantz, 1994; Chow & Eanes, 2001; Dorozhkin, 2012c, p. 850; Elliott, 1994; LeGeros, 1991).

7.3 Brief discussion of the important predeposition and postdeposition procedures

Prior to being coated by calcium orthophosphates, in the vast majority of cases, the surfaces of Mg and its biodegradable alloys need to be prepared. The preparation normally consists of cleaning and/or degreasing to remove any sort of surface contamination arising from manufacturing. This procedure can be performed in acetone (Abdal-hay et al., 2013; Cui et al., 2013; Hiromoto et al., 2008; Hiromoto & Tomozawa, 2010, 2011; Hiromoto, Tomozawa, & Maruyama, 2013; Hiromoto & Yamamoto, 2009; Jo et al., 2011; Jo, Li, Kim, Kim, & Koh, 2013; Kannan, 2013; Noorakma, Zuhailawati, Aishvarya, & Dhindaw, 2013; Ohtsu, Hiromoto, Yamane, Satoh, & Tomozawa, 2013;

Table 7.1 Existing calcium orthophosphates and their major properties (Dorozhkin, 2011b)

Ca/P molar ratio	Compound	Formula	Solubility at 25 °C, $-\log(K_s)$	Solubility at 25 °C, g/L	pH stability range in aqueous solutions at 25 °C
0.5	Monocalcium phosphate monohydrate (MCPM)	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	1.14	~ 18	0.0–2.0
0.5	Monocalcium phosphate anhydrous (MCPA or MCP)	$\text{Ca}(\text{H}_2\text{PO}_4)_2$	1.14	~ 17	^c
1.0	Dicalcium phosphate dihydrate (DCPD), mineral brushite	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	6.59	~ 0.088	2.0–6.0
1.0	Dicalcium phosphate anhydrous (DCPA or DCP), mineral monetite	CaHPO_4	6.90	~ 0.048	^c
1.33	Octacalcium phosphate (OCP)	$\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$	96.6	~ 0.0081	5.5–7.0
1.5	α -Tricalcium phosphate (α -TCP)	$\alpha\text{-Ca}_3(\text{PO}_4)_2$	25.5	~ 0.0025	^a
1.5	β -Tricalcium phosphate (β -TCP)	$\beta\text{-Ca}_3(\text{PO}_4)_2$	28.9	~ 0.0005	^a

1.2–2.2	Amorphous calcium phosphates (ACP)	$\text{Ca}_x\text{H}_y(\text{PO}_4)_z \cdot n\text{H}_2\text{O}$, $n = 3\text{--}4.5$; 15–20% H_2O	^b	^b	$\sim 5\text{--}12^{\text{d}}$
1.5–1.67	Calcium-deficient hydroxyapatite (CDHA or Ca-def HA) ^e	$\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}$ ($0 < x < 1$)	~ 85	~ 0.0094	6.5–9.5
1.67	Hydroxyapatite (HA, HAp, or OHAp)	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	116.8	~ 0.0003	9.5–12
1.67	Fluorapatite (FA or FAp)	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	120.0	~ 0.0002	7–12
1.67	Oxyapatite (OA, OAp, or OXA) ^f , mineral voelckerite	$\text{Ca}_{10}(\text{PO}_4)_6\text{O}$	~ 69	~ 0.087	^a
2.0	Tetracalcium phosphate (TTCP or TetCP), mineral hilgenstockite	$\text{Ca}_4(\text{PO}_4)_2\text{O}$	38–44	~ 0.0007	^a

^aThese compounds cannot be precipitated from aqueous solutions.

^bCannot be measured precisely. However, the following values were found: 25.7 ± 0.1 (pH = 7.40), 29.9 ± 0.1 (pH = 6.00), 32.7 ± 0.1 (pH = 5.28). The comparative extent of dissolution in acidic buffer is: ACP >> α -TCP >> β -TCP > CDHA >> HA > FA.

^cStable at temperatures above 100 °C.

^dAlways metastable.

^eOccasionally, it is called “precipitated HA (PHA).”

^fExistence of OA remains questionable.

Rojaee, Fathi, & Raeissi, 2013a; Rojaee et al., 2013b; Song et al., 2013; Sreekanth & Rameshbabu, 2012; Tomozawa & Hiromoto, 2011a, 2011b, 2011c; Tomozawa, Hiromoto, & Harada, 2010; Wang, Wei, et al., 2009; Wang et al., 2013; Wang, Guan, et al., 2011; Wang, Guan, Wang, Ren, & Wang, 2010; Wen et al., 2009; Wu et al., 2010; Xiao, Yu, et al., 2013; Xiao, Zhu, Su, & Li, 2013; Xu, Pan, et al., 2009; Yang, Jiao, Cui, et al., 2008; Yanovska, Kuznetsov, Stanislavov, Danilchenko, & Sukhodub, 2012; Zhang, Li, et al., 2012; Zhang, Zeng, et al., 2010), ethanol (Chai et al., 2012; Cui et al., 2013; Gan et al., 2013; Gao et al., 2011; Geng, Tan, Jin, Yang, & Yang, 2009; Grubač, Metikoš-Huković, & Babić, 2013; Guan et al., 2012; Hiromoto et al., 2008; Hu et al., 2010; Iskandar, Aslani, & Liu, 2013; Jo et al., 2011, 2013; Kannan, 2013; Kim et al., 2014; Li, Wang, Yan, & Lu, 2012a, 2012b; Liu, Hu, Ding, & Wang, 2011a; Liu, Tang, Wang, Hu, & Li, 2013; Onoki & Yamamoto, 2010; Rojaee et al., 2013b; Song, Zhang, Li, Zhao, & Zhang, 2010; Wang, Tan, et al., 2011; Wang et al., 2013; Waterman et al., 2011; Xu, Zhang, et al., 2009; Xu, Zhang, & Yang, 2012; Yang, Jiao, Cui, et al., 2008; Yanovska et al., 2012; Zhang, Ma, Chen, & Wei, 2013), mixtures thereof (Meng et al., 2011), trichloroethylene (Gray-Munro & Strong, 2009), aqueous solution of Na_2CO_3 (Gray-Munro & Strong, 2009), a mixture of 4% nitric acid + 96% ethylene glycol (Guan et al., 2012), or distilled water (Abdal-hay et al., 2013; Guan et al., 2012; Hahn et al., 2011; Li et al., 2012a, 2012b; Gray-Munro & Strong, 2009; Rojaee et al., 2013b; Sreekanth & Rameshbabu, 2012; Wang et al., 2013; Wu et al., 2010; Yang et al., 2008; Zhang, Zhang, & Wei, 2008; Zhang, Zeng, et al., 2010).

In addition, various types of physical modifications of the metallic surface are used. Examples comprise physical grinding and/or polishing (Abdal-hay et al., 2013; Chai et al., 2012; Chen, Biribilis, & Abbott, 2011, 2012; Cui et al., 2013; Du et al., 2011; Gan et al., 2013; Gao et al., 2011; Geng et al., 2009; Grubač et al., 2013; Guan et al., 2012; Hahn et al., 2011; Hiromoto & Tomozawa, 2010, 2011; Hiromoto et al., 2008; Hiromoto et al., 2013; Hu et al., 2010; Iskandar et al., 2013; Jo et al., 2011, 2013; Kannan, 2013; Kim et al., 2014; Li et al., 2012a, 2012b; Liu et al., 2011a; Liu, Hu, Ding, & Wang, 2011b; Liu, Tang, Li, & Hu, 2014; Meng et al., 2011; Gray-Munro & Strong, 2009; Noorakma et al., 2013; Ohtsu et al., 2013; Onoki & Yamamoto, 2010; Rojaee et al., 2013a; Song, Shan, & Han, 2008; Song et al., 2010, 2013; Sreekanth & Rameshbabu, 2012; Tomozawa & Hiromoto, 2011a, 2011b, 2011c; Tomozawa et al., 2010; Wang et al., 2010; Wang, Wei, et al., 2009; Wang et al., 2013; Wang, Guan, et al., 2011; Wang, Tan, et al., 2011; Waterman et al., 2011; Wen et al., 2009; Wu et al., 2010; Xiao, Yu, et al., 2013; Xiao, Zhu, et al., 2013; Xu, Pan, et al., 2009; Xu, Zhang, et al., 2009; Xu et al., 2012; Yang, Jiao, Cui, et al., 2008; Yanovska et al., 2012; Zhang, Dai, et al., 2012; Zhang et al., 2013; Zhang, Li, et al., 2012; Zhang et al., 2008; Zhang, Zheng, et al., 2010), drying (Abdal-hay et al., 2013; Gan et al., 2013; Geng et al., 2009; Jo et al., 2013; Kim et al., 2014; Li et al., 2012a, 2012b; Liu et al., 2013; Onoki & Yamamoto, 2010; Rojaee et al., 2013a, 2013b; Song et al., 2013; Wang et al., 2010; Wang, Guan, et al., 2011; Wang, Tan, et al., 2011; Waterman et al., 2011; Wen et al., 2009; Xu, Pan, et al., 2009; Xu, Zhang, et al., 2009; Yang, Jiao, Cui, et al., 2008; Yanovska et al., 2012; Zhang, Ma, et al., 2013; Zhang, Zeng, et al.,

2010), heat treatment (Geng et al., 2009; Hu et al., 2010; Gray-Munro & Strong, 2009), and/or autoclaving (Hiromoto et al., 2008).

Furthermore, prior deposition of calcium orthophosphates, the surface of Mg, and its alloys might be chemically treated (e.g., activated) (Chen, Birbilis, et al., 2012; Du et al., 2011; Wang, Guan, et al., 2011; Wang et al., 2010; Wang, Tan, et al., 2011; Wen et al., 2009), alkaline treated (Du et al., 2011; Guan et al., 2012; Gray-Munro & Strong, 2009; Wang, Wei, et al., 2009; Xu et al., 2012), anodized (Hiromoto et al., 2008; Zhang, Ma, et al., 2013), chemically polished (Hiromoto & Tomozawa, 2010, 2011; Hiromoto et al., 2013; Ohtsu et al., 2013; Tomozawa & Hiromoto, 2011a, 2011b, 2011c; Tomozawa et al., 2010), electrochemically polished (Meng et al., 2011), etched (Rojace et al., 2013b; Song et al., 2013), passivated (Cui et al., 2013; Grubač et al., 2013; Kannan & Orr, 2011; Waterman et al., 2011), or prephosphatized (Chai et al., 2012; Du et al., 2011; Zhang, Ma, et al., 2013), among others (Geng et al., 2009).

More to the point, prior deposition of calcium orthophosphates, the surface of Mg, and its alloys might be coated by an interlayer of another compound, such as poly(ϵ -caprolactone) (Jo et al., 2013), nicotinic acid (Song et al., 2013), $\text{Mg}(\text{OH})_2$ (Waterman et al., 2011), MgF_2 (Jo et al., 2011; Lalk et al., 2013), $\text{Ca}(\text{OH})_2$ (Waterman, Birbilis, Dias, Woodfield, & Staiger, 2012), or titania (Tang, Xin, & Wang, 2013) to enhance the corrosion resistance and coating flexibility. Precalcified coatings might be applied as well (Liu et al., 2013; Song et al., 2013). All types of the aforementioned treatments are usually performed by dipping, spraying, rinsing, and/or soaking, depending on both the quality requirements and the limitations of the product to be coated. Finally, the surface of Mg and its biodegradable alloys might be sterilized prior to deposition of calcium orthophosphates (Cui et al., 2013).

As seen from the amount of available references, grinding and/or polishing of Mg and its biodegradable alloys appear to be the most popular surface pretreatment techniques, followed by cleaning and/or degreasing.

In addition, after calcium orthophosphate coatings have been deposited, various types of postdeposition treatments might also be necessary to improve their properties. For example, postdeposition heat treatment (annealing) of calcium orthophosphates leads to conversion of the deposited amorphous (ACP) and nonapatite phases, such as dicalcium phosphate dihydrate (DCPD), into either hydroxyapatite (HA) (Yang, Jiao, Cui, et al., 2008) or $\text{Ca}_2\text{P}_2\text{O}_7$ (Xu et al., 2012) (this depends on the Ca/P ratio) with simultaneous increasing of coating crystallinity, enhancing corrosion resistance, as well as reducing the residual stress. Furthermore, for the same purposes, chemical treatment of the coated samples in either aqueous alkaline solutions (Chen et al., 2011; Grubač et al., 2013; Guan et al., 2012; Jamesh, Kumar, & Narayanan, 2012; Kannan & Orr, 2011; Song et al., 2008; Su, Li, & Lian, 2012; Wen et al., 2009; Zhang, Li, et al., 2012) or phosphate-buffered saline (PBS) (Wu et al., 2010; Zhang, Dai, et al., 2012; Zhang, Dai, et al., 2013) may be used (Figure 7.4). In addition, the coated samples may be kept in boiling water (Yang, Jiao, Cui, et al., 2008). Finally, to get even better protection, other compounds, such as stearic acid (Zhang, Li, et al., 2012), may be adsorbed on or deposited over the calcium orthophosphate coatings to form biocomposites.

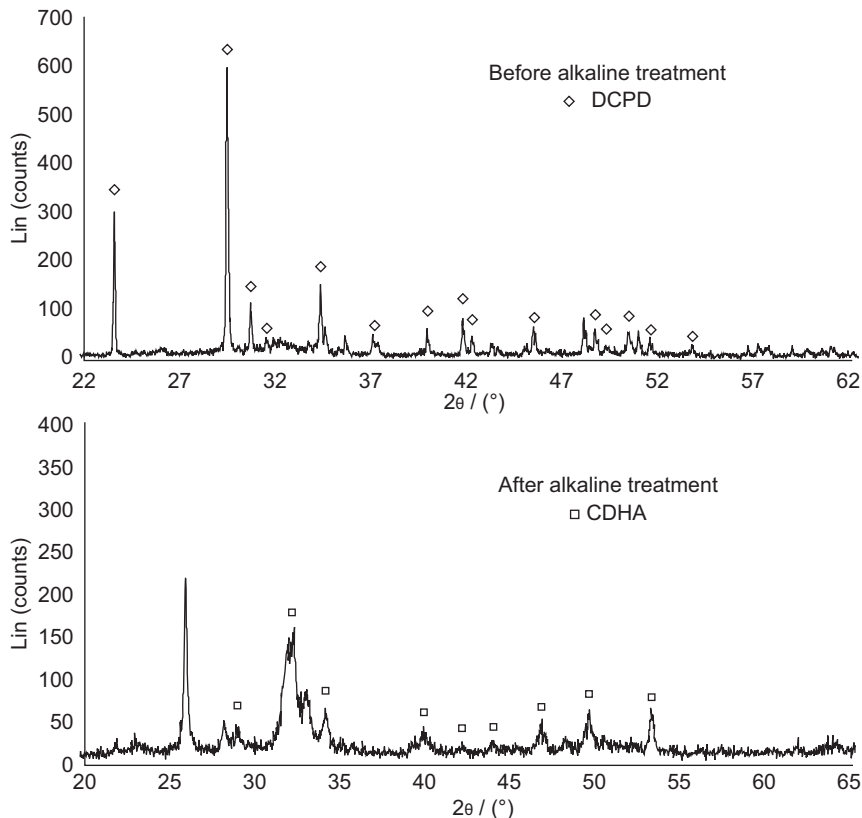


Figure 7.4 X-ray diffraction patterns of calcium orthophosphate coated AZ91 Mg alloy before (top) and after (bottom) an alkaline treatment. One can see that the initially deposited coating of DCPD was transformed into that of CDHA. DCPD, dicalcium phosphate dihydrate; CDHA, calcium-deficient hydroxyapatite.

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7.4 Deposition techniques

7.4.1 A brief historical background

Very briefly, the biomedical history of biodegradable Mg metallic implants started in 1878, when the physician Edward C. Huse used Mg wires as ligatures to stop the bleeding vessels of three human patients: once in a radial artery and twice in the operation for varicocele. He already observed that corrosion of Mg was slower *in vivo* and that the period until complete degradation was dependent on the size of the Mg wire used ([Huse, 1878](#)). The history of biomedical applications of calcium orthophosphates is much longer, because attempts to treat rickets (rachitis) by these compounds have been known since at least 1797 ([Sen & Jun, 1797](#)). Nevertheless, in spite of such long biomedical histories for both major constituents, they coexisted independently

until 2007, when the earliest papers on the protective calcium orthophosphate coatings on Mg were published (Cortés, López, & Mantovani, 2007; Wang et al., 2007). Therefore, the subject of this review appears to be new. Nevertheless, the substantial amount of available publications clearly indicates its importance.

7.4.2 Biomimetic deposition and wet chemical precipitation

From the preparation point of view, a spontaneous precipitation upon exposure to supersaturated solutions is the simplest way to deposit calcium orthophosphate coatings on Mg and its biodegradable alloys. Depending on the experimental conditions, the spontaneous precipitation can be divided into biomimetic deposition and wet chemical precipitation. Biomimetic deposition is carried out from artificially prepared simulating solutions, such as Hank's balanced salt solution (HBSS) (Hiromoto et al., 2008; Kuwahara et al., 2000), simulated body fluid (SBF) (Cortés et al., 2007; Hu et al., 2010; Liu et al., 2013; Lorenz et al., 2009; Rettig & Virtanen, 2008, 2009), and their modifications (Waterman et al., 2011, 2012; Yang, Jiao, Yin, Zhang, & Zhang, 2008; Zhang et al., 2008). Wet chemical deposition is performed from solutions of simpler composition (Chen et al., 2011; Chen, Biribilis, et al., 2012; Cui et al., 2013; Guan et al., 2012; Hu et al., 2010; Kang et al., 2013; Li et al., 2012a; Liu et al., 2011a, 2011b; Liu et al., 2013, 2014; Gray-Munro & Strong, 2009; Ohtsu et al., 2013; Wang et al., 2007; Wang, Wei, et al., 2009; Wang, Tan, et al., 2011; Xu et al., 2012; Yang et al., 2011; Yanovska et al., 2012; Zhang, Zeng, et al., 2010; Zhang, Ma, et al., 2013) and those containing non-biomimetic ions (Chai et al., 2012; Iskandar et al., 2013; Xu, Pan, et al., 2009; Xu, Zhang, et al., 2009). In addition, chemical deposition might also be performed from nonaqueous solutions, such as alcohol (Rojaei et al., 2013b).

Interestingly, the aforementioned biomimetic solutions HBSS (Abdal-hay et al., 2013; Cui et al., 2013; Gan et al., 2013; Geng et al., 2009; Grubač et al., 2013; Iskandar et al., 2013; Jo et al., 2013; Li et al., 2012a, 2012b; Tang, Xin, & Wang, 2013; Tomozawa & Hiromoto, 2011b; Wang, Tan, et al., 2011; Wang et al., 2013; Waterman et al., 2011; Xu, Zhang, et al., 2009; Zhang et al., 2007; Zhang, Zeng, et al., 2010) and SBF (Chen et al., 2011; Choudhary, Raman, & Nie, 2012; Gao et al., 2011; Guan et al., 2012; Hahn et al., 2011; James et al., 2012; Jo et al., 2011; Johnson et al., 2013; Kang et al., 2013; Kannan, 2012, 2013; Kim et al., 2014; Li et al., 2012a; Liu et al., 2011b, 2014; Meng et al., 2011; Gray-Munro et al., 2009; Noorakma et al., 2013; Pan, Chen, Wang, & Zhao, 2013; Rojaee et al., 2013a, 2013b; Shi, Qi, Chen, & Shi, 2011; Smith et al., 2012; Song et al., 2008, 2010, 2013; Sreekanth & Rameshbabu, 2012; Wang et al., 2007, 2010; Xiao, Zhu, et al., 2013; Xu, Zhang, et al., 2009; Xu et al., 2012; Yang et al., 2009; Zhang, Dai, et al., 2012; Zhang, Li, et al., 2012; Zhang, Dai, et al., 2013; Zhang, Ma, et al., 2013; Zhang et al., 2008; Zong et al., 2011), as well as Dulbecco's Modified Eagle Medium (DMEM) (Cui et al., 2013), minimum essential medium (MEM) (Chen, Kirkland, et al., 2012), and aqueous solutions (0.8–3.5 wt.%) of NaCl (Hiromoto & Tomozawa, 2011; Waterman et al., 2011; Xu et al., 2012; Yang, Jiao, Cui, et al., 2008) are commonly used to study *in vitro* corrosion of Mg and its alloys (Virtanen, 2011; Xin, Hu, & Chu, 2010) and, thus, the protective properties

of calcium orthophosphate coatings (Wang et al., 2012). The latter property can be measured *in vitro* by hydrogen evolution, increasing the solution pH, or following the concentration of released Mg^{2+} ions (Figure 7.5) (Jo et al., 2011; Kim et al., 2014). *In vivo* corrosion kinetics are much more difficult to measure; nevertheless, the typical results are presented in Figure 7.6 (Kim et al., 2014).

To continue differentiations between the biomimetic deposition and wet chemical precipitation, the former experiments are always performed under physiological conditions (temperature and solution pH), while the latter experiments might be performed at elevated temperatures and nonphysiological solution pH (Geng et al., 2009). Nevertheless, in all cases, calcium orthophosphates are precipitated and grown on the surface of Mg and its alloys. Both techniques are simple to set up and perform and are a cost-effective way of creating homogeneous coatings on several samples simultaneously. In addition, they do not require line of sight and thus allow complex shapes to be coated (Habibovic, Barrere, Blitterswijk, Groot, & Layrolle, 2002; Liu, de Groot, & Hunziker, 2009). Depending on the Ca/P ratio, temperature, and the solution pH, coatings of DCPD, octacalcium phosphate (OCP), or calcium-deficient hydroxyapatite (CDHA) might be precipitated on Mg and its alloys (Liu et al., 2014; Yanovska et al., 2012). For example, variations of ionic composition of the initial solutions were found to lead to deposition of various phases such as DCPD, DCPD + CDHA, and CDHA (Yanovska et al., 2012). This is similarly valid for the temperature: with temperature increases, the intensity of DCPD diffraction peaks in calcium orthophosphate coatings were found to decrease, while those of CDHA gradually increased (Liu et al., 2014). In addition, precipitation of β -tricalcium phosphate (β -TCP) on Mg was detected (Chai et al., 2012; Geng et al., 2009).

Because simulating solutions often contain a number of various ions, ion-substituted calcium orthophosphates are always deposited with a biomimetic approach. For example, amorphous carbonated calcium-magnesium orthophosphate coatings were formed in SBF (Cortés et al., 2007; Lorenz et al., 2009; Rettig & Virtanen, 2008, 2009). After incubation in SBF for 5 days, the deposited coatings had a thickness exceeding 20 μm and appeared to be highly permeable (Rettig & Virtanen, 2008, 2009; Song et al., 2013). In addition, the presence of highly reactive Mg results in the formation of Mg-enriched calcium orthophosphates (Gray-Munro & Strong, 2009), with simultaneous crystallization kinetics decreasing because Mg^{2+} ions are known inhibitors of apatite nucleation and growth (Bigi et al., 1993).

Various investigations indicated that prolonged immersion in supersaturated solutions resulted in the formation of thicker coatings, only if the supply of calcium and orthophosphate ions was plentiful. Under these circumstances, biomimetic deposition requires regular solution renewal (Cortés et al., 2007; Hiromoto et al., 2008; Hu et al., 2010; Kuwahara et al., 2000; Liu et al., 2013; Lorenz et al., 2009; Rettig & Virtanen, 2008, 2009; Waterman et al., 2011; Zhang et al., 2008). For example, controlling the biodegradation rate of Mg by biomimetic apatite coating was investigated (Zhang et al., 2008). The authors used both single-coated (one immersion for 24 h) and dual-coated (two immersions for 24 h each) Mg samples in modified SBF, as well as uncoated Mg as a control, followed by corrosion tests performed in the standard SBF. The findings demonstrated that two immersions resulted in the formation of

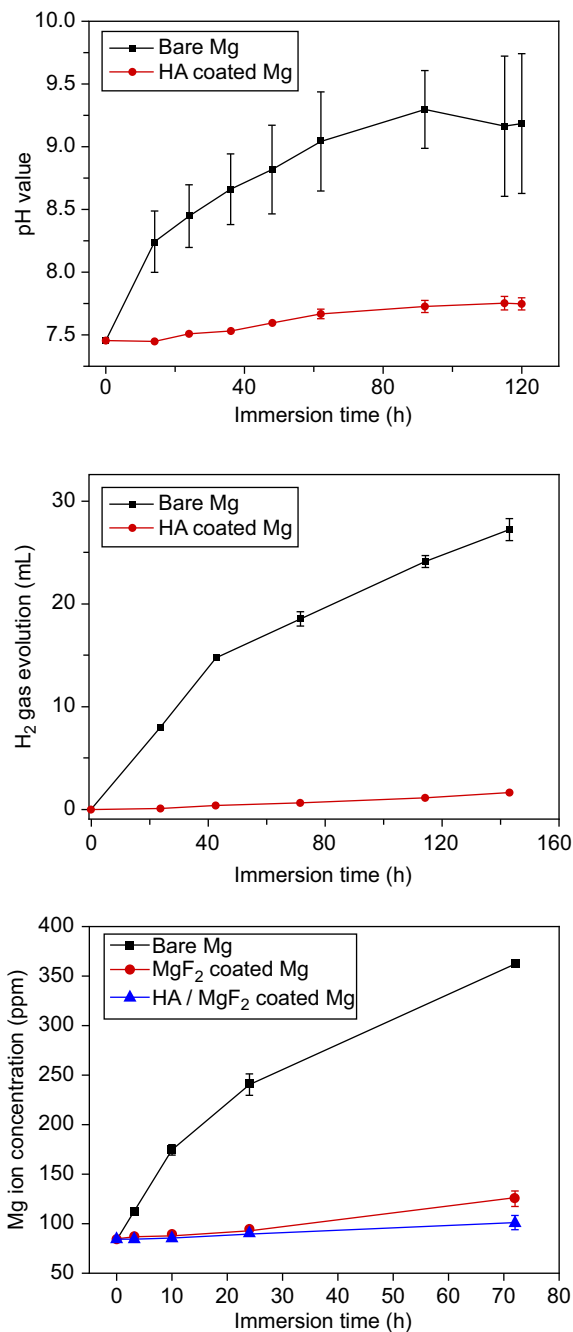


Figure 7.5 *In vitro* determination of the protective properties of calcium orthophosphate coatings on Mg and its alloys in SBF (corrosion tests). Variation of pH (top) and hydrogen gas evolution (middle) for bare and HA-coated Mg. Reprinted from Kim et al. (2014), with permission. Concentration of released Mg²⁺ ions (bottom) for bare Mg, MgF₂-coated Mg, and HA/MgF₂-coated Mg samples. Reprinted from Jo et al. (2011), with permission.

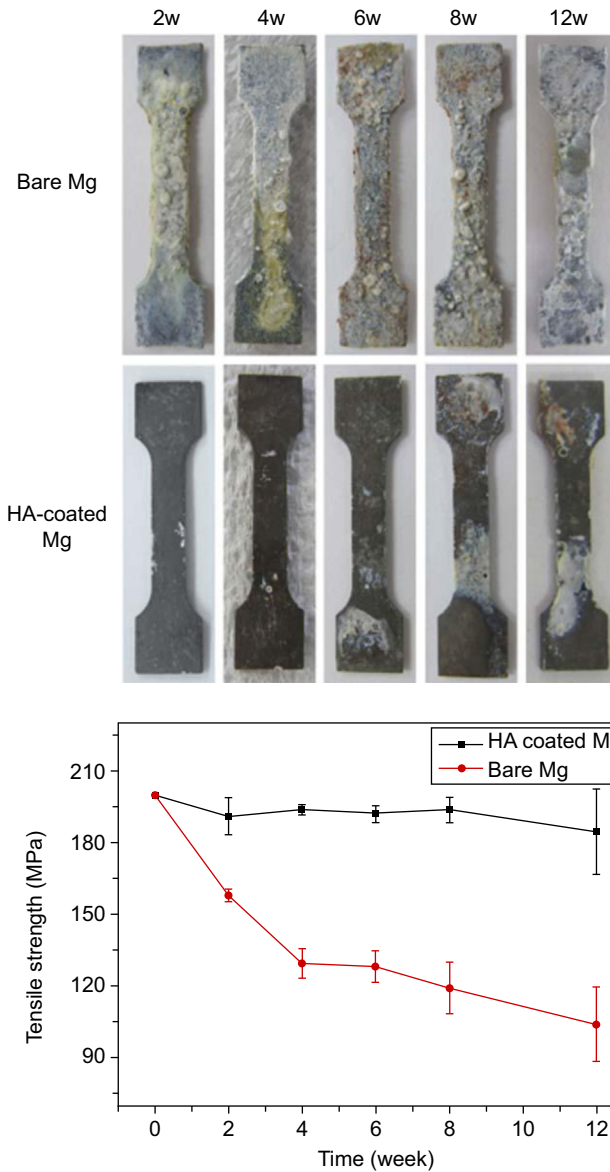


Figure 7.6 *In vivo* determination of the protective properties of calcium orthophosphate coatings on Mg and its alloys. Top: Optical images of the bare Mg and HA-coated Mg specimens after 2, 4, 6, 8, and 12 weeks of implantation. Bottom: Ultimate tensile strength of the bare Mg- and HA-coated Mg specimens after 2, 4, 6, 8, and 12 weeks of implantation. Reprinted from [Kim et al. \(2014\)](#), with permission.

thicker CDHA coatings, with increased corrosion protection in SBF compared to the controls. The authors concluded that the degradation rate of Mg could be tailored by controlling the thickness of apatite coatings (Zhang et al., 2008). Other researchers demonstrated comparable findings for the corrosion protection of calcium orthophosphate coated AZ31 and AZ91D Mg alloys using both immersion tests in SBF (Yang et al., 2009) and electrochemical tests (Hu et al., 2010), respectively. In support of this, still other investigators illustrated the corrosion protection of biomimetic CDHA-coated pure Mg, with subsequent cell adhesion increases (Keim et al., 2011; Lorenz et al., 2009). Furthermore, biomimetic precipitation of calcium orthophosphates on Mg might be performed under the magnetic field (Xu et al., 2013; Yanovska et al., 2012). A difference in particle morphology and crystal texture of precipitates in the north pole and the south pole proximities was observed. In the presence of a magnetic field, an increase of crystallite sizes in (0 2 0) and (0 4 0) planes was observed for precipitated DCPD, which allowed the authors to vary crystallinity of the coatings (Yanovska et al., 2012).

The spontaneous precipitation techniques have proven to be popular methods for coating Mg and its alloys. However, there are reports on the formation of nonuniform and porous calcium orthophosphate coatings on Mg substrates caused by coating formation occurring around hydrogen bubbles formed on the Mg surface during immersion (Cui et al., 2008).

7.4.3 Sol–gel preparation and dip coating

Sol–gel preparation combined with a dip coating technique has been widely investigated to coat Mg and its biodegradable alloys for both corrosion protection and increased adhesion. The technique involves a substrate immersion (dipping) into a liquid, which is a concentrated calcium orthophosphate solution with a gel-like texture. Requirements for the sol preparation are calcium and phosphorus precursors and one or two solvents, often ethanol (as the only solvent) or water and ethanol (if two solvents are used). The phosphorus precursor, regularly P_2O_5 or triethylphosphate, is dissolved in ethanol. The selected calcium precursor, most often calcium nitrate, is also dissolved in either water or ethanol and then both solutions are mixed. The obtained mixture is then refluxed at various temperatures and solvents are evaporated off until a more viscous solution is obtained to achieve a sol–gel. Samples of Mg and its alloys to be coated are then dipped into the sol–gel several times to acquire a calcium orthophosphate coating, which is then cured at high temperatures to increase the coating/substrate adhesion and to accomplish apatitic structures within the applied coatings. When adapting this coating system for Mg substrates and their alloys, the curing temperatures cannot exceed the melting point of pure Mg (650 °C) to avoid affecting the surface integrity of the Mg substrate. Therefore, curing of sol–gel coatings on Mg and its alloys has been reported anywhere in the range of 25–400 °C by different authors (Feil, Frbeth, & Schtze, 2009; Galio et al., 2010; Hu, Li, Zhong, Zhang & Chen, 2009; Rojaee et al., 2013a; Roy et al., 2011; Tan, Soutar, Annergren, & Liu, 2005; Tang, Xin, Luo, & Wang, 2013; Tang, Xin, & Wang, 2013).

A typical experimental example looks as follows: 3.94 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 0.71 g of P_2O_5 were dissolved separately in 10 ml of ethanol. Ca-precursor was added dropwise into the P-precursor to produce a mixture containing Ca/P ratio 1.67. The obtained suspension stirred at 400 rpm for 5 h at 26 °C in a closed beaker. Afterwards, the samples of an Mg alloy were dipped vertically into the suspension and withdrawn at a constant speed of 0.1 mm/s using an electric dip coater. The coated substrates were then maintained at room temperature for 24 h in order to complete aging. Then, they were gradually heated to 60 °C and maintained at this temperature for 24 h. Afterwards, the coated samples were calcined at 400 °C for 6 h (Rojae et al., 2013a).

To date, the sol–gel preparations combined with dip coating have been established as cost-effective and simple systems to set up, as well as possessing the ability to coat irregular shapes, similar to the spontaneous precipitation techniques. This approach shows the potential of using relatively low temperatures and short incubation times to achieve thick coatings on Mg and its alloys. Their primary advantage over the aforementioned spontaneous precipitation techniques is in the strength of the coating/substrate adhesion (Lamaka et al., 2008; Qu & Wei, 2008).

7.4.4 Electrodeposition

Electrodeposition is a broad range of deposition techniques by means of electrical current. It comprises electrochemical deposition (or cathodic deposition), electrophoretic deposition, and some other techniques. In general, electrodeposition is a low-cost and simple process that can be carried out at room temperature to form uniform coatings, which was also applied for deposition of calcium orthophosphate coatings on Mg and its biodegradable alloys (Choudhary et al., 2012; Grubač et al., 2013; Guan et al., 2012; Jamesh et al., 2012; Kannan & Orr, 2011; Kannan, 2013; Lu et al., 2013; Metikoš-Huković, Babić, Grubač, Petravić, & Peter, 2013; Salman, Kuroda, & Okido, 2013; Song et al., 2008, 2013; Wen et al., 2009; Zhang, Zeng, et al., 2010; Zhang, Li, et al., 2012). This technique is commonly performed from aqueous solutions similar to those used in wet-chemical deposition (see Section 7.4.2). For example, an AZ91D alloy was successfully coated by a biphasic combination of DCPD and β -TCP using cathodic deposition at room temperature for 2 h. Afterwards, a transformation step was carried out in 1 M aqueous solution of NaOH for 2 h to convert the biphasic mixture into the uniform CDHA coatings (Song et al., 2008). Similarly, another research group conducted cathodic deposition of calcium orthophosphate coatings on AZ31 alloy at 85 °C for a period of 4 h and obtained a combination of CDHA and DCPD phases. Afterwards, the coated samples were immersed into 0.25 M NaOH solution for 4 h at 60 °C to transform the biphasic (CDHA + DCPD) coatings into the single-phase CDHA ones (Figure 7.7) (Waterman et al., 2011). The authors of those studies demonstrated that the deposited CDHA coatings both improved corrosion protection (namely, the numerical value of corrosion potential $[E_{\text{corr}}]$ of AZ31 substrate increased from -1.6 to -1.42 V) (Wen et al., 2009) and improved bioactivity of the samples. Furthermore, the CDHA-coated samples exposed to SBF showed ~20% improvement in the mechanical strength as compared to that of the uncoated samples (Kannan & Orr, 2011).

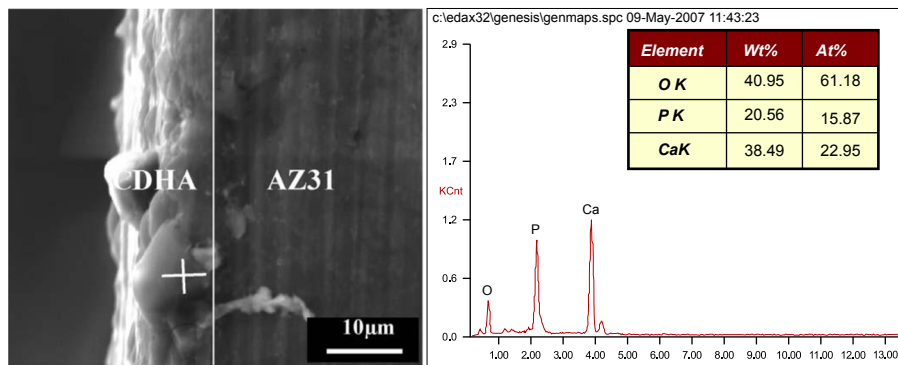


Figure 7.7 Left: A cross-sectional SEM image. Right: An EDS spectrum (performed in the cross on the left image) of a CDHA-coated specimen of Mg-based AZ31 alloy. The EDS shows that the coating consists of Ca, P, and O elements with the Ca/P atom ratio of ~ 1.45 . CDHA, calcium-deficient hydroxyapatite.

Reprinted from [Wen et al. \(2009\)](#), with permission.

The electrodeposition process of calcium orthophosphate coatings on Mg and its alloys can be modified to include pulse currents as opposed to the constant currents. This resulted in better performance of the pulse-potential coatings, which was attributed to a more closely packed morphology of the protective coatings, which decreased the anodic dissolution of Mg and its alloys ([Kannan, 2012](#); [Meng et al., 2011](#); [Srinivasan, Liang, Blawert, Stormer, & Dietzel, 2010](#); [Wang, Guan, et al., 2011](#); [Wang et al., 2010](#); [Zong et al., 2011](#)). Adjustments of both the pulse current parameters and electrolyte solutions were suggested as controlling effective ways of the coating structure. By these means, CDHA was successfully deposited on Mg–Zn–Ca alloy directly, without the need for a transformation step ([Wang et al., 2010](#)). In addition, dense and uniform fluorine-doped HA coatings were electrodeposited in the same way but with the addition of H_2O_2 to the electrolyte to reduce H_2 evolution by its oxidation ([Meng et al., 2011](#)). Furthermore, pulse electrophoresis at 85°C for 30 min revealed a greater adhesion of calcium orthophosphate coatings to Mg–Zn–Ca alloys ([Shadanbaz & Dias, 2012](#)), while pulse treatments of the coated samples of AM50 alloys at 20°C for 15 min displayed a higher corrosion resistance ([Srinivasan et al., 2010](#)). Other researchers used cathodic deposition to put DCPD coatings on Mg–Zn alloys ([Li et al., 2010](#); [Song et al., 2010](#); [Zhang, Li, Song, Zhao, & Zhang, 2010](#)). The DCPD coatings were deposited at room temperature by adding 10 ml/l H_2O_2 into the electrolyte and adjusting the pH value to 4.4. The authors stated that the DCPD phase could effectively decrease the degradation rate of the alloy as well as increase its biocompatibility. Further research indicated that the electrophoretically deposited DCPD on Mg–Zn alloys (which were then converted to CDHA via alkali treatment) were more stable and effective in corrosion resistance compared to the originally deposited DCPD. Similar results were obtained by other researchers ([Grubač et al., 2013](#)). However, coatings of fluoridated HA were found to possess even better corrosion protective properties ([Li et al., 2010](#); [Song et al., 2010](#)). Further

research analyzed the effect of different deposition times (20, 60, 120 or 240 min) in cathodic deposition. The authors concluded that the deposition time had a great influence on the coating's morphology; however, it did not influence the conversion of DCPD to CDHA or other calcium orthophosphates (Zhang, 2010).

Normally, electrodeposition of calcium orthophosphate coatings on Mg and its biodegradable alloys is performed from aqueous solutions (the aforementioned examples). However, to improve some properties of the coatings, studies are available on the addition of organic solvents, such as alcohol (Kannan, 2012, 2013; Song et al., 2013). For example, to reduce conductivity of the coating solutions (0.1 M $\text{Ca}(\text{NO}_3)_2$ and 0.06 M of $\text{NH}_4\text{H}_2\text{PO}_4$ dissolved in water), ethanol was added in different proportions: 10%, 30%, 50%, and 70% (v/v) and electrochemical deposition was carried out on AZ91 alloy using a constant-potential method. The author revealed a significant decrease of hydrogen bubble bursting during deposition from ethanol-containing solutions, which resulted in denser packing of the precipitated DCPD crystals and, thus, a higher degradation resistance of the DCPD coatings, as compared to those formed from ethanol-free solutions. The optimum results were obtained for 30% (v/v) ethanol-containing solutions, while further increasing in ethanol content in the solution produced thinner DCPD coatings possessing poorer protection degrees (Kannan, 2013).

Representative micro-computed tomography (CT) reconstruction images of *in vivo* biodegradation studies of the electrochemically deposited calcium orthophosphate coatings are presented in Figure 7.8 (Wang, Guan, et al., 2011). At 8 weeks of implantation, the surface morphology of the residual bare Mg alloy implant exhibited obvious

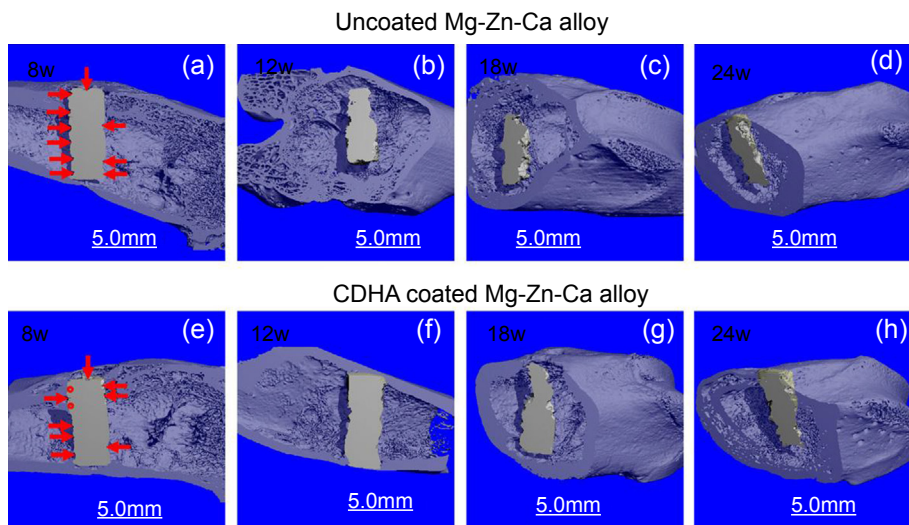


Figure 7.8 Representative micro-CT reconstruction images of the rabbit femora containing both uncoated (top) and CDHA-coated (bottom) Mg–Zn–Ca alloy implants at 8, 12, 18, and 24 weeks postoperatively.

Reprinted from Wang, Guan, et al. (2011), with permission.

corrosion pits (indicated by red arrows in [Figure 7.8\(a\)](#)), while there was only slight corrosion with superficial pits for CDHA-coated specimen (indicated by red arrows in [Figure 7.8\(e\)](#)). With the implantation time increasing, corrosion of both samples became gradually more severe due to the local failure of the CDHA coatings (shown in [Figure 7.8\(c\), \(d\), \(g\) and \(h\)](#)). Therefore, both uncoated and CDHA-coated Mg alloy implants were corroded in the rabbit femora; however, during the same implantation period, the bare Mg alloy implants experienced more serious corrosion than the CDHA-coated implants ([Wang, Guan, et al., 2011](#)).

Calcium orthophosphate coatings obtained by the electrochemical method have a uniform structure because they are formed gradually through a nucleation and growth process at relatively low temperatures.

7.4.5 Hydrothermal

Hydrothermal treatment is a simple process and one of the most cost-effective techniques for coating deposition on metallic surfaces. It is rather similar to the aforementioned biomimetic deposition and wet-chemical precipitation; however, because the hydrothermal treatment is performed at elevated ($>90^{\circ}\text{C}$) temperatures during a relatively prolonged period of time ($>1.5\text{ h}$), the calcium orthophosphate deposits are usually crystalline. However, it is difficult to form coatings of pure calcium orthophosphates on Mg and its biodegradable alloys because aqueous solutions at elevated temperatures cause heavy corrosion of Mg, while the released Mg^{2+} ions might both form surface layers of $\text{Mg}(\text{OH})_2$ and substitute Ca^{2+} ions in the structure of coatings.

To the best of my findings, until recently, there was only one research group located in Japan who actively pursued this approach ([Hiromoto & Tomozawa, 2010, 2011](#); [Hiromoto & Yamamoto, 2009](#); [Hiromoto et al., 2013](#); [Ohtsu et al., 2013](#); [Tomozawa & Hiromoto, 2011a, 2011b, 2011c](#); [Tomozawa et al., 2010](#)). However, in 2012 and 2014, research groups from China ([Li et al., 2012b](#)) and Korea ([Kim et al., 2014](#)), respectively, also published papers on this technique. Namely, using a hydrothermal treatment for 2 h at 363 K, the Japanese researchers succeeded in forming well-crystallized HA and OCP coatings on both pure Mg and Mg–Al–Zn alloys from a 0.25 M Ca-EDTA and KH_2PO_4 treatment solution in a wide pH range, from 5.9 to 11.9. According to the authors, the formation of highly crystalline coatings was achieved primarily due to using Ca-EDTA solutions, which could supply sufficiently high concentrations of Ca^{2+} ions to perform precipitation. Both HA and OCP coatings were found to consist of an outer porous layer and an inner continuous layer, while both the crystal phases and the microstructures of the coatings were found to vary with the pH of the treatment solutions. Namely, in weak acidic ($\text{pH} = 5.9$) solutions, a dual-layer structure was formed: an outer coarse layer consisted of plate-like OCP crystals and an inner dense layer consisted primarily of HA crystals. In weak alkaline ($\text{pH} = 8.9$) solutions, a dual-layer structure was also formed: an outer coarse layer consisted of rod-like HA crystals and an inner dense layer consisted of well-packed HA crystals ([Figure 7.9](#)). In strong alkaline ($\text{pH} = 11.9$) solutions, needle-like HA crystals were formed. Both layers were found to grow with an increase of the treatment periods. A thin $\text{Mg}(\text{OH})_2$ layer was also

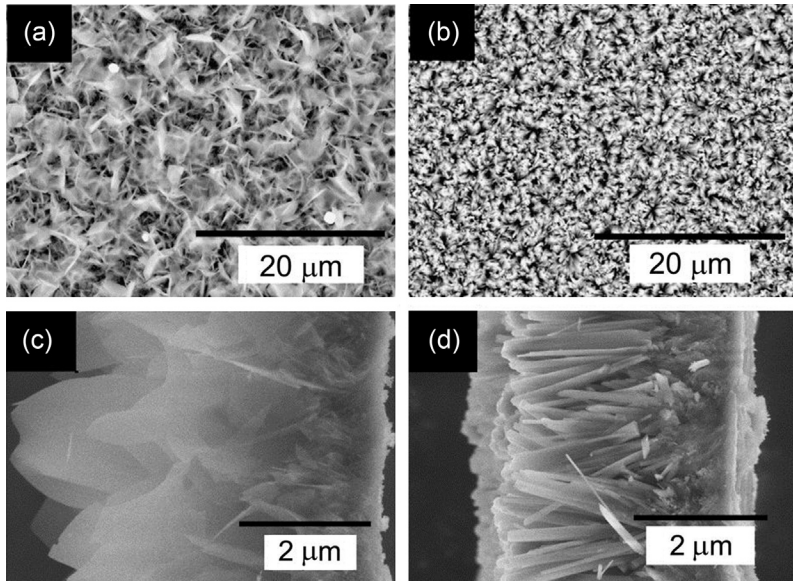


Figure 7.9 The surface (a, b) and cross-sectional (c, d) SEM images of calcium orthophosphate coatings deposited on Mg synthesized under the hydrothermal conditions in the treatment solutions with a pH value of 5.9 (a, c) and 8.9 (b, d). As seen in (c) and (d), the outer porous layer and the inner continuous layer are located in the left and right sides of the images, respectively. Reprinted from [Ohtsu et al. \(2013\)](#), with permission.

formed at the boundary between the calcium orthophosphate coatings and Mg substrates ([Figure 7.10](#)). The HA and OCP coatings were found to improve the corrosion resistance of both pure Mg and Mg–Al–Zn alloys in both HBSS and 3.5 wt% NaCl solutions; however, the corrosion resistance of HA coatings was always higher than that of OCP ones ([Hiromoto & Tomozawa, 2010, 2011](#); [Hiromoto & Yamamoto, 2009](#); [Hiromoto et al., 2013](#); [Ohtsu et al., 2013](#); [Tomozawa & Hiromoto, 2011a, 2011b, 2011c](#); [Tomozawa et al., 2010](#)). Similar results were obtained by other researchers ([Kim et al., 2014](#); [Li et al., 2012b](#)). In addition, such coatings showed good adhesive properties with slight plastic deformations under cyclic stresses below the fatigue limit. Neither cracks nor detachment were microscopically observed under 5% static elongation and under 3% cyclic elongation ([Hiromoto et al., 2013](#)). The authors revealed that the protection level of calcium orthophosphate coatings could be varied by their crystal phase, microstructure, and thickness. Thus, an optimization of the microstructure of the coatings is necessary to adjust the corrosion resistance of the coated Mg to the desired values.

7.4.6 Aerosol deposition

In addition, calcium orthophosphate coatings might be put down on Mg and its biodegradable alloys by an aerosol deposition technique. Namely, there are studies in which

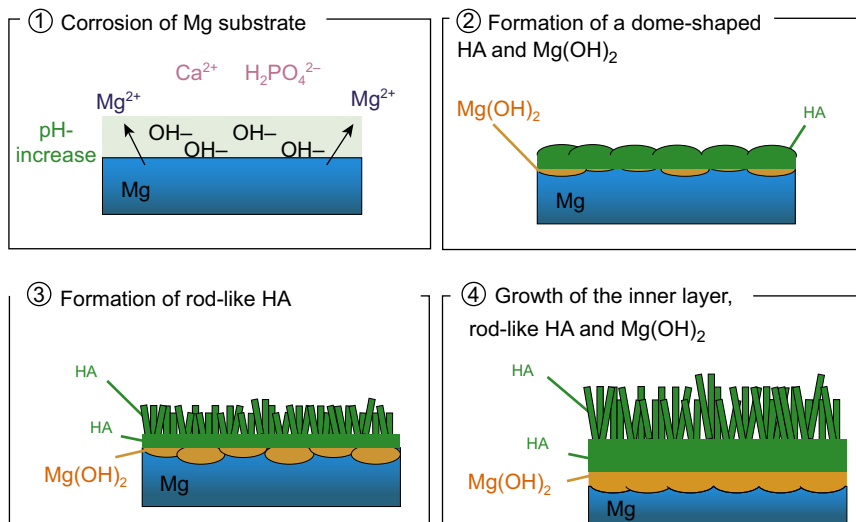


Figure 7.10 A schematic illustration of formation and growth mechanisms of HA coatings on Mg under the hydrothermal conditions.

Reprinted from [Tomozawa and Hiromoto \(2011a\)](#) with permission. Another illustration of this mechanism is available in [Hiromoto and Yamamoto \(2009\)](#).

the authors used this technique to deposit HA onto the surface of both pure Mg and Mg previously covered by either poly(ϵ -caprolactone) ([Jo et al., 2013](#)) or MgF_2 ([Jo et al., 2011](#)). To perform aerosol deposition, HA powder was sprayed onto Mg samples in a deposition chamber using oxygen carrier gas at a flow rate of $5 \times 10^{-4} \text{ m}^3/\text{s}$ under a pressure of 9.2 Torr. According to scanning electron microscopy (SEM) observations, when HA was deposited onto Mg with the poly(ϵ -caprolactone) interlayer, it was partially embedded into this interlayer, forming composite-like structures ([Jo et al., 2013](#)); however, when HA was deposited onto Mg with the MgF_2 interlayer, no composite-like structures were observed ([Jo et al., 2011](#)). The corrosion tests performed in SBF revealed the good corrosion resistance of such coatings ([Figure 7.5](#), bottom). In addition, the HA coatings on Mg with the poly(ϵ -caprolactone) interlayer were found to have better stability during deformation compared with the HA coatings on Mg without the interlayer. These results revealed that coating Mg by an HA/poly(ϵ -caprolactone) double layer might become a promising approach to reducing the corrosion rate of Mg and improving the coating flexibility ([Jo et al., 2013](#)).

In addition to aerosol deposition, Mg and its biodegradable alloys might be coated by calcium orthophosphate-based biocomposites. For example, there is a study on the deposition of HA/chitosan biocomposites on AZ31 alloy ([Hahn et al., 2011](#)). The authors employed a slit-type nozzle with a $10 \times 0.5 \text{ mm}^2$ rectangular opening and air as a carrier gas with a flow rate of 30 L/min. The $5 \text{ }\mu\text{m}$ -thick HA/chitosan coatings were deposited over the entire surface of the AZ31 Mg alloy substrates by scanning the substrates on the motorized X–Y stage for 1 min at a scanning speed of 1 mm/s. The biocomposite coatings were found to exhibit high adhesion strengths, ranging from

24.6 to 27.7 MPa, and showed good corrosion resistance. Although the addition of chitosan lowered the corrosion resistance of the HA coatings, their biocompatibility was improved (Hahn et al., 2011).

7.4.7 Spin coating

Just two publications were found on the subject of spin coating, both devoted to the deposition of calcium orthophosphate-based biocomposites on Mg alloys (Johnson et al., 2013; Wang et al., 2013). Initially, biocomposites of HA/collagen (HAC) (Wang et al., 2013) and HA/poly(lactic-co-glycolic acid) (Johnson et al., 2013), respectively, were prepared. Afterwards, to deposit HAC onto the surface of AZ31 alloy chips, a mixture of 2 g of poly(L-lactic acid) (PLLA) and HAC (at various PLLA/HAC ratios) was dissolved in 20 ml of dichloromethane and magnetically stirred for 30 min followed by ultrasonic dispersion for 15 min. The prepared suspension was spin coated on pretreated AZ31 alloy chips for 30 s at a rotating speed of 2000 r/min. The coated surface was immediately dried by blowing at room temperature and, in order to get thick coatings, the procedure was repeated five times. The corrosion studies performed in HBSS revealed that the biocomposite coatings suppressed the sharp rising of pH value and Mg^{2+} releasing from the substrates, while the degradation behavior of the alloy was correlated to microstructure of the coatings (Wang et al., 2013). Both the deposition technique and the obtained corrosion results appeared to be similar for Mg alloys covered by HA/poly(lactic-co-glycolic acid) coatings (Johnson et al., 2013). Thus, the spin coating technique appears to be a convenient tool to deposit composite coatings.

7.4.8 Spray coating

Again, just two publications were found on the topic of spray coating. One of them was devoted to deposition of HA-doped poly(lactic acid) porous coatings on AZ31 alloy (Abdal-hay et al., 2013), whereas the other one was devoted to deposition of HA coatings on AZ51 alloy (Noorakma et al., 2013). In the former paper, the authors dissolved poly(lactic acid) in dichloromethane solvent. Afterwards, colloids were prepared by adding nanosized HA particles to the poly(lactic acid) solutions, which were stirred for more than 24 h. Then, these colloids were sprayed onto the surface of AZ31 samples at room temperature and 50% humidity. The air pressure (400 kPa) was optimized to get fine droplets. The coated samples were dried in a vacuum oven at 40 °C for 12 h and then at 67 °C for 1.5 h (Abdal-hay et al., 2013). In the second paper, the deposition technique was almost the same, but the spraying process was performed onto heated to 400 °C AZ51 substrates (Noorakma et al., 2013).

The results of both studies revealed that the coated Mg alloy samples had better corrosion resistance compared with that of uncoated samples. Namely, during immersion tests performed for 15 days in HBSS, the numerical values of pH increases, weight loss, and bending strength decreases were found to be lower for the coated samples (with average values of 8.5%, 7.2%, and 10%, respectively) than the similar values for the uncoated samples (10.5%, 15.5%, and 25%, respectively) (Abdal-hay

et al., 2013). Similar trends were obtained in another study (Noorakma et al., 2013). In addition, cytocompatibility studies with MC3T3 cells revealed a continuous increase in cell growth on the coated samples (Abdal-hay et al., 2013).

7.4.9 Ion-beam assisted deposition

Just one publication was found on ion-beam assisted deposition of calcium orthophosphate coatings on Mg and its alloys. The publication was devoted to the deposition of calcium orthophosphates with Ca/P ratio >1.67 on AZ31 alloy (Yang, Jiao, Cui, et al., 2008). To do this, calcium orthophosphate evaporants were prepared by adding 37% CaO powder to HA powder. Prior to deposition, the surface of AZ31 substrates was cleaned by 120 V and 2 A Ar^+ beam bombardment for 20 min. Afterwards, vapor fluxes of evaporants were generated by an electron beam evaporator, which were deposited on the rotating AZ31 substrates. The substrate temperature during deposition was kept below 100°C . To convert amorphous phases (ACP) into HA after deposition, some specimens were subjected to annealing at 250°C for 2 h and then kept boiling in deionized water for 30 min. Compared with the uncoated AZ31 samples, the numerical values for both hardness and elastic modulus of the coated samples were found to increase for 77% and 55%, respectively. In addition, in degradation tests performed in 3% aqueous solutions of NaCl, the mass loss of the coated samples appeared to be just one-fifth of that of uncoated samples (Figure 7.11), which indicated that the ion-beam deposited calcium orthophosphate coatings decreased the degradation rates of AZ31 significantly (Yang, Jiao, Cui, et al., 2008).

However, in another study, nanostructured “HA coatings were deposited on polished Mg using the patented transonic particle acceleration (Spire Biomedical) process” (Iskandar et al., 2013; Abstract). Unfortunately, no information on the deposition process was disclosed. A search on the Spire Biomedical website revealed the following information: “Deposited at low temperature and offering a wide range of calcium phosphate formulations, IonTite™ coatings are ideal for promoting bone/implant interfacial bonding. These adherent coatings can be applied to dental, joint replacement and fixation products made of biomaterials such as Co-Cr, Ti, stainless steel and most other metals.” Further investigations have revealed that the company uses an ion beam-assisted deposition technology; therefore, with a reasonable level of probability, Iskandar et al. (2013) might be considered as the second publication on this technique. The results revealed that in comparison to the noncoated Mg

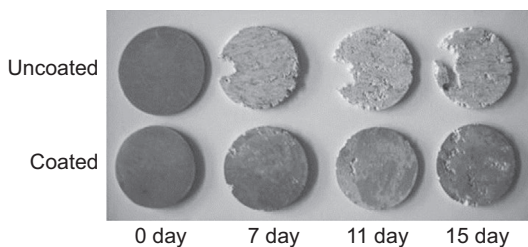


Figure 7.11 A mutual comparison of the degradation behavior of the uncoated and calcium orthophosphate coated samples of AZ31 alloy performed in 3% aqueous solution of NaCl at different immersion times. Reprinted from Yang et al. (2008), with permission.

samples, the coated ones showed significantly decreased degradation rates, indicating that the HA coating was protecting the Mg samples from rapid degradation (Iskandar et al., 2013).

7.4.10 Direct laser melting

Again, just one publication was found on the topic of direct laser melting. The publication was devoted to deposition of HA on AZ31B alloy (Santhanakrishnan et al., 2012). To perform the deposition, initially a precursor was prepared by mixing an HA powder with an aqueous solution containing a binder and a reducer. Afterwards, the obtained slurry was deposited onto the surface of AZ31B alloy substrates using an air-sprayed gun, followed by air-drying for 24 h to remove moisture. Later, the precursor deposited substrates were subjected to laser processing using an ytterbium (IPG YLS-3000) fiber laser (1064 nm) of continuous wave with Gaussian power distribution and beam focal spot of 1 mm. The results of further investigations revealed improvements of both corrosion resistance (+48%) and biodegradability (+180%) for HA-coated AZ31B samples for the selected laser process variables, such as power, scanning speed, and beam indexing (Santhanakrishnan et al., 2012).

7.4.11 A double-layered capsule hydrothermal hot pressing

One publication was found on the topic of hydrothermal hot pressing, which was devoted to the deposition of HA on AZ31 alloy (Onoki & Yamamoto, 2010). Firstly, the Mg alloy rod and the powder mixture of DCPD and $\text{Ca}(\text{OH})_2$ were placed into a polyethylene tube. The powder mixture was loaded into the tube such that the Mg alloy rod was concentrically positioned with respect to the tube axis. Both ends of the tube were fastened with paper staples. Secondly, the entire tube was further encapsulated using a poly-vinylidene-chloride film. Then, alumina powder was placed between the tube and film. The entire construction was put into a batch-type high temperature and pressure vessel for hydrothermal treatment. Then, the vessel was heated up to 150 °C for 3 h, while the pressure was kept at 40 MPa using a pressure regulator. After the treatment, the vessel was cooled down to a room temperature and the HA-coated AZ31 samples were removed. Afterwards, pullout tests were conducted in order to measure the adhesive properties of HA coating to AZ31 substrates. The average value of the maximum shear stress was determined to be 6.1 ± 1.0 MPa. In addition, it was revealed that HA remained on the surface of the Mg alloy after the pullout fracture tests. Thus, by means of this technique, HA coatings could be bonded to Mg and its alloys with good adhesive properties (Onoki & Yamamoto, 2010).

7.4.12 Micro-arc or plasma electrolytic oxidation

Micro-arc oxidation (also called plasma electrolytic oxidation, anodic spark deposition, or micro-arc discharge oxidation) is a combination of plasma-chemical and electrochemical processes. It combines an electrochemical oxidation with a high-voltage spark treatment performed in aqueous electrolytic baths, which also contain modifying

elements in the form of dissolved salts (e.g., silicates, borates) to be incorporated into the resulting coatings. This technique was found to be applicable to deposit ceramic coatings on Mg and its alloys with simultaneous corrosion resistance (Liu et al., 2011a, 2011b; Liu et al., 2014; Rojaee et al., 2013a; Shi et al., 2009, 2011; Sreekanth & Rameshbabu, 2012; Wang, Wang, et al., 2009; Wu et al., 2010; Zhang, Dai, et al., 2012; Zhang, Dai, et al., 2013; Zhang et al., 2007). Therefore, the protective coatings consist mainly of MgO combined with magnesium silicates, borates, etc., depending on the chemical composition of the electrolytic bath. In the case of Mg alloys, such coatings also contain oxides, silicates, borates, etc. of the alloying elements. In the presence of Ca- and P-containing salts, such coatings also contain various Ca- and P-containing compounds (but not calcium orthophosphates) (Gan et al., 2013; Gao et al., 2011; Ma, Zhang, Qu, & Li, 2010; Pan et al., 2013; Yao, Li, & Jiang, 2009). Namely, Ca- and P-containing coatings were prepared on AZ91D alloy in both NaOH- and Na₂SiO₃-containing electrolytes with the addition of sodium hexameta-phosphate and calcium hypophosphite.

According to the results of energy-dispersive spectroscopy (EDS), the coatings prepared in the NaOH system were mainly composed of oxides of Mg, Al, P, and Ca, while those prepared in the Na₂SiO₃ system also contained a substantial amount of Si oxides. The results of X-ray diffraction revealed MgO and Mg₂SiO₄ as the predominant phases in the coatings prepared in NaOH and Na₂SiO₃ systems, respectively (Yao et al., 2009). Similar results were obtained in other studies (Gan et al., 2013; Gao et al., 2011; Pan et al., 2013). However, once among other phases, the formation of CaNaPO₄ was detected because the electrolyte used in that study contained CaCO₃, Ca₃(PO₄)₂, and 20 g/L of orthophosphate ions (Ma et al., 2010). With the exception of Ma et al. (2010), the formation of calcium orthophosphates was not noticed in the coatings, so the micro-arc oxidation technique alone appears to be unsuitable for deposition of calcium orthophosphates on Mg and its biodegradable alloys. It might be considered as a predeposition technique (see Section 7.3).

However, using other techniques, such as chemical precipitation (Liu et al., 2011a, 2011b, 2014; Zhang, Dai, et al., 2013) or electrodeposition (Gao et al., 2011; Rojaee et al., 2013a; Shi et al., 2011; Sreekanth & Rameshbabu, 2012; Wu et al., 2010; Zhang, Dai, et al., 2012), calcium orthophosphate coatings might be deposited over the micro-arc oxidative coatings (Figures 7.12 and 7.13). Namely, Mg–Zn–Ca alloys coated with such composite coatings were found to induce rapid precipitation of calcium orthophosphates from simulated solutions, with simultaneous increasing of the corrosion resistance of Mg and its alloys (Gao et al., 2011). Similar results were obtained in other studies (Liu et al., 2011b; Rojaee et al., 2013a; Shi et al., 2011). In addition, micro-arc oxidation of the Mg surface might be performed simultaneously with the electrodeposition of calcium orthophosphates, which resulted in formation of composite MgO/calcium orthophosphate protective coatings on Mg and its alloys (Sreekanth & Rameshbabu, 2012). More to the point, calcium orthophosphate-based biocomposite coatings might be deposited over the micro-arc oxidative coatings (Wu et al., 2010; Zhang, Dai, et al., 2012; Zhang et al., 2013). Therefore, combinations of micro-arc oxidation (to provide good corrosion resistance) with any suitable deposition technique of calcium orthophosphates (Figure 7.14) appear to be the effective and promising

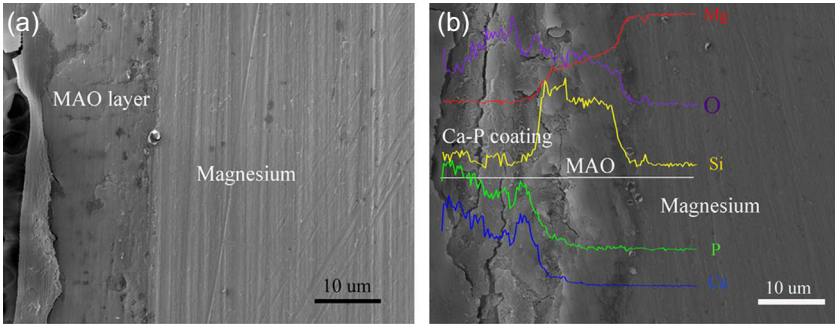


Figure 7.12 Cross-sectional SEM images of micro-arc oxidized (MAO) Mg substrates: initial (left) and with deposited calcium orthophosphate coatings (right). The line scanning of element distribution across the coatings is depicted. It is clearly seen that the MAO layer consists of magnesium silicates.

Reprinted from [Liu et al. \(2011b\)](#) with permission. Additional pictures of the element distributions across the coatings are available in [Hiromoto and Yamamoto \(2009\)](#) and [Pan et al. \(2013\)](#).

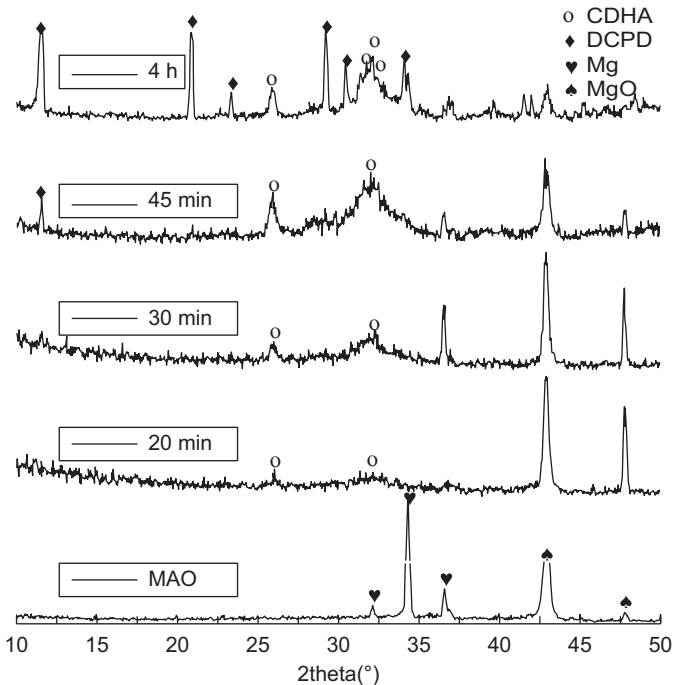


Figure 7.13 X-ray diffraction patterns of the calcium orthophosphate coatings formed on the surface of micro-arc oxidized (MAO) Mg substrates soaked in calcium orthophosphate-containing solutions. One can see that the initial surface of the MAO Mg covered by MgO (bottom pattern) was covered initially by CDHA (patterns at 20–45 min) and finally by a mixture of CDHA with DCPD (top pattern).

Reprinted from [Liu et al. \(2011a\)](#), with permission.

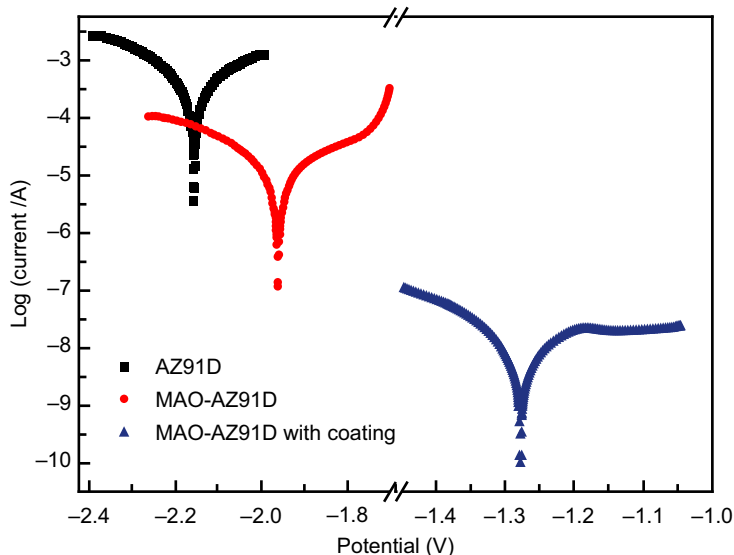


Figure 7.14 Tafel curves to measure the corrosion potential in SBF for bare AZ91D alloy, micro-arc oxidized AZ91D alloy (MAO-AZ91D), and MAO-AZ91D alloy covered by calcium orthophosphate coating. The more positive the value of the corrosion potential, the better corrosion resistance is.

Reprinted from [Zhang, Dai, et al. \(2012\)](#), with permission.

methods to construct biodegradable Mg-based metallic bone grafts, offering improved patient outcomes.

7.5 Conclusions

Due to their unique properties, the utilization of Mg and its biodegradable alloys as bone graft substitutes appears to be very promising. However, as identified in this chapter, for successful clinical applications, the corrosion of these metals must be slowed down. The development of nontoxic, biocompatible, and corrosion-resistant protective coatings seems to be the most promising route to solve the problem. Because the use of calcium orthophosphates is well established in the field of biomaterials, they appear to be excellent candidates to construct the required coatings on Mg and its biodegradable alloys. An additional advantage of using calcium orthophosphates as protective coatings is to provide the implants with surface biological properties for adsorption of proteins, adhesion of cells, and bone apposition. Therefore, the available knowledge on calcium orthophosphate coatings on Mg and its biodegradable alloys has been summarized in this review.

From the discussions in this chapter, the following conclusions can be made. Although the combination of calcium orthophosphates and Mg metal is a new area of research that has still to be thoroughly explored, the amount of available

publications on the topic clearly indicates that calcium orthophosphate coatings on Mg and its biodegradable alloys has rapidly become a common practice. However, in many cases, satisfactory results have not been achieved yet, typically due to an insufficient amount of studies performed. Namely, according to the available literature, calcium orthophosphate coatings, films, and layers might be deposited and/or created on various substrates by means of at least 22 different techniques; each of these techniques has both advantages and shortcomings of its own (Dorozhkin, 2012b). In addition, new deposition techniques are continuously being explored. However, as seen here, 12 deposition techniques have been tried to put calcium orthophosphates onto Mg and its biodegradable alloys; for five of these techniques, only one or two publications are available, which is not enough. Even less information is presently available on *in vivo* investigations. Therefore, although the development of appropriate techniques for covering Mg and its biodegradable alloys by calcium orthophosphate holds great potential for the development of novel biomaterials, currently available information on the subject appears to be insufficient to make serious conclusions.

References

- Abdal-hay, A., Barakat, N. A. M., & Lim, J. K. (2013). Hydroxyapatite-doped poly(lactic acid) porous film coating for enhanced bioactivity and corrosion behavior of AZ31 Mg alloy for orthopedic applications. *Ceramics International*, 39, 183–195.
- Amjad, Z. (Ed.). (1997). *Calcium phosphates in biological and industrial systems* (p. 529). Boston, MA: Kluwer.
- Anselme, K. (2000). Osteoblast adhesion on biomaterials. *Biomaterials*, 21, 667–681.
- Bigi, A., Falini, G., Foresti, E., Ripamonti, A., Gazzano, M., & Roveri, N. (1993). Magnesium influence on hydroxyapatite crystallization. *Journal of Inorganic Biochemistry*, 49, 69–78.
- Brown, P. W., & Constantz, B. (Eds.). (1994). *Hydroxyapatite and related materials* (p. 343). Boca Raton, FL: CRC Press.
- Chai, H., Guo, L., Wang, X., Gao, X., Liu, K., Fu, Y., et al. (2012). In vitro and in vivo evaluations on osteogenesis and biodegradability of a β -tricalcium phosphate coated magnesium alloy. *Journal of Biomedical Materials Research. Part A*, 100A, 293–304.
- Chen, X. B., Birbilis, N., & Abbott, T. B. (2011). A simple route towards a hydroxyapatite–Mg(OH)₂ conversion coating for magnesium. *Corrosion Science*, 53, 2263–2268.
- Chen, X. B., Birbilis, N., & Abbott, T. B. (2012). Effect of [Ca²⁺] and [PO₄³⁻] levels on the formation of calcium phosphate conversion coatings on die-cast magnesium alloy AZ91D. *Corrosion Science*, 55, 226–232.
- Chen, X. B., Kirkland, N. T., Krebs, H., Thiriat, M. A., Virtanen, S., Nisbet, D., et al. (2012). In vitro corrosion survey of Mg-xCa and Mg-3Zn-yCa alloys with and without calcium phosphate conversion coatings. *Corrosion Engineering, Science and Technology*, 47, 365–373.
- Choudhary, L., Raman, R. K. S., & Nie, J. F. (2012). In vitro evaluation of degradation of a calcium phosphate coating on a Mg-Zn-Ca alloy in a physiological environment. *Corrosion*, 68, 499–506.
- Chow, L. C., & Eanes, E. D. (Eds.). (2001). *Monographs in oral science: Vol. 18. Octacalcium phosphate* (p. 168). Basel, Switzerland: Karger.

- Cortés, D. A., López, H. Y., & Mantovani, D. (2007). Spontaneous and biomimetic apatite formation on pure magnesium. *Materials Science Forum*, 539–543, 589–594.
- Cui, F., Yang, J., Jiao, Y., Yin, Q., Zhang, Y., & Lee, I. (2008). Calcium phosphate coating on magnesium alloy for modification of degradation behavior. *Frontiers of Materials Science in China*, 2, 143–148.
- Cui, W., Beniash, E., Gawalt, E., Xu, Z., & Sfeir, C. (2013). Biomimetic coating of magnesium alloy for enhanced corrosion resistance and calcium phosphate deposition. *Acta Biomaterialia*, 9, 8650–8659.
- Czerwinski, F. (Ed.). (2011). *Magnesium alloys – Corrosion and surface treatments* (p. 344). Rijeka, Croatia: InTech.
- Davies, J. E. (1996). In vitro modeling of the bone/implant interface. *The Anatomical Record*, 245, 426–445.
- Davy, H. (1808a). The Bakerian lecture: on some new phenomena of chemical changes produced by electricity, particularly the decomposition of the fixed alkalies, and the exhibition of the new substances which constitute their bases; and on the general nature of alkaline bodies. *Philosophical Transactions of the Royal Society of London*, 98, 1–44.
- Davy, H. (1808b). Electro-chemical researches on the decomposition of the earths; with observations on the metals obtained from the alkaline earths, and on the amalgam procured from ammonia. *Philosophical Transactions of the Royal Society of London*, 98, 333–370.
- Dorozhkin, S. V. (2011a). Biocomposites and hybrid biomaterials based on calcium orthophosphates. *Biomatter*, 1, 3–56.
- Dorozhkin, S. V. (2011b). Calcium orthophosphates: occurrence, properties, biomineralization, pathological calcification and biomimetic applications. *Biomatter*, 1, 121–164.
- Dorozhkin, S. V. (2012a). Calcium orthophosphates and human beings. A historical perspective from the 1770s until 1940. *Biomatter*, 2, 53–70.
- Dorozhkin, S. V. (2012b). Calcium orthophosphate coatings, films and layers. *Progress in Biomaterials*, 1, 1–40.
- Dorozhkin, S. V. (2012c). *Calcium orthophosphates: Applications in nature, biology, and medicine*. Singapore: Pan Stanford.
- Dorozhkin, S. V. (2013). A detailed history of calcium orthophosphates from 1770s till 1950. *Materials Science and Engineering: C*, 33, 3085–3110.
- Du, H., Wei, Z., Wang, H., Zhang, E., Zuo, L., & Du, L. (2011). Surface microstructure and cell compatibility of calcium silicate and calcium phosphate composite coatings on Mg–Zn–Mn–Ca alloys for biomedical application. *Colloids and Surfaces. B, Bio-interfaces*, 83, 96–102.
- Elliot, J. C. (1994). Structure and chemistry of the apatites and other calcium orthophosphates. In *Studies in inorganic chemistry* (Vol. 18, p. 389). Amsterdam, Netherlands: Elsevier.
- Fathi, M. H., Meratian, M., & Razavi, M. (2011). Novel magnesium-nanofluorapatite metal matrix nanocomposite with improved biodegradation behavior. *Journal of Biomedical Nanotechnology*, 7, 441–445.
- Feil, F., Frbeth, W., & Schtze, M. (2009). Purely inorganic coatings based on nanoparticles for magnesium alloys. *Electrochimica Acta*, 54, 2478–2486.
- Galio, A., Lamaka, S., Zheludkevich, M., Dick, L., Mller, I., & Ferreira, M. (2010). Inhibitor-doped sol-gel coatings for corrosion protection of magnesium alloy AZ31. *Surface and Coatings Technology*, 204, 1479–1486.
- Gan, J., Tan, L., Yang, K., Hu, Z., Zhang, Q., Fan, X., et al. (2013). Bioactive Ca–P coating with self-sealing structure on pure magnesium. *Journal of Materials Science: Materials in Medicine*, 24, 889–901.

- Gao, J. H., Guan, S. K., Chen, J., Wang, L. G., Zhu, S. J., Hu, J. H., et al. (2011). Fabrication and characterization of rod-like nano-hydroxyapatite on MAO coating supported on Mg–Zn–Ca alloy. *Applied Surface Science*, 257, 2231–2237.
- Geng, F., Tan, L. L., Jin, X. X., Yang, J. Y., & Yang, K. (2009). The preparation, cytocompatibility, and in vitro biodegradation study of pure β -TCP on magnesium. *Journal of Materials Science: Materials in Medicine*, 20, 1149–1157.
- Gray, J., & Luan, B. (2002). Protective coatings on magnesium and its alloys – a critical review. *Journal of Alloys and Compounds*, 336, 88–113.
- Grubač, Z., Metikoš-Huković, M., & Babić, R. (2013). Electrocrystallization, growth and characterization of calciumphosphate ceramics on magnesium alloys. *Electrochimica Acta*, 109, 694–700.
- Gu, X. N., Li, N., Zhou, W. R., Zheng, Y. F., Zhao, X., Cai, Q. Z., et al. (2011). Corrosion resistance and surface biocompatibility of a microarc oxidation coating on a Mg–Ca alloy. *Acta Biomaterialia*, 7, 1880–1889.
- Guan, R. G., Johnson, I., Cui, T., Zhao, T., Zhao, Z. Y., Li, X., et al. (2012). Electrodeposition of hydroxyapatite coating on Mg–4.0Zn–1.0Ca–0.6Zr alloy and in vitro evaluation of degradation, hemolysis, and cytotoxicity. *Journal of Biomedical Materials Research Part A*, 100A, 999–1015.
- Guan, Y. C., Zhou, W., & Zheng, H. Y. (2009). Effect of laser surface melting on corrosion behaviour of AZ91D Mg alloy in simulated-modified body fluid. *Journal of Applied Electrochemistry*, 39, 1457–1464.
- Habibovic, P., Barrere, F., Blitterswijk, C., Groot, K., & Layrolle, P. (2002). Biomimetic hydroxyapatite coating on metal implants. *Journal of the American Ceramic Society*, 85, 517–522.
- Hahn, B. D., Park, D. S., Choi, J. J., Ryu, J., Yoon, W. H., Choi, J. H., et al. (2011). Aerosol deposition of hydroxyapatite–chitosan composite coatings on biodegradable magnesium alloy. *Surface and Coatings Technology*, 205, 3112–3118.
- Hamed, E., Jasiuk, I., Yoo, A., Lee, Y., & Liszka, T. (2012). Multi-scale modelling of elastic moduli of trabecular bone. *Journal of the Royal Society Interface*, 9, 1654–1673.
- Hamed, E., Novitskaya, E., Li, J., Chen, P. Y., Jasiuk, I., & McKittrick, J. (2012). Elastic moduli of untreated, demineralized and deproteinized cortical bone: validation of a theoretical model of bone as an interpenetrating composite material. *Acta Biomaterialia*, 8, 1080–1092.
- Hanawa, T. (1999). In vivo metallic biomaterials and surface modification. *Materials Science and Engineering: A*, 267, 260–266.
- Haynes, W. M. (Ed.). (2013). *CRC handbook of chemistry and physics* (94th ed., p. 2668). Boca Raton, FL: CRC Press.
- Hench, L. L. (1998). Bioceramics. *Journal of the American Ceramic Society*, 81, 1705–1728.
- Hiromoto, S. (2012). Corrosion of calcium phosphate coated AZ31 magnesium alloy under a salt spray test. *Materials Transactions*, 53, 700–706.
- Hiromoto, S., Shishido, T., Yamamoto, A., Maruyama, N., Somekawa, H., & Mukai, T. (2008). Precipitation control of calcium phosphate on pure magnesium by anodization. *Corrosion Science*, 50, 2906–2913.
- Hiromoto, S., & Tomozawa, M. (2010). Corrosion behavior of magnesium with hydroxyapatite coatings formed by hydrothermal treatment. *Materials Transactions*, 51, 2080–2087.
- Hiromoto, S., & Tomozawa, M. (2011). Hydroxyapatite coating of AZ31 magnesium alloy by a solution treatment and its corrosion behavior in NaCl solution. *Surface and Coatings Technology*, 205, 4711–4719.

- Hiromoto, S., Tomozawa, M., & Maruyama, N. (2013). Fatigue property of a bioabsorbable magnesium alloy with a hydroxyapatite coating formed by a chemical solution deposition. *Journal of the Mechanical Behavior of Biomedical Materials*, 25, 1–10.
- Hiromoto, S., & Yamamoto, A. (2009). High corrosion resistance of magnesium coated with hydroxyapatite directly synthesized in an aqueous solution. *Electrochimica Acta*, 54, 7085–7093.
- Hoog, O. C., Birbilis, N., Zhang, M. Z., & Estrin, Y. (2008). Surface grain size effects on the corrosion of magnesium. *Key Engineering Materials*, 384, 229–240.
- Hort, N., Huang, Y., Fechner, D., Störmer, M., Blawert, C., Witte, F., et al. (2010). Magnesium alloys as implant materials – principles of property design for Mg-RE alloys. *Acta Biomaterialia*, 6, 1714–1725.
- Hu, J., Li, Q., Zhong, X., Zhang, L., & Chen, B. (2009). Composite anticorrosion coatings for AZ91D magnesium alloy with molybdate conversion coating and silicon sol-gel coatings. *Progress in Organic Coatings*, 66, 199–205.
- Hu, J., Wang, C., Ren, W., Zhang, S., & Liu, F. (2010). Microstructure evolution and corrosion mechanism of dicalcium phosphate dihydrate coating on magnesium alloy in simulated body fluid. *Materials Chemistry and Physics*, 119, 294–298.
- Huse, E. C. (1878). A new ligature? *Chicago Medical Journal and Examiner*, 37, 171–172.
- Iskandar, M. E., Aslani, A., & Liu, H. (2013). The effects of nanostructured hydroxyapatite coating on the biodegradation and cytocompatibility of magnesium implants. *Journal of Biomedical Materials Research Part A*, 101A, 2340–2354.
- Jacobs, J. J., Gilbert, J. L., & Urban, R. M. (1998). Corrosion of metal orthopaedic implants. *Journal of Bone and Joint Surgery*, 80, 268–282.
- Jamsh, M., Kumar, S., & Narayanan, T. S. N. S. (2012). Electrodeposition of hydroxyapatite coating on magnesium for biomedical applications. *Journal of Coatings Technology and Research*, 9, 495–502.
- Jo, J. H., Kang, B. G., Shin, K. S., Kim, H. E., Hahn, B. D., Park, D. S., et al. (2011). Hydroxyapatite coating on magnesium with MgF₂ interlayer for enhanced corrosion resistance and biocompatibility. *Journal of Materials Science: Materials in Medicine*, 22, 2437–2447.
- Jo, J. H., Li, Y., Kim, S. M., Kim, H. E., & Koh, Y. H. (2013). Hydroxyapatite/poly(ϵ -caprolactone) double coating on magnesium for enhanced corrosion resistance and coating flexibility. *Journal of Biomaterials Applications*, 28, 617–625.
- Johnson, I., Akari, K., & Liu, H. (2013). Nanostructured hydroxyapatite/poly(lactic-co-glycolic acid) composite coating for controlling magnesium degradation in simulated body fluid. *Nanotechnology*, 24, art. no. 375103.
- Kammer, C. (2000). *Magnesium Taschenbuch*. Düsseldorf, Germany: Alu Media Verlag.
- Kang, M. H., Jung, H. D., Kim, S. W., Lee, S. M., Kim, H. E., Estrin, Y., et al. (2013). Production and bio-corrosion resistance of porous magnesium with hydroxyapatite coating for biomedical applications. *Materials Letters*, 108, 122–124.
- Kannan, M. B. (2012). Enhancing the performance of calcium phosphate coating on a magnesium alloy for bioimplant applications. *Materials Letters*, 76, 109–112.
- Kannan, M. B. (2013). Improving the packing density of calcium phosphate coating on a magnesium alloy for enhanced degradation resistance. *Journal of Biomedical Materials Research Part A*, 101A, 1248–1254.
- Kannan, M. B., & Orr, L. (2011). In vitro mechanical integrity of hydroxyapatite coated magnesium alloy. *Biomedical Materials*, 6, 045003 (p. 11).

- Keim, S., Brunner, J., Fabry, B., & Virtanen, S. (2011). Control of magnesium corrosion and biocompatibility with biomimetic coatings. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, 96B, 84–90.
- Kim, S. M., Jo, J. H., Lee, S. M., Kang, M. H., Kim, H. E., Estrin, Y., et al. (2014). Hydroxyapatite-coated magnesium implants with improved in vitro and in vivo biocorrosion, biocompatibility, and bone response. *Journal of Biomedical Materials Research Part A*, 102A, 429–441.
- Kraus, T., Fischerauer, S. F., Hanzi, A. C., Uggowitzer, P. J., Löffler, J. F., & Weinberg, A. M. (2012). Magnesium alloys for temporary implants in osteosynthesis: in vivo studies of their degradation and interaction with bone. *Acta Biomaterialia*, 8, 1230–1238.
- Kuwahara, H., Al-Abdullat, Y., Ohta, M., Tsutsumi, S., Ikeuchi, K., Mazaki, N., et al. (2000). Surface reaction of magnesium in Hank's solution. *Materials Science Forum*, 350, 349–358.
- Lalk, M., Reifenrath, J., Angrisani, N., Bondarenko, A., Seitz, J. M., Mueller, P. P., et al. (2013). Fluoride and calcium-phosphate coated sponges of the magnesium alloy AX30 as bone grafts: a comparative study in rabbits. *Journal of Materials Science: Materials in Medicine*, 24, 417–436.
- Lamaka, S., Montemor, M., Galio, A., Zheludkevich, M., Trindade, C., Dick, L., et al. (2008). Novel hybrid sol-gel coatings for corrosion protection of AZ31B magnesium alloy. *Electrochimica Acta*, 53, 4773–4783.
- LeGeros, R. Z. (1991). Calcium phosphates in oral biology and medicine. In *Monographs in oral science* (Vol. 15, p. 201). Basel, Switzerland: Karger.
- Lhotka, C., Szekeres, T., Steffan, I., Zhuber, K., & Zweymüller, K. (2003). Four-year study of cobalt and chromium blood levels in patients managed with two different metal-on-metal total hip replacements. *Journal of Orthopaedic Research*, 21, 189–195.
- Li, J., Song, Y., Zhang, S., Zhao, C., Zhang, F., Zhang, X., et al. (2010). In vitro responses of human bone marrow stromal cells to a fluoridated hydroxyapatite coated biodegradable Mg–Zn alloy. *Biomaterials*, 31, 5782–5788.
- Li, K. K., Wang, B., Yan, B., & Lu, W. (2012a). Microstructure, in vitro corrosion and cytotoxicity of Ca–P coatings on ZK60 magnesium alloy prepared by simple chemical conversion and heat treatment. *Journal of Biomaterials Applications*, 28, 375–384.
- Li, K. K., Wang, B., Yan, B., & Lu, W. (2012b). Preparing Ca–P coating on biodegradable magnesium alloy by hydrothermal method: in vitro degradation behavior. *Chinese Science Bulletin*, 57, 2319–2322.
- Liang, J., Srinivasan, P. B., Blawert, C., & Dietzel, W. (2010). Influence of pH on the deterioration of plasma electrolytic oxidation coated AM50 magnesium alloy in NaCl solutions. *Corrosion Science*, 52, 540–547.
- Liu, Y., de Groot, K., & Hunziker, E. (2009). Biomimetic mineral coatings in dental and orthopaedic implantology. *Frontiers of Materials Science in China*, 3, 154–162.
- Liu, G. Y., Hu, J., Ding, Z. K., & Wang, C. (2011a). Formation mechanism of calcium phosphate coating on micro-arc oxidized magnesium. *Materials Chemistry and Physics*, 130, 1118–1124.
- Liu, G. Y., Hu, J., Ding, Z. K., & Wang, C. (2011b). Bioactive calcium phosphate coating formed on micro-arc oxidized magnesium by chemical deposition. *Applied Surface Science*, 257, 2051–2057.
- Liu, G., Tang, S., Li, D., & Hu, J. (2014). Self-adjustment of calcium phosphate coating on micro-arc oxidized magnesium and its influence on the corrosion behaviour in simulated body fluids. *Corrosion Science*, 79, 206–214.

- Liu, G. Y., Tang, S. W., Wang, C., Hu, J., & Li, D. C. (2013). Formation characteristic of Ca–P coatings on magnesium alloy surface. *Transactions of Nonferrous Metals Society of China*, 23, 2294–2299.
- Lorenz, C., Brunner, J. G., Kollmannsberger, P., Jaafar, L., Fabry, B., & Virtanen, S. (2009). Effect of surface pre-treatments on biocompatibility of magnesium. *Acta Biomaterialia*, 5, 2783–2789.
- Lowenstam, H. A., & Weiner, S. (1989). *On biomineralization* (p. 324). New York, NY: Oxford University Press.
- Lu, W., Ou, C., Zhan, Z., Huang, P., Yan, B., & Chen, M. (2013). Microstructure and in vitro corrosion properties of ZK60 magnesium alloy coated with calcium phosphate by electrodeposition at different temperatures. *International Journal of Electrochemical Science*, 8, 10746–10757.
- Ma, C., Zhang, X., Qu, L., & Li, M. (2010). Calcium and phosphate biocoatings on magnesium alloy fabricated by micro-arc oxidation. *Advanced Materials Research*, 105–106, 565–568.
- Majumdar, J. D., Bhattacharyya, U., Biswas, A., & Manna, I. (2008). Studies on thermal oxidation of Mg-alloy (AZ91) for improving corrosion and wear resistance. *Surface and Coatings Technology*, 202, 3638–3642.
- Meng, E. C., Guan, S. K., Wang, H. X., Wang, L. G., Zhu, S. J., Hu, J. H., et al. (2011). Effect of electrodeposition modes on surface characteristics and corrosion properties of fluorine-doped hydroxyapatite coatings on Mg–Zn–Ca alloy. *Applied Surface Science*, 257, 4811–4816.
- Mensah-Darkwa, K., Gupta, R. K., & Kumar, D. (2013). Mechanical and corrosion properties of magnesium-hydroxyapatite (Mg-HA) composite thin films. *Journal of Materials and Science and Technology*, 29, 788–794.
- Metikoš-Huković, M., Babić, R., Grubač, Z., Petravić, M., & Peter, R. (2013). Potential assisted formation and characterization of hydroxyapatite coatings on biodegradable magnesium alloys. *Journal of Electrochemical Society*, 160, H674–H680.
- Mordike, B., & Ebert, T. (2001). Magnesium properties – applications – potential. *Materials Science and Engineering: A*, 302, 37–45.
- Mueller, W. D., Nascimento, M. L., & de Mele, M. F. L. (2010). Critical discussion of the results from different corrosion studies of Mg and Mg alloys for biomaterial applications. *Acta Biomaterialia*, 6, 1749–1755.
- Gray-Munro, J. E., Seguin, C., & Strong, M. (2009). Influence of surface modification on the in vitro corrosion rate of magnesium alloy AZ31. *Journal of Biomedical Materials Research Part A*, 91A, 221–230.
- Gray-Munro, J. E., & Strong, M. (2009). The mechanism of deposition of calcium phosphate coatings from solution onto magnesium alloy AZ31. *Journal of Biomedical Materials Research Part A*, 90A, 339–350.
- Nagels, J., Stokdijk, M., & Rozing, P. M. (2003). Stress shielding and bone resorption in shoulder arthroplasty. *Journal of Shoulder and Elbow Surgery*, 12, 35–39.
- Nassif, N., & Ghayad, I. (2013). Corrosion protection and surface treatment of magnesium alloys used for orthopedic applications. *Advances in Materials Science and Engineering*, 2013, 10, 532896.
- Niinomi, M. (2002). Recent metallic materials for biomedical applications. *Metallurgical and Materials Transactions A*, 33, 477–486.
- Niinomi, M. (2010). In *Metals for biomedical devices* (p. 432). Boca Raton, FL: CRC Press.

- Noorakma, A. C. W., Zuhailawati, H., Aishvarya, V., & Dhindaw, B. K. (2013). Hydroxyapatite-coated magnesium-based biodegradable alloy: cold spray deposition and simulated body fluid studies. *Journal of Materials Engineering and Performance*, 22, 2997–3004.
- Ohtsu, N., Hiromoto, S., Yamane, M., Satoh, K., & Tomozawa, M. (2013). Chemical and crystallographic characterizations of hydroxyapatite- and octacalcium phosphate-coatings on magnesium synthesized by chemical solution deposition using XPS and XRD. *Surface and Coatings Technology*, 218, 114–118.
- Ong, J. L., & Chan, D. C. N. (1999). Hydroxyapatite and their use as coatings in dental implants: a review. *Critical Reviews in Biomedical Engineering*, 28, 667–707.
- Onoki, T., & Yamamoto, S. Y. (2010). Hydroxyapatite ceramics coating on magnesium alloy via a double layered capsule hydrothermal hot-pressing. *Journal of the Ceramic Society of Japan*, 118, 749–752.
- Pan, Y. K., Chen, C. Z., Wang, D. G., & Zhao, T. G. (2013). Effects of phosphates on microstructure and bioactivity of micro-arc oxidized calcium phosphate coatings on Mg–Zn–Zr magnesium alloy. *Colloids and Surfaces B: Biointerfaces*, 109, 1–9.
- Qu, H., & Wei, M. (2008). Improvement of bonding strength between biomimetic apatite coating and substrate. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, 84B, 436–443.
- Razavi, M., Fathi, M. H., & Meratian, M. (2010). Microstructure, mechanical properties and bio-corrosion evaluation of biodegradable AZ91-FA nanocomposites for biomedical applications. *Materials Science and Engineering A*, 527, 6938–6944.
- Ren, M., Cai, S., Xu, G., Ye, X., Dou, Y., Huang, K., et al. (2013). Influence of heat treatment on crystallization and corrosion behavior of calcium phosphate glass coated AZ31 magnesium alloy by sol-gel method. *Journal of Non-Crystalline Solids*, 369, 69–75.
- Rettig, R., & Virtanen, S. (2008). Time-dependent electrochemical characterization of the corrosion of a magnesium rare-earth alloy in simulated body fluids. *Journal of Biomedical Materials Research Part A*, 85A, 167–175.
- Rettig, R., & Virtanen, S. (2009). Composition of corrosion layers on a magnesium rare-earth alloy in simulated body fluids. *Journal of Biomedical Materials Research Part A*, 88A, 359–369.
- Roach, P., Eglin, D., Rohde, K., & Perry, C. C. (2007). Modern biomaterials: a review – bulk properties and implications of surface modifications. *Journal of Materials Science: Materials in Medicine*, 18, 1263–1277.
- Robinson, D. A., Griffith, R. W., Shechtman, D., Evans, R. B., & Conzemius, M. G. (2010). In vitro antibacterial properties of magnesium metal against *Escherichia coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*. *Acta Biomaterialia*, 6, 1869–1877.
- Rojacee, R., Fathi, M., & Raeissi, K. (2013a). Electrophoretic deposition of nanostructured hydroxyapatite coating on AZ91 magnesium alloy implants with different surface treatments. *Applied Surface Science*, 285, 664–673.
- Rojacee, R., Fathi, M., & Raeissi, K. (2013b). Controlling the degradation rate of AZ91 magnesium alloy via sol–gel derived nanostructured hydroxyapatite coating. *Materials Science and Engineering: C*, 33, 3817–3825.
- Roy, A., Singh, S. S., Datta, M. K., Lee, B., Ohodnicki, J., & Kumta, P. N. (2011). Novel sol-gel derived calcium phosphate coatings on Mg4Y alloy. *Materials Science and Engineering: B*, 176, 1679–1689.
- Salman, S. A., Kuroda, K., & Okido, M. (2013). Preparation and characterization of hydroxyapatite coating on AZ31 Mg alloy for implant applications. *Bioinorganic Chemistry and Applications*, 2013, 6. 175756.

- Santhanakrishnan, S., Ho, Y. H., & Dahotre, N. B. (2012). Laser coating of hydroxyapatite on Mg for enhanced physiological corrosion resistance and biodegradability. *Materials Technology*, 27, 273–277.
- Sen, D. A., & Jun, D. A. (1798). Annals of medicine, for the year 1797. In *Exhibiting a concise view of the latest and most important discoveries in medicine and medical philosophy* (Vol. 2). Edinburgh: printed for Mudie, G. & son, South bridge; and for G. G. & J. Robinson, London. pp. 397–398.
- Shadanbaz, S., & Dias, G. J. (2012). Calcium phosphate coatings on magnesium alloys for biomedical applications: a review. *Acta Biomaterialia*, 8, 20–30.
- Shi, P., Ng, W. F., Wong, M. H., & Cheng, F. T. (2009). Improvement of corrosion resistance of pure magnesium in Hanks' solution by microarc oxidation with sol-gel TiO₂ sealing. *Journal of Alloys and Compounds*, 469, 286–292.
- Shi, Y., Qi, M., Chen, Y., & Shi, P. (2011). MAO–DCPD composite coating on Mg alloy for degradable implant applications. *Materials Letters*, 65, 2201–2204.
- Smith, M. R., Atkinson, P., White, D., Piersma, T., Gutierrez, G., Rossini, G., et al. (2012). Design and assessment of a wrapped cylindrical Ca-P AZ31 Mg alloy for critical-size ulna defect repair. *Journal of Biomedical Materials Research Part B*, 100B, 206–216.
- Song, G. L. (2007). Control of biodegradation of biocompatible magnesium alloys. *Corrosion Science*, 49, 1696–1701.
- Song, G. L. (Ed.). (2011). *Corrosion of magnesium alloys* (p. 480). Cambridge, UK: Woodhead Publishing.
- Song, G. L. (Ed.). (2013). *Corrosion prevention of magnesium alloys* (p. 592). Cambridge, UK: Woodhead Publishing.
- Song, G. L., & Atrous, A. (2003). Understanding magnesium corrosion. A framework for improved alloy performance. *Advanced Engineering Materials*, 5, 837–858.
- Song, Y., Shan, D., & Han, E. (2008). Electrodeposition of hydroxyapatite coating on AZ91D magnesium alloy for biomaterial application. *Materials Letters*, 62, 3276–3279.
- Song, Y., Shan, D., & Han, E. H. (2013). A novel biodegradable nicotinic acid/calcium phosphate composite coating on Mg–3Zn alloy. *Materials Science and Engineering: C*, 33, 78–84.
- Song, Y., Zhang, S., Li, J., Zhao, C., & Zhang, X. (2010). Electrodeposition of Ca–P coatings on biodegradable Mg alloy: in vitro biomineralization behavior. *Acta Biomaterialia*, 6, 1736–1742.
- Sreekanth, D., & Rameshbabu, N. (2012). Development and characterization of MgO/hydroxyapatite composite coating on AZ31 magnesium alloy by plasma electrolytic oxidation coupled with electrophoretic deposition. *Materials Letters*, 68, 439–442.
- Srinivasan, P., Liang, J., Blawert, C., Stormer, M., & Dietzel, W. (2010). Characterization of calcium containing plasma electrolytic oxidation coatings on AM50 magnesium alloy. *Applied Surface Science*, 256, 4017–4022.
- Staiger, M. P., Pietak, A. M., Huadmai, J., & Dias, G. (2006). Magnesium and its alloys as orthopedic biomaterials: a review. *Biomaterials*, 27, 1728–1734.
- Su, Y., Li, G., & Lian, J. (2012). A chemical conversion hydroxyapatite coating on AZ60 magnesium alloy and its electrochemical corrosion behavior. *International Journal of Electrochemical Science*, 7, 11497–11511.
- Suchanek, W., & Yoshimura, M. (1998). Processing and properties of hydroxyapatite-based biomaterials for use as hard tissue replacement implants. *Journal of Materials Research*, 13, 94–117.
- Tan, A., Soutar, A., Annergren, I., & Liu, Y. (2005). Multilayer sol-gel coatings for corrosion protection of magnesium. *Surface and Coatings Technology*, 198, 478–482.

- Tang, H., Xin, T. Z., Luo, Y., & Wang, F. P. (2013). In vitro degradation of AZ31 magnesium alloy coated with hydroxyapatite by sol-gel method. *Materials Science and Technology*, 29, 547–552.
- Tang, H., Xin, T. Z., & Wang, F. (2013). Calcium phosphate/titania sol-gel coatings on AZ31 magnesium alloy for biomedical applications. *International Journal of Electrochemical Science*, 8, 8115–8125.
- Tomozawa, M., & Hiromoto, S. (2011a). Growth mechanism of hydroxyapatite-coatings formed on pure magnesium and corrosion behavior of the coated magnesium. *Applied Surface Science*, 257, 8253–8257.
- Tomozawa, M., & Hiromoto, S. (2011b). Microstructure, corrosion resistance and adhesive strength of calcium phosphate coatings formed on pure magnesium by a simple immersion method. *ESC Transactions*, 33, 31–37.
- Tomozawa, M., & Hiromoto, S. (2011c). Microstructure of hydroxyapatite- and octacalcium phosphate-coatings formed on magnesium by a hydrothermal treatment at various pH values. *Acta Materialia*, 59, 355–363.
- Tomozawa, M., Hiromoto, S., & Harada, Y. (2010). Microstructure of hydroxyapatite-coated magnesium prepared in aqueous solution. *Surface and Coatings Technology*, 204, 3243–3247.
- Touyz, R. M. (2004). Magnesium in clinical medicine. *Frontiers in Bioscience*, 9, 1278–1293.
- Virtanen, S. (2011). Biodegradable Mg and Mg alloys: corrosion and biocompatibility. *Materials Science and Engineering: B*, 176, 1600–1608.
- Vormann, J. (2003). Magnesium: nutrition and metabolism. *Molecular Aspects of Medicine*, 24, 27–37.
- Wang, H., Estrin, Y., & Zúberová, Z. (2008). Bio-corrosion of a magnesium alloy with different processing histories. *Materials Letters*, 62, 2476–2479.
- Wang, H., Guan, S., Wang, Y., Liu, H., Wang, H., Wang, L., et al. (2011). In vivo degradation behavior of Ca-deficient hydroxyapatite coated Mg–Zn–Ca alloy for bone implant application. *Colloids and Surfaces B*, 88, 254–259.
- Wang, H., Guan, S., Wang, X., Ren, C., & Wang, L. (2010). In vitro degradation and mechanical integrity of Mg–Zn–Ca alloy coated with Ca-deficient hydroxyapatite by the pulse electrodeposition process. *Acta Biomaterialia*, 6, 1743–1748.
- Wang, J., Tang, J., Zhang, P., Li, Y., Wang, J., Lai, Y., et al. (2012). Surface modification of magnesium alloys developed for bioabsorbable orthopedic implants: a general review. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, 100B, 1691–1701.
- Wang, Q., Tan, L., Xu, W., Zhang, B., & Yang, K. (2011). Dynamic behaviors of a Ca–P coated AZ31B magnesium alloy during in vitro and in vivo degradations. *Materials Science and Engineering: B*, 176, 1718–1726.
- Wang, X., Cai, S., Liu, T., Ren, M., Huang, K., Zhang, R., et al. (2014). Fabrication and corrosion resistance of calcium phosphate glass-ceramic coated Mg alloy via a PEG assisted sol–gel method. *Ceramics International*, 40, 3389–3398.
- Wang, Y., Gao, J. C., Zhang, Y., Zhou, X. F., & Wu, S. (2007). Effect of dicalcium phosphate dihydrate (DCPD) coating on the corrosion behavior of pure magnesium in simulated body solution. *Gongneng Cailiao/Journal of Functional Materials*, 38, 1884–1886.
- Wang, Y. M., Wang, F. H., Xu, M. J., Zhao, B., Guo, L. X., & Ouyang, J. H. (2009). Microstructure and corrosion behavior of coated AZ91 alloy by microarc oxidation for biomedical application. *Applied Surface Science*, 255, 9124–9131.

- Wang, Y. M., Wei, M., & Gao, J. (2009). Improve corrosion resistance of magnesium in simulated body fluid by dicalcium phosphate dihydrate coating. *Materials Science and Engineering: C*, 29, 1311–1316.
- Wang, Z. L., Yan, Y. H., Wan, T., & Yang, H. (2013). Poly(L-lactic acid)/hydroxyapatite/collagen composite coatings on AZ31 magnesium alloy for biomedical application. *Proceedings of the Institution of Mechanical Engineers, Part H*, 227, 1094–1103.
- Waterman, J., Birbilis, N., Dias, G. J., Woodfield, T. B. F., & Staiger, M. P. (2012). Improving in vitro corrosion resistance of biomimetic calcium phosphate coatings for Mg substrates using calcium hydroxide layer. *Corrosion Engineering Science and Technology*, 47, 340–345.
- Waterman, J., Pietak, A., Birbilis, N., Woodfield, T., Dias, G., & Staiger, M. P. (2011). Corrosion resistance of biomimetic calcium phosphate coatings on magnesium due to varying pretreatment time. *Materials Science and Engineering: B*, 176, 1756–1760.
- Weiner, S., & Wagner, H. D. (1998). The material bone: structure-mechanical function relations. *Annual Review of Materials Science*, 28, 271–298.
- Wen, C., Guan, S., Peng, L., Ren, C., Wang, X., & Hu, Z. (2009). Characterization and degradation behavior of AZ31 alloy surface modified by bone-like hydroxyapatite for implant applications. *Applied Surface Science*, 255, 6433–6438.
- Witte, F., Feyerabend, F., Maier, P., Fischer, J., Störmer, M., Blawert, C., et al. (2007). Biodegradable magnesium-hydroxyapatite metal matrix composites. *Biomaterials*, 28, 2163–2174.
- Witte, F., Fischer, J., Nellesen, J., Crostack, H. A., Kaese, V., Pisch, A., et al. (2006). In vitro and in vivo corrosion measurements of magnesium alloys. *Biomaterials*, 27, 1013–1018.
- Witte, F., Hort, N., Vogt, C., Cohen, S., Kainer, K. U., Willumeit, R., et al. (2008). Degradable biomaterials based on magnesium corrosion. *Current Opinion in Solid State & Materials Science*, 12, 63–72.
- Witte, F., Kaese, V., Haferkamp, H., Switzer, E., Meyer-Lindenberg, A., Wirth, C. J., et al. (2005). In vivo corrosion of four magnesium alloys and the associated bone response. *Biomaterials*, 26, 3557–3563.
- Witte, F., Ulrich, H., Rudert, M., & Willbold, E. (2007). Biodegradable magnesium scaffolds: appropriate inflammatory response. *Journal of Biomedical Materials Research Part A*, 81A, 748–756.
- Wu, C., Wen, Z., Dai, C., Lu, Y., & Yang, F. (2010). Fabrication of calcium phosphate/chitosan coatings on AZ91D magnesium alloy with a novel method. *Surf Coat Technol*, 204, 3336–3347.
- Xiao, X., Yu, H., Zhu, Q., Li, G., Qu, Y., & Gu, R. (2013). In vivo corrosion resistance of Ca–P coating on AZ60 magnesium alloy. *Journal of Bionic Engineering*, 10, 156–161.
- Xiao, X., Zhu, Q. S., Su, Y. C., & Li, G. Y. (2013). In vitro degradation and biocompatibility of Ca–P coated magnesium alloy. *Chemical Research in Chinese Universities*, 29, 285–289.
- Xin, R., Wang, M., Gao, J., Liu, P., & Liu, Q. (2009). Effect of microstructure and texture on corrosion resistance of magnesium alloys. *Materials Science Forum*, 610–613, 1160–1163.
- Xin, Y., Hu, T., & Chu, P. K. (2010). Influence of test solutions on in vitro studies of biomedical magnesium alloys. *Journal of Electrochemical Society*, 157, C238–C243.
- Xin, Y., Hu, T., & Chu, P. K. (2011). In vitro studies of biomedical magnesium alloys in a simulated physiological environment: a review. *Acta Biomaterialia*, 7, 1452–1459.
- Xu, C. Y., Xu, X. L., Gao, F., Chu, F. X., Wang, Q., & Guo, Q. N. (2013). The crystal orientation of hydroxyapatite coatings affected by the magnetic fields on magnesium alloy. *Applied Mechanics and Materials*, 395–396, 751–754.

- Xu, L., Pan, F., Yu, G., Yang, L., Zhang, E., & Yang, K. (2009). In vitro and in vivo evaluation of the surface bioactivity of a calcium phosphate coated magnesium alloy. *Biomaterials*, 30, 1512–1523.
- Xu, L. P., Zhang, E., & Yang, K. (2009). Phosphating treatment and corrosion properties of Mg–Mn–Zn alloy for biomedical application. *Journal of Materials Science: Materials in Medicine*, 20, 859–867.
- Xu, L. P., Zhang, E. L., & Yang, K. (2012). Biocorrosion property and cytocompatibility of calcium phosphate coated Mg alloy. *Transactions of Nonferrous Metals Society of China*, 22, 2014–2020.
- Xue, D., Yun, Y., Schulz, M. J., & Shanov, V. (2011). Corrosion protection of biodegradable magnesium implants using anodization. *Materials Science and Engineering: C*, 31, 215–223.
- Yang, J. X., Cui, F. Z., Lee, I. S., Zhang, Y., Yin, Q. S., Xia, H., et al. (2011). In vivo biocompatibility and degradation behavior of Mg alloy coated by calcium phosphate in a rabbit model. *Journal of Biomaterials Applications*, 27, 153–164.
- Yang, J. X., Cui, F. Z., Yin, Q., Zhang, Y., Zhang, T., & Wang, X. (2009). Characterization and degradation study of calcium phosphate coating on magnesium alloy bone implant. *IEEE Transactions on Plasma Science*, 37, 1161–1168.
- Yang, J. X., Jiao, Y. P., Cui, F. Z., Lee, I. S., Yin, Q. S., & Zhang, Y. (2008). Modification of degradation behavior of magnesium alloy by IBAD coating of calcium phosphate. *Surface and Coatings Technology*, 202, 5733–5736.
- Yang, J. X., Jiao, Y. P., Yin, Q. S., Zhang, Y., & Zhang, T. (2008). Calcium phosphate coating on magnesium alloy by biomimetic method: Investigation of morphology, composition and formation process. *Frontiers of Materials Science in China*, 2, 149–155.
- Yang, K., & Tan, L. (2013). Control of biodegradation of magnesium (Mg) alloys for medical applications. In G. L. Song (Ed.), *Corrosion prevention of magnesium alloys* (pp. 509–543). Cambridge, UK: Woodhead Publishing.
- Yanovska, A., Kuznetsov, V., Stanislavov, A., Danilchenko, S., & Sukhodub, L. (2012). Calcium–phosphate coatings obtained biomimetically on magnesium substrates under low magnetic field. *Applied Surface Science*, 258, 8577–8584.
- Yao, Z., Li, L., & Jiang, Z. (2009). Adjustment of the ratio of Ca/P in the ceramic coating on Mg alloy by plasma electrolytic oxidation. *Applied Surface Science*, 255, 6724–6728.
- Zberg, B., Uggowitzer, P. J., & Löffler, J. F. (2009). MgZnCa glasses without clinically observable hydrogen evolution for biodegradable implants. *Nature Materials*, 8, 887–891.
- Zeng, R., Dietzel, W., Witte, F., Hort, N., & Blawert. (2008). Progress and challenge for magnesium alloys as biomaterials. *Advanced Engineering Materials*, 10, B3–B14.
- Zhang, C. Y. (2010). Preparation of calcium phosphate coatings on Mg–1.0 Ca alloy. *Transactions of Nonferrous Metals Society of China*, 20, s655–s659.
- Zhang, C. Y., Zeng, R. C., Liu, C. L., & Gao, J. C. (2010). Comparison of calcium phosphate coatings on Mg–Al and Mg–Ca alloys and their corrosion behavior in Hank's solution. *Surface and Coatings Technology*, 204, 3636–3640.
- Zhang, J., Dai, C. S., Wei, J., & Wen, Z. H. (2012). Study on the bonding strength between calcium phosphate/chitosan composite coatings and a Mg alloy substrate. *Applied Surface Science*, 261, 276–286.
- Zhang, J., Dai, C. S., Wei, J., Wen, Z. H., Zhang, S., & Chen, C. (2013). Degradable behavior and bioactivity of micro-arc oxidized AZ91D Mg alloy with calcium phosphate/chitosan composite coating in m-SBF. *Colloids and Surfaces B*, 111, 179–187.

- Zhang, S., Li, J., Song, Y., Zhao, C., & Zhang, X. (2010). Influence of dicalcium phosphate dihydrate coating on the in vitro degradation of Mg-Zn alloy. *Frontiers of Materials Science in China*, 4, 116–119.
- Zhang, X., Li, Q., Li, L., Zhang, P., Wang, Z., & Chen, F. (2012). Fabrication of hydroxyapatite/stearic acid composite coating and corrosion behavior of coated magnesium alloy. *Materials Letters*, 88, 76–78.
- Zhang, X. P., Zhao, Z. P., Wu, F. M., Wang, Y. L., & Wu, J. (2007). Corrosion and wear resistance of AZ91D magnesium alloy with and without microarc oxidation coating in Hank's solution. *Journal of Materials Science*, 42, 8523–8528.
- Zhang, Y., Ma, Y., Chen, M., & Wei, J. (2013). Effects of anodizing biodegradable Mg–Zn–Zr alloy on the deposition of Ca–P coating. *Surface and Coatings Technology*, 228, S111–S115.
- Zhang, Y., Zhang, G., & Wei, M. (2008). Controlling the biodegradation rate of magnesium using biomimetic apatite coating. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, 89B, 408–414.
- Zong, Y., Niu, J. L., Mao, L., Zhang, X. B., Yuan, G. Y., & Ding, W. J. (2011). Improvement of corrosion performance in simulated body fluid solution of Mg–Nd–Zn–Zr alloy coated with hydroxyapatite by pulse eletrodeposition. *Coosion and Protection*, 32, 430–437.

Plasma electrolytic oxidation/micro-arc oxidation of magnesium and its alloys

8

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8.1 Introduction

Although plasma electrolytic oxidation (PEO), magnesium anodic oxidation and micro-arc oxidation (MAO) processes have been used for the surface protection of magnesium in industrial applications for a couple of decades, their use in biomedical applications is relatively new. Special requirements, such as biocompatibility and controlled degradation, may need to be considered as they differ from the classic treatments that simply focus on the best corrosion and wear protection for the intended application. This chapter provides an overview of state-of-the-art PEO processing for magnesium biomedical applications, including processing parameters, coating compositions and properties.

8.2 Principles of PEO processing

The coating process by PEO is very simple, involving simple immersion of a metallic sample into an electrolyte. The sample piece acts as the anode and is usually a large inert metal sheet; often an electrolyte container made of stainless steel acts as a counter electrode. A high-voltage power supply is used to apply voltage between the metallic sample and the counter electrode. A large amount of heat is evolved in the process, so a cooling system is frequently employed to cool the electrolyte. PEO coating commences after the dielectric breakdown of the anodic oxide film. The prerequisite of a metal or an alloy for the PEO treatment is the formation of a resistive barrier layer on the metallic substrate during anodic oxidation, because dielectric breakdown occurs only when such a barrier layer exists. Anodic films with resistive barrier layers are formed in aqueous electrolytes only on valve metals, namely Al, Mg, Ti, Zr, Nb, Ta, W and Hf (Young, 1961). However, PEO coatings are frequently studied only on light valve metals like Mg, Al and Ti and their alloys because of the attractive

properties of the light metals for automobile, computer, and biomedical applications. During anodic oxidation, the electric field across growing anodic film exceeds a critical voltage called *dielectric breakdown voltage* and dielectric breakdown of anodic film occurs, which is usually noticed because of spark discharge, gas evolution and changes in the slope of the voltage–time curve of anodizing (Albella, Montero, & Martinez-Duart, 1987; Wood & Pearson, 1967). In PEO, dielectric breakdown voltage is considered to be the voltage at which the first spark is observed (Wood & Pearson, 1967). The breakdown voltage (U_B) is specific for electrode/electrolyte systems; for a particular system, its value can be adjusted by changing the resistivity (ρ) of the electrolyte because breakdown voltage is directly proportional to the logarithm of the resistivity of the electrolyte (Ikonopisov, 1977), given as

$$U_B = a_B + b_B \log \rho \quad \text{where } a_B, b_B \text{ are constants}$$

The coating material is formed mainly due to dielectric discharges. Anodic film is locally damaged by dielectric breakdown and local ionic transport of electrolyte species at high voltage leads to the formation of a thicker layer at breakdown sites (Sah, Tatsuno, Aoki, & Habazaki, 2011; Shimizu, Thompson, & Wood, 1982). Dielectric breakdown is a discrete and visually dynamic phenomenon; therefore, the coating grows with process time, which multiplies dielectric discharges. The dielectric discharges create local and instantaneous high-temperature plasma that leads to rapid heating and cooling of the oxide layer and results in the formation of high-temperature oxide phases of the coatings. Although the electron temperature of plasma ranges up to $\sim 10^4$ K (Yerokhin, Nie, Leyland, Matthews, & Dowey, 1999), the actual temperature of exposed oxide is lower. A study by Matykina et al. showed that monoclinic zirconia from the electrolyte is incorporated in the PEO coating and it is changed to tetragonal/orthorhombic; thus, the transition temperature of $\sim 1710^\circ\text{C}$ should be reached at least (Matykina, Arrabal, Monfort, Skeldon, & Thompson, 2008). This high-temperature exposure creates PEO coatings with phases as hard as diamond.

The high hardness and stability of the phases building the coating materials are the main features of PEO coatings. However, the most intriguing part of PEO is the formation of uniform and dense coatings. The dielectric breakdown phenomenon seems, at a glance, to be a random and uncontrolled process as it occurs randomly and instantaneously, giving a dynamic view of sparking. The coating material is synthesized mainly by dielectric discharges (McNeill & Nordbloom, 1958), and sparking in the coating remains a magnificent feature; therefore, understanding the sparking in PEO remains a hot topic of research toward understanding and monitoring the process of PEO. Sparking has been studied by video imaging and optical emission spectroscopy.

Different models to explain the coating formation by PEO have been proposed, such as oxide film dielectric breakdown (Van, Brown, & Wirtz, 1977), a discharge-in-pore model (Krysmann, Kurze, Dittrich, & Schneider, 1984) and contact glow electrolysis (Hickling & Ingram, 1964). The most accepted and verified model is the oxide film dielectric breakdown model. According to this model, oxide film is locally broken due to high currents caused by electron avalanches, and new coating material is formed

at the coating/substrate interface by high ionic transport. Strong support for this model comes from the study by [Monfort et al. \(2007\)](#), which employed sequential anodizing of Al in silicate and phosphate electrolytes. A PEO coating was first formed in a silicate electrolyte and then in the phosphate electrolyte. The very presence of phosphorus, observed by EPMA (electron probe micro analysis), at the metal/coating interface shows that new coating material is formed in the vicinity of the metal/coating interface by short-circuit paths formed by discharge events.

High-speed video imaging ([Martin et al., 2013](#)) and megahertz sampling of current and voltage transients ([Dunleavy, Golosnoy, Curran, & Clyne, 2009](#)) have revealed that the duration of a single discharge is on the order of $\sim 10 \mu\text{s}$, compared with the lifespan of a discharge of 0.25–3.5 ms ([Yerokhin et al., 2003](#)) or 35–800 ms ([Matykina, Berkani, Skeldon, & Thompson, 2007](#)) being recorded by low-resolution video imaging. This shows that the lifetime of a discharge recorded by video imaging should not be for a single discharge event but for a cascade (or group) of discharge events likely to occur in the same physical location of the coating. A cascade of discharges occurring in the same physical location is likely to be recorded as a single event by video imaging. The similar lifetime of sparks of PEO and that of insulator breakdown shows that the discharge in PEO is filamentary discharge.

Significant control has been achieved in controlling the discharge behaviour of PEO. Pulsed DC, AC or bipolar power supplies are suitable to tailor rather less defective and compact coatings ([Hussein, Nie, & Northwood, 2010](#); [Hussein, Zhang, Nie, Xia, & Northwood, 2011](#); [Xin, Song, Zhao, & Hu, 2006](#)). However, PEO coatings still contain detrimental discharge pores to weaken the corrosion resistance of the coating for promising commercial applications. Large micropores that develop at the later stage of coating formation are largely due to arcing. The destructive arcing can be turned even milder than micro-arcing by increasing the cathodic-to-anodic current ratio, and a PEO coating with a highly dense intermediate layer is formed when AC or bipolar pulse power supply is employed to coat Al or Mg alloys in alkaline silicate-based electrolytes ([Arrabal, Matykina, Hashimoto, Skeldon, & Thompson, 2009](#); [Jaspard-Mécuson et al., 2007](#)). The specific roles of alkaline silicate-based electrolyte and cathodic currents to form dense PEO coatings were studied by the application of single-pulse voltages on aluminium microelectrodes. Alkaline silicate electrolytes promote weak dielectric discharges that promote healing of breakdown sites ([Sah et al., 2011](#)). Additionally, the cathodic current produces a nanoporous layer at previous dielectric breakdown sites, and such a nanoporous layer is highly resistive for further dielectric breakdown. Hence, cathodic breakdown suppresses repeated dielectric breakdown at the same sites and may cause the formation of a rather dense coating ([Sah, 2012](#); [Sah, Tsuji, Aoki, & Habazaki, 2012](#)). However, dense coating formation by 'soft' PEO is highly selective in terms of power supply, electrolytes and substrate, so it is not applicable for forming protective coatings of desired composition on every substrate.

The role of electrolytes is as important as the mode of power supply to control the process of PEO. Currently, much attention is being paid to forming a rather dense and uniform PEO coating by modifying electrolytes and process conditions. KOH or NaOH serves to promote electrolytic conductivity and to adjust the pH of the

electrolyte. Silicates accelerate the growth of the coatings (Raj & Mubarak Ali, 2009). The phosphate of the electrolyte enhances the formation of α -Al₂O₃ in the coatings on aluminium (Lv et al., 2006). Phosphate also accelerates dielectric discharges and promotes the rapid growth of PEO coatings (Sah, 2012; Sah, Aoki, & Habazaki, 2010). The number and size of discharge channels decrease with the addition of aluminate to the electrolyte (Liang et al., 2005a). To improve the tribological properties of PEO coatings, several studies of the incorporation of particulate matters from electrolyte into the coating, such as the incorporation of zirconia nanoparticles (Matykina, Arrabal, Monfort, et al., 2008), Fe micrograins (Jin, Chu, Tong, & Zhao, 2006), carbon nanotubes (Lee, Jo, Lee, Yoo, & Shin, 2011) and WC/TiC nanopowder (Aliofkhazraei & Sabour Rouhaghdam, 2010), were reported. However, complete integration of particulate matters of the electrolyte in the coating phases was rarely observed; generally, a composite coating is formed.

Recently, it was found that low melting point clay particles, which were added to the electrolyte, integrated completely in the coating causing significant changes in the microstructure of the coating and also seal markedly the open discharge pores. The integration of clay particles is also strong evidence for the growth of coating at the coating/electrolyte interface. However, the addition of the clay particles turns the crystalline coating to amorphous, thereby causing the PEO coating to lose its hardness, which is one of the important properties of PEO coatings (Blawert, Sah, Liang, Huang, & Höche, 2012). Like many PEO coatings, this coating has the potential for dual use: technical and biomedical applications. However, in contrast to industrial applications, the biomedical coatings require additional features depending on the intended application, which are mainly biocompatibility and controlled degradation. In the following sections, an overview of the state-of-the art PEO coatings for biomedical use is given and the advantages/disadvantages are discussed.

8.3 Coating requirements for biomedical applications

The design and selection of a coating material for biomaterials critically depend on the intended application. Poor selection of a coating material can lead to clinical problems. Generally, biomaterials should exhibit various degrees of compatibility with the environment in the human body. The extent of compatibility varies based on the application and service life of the material. A coating material for biodegradable implants requires various properties. Firstly, the coating material should be biocompatible, which encompasses many aspects such as physical, chemical and mechanical properties; it also needs to integrate with the surrounding tissues. The coating should satisfy the required functions without eliciting any undesirable effects in the patient. It should possess beneficial cellular or tissue response, as well as cell proliferation. Coatings are exposed to human tissues and fluids; hence, it is important to understand the possible interactions between host and material. A direct anchoring of the coating, known as osseointegration, by the formation of bone tissue around it without the growth of fibrous tissue at the bone-coating interface is required for performing successfully under loading conditions (Albrektsson & Johansson, 2001). Thrombosis, which

involves blood coagulation and adhesion of blood platelets to the biomaterials, is an important issue for biocompatibility.

The cytotoxicity of coating materials is another critical property. The elements present in the coating or the byproducts should not be toxic, and ideally they should be essential for the physiological system. In recent years, ceramic materials have been widely used for their unique features, such as excellent tribological properties and biocompatibility. PEO coatings, such as phosphate- and silicate-based coatings, are biocompatible (Gu, Bandopadhyay, Chen, Guo, & Ning, 2012; Gu, Chen, et al., 2012). Gu et al. (2011) reported improvement in the cell adhesion of a silicate-based PEO-coated magnesium alloy. Silicon containing PEO-coated magnesium alloy has been shown to promote cell proliferation and differentiation of osteoblasts and hence exhibits good biocompatibility (Yang, Yin, et al., 2013). However, the biocompatibility of PEO coatings can be further enhanced by incorporating elements such as calcium in the form of ions/particles into the coating, because calcium is naturally present in bone and improves biocompatibility and osseointegration (Shi, 2005).

The main purpose of the coating is to delay the degradation rate of magnesium-based implant materials; hence, it is critical that the coating material should have a lower degradation rate than that of the substrate material. It is equally important that the coating material must not be nondegradable in body fluid. The coating should have a predictable degradation rate to provide progressive bone loading and prevent stress shielding to aid better bone healing. Preferably, the coating should not be a conducting material. Magnesium is the most active metal in the galvanic series; hence, a conducting coating would result in bimetallic corrosion (galvanic corrosion) (Zeng, Dietzel, Witte, Hort, & Blawert, 2008) when the coating starts to corrode. This would, in fact, accelerate the corrosion of the substrate material. In one of the early trials using magnesium metal for implant applications, gold-plated steel nails were used along with magnesium metal. As a consequence of galvanic corrosion, the magnesium metal corroded rapidly (Staiger, Pietak, Huadmai, & Dias, 2006). However, PEO coatings, in general, are nonconducting; hence, galvanic corrosion would not be an issue.

For desirable protection of the base materials from corrosion, the coating should be uniform and compact. Micropores, which form due to microdischarge during the coating, can be an issue with PEO coatings. The pores can expose the substrate to the harsh body fluids by allowing the fluid to penetrate through the pores. Consequently, the functional properties of the coating could reduce, for example, mechanical properties such as tensile strength, and adhesion can be affected. Hence, it is critical to control the porosity of the coating. A significant amount of work has been done to minimize the porosity in PEO coatings (Blawert, Dietzel, Ghali, & Song, 2006; Wei Zhang, Du, Zhang, & Wang, 2011), especially for engineering applications. Alteration of the process parameters has been shown to reduce the porosity of PEO coatings. Postcoating sealants have also been used to block the pores (Guo-Hua et al., 2010). For the intended implant applications, biocompatible and biodegradable polymers, such as polylactic acid (PLA), polyglycolic acid (PGA) or its copolymers, can be used as a sealant material on PEO coating. The degradation rate of polymers in the body can be adjusted using copolymers (Nair & Laurencin, 2007). Furthermore, the dissolution of the polymers can be tailored to suit different applications by altering

the crystallinity or molecular weight of the polymer (Chandra & Rustgi, 1998; Nair & Laurencin, 2007).

Although it has been discussed that porosity in the coating deteriorates the performance of the coating (corrosion protection), it is interesting to note that porous structured biomaterials are intentionally made for scaffolding. The porous structures play an important role in bone formation. The pores allow new blood capillaries that develop during healing to grow into the graft. The blood provides essential nutrients for fibroblasts and other cells to survive on the biomaterial. It has been shown that higher porosity and pore size result in greater bone ingrowth (Rhalimi et al., 1999). However, if the porosity is too high, the mechanical properties of the scaffolds would reduce. For coatings, the size, shape and locality of the porosity are important. It has been reported that Ti-based alloy with 70% porosity has the optimum mechanical properties, as well as suitable pore size and porosity to allow more bone ingrowth (Xu et al., 2013). In the case of coatings on biodegradable materials, pore connectivity to the substrate would deteriorate the coating rapidly. A relatively protective intermediate layer between the porous structure and the substrate would be beneficial for delaying the corrosion and also enhancing bone formation.

Typically, the pH of body fluid is between 7.4 and 7.6. The pH of the body fluid near the implant should not change significantly during the dissolution of the coating for two reasons: (1) acidity or alkalinity would affect the living cells in that region (i.e., unbalanced pH can affect the biocompatibility), and (2) the dissolution of the substrate magnesium material is influenced by the pH of the environment (Zeng et al., 2008). Magnesium corrosion accelerates when the pH of the environment is low and it passivates when the environment is alkaline.

Another potential challenge with PEO coating is optimizing the coating thickness depending on the degradability of the coating. If the thickness of the PEO layer is significantly high, the dissolution of the implant would reduce to an undesirably low rate. The parameters for obtaining a thin layer, typically around 5–10 μm , should be optimized. The thickness and morphology of the coating and the size of the pores can be altered by varying the voltage and the composition of the electrolyte used in the process for obtaining desirable results (Gu et al., 2011).

Generally, the longevity of coatings is of prime importance in many applications. One of the main factors that governs the longevity is adhesion (Baglin, 1988). Although the coating is expected to degrade over time in these implant applications, the coating should have adequate adhesive strength. To perform its functions, its adhesion to the substrate must tolerate mechanical stresses and the corrosive environment. Good adhesion of a coating depends on various factors, such as atomic bonding structure, elastic moduli, thickness and fracture toughness (Baglin, 1988). When the adhesion is poor, cyclic loading can cause failure at the coating/substrate interface, which could lead to blistering or even complete spalling of the coating (Gupta, Kulshrestha, & Agarwal, 1987). Good adhesion is promoted by a strong bonding across the interfacial region and low stress gradients when experiencing stress. Generally, intermolecular attraction is the basis for adhesion; hence, increasing the actual area of contact will increase the total energy of surface interaction by a proportional amount (Davies & Whittaker, 1967). Interestingly, in PEO

coatings, the ceramic layer grows inwards and outwards. Thus, the coating is an integral part of the metal substrate and should exhibit good adhesion.

Generally, orthopaedic implants are subjected to cyclic loading. The coating should have good mechanical properties such as hardness, tensile strength and elastic modulus that enable them to withstand repetitive loads or strains. Hence, the fatigue strength of the coating material should be taken into consideration. Due to their brittle nature, ceramics may be susceptible to cracking under loading conditions. Even fine cracks in the coating could allow the body fluid to penetrate through and initiate substrate corrosion. This could lead to localized corrosion and then spallation of the coating, eventually affecting the mechanical integrity of the implant. This could be avoided by using a thin layer of biodegradable polymer top coat, as described earlier.

Wear is another important property to be considered for implant coatings. Wear and abrasion can act in synergy with corrosion and could lead to dimensional instability of the implant (Richard, Kowandy, Landoulsi, Geetha, & Ramasawmy, 2010). Furthermore, wear debris can cause aseptic loosening due to osteolysis (Kowandy, Mazouz, & Richard, 2006). Although ceramics, in general, have high wear resistance, it has been reported that surface roughness of ceramics affects the wear properties; that is, ceramics with a rough surface cause excessive wear (Monasky & Taylor, 1971). Nano-structured coatings could overcome this issue, and in fact they have attractive physical and mechanical properties for biomedical applications.

In summary, a coating material for biodegradable implants requires various properties; however, the key requirements are biocompatibility, controlled degradation rate, good adhesion and wear resistance, as shown in Figure 8.1. Although certain PEO coatings that are phosphate- and silicate-based satisfy all the key requirements, tailoring of the PEO coatings would be required to further enhance the biocompatibility and achieve desirable results.

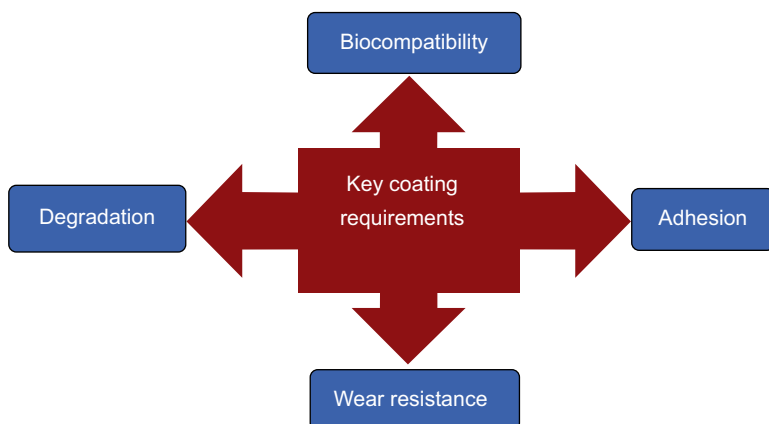


Figure 8.1 Key coating requirements for biodegradable magnesium-based implants.

8.4 Controlling coating composition, microstructure and properties for biomedical applications

The degradation rate of a PEO-coated Mg biomedical device is determined mainly by microstructure and composition of PEO coating; this section is devoted to the recent investigations in this context. An extended review was published elsewhere, focusing on strategies to improve the corrosion resistance of micro-arc oxidation-coated magnesium alloys for degradable implants (Sankara Narayanan, Park, & Lee, 2014). The interested reader can find there an extended range of references, especially regarding the influence of electrolyte composition, including additives and particles and processing parameters on microstructure and performance.

8.4.1 Energy input

The formation of PEO coatings is caused by dielectric discharges and microstructure, and properties of PEO coating can be controlled by the energy of discharges. The electric energy (mainly adjustable by voltage and current) is thereby converted into thermal energy. Generally, the energy of a discharge is sufficient enough to melt the coating material so that a highly crystalline oxide coating is obtained after the discharges are stopped and the coating material is quenched (Van et al., 1977). The energy of a discharge can be controlled by the parameters of power supply as well as electrolytes used. Pulsed DC and AC are preferred because they allow better control of the energy input by the discharges and they reduce the likelihood of damaging the coating by severe burning. Thus, pulse frequency, pulse length and duty cycle are additional options to control energy input and as a consequence the microstructure, but so far they have not been studied much for biomedical applications of PEO coatings.

PEO processing is normally performed in either constant voltage or constant current mode, resulting in specific time dependences. In constant voltage mode, the total energy input is often decreasing with treatment time. While the coating is growing in thickness, its resistance is increasing; therefore, the current is decreasing if the voltage is fixed. Contrary, in constant current mode, the total energy input is normally increasing with time because the voltage is increasing to compensate for the increasing resistance of the coating to maintain the selected current. However, the total energy input is not directly related to the energy in one single discharge. In the beginning of the process, normally a large number of small discharges occur; in the later stages, the total number is reduced but the size and lifetime is increasing, supposing that the energy transferred by a single discharge event at the end of the process is higher than at the beginning (Bala Srinivasan, Blawert, Störmer, & Dietzel, 2010).

Bala Srinivasan, Liang, Blawert, Störmer, and Dietze (2009) applied different current density to control the microstructure and properties of PEO coatings. DC currents of 15 mA/cm², 75 mA/cm² and 150 mA/cm² were applied and the thickness, roughness, microstructure, morphology, phase composition and corrosion resistance were characterized. The thickness along with the roughness of PEO coatings increased with increasing current density. PEO coating with very large discharge pores (Figure 8.2) was formed with 150 mA/cm² applied current; however, the density of

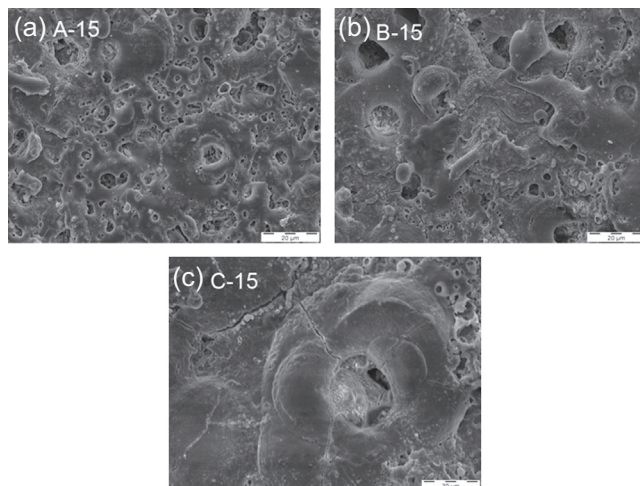


Figure 8.2 Scanning electron micrographs showing the surface morphologies of the specimens PEO coated at different current densities for 15 min (A: 15 mA/cm², B: 75 mA /cm² and C: 150 mA/cm²).

Reprinted from [Bala Srinivasan et al. \(2009\)](#) with permission from Elsevier.

discharge channels appeared to decrease with increasing applied current. This showed that high current application is responsible for strong discharges. Such strong discharges leave large pores, which were observed in cross-sections of the coatings. However, shorter treatment under higher currents formed compact coatings. Prolonged treatment at higher currents may cause repeated discharges at the same location and thereby formation of rather highly defective coating. Formation of large discharge pores, on the other hand, increased the roughness of the coating. Impedance and potentiodynamic polarization measurements of the coated Mg alloys showed that coatings with denser and more compact morphology are more protective in the aggressive chloride solution. Large discharge pores act as channels for corrosive media to reach the underlying substrate easily and thereby weaken the corrosion protection property of PEO coatings. On the other hand, a certain energy level is required to incorporate all components of the electrolyte into the final coating. At a low current density, the coating is mainly composed of MgO, and it requires at least a medium current density to produce the Mg₂SiO₄ phase as well; the content of the latter increases with increasing current density. A similar effect is observed when the energy input is controlled by the final voltage ([Bala Srinivasan et al., 2010](#)). At the same current density of 15 mA/cm², at least a final voltage of 440 V was required to produce larger amounts of the Mg₂SiO₄ phase instead of MgO. Therefore, it is important to find the right balance between the destructive and constructive energy of discharges to produce microstructures that have the desired degradation properties.

[Gu et al. \(2011\)](#) formed PEO coatings on a biomedical Mg-Ca alloy in alkaline silicate solution at fixed voltages (300–400 V), 700 Hz, 30% duty cycle and 600 s processing time. The microstructure of the coating changed significantly with applied

voltage (Figure 8.3). With increasing applied voltage, the pore size and the thickness of the PEO layer increased. When 300 V was applied (Figure 8.3(a)), a porous oxide coating with an average coating thickness of 4.5 μm and a pore diameter of 0.4 μm was formed on the alloy surface. As the applied voltage was increased to 360 V (Figure 8.3(b)), the thickness and pore size of the coating increased to 6 μm and 1.2 μm , respectively. While increasing the voltage to 400 V, the resulting coating became still thicker while the pore size increased slightly in diameter. The presence of microchannels in the cross-section (marked by an arrow in Figure 8.3(c)) of the coating obtained at 400 V revealed the presence of strong discharges. Strong evidence for the formation of high-energy discharges also came from the evolution of high dielectric breakdown current and the formation of large discharge channels when breakdown is caused by high-voltage pulses (Sah, 2012; Sah et al., 2011). Thus, increasing applied voltage results in high-energy dielectric discharges, and increased amounts of molten product may be erupted from and rapidly deposited around the discharge channels. As a result of this series of reactions, the pore size and the thickness of the layer increased with higher applied voltage. At the same time, the trapping

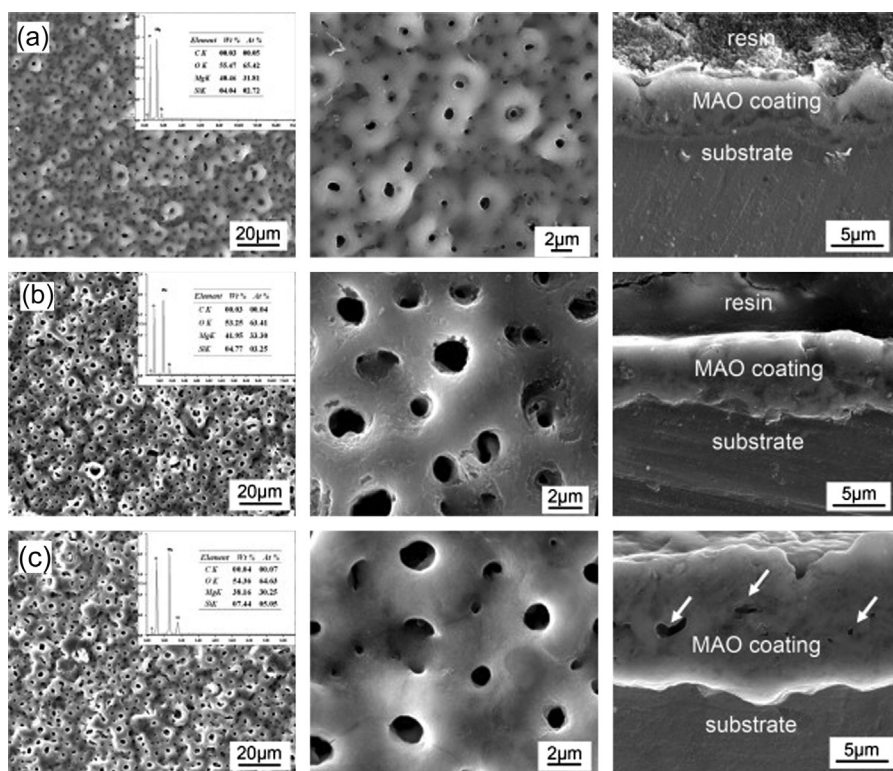


Figure 8.3 The surface and cross-sectional morphologies of (a) 300 V, (b) 360 V and (c) 400 V MAO-treated Mg–Ca alloy samples. (Insets) EDS results.

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of gas bubbles in the growing oxide layer might be responsible for the micropores inside the PEO layer (Guo & An, 2005).

The microstructure that develops at different voltages has a strong influence on the properties of the coating (Gu et al., 2011). Figure 8.4 presents the variations in pH and the volume of hydrogen evolved as a function of immersion time. Hydrogen evolves much more slowly from PEO-treated than untreated Mg-Ca alloy specimens

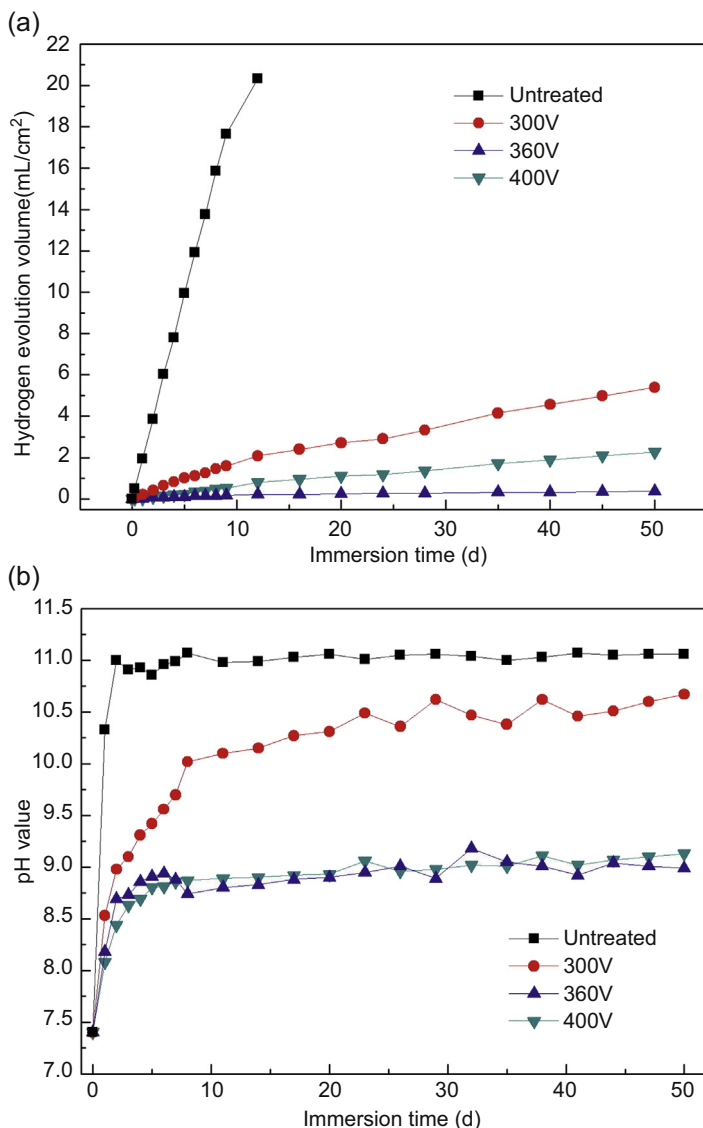


Figure 8.4 (a) The hydrogen evolution volume and (b) change in pH value of Hank's solution containing untreated and MAO-treated Mg-Ca alloy samples as a function of immersion time. Reprinted from Gu et al. (2011) with permission from Elsevier.

(1.694 ml /cm²/day). Among the three specimens that were PEO treated at different applied voltages, the one treated at 360 V exhibited the slowest hydrogen evolution rate (0.007 ml cm²/day), whereas the one treated at 300 V showed the highest evolution rate (0.108 ml cm²/day), followed by the 400 V PEO-treated specimen (0.045 ml cm²/day). The change in the pH value of the Hank's solution indicated a tendency similar to that of the hydrogen evolution results. The variation in the corrosion rates of the PEO-treated specimen is attributed to changes in the microstructure of the samples obtained at different applied voltages. On the one hand, the change in corrosion resistance of the PEO coatings depends on the coating thickness. The 300-V treated PEO coating showed the poorest corrosion resistance, which is due mainly to its low thickness (4.5 µm). On the other hand, the integrity of an MAO coating also influences the corrosion resistance. The 400-V treated PEO coating has more micropores and larger discharge channels inside the coating, permitting more corrosive medium to be absorbed into the PEO coating, reducing its corrosion resistance. Thus, the specimen treated at 360 V has the best combination of thickness and integrity. The surface morphology observed after immersion in a corrosive medium confirmed that PEO coating formed at 360 V has the best protective ability. The corrosion behaviour of PEO-coated alloy significantly influenced the cell proliferation. The most protective coating also showed the best cell proliferation and bioactivity.

The compactness of coating formed at higher voltages may also depend on the electrolyte, pulse frequency, duty cycle or type of supply (bipolar pulses) used. [Lin, Tan, Zhang, et al. \(2013\)](#) reported PEO coating formation on ZK60 Mg alloy in alkaline silicate solution containing fluoride at different constant voltages of 230, 300, 370 and 450 V using 1000 Hz pulse frequency and 40% duty cycle. Thicker and denser coatings were formed at higher voltages, contrary to the result of [Gu et al. \(2011\)](#) discussed above. The formation of a dense coating at 450 V is explained by the rather long melt quench time and reduced gas evolution. However, the role of electrolytes in PEO is discussed in the next section. It should be noted that the compact PEO coating formed at 450 V showed the best corrosion protection in Hank's solution and, because of its highest degradation resistance, also the least cytotoxicity and haemolytic ratio.

Summarizing, it is obvious that the energy input by the discharges is a very important parameter to control the microstructure and properties of PEO coatings, because it determines what phases will form, how quick the coating grows and how much damage to the coating is generated. The interaction of the processing parameters (voltage, current, pulse form, frequency, length, duty cycle) are very complex, and even the electrolyte interacts by determining the breakdown voltage; thus, there is no clear indication of the best processing window.

8.4.2 Electrolyte composition

Like the applied current and voltage during PEO processing, electrolyte composition also controls the microstructure of PEO coatings. The first evidence that electrolyte species are incorporated in PEO coating, unlike classical anodic films, came from

the formation of $\text{Cd}_2\text{Nb}_2\text{O}_7$ on a cadmium anode in an aqueous solution of potassium niobate (McNeill & Nordbloom, 1958). Later, the mechanistic study by Monfort et al. (2007) using sequential PEO of Al in silicate and phosphate electrolytes showed that electrolyte species are incorporated in the coating due to short-circuit transport caused by dielectric breakdown. Therefore, the composition of PEO coatings should mainly depend on electrolyte and substrate composition.

Generally, a large number of electrolytes are available for PEO processing of magnesium alloys. Strong alkaline solutions are preferred, but under certain conditions even acidic solutions can be used. However, they can be divided into two main groups according to the main coating-forming addition in the electrolyte. In that sense, phosphate- and silicate-based electrolytes are available, to which various additions are possible, such as hydroxides, fluorides, borates and aluminates (to name just a few). Hydroxides are normally used to adjust the pH value and conductivity of the electrolyte solution. Additionally, the concentration of all these additions has an influence on the surface modification that can be obtained, by controlling the breakdown voltage but also determining the amount of possible conversion products added to the coating. Thus, there is a direct influence on coating composition, morphology and structure, and thus on the properties of the coating as well. Altogether, a large number of studies of electrolyte influence on microstructure and properties were performed, but just a few can be presented here. A more complete review can be found elsewhere (Sankara Narayanan et al., 2014).

Duan, Yan, and Wang (2007) formed PEO coating on AZ91D magnesium alloy in three different electrolytes – namely, alkaline silicate-phosphate, alkaline silicate-borate and alkaline silicate-borate-fluoride (Figure 8.5). Depending on the different electrolytes, characteristic microstructures of PEO coatings were observed. Large discharge pores with bigger voids near the coating/substrate interface were developed in alkaline silicate-phosphate coating, while the surface morphology of coatings developed in the latter two electrolytes remains the same with improved cross-sectional morphology. The inner region of the coating formed in alkaline silicate-borate-fluoride was denser than that formed in alkaline silicate-borate electrolyte. The corrosion performance of the coatings produced in the three electrolytes is closely related to the microstructure. The coating with denser coating/substrate interface formed in alkaline silicate-borate-fluoride showed the best corrosion protection. The formation of an inner dense layer in fluoride-containing electrolyte may be due to fluoride-assisted suppression of localized galvanic corrosion of the substrate during the coating process (Němcová, Skeldon, Thompson, & Pacal, 2013). A coating with dense and uniform microstructures has a higher potential to show promising corrosion protection of the substrate in body fluid as well.

Not only the composition of the electrolyte but also the concentration of the electrolyte is effective in controlling the microstructure of PEO coatings. Zhang, Zhang, et al. (2012) studied the effect of silicate concentration on PEO of AZ91HP Mg alloy in a sodium hydroxide and phytic acid solution. The latter is an acid suitable for forming insoluble salts of magnesium, which would be incorporated into the coating; it has a variety of beneficial effects for human health, including as an anti-cancer agent, inhibitor for renal stone development and anti-oxidation agent. With increasing

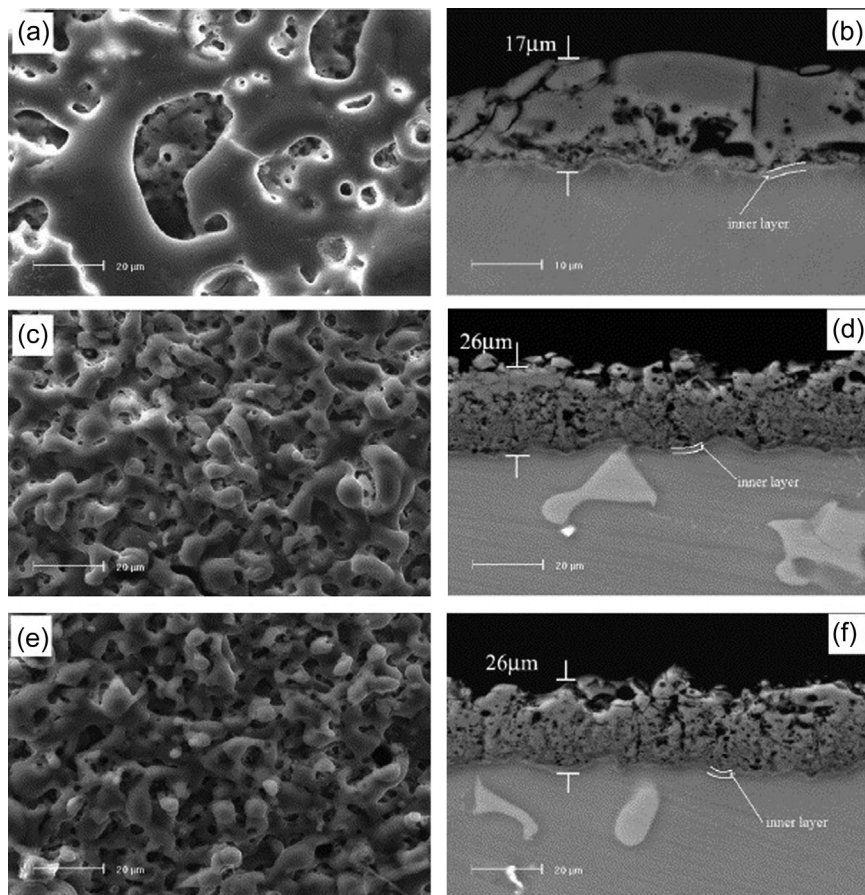


Figure 8.5 Morphologies of PEO films on magnesium alloy AZ91D, respectively, treated in solutions containing phosphate (a), borate (c) and both borate and fluoride (e); (b), (d) and (f) were their cross-sectional morphologies.

Reprinted from [Duan et al. \(2007\)](#) with permission from Elsevier.

concentration of silicate in the electrolyte, the growth of thicker MgO-based PEO coating was observed. Unfortunately, the size of discharge channels, which are potential defects of the coating, was also increasing. Thus, the coating formed in the electrolyte containing 10 g/l silicate possessed the best combination of thickness and compactness, showing the least corrosion current in 3.5% NaCl solution when potentiodynamic polarization was carried out.

[Sah et al. \(2010\)](#) formed MgAl_2O_4 -based PEO coatings on AZ80 Mg alloy in alkaline aluminate solution ($0.15 \text{ mol} \cdot \text{dm}^{-3} \text{ K}_2\text{Al}_2\text{O}_4 + 0.01 \text{ mol} \cdot \text{dm}^{-3} \text{ KOH}$) with different concentrations of Na_3PO_4 . The concentration of phosphate in alkaline aluminate electrolyte significantly controlled the discharge characteristics and the microstructure of the coatings developed. The coatings formed in the phosphate-free electrolyte were

highly porous and very thin. The addition of phosphate to the electrolyte accelerated the growth of the coating and at the same time increased defects, such as cracks and large discharge pores in the coating. EDS (energy dispersive X-ray spectroscopy) mapping showed that phosphor was mainly present in the inner half of the coating. An optimized concentration of $0.05 \text{ mol} \cdot \text{dm}^{-3}$ phosphate in alkaline aluminate solution enabled formation of a uniform and rather dense coating. This coating showed the lowest anodic current during anodic polarization in 0.5 M NaCl solution.

However, calcium and phosphor are likely the two most interesting elements for biomedical applications. The easiest way to control the ratio of the two elements in PEO coatings is by variation of the concentration of the two elements in the electrolyte. Different sources were successfully used, such as sodium hexametaphosphate and calcium hypophosphite (Yao, Li, & Jiang, 2009) or sodium phosphate and calcium hydroxide (Srinivasan, Liang, Blawert, Störmer, & Dietzel, 2010). The latter results suggest that the incorporation of calcium into the layer occurs mainly via formation of an amorphous phase, while phosphate is incorporated in crystalline (Mg_3PO_4) and together with Ca in the amorphous phase. In contrast, although using a similar electrolyte, it was not possible to incorporate Ca into PEO coatings while using a DC power supply (Gao, Yerokhin, & Matthews, 2013). This stresses the importance of the combination of electrolyte and electrical processing parameters to control the composition and properties of the PEO coatings.

However, there are more options available than a simple replacement of standard NaOH or KOH electrolyte additions by $\text{Ca}(\text{OH})_2$. Thus, strontium ($3 \text{ g/L } (\text{NaPO}_3)_6 + 8 \text{ g/L } \text{KF} \cdot 2\text{H}_2\text{O} + 1 \text{ g/L } \text{Sr}(\text{OH})_2$) was introduced to an MAO coating to improve the bioactivity of the coating (Lin et al., 2014). The Sr-P coated ZK60 alloy had a better corrosion resistance than the only P-coated reference, which was mainly attributed to the superior inner barrier layer of the Sr-P coating. The long-term protective ability of Sr-P coating was better than that of the P coating, probably owing to its greater thickness, superior inner barrier layer and superior apatite formation ability.

Summarizing, one can state that biospecific modifications of PEO coatings via electrolyte modifications have just started, and further improvements can be expected in the future.

8.4.3 Particle additions

To improve the tribological properties and growth rate of PEO coatings, but also to add new functionalities, several studies were devoted to the incorporation of particles and the production of composite PEO coatings. Different types of particles, including metals, ceramics and polymers, were successfully incorporated in PEO coatings directly from the treatment electrolytes. There are several reports of particle incorporation in PEO coatings on Al alloys (Jin et al., 2006; Lee, Jo, et al., 2011; Malyshev & Zorin, 2007; Matykina, Arrabal, Monfort, et al., 2008; Matykina, Arrabal, Skeldon, & Thompson, 2008; Matykina, Arrabal, Skeldon, & Thompson, 2009; Wu, Qin, Guo, & Xie, 2008). However, the interest in particle incorporation in PEO coatings on Mg alloys is also increasing (Arrabal, Matykina, Skeldon, et al., 2008a; Arrabal, Matykina, et al., 2008b; Blawert et al., 2012; Guo et al., 2009; Lee, Shin, Namgung, Yoo, & Shin, 2011; Lim,

Ryu, & Hong, 2012; Lu, submitted for publication; Necula, Fratila-Apachitei, Berkani, Apachitei, & Duszczek, 2009; Song, Sun, & Liu, 2012; Wang et al., 2009).

The first report of zirconia nanoparticle incorporation in PEO coatings on Mg alloy was made by Arrabal, Matykina, et al. (2008a,b). They found that the addition of zirconia to the electrolyte generally enhanced coating growth. Basically, a two-layered PEO coating was formed under the given condition and zirconia was preferentially present in the outer coating layer (Figure 8.6). The preferential presence of zirconia was explained by the local heating of microdischarges, under which the zirconia reacts with magnesium species to form $\text{Mg}_2\text{Zr}_5\text{O}_{12}$ in the outer coating layer. The presence of both zirconia and $\text{Mg}_2\text{Zr}_5\text{O}_{12}$ showed that both inert as well as reactive incorporation of zirconia occurs in PEO coating

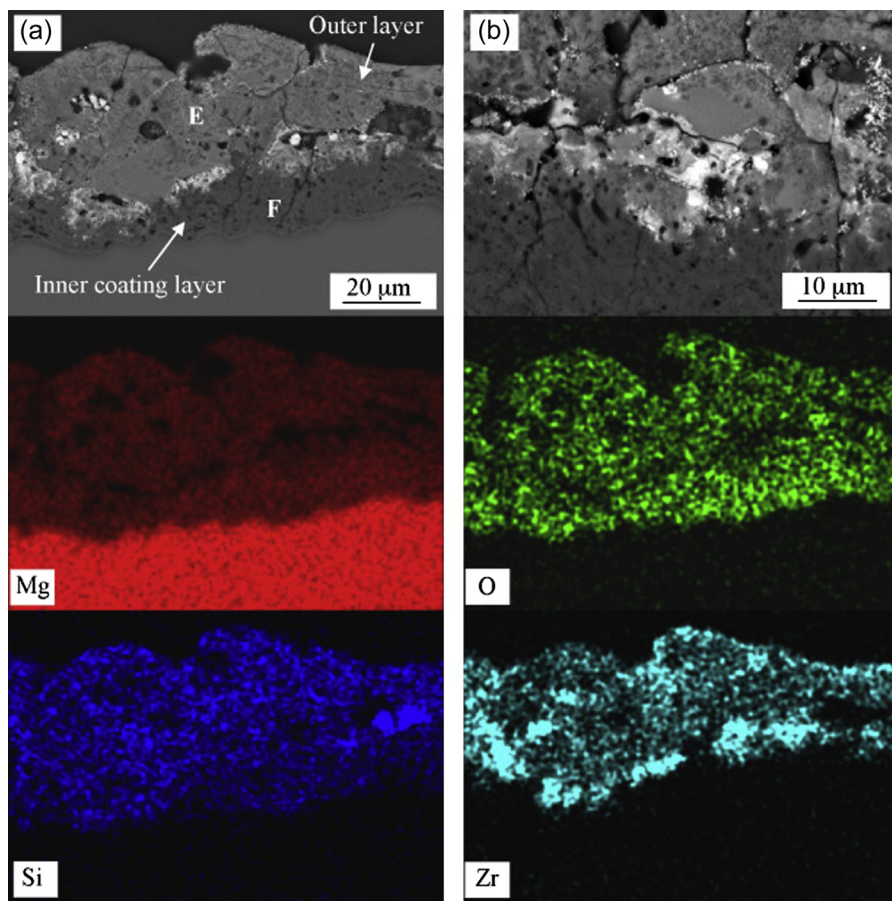


Figure 8.6 (a) Scanning electron micrograph (backscattered electrons) of a cross-section of magnesium following AC PEO treatment for 2400 s at 200 mA/cm^2 (rms) in $0.025 \text{ M Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}/0.05 \text{ M KOH}$ with addition of 10 g/L of monoclinic zirconia. (b) Detail of region between the inner and outer coating layers. EDX elemental maps are shown for magnesium, oxygen, silicon and zirconium of the cross-section of (a).

Reprinted from Arrabal, Matykina, et al. (2008a,b) with permission from Elsevier.

formed by AC current. However, in DC processing, zirconia particle incorporation in PEO coatings can also reveal phase transition. The original monoclinic zirconia was also present in tetragonal modifications when the PEO process was performed in the same silicate-based electrolyte. In a phosphate-based electrolyte under the same processing conditions, the phase transformation and the reactive incorporation to $\text{Mg}_2\text{Zr}_5\text{O}_{12}$ occurred (Arrabal, Matykina, et al., 2008a).

This generally demonstrates how complex the conditions and interactions of the various parameters during PEO processing are and how difficult it is to predict the outcome of the treatment in the sense of coating composition.

To introduce antibacterial/antimicrobial properties, Necula et al. (2009) produced MgO-Ag nanocomposite coatings on Mg alloys by PEO treatment in alkaline silicate-based solutions containing Ag-nanoparticles. EDS analysis showed that the surface content of Ag as well as the roughness of the coating increased with increasing concentration of Ag in the electrolyte. The GDOES (glow discharge optical emission spectroscopy) elemental profile showed that Ag was incorporated throughout the coating and Ag enrichment occurred mainly at the coating/substrate interface. The morphology of the coating also changed with varying concentrations of Ag nanoparticles in the electrolyte. The surface density of pores seems to be reduced with increasing concentration of Ag in the electrolyte. However, a rough and fragile coating was formed with higher concentration of Ag nanoparticles.

Calcium phosphate is another interesting phase for biomedical applications. Seyfoori, Mirdamadi, Seyedraoufi, Khavandi, and Aliofkhazraei (2013) have demonstrated that a nanocomposite PEO coating containing biphasic calcium phosphate can be obtained if 10 g/L hydroxyapatite nanopowder is added to the treatment electrolyte (7 g/L Na_2SiO_3 + 5 g/L NaF and 2 g/L KOH). Incorporation of these nanoparticles could alter the microstructure of the coatings by blocking the structural pores of the MAO-derived films; in this way, it could enhance significantly the corrosion resistance and apatite-forming ability of the pure MAO film.

To enhance the corrosion resistance of the coating, the sealing of pores is quite crucial. A study by Song et al. (2012) showed that PEO coating formed in alkaline aluminate electrolyte containing increasing concentration of titania nanoparticles forms denser and thicker PEO coating, which showed improved corrosion protection. However, PEO coating formed in alkaline silicate-fluoride electrolyte with glycerol showed a slightly decreased growth rate with increasing concentration of titania (TiO_2) sol (Wang et al., 2009). The surface morphology of the coating showed that the size of discharge channels decreased with the addition of titania sol in the electrolyte. The x-ray diffraction (XRD) pattern of latter study showed that peaks corresponding to Mg_2SiO_4 became broader with addition of titania sol in the electrolyte, indicating formation of amorphous phases in the coating. However, the coating formed with the highest concentration of titania showed the worst corrosion protection in simulated body fluid. The presence of the amorphous phase in the coating was made responsible for the lowest corrosion protection.

Blawert et al. (2012) showed that clay particles can be added to the electrolyte and significant sealing of the pores can be achieved. It was also discussed that the formation of coating material not only occurs at the coating/substrate interface but also at the

coating/electrolyte interface. However, incorporation of clay particles in the PEO coating significantly turned crystalline phases into amorphous ones. The presence of amorphous phases in the coatings accelerated degradation of the coatings (Lu, submitted for publication).

From these observations, it can be concluded that a dense PEO coating with crystalline microstructure might be more promising for durable corrosion protection of Mg-based biomedical implants. The positive effect of amorphous phases can result in a more uniform but faster degradation. However, one should also keep in mind that Mg alloys are considered to be degradable implants, and therefore a completely protective coating should not be developed. If the coating is not soluble, it can have negative effects on the human body if the coating fractures and insoluble coating particles remain after the substrate is dissolved.

8.5 Duplex treatments

PEO coatings are generally porous, and pores resulting from the discharge channels often connect the coating/substrate interface with the outside. Such porous coatings can cause early degradation of the PEO-coated Mg implants. Therefore, pores must be sealed to enhance the durability of PEO-coated Mg implants in corrosive environments; in addition, the sealants should also be biomaterials. Commonly used sealants are TiO_2 , hydroxyapatite (HA), phosphate, silicate and chitosan, which are often applied by either dip-coating or electrodeposition processes. There are several reports of duplex treatment of PEO-coated Mg metal/alloys.

An attempt at sealing the open pores of PEO coating on Mg alloys by immersion in alkaline phosphate, alkaline silicate or silicate-based sol-gel did not cover all the discharge pores. However, the corrosion resistance of the sealed PEO coatings was improved (Malayoglu, Tekin, & Shrestha, 2010). Shi, Ng, Wong, and Cheng (2009) fabricated a composite coating on a pure Mg metal for improving its corrosion resistance in Hank's solution. A thick and porous oxide layer was first formed by PEO in a silicate/fluoride containing electrolyte, and then a top TiO_2 sealing layer was formed on the porous layer by sol-gel dip-coating followed by hydrothermal treatment. Figure 8.7 shows that all the discharge pores are sealed after TiO_2 sealing and hydrothermal treatment. However, several cracks developed after sealing. The formation of cracks was suggested to be due to the stress generated by filling the pores. Both electrochemical impedance spectroscopic and anodic polarization measurements showed an increase in the initial corrosion resistance by about 30 times due to the composite coating. Immersion tests also showed that the coated samples were more stable over time, and the degree of corrosion damage was much reduced compared to that of bare Mg. However, the coating failed in 10 days, which is not enough protection for practical purposes.

Zhang, Bai, et al. (2012) devised a scheme to avoid cracking of the sealant layer. They employed PEO treatment of Mg alloy followed by sol-gel TiO_2 sealing. After sealing, samples were annealed to 250 °C. Figure 8.8 shows the surface of the PEO coating before and after sealing and subsequent mechanical scratching. No cracks

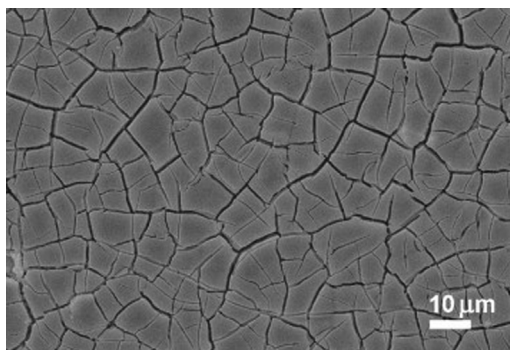


Figure 8.7 SEM micrograph showing surface morphology of PEO-TiO₂. Reprinted from [Shi et al. \(2009\)](#) with permission from Elsevier.

were observed due to sealing (right image). Furthermore, it was observed that filled discharge pores were tightly filled. Such sealed discharge pores enhanced the corrosion resistance in simulated body fluid significantly. The corrosion current of the sealed PEO coatings decreased remarkably by about three orders of magnitude compared to the bare alloy, and the coating remained intact for a longer time in corrosive simulated body fluid.

Like TiO₂, HA is another highly biocompatible and bioactive material, which can also be incorporated in PEO coatings by duplex treatment. A PEO coating was formed on the Mg-Zn-Ca alloy and a layer of HA was deposited on the coating by electrodeposition ([Gao, Guan, et al., 2011](#)). The HA layer effectively filled all the defects, such as pores and cracks; furthermore, no cracks developed after sealing, as shown in [Figure 8.9](#). EDS mapping showed the presence of Ca in the outer layer, suggesting that the outer layer is HA. In addition, scanning electron microscopy (SEM) showed

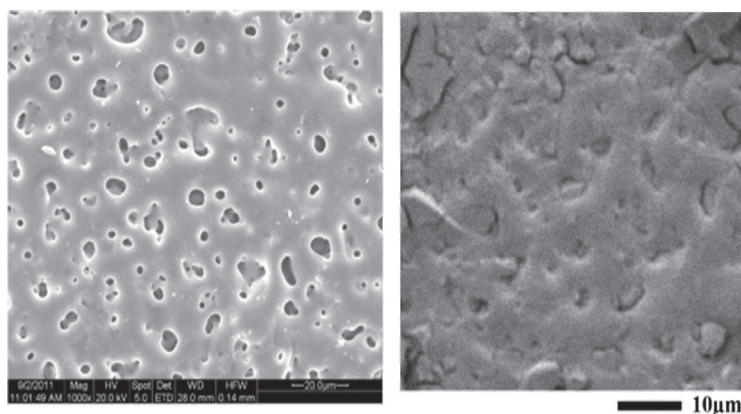


Figure 8.8 SEM image PEO coating before (left) and after (right) sealing. Adapted from [Zhang, Bai, et al. \(2012\)](#) with permission from Elsevier.

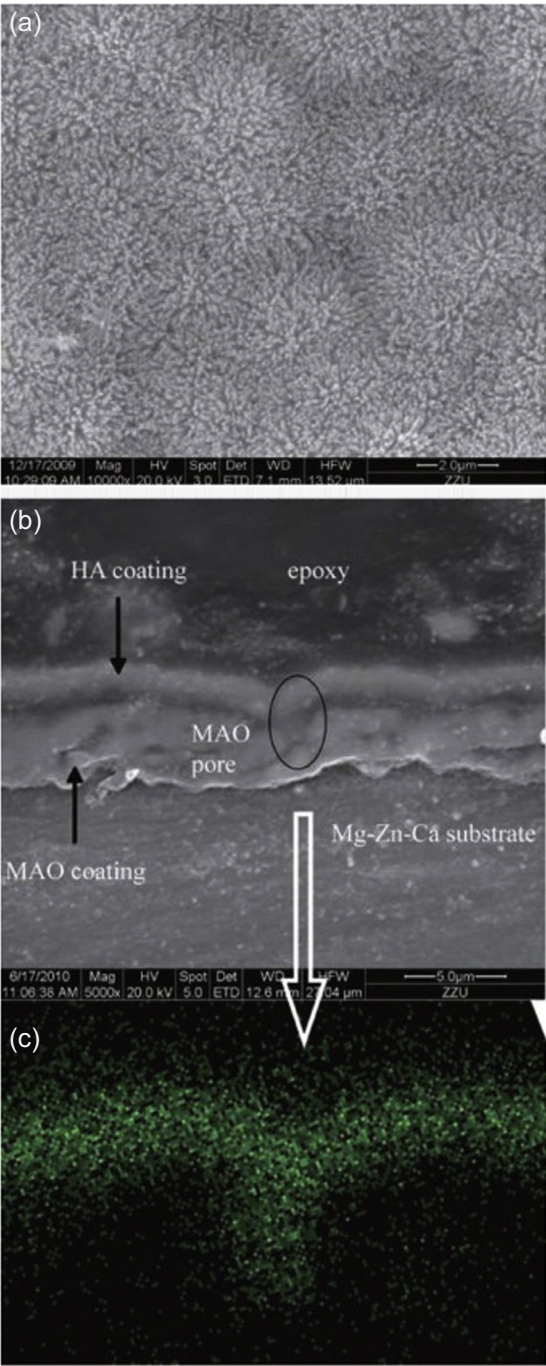


Figure 8.9 (a) Surface morphology and (b) cross-section morphology of composite coatings on Mg-Zn-Ca alloy. (c) EDS mapping showing the presence of Ca in the outer layer, suggesting that the outer layer is HA.

Reprinted from [Gao, Guan, et al. \(2011\)](#) with permission from Elsevier.

that HA appears in the form of nanorods. This duplex coating remarkably decreased the corrosion current by about three orders of magnitude and ennobled the corrosion potential by more than 100 mV in SBF. Immersion in SBF also promoted the formation of nanoflakes of HA from nanorods, revealing a phenomenon of biomineralization by precipitation of calcium phosphates. This phenomenon was reported only for HA nanorods.

A similar study by [Sreekanth & Rameshbabu \(2012\)](#) also showed the improvement of biodegradation resistance in PEO-coated AZ31 Mg alloy by the electrodeposition of HA. However, HA can also be derived from calcium phosphate coating, even by immersion in SBF. [Liu, Hu, Ding, and Wang \(2011\)](#) formed a PEO coating on pure Mg samples and a calcium phosphate layer was formed by a chemical method (calcification). X-ray crystallography revealed that the duplex coating was composed of a mixture of HA, dicalcium phosphate dehydrate (DCPD) and MgO. In a later study, Liu et al. reported the influence of the deposition temperature. At low temperatures, the previously mentioned mixture is formed, whereas at higher temperature (67 °C) mainly the formation of HA is observed ([Liu, Tang, Li, & Hu, 2014](#)).

After immersion of the duplex-coated Mg in SBF for 147 h, large flake-like structures of dicalcium phosphate dihydrate possibly dissolved in SBF and the fine porous structure was changed to needle-like structures of HA ([Liu et al., 2011](#)). Longer immersion times in SBF confirmed the already observed change of the coating. The authors called the change from the original HA/DCPD coating to bonelike apatite ‘self-adjustment’, which should result in better corrosion resistance as well ([Liu et al., 2014](#)). A PEO coating containing dicalcium phosphate dihydrate was also formed when PEO treatment was carried out in an electrolyte containing EDTA-Ca with subsequent hydrothermal treatment of the coating at low temperature. However, high-temperature hydrothermal treatment led to filling of the discharge channels and densification of the coating accompanied with disappearance of the dihydrate. Potentiodynamic polarization measurements of the hydrothermally treated coating showed a remarkable decrease in anodic current in Hank’s solution over a wide range of polarized potential ([Chang, Tian, Liu, & Duan, 2013](#)). In contrast, [Zhang, Ma, Chen, and Wei \(2013\)](#) have produced Ca-P coatings on Mg-Zn-Zr alloy using a three-step process, consisting of anodizing, pre-phosphatizing (5 h, 37 °C, saturated Na₂HPO₄ solution) and deposition of Ca-P coating (up to 48 h, 70 °C, solution of Na₂HPO₄·12H₂O + Ca(NO₃)₂·4H₂O). Compared with direct deposition, anodizing as the pretreatment followed by pre-phosphatizing makes the Ca-P coating denser and the binding force with the Mg alloy increases remarkably, while the corrosion potential shifts to higher values.

As demonstrated by Lin et al., posttreatment with HF (dipping for 48 h, 30 °C, 48 wt% HF) can be another option to seal or modify an MAO coating on a biodegradable magnesium alloy ([Lin, Tan, Wan, et al., 2013](#)). After the treatment, the porous structure of the MAO coating disappeared, and magnesium fluoride became the main component of the coating. The wear resistance was not affected much. A slightly reduced corrosion resistance was observed, but the initial alkalization effect of the MAO coating was well controlled; thus, no haemolysis took place for the HF-treated MAO coating.

Another option to increase the corrosion resistance and reduce the degradation rate is the combination of PEO coatings with polymer coatings. The combination of a PEO coating and a polyether imide (PEI) top-coat improved the corrosion resistance in 0.1 M NaCl solution (electrochemical impedance spectroscopy, EIS) and salt spray (5% NaCl) remarkably (Srinivasan, Scharnagl, Blawert, & Dietzel, 2010). However, corrosion tests in physiological solutions have not been performed yet. An interesting feature for biomedical applications is the controlled and adjustable degradation behaviour of this PEI polymer over a wide range (Scharnagl & Blawert, 2013b); thus, biodegradation should be still available for the whole coating system.

Chitosan can be also used for successful sealing of MAO coatings on Mg-Zn-Ca alloys. The sealing is obtained by a 5-min dipping of the MAO specimen in a chitosan solution (1% chitosan dissolved in 1 wt% acetic acid) and subsequent drying at room temperature. The duplex treatment reduces the corrosion current density in SBF by nearly three orders of magnitude compared to the uncoated alloy (Bai et al., 2012). An example for the combination of MAO and multilayers composed out of subsequent layers of chitosan and polystyrene sulfonate was given by Liu, Pan, Yang, Cai, and Chen (2012). With duplex treatment, the corrosion resistance of the WE43 alloy in SBF could be significantly increased.

8.6 Performance of PEO coatings in biomedical applications

In actual human physiological environments, orthopaedic implants and cardiovascular stents are under mechanical stress and are subject to corrosion and wear. Even if the main mechanical properties are generally provided by the substrate, the biomedical coatings should have adapted mechanical properties; for example, they should be able to follow the strain of the magnesium substrate without failure, protect the substrate for a certain time and also be biodegradable. The PEO coatings' morphology and composition can be controlled over a wide range; thus, the properties can be fine-tuned to offer reasonable mechanical strength, wear and corrosion resistance. Therefore, they have a high potential for biomedical applications. However, characterization of PEO coatings in *in-vivo* environments is still limited. This section gives a general overview of recent studies of *in vitro* and *in vivo* performances of PEO-coated magnesium alloys.

8.6.1 Mechanical properties

Mg alloys have excellent mechanical properties for application as implants in load-bearing parts of the body, such as the human tibia. The fracture toughness of Mg alloys is higher than that of ceramic biomaterials, and the elastic modulus and compressive yield strength of magnesium are closer to those of natural bone than other metallic implants. Thus, Mg alloys help to reduce or avoid the 'stress shielding effect'—a factor that reduces the stimulation of new bone growth (Staiger et al., 2006). To endure the stress during movement of bones, PEO-coated Mg alloys should have similar

mechanical properties to that of substrate alloys. PEO coatings are formed due to the conversion of metallic substrates into oxide, so there is strong adhesion of the coating with substrate. The average compressive stress in human tibia is about 4.047 ± 0.217 MPa (Fukubayashi & Kurosawa, 1980; Wang Fei, 2006). PEO coatings are hard enough to resist compressive stress. However, degradation properties may be different under stress. Wang, Gao, Wang, Zhu, and Guan (2012) studied the biodegradation of a PEO-coated cast Mg alloy under compressive stress in Kokubo's SBF and found that the applied compressive stress changed the degradation mode of coated samples. The applied stress caused certain peeling-off locations on the coating, and continuous increase of pH value demonstrated faster degradation of the coating under stress. However, precipitation of Ca-P salts inside the micropores and on the surface of coated samples bearing stress was still observed, suggesting that the coating still had protective and osteoconductive abilities.

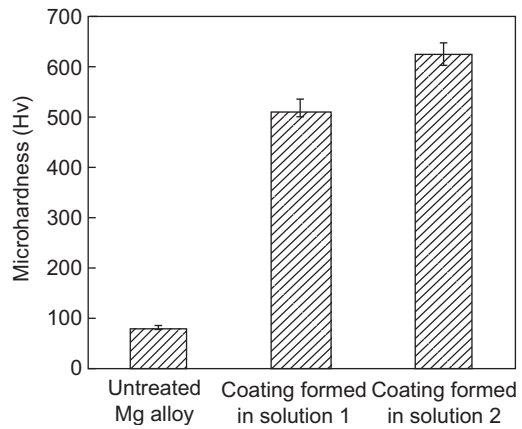
The effect of a PEO coating on the strength retention of *in vivo* and *in vitro* degraded magnesium implants (WE43) was studied by Imwinkleried, Beck, Iizuka, and Schaller (2013). The difference in strength retention of coated and noncoated implants was most pronounced after 12 weeks and vanished with longer implantation times. The authors found that approximately 80% of the strength was retained at 12 weeks of implantation, which should allow a stable fracture fixation during the period typically needed for fracture healing. Another study reported by Xia, Zhang, Lu, and Geng (2013) came to similar conclusions. In spite of the loss of corrosion resistance and loss of strength of PEO-coated Mg–4.0Zn–0.2Ca alloy after 30 days of immersion in SBF, its mechanical integrity was still judged to be enough for bone fixtures.

However, under bending load conditions, PEO coatings are also exposed to tensile stresses. Coatings may crack if they cannot follow the strain of the substrate. However, SCC (stress corrosion cracking) experiments with PEO-coated Mg alloys in very mild chloride containing test solutions (ASTM D1384 solution) have demonstrated that the coatings may crack, but they do not severely flake off and they do improve the SCC resistance compared to the uncoated alloy (Bala Srinivasan, Blawert, & Dietzel, 2008; Srinivasan, Blawert, Dietzel, & Kainer, 2008).

If the coatings are exposed to alternating loads, the fatigue properties are important. Unfortunately, there is no information available on the performance in physiological solutions. The performance of PEO-coated magnesium alloys in air and in technological chloride solutions suggests that the performance is similar compared to uncoated material as long as the coatings are not too thick (<20 μm). For more information, see the review by Blawert et al. (2006).

PEO coatings are normally composed of hard crystalline oxides. Therefore, PEO coatings are highly resistant to mechanical wear. The wear properties of PEO coatings are also controlled by the microstructure of the coatings. There are several reports about the characterization of mechanical (wear) properties and microstructure of PEO coatings formed on Mg alloys for industrial and biomedical applications. The hardness of PEO-coated Mg alloys is controlled by crystalline phases present in the coatings, which in turn can be controlled by processing parameters, electrolytes and substrate composition. Liang et al. (2005b) fabricated PEO coatings in alkaline silicate electrolyte with and without KF; they found that the microhardness of the coating is

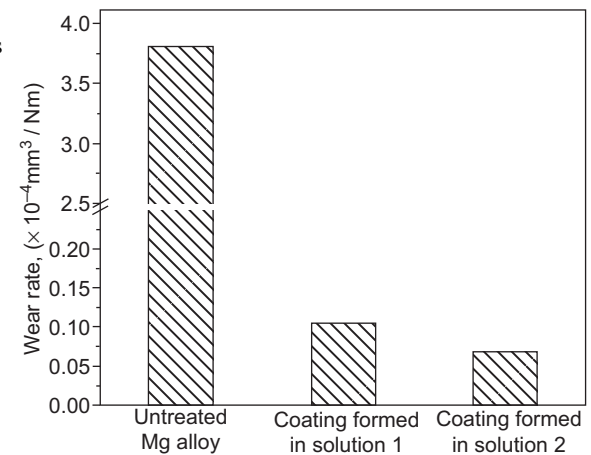
Figure 8.10 Microhardness of Mg alloy substrate and PEO coatings formed in different solutions. Reprinted from [Liang et al. \(2005b\)](#) with permission from Elsevier.



higher for the PEO coating formed with KF addition ([Figure 8.10](#)). The higher microhardness may be due to the formation of dense microstructure and crystalline MgF_2 phases in the coating. The wear rate for the coating formed in the electrolyte containing fluoride is lower, and the reason should be the formation of additional crystalline phases ([Figure 8.11](#)). Wear resistance of PEO coating formed in silicate electrolyte is higher than that formed in phosphate electrolyte, which is related to the higher hardness of the silicate-based coating ([Rapheal, Kumar, Blawert, & Dahotre, 2011](#)).

Finally, the knowledge about the influence of PEO coatings on the mechanical properties of Mg alloys under *in vitro* and *in vivo* test conditions is still quite limited. The tests available suggest that the performance is at least better than the performance of the uncoated alloys and sufficient for certain applications, such as fracture fixation.

Figure 8.11 Wear rates of Mg alloy substrate and PEO coatings formed in different solutions. Reprinted from [Liang et al. \(2005b\)](#) with permission from Elsevier.



However, alternating loads and fatigue properties have not been studied to the knowledge of the authors and are still a concern.

8.6.2 Corrosion/biodegradation

Mg is a highly electropositive metal and is readily corroded in aqueous medium containing chloride ions. In body fluids, there is a considerable amount of chloride ions and magnesium is easily corroded. In an early test of magnesium as a biomaterial, [Lambotte \(1932\)](#) reported that Mg corroded too rapidly *in vivo*, leading to complete disintegration within 8 days and producing a significant amount of gas beneath the skin. Such a fast disintegration of Mg led to failure of the fracture healing and a significant amount of gas liberated at the detached implant/tissue interface, which further hindered fracture healing. PEO coatings have the potential to control the degradation rate of the substrate. Corrosion of PEO-coated Mg alloys is controlled by the micro-structure and composition of the coating. There are several reports about the biodegradation of PEO-coated Mg alloys.

[Zhang, Zhao, Wu, Wang, and Wu \(2007\)](#) reported that the degradation and hydrogen evolution in Hank's solution was significantly suppressed by PEO coating of AZ91D alloys. Electrochemical polarization showed that open-circuit potential shifted significantly to the positive direction by PEO coating, showing significant passivation by the coating ([Figure 8.12](#)). The corrosion current of the alloy was dramatically decreased by five orders of magnitude due to the PEO coating. However, the PEO coating degraded just after immersing the coated sample for 1 day in Hank's solution because the coating was porous. [Lin, Tan, Zhang, et al. \(2013\)](#) produced PEO coatings at different voltages of 230, 300, 370 and 450 V on ZK60 Mg alloys in

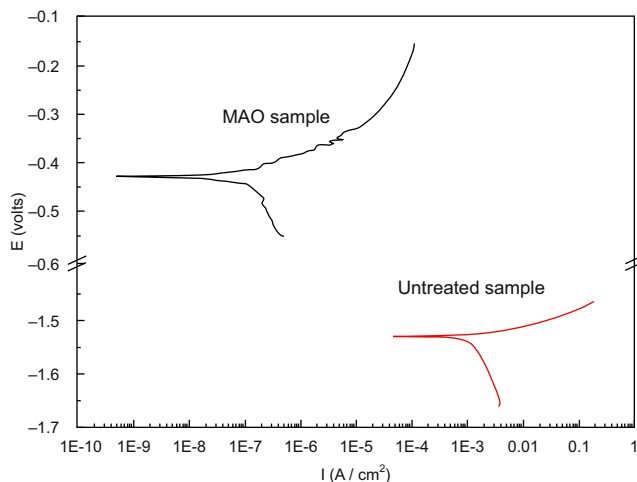


Figure 8.12 Polarization curves for PEO-treated sample and untreated one (potential measured against saturated Hg-Hg₂Cl₂ electrode).

Reprinted from [Zhang et al. \(2007\)](#) with kind permission from Springer Science and Business Media.

alkaline silicate-fluoride electrolyte. PEO coatings with different microstructures were identified, but only the coating formed at 450 V was highly dense and uniform and showed the best corrosion protection. However, after immersion of this coating for 1 month in Hank's solution, several voids appeared in the coating, and formation of these voids might be due to dissolution of MgO.

Therefore, further improvement in PEO coating composition and microstructure is required to decrease the degradation rate of PEO-coated Mg alloys. Most of the PEO coatings contain MgO as a major phase, and MgO is unstable in aqueous medium. Therefore, replacing or reducing the content of MgO would be a strategy to slow down the degradation if required. This can be achieved by modifying the electrolyte for PEO, producing other phases that are supposed to be more biocompatible.

PEO coating containing CaSiO_3 was formed in alkaline silicate electrolyte with different concentrations of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ at different constant voltage modes. The pore density and morphology of coatings largely changed with varying concentrations of phosphate as well as the magnitude of constant voltage, as shown in [Figure 8.13](#). Increasing the concentration of the phosphate is effective in enhancing the coating growth rate and reducing the pore density. The coating formed in the electrolyte containing 15 g/l phosphate at 500 V showed the lowest biodegradation over 4 weeks of immersion in SBF ([Wang et al., 2013](#)). [Tang and Wang \(2013\)](#) reported that a CaTiO_3 -based PEO coating can be formed on AZ31 magnesium alloys by using an electrolyte consisting of sodium hydroxide NaOH (6 g/L), potassium fluorotitanate K_2TiF_6 (4 g/L) and calcium glycerophosphate $\text{C}_3\text{H}_7\text{O}_6\text{PCa}$ (6 g/L). The PEO coating containing bioactive and biocompatible CaTiO_3 significantly suppressed the biodegradation rate of the alloy substrate. Additionally, a uniform layer containing spherical particles with a high potential to form apatite was observed on the coating surface after biocorrosion (7 days of exposure to SBF). It was reported that the formation of this layer could enhance the biocompatibility of the coated Mg alloy.

An electrochemical corrosion study (pot.-dyn. polarization and EIS) of the performance of a pulsed constant current silicate-based PEO coating on pure Mg in simulated body fluid revealed the much better corrosion performance compared to the uncoated specimen ([Alabbasi, Bobby Kannan, Walter, Störmer, & Blawert, 2013](#)). The coating is composed out of a thin dense inner layer, which offers the main corrosion resistance, and a thick porous outer layer. Postdegradation analysis and similar breakdown potential observed in the potentiodynamic polarization curves of the uncoated and the PEO-coated magnesium suggest that the porous outer layer has stabilized the inner compact layer, most likely by inhibiting the free flow of aggressive ions towards the inner layer by promoting precipitation ($\text{Mg}_2\text{PO}_4\text{OH}$ and $\text{Ca}_3(\text{PO}_4)_2$) on the porous layer surface.

However, the performance depends very much on the open porosity. Sealing is required if the lifetime of PEO coatings in physiological solutions should be extended and the dissolutions should be retarded or slowed down. Sealing treatments can always be considered as duplex treatments, and possible improvements have already been discussed. However, one should keep in mind that the various sealing techniques available have to be carefully selected for the intended application to obtain the best performance. Chu et al. have tested the degradation behaviour in SBF and simulated

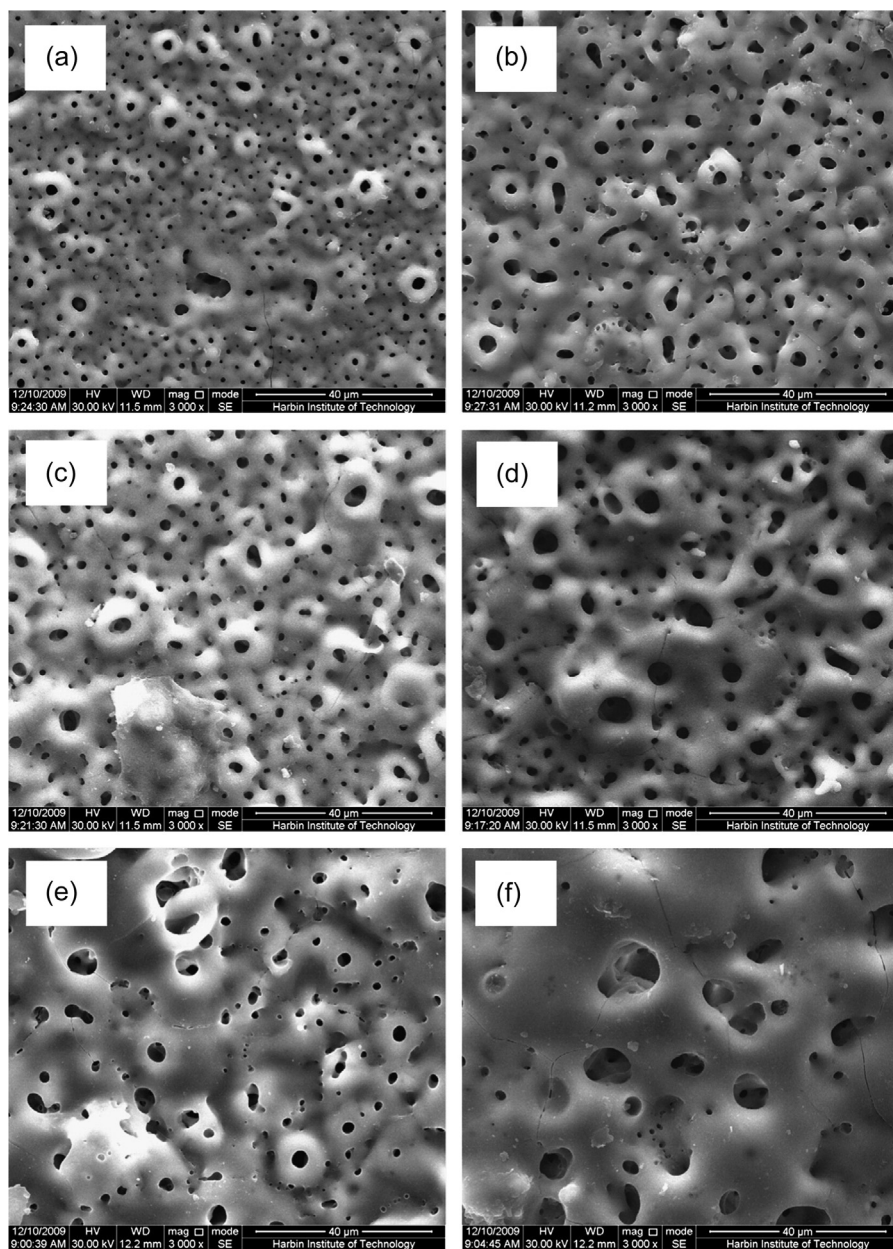


Figure 8.13 Surface morphologies of coatings formed on AZ91D alloy with different $\text{Ca}(\text{H}_2\text{PO}_4)_2$ concentration and various applied voltages: (a) Si-Ca5 @ 450 V; (b) Si-Ca5 @ 500 V; (c) Si-Ca10 @ 450 V; (d) Si-Ca10 @ 500 V; (e) Si-Ca15 @ 450 V and (f) Si-Ca15 @ 500 V.

Reprinted from [Wang et al. \(2013\)](#) with permission from Elsevier.

intestinal fluid (SIF) of three different sealing treatments on MAO medical magnesium alloy wires using boiling water, zirconia sol–gel and organic gelatin–hydroxyapatite coatings. Only those two coatings involving boiling water and gelatin–HA coating can effectively close the MAO discharge channels on the MAO Mg alloy wires. However, the overall best result was obtained from the samples with gelatin–HA coatings. In both SIF and SBF, the gelatin–HA coating can significantly retard the degradation rate and improve the corrosion resistance (Chu, Han, Xue, Bai, & Chu, 2013).

For *in vitro* testing, the results of PEO-coated specimens depend very much on the composition of the test solution, which was demonstrated by the work of Wan et al. (2013). In their study, the plasma electrolytic oxidation coated magnesium (silicate-based coating produced in an electrolyte of 10 g/L $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ + 8 g/L $\text{KF} \cdot 2\text{H}_2\text{O}$ + 1 g/L KOH) was immersed in four different simulated body fluids at 37 °C: NaCl (0.9 wt%), phosphate buffered saline (0.14 M NaCl + 1 mM KH_2PO_4 + 3 mM KCl + 10 mM Na_2HPO_4 at a pH = 7.4), and each with the addition of albumin to investigate the influence of protein and inorganic ions on the degradation behaviour of the coating. The degradation behaviour was determined by electrochemical methods. The results of the tests showed that aggressive corrosion took place in the NaCl solution, whereas albumin can act as an inhibitor and its adsorption impeded further dissolution of the coating. The mechanism was attributed to the synergistic effect of protein adsorption and precipitation of insoluble salts (phosphates).

8.6.3 Biocompatibility

Magnesium alloys are generally considered to be biocompatible; however, the local pH increase during degradation of Mg alloys causes inflammation, thrombogenic reactions and toxicity to cells (Delva, 2003; Gao, Shi, et al., 2011). Therefore, control of both corrosion and the resulting pH is necessary to enhance the biocompatibility of Mg alloys. Thus, the deposition of PEO coating, which controls corrosion via its microstructure and composition, would have direct impact on the biocompatibility of Mg alloys. Recently, Jo, Hong, Shin, Kim, and Koh (2012) observed that PEO-coated pure Mg has the highest cell attachment, cell proliferation, cell differentiation and biodegradation resistance compared with bare and anodized Mg after a posttreatment was performed. The posttreatment consisted of simple immersion of the specimens into the cell culturing medium to dissolve all unstable phases from the coatings. The enhanced biocompatibility of PEO-coated Mg should be due to higher coating thickness (revealed from reduced substrate peaks in the XRD pattern) and roughness.

However, mainly MgO-based PEO coating does not offer corrosion resistance for the long term, as would be suitable for biomedical applications. Recently, forsterite (Mg_2SiO_4), a bioceramic-based PEO coating, was formed on ZK60 magnesium alloy and its detailed biological performance was studied (Yang, Li, et al., 2013). *In vitro* biocompatibility/bioactivity evaluation of the PEO-coated alloy in comparison with the naked alloy was performed using murine bone marrow stem cells (BMSCs). The results revealed that the extract of PEO-coated alloy had no obvious cytotoxicity during the 5 days of culturing, and the surface of the PEO coating exhibited better cell

adhesion and affinity. Alkaline phosphatase (ALP) activity assay, a test to show cell differentiation, demonstrated that the ALP level of the BMSCs in the extract of PEO-coated alloy was much higher than that of the naked alloy, indicating that the release of Mg and Si ions from the coating was beneficial for the differentiation of BMSCs. Additionally, a hemolysis test showed that the PEO-coated alloy group drastically decreased the hemolytic ratio compared with the naked alloy group, indicating a great improvement of hemocompatibility. The better biocompatibility of this PEO coating could be due to the reduced degradation rate, higher surface roughness and porosity, as well as its biocompatible coating composition that mainly contains Mg, Si and O.

However, the biocompatibility of PEO-coated Mg alloys can be improved in various ways. One option is the intended integration of elements enhancing the bioactivity of the coating directly. This approach was followed by [Lin et al. \(2014\)](#). Strontium (Sr) was incorporated into the coating in order to improve bioactivity. The *in vitro* degradation studies showed that the MAO coating containing Sr had a better overall corrosion resistance and the *in vitro* cell tests demonstrated that the incorporation of Sr into the MAO coating enhanced both the proliferation of preosteoblast cells and the ALP activity of the murine bone marrow stromal cells. In the conclusion of the authors, the MAO coating with Sr is a promising surface treatment for biodegradable magnesium alloys.

Another option to improve biocompatibility is a duplex treatment of the selected Mg alloy. The effect of combining a PEO-coated Mg alloy with a propolis top layer on degradation and biocompatibility was studied by [Gao, Shi, et al. \(2011\)](#). It was found that the composite layer of PEO-coating and propolis layer remarkably enhanced the corrosion resistance of the alloy. The higher biocompatibility of composite coating was determined by observing the surface morphology after tissue culture of 24 h. Cells grew well and more branches appeared on composite coating than on the only PEO-coated sample, confirming the lesser toxicity of the composite coating ([Figure 8.14](#)). The biocompatibility was further assessed by MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay, and it was pointed out that the higher biocompatibility is due to a suppressed corrosion rate and the antibiotic and acidic nature of propolis.

From the results above, it appears as if the reduced degradation rate compared to naked magnesium alloys is the main issue that improves the biocompatibility. Nevertheless, further improvements should be possible by fine-tuning the composition and surface morphology of the coatings.

8.6.4 *In vivo* testing

To assess the *in vivo* degradation of PEO-coated Mg alloys, microfocus computed tomography (μ CT) is often used. [Fischerauer et al. \(2013\)](#) employed μ CT to study the biocorrosion of PEO-coated ZX50 Mg alloys. Machined cylindrical ZX50 Mg alloy pins were PEO-treated using the MAGOXID-COAT[®] process. Twenty PEO-coated pins as test samples and 20 untreated pins as controls were implanted in the femoral bones of 25-week-old Sprague–Dawley rats with a body weight of 140–160 g. Each rat was implanted with two identical pins. The degradation performance of

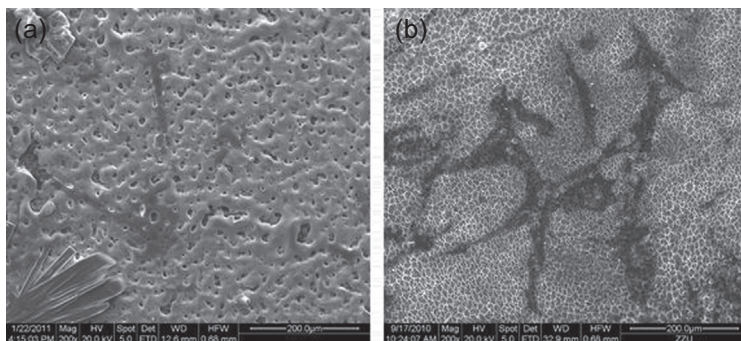


Figure 8.14 The typical WJCs morphologies of all the materials seeded with a density of 1×10^4 /disk and cultured for 48 h. (a) The typical SEM image of MAO coating and (b) the typical SEM image of composite coatings.

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PEO-coated ZX50 pins and untreated ZX50 control implants in rat femurs and their influence on living tissue was assessed in this study by means of μ CT measurements and histological analysis. The μ CT study demonstrated that PEO-treated samples showed almost no corrosion in the first week, but they revealed an accelerated degradation rate after the third week—even faster than that of the untreated ZX50 implants ([Figure 8.15](#)). This increased degradation might be due to localized corrosion. The histological analyses ([Figure 8.16](#)) showed that the initial improved corrosion resistance of the PEO implants has a positive effect on bone and tissue response. The reduced hydrogen evolution by the coating allowed increased osteoblast apposition from the very beginning and thus generated a stable bone/implant interface, which was considered to be responsible for fracture stabilization and healing.

A similar enhanced *in vivo* degradation of PEO-coated ZK60 alloy (forsterite-based coating) prepared in an electrolyte composed out of 10 g/L $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ + 1 g/L KOH and 8 g/L $\text{KF} \cdot 2\text{H}_2\text{O}$ was also observed by [Lin, Tan, Wang, et al. \(2013\)](#).

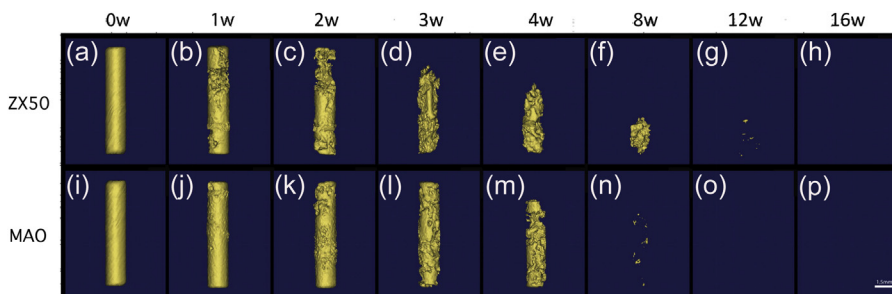


Figure 8.15 μ CT images (3-D reconstruction) of implanted ZX50 (a–h) and MAO (i–p) pins. The pins degrade over time and vanish completely after 12–16 weeks.

Reprinted from [Fischerauer et al. \(2013\)](#) with permission from Elsevier.

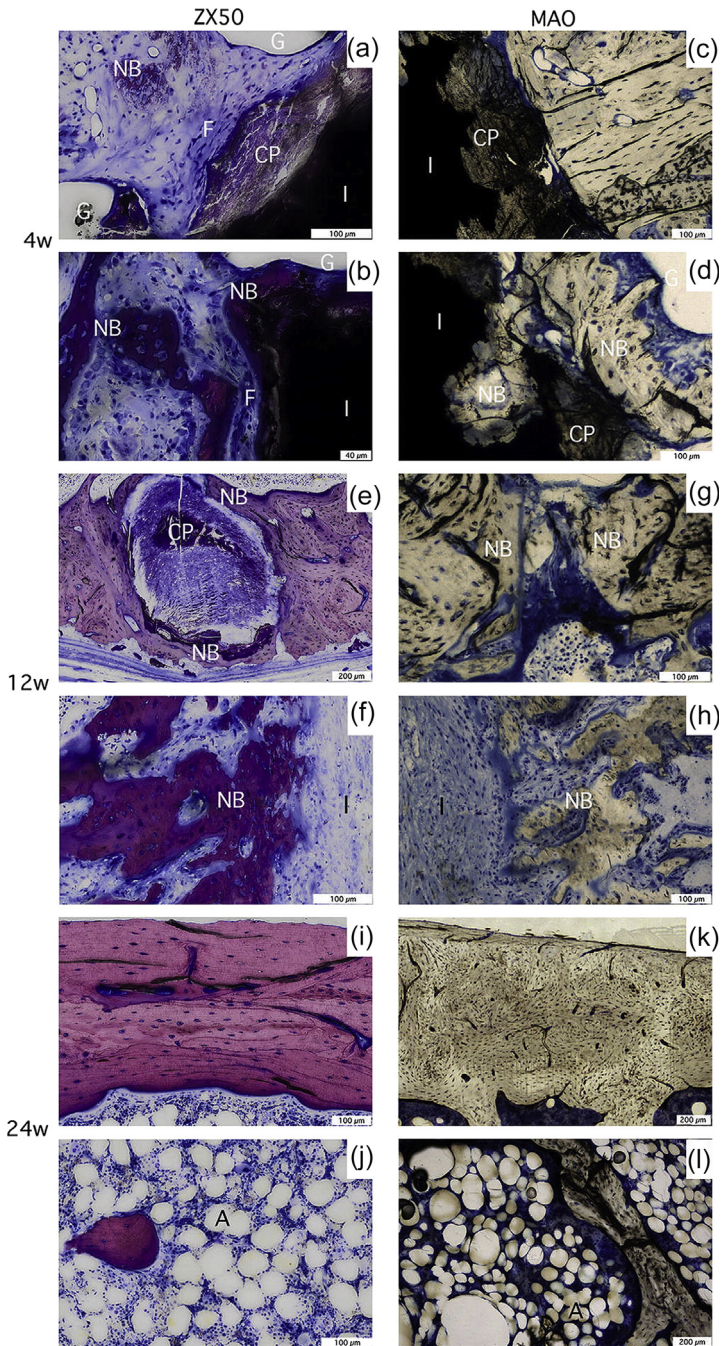


Figure 8.16 Histological thin slides of ZX50 and MAO pins in Levai-Laczko staining for ZX50 samples (left) and Toluidine Blue O for the MAO implants (right). Situation after 4 weeks (a–d), 12 weeks (e–h) and 24 weeks (i–l). I = implant/initial implant site, CP = corrosion products, G = hydrogen gas bubble, NB = new bone formation, F = fibroblast band, A = adipocytes. Reprinted from [Fischerauer et al. \(2013\)](#) with permission from Elsevier.

A transcortical model in rabbits was used to study the *in vivo* degradation behaviours and biological compatibilities of ZK60 alloys with and without MAO treatment. The implant and the surrounding bone tissues were characterized by CT, SEM and histological methods at 2, 4 and 12 weeks after the implantation. The results revealed that both the bare and MAO-coated ZK60 alloys completely degraded within 12 weeks in this animal model. Within the first 2 weeks, the MAO coating decreased the degradation rate of ZK60 alloy and enhanced the response of the surrounding tissues; after that, an acceleration of the degradation of the MAO-coated ZK60 alloy was observed. It was found that the alloy could be degraded before the complete degradation of the MAO coating, leading to local peeling-off of the coating without much dissolution of the coating. The conclusion of the authors was that although promising for biomedical application, the ZK60 alloy degrades too fast in the transcortical model to meet the clinical requirement. The present forsterite-containing MAO coating could protect the substrate in the short term, but the long-term protective ability should be further improved.

The lack of long-term corrosion resistance of PEO coatings was also realized in the study of [Imwinkelried et al. \(2013\)](#). The strength decrease of magnesium implants produced from WE43 alloy was studied *in vitro* and *in vivo*, with and without a protective PEO coating. *In vivo*, degradation was examined by implanting rectangular plates on top of the nasal bone of miniature pigs; after 12 and 24 weeks of *in vivo* degradation, the large rectangular plates were removed and mechanically tested in three-point bending. *In vitro*, identical plates were immersed in simulated body fluid for 4, 8 and 12 weeks. The results revealed that the coating did not prevent degradation, but it was effective in delaying gas release and in improving the formation of calcium phosphate at the implant surface. Altogether, the *in vivo* degradation was about four times slower than that observed during static immersion in SBF. However, despite the slow degradation, the formation of gas pockets in the overlying soft tissue could not be avoided. According to the authors, uniformity of degradation and reliable strength retention (approximately 80% after 12 weeks implantation) make this alloy a prime candidate for the use of magnesium in craniomaxillofacial surgery.

As already mentioned, the *in vivo* corrosion resistance of PEO coatings can be further enhanced by duplex treatments. [Chen et al. \(2012\)](#) produced a PEO coating on Mg-Zn-Ca alloy and deposited a thin layer of HA by electrodeposition on top of it. The *in vivo* degradation behaviour and a detailed osteogenesis were studied by μ CT, radiography, fluorescence microscopy, electron microscopy and energy-dispersive X-ray spectroscopy. It was found that a void, probably filled with hydrogen gas, developed between the bone and untreated Mg alloy ([Figure 8.17](#)). Significant lymphocytic infiltration ([Figure 8.18](#)) showed troubled healing of the bone fracture. However, no voids were observed at the duplex coating/bone interface. Additionally, the absence of lymphocytic and plasmablastic inflammations showed that fracture healing occurred successfully due to the duplex-coated Mg alloy. Therefore, corrosion-resistant coatings are considered to be useful for implant applications.

The *in vivo* tests are still very limited, but they clearly show that the PEO coatings can improve the initial degradation rate of the substrate material. Long-term protection

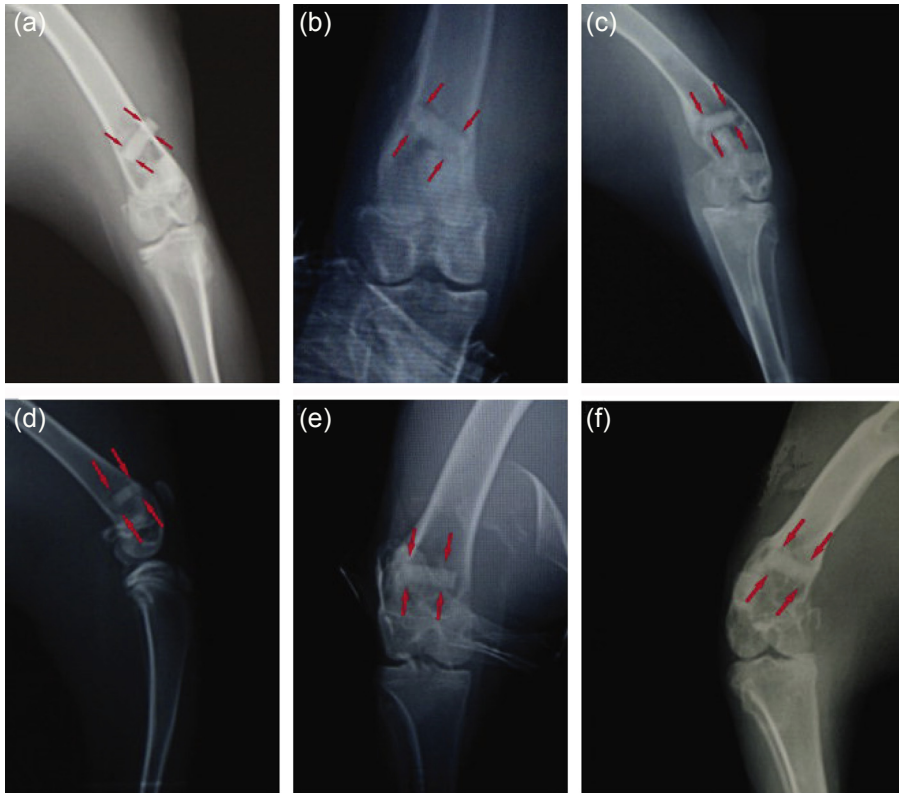


Figure 8.17 Radiographs of the substrates (a–c) and coated (d–f) samples at 1, 4 and 8 weeks, postoperatively.
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of single PEO coatings in the various models studied so far was not obtained, and effective sealing might be required for certain applications.

8.7 Applications

Up to now, a number of biomedical components have been treated successfully by PEO processes:

- biomedical magnesium alloy wires as PEO treated ([Chu, Han, Bai, Xue, & Chu, 2012](#)) and additionally sealed ([Chu et al., 2013](#));
- stents and other metallic supports ([Dong, Zhang, Xu, & Pu, 2008](#)); and
- bone screws ([Scharnagl & Blawert, 2013a](#)).

However, none of these components have made their way into commercial medical applications so far. This is not only because of their poor performance but also because

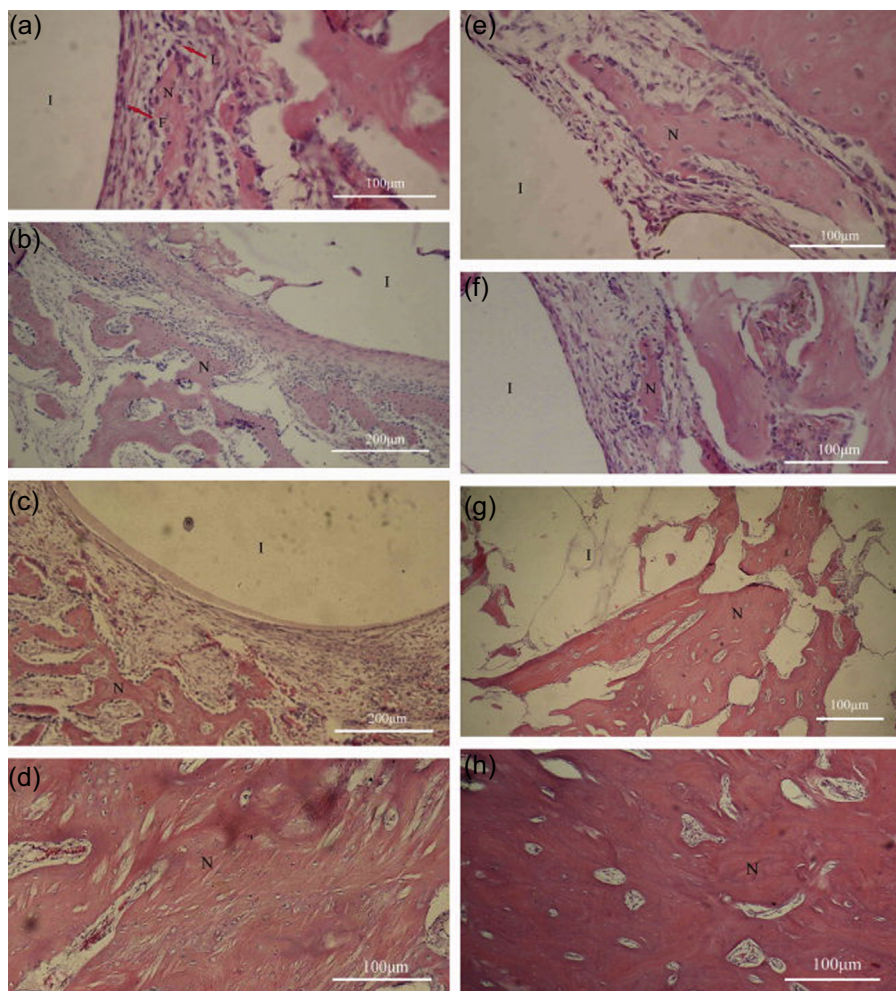


Figure 8.18 Histological photographs of the implant/bone interface around the substrates (a–d) and coated (e–h) samples at 8, 12, 18 and 50 weeks. I-implant, L-lymphocytic infiltration, F-fibroblast band, N-new bone tissue.

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of the relatively short time period that has occurred since intensive research in the PEO treatment of degradable magnesium components began. It is most likely that this will change in the future when more biospecific PEO coatings are designed.

8.8 Summary and conclusions

There is no question that PEO coatings have great potential for the surface treatment of magnesium-based degradable biomaterials. The properties and the

composition of the coatings can be tailored over a wide range so that the degradation can be adjusted and biocompatibility can be obtained. Coatings are available that have property profiles reaching from nearly inert to soluble. In the latter case, the degradation rate can be controlled by the phase composition and thickness. Good adhesion of the coatings to the substrate also allows their use in stress-loaded conditions. The relatively high hardness gives enough wear resistance to protect the relatively soft magnesium substrate from mechanical damage during implantation or during the final use.

The current performance of stand-alone PEO coatings *in vivo* environments appears to not be good enough for long-term protection and requires further improvements. There are many unexplored options, ranging from electrolytes to processing modifications. However, the most promising approach appears to be the wide variety of duplex treatments, which can provide the required sealing of the PEO coating while the PEO coating provides good adhesion for the top-coat.

However, the main problems for use in biomedical applications appear to be the missing standard for PEO coatings and the varying treatment results depending on the power supply, electrolyte and processing parameters used to produce the coatings. On the other hand, there are no requirement specifications from the biomedical side on what composition and properties such a coating actually should have. Therefore, an increasing number of studies appear to be unfocussed, and it is impossible to give an outlook on what coating might make its way into an application, especially considering the strict regulations for medical approval. Currently, the full potential of PEO coatings does not even appear to be used. The open porosity of the coatings might be used as containers for drug delivery, where the release can be adjusted by biodegradable top coats. This also demonstrates the importance of duplex treatments. Combinations of PEO with other biodegradable coatings might be an option to extend the field of applications further. However, much more research is required to bring PEO coatings (stand-alone or duplex-treated/sealed) into biomedical application.

References

- Alabbasi, A., Bobby Kannan, M., Walter, R., Störmer, M., & Blawert, C. (2013). Performance of pulsed constant current silicate-based PEO coating on pure magnesium in simulated body fluid. *Materials Letters*, 106, 18–21.
- Albella, J. M., Montero, I., & Martinez-Duart, J. M. (1987). A theory of avalanche breakdown during anodic oxidation. *Electrochimica Acta*, 32, 255–258.
- Albrektsson, T., & Johansson, C. (2001). Osteoinduction, osteoconduction and osseointegration. *European Spine Journal*, 10, S96–S101.
- Aliofkhazraei, M., & Sabour Rouhaghdam, A. (2010). Fabrication of TiC/WC ultra hard nanocomposite layers by plasma electrolysis and study of its characteristics. *Surface and Coatings Technology*, 205(Suppl. 1), S51–S56.
- Arrabal, R., Matykina, E., Hashimoto, T., Skeldon, P., & Thompson, G. E. (2009). Characterization of AC PEO coatings on magnesium alloys. *Surface and Coatings Technology*, 203, 2207–2220.

- Arrabal, R., Matykina, E., Skeldon, P., & Thompson, G. E. (2008a). Incorporation of zirconia particles into coatings formed on magnesium by plasma electrolytic oxidation. *Journal of Materials Science*, 43, 1532–1538.
- Arrabal, R., Matykina, E., Viejo, F., Skeldon, P., Thompson, G. E., & Merino, M. C. (2008b). AC plasma electrolytic oxidation of magnesium with zirconia nanoparticles. *Applied Surface Science*, 254, 6937–6942.
- Baglin, J. E. E. (1988). Thin film adhesion: new possibilities for interface engineering. *Materials Science and Engineering: B*, 1, 1–7.
- Bai, K., Zhang, Y., Fu, Z., Zhang, C., Cui, X., Meng, E., et al. (2012). Fabrication of chitosan/magnesium phosphate composite coating and the in vitro degradation properties of coated magnesium alloy. *Materials Letters*, 73, 59–61.
- Bala Srinivasan, P., Blawert, C., & Dietzel, W. (2008). Effect of plasma electrolytic oxidation treatment on the corrosion and stress corrosion cracking behaviour of AM50 magnesium alloy. *Materials Science and Engineering: A*, 494, 401–406.
- Bala Srinivasan, P., Blawert, C., Störmer, M., & Dietzel, W. (2010). Characterisation of tribological and corrosion behaviour of plasma electrolytic oxidation coated AM50 magnesium alloy. *Surface Engineering*, 26, 340–346.
- Bala Srinivasan, P., Liang, J., Blawert, C., Störmer, M., & Dietzel, W. (2009). Effect of current density on the microstructure and corrosion behaviour of plasma electrolytic oxidation treated AM50 magnesium alloy. *Applied Surface Science*, 255, 4212–4218.
- Blawert, C., Dietzel, W., Ghali, E., & Song, G. (2006). Anodizing treatments for magnesium alloys and their effect on corrosion resistance in various environments. *Advanced Engineering Materials*, 8, 511–533.
- Blawert, C., Sah, S. P., Liang, J., Huang, Y., & Höche, D. (2012). Role of sintering and clay particle additions on coating formation during PEO processing of AM50 magnesium alloy. *Surface and Coatings Technology*, 213, 48–58.
- Chandra, R., & Rustgi, R. (1998). Biodegradable polymers. *Progress in Polymer Science*, 23, 1273–1335.
- Chang, L., Tian, L., Liu, W., & Duan, X. (2013). Formation of dicalcium phosphate dihydrate on magnesium alloy by micro-arc oxidation coupled with hydrothermal treatment. *Corrosion Science*, 72, 118–124.
- Chen, S., Guan, S., Li, W., Wang, H., Chen, J., Wang, Y., et al. (2012). In vivo degradation and bone response of a composite coating on Mg–Zn–Ca alloy prepared by microarc oxidation and electrochemical deposition. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, 100B, 533–543.
- Chu, C. L., Han, X., Bai, J., Xue, F., & Chu, P. K. (2012). Fabrication and degradation behavior of micro-arc oxidized biomedical magnesium alloy wires. *Surface and Coatings Technology*, 213, 307–312.
- Chu, C. L., Han, X., Xue, F., Bai, J., & Chu, P. K. (2013). Effects of sealing treatment on corrosion resistance and degradation behavior of micro-arc oxidized magnesium alloy wires. *Applied Surface Science*, 271, 271–275.
- Davies, D., & Whittaker, J. A. (1967). Methods of testing the adhesion of metal coating. *Metallurgical Reviews*, 112, 12–15.
- Delva, P. (2003). Magnesium and heart failure. *Molecular Aspects of Medicine*, 24, 79.
- Dong, S., Zhang, Z., Xu, Y., & Pu, Z. (2008). *Biodegradable micro-arc oxidized metal stent and its preparation method*. CN101239009A.
- Duan, H., Yan, C., & Wang, F. (2007). Effect of electrolyte additives on performance of plasma electrolytic oxidation films formed on magnesium alloy AZ91D. *Electrochimica Acta*, 52, 3785–3793.

- Dunleavy, C. S., Golosnoy, I. O., Curran, J. A., & Clyne, T. W. (2009). Characterisation of discharge events during plasma electrolytic oxidation. *Surface and Coatings Technology*, 203, 3410–3419.
- Fischerauer, S. F., Kraus, T., Wu, X., Tangl, S., Sorantin, E., Hänzli, A. C., et al. (2013). In vivo degradation performance of micro-arc-oxidized magnesium implants: a micro-CT study in rats. *Acta Biomaterialia*, 9, 5411–5420.
- Fukubayashi, T., & Kurosawa, H. (1980). The contact area and pressure distribution pattern of the knee: a study of normal and osteoarthrotic knee joints. *Acta Orthopaedica*, 51, 871–879.
- Gao, J. H., Guan, S. K., Chen, J., Wang, L. G., Zhu, S. J., Hu, J. H., et al. (2011). Fabrication and characterization of rod-like nano-hydroxyapatite on MAO coating supported on Mg–Zn–Ca alloy. *Applied Surface Science*, 257, 2231–2237.
- Gao, J. H., Shi, X. Y., Yang, B., Hou, S. S., Meng, E. C., Guan, F. X., et al. (2011). Fabrication and characterization of bioactive composite coatings on Mg–Zn–Ca alloy by MAO/sol–gel. *Journal of Materials Science: Materials in Medicine*, 22, 1681–1687.
- Gao, Y., Yerokhin, A., & Matthews, A. (2013). DC plasma electrolytic oxidation of biodegradable cp-Mg: In-vitro corrosion studies. *Surface and Coatings Technology*, 234, 132–142.
- Gu, X. N., Li, N., Zhou, W. R., Zheng, Y. F., Zhao, X., Cai, Q. Z., et al. (2011). Corrosion resistance and surface biocompatibility of a microarc oxidation coating on a Mg–Ca alloy. *Acta Biomaterialia*, 7, 1880–1889.
- Gu, Y., Bandopadhyay, S., Chen, C.-F., Guo, Y., & Ning, C. (2012). Effect of oxidation time on the corrosion behavior of micro-arc oxidation produced AZ31 magnesium alloys in simulated body fluid. *Journal of Alloys and Compounds*, 543, 109–117.
- Gu, Y., Chen, C.-F., Bandopadhyay, S., Ning, C., Zhang, Y., & Guo, Y. (2012). Corrosion mechanism and model of pulsed DC microarc oxidation treated AZ31 alloy in simulated body fluid. *Applied Surface Science*, 258, 6116–6126.
- Guo, H. F., & An, M. Z. (2005). Growth of ceramic coatings on AZ91D magnesium alloys by micro-arc oxidation in aluminate–fluoride solutions and evaluation of corrosion resistance. *Applied Surface Science*, 246, 229–238.
- Guo, J., Wang, L., Wang, S. C., Liang, J., Xue, Q., & Yan, F. (2009). Preparation and performance of a novel multifunctional plasma electrolytic oxidation composite coating formed on magnesium alloy. *Journal of Materials Science*, 44, 1998–2006.
- Guo-Hua, L., Huan, C., Xing-Quan, W., Hua, P., Gu-Ling, Z., Bin, Z., et al. (2010). Characteristics of sealed plasma electrolytic oxidation coatings with electrochemical impedance spectroscopy. *Chinese Physics B*, 19, 085202. <http://dx.doi.org/10.1088/1674-1056/19/8/085202>.
- Gupta, B. K., Kulshrestha, S., & Agarwal, A. K. (1987). Friction and wear behavior of ion-plated lead–tin coatings. *Journal of Vacuum Science & Technology A*, 5, 358–363.
- Hickling, A., & Ingram, M. D. (1964). Contact glow-discharge electrolysis. *Transactions of the Faraday Society*, 60, 783–793.
- Hussein, R. O., Nie, X., & Northwood, D. O. (2010). Influence of process parameters on electrolytic plasma discharging behaviour and aluminum oxide coating microstructure. *Surface and Coatings Technology*, 205, 1659–1667.
- Hussein, R. O., Zhang, P., Nie, X., Xia, Y., & Northwood, D. O. (2011). The effect of current mode and discharge type on the corrosion resistance of plasma electrolytic oxidation (PEO) coated magnesium alloy AJ62. *Surface and Coatings Technology*, 206, 1990–1997.

- Ikonopisov, S. (1977). Theory of electrical breakdown during formation of barrier anodic films. *Electrochimica Acta*, 22, 1077–1082.
- Imwinkleried, T., Beck, S., Iizuka, T., & Schaller, B. (2013). Effect of a plasmaelectrolytic coating on the strength retention of in vivo and in vitro degraded magnesium implants. *Acta Biomaterialia*, 9, 8643–8649.
- Jaspard-Mécuson, F., Czerwicz, T., Henrion, G., Belmonte, T., Dujardin, L., Viola, A., et al. (2007). Tailored aluminium oxide layers by bipolar current adjustment in the plasma electrolytic oxidation (PEO) process. *Surface and Coatings Technology*, 201, 8677–8682.
- Jin, F., Chu, P. K., Tong, H., & Zhao, J. (2006). Improvement of surface porosity and properties of alumina films by incorporation of Fe micrograins in micro-arc oxidation. *Applied Surface Science*, 253, 863–868.
- Jo, J.-H., Hong, J.-Y., Shin, K.-S., Kim, H.-E., & Koh, Y.-H. (2012). Enhancing biocompatibility and corrosion resistance of Mg implants via surface treatments. *Journal of Biomaterials Applications*, 27, 469–476.
- Kowandy, C., Mazouz, H., & Richard, C. (2006). Isolation and analysis of articular joints wear debris generated in vitro. *Wear*, 261, 966–970.
- Krysmann, W., Kurze, P., Dittich, K. H., & Schneider, H. G. (1984). Process characteristics and parameters of anodic oxidation by spark discharge (ANOF). *Crystal Research and Technology*, 19, 973–979.
- Lambotte, A. (1932). L'utilisation du magnesium comme materiel perdu dans l'osteosynthèse. *Bulletins et Memoires de la Societe Nationale de Chirurgie*, 28, 1325–1334.
- Lee, K. M., Jo, J. O., Lee, E. S., Yoo, B., & Shin, D. H. (2011). Incorporation of carbon nanotubes into oxide layer on 7075 Al Alloy by plasma electrolytic oxidation. *Journal of The Electrochemical Society*, 158, C325–C328.
- Lee, K. M., Shin, K. R., Namgung, S., Yoo, B., & Shin, D. H. (2011). Electrochemical response of ZrO₂-incorporated oxide layer on AZ91 Mg alloy processed by plasma electrolytic oxidation. *Surface and Coatings Technology*, 205, 3779–3784.
- Liang, J., Guo, B., Tian, J., Liu, H., Zhou, J., Liu, W., et al. (2005a). Effects of NaAlO₂ on structure and corrosion resistance of microarc oxidation coatings formed on AM60B magnesium alloy in phosphate–KOH electrolyte. *Surface and Coatings Technology*, 199, 121–126.
- Liang, J., Guo, B., Tian, J., Liu, H., Zhou, J., & Xu, T. (2005b). Effect of potassium fluoride in electrolytic solution on the structure and properties of microarc oxidation coatings on magnesium alloy. *Applied Surface Science*, 252, 345–351.
- Lim, T. S., Ryu, H. S., & Hong, S.-H. (2012). Electrochemical corrosion properties of CeO₂-containing coatings on AZ31 magnesium alloys prepared by plasma electrolytic oxidation. *Corrosion Science*, 62, 104–111.
- Lin, X., Tan, L., Wan, P., Yu, X., Yang, K., Hu, Z., et al. (2013). Characterization of micro-arc oxidation coating post-treated by hydrofluoric acid on biodegradable ZK60 magnesium alloy. *Surface and Coatings Technology*, 232, 899–905.
- Lin, X., Tan, L., Wang, Q., Zhang, G., Zhang, B., & Yang, K. (2013). In vivo degradation and tissue compatibility of ZK60 magnesium alloy with micro-arc oxidation coating in a transcortical model. *Materials Science and Engineering: C*, 33, 3881–3888.
- Lin, X., Tan, L., Zhang, Q., Yang, K., Hu, Z., Qiu, J., et al. (2013). The in vitro degradation process and biocompatibility of a ZK60 magnesium alloy with a forsterite-containing micro-arc oxidation coating. *Acta Biomaterialia*, 9, 8631–8642.
- Lin, X., Yang, X., Tan, L., Li, M., Wang, X., Zhang, Y., et al. (2014). In vitro degradation and biocompatibility of a strontium-containing micro-arc oxidation coating on the biodegradable ZK60 magnesium alloy. *Applied Surface Science*, 288, 718–726.

- Liu, G. Y., Hu, J., Ding, Z. K., & Wang, C. (2011). Bioactive calcium phosphate coating formed on micro-arc oxidized magnesium by chemical deposition. *Applied Surface Science*, 257, 2051–2057.
- Liu, G. Y., Tang, S., Li, D., & Hu, J. (2014). Self-adjustment of calcium phosphate coating on micro-arc oxidized magnesium and its influence on the corrosion behaviour in simulated body fluids. *Corrosion Science*, 79, 206–214.
- Liu, P., Pan, X., Yang, W., Cai, K., & Chen, Y. (2012). Improved anticorrosion of magnesium alloy via layer-by-layer self-assembly technique combined with micro-arc oxidation. *Materials Letters*, 75, 118–121.
- Lu X, Sah, S.P., Scharnagl, N., Störmer, M., Sarykevich, M., Mohedano, M., Blawert, C., Zheludkevich, M.L., Kainer, K.U. Degradation behavior of PEO coating on AM50 magnesium alloy produced from electrolytes with clay particle addition. Submitted for publication to *Surface & Coatings Technology*.
- Lv, G., Gu, W., Chen, H., Feng, W., Khosa, M. L., Li, L., et al. (2006). Characteristic of ceramic coatings on aluminum by plasma electrolytic oxidation in silicate and phosphate electrolyte. *Applied Surface Science*, 253, 2947–2952.
- Malayoglu, U., Tekin, K. C., & Shrestha, S. (2010). Influence of post-treatment on the corrosion resistance of PEO coated AM50B and AM60B Mg alloys. *Surface and Coatings Technology*, 205, 1793–1798.
- Malyshev, V. N., & Zorin, K. M. (2007). Features of microarc oxidation coatings formation technology in slurry electrolytes. *Applied Surface Science*, 254, 1511–1516.
- Martin, J., Melhem, A., Shchedrina, I., Duchanoy, T., Nominé, A., Henrion, G., et al. (2013). Effects of electrical parameters on plasma electrolytic oxidation of aluminium. *Surface and Coatings Technology*, 221, 70–76.
- Matykina, E., Arrabal, R., Monfort, F., Skeldon, P., & Thompson, G. E. (2008). Incorporation of zirconia into coatings formed by DC plasma electrolytic oxidation of aluminium in nanoparticle suspensions. *Applied Surface Science*, 255, 2830–2839.
- Matykina, E., Arrabal, R., Skeldon, P., & Thompson, G. E. (2008). Incorporation of zirconia nanoparticles into coatings formed on aluminium by AC plasma electrolytic oxidation. *Journal of Applied Electrochemistry*, 38, 1375–1383.
- Matykina, E., Arrabal, R., Skeldon, P., & Thompson, G. E. (2009). Investigation of the growth processes of coatings formed by AC plasma electrolytic oxidation of aluminium. *Electrochimica Acta*, 54, 6767–6778.
- Matykina, E., Berkani, A., Skeldon, P., & Thompson, G. E. (2007). Real-time imaging of coating growth during plasma electrolytic oxidation of titanium. *Electrochimica Acta*, 53, 1987–1994.
- McNeill, W., & Nordbloom, G. F. (1958). US2854390.
- Monasky, G. E., & Taylor, D. F. (1971). Studies on the wear of porcelain, enamel, and gold. *Journal of Prosthetic Dentistry*, 25, 299–306.
- Monfort, F., Matykina, E., Berkani, A., Skeldon, P., Thompson, G. E., Habazaki, H., et al. (2007). Species separation during coating growth on aluminium by spark anodizing. *Surface and Coatings Technology*, 201, 8671–8676.
- Nair, L. S., & Laurencin, C. T. (2007). Biodegradable polymers as biomaterials. *Progress in Polymer Science*, 32, 762–798.
- Necula, B. S., Fratila-Apachitei, L. E., Berkani, A., Apachitei, I., & Duszczyk, J. (2009). Enrichment of anodic MgO layers with Ag nanoparticles for biomedical applications. *Journal of Materials Science: Materials in Medicine*, 20, 339–345.
- Němcová, A., Skeldon, P., Thompson, G. E., & Pacal, B. (2013). Effect of fluoride on plasma electrolytic oxidation of AZ61 magnesium alloy. *Surface and Coatings Technology*, 232, 827–838.

- Raj, V., & Mubarak Ali, M. (2009). Formation of ceramic alumina nanocomposite coatings on aluminium for enhanced corrosion resistance. *Journal of Materials Processing Technology*, 209, 5341–5352.
- Rapheal, G., Kumar, S., Blawert, C., & Dahotre, N. B. (2011). Wear behavior of plasma electrolytic oxidation (PEO) and hybrid coatings of PEO and laser on MRI 230D magnesium alloy. *Wear*, 271, 1987–1997.
- Rhalmi, S., Odin, M., Assad, M., Tabrizian, M., Rivard, C. H., & Yahia, L. H. (1999). Hard, soft tissue and in vitro cell response to porous nickel-titanium: a biocompatibility evaluation. *Bio-Medical Materials and Engineering*, 9, 151–162.
- Richard, C., Kowandy, C., Landoulsi, J., Geetha, M., & Ramasawmy, H. (2010). Corrosion and wear behavior of thermally sprayed nano ceramic coatings on commercially pure Titanium and Ti–13Nb–13Zr substrates. *International Journal of Refractory Metals and Hard Materials*, 28, 115–123.
- Sah, S.P.(2012). *Fundamental study of plasma electrolytic oxidation of light metals by single pulse technique* (Ph.D. thesis). Japan: Hokkaido University.
- Sah, S. P., Aoki, Y., & Habazaki, H. (2010). Influence of phosphate concentration on plasma electrolytic oxidation of AZ80 magnesium Alloy in alkaline aluminate solution. *Materials Transactions*, 51, 94–102.
- Sah, S. P., Tatsuno, Y., Aoki, Y., & Habazaki, H. (2011). Dielectric breakdown and healing of anodic oxide films on aluminium under single pulse anodizing. *Corrosion Science*, 53, 1838–1844.
- Sah, S. P., Tsuji, E., Aoki, Y., & Habazaki, H. (2012). Cathodic pulse breakdown of anodic films on aluminium in alkaline silicate electrolyte – understanding the role of cathodic half-cycle in AC plasma electrolytic oxidation. *Corrosion Science*, 55, 90–96.
- Sankara Narayanan, T. S. N., Park, I. S., & Lee, M. H. (2014). Strategies to improve the corrosion resistance of microarc oxidation (MAO) coated magnesium alloys for degradable implants: prospects and challenges. *Progress in Materials Science*, 60, 1–71.
- Scharnagl, N., & Blawert, C. (2013a). Funktionale Schichtsysteme - Verbesselter Schutz für Magnesiumoberflächen. *JOT, Journal für Oberflächentechnik*, 53, 28–30.
- Scharnagl, N., & Blawert, C. (2013b). *Method of treating a magnesium component*. EP2093308B1.
- Seyfoori, A., Mirdamadi, S., Seyedraoufi, Z. S., Khavandi, A., & Aliofkhazraei, M. (2013). Synthesis of biphasic calcium phosphate containing nanostructured films by micro arc oxidation on magnesium alloy. *Materials Chemistry and Physics*, 142, 87–94.
- Shi, D. (2005). *Introduction to biomaterials*. Tsinghu University Press, Word Scientific Publishing Co. Pte. Ltd., Beijingh.
- Shi, P., Ng, W. F., Wong, M. H., & Cheng, F. T. (2009). Improvement of corrosion resistance of pure magnesium in Hanks' solution by microarc oxidation with sol–gel TiO₂ sealing. *Journal of Alloys and Compounds*, 469, 286–292.
- Shimizu, K., Thompson, G. E., & Wood, G. C. (1982). The electrical breakdown during anodizing of high purity aluminium in borate solutions. *Thin Solid Films*, 92, 231–241.
- Song, Y. L., Sun, X. Y., & Liu, Y. H. (2012). Effect of TiO₂ nanoparticles on the microstructure and corrosion behavior of MAO coatings on magnesium alloy. *Materials and Corrosion*, 63, 813–818.
- Srekanth, D., & Rameshbabu, N. (2012). Development and characterization of MgO/hydroxyapatite composite coating on AZ31 magnesium alloy by plasma electrolytic oxidation coupled with electrophoretic deposition. *Materials Letters*, 68, 439–442.
- Srinivasan, P. B., Blawert, C., Dietzel, W., & Kainer, K. U. (2008). Stress corrosion cracking behaviour of a surface-modified magnesium alloy. *Scripta Materialia*, 59, 43–46.

- Srinivasan, P. B., Liang, J., Blawert, C., Störmer, M., & Dietzel, W. (2010). Characterization of calcium containing plasma electrolytic oxidation coatings on AM50 magnesium alloy. *Applied Surface Science*, 256, 4017–4022.
- Srinivasan, P. B., Scharnagl, N., Blawert, C., & Dietzel, W. (2010). Enhanced corrosion protection of AZ31 magnesium alloy by duplex plasma electrolytic oxidation and polymer coatings. *Surface Engineering*, 26, 354–360.
- Staiger, M. P., Pietak, A. M., Huadmai, J., & Dias, G. (2006). Magnesium and its alloys as orthopedic biomaterials: a review. *Biomaterials*, 27, 1728–1734.
- Tang, H., & Wang, F. (2013). Synthesis and properties of CaTiO₃-containing coating on AZ31 magnesium alloy by micro-arc oxidation. *Materials Letters*, 93, 427–430.
- Van, T. B., Brown, S. D., & Wirtz, G. P. (1977). Mechanism of anodic spark deposition. *American Ceramic Society Bulletin*, 56, 563–566.
- Wan, P., Lin, X., Tan, L., Li, L., Li, W., & Yang, K. (2013). Influence of albumin and inorganic ions on electrochemical corrosion behavior of plasma electrolytic oxidation coated magnesium for surgical implants. *Applied Surface Science*, 282, 186–194.
- Wang, B., Gao, J., Wang, L., Zhu, S., & Guan, S. (2012). Biocorrosion of coated Mg–Zn–Ca alloy under constant compressive stress close to that of human tibia. *Materials Letters*, 70, 174–176.
- Wang, Y. M., Guo, J. W., Shao, Z. K., Zhuang, J. P., Jin, M. S., Wu, C. J., et al. (2013). A metasilicate-based ceramic coating formed on magnesium alloy by microarc oxidation and its corrosion in simulated body fluid. *Surface and Coatings Technology*, 219, 8–14.
- Wang, Y. M., Wang, F. H., Xu, M. J., Zhao, B., Guo, L. X., & Ouyang, J. H. (2009). Microstructure and corrosion behavior of coated AZ91 alloy by microarc oxidation for biomedical application. *Applied Surface Science*, 255, 9124–9131.
- Wang Fei, & Zhang Qi (2006). Effect of high tibial osteotomy on tibiofemoral contact pressures: a biomechanical study at human cadaveric knees. *Journal of Hebei Medical University*, 2, 83–85.
- Wei Zhang, Bo Tian, Ke-Qin Du, Hui-Xia Zhang, & Fu-Hui Wang (2011). Preparation and corrosion performance of PEO coating with low porosity on magnesium Alloy AZ91D in acidic KF system. *International Journal of Electrochemical Science*, 6, 5228–5248.
- Wood, G. C., & Pearson, C. (1967). Dielectric breakdown of anodic oxide films on valve metals. *Corrosion Science*, 7, 119–125.
- Wu, X., Qin, W., Guo, Y., & Xie, Z. (2008). Self-lubricative coating grown by micro-plasma oxidation on aluminum alloys in the solution of aluminate–graphite. *Applied Surface Science*, 254, 6395–6399.
- Xia, Y. H., Zhang, B. P., Lu, C. X., & Geng, L. (2013). Improving the corrosion resistance of Mg–4.0Zn–0.2Ca alloy by micro-arc oxidation. *Materials Science and Engineering: C*, 33, 5044–5050.
- Xin, S., Song, L., Zhao, R., & Hu, X. (2006). Influence of cathodic current on composition, structure and properties of Al₂O₃ coatings on aluminum alloy prepared by micro-arc oxidation process. *Thin Solid Films*, 515, 326–332.
- Xu, J., Weng, X.-J., Wang, X., Huang, J.-Z., Zhang, C., Muhammad, H., et al. (2013). Potential use of porous titanium–niobium alloy in orthopedic implants: preparation and experimental study of its biocompatibility in vitro. *PLoS ONE*, 8, e79289.
- Yang, X., Li, M., Lin, X., Tan, L., Lan, G., Li, L., et al. (2013). Enhanced in vitro biocompatibility/bioactivity of biodegradable Mg–Zn–Zr alloy by micro-arc oxidation coating contained Mg₂SiO₄. *Surface and Coatings Technology*, 233, 65–73.
- Yang, X., Yin, Q., Zhang, Y., Li, M., Lan, G., Lin, X., et al. (2013). [Biocompatibility of silicon containing micro-arc oxidation coated magnesium alloy ZK60 with osteoblasts cultured in vitro]. *Zhongguo xiu fu chong jian wai ke za zhi* = *Zhongguo xiu fu*

- chongjian waike zazhi* = *Chinese Journal of Reparative and Reconstructive Surgery*, 27, 612–618.
- Yao, Z., Li, L., & Jiang, Z. (2009). Adjustment of the ratio of Ca/P in the ceramic coating on Mg alloy by plasma electrolytic oxidation. *Applied Surface Science*, 255, 6724–6728.
- Yerokhin, A. L., Nie, X., Leyland, A., Matthews, A., & Dowey, S. J. (1999). Plasma electrolysis for surface engineering. *Surface and Coatings Technology*, 122, 73–93.
- Yerokhin, A. L., Snizhko, L. O., Gurevina, N. L., Leyland, A., Pilkington, A., & Matthews, A. (2003). Discharge characterization in plasma electrolytic oxidation of aluminium. *Journal of Physics D: Applied Physics*, 36, 2110.
- Young, L. (1961). *Anodic oxide films*. New York, NY: Academic Press.
- Zeng, R., Dietzel, W., Witte, F., Hort, N., & Blawert, C. (2008). Progress and Challenge for magnesium alloys as biomaterials. *Advanced Engineering Materials*, 10, B3–B14.
- Zhang, R. F., Zhang, S. F., Xiang, J. H., Zhang, L. H., Zhang, Y. Q., & Guo, S. B. (2012). Influence of sodium silicate concentration on properties of micro arc oxidation coatings formed on AZ91HP magnesium alloys. *Surface and Coatings Technology*, 206, 5072–5079.
- Zhang, X. P., Zhao, Z. P., Wu, F. M., Wang, Y. L., & Wu, J. (2007). Corrosion and wear resistance of AZ91D magnesium alloy with and without microarc oxidation coating in Hank's solution. *Journal of Materials Science*, 42, 8523–8528.
- Zhang, Y., Bai, K., Fu, Z., Zhang, C., Zhou, H., Wang, L., et al. (2012). Composite coating prepared by micro-arc oxidation followed by sol–gel process and in vitro degradation properties. *Applied Surface Science*, 258, 2939–2943.
- Zhang, Y., Ma, Y., Chen, M., & Wei, J. (2013). Effects of anodizing biodegradable Mg–Zn–Zr alloy on the deposition of Ca–P coating. *Surface and Coatings Technology*, 228(Suppl. 1), S111–S115.

Strategies to improve the corrosion resistance of microarc oxidation coatings on magnesium and its alloys: Implications for biomedical applications

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9.1 Introduction

The development of biodegradable implants is one of the most interesting research topics in the area of biomaterials (Brar, Platt, Sarntinoranont, Martin, & Manuel, 2009; Hermawan, Purnama, Dube, Couet, & Mantovani, 2010; Hermawan, Dube, & Mantovani, 2010; Kirkland, Birbilis, & Staiger, 2012; Kirkland, Lespagnol, Birbilis, & Staiger, 2010; Moravej, Purnama, Fiset, Couet, & Mantovani, 2010; Moravej, Prima, Fiset, & Mantovani, 2010; Shaw, Sikora, & Virtanen, 2008; Song and Song, 2007; Staiger, Pietaket, Huadmai, & Dias, 2006; Virtanen, 2011; Witte, 2010; Witte et al., 2008; Xin, Hu, & Chu, 2011; Zeng, Dietzel, Witte, Hort, & Blawert, 2008). The idea that, once implanted, the biodegradable implant would stay in the human body only for the time it takes to fix the problem and subsequently be gradually dissolved, absorbed, consumed, or excreted, without warranting a secondary surgery, is indeed fascinating (Shaw et al., 2008). This approach considers corrosion to be a desirable material property rather than a limitation. Their biodegradable properties in combination with a nontoxic nature means that Mg and its alloys are potential candidate materials for biodegradable implants. However, the rapid corrosion, generation of a large volume of hydrogen gas, accumulation of hydrogen bubbles in gas pockets adjacent to the implant, and increase in the local pH value of body fluid are the most critical limitations in using them as implant materials. A variety of surface modification methods were explored to control the rate of corrosion of Mg and its alloys (Hornberger, Virtanen, & Boccaccini, 2012; Wang, Tang, et al., 2012; Yang, Cui, & Lee, 2011); among them, microarc oxidation (MAO) has received considerable attention.

9.2 Surface modification of Mg and its alloys by microarc oxidation (MAO)

MAO, also referred to as plasma electrolytic oxidation or micro-plasma oxidation, is a high-voltage plasma-assisted anodic oxidation process, widely employed for the surface modification of magnesium and its alloys (Blawert, Dietzel, Ghali, & Song, 2006; Cai et al., 2011; Ghasemi, Raja, Blawert, Dietzel, & Kainer, 2008; Gu, Chen, et al., 2012; Guo and An, 2005; Guo, An, Huo, Xu, & Wu, 2006; Han, Zhu, & Lei, 2011; Hussein, Zhang, Nei, Xia, & Northwood, 2011; Liang, Hu, & Hao, 2007; Liu, Lu, Jing, Yuan, & Zhang, 2009; Malayoglu, Tekin, & Shrestha, 2010; Wu, Su, Jiang, & Meng, 2010; Yao, Li, Liu, & Jiang, 2010). The plasma discharges generated during the process cause partial short-term melting of the oxide layer and promote the formation of a highly adherent ceramic oxide coating (Malayoglu et al., 2010). The MAO coating possesses high hardness, good wear resistance, moderate corrosion resistance, better thermal stability, and dielectric properties (Blawert et al., 2006; Cai et al., 2011; Hussein et al., 2011; Yao et al., 2010).

9.2.1 Characteristics and architecture of MAO coatings

The mechanism of deposition of MAO coatings involves the following stages: (1) formation of an anodic barrier film during the first few seconds of oxidation; (2) dielectric breakdown of the barrier film; (3) local thickening of the oxide film at locations of sparking; (4) formation of pores in the oxide layer; (5) sustained growth of the oxide layer in the presence of sparking; and (6) formation of discrete larger sparks and breakdown channels. The cavities/pores are formed when the molten oxide and gas bubbles are thrown out of microarc discharge channels (Duan, Du, Yan, & Wang, 2006; Guo and An, 2005). The rapid solidification of the molten oxide by the relatively cool electrolyte imparts thermal stress in the oxide film; when the stress is relieved, microcracks are formed (Duan et al., 2006; Han et al., 2011). The lower value of the Pilling-Bedworth ratio is also considered as one of the reasons for the higher porosity of MAO coatings on Mg and its alloys (Duan et al., 2006; Su, Wu, Guo, & Jiang, 2009). The pores are generally classified as open pores and closed pores. The open pores are relatively larger and are concentrated on the surface of the MAO coatings, while the closed pores are present in the middle region of the coating (Malayoglu et al., 2010). In addition, numerous hairline crack-like networks formed by the discharge paths that are extended almost down to the base metal are observed (Malayoglu et al., 2010).

The architecture of MAO coatings on Mg and its alloys has a three-layered structure: a porous outer layer with several large-sized, deep pores/cavities; a middle layer with less porosity; and a thin barrier layer (Han et al., 2011) (Figure 9.1). The barrier layer, which is about one-third of the total thickness, is compact, free of pores and cracks, and integrated firmly with the substrate by sintered interlocking (Duan et al., 2006; Guo, Cao, Lu, Liu, & Xu, 2011). The absence of any apparent discontinuity between the substrate and the barrier layer in the bonding zone confirms the occurrence of an excellent metallurgical bonding between the ceramic coating and the substrate

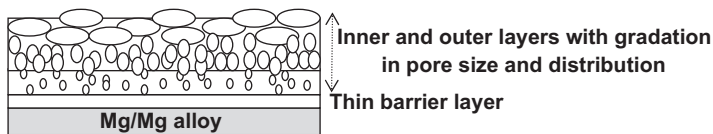


Figure 9.1 Schematic of the architecture of microarc oxidation (MAO) coatings on Mg and its alloys.

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(Pan, Chen, Wang, Yu, & Lin, 2012). The micropores and microcracks are randomly distributed on the surface of MAO coating, and they do not penetrate the entire coating layer (Gu, Xiong, Ning, & Zhang, 2012). The evolution of pores with time is largely a function of the applied potential/current.

9.2.2 Advantages and limitations of the porous structure of MAO coatings

The pores and cracks formed in the MAO coatings on Mg and its alloys have both beneficial and detrimental effects. The micropores and cracks generated during the microarc discharges help to release the residual stress of the coating (Gu, Xiong, et al., 2012). The presence of a porous outer layer in MAO coatings would significantly improve the mechanical interlocking effect, the bonding area, and stress distribution across the adhesive–substrate interface of the joints, resulting in higher bond strength (Tang, Zhao, Jiang, Chen, & Zuo, 2010). However, the presence of a higher pore density on the surface of the MAO coatings of Mg and its alloys increases the effective surface area and thus the tendency of the corrosive medium to adsorb and concentrate into these pores. This would facilitate quicker infiltration of the corrosive medium into the inner regions of the coating and subsequently down to the substrate, thus deteriorating the corrosion resistance of the coating by changing its local pH. The pore density, distribution of pores, and interconnectivity of the pores with the substrate are the important factors that decide its corrosion protective ability (Malayoglu et al., 2010). Hence, it is not just essential but mandatory to increase the corrosion resistance of MAO coatings. In this perspective, this review aims to address the various strategies explored in improving the corrosion resistance of MAO coatings on Mg and its alloys.

9.3 Strategies to improve the corrosion resistance of MAO-coated Mg and its alloys

9.3.1 Choice of electrolytes

The concentration and composition of the electrolytes used has a significant influence on the morphological characteristics, porosity, thickness, and corrosion resistance of MAO coatings (Liang et al., 2005). Hence, a proper choice of the electrolyte

composition and concentration is imperative to impart a rapid metal passivation and to promote an earlier attainment of sparking voltage (Liang et al., 2005). An alkaline electrolyte is commonly used for the deposition of MAO coatings on Mg and its alloys to prevent excessive metal dissolution from the anode. NaOH/KOH is used as the base electrolyte while phosphate, silicate, fluoride, aluminate, zirconate, permanganate, etc. are used as the primary electrolyte additives.

The concentration of the electrolyte is an important parameter in deciding the discharge characteristics and quality of MAO coating. An increase in concentration of KOH increased the conductivity of the electrolyte, decreased the ignition/breakdown voltage, enabled quicker passivation of the substrate, and promoted the formation of a less porous and more compact oxide layer (Cheng, Qin, Li, Wang, & Zhang, 2011; Ko, Namgung, & Shin, 2010). The increase in viscosity with the concentration of the electrolyte has enabled an enrichment of Mg^{2+} ions at the interface, allowed the formation of more concentrated plasma of Mg, and induced a more efficient deposition of the MAO coating (Barchiche, Rocca, Juers, Hazan, & Steinmetz, 2007). In dilute electrolytes, the sparking is relatively more intense (Ko et al., 2010) and the temperature increment is more than twice those observed with concentrated electrolytes (Chang et al., 2011). The findings of Cheng et al. (2011), Ko et al. (2010), and Barchiche et al. (2007) clearly revealed that the corrosion resistance of MAO coatings prepared using concentrated electrolytes is much better than those obtained using dilute electrolytes. The better corrosion resistance offered by the coatings prepared using concentrated electrolytes is due to the decrease in porosity, increase in compactness of the coating, and increase in volume fraction of the MgO phase (Ko et al., 2010). Blawert et al. (2007) have also recommended that one of the potential ways to reduce the pore density and to improve the corrosion performance of MAO-coated Mg alloys is to increase the concentration of the components in the electrolyte. According to them, an increase in the concentration of KOH (from 3 to 10 g/l) and Na_2SiO_3 (from 2 to 15 g/l) decreased the pore density from 136 to 24 pores/mm². In addition, an increase in the concentration of the electrolyte increased the reactivity and increased the volume fraction of the Mg_2SiO_4 (Forsterite) phase at the expense of the MgO phase.

The addition of the phosphate, silicate, fluoride, aluminate, zirconate, permanganate, etc. to the base electrolyte (NaOH/KOH) increased the conductivity of the electrolyte solution, decreased the breakdown voltage, and offered an extended window of opportunity for deposition of MAO coatings with desirable characteristics. Diffusion of the anions through the pores, formation of the corresponding oxides, and their reaction with MgO at high temperatures, which prevails during the MAO process, has led to the formation of additional phases other than MgO. The formation of magnesium phosphate, magnesium silicate, magnesium fluoride, etc. helped to increase the corrosion resistance of MAO coatings. The effect of electrolyte chemistry on the size and density of the pores, the various phases formed, their volume fractions, and how they are going to influence corrosion resistance of the resultant MAO coating is quite complex and still not fully understood (Rama Krishna, Poshal, & Sundararajan, 2010) because they are dependent on each other.

Among the various types of electrolytes used for preparing MAO coatings, the use of calcium- and phosphorus-containing compounds, such as $\text{Ca}(\text{OH})_2$ and Na_3PO_4 , as electrolytes assumes significance in terms of biomedical applications because these coatings could offer better biocompatibility and biological activity than those prepared using the conventional alkaline electrolytes (Bala Srinivasan, Liang, & Balajee, 2010; Bala Srinivasan, Liang, Blawert, Stormer, & Dietzel, 2010). The pore diameter and roughness of the coatings obtained from $\text{Ca}(\text{OH})_2$ -based electrolytes are relatively less when compared to those prepared using the conventional KOH-based electrolyte. In spite of its lower thickness, the compactness and presence of calcium-based compounds offered a better corrosion resistance for MAO coatings obtained from a $\text{Ca}(\text{OH})_2$ -based electrolyte. Because calcium-based compounds are biocompatible as well as bioactive, it appears that it would be a better strategy to prepare MAO coatings using electrolytes having calcium- and phosphorus-based compounds.

9.3.2 Process parameters and conditions

The process parameters, such as applied voltage/current density, frequency, and duty cycle, have a significant influence on the surface morphology, porosity, and thickness of the MAO coatings. In general, the MAO coating is thin, smooth, and uniform when the applied voltage/current density is low. An increase in voltage/current density increases the potential of oxidation and increases the thickness of the oxide coating. In addition, it also increases the reactivity between the Mg/Mg alloy and oxygen, leading to a better bonding at the interface, and increases the bond strength. However, an increase in spark size with voltage increases the porosity of the resultant coatings. An increase in voltage/current density beyond a critical level would increase the porosity of the outer layer and make the resultant coating rough and nonuniform (Chang et al., 2011; Zhang, Shan, Chen, & Han, 2008).

It is a common practice to carry out MAO of Mg/Mg alloys at a constant current density mode because it is generally believed that this methodology offers better process control and considerable savings in treatment time (Liang et al., 2007). With the application of a constant current density, however, the intensity of the spark discharge is increased and the number of spark discharges is decreased with an increase in process time. Hence, the resultant coating has a coarse and porous microstructure with large micropores. Instead, if the current density were allowed to decay freely at the later stage of the MAO process, then it would help reduce intensity of spark discharges and enable the formation of smaller sparks distributed over the entire surface of the oxide coating. Coatings obtained under such conditions would be intact, relatively smooth, possess a homogeneous microstructure, and be less porous (Liang et al., 2007). Obviously, the decrease in porosity, heterogeneity, and roughness would offer a better corrosion resistance. Hence, adopting suitable current density waveforms, such as freely decaying current density at the later stages or a step down in current density at a programmed time interval, appears to be one of the useful strategies for improving the corrosion resistance of MAO coatings on Mg and Mg alloys (Liang et al., 2007).

Different current modes such as direct current (DC), alternating current (AC), and pulse current (unipolar and bipolar modes) are used for MAO of Mg/Mg alloys

(Arrabal, Matykina, Hashimoto, Skeldon, & Thompson, 2009; Hussein et al., 2011). The characteristics of spark discharge vary considerably with the type of current mode employed. When the MAO coatings are prepared under unipolar current mode, the strong spark discharges increase the porosity and microcracks and an increase in the T_{off} period provides little help to resolve the defects. For coatings prepared under the bipolar mode, the cathodic component helps to reduce the strong spark discharges between the anodic periods. In addition, this current mode provides sufficient time for the oxide to cool down before the initiation of subsequent anodic pulses (long T_{off}). The increase in sintering time (T_{on}) would enable the formation of a dense oxide coating with minimum porosity. Hence, by suitably combining the cathodic current pulses with the T_{on} and T_{off} periods, it will be possible to control the porosity and other structural defects. Hussein et al. (2011) have studied the influence of direct current and pulse unipolar and bipolar current modes on the characteristics and corrosion resistance of MAO coatings on AJ62 Mg alloy. MAO coatings prepared under DC mode offered an i_{corr} of 2.24×10^{-5} A/cm² in 3.5% NaCl. The use of pulsed current unipolar mode instead of DC decreased the i_{corr} from 2.24×10^{-5} to 5.39×10^{-7} A/cm², whereas bipolar mode leads to a further decrease in i_{corr} to 4.30×10^{-8} A/cm². The corrosion behavior of coatings prepared under different current modes is correlated to the porosity and defects of the coating.

Su et al. (2009) have also recommended the use of cathodic current pulses to improve the characteristics of the MAO coatings deposited on ZK60 Mg alloy. An increase in cathodic current pulse leads to dissolution of the oxide coatings and a decrease in coating thickness. However, it enables the formation of a compact coating with reduced porosity. An increase in the anodic/cathodic (j_a/j_c) current ratios from 100/50 (2/1) to 100/150 (2/3) mA/cm² has led to a decrease in the number and size of the pores, a decrease in the extent of penetration of the electrolyte through to the coating-metal interface, and a decrease in i_{corr} from 9.246×10^{-7} to 1.098×10^{-8} A/cm².

Hussein, Northwood, and Nei (2012) studied the effect of unipolar, bipolar, and hybrid (a combination of both) current modes on the properties and corrosion resistance of MAO coatings deposited on AM60 Mg alloy. MAO coatings fabricated using unipolar current mode contain relatively larger pores due to the strong spark discharges (type B) (Hussein, Nei, Northwood, Yerokhin, & Matthews, 2010). Unlike the unipolar mode, the cathodic component and the longer T_{off} duration provide a balance of the discharge effect under bipolar current mode (Hussein et al., 2011) that enables the formation of MAO coating with minimum porosity. However, the coating growth rate is low under the bipolar current mode. Coatings prepared using a hybrid current mode enable a significant reduction in pore density and size due to the ability of the bipolar mode to decrease both the number and intensity of strong B-type discharges. MAO coatings obtained under the hybrid current mode are dense with a minimal amount of pores, through-coating cracks, and other defects. MAO coatings prepared using the hybrid current mode that consists of unipolar (for 15 min) followed by bipolar (for 15 min) are more compact, uniform, and offer a better corrosion resistance. The ability of the bipolar mode to repair the damages caused by the unipolar mode and to produce a dense coating with minimum defects combined with the ability of the unipolar mode to

provide chemically stable phases are considered to be responsible for the improved corrosion resistance of coatings obtained under this hybrid current mode.

Pulse frequency is another important electrical parameter that could influence the characteristics of MAO coatings deposited on Mg and its alloys. The effect of frequency on the structural characteristics and corrosion resistance of MAO coatings deposited on ZM5 Mg alloy using 0.018 M NaOH, 0.016 M $(\text{NaPO}_3)_6$, and 0.190 M NaF at 2 A/dm^2 with a frequency of 800 Hz for 60 min and 100 Hz for 110 min was studied by [Lv et al. \(2008\)](#). The thicknesses of the MAO coating prepared at 100 Hz for 60 and 110 min were 8 and $26 \mu\text{m}$, respectively, whereas those obtained at 800 Hz were only 2.7 and $4 \mu\text{m}$, respectively, at similar time intervals. A lower frequency provides a longer time for one single pulse, which induced continuous discharge and enabled faster growth of the coating. For MAO coatings prepared at 100 Hz, the pore size is much larger while the density is lower compared with those prepared at 800 Hz ([Figure 9.2](#)). With an increase in treatment time, the pore size of the coatings prepared at 100 Hz is increased along with the formation of some microcracks, which make the coating rougher. For MAO coatings obtained at 800 Hz, an increase in treatment time has resulted in a slight increase in pore size, while no distinct cracks were evident.

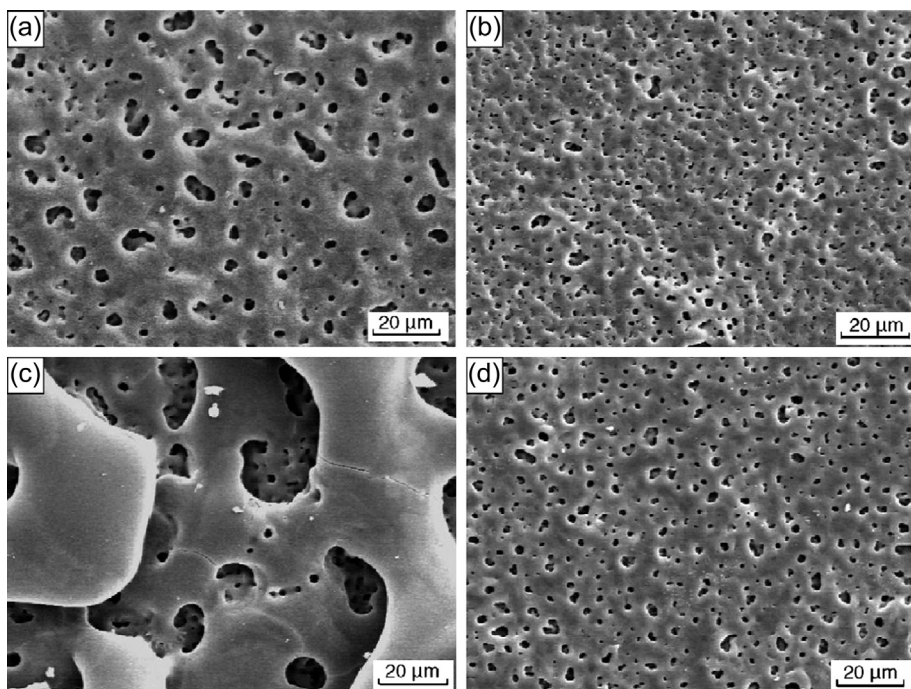


Figure 9.2 Surface morphology of microarc oxidation (MAO) coatings deposited on ZM5 Mg alloy using 0.018 M NaOH + 0.016 M $(\text{NaPO}_3)_6$ + 0.190 M NaF at 2 A/dm^2 at various pulse frequencies and time: (a, c) 100 Hz and (b, d) 800 Hz; (a, b) 60 min and (c, d) 110 min. Adapted from [Lv et al. \(2008\)](#) with permission from Elsevier.

Van, Brown, and Wirtz (1977) reported that the lifetime of a single spark during MAO is about 0.17 ms. The pulse width at 800 Hz is 0.6 ms, which is comparable with the spark lifetime. Hence, during one pulse, either one or two spark discharges occur at the same place; during the next pulse, the discharge would occur at a different place. The continuous movement of spark discharges during deposition enables the formation of MAO coatings with a small pore size and higher density at 800 Hz. In contrast, at 100 Hz, the pulse width is 5 ms, which is much longer than the lifetime of the spark. Hence, the continuous breakdown of a large period leads to the formation of MAO coatings with larger pore sizes. The higher temperature generated during spark discharges and subsequent quenching by the surrounding electrolyte induces the formation of microcracks on coatings prepared at 100 Hz. The higher energy per pulse and higher degree of plasma chemical reactions enables a higher coating thickness at low frequencies, whereas the coating thickness is decreased with an increase in frequency. Moreover, at higher frequencies, with shorter pulses on time and lower energy per pulse, the movement of cations and anions towards the growth front and the incorporation of the corresponding elements in the resultant coating are decreased.

Duty cycle is an important electrical parameter that influences the characteristics of MAO coatings deposited on Mg/Mg alloys. An increase in duty cycle refers to an increase in the time of application of current/voltage during each cycle, and it has a similar effect as the applied voltage on the characteristics of MAO coatings. An increase in duty cycle increases the energy density of the sparks, the amount of heat released during the process, and the amount of molten oxide that is thrown out to the electrolyte (Wang, Zhu, et al., 2009; Tang et al., 2010). Hence, an increase in duty cycle increases the porosity and decreases the coating thickness. For a duty cycle of 0.1, the coating is thin, smooth, and uniform, whereas it becomes very rough with large pores and cracks for a duty cycle of 0.9 (Chang et al., 2011). The duty cycle has to be carefully optimized to deposit MAO coatings with a reasonable thickness and relatively smooth coating, with a lesser number of pores and better corrosion resistance.

The effect of treatment time is also an important parameter that influences the thickness, morphological features, size, and distribution of pores and corrosion resistance of MAO coatings. An increase in treatment time provides enough opportunity for the buildup of the coating, resulting in an increase in coating thickness. However, with an increase in time, the spark discharges become more energetic, more violent, and move slowly over the sample surface, thus resulting in the formation of nonuniform coatings with higher roughness and larger pores (Figure 9.3). With an increase in treatment time, the accumulation of liquid melt around the micropores could cover the small micropores, which would help to increase the corrosion resistance. However, an increase in surface roughness could cause a deleterious influence on corrosion resistance. According to Lv et al. (2009), MAO coatings deposited on AZ91D Mg alloy using 10 g/l Na_2SiO_3 , 8 g/l NaF, and 2 g/l NaOH at 2 A/dm^2 with a pulse frequency of 800 Hz for 2.5, 5, 20, and 30 min offered an i_{corr} of 1.9687×10^{-9} , 8.3312×10^{-8} , 3.1357×10^{-10} , and $1.4768 \times 10^{-9} \text{ A/cm}^2$, respectively.

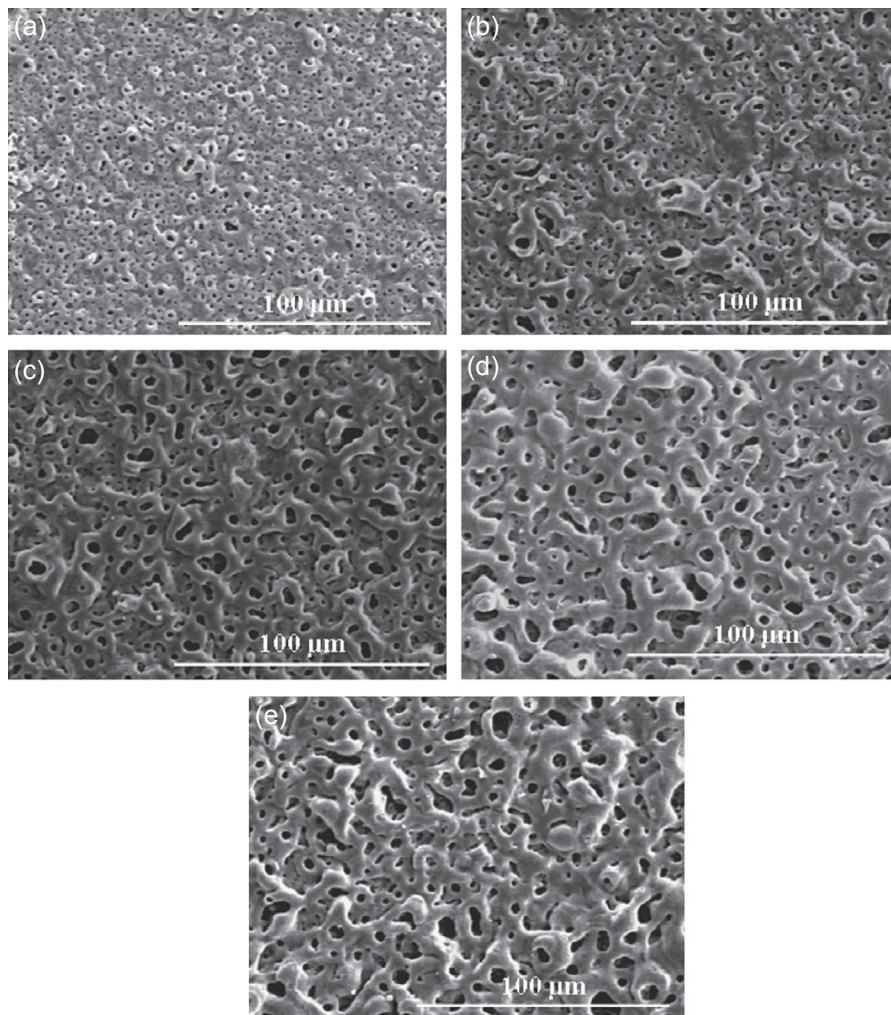


Figure 9.3 Surface morphology of microarc oxidation (MAO) coatings deposited on AZ91D Mg alloy using 10 g/l Na_2SiO_3 + 8 g/l NaF + 2 g/l NaOH at 2 A/dm^2 for various durations of time: (a) 2.5 min; (b) 5 min; (c) 15 min; (d) 20 min; (e) 30 min.

Adapted from [Lv et al. \(2009\)](#) with permission from Elsevier.

9.3.3 Pretreatment

[Wang, Zhou, Liang, and Chen \(2012\)](#) explored the use of laser surface melting (LSM) as a pretreatment of AZ91D Mg alloy for MAO coating. The LSM was performed using a 10 kW transverse-flow, continuous-wave CO_2 laser using Ar as shielding gas at a pressure of 0.2 MPa. A constant beam diameter of 3 mm with 50% track overlapping was used while the energy density was varied between 32 and 89 J/mm^2 so as to achieve a melting depth of 969.5–1503 μm. LSM enabled refinement of

microstructure, altered the crystal orientation of Mg from (101) to (112), enriched Al at the surface, and allowed redistribution of β -phase ($\text{Mg}_{17}\text{Al}_{12}$) on the AZ91 Mg alloy matrix, all of which promoted a better reactivity of the alloy surface during MAO treatment. The resultant coatings are more compact, have fewer cracks on the surface, possess higher volume fraction of MgAl_2O_4 , and offered a decrease in i_{corr} from 6.40×10^{-8} to 5.00×10^{-9} A/cm², when compared to those obtained on the alloy not pretreated with LSM.

Jiang et al. (2013) have shown that equal-channel angular pressing of AZ91D Mg alloy leads to a change in microstructure and a homogeneous distribution of the β -phase ($\text{Mg}_{17}\text{Al}_{12}$) in the matrix. This increased the reactivity of the alloy during MAO treatment, resulting in the formation of a compact coating with uniform micropores and better corrosion resistance. The findings of Jiang et al. (2013) suggest that other deformation processes could also be explored as a pretreatment of Mg alloys for MAO coating.

Cerium conversion coating has been explored as a pretreatment for MAO coatings on AZ91D Mg alloy (Cai et al., 2011). During the initial periods of MAO treatment, which is similar to conventional anodizing, the cerium from the conversion coating becomes available at the growth front and is likely to be incorporated in the passive oxide film as it grows. The barrier layer of MAO coating formed on AZ91D Mg alloy pretreated with cerium conversion coating is more compact and exhibits better bonding with the matrix than those obtained without pretreatment. Unlike those formed on untreated AZ91D Mg alloy, MAO coatings deposited on the Mg alloy subjected to cerium conversion coating pretreatment are uniform, have a fewer number of smaller size pores, and lead to a decrease in i_{corr} from 1.3×10^{-6} to 1.20×10^{-7} A/cm².

The role of immersion pretreatment in $\text{Al}(\text{NO}_3)_3$ with or without ultrasound (40 kHz) has been explored as a pretreatment for MAO coating of AZ91D Mg alloy (Ximei, Liquan, Huicong, & Weiping, 2008). Pretreatment in 0.1 M $\text{Al}(\text{NO}_3)_3$ (pH: 4.0) for 30 min promoted the formation of oxides and hydroxides of magnesium and aluminum, decreased the breakdown voltage, decreased the thickness, and enabled the formation of a more uniform oxide layer. Ultrasonic treatment increased the uniformity and decreased the diameter of the micropores of the oxide layer. Immersion pretreatment in $\text{Al}(\text{NO}_3)_3$ without ultrasonic treatment offered an i_{corr} of 1540×10^{-6} A/cm²; with ultrasonic treatment, the i_{corr} is decreased to 180×10^{-6} A/cm².

9.3.4 Additives

A variety of organic and inorganic compounds and other special additives, in addition to the primary electrolyte additives, have been used to modify the electrolyte solution to impart desirable qualities in MAO coatings, particularly a better corrosion resistance. The effect of various additives on the characteristics of MAO coatings deposited on Mg alloy and the extent of improvement in corrosion resistance are compiled in Table 9.1. Among the various types of additives studied, surfactants have the ability to modify the interfacial tension, decrease the contact angle and diameter of the oxygen bubbles, and enable an easy release of oxygen so that the resultant coatings have a lower porosity and better quality (Guo & An, 2006). The addition of glycerol

Table 9.1 Effect of various additives on the characteristics of microarc oxidation (MAO) coatings deposited on Mg and its alloys and the extent of improvement in corrosion resistance

Number	Composition of the base electrolyte and operating conditions	Additives used and their concentration	Effect of additives, coating characteristics, and extent of improvement in corrosion resistance of the Mg alloy	Reference
1	6 g/l Na_2SiO_3 ; 3 g/l of Na_3PO_4 ; 1.5 g/l NaF; 1.5 g/l NaOH Current density: 2 A/dm ² Pulse frequency: 300 Hz Duty cycle: 45%; time: 15 min	$\text{Na}_2\text{B}_4\text{O}_7$ (1 g/l); EDTA (0.5 g/l)	Addition of $\text{Na}_2\text{B}_4\text{O}_7$ and EDTA prevented the generation of nodules, altered the topography of the resultant coatings, and decreased the i_{corr} of MAO coatings deposited on Mg-5Li-3.5Al-1.2Zn-1.2Ce alloy in 3.5% NaCl from 1.37×10^{-6} to 5.92×10^{-7} A/cm ² and 3.76×10^{-8} A/cm ² , respectively	Shi et al. (2010)
2	6 g/l Na_2SiO_3 ; 2 g/l KF; 2 g/l KOH; 10 ml/l glycerol Current density: 100 mA/cm ² Time: 10 min	Dodecyl sodium sulfate (0.25 g/l); diphenylamine- 4-sulfonic acid sodium (0.25 g/l); Dodecyl phenyl sodium sulfonate (0.25 g/l)	Addition of these surfactants (0.25 g/l) modified the interfacial tension, decreased the contact angle and diameter of the oxygen bubbles, and enabled an easy release of oxygen so that the resultant MAO coatings deposited on AZ31B Mg alloy possess a lower porosity and better quality	Guo and An (2006)
3	15 g/l NaOH; 12 g/l phytic acid Current density: 40 mA/cm ² Pulse frequency: 2000 Hz Duty cycle: 20%; time: 3 min	Sodium borate (10, 20, 30, and 40 g/l)	Addition of sodium borate (10–40 g/l) increased the coating thickness (from 3 to 8.5 μm), promoted the formation of $\text{Mg}_3\text{B}_2\text{O}_6$ phase besides MgO and $\alpha\text{-Al}_2\text{O}_3$, increased the porosity and roughness, and increased the i_{corr} of MAO coatings deposited on Mg alloy in 3.5% NaCl from 0.49 to 11.9 $\mu\text{A/cm}^2$	Zhang, Zhang, Shen, et al. (2012)
4	10 g/l NaOH Current density: 40 mA/cm ² Pulse frequency: 2000 Hz Duty cycle: 20%; time: 3 min	Phytic acid (4, 8, and 12 g/l)	Addition of phytic acid increased the coating thickness from 3 to 7 μm . MAO coatings deposited using 4 g/l phytic acid offered an i_{corr} of 7.696×10^{-6} A/cm ² while an increase in its concentration from 4 to 8 g/l decreased the i_{corr} to 2.559×10^{-6} A/cm ²	Zhang, Zhang, and Duo. (2009)

Continued

Table 9.1 Continued

Number	Composition of the base electrolyte and operating conditions	Additives used and their concentration	Effect of additives, coating characteristics, and extent of improvement in corrosion resistance of the Mg alloy	Reference
5	10 g/l Na ₂ SiO ₃ ; 2 g/l NaOH; 2 g/l Na ₂ EDTA Pulse-reverse voltage: 400/120 V Pulse frequency: 100 Hz Time: 15 min	Glycerol (2, 4, and 6 ml/l)	Addition of glycerol decreased the interfacial tension, changed the anode-electrolyte interface, increased the adsorptive capacity of negative ions, and promoted the formation of numerous intensive discharge sparks with small size, a smooth coating with reduced pore size, and cracks with higher volume fraction of MgO. Addition of 4 ml/l of glycerol has decreased the i_{corr} of MAO coatings deposited on AZ91D Mg alloy in 3.5% NaCl from 6.16×10^{-5} to 5.18×10^{-7} A/cm ² . Addition of 6 ml/l of glycerol limited the diffusion of anions, decreased the coating thickness from 111 to 64 μm , and restricted the improvement in corrosion resistance	Wu et al. (2009)
6	15 g/l Na ₂ SiO ₃ ; 10 g/l NaOH; 8 g/l KF; 5 ml/l glycerin Voltage: 500 V Pulse frequency: 600 Hz Duty cycle: 8% Time: 5 min	TiO ₂ sol (5 and 10 vol.%)	Addition of TiO ₂ sol has decreased the coating thickness from 22 to 18 μm and reduced the pore size. Nevertheless, the i_{corr} of MAO coating deposited AZ91D Mg alloy in SBF is increased from 3.16×10^{-8} A/cm ² to 7.76×10^{-8} A/cm ² (for 5 vol. % TiO ₂ sol) and 1.51×10^{-7} A/cm ² (for 10 vol. % TiO ₂ sol). Extent of corrosion damage after 312 h of immersion in SBF is also relatively higher for MAO coatings prepared using TiO ₂ sol	Wang, Wang, et al. (2009)
7	10 g/l NaSiO ₃ ; 3 g/l NaOH; 10 ml/l triethanolamine Current density: 5 A/dm ² Pulse frequency: 2000 Hz Duty cycle: 15% Time: 10 min	SiO ₂ sol (1 vol. %)	Addition of SiO ₂ sol decreased the coating thickness from 17 to 14 μm , decreased the micropores and structural imperfections, enabled the formation of a uniform coating, promoted the formation of Mg ₂ SiO ₄ at the expense of MgO, and decreased the i_{corr} of MAO coatings deposited on Mg-Li alloy in 3.5% NaCl from 6.29×10^{-7} A/cm ² to 1.00×10^{-7} A/cm ²	Liu et al. (2009)

8	10 g/l Na ₂ SiO ₃ ; 10 g/l KOH Current density: 10 A/dm ² Pulse frequency: 200 Hz Duty cycle: 15% Time: 20 min	ZrO ₂ sol (5 vol. %)	Addition of ZrO ₂ sol lead a marginal increase in thickness from 36 to 40 µm, altered the morphological features, enabled the formation of a uniform coating with less micropores and cracks, promoted the formation of Mg ₂ Zr ₅ O ₁₂ phase besides MgO and Mg ₂ SiO ₄ phases, and decreased the i_{corr} of MAO coatings deposited on AZ91D Mg alloy in 3.5% NaCl from 5.38×10^{-7} A/cm ² to 1.436×10^{-8} A/cm ²	Tang, Liu, Li, and Zhu (2011)
9	15 g/l NaAlO ₂ and 1.2 g/l KOH at 25 mA/cm ² for 25 min	CeCl ₃ (0.08 g/l)	Addition of CeCl ₃ enabled the formation of a uniform coating, decreased the porosity from 27% to 1.7%, and decreased the i_{corr} of MAO coatings deposited on AZ91D Mg alloy from 1.607×10^{-6} A/cm ² to 0.179×10^{-6} A/cm ²	Laleh, Kargar, and Sabour Rouhaghdam (2011a)
10	40 g/l NaOH; 50 g/l NaSiO ₃ ; 30 g/l Na ₂ B ₄ O ₇ ; 10 g/l C ₆ H ₅ O ₇ Na ₃ Current density: 10 mA/cm ² Time: 10 min	Ethylene glycol (EG) (10 g/l); Polyethylene glycol (PEG 400, PEG 1000, and PEG 4000) (10 g/l)	Addition of EG, PEG 400, and PEG 1000 decreased the pore size, nodule size, and average surface roughness. PEG 4000 exhibits poor solubility in the electrolyte. Addition of 10 g/l of EG, PEG 400, PEG 1000, and PEG 4000 decreased the i_{corr} of MAO coatings deposited on AZ31B Mg alloys in 3.5% NaCl from 3.67×10^{-6} A/cm ² to 1.97×10^{-6} A/cm ² , 1.54×10^{-7} , 1.23×10^{-7} , and 3.83×10^{-7} A/cm ² , respectively	Zhu, Wang, Li, and Zhang (2012)
11	1.5 M KOH 0.04 M Sodium citrate 0.1 M H ₃ PO ₄ ; 0.08 M NaSiO ₃ Current density: 0.02 A/cm ² Time: 2 h	Hexamethylenetetramine (HMTA) (0.1 M); sodium borate (0.1 M)	Addition of HMTA decreased the average surface roughness (R_a) from 10.12 to 1.22 µm, decreased the pore size, reduced the thermal stress and cracks, enabled the formation of a homogenous coating, and increased the corrosion resistance of the MAO coatings deposited on AZ91D Mg alloy in 5% NaCl. Addition of sodium borate changed the composition but was not able to influence the morphology and roughness. MAO coatings obtained with the addition of HMTA and borate offered an i_{corr} of 4.2×10^{-7} A/cm ²	Bai and Chen (2009)
12	15.0 g/l Na ₂ SiO ₃ ; 2 g/l NaOH 5 ml/l triethanolamine Current density: 5 A/dm ² Pulse frequency: 2000 Hz Duty cycle: 15% Time: 10 min	Na ₂ WO ₄ (0.6 g/l)	Addition of tungstate increased the coating thickness, decreased the size and number of pores and microcracks, provoked the formation of a dense coating with less structural imperfections, and decreased the i_{corr} of MAO coatings deposited on Mg-Li alloy from 2.0×10^{-5} to 8.8×10^{-6} A/cm ²	Li, Yuan, Sun, and Jing (2011)

Continued

Table 9.1 Continued

Number	Composition of the base electrolyte and operating conditions	Additives used and their concentration	Effect of additives, coating characteristics, and extent of improvement in corrosion resistance of the Mg alloy	Reference
13	10 g/l NaOH; 18 g/l Na ₂ SiO ₃ Current density: 40 mA/cm ² Pulse frequency: 2000 Hz Duty cycle: 20%; time: 3 min	8-hydroxyquinoline (8-HQ) (2, 5, and 8 g/l)	Addition of 2 g/l of 8-HQ decreased the number of micropores from 0.17 to 0.12/μm ² , increased the uniformity of the coating, and decreased the i_{corr} of MAO coatings from 40 to 2.2 μA/cm ² , whereas addition of 5 and 8 g/l of 8-HQ increased the heterogeneity of the coating and decreased the corrosion resistance	Zhang, Zhang, Yang, et al. (2012)
14	10 g/l NaOH; 18 g/l Na ₂ SiO ₃ ·9H ₂ O Current density: 40 mA/cm ² Pulse frequency: 2000 Hz Duty cycle: 20%; time: 3 min	Tannic acid (4 g/l)	Tannic acid decreased the interfacial tension of gas–liquid and solid–liquid interface, promoted the formation of a uniform coating with higher thickness, and decreased the i_{corr} of MAO coatings deposited on AZ91 Mg alloy in 3.5% NaCl from 6.125×10^{-7} A/cm ² to 1.385×10^{-7} A/cm ²	Zhang, Zhang, Li, et al. (2012)
15	0.18 M KOH 0.09 M KF 0.08 Na ₂ SiO ₄ Current density: 100 mA/dm ² Time: 300 s	KMnO ₄ (0.07 M)	MAO coatings obtained in the presence of KMnO ₄ lead to closure of many of the pores, a decrease in thickness from 11 to 3 μm, formation of Mn ₂ O ₃ phase along with MgO, MgF ₂ , and Mg ₂ SiO ₄ , an increase in coating density, and a significant decrease in i_{corr} from 1.78×10^{-7} A/cm ² to 6.95×10^{-9} A/cm ²	Hwang, Kim, Park, Yoo, and Shin (2009)
16	45 g/l NaOH; 100 g/l Na ₂ SiO ₃ Current density: 20 mA/cm ² Time: 30 min	Polyaspartic acid (PASP) (9.6, 19.2, 28.8, and 38.4 g/l)	Addition of 9.6, 19.2 and 29.8 g/l of PASP increased the coating thickness from 6.4 to 7.5, 14.6, and 23.5 μm while at 38.4 g/l the increase in coating thickness is limited to 16.2 μm. Addition of 9.6, 19.2, 28.8, and 38.4 g/l of PASP decreased the i_{corr} of MAO coatings deposited on AZ31 Mg alloy in 3.5% NaCl from 1.831×10^{-5} A/cm ² to 1.071×10^{-6} , 2.229×10^{-7} , 2.204×10^{-7} , and 1.388×10^{-7} A/cm ² , respectively	Liu, Zhag, et al. (2011)

Data compiled from Sankara Narayanan et al. (2014) with permission from Elsevier.

decreased the extent of oxygen evolution, increased the coating adhesion, and offered a better corrosion resistance for the MAO coating (Pan et al., 2012). However, when the concentration of glycerol is increased beyond a threshold level, it prevents diffusion of anions to the growth front and decreases the corrosion resistance of the MAO coatings. Wu, Liu, Lu, Zhang, and Wang (2009) have also pointed out that the beneficial influence of addition of glycerol on corrosion resistance of MAO coatings could not be fully realized when the concentration of glycerol in the electrolyte is increased from 4 ml/l to 6 ml/l. The addition of hydrogen peroxide has prolonged the duration of spark discharge and increased the extent of oxygen evolution and the roughness of the MAO coatings, resulting in a decrease in corrosion resistance (Pan et al., 2012).

The various types of additives could change the coating thickness to varying degrees and promote the formation of additional phases. However, the corrosion protective ability of MAO coating appears to be largely a function of the porosity, homogeneity, and roughness of the coating rather than the thickness and the type of phases formed (Shi, Xu, Li, Yao, & Wu, 2010; Zhang, Zhang, Shen, et al., 2012; Zhang, Zhang, Yang, et al., 2012). In spite of their influence on thickness, composition, morphological features, and pore density, additives could not completely eliminate the pores and cracks of the MAO coating. Hence, it appears that additives will be of little help in improving the corrosion resistance of MAO coatings. In addition, the stability of these additives at the temperature experienced in the growth front of the coating is not known. Thermal decomposition of surfactants and organic and polymeric additives could lead to carbonaceous contamination, which is a matter of concern regarding the suitability of MAO coatings in biomedical applications. The cytocompatibility of these additives, their reaction intermediates, and decomposition products are also matters of concern.

9.3.5 Incorporation of ceramic particles

The incorporation of ceramic oxide particles, such as ZrO_2 , CeO_2 , TiO_2 , Al_2O_3 , etc. and hydroxyapatite (HA) has been explored as a strategy to increase the corrosion resistance of MAO coatings on Mg and its alloys by many researchers (Arrabal, Matykina, Viejo, et al., 2008; Arrabal, Matykina, Skeldon, & Thompson, 2008; Lee et al., 2012; Lee, Shin, Namgung, Yoo, & Shin, 2011; Li and Luan, 2012; Lim, Ryu, & Hong, 2012; Liu, Shan, Song, Han, & Ke, 2011; Mandelli et al., 2011; Necula, Fratila-Apachitei, Berkani, Apachitei, & Duszczuk, 2009; Salman, Ichino, & Okido, 2008; Song, Sun, & Liu, 2012; Sreekanth and Rameshbabu, 2012). This approach is aimed at the simultaneous incorporation of particles in the oxide layer as they grow so that the cavities/pores of the MAO coating are sealed with the incorporated particles. In addition, the resultant coating becomes a composite of MgO along with other phases formed during the MAO process, depending on the type of electrolyte used and the incorporated particles. The choice of the particles to be incorporated has been made based on their zeta potential in the type of alkaline electrolytes ($\sim \text{pH } 13$) used for the deposition. Although the size of the cavities/pores in the MAO coating is on the order of a few microns, many researchers have used nanosized particles with an average particle size of 150–200 nm. In spite of their initial size,

these particles are agglomerated in the electrolyte solution. The addition of these particles in the electrolyte, in general, has no significant influence on the oxidation behavior during the initial stages of MAO process and the kinetics of coating formation.

It is generally agreed that the preferential location of these particles in the MAO coating is at the surface, near the interface between the inner and outer layers, and within larger cavities/pores in the outer layer (Figure 9.4) (Arrabal, Matykina, Viejo, et al., 2008; Arrabal, Matykina, Skeldon, et al., 2008; Lee et al., 2012, 2011; Li and Luan, 2012; Lim et al., 2012; Liu, Shan, et al., 2011; Mandelli et al., 2011; Necula et al., 2009; Salman et al., 2008; Song et al., 2012; Sreekanth and Rameshbabu, 2012). Particle incorporation is seldom observed in the barrier layer, while very few particles are identified in the inner layer. The ability of the particles to withstand the thermal aggressions generated during the microarc discharge process is an important factor that decides the quality of the resultant coating. The thermal condition experienced at the site of microdischarges determines the formation of new phases and transformation of the existing phases. Incorporation of particles in the MAO coatings helps to reduce the porosity, seal the cracks, and decrease the effective metallic area prone to corrosion attack. The corrosion resistance of coatings obtained with the addition of particles is better than the one prepared in their absence. The inferences made from the study of Liu, Shan, et al. (2011) and Lim et al. (2012) suggest that a higher level of particle incorporation is likely to increase the corrosion resistance. However, an increase in the level of incorporation of particles will increase the surface roughness, which has a deleterious influence on the corrosion resistance. It is difficult to control the level of particle incorporation because it depends on particle characteristics, particularly the charge (zeta potential) and extent of agglomeration, which varies with the type of electrolytes used for deposition of MAO coatings.

There are many concerns in using this approach. The incorporation of particles fails to completely seal or fill the pores of the MAO coating. In addition, particle incorporation increases the heterogeneity of the coating, which has a deleterious influence on the corrosion resistance. Phase transformation and reversible transformation of incorporated particles is also a matter of concern because it could increase the residual stress of the coating, leading to cracking of the coated layer. The formation of additional phases, such as $\text{Mg}_2\text{Zr}_5\text{O}_{12}$, following the reaction between magnesium and ZrO_2 nanoparticles, increases the volume of the coating that would also lead to cracking of the coating.

9.3.6 Sealing and posttreatment

A variety of postsealing treatments were explored to improve the corrosion resistance of MAO coatings on Mg and its alloys. The effect of various postsealing treatments on the characteristics of MAO coatings deposited on Mg alloy and the extent of improvement in corrosion resistance are compiled in Table 9.2.

The major concern in adopting a sealing treatment by polymeric molecules and layer-by-layer (LBL) self-assembly techniques is the thickness of the sealant. The thickness of the LBL multilayers (50 layers) is of the order of a few nanometers, which is not sufficient to fill the pores of the MAO coating and to reduce the surface

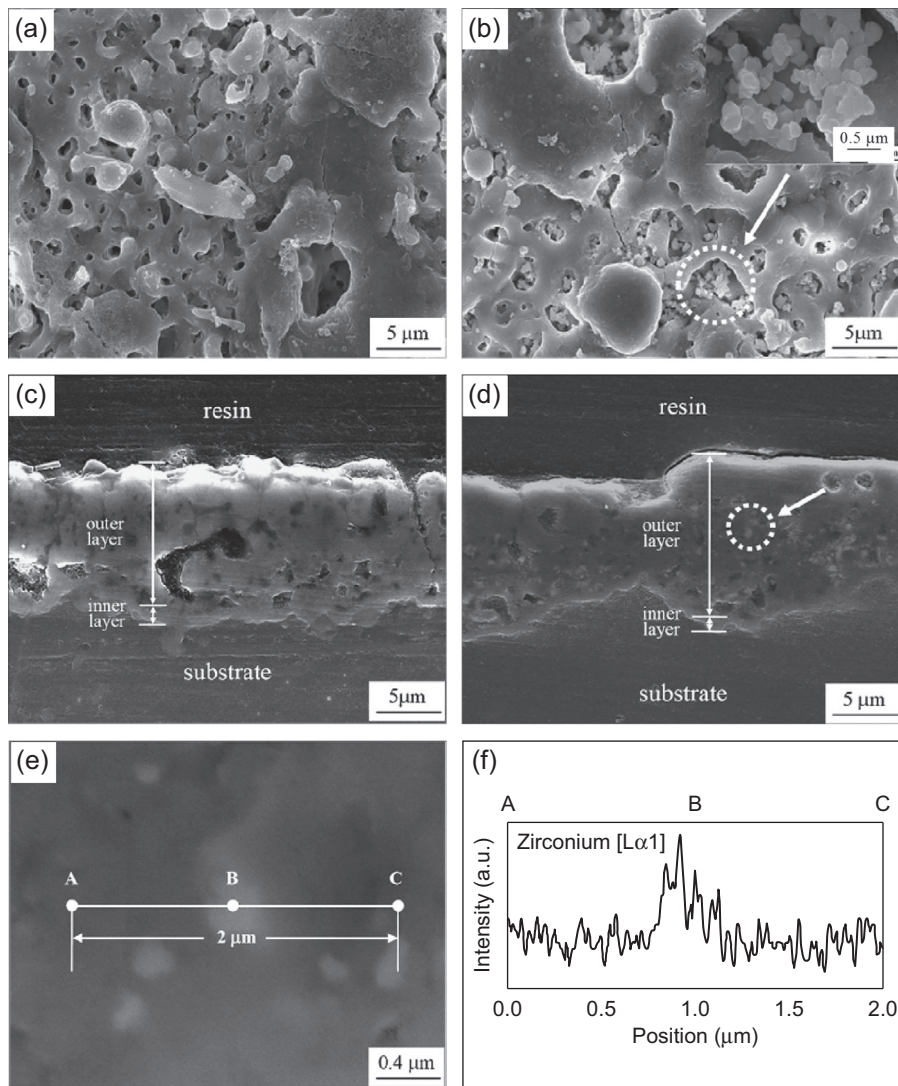


Figure 9.4 Surface and cross-sectional morphologies of the MAO-coated AZ91 Mg alloy without (a, c) and with (b, d) the addition of ZrO_2 particles. (e) Area of the oxide layer analyzed by energy-dispersive X-ray spectroscopy; and (f) energy-dispersive X-ray spectra line scanning profile of ZrO_2 nanoparticles in the oxide layers acquired from the area marked in (e). Adapted from Lee et al. (2011) with permission from Elsevier.

roughness (Liu, Pan, Yang, Cai, & Chen, 2012). In the case of polymeric sealing, a single layer would not offer sufficient corrosion protection and warrants multiple immersion cycles (Duan et al., 2006; Guo et al., 2011; Lu, Cao, Lin, Xu, & Wu, 2011; Wang, Tang, & He, 2010). An increase in the thickness of the sealant layer could cause cohesive failure. In addition, some of the essential properties, such as rigidity and wear

Table 9.2 Effect of various postsealing treatments on the characteristics of MAO coatings deposited on Mg and its alloys and the extent of improvement in corrosion resistance

No.	Type of postsealing treatment and operating conditions	Effect of postsealing on the characteristics of MAO coatings and extent of improvement in corrosion resistance of the Mg alloy	Reference
1	Immersion in organic sealing agent MAO coated AZ91D Mg alloy is immersed in organic sealing agent (ratio of organic material to solvent is 1:20) for 1 min followed by curing at 50 °C for 30 min. Number of cycles: 2 or 3 (thickness: 3–5 µm)	The organic sealing agent has penetrated into most of the pores and microcracks of the outer coarse layer, plugged the pores, integrated with the MAO coating by physical interlocking, and reduced its absorbent capacity. Post sealing with organic sealing agent has decreased the i_{corr} of MAO coatings deposited on AZ91D Mg alloy in 3.5% NaCl from $2.962 \times 10^{-7} \text{ A/cm}^2$ to $4.107 \times 10^{-10} \text{ A/cm}^2$.	Duan et al. (2006)
2	Infiltration of polymers MAO coated AZ31 Mg alloy is immersed in a mixture of 30 g Maleic anhydride-g-liquid polybutadiene (MALPB) (Mol wt.: 1020 and low viscosity), 100 g ethylene glycol monobutyl ether, 0.25% benzoyl peroxide (wt% of MALPB; peroxide initiator), and 1% dicumyl peroxide (wt% of MALPB; curing agent) for 1 min, cured at 180 °C for 15 min (30–180 °C at 10 °C/min) Thicknesses of the MALPB film: $10 \pm 0.5 \text{ µm}$	The infiltrated MALPB molecule after curing promotes the formation of a network structure that helps to seal the pores and cracks of the MAO coating. MAO coated AZ31 Mg alloy after infiltration with MALPB exhibits an impedance value of $>1 \text{ M}\Omega$ after 12 h of immersion in 3.5% NaCl. With increase in immersion time from 12 to 36, 48, 72, and 168 h, the impedance value is decreased from $>1 \text{ M}\Omega$ to 100, 5, 3, and 1 k Ω , respectively.	Wang et al. (2010)
3	Sealing using poly-L-lactic acid (PLLA) MAO coated WE42 Mg alloy was immersed vertically in PLLA-dichloromethane solution and withdrawn at a speed of 5 cm/min for 3 cycles	PLLA coating overlaid most of the pores and microcracks on the surface of the MAO coated WE42 Mg alloy and the coating is smooth and uniform without any tiny cracks and pores. PLLA sealing restricted the change in resistance of MAO coated WE42 Mg alloy from 1.4×10^5 to $1.3 \times 10^5 \Omega \cdot \text{cm}^2$ with no signs of corrosion after 4 weeks of immersion in Hank's solution (pH 7.4) at 37 °C.	Lu, Cao, et al. (2011); Guo et al. (2011)
4	Layer-by-layer (LBL) self-assembly technique MAO coated WE43 Mg alloy was coated uniformly with a layer of chitosan (CHI) and poly (styrene sulfonate) (PSS) polyelectrolyte multilayers using 5 mg/ml of their precursors by spin coating at 2000 rpm for 15 s and this procedure is repeated for 50 cycles	Deposition of CHI/PSS multilayers on MAO coated WE43 Mg alloy enabled a decrease in i_{corr} in SBF at 37 °C from 5.741×10^{-5} to $2.796 \times 10^{-6} \text{ A/cm}^2$. The ability of the polyelectrolytes to offer pH buffering in the damaged area is an added advantage of this type of sealing treatment.	Liu et al. (2012)
5	Sealing using alkaline phosphate (AP) and alkaline silicate (AS) based solutions Sealing using AP immersion in 12% KH_2PO_4 solution at 60 °C for 5 min Sealing using AS immersion in 5% water-glass (Na_2SiO_3) at 95 °C for 15 min	Both AP and AS sealing treatments plugged the open micropores of the MAO coated AM50B and AM60B Mg alloys and reduced their surface roughness. AP and AS treatment on MAO coated AM50B Mg alloy decreased the i_{corr} in 3.5% NaCl from 0.145 $\mu\text{A/cm}^2$ to 0.026 and 0.024 $\mu\text{A/cm}^2$, respectively, whereas for AM60B Mg alloy, the corresponding decrease in i_{corr} is from 0.104 $\mu\text{A/cm}^2$ to 0.032 and 0.022 $\mu\text{A/cm}^2$, respectively.	Malayoglu et al. (2010)

6	TiO ₂ sol–gel coating followed by hydrothermal treatment	The pores present in the MAO coated Mg provide an anchorage for the TiO ₂ sol-gel coating to hold on to the substrate during hydrothermal treatment, which would otherwise detach from the substrate. The TiO ₂ sol-gel coating has decreased the i_{corr} of MAO coated Mg in Hank's solution (pH: 7.4) at 37 °C from 400 to 12.5 $\mu\text{A}/\text{cm}^2$, which is also reflected in the increase in resistance value from $\sim 0.12 \text{ k}\Omega \cdot \text{cm}^2$ (uncoated Mg) to $\sim 4.20 \text{ k}\Omega \cdot \text{cm}^2$ (MAO-TiO ₂ sol-gel coating).	Shi et al. (2009)
7	TiO ₂ sol–gel coating followed by heat treatment MAO coated Mg-Li alloy was submerged vertically in titanium sol for 5 min, withdrawn at a speed of 6 cm/min for four cycles, and subsequently dried at 170 °C for 3 h	TiO ₂ sol-gel coating (thickness: 16 μm) helped to seal the micropores and microcracks of the MAO coating and enabled a smooth and uniform surface. Nevertheless, the thermal stress generated in the sol-gel coating during drying has resulted in the formation of cracks. Sealing of the MAO coated Mg-Li alloy with TiO ₂ sol-gel coating has enabled a decrease in i_{corr} from 5.56×10^{-6} to $5.64 \times 10^{-7} \text{ A}/\text{cm}^2$ with a corresponding increase in R_p from 23899 to 106800 $\Omega \cdot \text{cm}^2$.	Li, Jing, Yuan, and Zhang (2012)
8	TiO ₂ sol–gel coating followed by heat treatment MAO coated AZ91D Mg alloy was submerged vertically in the TiO ₂ sol for 1 min, withdrawn at a speed of 3 cm/min for 3 cycles, dried in air for 2 h, and heat-treated at 150 and 350 °C for 1 h	Multiple immersions of MAO coated AZ91D Mg alloy in the TiO ₂ sol though help to increase the thickness of the TiO ₂ sol-gel coating, it promote cracks in the coating Heat-treatment at 150 and 350 °C for 1 h helps to reduce the porosity of the coating from 27% to 0.184% and 0.002%, respectively. Sealing of the MAO coated AZ91D Mg alloy with TiO ₂ sol-gel coating followed by heat treatment at 150 °C for 1 h has lead to a decrease in i_{corr} from 1.607 to 0.0796 $\mu\text{A}/\text{cm}^2$ and a decrease in impedance value from 8×10^3 to $1 \times 10^3 \Omega \cdot \text{cm}^2$ in 3.5% NaCl. TiO ₂ sol-gel coating heat-treated at 350 °C for 1 h has lead to an increase in i_{corr} to 0.48 $\mu\text{A}/\text{cm}^2$.	Laleh, Kargar, and Sabour Rouhaghdam (2011b)
9	SiO ₂ sol–gel coating followed by heat treatment MAO coated AM50B and AM60B alloys were immersed vertically in the SiO ₂ sol for 1 min, slowly withdrawn upwards, aged at 160 °C for 3 h, cooled inside the oven to promote a polymerized network structure for three cycles, and subsequently rinsed in deionized water for 3 min and dried at ambient temperature for 24 h	SiO ₂ sol–gel coating effectively plugs the open micropores and reduces the surface roughness and active surface area of the MAO coated AM50 and AM60 Mg alloys. Sealing of the pores of MAO coated AM50 Mg alloy by SiO ₂ sol-gel coating has enabled a decrease in i_{corr} from 0.145 to 0.00657 $\mu\text{A}/\text{cm}^2$ whereas the corresponding decrease i_{corr} for AM60 Mg alloy is from 0.104 to 0.012 $\mu\text{A}/\text{cm}^2$ in 3.5% NaCl.	Malayoglu et al. (2010)

Continued

Table 9.2 Continued

No.	Type of postsealing treatment and operating conditions	Effect of postsealing on the characteristics of MAO coatings and extent of improvement in corrosion resistance of the Mg alloy	Reference
10	Sol-gel coating of propolis and polylactic acid MAO coated Mg-Zn-Ca alloy was immersed vertically in the propolis-polylactic acid sol (mixture of 0.8 g of propolis in 50 ml of ethyl alcohol + 0.5 g polylactic acid dissolved in 50 ml of chloroform) for 1 h, withdrawn at a speed of 3 cm/min, and dried in air for 15 min in the first cycle. In the subsequent three cycles, the airing period was kept as 10 min and the samples were withdrawn at a speed of 4.5 cm/min	The propolis-polylactic acid sol-gel coating effectively seals the pores in the MAO coated Mg-Zn-Ca alloy. Sealing of the MAO coating using propolis-polylactic acid sol-gel coating has enabled a decrease in i_{corr} in SBF at $36.5 \pm 0.5^\circ\text{C}$ from 5.37×10^{-5} to 1.10×10^{-6} A/cm ² .	Gao, Shi, et al. (2011)
11	High-intensity pulsed ion beam (HIPIB) radiation Ion energy: 300 keV; current density: 200 A/cm ² ; number of shots: 1 to 5	Re-melting of the MAO coating deposited on AZ31 Mg alloy followed by rapid solidification enables the formation of a smooth surface with decrease in pore density. Increase in the number of shots from 1 to 5 eliminates the pores in the outer layer and considerably decreases the size of the pores in the inner layers. In the absence of formation of any new phases, structural rearrangement promotes the compactness of the MAO coated AZ31 Mg alloy. Increase in the number of HIPIB radiation shots from 1 to 5 shifts the passivation—pitting breakdown voltage from -1.420 to -0.80 V vs SCE and a two-fold decrease in i_{corr} from 3×10^{-7} to 4×10^{-9} A/cm ² in 3.5% NaCl.	Han et al. (2011)
12	Post baking Annealing treatment of MAO coated AZ91D Mg alloy at 100, 150, and 200 °C for 10 h in high purity Ar gas	The amount of MgO content in the MAO coating increased with increasing annealing temperature. However, at temperatures higher than 150 °C, shrinkage of the oxide layer following the dehydration reaction has caused the formation of significant cracks in the coating. Annealing of the MAO coated AZ91D Mg alloy at 100 °C for 10 h offered an i_{corr} of 3.45×10^{-8} A/cm ² . Increase in annealing temperature from 100 to 150 °C lead to a decrease in i_{corr} from 3.45×10^{-8} A/cm ² to 9.61×10^{-9} A/cm ² . Increase in temperature from 150 to 200 °C increased the i_{corr} from 9.61×10^{-9} to 3.96×10^{-8} A/cm ² in 3.5% NaCl (pH: 7.0).	Ko, Lee, Lee, et al. (2011); Ko, Lee, and Shin (2011)

Data compiled from Sankara Narayanan et al. (2014) with permission from Elsevier.

resistance of the MAO coating, could be shielded by the relatively large thickness (Duan et al., 2006). The biocompatibility of the polymeric coatings under *in vivo* conditions also warrants attention (Lu, Cao, et al., 2011).

The major concern in adopting sol-gel coating as a sealing/posttreatment to seal the pores of the MAO coating on Mg and Mg alloys is the inability of the thickness of the single layer to provide a reasonable long-term corrosion protection, while cracking of the sol-gel coating limits the choice of multiple immersion to build its thickness. The cracks in the sol-gel layer permit penetration of the corrosive medium and promote localized corrosion attack. Heat treatment after the sol-gel coating increases the surface roughness. The occurrence of severe localized corrosion at the cracked regions and the increase in surface roughness of the coating after heat treatment leads to the question of whether sol-gel coating will be a useful strategy for improving the corrosion resistance of MAO coatings.

The use of high-intensity pulsed ion beam (HIPIB) radiation of MAO-coated AZ31 Mg alloy helps to increase the corrosion resistance. However, the decrease in corrosion resistance after 48 h of immersion in 3.5% NaCl suggests that most of the pores in the middle layer are not sealed and allowed permeation of the corrosive medium through them to the base metal (Han et al., 2011). This inference also suggests that the thickness of the remelted layer during HIPIB is not sufficient to achieve long-term corrosion resistance. The use of higher energy density or an increase in the number of irradiation shots to more than five could increase the thickness of the remelted layer and seal the pores in the middle layer. However, its effect on the microstructural characteristics of the Mg alloy is not known.

In spite of the sealing of the pores of the MAO coating, none of these sealing treatments could offer a long-term corrosion protection of the Mg alloy. This inference indicates that the sealants are effective only in sealing the pores at the top surface, and they would not be able to penetrate through the pores and seal the pores at the intermediate layers. In addition, sealing the pores at the top surface decreases the chances for cell adhesion and growth. Hence, it appears that sealing the pores using organic, polymeric, and other similar strategies has limited scope in achieving a better corrosion resistance of MAO coatings.

9.3.7 Multifunctional approaches

Improving the corrosion resistance is one of the key issues in MAO coatings deposited on Mg and its alloys. However, when they are used for biomedical applications, imparting other functionalities together with better corrosion resistance would always be beneficial, and any such approaches will be fascinating. Xu, Lu, Guo, and Fang (2010) explored the possibility of preparing MAO coatings with a multifunctional approach to achieve better corrosion resistance and controlled drug release. Known volumes of cross-linked gelatin/Paclitaxel-loaded Poly(DL-lactide-co-glycolide) (PLGA) nanoparticle (NP) solutions were dropped onto the surface of the MAO-coated WE42 Mg alloy and dried at room temperature. The cross-linked gelatin/PGLA NPs composite coating covers most pores and microcracks present on the surface of the MAO-coated WE42 Mg alloy, thus making it smooth and uniform,

offering a better corrosion resistance in Hank's solution at 37 °C, and exhibiting a nearly linear sustained-release profile with no significant burst release. The development of such multifunctional coatings for biomedical applications is likely to be explored further by many researchers, and it is indeed a useful strategy beyond achieving better corrosion resistance.

Lu, Liu, Guo, Fang, and Xu (2011) and Lu, Fan, et al. (2011) have also reported a similar multifunctional coating approach in which they have used either an electroless nickel or a poly-L-lactic acid (PLLA) coating as the first layer, a paclitaxel (PTX) loaded (8%, 10%, and 12%) organic poly(DL-lactide-co-glycolide) (PLGA with LA/GA 90:10) drug-releasing coating as the second layer, and a PTX-free drug-controlled releasing coating consisting of PLGA with different LA/GA ratio (90/10, 75/25, 50/50) deposited as the top layer on MAO-coated AZ81 Mg alloy to control the drug release rate. The PLGA-based drug-controlled release coating was also prepared using different concentrations (3%, 6%, and 12%) of polyethylene glycol (PEG) with different molecular weights (2000, 4000, and 6000) as plasticizers. The double-layered PLGA/PTX drug-releasing coating with a top-layered PLGA drug-controlled releasing coating deposited on electroless nickel or PLLA coating exhibited a nearly linear sustained-release profile with no significant burst releases. The PLGA-based drug-controlled release coating prepared using PEG exhibited increased drug release kinetics compared with those prepared using PLGA alone. In spite of its ability to provide a very good improvement in corrosion resistance, the acceptability of using an electroless nickel coating to seal the pores of MAO coatings (Lu, Liu, et al., 2011) becomes a questionable issue for biomedical applications because nickel is carcinogenic in nature. In addition, the extent of corrosion resistance offered by the electroless nickel coating is too high, so it may deviate from the basic objective of adopting these strategies to develop degradable implants.

Liu et al. (2011a) and Liu et al. (2011b) studied the formation mechanism of calcium phosphate coating on the surface of MAO-coated Mg. When the MAO-coated Mg is immersed in $\text{Ca}(\text{NO}_3)_2$, dissolution of $\text{MgO}/\text{Mg}(\text{OH})_2$ causes local alkalization, while the subsequent addition of K_2HPO_4 leads to the formation of HA with a spherical morphology (Figure 9.5(a) and 9.5(b)). With an increase in calcification time, the formation of HA is promoted (Figure 9.5(c) and 9.5(d)). Nevertheless, when the MAO-coated Mg surface is covered with HA crystals, dissolution of $\text{MgO}/\text{Mg}(\text{OH})_2$ and the extent of local alkalization are decreased, which hinders the nucleation and growth of HA. Continuous addition of K_2HPO_4 promotes direct reaction with Ca^{2+} ions, resulting in the formation of dicalcium phosphate dihydrate (DCPD) with a flake-like morphology (Figure 9.5(e)). Hence, the resultant coating consists of a mixture of HA and DCPD (Figure 9.5(f)). When the order of addition is reversed, only DCPD, initially with a flake-like morphology (Figure 9.6(a)) that changed into a plate-like morphology with increase in calcification time (Figure 9.6(b)), is observed. Hence, the use of an acidic calcification solution appears to be essential to induce the deposition of HA. However, acidic solutions could promote the dissolution of $\text{MgO}/\text{Mg}(\text{OH})_2$ and the Mg^{2+} ions would hinder apatite formation, which is reflected in the low Ca/P ratio of the coating during the initial stages of calcification. If the Ca^{2+} ion concentration is higher, then it could establish a

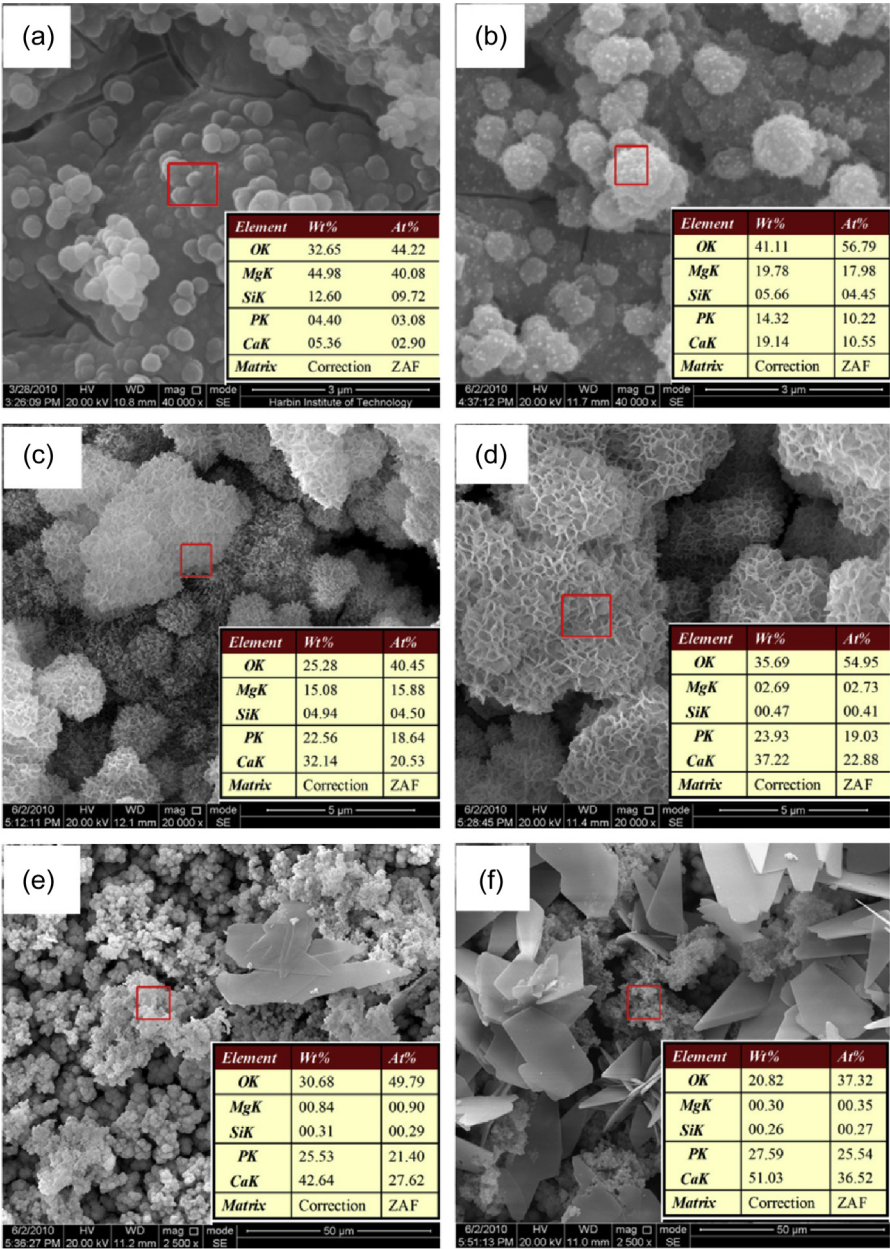


Figure 9.5 Evolution of morphological features of calcium phosphate coating deposited on MAO-coated Mg by calcification as a function of time: (a) 5 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 45 min, and (f) 4 h. Condition: addition of 0.1 M K_2HPO_4 to 0.17 M $Ca(NO_3)_2$. Adapted from Liu et al. (2011a) with permission from Elsevier.

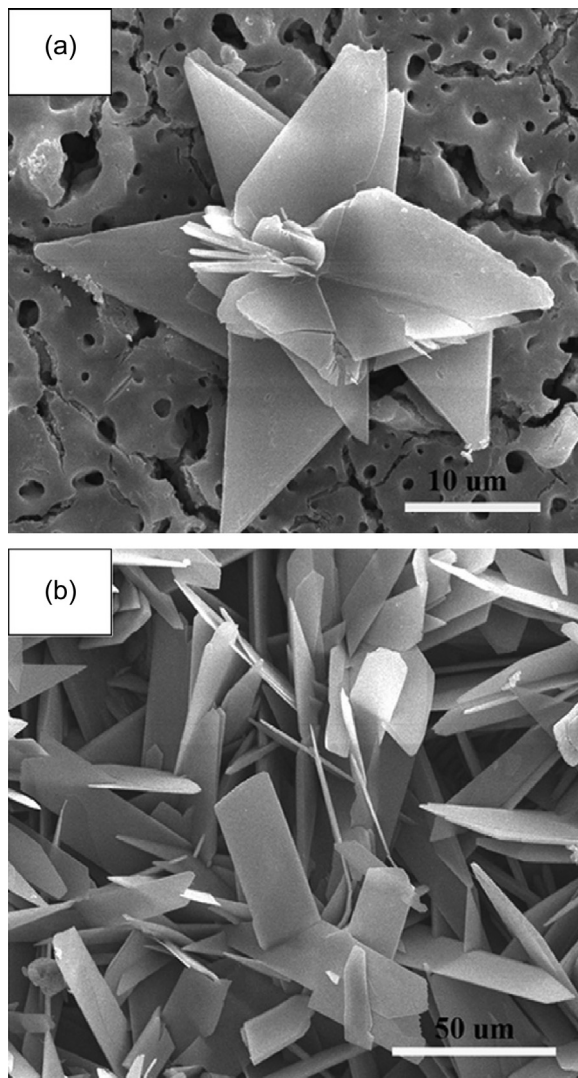


Figure 9.6 Evolution of morphological features of calcium phosphate coating deposited on MAO-coated Mg by calcification as a function of time: (a) 30 min and (b) 4 h.

Condition: addition of 0.17 M $\text{Ca}(\text{NO}_3)_2$ to 0.1 M K_2HPO_4 .

Adapted from [Liu et al. \(2011a\)](#) with permission from Elsevier.

bonding with hydroxyl group of $\text{Mg}(\text{OH})_2$, followed by PO_4^{3-} ions near the substrate surface. Once HA nuclei are formed, then the growth of HA would become easy in a local alkali environment. These inferences make evident the fact that pH and Ca^{2+} ion concentration could significantly influence the formation of calcium phosphate coating. MAO-coated Mg modified by calcium phosphate coating offered a good

corrosion resistance when immersed in simulated body fluid (SBF) (with no refreshment of the solution) at 37 °C for 132 h, as evidenced by the volume of hydrogen evolution, which is limited to $\sim 1 \text{ ml/cm}^2$ from 0 to 132 h. Conversely, for uncoated Mg, the volume of hydrogen evolution increased rapidly with an increase in immersion time from 0 to 60 h and reached $\sim 8 \text{ ml/cm}^2$ at 60 h; beyond 60 h, it exhibited a very slow increase until 132 h.

Gao, Guan, et al. (2011) have explored a multifunctional approach of depositing rod-like nano hydroxyapatite (RNHA) by electrodeposition (ED) on MAO-coated Mg alloy so that it would be possible to increase the corrosion resistance of MAO coating as well as its biocompatibility. The MAO-ED RNHA composite coating exhibits a much higher bonding strength of 12.3 MPa when compared to ED HA coating, which has a bond strength of 6.2 MPa (Ban and Hasegawa, 2002). The pinning force generated by the accommodation of RNHA within the pores of MAO coating and similarity in chemical bonding between these two coatings are considered to be responsible for the increase in bonding strength. Plugging of the pores by RNHA decreased the permeation of the corrosive medium, while the better compatibility between the MAO and HA coatings eliminates peeling of the coating and provides a better stability. In addition, the RNHA coating induced rapid precipitation of calcium orthophosphates on the HA rods, following their ability to increase the specific surface area to promote absorption of Ca^{2+} and PO_4^{3-} from SBF solution (Gao, Guan, et al., 2011). Hence, ED of RNHA on MAO-coated Mg alloy appears to be a good strategy because it not only increases the corrosion resistance by three orders of magnitude but also increases the bonding strength and promotes apatite growth.

Shi, Qi, Chen, and Shi (2011) have also used a similar multifunctional approach to deposit DCPD by ED to increase the corrosion resistance and bioactivity of MAO-coated Mg alloy. The porous nature of the MAO coating provides an anchoring effect for the flake-like DCPD crystals and improves the bonding between the top DCPD layer and the inner MAO layer. Plugging of the pores by DCPD enables a significant improvement in corrosion resistance of MAO-DCPD composite coating in SBF (pH: 7.4) at 37 °C. In addition, DCPD enables an increase in apatite-forming ability when compared to the MAO coating.

Chen et al. (2012) explored ED of HA as a strategy to seal the pores of the MAO coating on Mg alloys. The MAO-ED HA composite-coated Mg alloy effectively slows down the rate of degradation. *In vivo* studies indicate that during the early period, the MAO-ED HA composite-coated Mg alloy decreased the extent of release of Mg^{2+} ions and induced the growth of bone cells when compared to that of the uncoated one, thus satisfying one of the important requirements of degradable implants. The ability to show good bioactivity and rapid bone response that is evident from the newly formed bone tissues and its faster maturity, improved adhesion strength ($>40 \text{ MPa}$), and complete degradability of all the components of the coating (i.e., HA, octacalcium phosphate, $\text{Mg}_3(\text{PO}_4)_2$, and MgO) are some of the important attributes of this type of composite coatings.

Formation of a composite coating using a methodology that fundamentally combines the advantages of MAO coating and ED has been addressed by

Zhao et al. (2013). The combination of MAO coating and ED HA coatings lead to a four-fold decrease in i_{corr} when compared to the uncoated Mg alloy. The multifunctional ability of the MAO-ED HA composite coating not only improves the corrosion resistance but also endows the Mg alloys with a potential bioactivity following the chemical and biological similarity of HA to human bone tissues.

9.4 Summary and concluding remarks

The formation of pores and cracks in MAO coatings is inevitable. The pores in MAO coatings can be considered to be an opportunity because they could significantly improve the mechanical interlocking effect, the bonding area, and stress distribution across the adhesive—substrate interface of the joints, resulting in higher bond strength. However, it is a serious limitation in terms of the corrosion resistance of the resultant coatings. Several strategies were explored to improve the corrosion resistance of MAO coatings. The concern of the researchers is to employ a suitable strategy to overcome the deleterious influence of pores and cracks on the corrosion resistance of MAO coatings. The choice of suitable electrical parameters appears to hold a key because a hybrid (unipolar followed by bipolar) current mode, increase in cathodic current pulse, and increase in frequency enabled the formation of good-quality coatings with a considerable reduction in pore size and density. Because the MAO coatings are invariably porous, increasing the thickness of the barrier layer is very critical to imparting a better corrosion resistance.

Multifunctional approaches seem to be logical in terms of achieving an acceptable corrosion protection and biocompatibility. However, the acceptability of certain types of coatings, such as electroless nickel coating to seal the pores of MAO coatings, becomes a questionable issue for biomedical applications because they are carcinogenic in nature. A similar argument is also valid for many additives used to modify the electrolyte where the toxicity of an incorporated additive or its decomposition products is a matter of concern. Likewise, the sealants used to seal the pores of the MAO coatings, particularly polymeric compounds, should possess an acceptable self-degradation rate in the body fluid.

The major challenge is the susceptibility of magnesium and its alloys towards localized corrosion attacks when MAO coating or corrosion products cover their surface. In fact, the dominance of localized corrosion mechanisms when the corrosion products start to deposit on the surface has been the biggest challenge in developing magnesium-based degradable implants. A combination of strategies — increasing the thickness of the barrier layer, adopting suitable current parameters to prepare better-quality coatings, and imparting multifunctionality — could offer better corrosion resistance for MAO coatings on Mg/Mg alloys. In spite of numerous attempts to improve the corrosion performance of MAO coatings, the difficulty in eliminating the inhomogeneous degradation and maintaining sufficient mechanical integrity of Mg/Mg alloys for a reasonable time remains unsolved, and the quest for the perfect strategy continues.

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References

- Arrabal, R., Matykina, E., Hashimoto, T., Skeldon, P., & Thompson, G. E. (2009). Characterization of AC PEO coatings on magnesium alloys. *Surface and Coatings Technology*, 203, 2207–2220.
- Arrabal, R., Matykina, E., Skeldon, P., & Thompson, G. E. (2008). Incorporation of zirconia particles into coatings formed on magnesium by plasma electrolytic oxidation. *Journal of Materials Science*, 43, 1532–1538.
- Arrabal, R., Matykina, E., Viejo, F., Skeldon, P., Thompson, G. E., & Merino, M. C. (2008). AC plasma electrolytic oxidation of magnesium with zirconia nanoparticles. *Applied Surface Science*, 254, 6937–6942.
- Bai, A., & Chen, Z. J. (2009). Effect of electrolyte additives on anti-corrosion ability of micro-arc oxide coatings formed on magnesium alloy AZ91D. *Surface and Coatings Technology*, 203, 1956–1963.
- Bala Srinivasan, P., Liang, J., Balajee, R. G., Blawert, C., Störmer, M., & Dietzel, W. (2010). Effect of pulse frequency on the microstructure, phase composition and corrosion performance of a phosphate-based plasma electrolytic oxidation coated AM50 magnesium alloy. *Applied Surface Science*, 256, 3928–3935.
- Bala Srinivasan, P., Liang, J., Blawert, C., Störmer, M., & Dietzel, W. (2010). A preliminary study of calcium containing plasma electrolytic oxidation coatings on AM50 magnesium alloy. *Journal of Material Science*, 45, 1406–1410.
- Ban, S., & Hasegawa, J. (2002). Morphological regulation and crystal growth of hydrothermal electrochemically deposited apatite. *Biomaterials*, 23, 2965–2972.
- Barchiche, C. E., Rocca, E., Juers, C., Hazan, J., & Steinmetz, J. (2007). Corrosion resistance of plasma-anodized AZ91D magnesium alloy by electrochemical methods. *Electrochimica Acta*, 53, 417–425.
- Blawert, C., Dietzel, W., Ghali, E., & Song, G. (2006). Anodizing treatments for magnesium alloys and their effect on corrosion resistance in various environments. *Advanced Engineering Materials*, 8, 511–533.
- Blawert, C., Heitmann, V., Dietzel, W., Nykyforchyn, H. M., & Klapkiv, M. D. (2007). Influence of electrolyte on corrosion properties of plasma electrolytic conversion coated magnesium alloys. *Surface and Coatings Technology*, 201, 8709–8914.
- Brar, H. S., Platt, M. O., Sarntinoranont, M., Martin, P. I., & Manuel, M. V. (2009). Magnesium as a biodegradable and bioabsorbable material for medical implants. *Journal of Operations Management*, 61, 31–34.
- Cai, J., Cao, F., Chang, L., Zheng, J., Zhang, J., & Cao, C. (2011). The preparation and corrosion behaviors of MAO coating on AZ91D with rare earth conversion precursor film. *Applied Surface Science*, 257, 3804–3811.
- Chang, L. R., Cao, F. H., Cai, J. S., Liu, W. J., Zhang, Z., & Zhang, J. G. (2011). Influence of electric parameters on MAO of AZ91D magnesium alloy using alternative square-wave power source. *Transactions of Nonferrous Metals Society of China*, 21, 307–316.

- Chen, S., Guan, S., Li, W., Wang, H., Chen, J., Wang, Y., et al. (2012). In vivo degradation and bone response of a composite coating on Mg–Zn–Ca alloy prepared by microarc oxidation and electrochemical deposition. *Journal of Biomedical Materials Research B*, 100B, 533–543.
- Cheng, Y. L., Qin, T. W., Li, L. L., Wang, H. M., & Zhang, Z. (2011). Comparison of corrosion resistance of microarc oxidation coatings prepared with different electrolyte concentrations on AM60 magnesium alloy. *Corrosion Engineering, Science and Technology*, 46, 17–23.
- Duan, H., Du, K., Yan, C., & Wang, F. (2006). Electrochemical corrosion behavior of composite coatings of sealed MAO film on magnesium alloy AZ91D. *Electrochimica Acta*, 51, 2898–2908.
- Gao, J. H., Guan, S. K., Chen, J., Wang, L. G., Zhu, S. J., Hu, J. H., et al. (2011). Fabrication and characterization of rod-like nano-hydroxyapatite on MAO coating supported on Mg–Zn–Ca alloy. *Applied Surface Science*, 257, 2231–2237.
- Gao, J. H., Shi, X. Y., Yang, B., Hou, S. S., Meng, E. C., Guan, F. X., et al. (2011). Fabrication and characterization of bioactive composite coatings on Mg–Zn–Ca alloy by MAO/sol–gel. *Journal of Materials Science: Materials in Medicine*, 22, 1681–1687.
- Ghasemi, A., Raja, V. S., Blawert, C., Dietzel, W., & Kainer, K. U. (2008). Study of the structure and corrosion behavior of PEO coatings on AM50 magnesium alloy by electrochemical impedance spectroscopy. *Surface and Coatings Technology*, 202, 3513–3518.
- Gu, Y., Chen, C. F., Bandopadhyay, S., Ning, C., Zhang, Y., & Guo, Y. (2012). Corrosion mechanism and model of pulsed DC microarc oxidation treated AZ31 alloy in simulated body fluid. *Applied Surface Science*, 258, 6116–6126.
- Gu, Y., Xiong, W., Ning, C., & Zhang, J. (2012). Residual stresses in microarc oxidation ceramic coatings on biocompatible AZ31 magnesium alloys. *Journal of Materials Engineering and Performance*, 21, 1085–1090.
- Guo, H. F., & An, M. Z. (2005). Growth of ceramic coatings on AZ91D magnesium alloys by micro-arc oxidation in aluminate–fluoride solutions and evaluation of corrosion resistance. *Applied Surface Science*, 246, 229–238.
- Guo, H. F., & An, M. Z. (2006). Effect of surfactants on surface morphology of ceramic coatings fabricated on magnesium alloys by micro-arc oxidation. *Thin Solid Films*, 500, 186–189.
- Guo, H. F., An, M. Z., Huo, H. B., Xu, S., & Wu, L. J. (2006). Microstructure characteristic of ceramic coatings fabricated on magnesium alloys by micro-arc oxidation in alkaline silicate solutions. *Applied Surface Science*, 252, 7911–7916.
- Guo, M., Cao, L., Lu, P., Liu, Y., & Xu, X. (2011). Anticorrosion and cytocompatibility behavior of MAO/PLLA modified magnesium alloy WE42. *Journal of Materials Science: Materials in Medicine*, 22, 1735–1740.
- Han, X. G., Zhu, X. P., & Lei, M. K. (2011). Electrochemical properties of microarc oxidation films on a magnesium alloy modified by high-intensity pulsed ion beam. *Surface and Coatings Technology*, 206, 874–878.
- Hermawan, H., Dubé, D., & Mantovani, D. (2010). Developments in metallic biodegradable stents. *Acta Biomaterialia*, 6, 1693–1697.
- Hermawan, H., Purnama, A., Dube, D., Couet, J., & Mantovani, D. (2010). Fe–Mn alloys for metallic biodegradable stents: degradation and cell viability studies. *Acta Biomaterialia*, 6, 1852–1860.
- Hornberger, H., Virtanen, S., & Boccaccini, A. R. (2012). Biomedical coatings on magnesium alloys - a review. *Acta Biomaterialia*, 8, 2442–2455.
- Hussein, R. O., Nie, X., Northwood, D. O., Yerokhin, A., & Matthews, A. (2010). Spectroscopic study of electrolytic plasma and discharging behaviour during the plasma electrolytic oxidation (PEO) process. *Journal of Physics D*, 43, 105203.

- Hussein, R. O., Northwood, D. O., & Nie, X. (2012). The influence of pulse timing and current mode on the microstructure and corrosion behaviour of a plasma electrolytic oxidation (PEO) coated AM60B magnesium alloy. *Journal of Alloys and Compounds*, 541, 41–48.
- Hussein, R. O., Zhang, P., Nie, X., Xia, Y., & Northwood, D. O. (2011). The effect of current mode and discharge type on the corrosion resistance of plasma electrolytic oxidation (PEO) coated magnesium alloy AJ62. *Surface and Coatings Technology*, 206, 1990–1997.
- Hwang, D. Y., Kim, Y. M., Park, D. Y., Yoo, B., & Shin, D. H. (2009). Corrosion resistance of oxide layers formed on AZ91 Mg alloy in KMnO_4 electrolyte by plasma electrolytic oxidation. *Electrochimica Acta*, 54, 5479–5485.
- Jiang, J., Zhou, Q., Yu, J., Ma, A., Song, D., Lu, F., et al. (2013). Comparative analysis for corrosion resistance of micro-arc oxidation coatings on coarse-grained and ultra-fine grained AZ91D Mg alloy. *Surface and Coatings Technology*, 216, 259–266.
- Kirkland, N. T., Birbilis, N., & Staiger, M. P. (2012). Assessing the corrosion of biodegradable magnesium implants: a critical review of current methodologies and their limitations. *Acta Biomaterialia*, 8, 925–936.
- Kirkland, N. T., Lespagnol, J., Birbilis, N., & Staiger, M. P. (2010). A survey of bio-corrosion rates of magnesium alloys. *Corrosion Science*, 52, 287–291.
- Ko, Y. G., Lee, K. M., Lee, B. U., & Shin, D. H. (2011). An electrochemical analysis of AZ91 Mg alloy processed by plasma electrolytic oxidation followed by static annealing. *Journal of Alloys and Compounds*, 509S, S468–S472.
- Ko, Y. G., Lee, K. M., & Shin, D. H. (2011). Electrochemical corrosion properties of AZ91 Mg Alloy via plasma electrolytic oxidation and subsequent annealing. *Materials Transactions*, 52, 1697–1700.
- Ko, Y. G., Namgung, S., & Shin, D. H. (2010). Correlation between KOH concentration and surface properties of AZ91 magnesium alloy coated by plasma electrolytic oxidation. *Surface and Coatings Technology*, 205, 2525–2531.
- Laleh, M., Kargar, F., & Sabour Rouhaghdam, A. (2011a). Formation of a compact oxide layer on AZ91D magnesium alloy by microarc oxidation via addition of cerium chloride into the MAO electrolyte. *Journal of Coatings Technology and Research*, 8, 765–771.
- Laleh, M., Kargar, F., & Sabour Rouhaghdam, A. (2011b). Improvement in corrosion resistance of micro arc oxidation coating formed on AZ91D magnesium alloy via applying a nano-crystalline sol–gel layer. *Journal of Sol-Gel Science and Technology*, 59, 297–303.
- Lee, K. M., Lee, B. U., Yoon, S. I., Lee, E. S., Yoo, B., & Shin, D. H. (2012). Evaluation of plasma temperature during plasma oxidation processing of AZ91 Mg alloy through analysis of the melting behavior of incorporated particles. *Electrochimica Acta*, 67, 6–11.
- Lee, K. M., Shin, K. R., Namgung, S., Yoo, B., & Shin, D. H. (2011). Electrochemical response of ZrO_2 -incorporated oxide layer on AZ91 Mg alloy processed by plasma electrolytic oxidation. *Surface and Coatings Technology*, 205, 3779–3784.
- Li, X., & Luan, B. L. (2012). Discovery of Al_2O_3 particles incorporation mechanism in plasma electrolytic oxidation of AM60B magnesium alloy. *Materials Letters*, 86, 88–91.
- Li, Z., Jing, X., Yuan, Y., & Zhang, M. (2012). Composite coatings on a Mg-Li alloy prepared by combined plasma electrolytic oxidation and sol-gel techniques. *Corrosion Science*, 63, 358–366.
- Li, Z., Yuan, Y., Sun, P., & Jing, X. (2011). Ceramic coatings of LA141 alloy formed by plasma electrolytic oxidation for corrosion protection. *ACS Applied Materials & Interfaces*, 3, 3682–3690.
- Liang, J., Guo, B., Tian, J., Liu, H., Zhou, J., & Xu, T. (2005). Effect of potassium fluoride in electrolytic solution on the structure and properties of microarc oxidation coatings on magnesium alloy. *Applied Surface Science*, 252, 345–351.

- Liang, J., Hu, L., & Hao, J. (2007). Improvement of corrosion properties of microarc oxidation coating on magnesium alloy by optimizing current density parameters. *Applied Surface Science*, 253, 6939–6945.
- Lim, T. S., Ryu, H. S., & Hong, S. H. (2012). Electrochemical corrosion properties of CeO₂-containing coatings on AZ31 magnesium alloys prepared by plasma electrolytic oxidation. *Corrosion Science*, 62, 104–111.
- Liu, F., Shan, D., Song, Y., Han, E. H., & Ke, W. (2011). Corrosion behavior of the composite ceramic coating containing zirconium oxides on AM30 magnesium alloy by plasma electrolytic oxidation. *Corrosion Science*, 53, 3845–3852.
- Liu, G. Y., Hu, J., Ding, Z. K., & Wang, C. (2011a). Formation mechanism of calcium phosphate coating on micro-arc oxidized magnesium. *Materials Chemistry and Physics*, 130, 1118–1124.
- Liu, G. Y., Hu, J., Ding, Z. K., & Wang, C. (2011b). Bioactive calcium phosphate coating formed on micro-arc oxidized magnesium by chemical deposition. *Applied Surface Science*, 257, 2051–2057.
- Liu, J., Lu, Y., Jing, X., Yuan, Y., & Zhang, M. (2009). Characterization of plasma electrolytic oxidation coatings formed on Mg–Li alloy in an alkaline silicate electrolyte containing silica sol. *Materials and Corrosion*, 60, 865–870.
- Liu, P., Pan, X., Yang, W., Cai, K., & Chen, Y. (2012). Improved anticorrosion of magnesium alloy via layer-by-layer self-assembly technique combined with micro-arc oxidation. *Materials Letters*, 75, 118–121.
- Liu, Y. P., Zhag, D. F., Chen, C. G., Zhang, J. G., & Cui, L. (2011). Adsorption orientation of sodium of polyaspartic acid effect on anodic films formed on magnesium alloy. *Applied Surface Science*, 257, 7579–7585.
- Lu, P., Cao, L., Lin, Y., Xu, X., & Wu, X. (2011). Evaluation of magnesium ions release, biocorrosion, and hemocompatibility of MAO/PLLA-modified magnesium alloy WE42. *Journal of Biomedical Materials Research*, 96B, 101–109.
- Lu, P., Fan, H., Liu, Y., Cao, L., Wu, X., & Xu, X. (2011). Controllable biodegradability, drug release behavior and hemocompatibility of PTX-eluting magnesium stents. *Colloids and Surfaces, B: Biointerfaces*, 83, 23–28.
- Lu, P., Liu, Y., Guo, M., Fang, H., & Xu, X. (2011). Corrosion and drug release properties of EN-plating/PLGA composite coating on MAO film. *Materials Science and Engineering: C*, 31, 1285–1289.
- Lv, G. H., Chen, H., Gu, W. C., Li, L., Niu, E. W., Zhang, X. H., et al. (2008). Effects of current frequency on the structural characteristics and corrosion property of ceramic coatings formed on magnesium alloy by PEO technology. *Journal of Materials Processing Technology*, 208, 9–13.
- Lv, G. H., Chen, H., Li, L., Niu, E. W., Pang, H., Zou, B., et al. (2009). Investigation of plasma electrolytic oxidation process on AZ91D magnesium alloy. *Current Applied Physics*, 9, 126–130.
- Malayoglu, U., Tekin, K. C., & Shrestha, S. (2010). Influence of post-treatment on the corrosion resistance of PEO coated AM50B and AM60B Mg alloys. *Surface and Coatings Technology*, 205, 1793–1798.
- Mandelli, A., Bestetti, M., Da Forno, A., Lecis, N., Trasatti, S. P., & Trueba, M. (2011). A composite coating for corrosion protection of AM60B magnesium alloy. *Surface and Coatings Technology*, 205, 4459–4465.
- Moravej, M., Prima, F., Fiset, M., & Mantovani, D. (2010). Electroformed iron as new biomaterial for degradable stents: development process and structure–properties relationship. *Acta Biomaterialia*, 6, 1726–1735.

- Moravej, M., Purnama, A., Fiset, M., Couet, J., & Mantovani, D. (2010). Electroformed pure iron as a new biomaterial for degradable stents: In vitro degradation and preliminary cell viability studies. *Acta Biomaterialia*, 6, 1843–1851.
- Necula, B. S., Fratila-Apachitei, L. E., Berkani, A., Apachitei, I., & Duszczek, J. (2009). Enrichment of anodic MgO layers with Ag nanoparticles for biomedical applications. *Journal of Materials Science: Materials in Medicine*, 20, 339–345.
- Pan, Y. K., Chen, C. Z., Wang, D. G., Yu, X., & Lin, Z. Q. (2012). Influence of additives on microstructure and property of microarc oxidized Mg–Si–O coatings. *Ceramics International*, 38, 5527–5533.
- Rama Krishna, L., Poshal, G., & Sundararajan, G. (2010). Influence of electrolyte chemistry on morphology and corrosion resistance of micro arc oxidation coatings deposited on magnesium. *Metallurgical and Materials Transactions A*, 41, 3499–3508.
- Salman, S. A., Ichino, R., & Okido, M. (2008). Production of alumina-rich surface film on AZ31 magnesium Alloy by anodizing with co-precipitation of nano-sized alumina. *Materials Transactions*, 49, 1038–1041.
- Shaw, B. A., Sikora, E., & Virtanen, S. (2008). Fix, heal, and disappear: a new approach to using metals in the human body. *Electrochemical Society Interface Summer*, 45–49.
- Shi, L., Xu, Y., Li, K., Yao, Z., & Wu, S. (2010). Effect of additives on structure and corrosion resistance of ceramic coatings on Mg–Li alloy by microarc oxidation. *Current Applied Physics*, 10, 719–723.
- Shi, P., Ng, W. F., Wong, M. H., & Cheng, F. T. (2009). Improvement of corrosion resistance of pure magnesium in hanks' solution by microarc oxidation with sol–gel TiO₂ sealing. *Journal of Alloys and Compounds*, 469, 286–292.
- Shi, Y., Qi, M., Chen, Y., & Shi, P. (2011). MAO-DCPD composite coating on Mg alloy for degradable implant applications. *Materials Letters*, 65, 2201–2204.
- Song, G., & Song, S. (2007). A possible biodegradable magnesium implant material. *Advanced Engineering Materials*, 9, 298–302.
- Song, Y. L., Sun, X. Y., & Liu, Y. H. (2012). Effect of TiO₂ nanoparticles on the microstructure and corrosion behavior of MAO coatings on magnesium alloy. *Materials and Corrosion*, 63, 813–818.
- Sreekanth, D., & Rameshbabu, N. (2012). Development and characterization of MgO/hydroxyapatite composite coating on AZ31 magnesium alloy by plasma electrolytic oxidation coupled with electrophoretic deposition. *Materials Letters*, 68, 439–442.
- Staiger, M. P., Pietak, A. M., Huadmai, J., & Dias, G. (2006). Magnesium and its alloys as orthopedic biomaterials: a review. *Biomaterials*, 27, 1728–1734.
- Su, P., Wu, X., Guo, Y., & Jiang, Z. (2009). Effects of cathode current density on structure and corrosion resistance of plasma electrolytic oxidation coatings formed on ZK60 Mg alloy. *Journal of Alloys and Compounds*, 475, 773–777.
- Tang, M., Liu, H., Li, W., & Zhu, L. (2011). Effect of zirconia sol in electrolyte on the characteristics of microarc oxidation coating on AZ91D magnesium. *Materials Letters*, 65, 413–415.
- Tang, Y., Zhao, X., Jiang, K., Chen, J., & Zuo, Y. (2010). The influences of duty cycle on the bonding strength of AZ31B magnesium alloy by microarc oxidation treatment. *Surface and Coatings Technology*, 205, 1789–1792.
- Van, T. B., Brown, S. D., & Wirtz, P. G. (1977). Mechanism of anodic spark deposition. *American Ceramic Society Bulletin*, 56, 563–566.
- Virtanen, S. (2011). Biodegradable Mg and Mg alloys: corrosion and biocompatibility. *Materials Science and Engineering: B*, 176, 1600–1608.

- Wang, J., Tang, J., & He, Y. (2010). Top coating of low-molecular weight polymer MALPB used for enhanced protection on anodized AZ31B Mg alloys. *Journal of Coatings Technology and Research*, 7, 737–746.
- Wang, J., Tang, J., Zhang, P., Li, Y., Wang, J., Lai, Y., et al. (2012). Surface modification of magnesium alloys developed for bioabsorbable orthopedic implants: a general review. *Journal of Biomedical Materials Research Part B*, 100, 1691–1701.
- Wang, L., Zhou, J., Liang, J., & Chen, J. (2012). Microstructure and corrosion behavior of plasma electrolytic oxidation coated magnesium alloy pre-treated by laser surface melting. *Surface and Coatings Technology*, 206, 3109–3115.
- Wang, X., Zhu, L., Li, W., Liu, H., & Li, Y. (2009). Effects of half-wave and full-wave power source on the anodic oxidation process on AZ91D magnesium alloy. *Applied Surface Science*, 255, 5721–5728.
- Wang, Y. M., Wang, F. H., Xu, M. J., Zhao, B., Guo, L. X., & Ouyang, J. H. (2009). Microstructure and corrosion behavior of coated AZ91 alloy by microarc oxidation for biomedical application. *Applied Surface Science*, 255, 9124–9131.
- Witte, F. (2010). The history of biodegradable magnesium implants: a review. *Acta Biomaterialia*, 6, 1680–1692.
- Witte, F., Hort, N., Vogt, C., Cohen, S., Kainer, K. U., Willumeit, R., et al. (2008). Degradable biomaterials based on magnesium corrosion. *Current Opinion in Solid State & Materials Science*, 12, 63–72.
- Wu, D., Liu, X., Lu, K., Zhang, Y., & Wang, H. (2009). Influence of $C_3H_8O_3$ in the electrolyte on characteristics and corrosion resistance of the microarc oxidation coatings formed on AZ91D magnesium alloy surface. *Applied Surface Science*, 255, 7115–7120.
- Wu, X., Su, P., Jiang, Z., & Meng, S. (2010). Influences of current density on tribological characteristics of ceramic coatings on ZK60 Mg Alloy by plasma electrolytic oxidation. *ACS Applied Materials & Interfaces*, 2, 810–812.
- Ximei, W., Liqun, Z., Huicong, L., & Weiping, L. (2008). Influence of surface pretreatment on the anodizing film of Mg alloy and the mechanism of the ultrasound during the pretreatment. *Surface Coatings and Technology*, 202, 4210–4217.
- Xin, Y., Hu, T., & Chu, P. K. (2011). In vitro studies of biomedical magnesium alloys in a simulated physiological environment: a review. *Acta Biomaterialia*, 7, 1452–1459.
- Xu, X., Lu, P., Guo, M., & Fang, M. (2010). Cross-linked gelatin/nanoparticles composite coating on micro-arc oxidation film for corrosion and drug release. *Applied Surface Science*, 256, 2367–2371.
- Yang, J., Cui, F., & Lee, I. S. (2011). Surface modifications of magnesium alloys for biomedical applications. *Annals of Biomedical Engineering*, 39, 1857–1871.
- Yao, Z. P., Li, L. L., Liu, X. R., & Jiang, Z. H. (2010). Preparation of ceramic conversion layers containing Ca and P on AZ91D Mg alloys by plasma electrolytic oxidation. *Surface Engineering*, 26, 317–320.
- Zeng, R., Dietzel, W., Witte, F., Hort, N., & Blawert, C. (2008). Progress and challenge for magnesium alloys as biomaterials. *Advanced Engineering Materials*, 10, B3–B14.
- Zhang, R. F., Shan, D. Y., Chen, R. S., & Han, E. H. (2008). Effects of electric parameters on properties of anodic coatings formed on magnesium alloys. *Materials Chemistry and Physics*, 107, 356–363.
- Zhang, R. F., Zhang, S. F., & Duo, S. W. (2009). Influence of phytic acid concentration on coating properties obtained by MAO treatment on magnesium alloys. *Applied Surface Science*, 255, 7893–7897.

- Zhang, R. F., Zhang, S. F., Shen, Y. L., Zhang, L. H., Liu, T. Z., Zhang, Y. Q., et al. (2012). Influence of sodium borate concentration on properties of anodic coatings obtained by micro arc oxidation on magnesium alloys. *Applied Surface Science*, 258, 6602–6610.
- Zhang, R. F., Zhang, S. F., Yang, N., Yao, L. J., He, F. X., Zhou, Y. P., et al. (2012). Influence of 8-hydroxyquinoline on properties of anodic coatings obtained by micro arc oxidation on AZ91 magnesium alloys. *Journal of Alloys and Compounds*, 539, 249–255.
- Zhang, S. F., Zhang, R. F., Li, W. K., Li, M. S., & Yang, G. L. (2012). Effects of tannic acid on properties of anodic coatings obtained by microarc oxidation on AZ91 magnesium alloy. *Surface and Coatings Technology*, 207, 170–176.
- Zhao, Q., Guo, X., Dang, X., Hao, J., Lai, J., & Wang, K. (2013). Preparation and properties of composite MAO/ECD coatings on magnesium alloy. *Colloids and Surfaces B: Biointerfaces*, 102, 321–326.
- Zhu, F., Wang, J., Li, S., & Zhang, J. (2012). Preparation and characterization of anodic films on AZ31B Mg alloy formed in the silicate electrolytes with ethylene glycol oligomers as additives. *Applied Surface Science*, 258, 8985–8990.

Biomimetic surface modifications of magnesium and magnesium alloys for biomedical applications

10

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10.1 Introduction

The term “biomimetic” refers to any system that mimics a naturally occurring biological system. Many organisms have developed multifunctional surfaces with hierarchical topographies and unique surface chemistries that enable them to survive and adapt to environmental influences. As our understanding of these processes has grown, we have developed technologies that allow us to take advantage of nature’s elegant solutions to everyday problems. A few examples include the following:

1. the surface patterning of aircraft materials to resemble the surface micron-scale pattern of shark skin for reduced drag (Scardino & de Nys, 2011);
2. the development of catechol-based polymer derivatives that mimic natural mussel adhesives, which have the remarkable ability to strongly adhere even under wet conditions (Sedo, Saiz-Poseu, Busque, & Ruiz-Molina, 2013);
3. surface modifications of implant materials to emulate the structure and chemical composition of the extracellular matrix (ECM) for optimized biocompatibility (Rahmany & Van Dyke, 2013); and
4. the development of superhydrophobic self-cleaning surfaces that mimic the hierarchical topography and surface chemistry of the lotus leaf (Guo, Liu, & Su, 2011; Yan, Gao, & Barthlott, 2011).

Biomimetic surface modifications can either mimic biology in terms of the modified surface itself or in the way that the coating is produced. The examples given above all fit into the former category, where the surface topography and/or surface chemistry mimic a biological system. A key example of the latter is in the deposition of calcium phosphate coatings on the surface of orthopedic implants in order to improve osseointegration. Calcium phosphate coatings deposited under conditions that mimic physiological conditions have been shown to have increased biocompatibility in comparison to spray-coated calcium phosphates that are deposited under far from natural conditions (Avila, Misch, Galindo-Moreno, & Wang, 2009).

In this chapter, biomimetic surface modification of magnesium and its alloys is discussed. To date, three key areas of research have been explored for these materials, including the following:

1. surface modifications that mimic the ECM for control of biodegradation and biocompatibility of magnesium alloy implant materials,

2. deposition of calcium phosphate coatings on magnesium and its alloys using a biomimetic coating strategy, and
3. superhydrophobic coatings for corrosion control that mimic the topography and surface chemistry of the lotus leaf.

10.1.1 General challenges in the development of coatings for magnesium and its alloys

There are two key challenges in the development of coatings for magnesium alloys. First, magnesium is a highly reactive metal that readily undergoes oxidation in contact with air or aqueous solutions. This results in the formation of a magnesium oxide/hydroxide layer at the surface. To further complicate matters, magnesium also undergoes a reaction with atmospheric CO_2 to produce magnesium carbonate at the surface. This $\text{Mg}(\text{OH})_2/\text{MgO}/\text{MgCO}_3$ surface layer can impede the adhesion and uniformity of surface coatings deposited on these materials, resulting in poor coating performance. A careful choice of pretreatment driven by the expected chemistry at the magnesium alloy/coating bath interface is therefore essential for optimized coating performance. Furthermore, magnesium reacts violently with most acids and readily dissolves in aqueous media at pH values less than 11. This effectively eliminates the use of many traditional coatings due to underlying dissolution of the substrate during coating deposition, resulting in poor coating adhesion.

Second, the surface chemistry of these materials is not homogeneous. This is illustrated in Figure 10.1, which shows the surface microchemistry of three different magnesium aluminum alloys with 3%, 6%, and 9% aluminum, respectively. The β phase (intermetallic, $\text{Mg}_{17}\text{Al}_{12}$) precipitates at the grain boundaries during cooling of these alloys, resulting in a non-uniform surface chemistry. On the AZ31 alloy, this phase is present as discrete bright spots in the image. As the amount of aluminum in the alloy is increased, the β phase gradually becomes an interconnected network on the surface. Therefore, the chemistry at the coating bath/alloy surface varies spatially across the sample. Moreover, the surface chemistry of magnesium alloys varies dramatically depending on the particular alloy to be coated. This means that coating strategies are not necessarily applicable from alloy to alloy.

10.2 Modification of biodegradable magnesium alloy implant surfaces

In recent years, magnesium alloys have been proposed as a potential biodegradable metallic implant material for orthopedic and cardiovascular applications (Brar et al., 2009; Staiger, Pietak, Huadmai, & Dias, 2006; Witte et al., 2008). They are an excellent material for this purpose because they have mechanical properties that are similar to bone (Staiger et al., 2006), have been shown to corrode in biological fluids (Song et al., 2009; Xin et al., 2009; Yang & Zhang, 2009), and are inherently biocompatible (Brar et al., 2009; Witte et al., 2008; Staiger et al., 2006). Magnesium-based metals readily corrode in aqueous solutions at pH values below 11; therefore, under

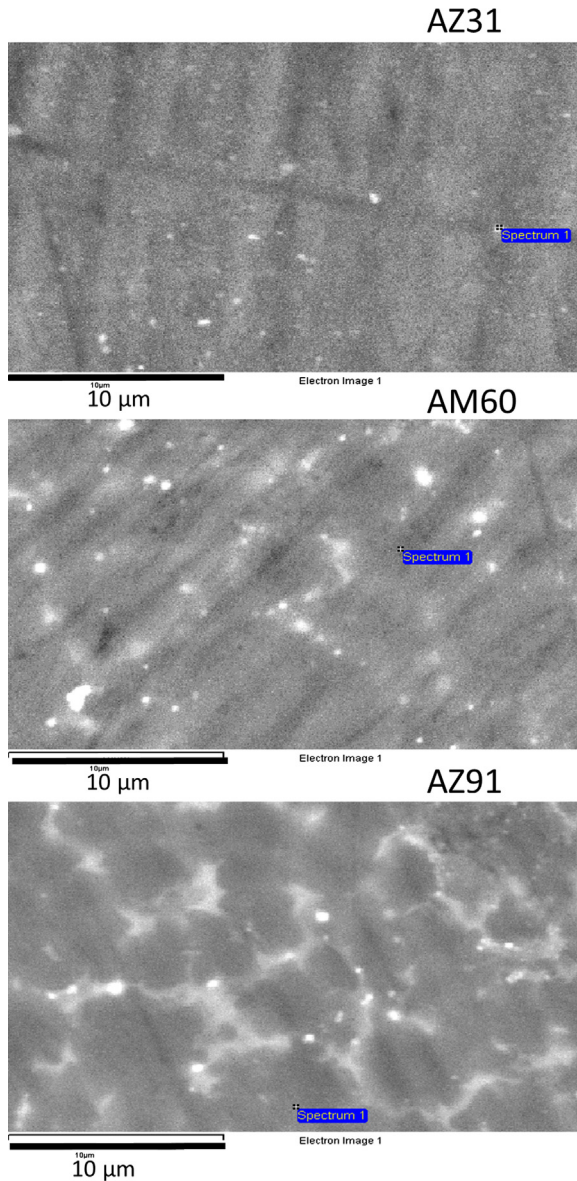
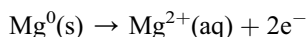


Figure 10.1 Backscattered electron microscopy images of magnesium alloy AZ31 (top), magnesium alloy AM60 (middle), and magnesium alloy AZ91 (bottom). The bright areas are the aluminum-rich β phase of the alloy; the dark areas are the magnesium-rich α phase of the alloy.

physiological conditions, these materials will readily degrade according to the following reactions (Makar & Kruger, 1993):



Alloying with aluminum and zinc has been shown to improve the corrosion resistance of magnesium by increasing the stability of the oxide layer and the open circuit potential (Anik & Celikten, 2007; Ghali, Dietzel, & Kainer, 2004a,b; Makar & Kruger, 1993; Mathieu, Rapin, Steinmetz, & Steinmetz, 2003; Song & Atrens, 1999; Song, Atrens, & Dargusch, 1999). Alloying leads to the formation of both a magnesium-rich phase (α phase) and an aluminum-rich intermetallic phase with a composition of $\text{Mg}_{17}\text{Al}_{12}$ (β phase) in the alloyed material (Mathieu et al., 2003; Unigovski & Gutman, 1999). The corrosion resistance of magnesium alloys has been shown to be related to the stability of the oxide layer that forms over the aluminum rich phase of the material (Anik et al., 2006; Anik & Celikten, 2007; Mathieu et al., 2003; Song et al., 1999; Song & Atrens, 1999). Although alloying slows the corrosion rate, hydrogen gas evolution and an increase in alkalinity are still by-products of the corrosion reaction and pose significant health risks for the patient. Therefore, surface modification of these materials to control the degradation rate in the early stages of healing and improve their biocompatibility is crucial to the successful implementation of magnesium alloy implants in medicine.

10.2.1 Surface modification to mimic the ECM

Cell adhesion and proliferation at the implant surface is a vital factor for successful integration of a biomaterial within the body (Hersel, Dahmen, & Kessler, 2003). In recent years, an improved understanding of the interactions of cells with the ECM has led to the development of coatings that mimic the structure and/or surface chemistry of the ECM. The ECM is an organized three-dimensional network of macromolecules with both micro and nanoscale surface features that provide cell support and cell adhesion sites and regulate cell communication (Wang & Carrier, 2011). It is composed primarily of polysaccharide chains of glycosaminoglycans and fibrous proteins such as collagen, elastin, and fibronectin. Several review articles detail biomimetic approaches for modulating cell adhesion on biomaterials (Avila et al., 2009; Rahmany & Van Dyke, 2013). From these reviews, three general strategies for optimizing cell adhesion, proliferation, and differentiation emerge: nanoscale patterning of surfaces, the incorporation of bioactive molecules into surface coatings, and covalent bonding of bioadhesive ECM macromolecules/binding motifs to the biomaterials surface.

Two research articles have highlighted the importance of nanoscale topography on cell/magnesium surface interactions (Weng & Webster, 2012, 2013). In these articles, the surface of magnesium ribbon was roughened by immersion in high concentration sodium hydroxide solutions. The resulting surfaces were shown to have increased

nanoscale surface roughness in comparison to the control sample. The increased surface roughness was correlated to improved cell adhesion and cell function on the modified surfaces. This is a promising area of future research; however, few studies on the influence of magnesium surface topography on cell response have been reported.

To date, two types of biomimetic surface modifications that mimic the ECM have been the main focus of research efforts to improve both the corrosion resistance and biocompatibility of magnesium alloys: biodegradable polymer coatings and covalent attachment of ECM proteins/binding motifs to magnesium alloy surfaces.

10.2.1.1 *Biodegradable polymer coatings*

Chitosan is a long-chain natural biopolymer obtained from chemical modification of chitin, the main component of crustacean shells. This linear polysaccharide is made up of randomly distributed β -linked D-glucosamine and N-acetyl-D-glucosamine sub-units, and it is similar in chemical composition to the glycosaminoglycans found in the ECM. Chitosan has been shown to have good biocompatibility, which makes it an attractive coating material for biomaterial applications. Several articles have been published on the deposition and properties of chitosan coatings on magnesium alloys (Bai et al., 2012; Gu et al., 2009; Hahn et al., 2011; Wu et al., 2010; Zhang, Dai, Wei, & Wen, 2012). It has been observed that pure chitosan coatings produced via dip-coating do not exhibit sufficient corrosion resistance for practical purposes (Bai et al., 2012; Gu et al., 2009). The topography and corrosion resistance of the coatings produced via dip-coating have been shown to be strongly influenced by the molecular weight of the chitosan polymer and the number of deposited layers. These coatings vary from smooth and compact to porous at the microscale as a function of coating procedure (Bai et al., 2012; Gu et al., 2009).

To overcome their limited corrosion resistance, micro-arc oxidation (MAO) followed by deposition of a chitosan-based coating has been proposed. An MAO magnesium phosphate layer was produced in one study, followed by pore sealing with a dip-coated chitosan layer (Bai et al., 2012). The coatings produced by this combined method had better corrosion resistance than either MAO or chitosan coating alone due to both the enhanced stability of the chitosan layer through cross-linking reactions with surface phosphate ions and the barrier effect of the chitosan on the microporous MAO layer (Bai et al., 2012). Several articles have reported the surface modification of magnesium alloys through MAO followed by electrophoretic deposition of composite calcium phosphate/chitosan coatings (Wu et al., 2010; Zhang et al., 2012). In these articles, it was demonstrated that the coating adhesion depended strongly on the electrolyte composition and the voltage range employed.

Finally, aerosol deposition has also been proposed as a viable method for producing hydroxyapatite (HA)-chitosan composite coatings on magnesium alloys (Hahn et al., 2011). Aerosol deposition is a type of spray coating whereby dense, well ordered ceramic coatings are formed by collision of solid particles of the coating material with the substrate to be coated (Hahn et al., 2011). The deposition is done at room temperature, which allows this technique to be used to produce hybrid organic/inorganic

coatings. Aerosol deposition has been successfully used to produce HA-chitosan coatings on the AZ31 magnesium alloy. The topography of the coatings produced had a rough surface, with a network structure that became denser and smoother as the concentration of chitosan in the coating feedstock increased. Improved corrosion resistance and biocompatibility was observed for the composite coatings (Hahn et al., 2011).

The development of biodegradable organic coatings on magnesium alloys using several other polymers has also been reported. Alginate, a natural anionic polysaccharide that crosslinks to form a hydrogel upon exposure to calcium ions, has been proposed as a potentially biocompatible coating for magnesium alloys (Sangeetha et al., 2011). Although these coatings were shown to have good biocompatibility, they were not particularly corrosion resistant due to their poor stability *in vitro*. Similarly, dip-coated poly(lactide-co-glycolide) coatings were observed to significantly enhance cell adhesion and proliferation but with limited improvement in corrosion resistance due to poor alloy-polymer adhesion (Ostrowski et al., 2013). Spray-coated poly(lactic acid) and poly (DTH carbonate) films also yielded only modest improvements for *in vitro* corrosion resistance (Gray-Munro, Seguin, & Strong, 2009).

Other research has demonstrated that coating using polymers with functional groups that can interact strongly with the magnesium alloy substrate, such as poly(vinyl acetate) (PVA), can result in improved adhesion and consequently improved corrosion resistance (Abdal-hay, Dewidar, & Lim, 2012). Furthermore, the influence of morphology of the polymeric coating has also been shown to be an important factor for optimum corrosion resistance and biocompatibility. The coating morphology is strongly influenced by the solvent, polymer concentration, and method of deposition.

In one article, dip-coated PVA films were deposited on a magnesium alloy from three different solvents (Abdal-hay et al., 2012). The coatings where the polymer was dissolved in either tetrahydrofuran or dimethylformamide were a uniform, dense layer, whereas those deposited from a dichloromethane/PVA solution were porous. The porous coatings were observed to have the best corrosion resistance and improved cell adhesion. Likewise, spray-coated poly(lactic acid) coatings with a porous structure were also found to have improved corrosion resistance with no cytotoxicity (Abdal-hay, Barakat, & Lim, 2013b). Poly(lactic acid) coatings on magnesium alloys produced by dip-coating and electrospinning have also been compared (Abdal-hay et al., 2013a). The dip-coated samples were shown to have a porous structure, while electrospinning resulted in a fibrous structure similar to the ECM. Increased cell proliferation and decreased corrosion rates were observed on both coated samples. The authors postulated that the porous structure prevents the build-up of hydrogen gas at the substrate/coating interface, thus preventing the coating delamination that has been observed for smooth dense polymer films.

The level of porosity in the biodegradable polymer films has also been shown to be an important factor for optimum *in vivo* performance. Porous poly(caprolactone) coatings with both high and low porosity have been reported (Wong et al., 2010). Both coatings had improved corrosion resistance, excellent cell viability, and helped retain the mechanical strength of the magnesium alloy implant during immersion testing.

However, the low porosity coatings were observed to result in the most new bone formation, with no implant volume reduction for *in vivo* animal tests. In general, biodegradable polymer coatings have been shown to improve the corrosion resistance and biocompatibility of magnesium and its alloys. However, future research efforts should aim to improve the adhesion of these coatings and to better understand the role of surface topography on corrosion resistance and biocompatibility.

10.2.1.2 Attachment of ECM proteins or peptides

Surface modification strategies that mimic the properties of the ECM through the attachment of ECM proteins or peptide sequences present in ECM proteins have been shown to dramatically improve the biocompatibility of implant surfaces (Hersel et al., 2003; Rahmany & Van Dyke, 2013). Although this is a promising avenue of research for magnesium alloys, it has not been extensively explored to date. One article reported on the surface modification of the AZ31B magnesium alloy surface with a peptide sequence designed to mimic the acidic bone protein, dentin sialophosphoprotein (Cui et al., 2013). The coating was deposited by dip-coating from a solution of the peptide dissolved in tetrahydrofuran. This biomimetic peptide coating did have a positive impact on the corrosion resistance of the substrate and was shown to facilitate calcium phosphate precipitation in an organized crystal structure. Further research is needed to optimize the corrosion resistance and to characterize the *in vitro* cell behavior and *in vivo* tissue-regenerating ability of these coatings.

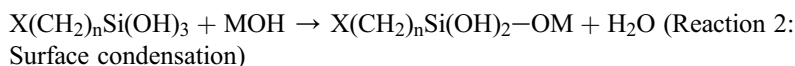
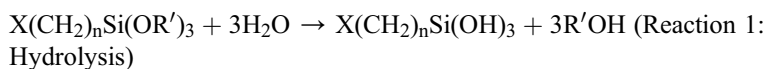
In the next section, preliminary results from my laboratory on two possible biomimetic surface modification strategies for magnesium alloys are discussed. The first is the covalent attachment of the arginine-glycine-aspartic acid peptide sequence (RGD) to the magnesium alloy surface. Cells bind to surfaces through specific ligands found in proteins of the ECMs. One of these ligands is RGD, commonly found in adhesive proteins such as fibronectin (Hersel et al., 2003; Rahmany & Van Dyke, 2013). The bonding of peptide chains containing the RGD sequence to biomaterials surfaces has been shown to significantly improve osteoblast attachment to titanium and polymers (Chollet et al., 2009; Dettin et al., 2009). Furthermore, it has been shown that factors such as the surface density and distribution of the RGD peptide, the peptide sequence, the surface topography, and method of covalent immobilization play a key role in mediating the observed cell response (Hersel et al., 2003; Le Saux et al., 2011).

The second strategy is the covalent immobilization of collagen layers to the magnesium alloy surface. Bone tissue is a composite material consisting mainly of collagen proteins and calcium phosphate. It is anticipated that chemisorbed collagen coatings could provide a corrosion-resistant and biocompatible surface layer for improved cell adhesion on magnesium alloys destined for orthopedic applications.

To achieve optimum stability of biomimetic coatings, covalent bonding to the surface is essential. In this regard, organosilane coatings give a unique opportunity to provide both the required corrosion resistance and the ability to biofunctionalize the magnesium implant surface. These molecules can be synthesized with a wide variety of functional groups at the end of the alkyl chain; an appropriate choice of

functional group will allow us to covalently attach biomolecules of interest. Two papers have successfully demonstrated the attachment of protein molecules to the surface of metallic magnesium using this strategy (Killian, Wagener, Schmuki, & Virtanen, 2010; Wagener, Killian, Turhan, & Virtanen, 2013). The authors further showed that their modified surfaces resulted in a significant decrease in the initial corrosion rate of samples immersed in simulated body fluid (SBF).

Surface attachment of organosilane occurs when hydrolyzed organosilane molecules undergo a condensation reaction with surface hydroxyl groups to form Si-O-Metal bonds (Abel et al., 2006; Torry, Campbell, & Cunliffe, 2006). The relevant reactions are given below, where R' is typically CH₃ or CH₂CH₃ and X is a functional group such as a thiol, alcohol, alkyl group, carboxylic acid, or amine:



Preliminary results from my research using organosilane coupling agents to covalently bond two different biomolecules to the AZ31 magnesium alloy surface are discussed in the next section.

Covalent attachment of the RGD peptide sequence through an amino-functionalized organosilane

In this research, the RGD peptide motif has been covalently attached to the surface of magnesium alloy AZ31 through an aminopropyltriethoxysilane (APTES) layer using a linker molecule, 3-maleimidopropionic acid n-hydroxysuccinimide ester (SMP), and an RGD peptide sequence that contains a cysteine moiety. The SMP linker preferentially bonds to primary amines through its succinimide functional group and to thiols through its maleimide functional group. This bifunctional crosslinker can thus covalently bond to the primary amine group of APTES at one end and to the cysteine residue of the peptide at the other.

The Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectrum for the APTES-coated magnesium alloy coupon is shown in Figure 10.2(a). This spectrum shows the characteristic absorption bands expected for an APTES film. The bands at 1136 cm⁻¹ (Si-O), 1044 cm⁻¹ (Si-O-Si), and 1408 cm⁻¹ (Si-CH₂) confirm the presence of APTES on the surface (Kim & Seidler, 2009). The two peaks at 1475 cm⁻¹ and 1578 cm⁻¹ are due to the amine functional groups. The ATR-FTIR spectrum for APTES-coated AZ31 exposed to the linker molecule alone and then to the linker molecule and the peptide are shown in Figure 10.2(b) and (c), respectively. The infrared spectrum for pure SMP has a major infrared band at 1727 cm⁻¹. This appears as a weak shoulder at 1724 cm⁻¹ (Figure 10.2(b)). Furthermore, a shift in the peak due to -NH₂ peak (1578 cm⁻¹) to lower wavenumbers (1566 cm⁻¹) is indicative of interaction of the SMP molecules with the surface through the amine group. The ATR-FTIR spectrum for the APTES-coated AZ31 after modification with both SMP and RGDC is

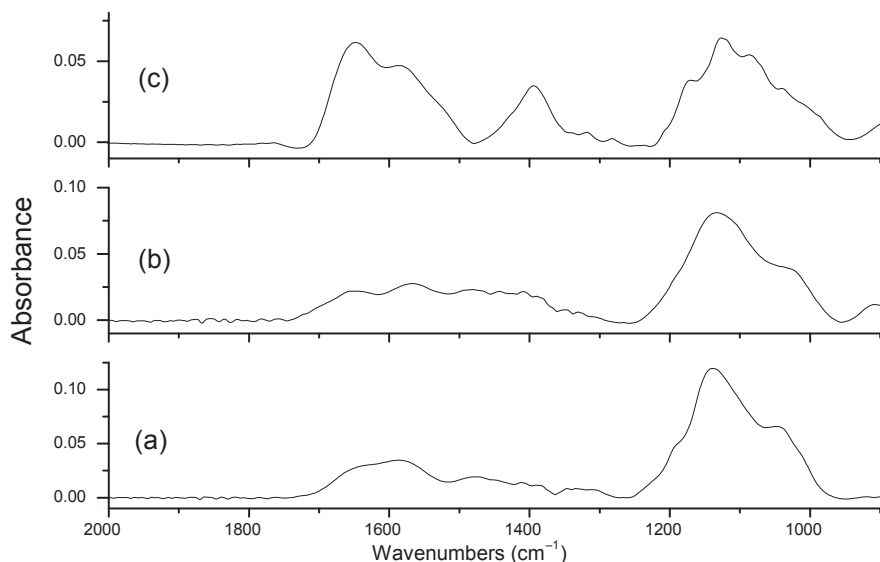


Figure 10.2 ATR-FTIR spectra of (a) APTES-coated AZ31, (b) SMP-modified APTES-coated AZ31, and (c) RGD-modified APTES-coated AZ31.

shown in [Figure 10.2\(c\)](#). In this spectrum, the signals from the weaker bands due to APTES and SMP in the $1400\text{--}750\text{ cm}^{-1}$ region have been attenuated. Only the strong Si-O bands are still observed. Furthermore, two new strong vibrational bands at 1647 cm^{-1} and 1586 cm^{-1} are present on the surface. These are the characteristic amide bands associated with peptides. This indicates that the RGD peptide has been successfully bonded to the surface. Sonication of the modified surface in water for 10 min did not result in any change in the spectrum, indicating that the peptide is covalently bonded.

The influence of APTES coating on the degradation rate of the magnesium AZ31 alloy in SBF was evaluated by comparing the surface chemistry and morphologies of the uncoated and coated material after immersion in SBF for 24 and 72 h. The concentration of magnesium released into solution was also evaluated. The corresponding scanning electron microscopy (SEM) images are shown in [Figure 10.3](#). It is clear that after 24 h immersion in SBF, there is a significant amount of pitting on the bare magnesium surface ([Figure 10.3\(a\)](#)), while the APTES-coated surface shows no apparent evidence of corrosion ([Figure 10.3\(c\)](#)). After 72 h, both samples ([Figure 10.3\(b\)](#) and [\(d\)](#)) show evidence of the deposition of a corrosion layer. However, the corrosion layer on the bare magnesium surface appears to be thicker, as evidenced by the increased cracking in the layer upon dehydration ([Figure 10.3\(b\)](#)) and the increased Ca/Mg ratio observed by EDS ([Figure 10.4](#)). The increase in pH during corrosion results in precipitation of insoluble calcium phosphate phases at the surface of magnesium alloys in SBF ([Gray-Munro & Strong, 2009](#)). These calcium phosphate precipitates are calcium deficient, as evidenced by the low Ca/P ratio observed ([Figure 10.4](#)).

[Figure 10.4](#) also shows the overall amount of magnesium ions released into solution for each sample. After 24 h, the amount of magnesium released is similar for coated

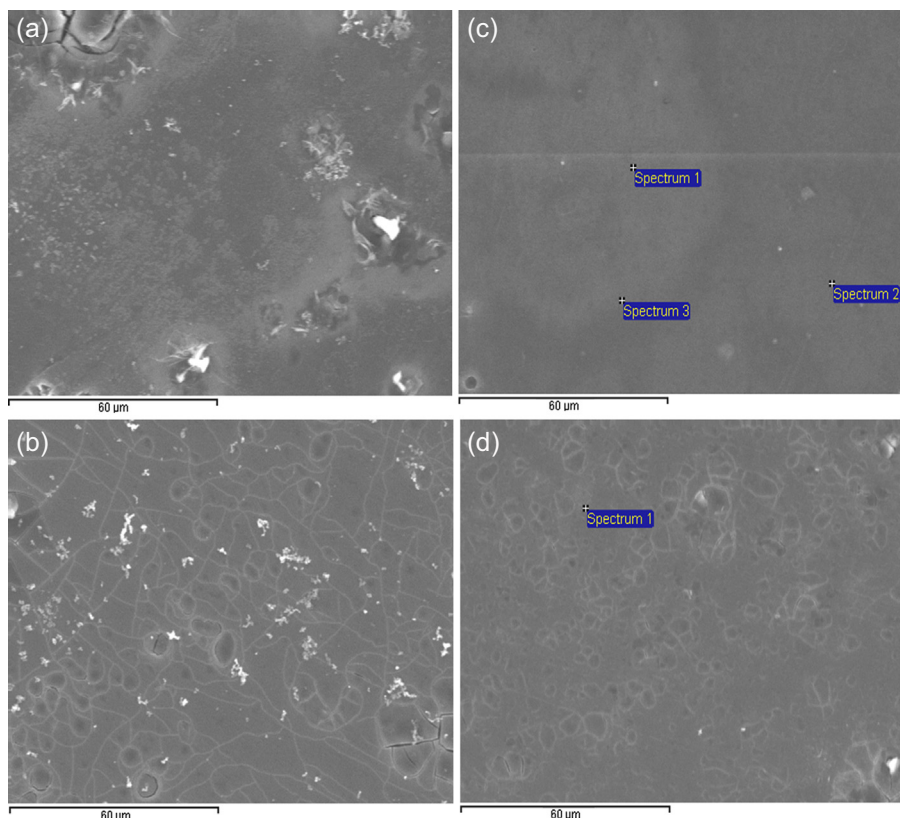


Figure 10.3 Scanning electron microscopy images of samples after immersion in Hanks' balanced salt solution: (a) Mg AZ31 after 24 h in SBF, (b) Mg AZ31 after 72 h in SBF, (c) APTES-coated Mg AZ31 after 24 h in SBF, and (d) APTES-coated Mg AZ31 after 72 h in SBF.

and uncoated samples. However, after 72 h a noticeable decrease in the overall amount of corrosion was observed for APTES-coated samples. This is likely due to defects in the APTES layer that result in some localized corrosion of the alloy in the initial stages of immersion. As these defects are filled in with insoluble calcium phosphates, the corrosion rate slows. This indicates that the APTES films are stable in SBF, but that film uniformity is an important factor in determining the overall corrosion resistance of the material.

Covalent immobilization of collagen

One of the main components of bone tissue is collagen proteins. The biocompatibility of implant materials is strongly influenced by the nature of the protein layers that adsorb upon implantation in the body because this layer governs cell response. To increase biocompatibility, it is essential to control the nature of these adsorbed protein layers. Proteins do not tend to adsorb to other proteins; therefore, one way to control the adsorption is to preadsorb a protein layer that will elicit a desired cell response. Because

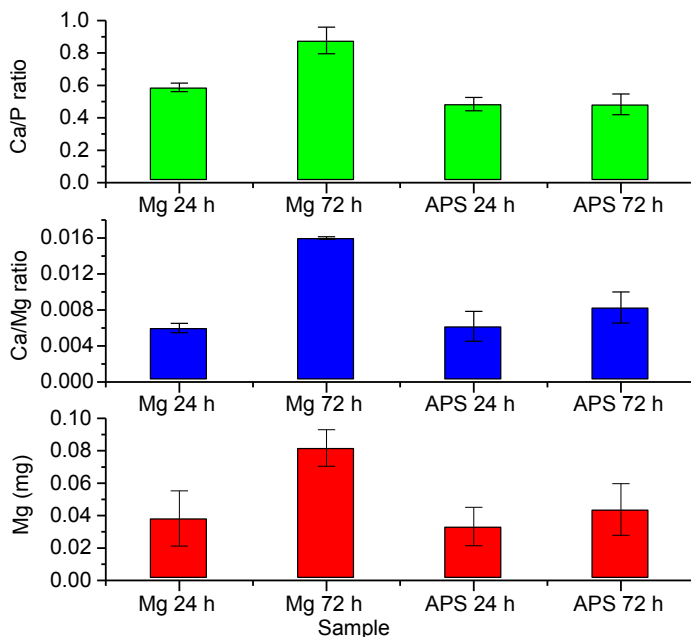


Figure 10.4 Amount of magnesium released into solution, Ca/Mg EDS ratios, and Ca/P EDS ratios for untreated magnesium alloy coupons and APTES-coated samples after immersion in simulated body fluid for 24 and 72 h.

biodegradation followed by growth of new bone tissue is the target of magnesium alloy implants, collagen coating may be one way to improve integration of these materials into the body. In this project, collagen has been covalently attached to the surface of magnesium alloy AZ31 through a silane layer using a linker molecule (ascorbic acid), as described by Killian *et al.* (2010), where albumin was covalently bonded to a magnesium surface. The ascorbic acid contains two functional groups capable of bonding to primary amines, thus enabling covalent bonding to the primary amine group of APTES at one end and to primary amine containing amino acids on the protein molecule at the other.

Figure 10.5 shows the infrared spectra for APTES-coated AZ31 (the peak assignments were discussed in Section 10.2.1.2.1) and APTES treated with ascorbic acid (Figure 10.5(b)). Two important changes were observed. The first is that most of the organosilane peaks are attenuated in comparison to the unmodified APTES layer, confirming that the film is being covered. The second is the increase in relative peak intensity of the peak at 1575 cm^{-1} . This peak was previously attributed to protonated amine groups interacting with HCO_3^- . The increase in intensity is likely due to the interaction of primary amine groups with ascorbic acid, which results in the formation of a protonated amine species.

Figure 10.5(c) shows the infrared spectrum of the APTES-coated alloy modified with ascorbic acid followed by dip coating in a collagen solution. The peaks due to APTES are fully attenuated and two new peaks at $\approx 875\text{ cm}^{-1}$ and 1400 cm^{-1} are

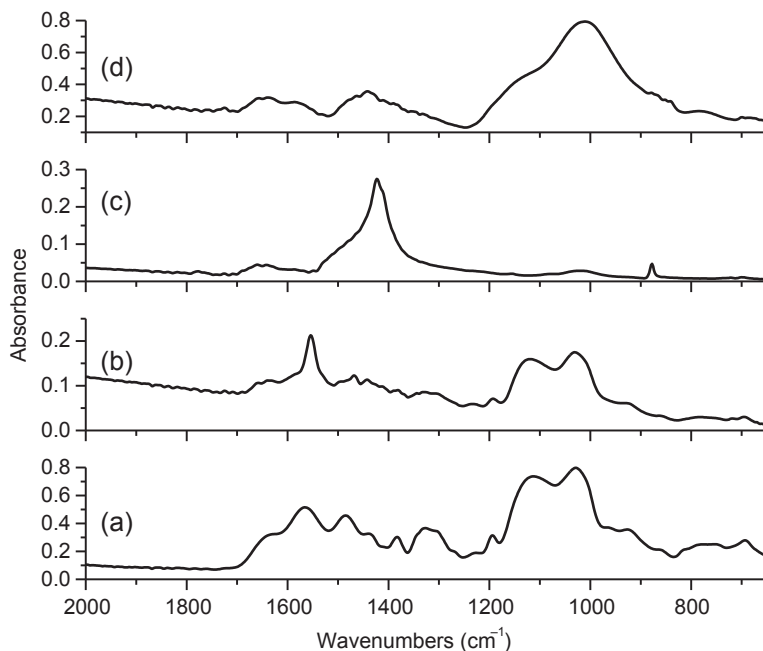


Figure 10.5 Glancing angle FTIR spectra of (a) APTES-coated AZ31, (b) L-ascorbic acid modified APTES-coated AZ31, (c) collagen deposited on L-ascorbic acid modified APTES-coated AZ31, and (d) collagen deposited on APTES-coated AZ31 (no ascorbic acid treatment).

observed. A reference spectrum confirmed that these two peaks are the most intense peaks in the infrared spectrum for collagen. To confirm that this collagen is chemically bonded to the surface and not simply physisorbed, a control experiment was performed. Figure 10.5(d) is an infrared spectrum for an APTES sample exposed to the collagen solution but without ascorbic acid treatment. The infrared spectrum clearly indicates that collagen is not deposited without the ascorbic acid linker molecule. This confirms that the collagen is covalently attached to the APTES coating through the ascorbic acid molecule.

The deposition of collagen on the surface is confirmed in Figure 10.6, which is an SEM image of the collagen coated surface. The collagen coating is fibrous in nature; although it distributed over the whole surface, the coating is nonuniform.

These two examples demonstrate that it is possible to biomimetically modify magnesium surfaces through the covalent attachment of ECM proteins or binding motifs. Further research is needed to optimize the corrosion resistance and characterize the influence of these surface modification strategies on cell/surface interactions.

10.2.2 Biomimetically deposited calcium phosphate coatings

Bone tissue is a complex composite material composed of mineralized collagen fibers with an assortment of other proteins and cells. The mineral phase is composed of

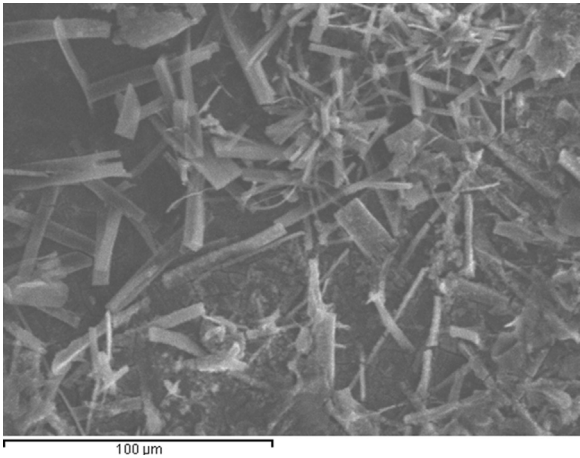


Figure 10.6 Scanning electron microscopy image of collagen fibers attached to an APTES-coated magnesium alloy coupon.

calcium-deficient carbonated HA (Liu, Wu, & de Groot, 2010). Calcium phosphate (CaP) coatings have been widely applied to various implant materials, such as titanium and stainless steel, in order to improve their biocompatibility and to increase bone growth at the implantation site (Avila et al., 2009). In particular, biomimetically deposited coatings have been observed to have excellent biocompatibility and the ability to promote osseointegration (Avila et al., 2009; Liu, Wu, & de Groot, 2010). The biomimetic approach is a low-temperature solution deposition technique that involves immersing the substrate material in SBF.

A typical composition for SBF (Table 10.1) is based on the inorganic ions present in blood plasma. The exact composition is highly variable in the literature, where attempts to improve deposition rates, promote the deposition of specific CaP phases,

Table 10.1 Typical composition of a simulated body fluid

Component	Concentration (mM)
CaCl ₂ · 2H ₂ O	1.26
MgSO ₄ (anhydrous)	0.81
KCl	5.37
KH ₂ PO ₄	0.44
NaHCO ₃	4.17
NaCl	136.9
Na ₂ HPO ₄ (anhydrous)	0.337
D-Glucose	5.55

and optimize biocompatibility have led to research with modified SBF solutions. The underlying theme for these coatings is that the inorganic ions present in the coating bath are also present in physiological solutions.

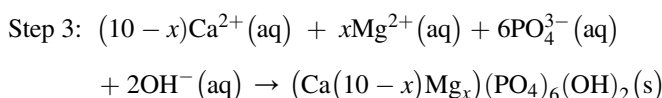
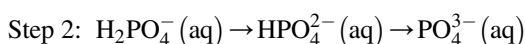
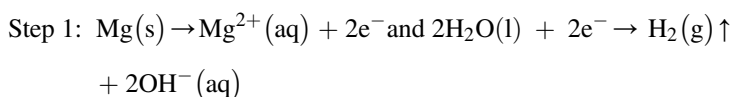
The key advantages of a biomimetic coating strategy include the following:

1. The coating bath temperatures are low, allowing co-deposition of biological molecules such as proteins and growth factors that would decompose at higher temperatures. Furthermore, this low-temperature process does not alter the substrate significantly during coating.
2. The crystallinity and composition of the deposited calcium phosphate coatings are similar to the mineral phase observed in natural bone tissue, resulting in improved bioactivity and good resorption characteristics.
3. This technique is not line of sight, allowing implants with complex or porous geometries to be uniformly coated.

The composition, pH, and temperature of the coating bath as well as the surface chemistry of the implant have both been shown to play a key role in the nucleation and growth of CaP coatings from SBF. The deposition rate and phase of CaP deposited are influenced by numerous factors such as the Ca/P ratio, concentration of inorganic ions, pH, the presence of crystal growth inhibitors such as Mg^{2+} , surface pretreatment, and coating post-treatments (Barrere, van Blitterswijk, de Groot, & Layrolle, 2002a,b; Feng et al., 2000; Hu et al., 2006; Kuroda, Ichino, Okido, & Takai, 2002; Liu, et al., 2002).

10.2.2.1 Biomimetic calcium phosphate coatings on magnesium alloys

Calcium phosphate coatings have been reviewed as a means of controlling both the degradation rate and the biocompatibility of magnesium alloy implant materials (Shadanbaz & Dias, 2012). The deposition of CaP on magnesium alloys is both helped and hindered by the nature of the substrate itself. A general mechanism for biomineralization is outlined below (Gray-Munro & Strong, 2009):



Upon immersion in an aqueous CaP solution, anodic dissolution of magnesium accompanied by cathodic reduction of water readily occurs (Step 1). The corrosion of the substrate surface gives an increase in magnesium ion concentration and pH near the solution/metal interface. The increase in pH results in a shift in the phosphate ion equilibrium toward deprotonated species (Step 2). This increase in pH further

affects the solubility of calcium phosphate, resulting in heterogeneous nucleation and growth of calcium-deficient, magnesium-rich HA at the interface (Step 3).

It has been well documented that magnesium ions can readily substitute into the crystal lattice of HA. The biomimetic process is typically done under ambient conditions; therefore, carbonate ions are also introduced into the crystal structure of the deposited CaP. As the pH of the bulk solution increases, homogeneous nucleation and growth of calcium phosphate crystals in solution can also occur, resulting in the deposition of additional CaP crystals at the surface. Due to its high reactivity, the magnesium alloy substrate is an active participant in the coating deposition mechanism, resulting in faster deposition rates and no need for complex surface modification strategies to induce CaP nucleation at the surface. The disadvantage is that the CaP layers produced at the interface are essentially a corrosion product; therefore, they tend to be amorphous, non-uniform, poorly adhered layers. This has a detrimental impact on their corrosion resistance. Moreover, the composition of this initially deposited inner CaP layer is often the same regardless of coating bath composition. This is illustrated in [Figures 10.7 and 10.8](#). [Figure 10.7](#) is an SEM image of a biomimetic CaP coating deposited on the AZ31 magnesium alloy. These figures are results from experiments conducted in our research laboratory. The coating bath was a mixture of 3 mM CaCl_2 and 1.8 mM Na_2HPO_4 to give a Ca/P ratio of 1.67/1, the stoichiometric ratio of HA. Two distinct layers were observed. The inner layer is composed of a uniform layer of agglomerated CaP particles. The observed

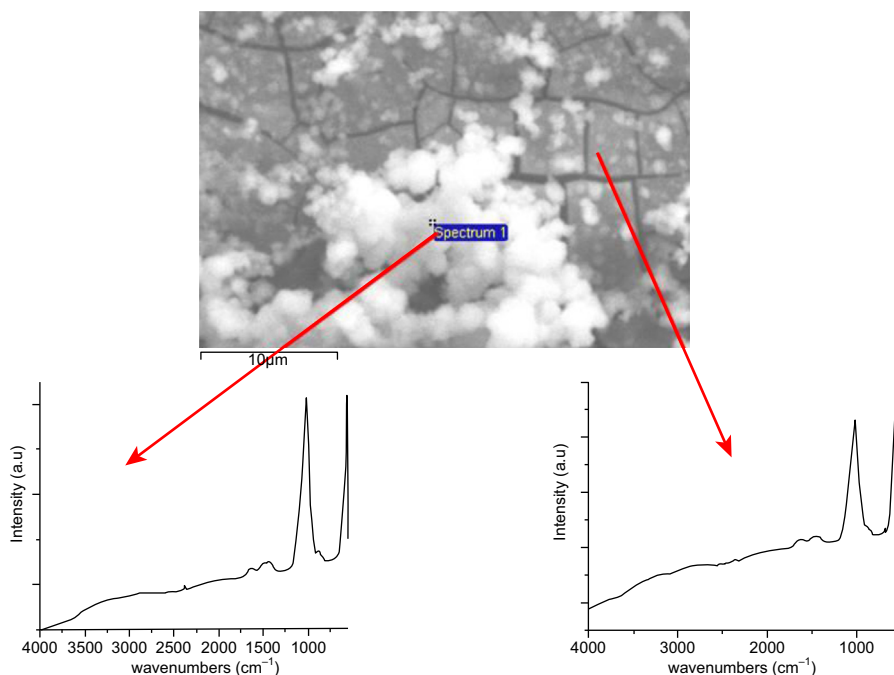


Figure 10.7 SEM image and ATR-FTIR spectra of calcium phosphate coating on Mg AZ31 deposited from a 3 mM CaCl_2 /1.8 mM Na_2HPO_4 solution.

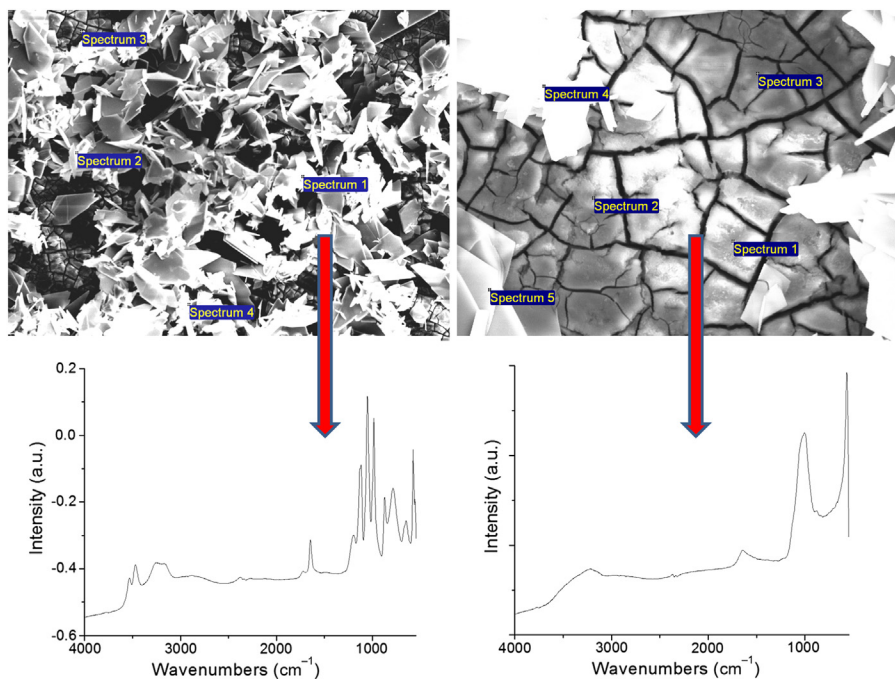


Figure 10.8 SEM image and ATR-FTIR spectra of calcium phosphate coating on Mg AZ31 deposited from a 2 mM CaHPO_4 solution (pH adjusted to 5 with H_3PO_4).

cracks are most likely due to dehydration of the inner layer. The outer layer is composed of larger agglomerates of spherical particles that deposit on the surface after formation in the bulk solution. Infrared microscopy confirmed that both the inner layer and outer layer are HA minerals.

Figure 10.8 is an SEM image of a biomimetic calcium coating deposited from a chloride-free solution of CaHPO_4 . It can again be readily observed from these images that two distinct layers are formed. The inner layer is identical in morphology and chemistry to that observed from the $\text{CaCl}_2/\text{Na}_2\text{HPO}_4$ coating bath, indicating that the nature of this layer is mainly controlled by dissolution of the substrate itself. However, the outer layer is composed of plate-like crystals of brushite. The deposition of brushite crystals rather than apatite in this instance is likely due to the decreased degradation rate of the magnesium alloy surface in the absence of chloride ions. This results in a slower increase in pH of the bulk solution and homogeneous precipitation of brushite crystals in the coating bath.

This type of duplex coating structure—consisting of a thin, compact inner layer and a porous crystalline outer layer—has also been reported in the literature for biomimetic calcium phosphate coatings on magnesium and its alloys (Yang, Cui, & Lee, 2011).

The study of biomimetic CaP coatings on magnesium alloys has been the subject of several research articles in the last decade. The exact surface pretreatment, coating bath composition, and coating deposition conditions vary widely. In particular, the coating

times range from several hours to several days. However, there are some common themes:

1. The deposition temperature is typically 37 °C.
2. The initial coating bath pH is typically between 7 and 7.4. A couple of articles reported the use of lower pH values, from 5 to 7. Notably, one paper reported that CaP coatings deposited from a pH 6 coating bath are more uniform, less porous, and have improved corrosion resistance over those deposited at physiological pH (Lu, Chen, Huang, & Yan, 2012).
3. The coating bath composition varies, but for the most part it consists of either SBF (Table 10.1) or modified simulated body fluid (m-SBF), which contains higher concentrations of Ca^{2+} and HPO_4^{2-} .

In the absence of surface pretreatment, CaP is readily deposited on magnesium and its alloys via the previously presented mechanism. It has been observed that the number of biomimetic layers deposited (Zhang, Zhang, & Wei, 2008) has a significant impact on the degradation rate of the coated material. The degradation rate of a poorly crystalline HA coating deposited from m-SBF decreased significantly when a second layer was deposited on top of the first. Coating bath chemistry can also affect the nature of the calcium phosphate phases formed. In a coating bath where CaCl_2 was used as the calcium source, a dicalcium phosphate dihydrate coating was reported (Yanovska et al., 2012), whereas a $\text{Ca}(\text{NO}_3)_2$ -containing solution resulted in the deposition of HA (Yang et al., 2009; Yanovska et al., 2012). The crystallinity of the deposited coatings was also shown to increase in the presence of a magnetic field (Yanovska et al., 2012). Finally, when pure magnesium, the AZ21 alloy, and a 0.5 wt% Ca magnesium alloy were exposed to bone cells in cell culture medium for 18 days, a bone-like matrix was deposited on the surface of these materials (Pietak, Mahoney, Dias, & Staiger, 2008). Although the concept of depositing coatings using bone cells has not been widely explored due to the risk of immunogenicity (Rahmany & Van Dyke, 2013), it could be a promising method for optimizing the biocompatibility and degradation rate of these materials.

A variety of surface pretreatments have been explored as a means for improving the adhesion and corrosion resistance of these biomimetically deposited CaP coatings. Some general pretreatment strategies that have been reported on magnesium alloys include polishing, acid etching, pre-calcification, anodizing, heat treatments, hydrothermal treatment, and MAO.

It has been reported that surface roughness has an impact on the corrosion resistance of CaP coatings. Good corrosion resistance was observed for polished samples, whereas the decrease in degradation rate was not as significant for roughened samples (Nguyen, Waterman, Staiger, & Woodfield, 2012). A CaP coating deposited from m-SBF for 5 days on a polished magnesium alloy AZ91 surface was found to consist of amorphous, calcium-deficient, carbonate-substituted HA. The coating was found to decrease the dissolution rate of the magnesium alloy by a factor of 5. The coating also enhanced cell adhesion in the short term (Lorenz et al., 2009). Likewise, biomimetic CaP coatings with some corrosion resistance were deposited on rough acid etched samples from both a simple calcium phosphate solution (Gray-Munro & Strong, 2009) and m-SBF (Lu et al., 2012). These coatings were both observed to consist of amorphous, calcium-deficient, carbonate-substituted hydroxyapatite.

Anodizing, MAO, and heat treatment have also been proposed as pretreatments (Cortes, Lopez, & Mantovani, 2007; Hiromoto et al., 2008; Liu, Hu, Ding, & Wang, 2011). In each case, calcium phosphate coatings were deposited on the pretreated surface upon immersion in SBF or m-SBF solutions, and improved corrosion resistance was observed.

Hydrothermal treatment of pure magnesium by immersion in 100 °C water for various times was also investigated to increase the number of hydroxyl groups at the surface (Waterman et al., 2011). Surface modification of titanium implants with hydroxyl groups is essential for the nucleation of CaP, although this is not critical for CaP nucleation on magnesium. However, hydrothermal pretreatment did impart improved corrosion resistance to the CaP-coated magnesium in SBF in comparison to non-pretreated samples.

The most popular pretreatment strategy reported thus far is precalcification of the surface prior to biomimetic CaP coating. Precalcification involves deposition of a calcium-rich layer via a chemical method. In several cases, a prelayer of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (brushite) was deposited prior to immersion in SBF or m-SBF (Hu et al., 2010; Shadanbaz et al., 2013; Xu et al., 2012a,b). Precalcification was shown to increase the deposition rate of biomimetic calcium phosphate coatings. Furthermore, the existing brushite precalcification layer was converted to hydroxyapatite during final coating formation. Precalcification by deposition of CaHPO_4 (monetite) was also reported (Shadanbaz et al., 2013). The monetite pretreatment was shown to have better corrosion resistance than brushite in several different types of cell culture media. This may be due to its decreased solubility in aqueous solution. Finally, precalcification by deposition of a $\text{Ca}(\text{OH})_2$ underlayer has been shown to produce biomimetic CaP coatings with fewer defects, better corrosion resistance, and self-healing capability (Waterman et al., 2012).

Post-treatment via sealing of biomimetic CaP coatings has also been attempted (Keim, Brunner, Fabry, & Virtanen, 2011). Four different post-treatments were applied to SBF-formed layers:

1. soaking in 1 M NaOH at room temperature for 24 h,
2. heat treatment at 150 °C in air for 1 h,
3. heat treatment in steam for 1 h, and
4. soaking in boiling water for 1 h.

Only soaking in NaOH and heating in steam resulted in noticeable sealing of cracks and pores in the CaP coating. Furthermore, post-treatment with these methods did not improve the corrosion resistance of the magnesium substrate. Interestingly, the authors determined that deposition of CaP coatings from Dulbecco's Modified Eagle cell culture medium resulted in more protective CaP coatings with increased biocompatibility. The exact mechanism of this increased corrosion resistance was not reported; however, the composition of the cell culture medium is significantly different than traditional SBF solutions because it is rich in amino acids and sugars.

Biomimetically deposited calcium phosphate coatings have been shown to significantly improve both the corrosion resistance and biocompatibility of a variety of different magnesium alloys. Further research is needed to optimize the corrosion

resistance, learn to control the phase of CaP deposited, and enhance long-term cell adhesion and proliferation.

10.3 Biomimetic superhydrophobic coatings on magnesium and its alloys

The term *superhydrophobic* refers to materials that exhibit contact angles with water that are greater than 150° . The inspiration for these coatings comes from nature, where self-cleaning plants such as the lotus leaf have garnered much attention. Several detailed reviews on superhydrophobic surfaces have been published (Guo et al., 2011; Yan et al., 2011). In general, the lotus leaf and other plants make use of a unique combination of surface topography and surface chemistry to achieve their superhydrophobicity. The surfaces of their leaves have a hierarchical topography with surface structures at both the micro and nanoscale. The surface of the lotus leaf has many microscale papillae, separated from each other by about 20–40 μm . Each of these papillae is coated with nanoscale crystals of a hydrophobic waxy compound. It is believed that the superhydrophobicity of these rough surfaces originates from trapping of air in the pores, which effectively limits water contact with the surface. In fact, smooth surfaces with similar surface chemistry are hydrophobic but do not exhibit superhydrophobicity.

There are two basic approaches for engineering superhydrophobic coatings: the surfaces of hydrophobic materials can be roughened or the surface of non-hydrophobic material is first roughened, followed by surface modification with a hydrophobic molecule. The second method is by far the most popular due to the fact it is the most versatile in terms of materials that can be modified for a variety of different applications. A number of different surface modification strategies have been proposed, including phase separation, electrochemical deposition, chemical vapor deposition, wet chemistry, sol–gel chemistry, lithography, and electrospinning (Guo et al., 2011; Yan et al., 2011). The extreme water repellence of superhydrophobic coatings has made them attractive for a number of industrial applications due to their self-cleaning, anti-icing, and antifouling properties (Guo et al., 2011; Yan et al., 2011). These coatings have also been reported to have excellent lubricity and good corrosion resistance (Guo et al., 2011; Yan et al., 2011).

The development of superhydrophobic coatings on magnesium and its alloys is an emerging field of research. Table 10.2 is a summary of published research on the coating strategies used to produce superhydrophobic films on magnesium alloys. In all but two of these articles, a multi-step method is employed, whereby the surface is first roughened followed by surface modification to improve hydrophobicity.

The two articles that use a single-step surface modification both report methods for depositing rough, hydrophobic polymer films directly on the surface of the magnesium alloy. In the first of these (Ishizaki et al., 2010), the authors use microwave plasma-enhanced chemical vapor deposition to produce superhydrophobic trimethylmethoxysilane (TMMOS) films on magnesium alloy AZ31. Aggregation of the TMMOS molecules in the plasma led to the deposition of many polymeric clusters on the surface.

Table 10.2 Summary of superhydrophobic coating methods on magnesium alloys

Alloy	General coating method	Reference
Mg-Li	Step 1 – Etching in 0.1 M HCl Step 2 – Fluoroalkylsilane modification	Liu et al. (2008)
AZ91D	Step 1 – Acid activation in $\text{CrO}_3/\text{HNO}_3$ Step 2 – Immersion in AgNO_3 solution Step 3 – Electroless Ni-P plating	Liu, Li, Lu, & Yu (2010)
AZ31	Step 1 – Etching in $\text{HNO}_3/\text{Cu}(\text{NO}_3)_2$ Step 2 – Triethoxyoctylsilane modification	Yin et al. (2010)
Pure Mg	Step 1 – Etching in H_2SO_4 Step 2 – Etching in H_2O_2 Step 3 – Stearic acid modification	Y. Wang et al. (2010)
AZ31	Step 1 – Immersion in $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ Step 2 – Fluoroalkylsilane modification	Ishizaki and Saito (2010)
AZ31	Step 1 – Conversion coating of hydrotalcite/hydromagnesite Step 2 – Bis-(3-triethoxysilyl propyl) tetra-sulfide modification	J. Wang et al. (2010)
AZ31	Step 1 – Microwave plasma-enhanced chemical vapor deposition of trimethylmethoxysilane (argon carrier gas)	Ishizaki et al. (2010)
Mg-Mn-Ce	Step 1 – Polymer plating with fluorine functionalized triazine dithiol monomers	Kang et al. (2011)
AZ61	Step 1 – Electrochemical machining in 0.2 M NaCl Step 2 – Fluoroalkylsilane modification	Xu et al. (2011)
AZ31	Step 1 – Hydrothermal treatment in ultrapure H_2O Step 2 – Octadecylsilane modification	Ishizaki and Sakamoto (2011)
AZ31	Step 1 – Immersion in $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ Step 2 – Fluoroalkylsilane modification	Ishizaki, Masuda, and Sakamoto (2011)
AZ91D	Step 1 – Electroless nickel plating Step 2 – Copper electrodeposition Step 3 – Lauric acid modification	Z. Wang et al. (2012)
AZ91D	Step 1 – Electroless nickel plating Step 2 – Cu-Zn electrodeposition	She et al. (2012)

Table 10.2 Continued

Alloy	General coating method	Reference
NZ30K	Step 3 – Electrochemical deposition of CuO Step 4 – Lauric acid modification Step 1 – Micro-arc oxidation Step 2 – Hydrophobic silica sol–gel coating	S. Wang et al. (2012)
AZ91D	Step 1 – Immersion in $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ Step 2 – Dodecyltriethoxysilane modification	Liu et al. (2013)
AZ91D	Step 1 – Etching in mixed acetic acid/phosphoric acid/nitric acid solution Step 2 – Electroless deposition of zinc Step 3 – Stearic acid modification	Wang et al. (2013)
AZ61	Step 1 – Immersion in CuSO_4 Step 2 – Sonication in H_2O Step 3 – Stearic acid modification	Song et al. (2013)
AZ91D	Step 1 – Hydrothermal treatment Step 2 – Perfluorooctyltriethoxysilane modification	Ou, Hu, Wang, and Li (2013)

The resulting rough topography coupled with the presence of hydrophobic functional groups led to films with contact angles greater than 150° , improved corrosion resistance, and high chemical stability in acidic and neutral aqueous solutions. The second article ([Kang, Lai, Sang, & Li, 2011](#)) discusses superhydrophobic polymer nanofilms produced by polymer plating with the triazine dithiol monomer, $\text{C}_3\text{N}_3\text{S}_2\text{HNa-N}(\text{CH}_2\text{CH}=\text{CH}_2)\text{C}_2\text{H}_4(\text{CF}_2)_7\text{CF}_3$ (ATP). The polymeric nanofilm produced contained both nanostructures and microstructures, had a contact angle greater than 150° , and improved corrosion resistance.

The remaining articles can be grouped predominantly according to the method of surface roughening employed prior to modification with a hydrophobic molecule. The key strategies involve chemical etching, hydrothermal treatments, or deposition of a structured prelayer on the magnesium alloy surface.

Surface roughening by chemical etching has been employed by a number of researchers to produce a hierarchical surface topography on magnesium alloys ([Liu et al., 2008](#); [Song et al., 2013](#); [Y. Wang et al., 2010](#); [Xu et al., 2011](#); [Yin et al., 2010](#)). Regardless of the chemical composition of the etching solution, the resulting surface topography included both micro and nanoscale surface features. Randomly distributed micro-scale papillae composed of petal-like nanosheets similar to the lotus leaf were observed ([Liu et al., 2008](#); [Y. Wang et al., 2010](#)) in some cases. In all

reported cases, the combination of chemical etching to produce micro/nanoscale hierarchical structures and surface modification resulted in coatings that exhibited superhydrophobicity.

Hydrothermal treatments have also been successfully used to generate oxide/hydroxide barrier layers with micronanoscale hierarchical topography. These layers are formed by dissolution and reprecipitation reactions that occur upon exposure of the alloy to aqueous solution at high temperatures for periods of several hours or more. Several authors have used hydrothermal treatment of magnesium alloys in pure water, producing surfaces covered with magnesium hydroxide nanosheets with typical thicknesses of approximately 100 nm (Ishizaki & Sakamoto, 2011; Ou et al., 2013). One interesting advantage of this method is that the hydroxide layer can be color tuned depending on the immersion time. A paper demonstrated that these coatings exhibit colors ranging from metallic silver to orange, green, or orchid as a function of hydrothermal treatment time (Ishizaki & Sakamoto, 2011). The hydrothermal method has also been used to create a hydrotalcite/hydromagnesite conversion coating on the AZ31 alloy (J. Wang et al., 2010). This conversion coating consisted of nanoscale flake-like structures that completely covered the surface. Randomly distributed microscale papillae were also observed.

The deposition of structured prelayers has also been explored as a way of producing hierarchical topography on magnesium alloy surfaces. Microarc oxidation followed by coating with hydrophobic nanoscale silica particles fabricated via the sol–gel method has showed promise as an adherent, corrosion-resistant superhydrophobic coating (S. Wang et al., 2012). Another promising method is the deposition of crystalline nanosheets of cerium oxide as a coating via a simple immersion process (Ishizaki et al., 2011; Ishizaki & Saito, 2010; Liu et al., 2013). In each case, the superhydrophobic films prepared by this method exhibited better corrosion resistance in sodium chloride solutions than the unmodified magnesium alloy; however, due to the presence of cracks in the coating, they did not have adequate long-term corrosion resistance. The deposition of metallic layers by electroless plating and/or electrochemical deposition has also been shown to be an effective surface roughening strategy (She et al., 2012; Z. Wang et al., 2012) leading to the desired micronanoscale hierarchical topography. Wang et al. (2013) used a combination of selective chemical etching followed by electroless zinc deposition for this purpose. The selective chemical etching resulted in preferential etching of the magnesium-rich phase of the alloy, the α phase. Upon exposure to the electroless zinc-plating solution, zinc deposited on both phases of the alloy but preferentially on the $\text{Mg}_{17}\text{Al}_{12}$, β phase, leading to a micronanoscale hierarchical topography.

In each of the articles discussed, the roughened surface is subsequently modified with a hydrophobic molecule. The use of two classes of hydrophobic molecules has been reported, including organosilanes and long-chain fatty acids. Modification with organosilanes is by far the most widely used method. Organosilanes have the structure $(\text{RO})_3\text{-Si-X}$, where R is a methoxy or ethoxy group and the nature of X depends on the desired application. These molecules undergo a series of hydrolysis and condensation reactions, resulting in the formation of covalent bonds between the organosilane molecules and magnesium surface hydroxyl groups. When the roughening procedure

involves deposition of a surface layer that does not contain a significant number of surface hydroxyl groups, a catalyst is added to the coating bath to promote hydrolysis and condensation (Ishizaki & Saito, 2010). In the case of superhydrophobic coatings, the X group of the organosilane is typically a long-chain hydrocarbon or a long-chain hydrocarbon containing low surface energy $-\text{CF}_2-$ and $-\text{CF}_3-$ functional groups. Surface modification with fluoroalkylsilanes has been shown to result in superhydrophobic coatings that have long-term stability in air and high chemical stability in acidic, basic, and salt solutions, as well as improved corrosion resistance compared to untreated magnesium alloys (Ishizaki et al., 2011; Ishizaki & Saito, 2010; Liu et al., 2008; Ou et al., 2013; Xu et al., 2011). Improved corrosion resistance has also been observed with alkylsilane surface treatments (Ishizaki & Sakamoto, 2011; Liu et al., 2013; Yin et al., 2010).

The long-chain fatty acids, stearic acid and lauric acid, have also been used to impart hydrophobicity to the surface of magnesium alloys (She et al., 2012; Song et al., 2013; Y. Wang et al., 2010; Z. Wang et al., 2012; Wang et al., 2013). When these molecules are adsorbed to the magnesium alloy surface by a simple immersion process, an acid/base interaction is established between the magnesium hydroxide surface and the carboxylic acid functional group of the molecule. The films produced by this method are stable in air (Song et al., 2013; Y. Wang et al., 2010) but have been shown to have poor corrosion resistance in sodium chloride solutions (Y. Wang et al., 2010). However, the use of long-chain fatty acids is desirable due to their decreased cost and increased environmental friendliness compared to organosilanes. Therefore, several researchers have employed electrodeposition (Z. Wang et al., 2012; Wang et al., 2013) or electrostatic adsorption (She et al., 2012) methods to improve the stability of these hydrophobic coatings. The electrodeposition method has been shown to result in the deposition of zinc stearate (Wang et al., 2013) and copper laurate (Z. Wang et al., 2012) compounds on the magnesium alloy surface. In each case significantly improved corrosion resistance was observed. However, it was reported that the copper laurate films were unstable in basic solution.

Biomimetic superhydrophobic coatings mimic nature through a combination of hierarchical topography at the micro and nanoscale coupled with the presence of hydrophobic molecules. These coatings have shown promise as a surface modification strategy for engineering surface treatments on magnesium alloys with optimum corrosion resistance.

10.4 Conclusions

In comparison to other materials, relatively little research has been done on biomimetic surface modifications of magnesium and its alloys. As this field develops, the ability to mimic nature through surface modifications that combine hierarchical topographies with specific surface chemistries will provide us with biodegradable implants that have controlled degradation rates. These biomimetically modified surfaces will also be designed to elicit desired cell responses for implants that readily integrate into the host tissue. Furthermore, the development of superhydrophobic coatings with

optimized corrosion resistance will lead to increased use of magnesium alloys in applications where high strength- to-weight ratios are advantageous.

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References

- Abdal-hay, A., Barakat, N., & Lim, J. (2013a). Influence of electrospinning and dip-coating techniques on the degradation and cytocompatibility of Mg-based alloy. *Colloids and Surfaces A: Physicochemical Engineering Aspects*, 420, 37–45.
- Abdal-hay, A., Barakat, N., & Lim, J. (2013b). Hydroxyapatite-doped poly(lactic acid) porous film coating for enhanced bioactivity and corrosion behavior of AZ31 Mg alloy for orthopedic applications. *Ceramics International*, 39(1), 183–195.
- Abdal-hay, A., Dewidar, M., & Lim, J. (2012). Biocorrosion behaviour and cell viability of adhesive polymer coated magnesium based alloys for medical implants. *Applied Surface Science*, 261, 536–546.
- Abel, M., Allington, R., Digby, R., Porritt, N., Shaw, S., & Watts, J. (2006). Understanding the relationship between silane application conditions, bond durability and locus of failure. *International Journal of Adhesives and Adhesion*, 26(1–2), 2–15.
- Anik, A., & Celikten, G. (2007). Analysis of the electrochemical reaction behaviour of alloy AZ91 by EIS technique in H₃PO₄/KOH buffered K₂SO₄ solution. *Corrosion Science*, 49(4), 1878–1894.
- Anik, M., Tanverdi, A., Celiyurek, I., Baksan, B., & Gurler, R. (2006). Effect of the eutectic phase mixture on the anodic behaviour of alloy AZ91. *Materials and Design*, 27(5), 347–355.
- Avila, G., Misch, K., Galindo-Moreno, P., & Wang, H.-L. (2009). Implant surface treatment using biomimetic agents. *Implant Dentistry*, 18(1), 17–26.
- Bai, K., Zhang, Y., Fu, Z., Zhang, C., Cui, X., Meng, E., et al. (2012). Fabrication of chitosan/magnesium phosphate composite coating and the in vitro degradation properties of coated magnesium alloy. *Materials Letters*, 73, 59–61.
- Barriere, F., van Blitterswijk, C., de Groot, K., & Layrolle, P. (2002a). Influence of ionic strength and carbonate on the Ca-P coating formation from SBFx5 solution. *Biomaterials*, 23(9), 1921–1930.
- Barriere, F., van Blitterswijk, C., deGroot, K., & Layrolle, P. (2002b). Nucleation of biomimetic Ca-P coatings on Ti6Al4V from a SBFx5 solution: influence of magnesium. *Biomaterials*, 23(10), 2211–2220.
- Brar, H., Platt, M., Sarntinoranont, M., PI, M., & Manuel, M. (2009). Magnesium as a biodegradable and bioabsorbable material for medical implants. *JOM*, 61(9), 31–34.
- Chollet, C., Chanseau, C., Remy, M., Guignandon, A., Bareille, R., Labrugere, C., et al. (2009). The effect of RGD density on osteoblast and endothelial cell behaviour on RGD-grafted polyethylene terephthalate surfaces. *Biomaterials*, 30(5), 711–720.

- Cortes, D., Lopez, H., & Mantovani, D. (2007). Spontaneous and biomimetic apatite formation on pure magnesium. *Materials Science Forum*, 539-543, 589–594.
- Cui, W., Beniash, E., Gawalt, E., Xu, Z., & Sfeir, C. (2013). Biomimetic coating of magnesium alloy for enhanced corrosion resistance and calcium phosphate deposition. *Acta Biomaterialia*, 9(10), 1–10.
- Dettin, M., Bagno, A., Gambaretto, R., Iucci, G., Conconi, M., Tuccitto, N., et al. (2009). Covalent surface modification of titanium oxide with different adhesive peptides: surface characterization and osteoblast-like cell adhesion. *Journal of Biomedical Materials Research A*, 90A(1), 35–45.
- Feng, Q., Cui, F., Wang, H., Kim, T., & Kim, J. (2000). Influence of solution conditions on deposition of calcium phosphate on titanium by NaOH treatment. *Journal of Crystal Growth*, 210(4), 735–740.
- Ghali, E., Dietzel, W., & Kainer, K. (2004a). Testing of general and localized corrosion of magnesium alloy: a critical review. *Journal of Materials Engineering and Performance*, 13(5), 517–529.
- Ghali, E., Dietzel, W., & Kainer, K. (2004b). General and localized corrosion of magnesium alloys: a critical review. *Journal of Materials Engineering and Performance*, 13(1), 7–23.
- Gray-Munro, J., Seguin, C., & Strong, M. (2009). Influence of surface modification on the in vitro corrosion rate of magnesium alloy AZ31. *Journal of Biomedical Materials Research A*, 91A(1), 221–230.
- Gray-Munro, J., & Strong, M. (2009). The mechanism of deposition of calcium phosphate coatings from solution onto magnesium alloy AZ31. *Journal of Biomedical Materials Research A*, 90A(2), 339–350.
- Gu, X., Zheng, Y., Lan, Q., Cheng, Y., Zhang, Z., Xi, T., et al. (2009). Surface modification of an Mg-1Ca alloy to slow down its biocorrosion by chitosan. *Biomedical Materials*, 4(4), 1–4.
- Guo, Z., Liu, W., & Su, B.-L. (2011). Superhydrophobic surfaces: from natural to biomimetic to functional. *Journal of Colloid and Interface Science*, 353(2), 335–355.
- Hahn, B., Park, D., Choi, J., Ryu, J., Yoon, W., Choi, J., et al. (2011). Aerosol deposition of hydroxyapatite-chitosan composite coatings on biodegradable magnesium alloy. *Surface and Coatings Technology*, 205(8–9), 3112–3118.
- Hersel, U., Dahmen, C., & Kessler, H. (2003). RGD modified polymers: biomaterials for stimulated cell adhesion and beyond. *Biomaterials*, 24(24), 4385–4415.
- Hiromoto, S., Shishido, T., Yamamoto, A., Maruyama, N., Somekawa, H., & Mukai, T. (2008). Precipitation control of calcium phosphate on pure magnesium by anodization. *Corrosion Science*, 50(10), 2906–2913.
- Hu, J., Wang, C., Ren, W., Zhang, S., & Liu, F. (2010). Microstructure evolution and corrosion mechanism of dicalcium phosphate dihydrate coating on magnesium alloy in simulated body fluid. *Materials Chemistry and Physics*, 119(1–2), 294–298.
- Hu, K., Yang, X., Cai, Y., Cui, Z., & Wei, Q. (2006). Preparation of bone-like composite coating using a modified simulated body fluid with high Ca and P concentrations. *Surface and Coatings Technology*, 201(3–4), 1902–1906.
- Ishizaki, T., Hieda, J., Saito, N., Saito, N., & Takai, O. (2010). Corrosion resistance and chemical stability of super-hydrophobic film deposited on magnesium alloy AZ31 by microwave plasma-enhanced chemical vapor deposition. *Electrochimica Acta*, 55(23), 7094–7101.
- Ishizaki, T., Masuda, Y., & Sakamoto, M. (2011). Corrosion resistance and durability of superhydrophobic surface formed on magnesium alloy coated with nanostructured cerium oxide film and fluoroalkylsilane molecules in corrosion NaCl aqueous solution. *Langmuir*, 27(8), 4780–4788.

- Ishizaki, T., & Saito, N. (2010). Rapid formation of a superhydrophobic surface on a magnesium alloy coated with a cerium oxide film by a simple immersion process at room temperature and its chemical stability. *Langmuir*, 26(12), 9749–9755.
- Ishizaki, T., & Sakamoto, M. (2011). Facile formation of biomimetic color-tuned superhydrophobic magnesium alloy with corrosion resistance. *Langmuir*, 27(6), 2375–2381.
- Kang, Z., Lai, X., Sang, J., & Li, Y. (2011). Fabrication of hydrophobic/super-hydrophobic nanofilms on magnesium alloys by polymer plating. *Thin Solid Films*, 520(2), 800–806.
- Keim, S., Brunner, J., Fabry, B., & Virtanen, S. (2011). Control of magnesium corrosion and biocompatibility with biomimetic coatings. *Journal of Biomedical Materials Research B*, 96B, 84–90.
- Killian, M., Wagener, V., Schmuki, P., & Virtanen, S. (2010). Functionalization of metallic magnesium with protein layers via linker molecules. *Langmuir*, 26(14), 12044–12048.
- Kim, J., & Seidler, J. (2009). Formation, structure, and reactivity of amino-terminated organic films on silicon substrates. *Journal of Colloid and Interface Science*, 329(1), 114–119.
- Kuroda, K., Ichino, R., Okido, M., & Takai, O. (2002). Effects of ion concentration and pH on hydroxyapatite deposition from aqueous solution onto titanium by the thermal substrate method. *Journal of Biomedical Materials Research*, 61(3), 354–359.
- Le Saux, G., Magneau, A., Bocking, T., Gaus, K., & Gooding, J. (2011). The relative importance of topography and RGD ligand density for endothelial cell adhesion. *PLOS One*, 6(7), e21869.
- Liu, G., Hu, J., Ding, Z., & Wang, C. (2011). Bioactive calcium phosphate coating formed on micro-arc oxidized magnesium by chemical deposition. *Applied Surface Science*, 257(6), 2051–2057.
- Liu, K., Zhang, M., Zhai, J., Wang, J., & Jiang, L. (2008). Bioinspired construction of Mg-Li alloys surfaces with stable superhydrophobicity and improved corrosion resistance. *Applied Physics Letters*, 92(18), e18310.
- Liu, Q., Ding, J., Mante, F., Wunder, S., & Baran, G. (2002). The role of surface functional groups in calcium phosphate nucleation on titanium foil: a self-assemble monolayer technique. *Biomaterials*, 23(15), 3103–3111.
- Liu, Y., Li, L., Lu, G., & Yu, S. (2010). Preparation of biomimetic hydrophobic coatings on AZ91D magnesium alloy surface. *Science China Technological Sciences*, 53(11), 2972–2975.
- Liu, Y., Lu, G., Liu, J., Han, Z., & Liu, Z. (2013). Fabrication of biomimetic hydrophobic films with corrosion resistance on magnesium alloy by immersion process. *Applied Surface Science*, 264, 527–532.
- Liu, Y., Wu, G., & de Groot, K. (2010). Biomimetic coatings for bone tissue engineering of critical-sized defects. *Journal of the Royal Society Interface*, 7(5), S631–S647.
- Lorenz, C., Brunner, J., Kollmannsberger, P., Jaafar, L., Fabry, B., & Virtanen, S. (2009). Effect of surface pre-treatments on biocompatibility of magnesium. *Acta Biomaterialia*, 5(7), 2783–2789.
- Lu, W., Chen, Z., Huang, P., & Yan, B. (2012). Microstructure, corrosion resistance and biocompatibility of biomimetic HA based CaP coatings on ZK60 magnesium alloy. *International Journal of the Electrochemical Society*, 7(12), 12668–12679.
- Makar, G., & Kruger, J. (1993). Corrosion of magnesium. *International Materials Reviews*, 38(3), 138–153.
- Mathieu, S., Rapin, S., Steinmetz, J., & Steinmetz, P. (2003). A corrosion study of the main constituent phases of AZ91 magnesium alloys. *Corrosion Science*, 45(12), 2741–2755.
- Nguyen, T., Waterman, J., Staiger, M., & Woodfield, T. (2012). Controlling in vitro corrosion rate of pure Mg with rough surface texture via biomimetic coating systems. *Corrosion Engineering Science and Technology*, 47(5), 358–364.

- Ostrowski, N., Lee, B., Roy, A., Ramanathan, M., & Kumta, P. (2013). Biodegradable poly(lactide-co-glycolide) coatings on magnesium alloys for orthopedic applications. *Journal of Materials Science: Materials in Medicine*, 24(1), 85–96.
- Ou, J., Hu, W., Xue, M., Wang, F., & Li, W. (2013). Superhydrophobic surfaces on light alloy substrates fabricated by a versatile process and their corrosion protection. *AES Applied Materials and Interfaces*, 5(8), 3101–3107.
- Pietak, A., Mahoney, P., Dias, G., & Staiger, M. (2008). Bone-like matrix formation on magnesium and magnesium alloys. *Journal of Materials Science: Materials in Medicine*, 19(1), 407–415.
- Rahmany, M., & Van Dyke, M. (2013). Biomimetic approaches to modulate cellular adhesion in biomaterials: a review. *Acta Biomaterialia*, 9(3), 5431–5437.
- Sangeetha, K., Roy, A., Singh, S., Lee, B., & Kumta, P. (2011). Novel alginate based coatings on Mg alloys. *Materials Science and Engineering B*, 176(20), 1703–1710.
- Scardino, A., & de Nys, R. (2011). Mini Review: biomimetic models and bioinspired surfaces for fouling control. *Biofouling*, 27(1), 73–86.
- Sedo, J., Saiz-Poseu, J., Busque, F., & Ruiz-Molina, D. (2013). Catechol-based biomimetic functional materials. *Advanced Materials*, 25(5), 653–701.
- Shadanbaz, S., Walker, J., Staiger, M., Dias, G., & Pietak, A. (2013). Growth of calcium phosphates on magnesium substrates for corrosion control in biomedical applications via immersion techniques. *Journal of Biomedical Materials Research B*, 101B(1), 162–172.
- Shadanbaz, S., & Dias, G. (2012). Calcium phosphate coatings on magnesium alloys for biomedical applications: a review. *Acta Biomaterialia*, 8(1), 20–30.
- She, Z., Li, Q., Wang, Z., Li, L., Chen, F., & Zhou, J. (2012). Novel method for controllable fabrication of a superhydrophobic CuO surface on AZ91D magnesium alloy. *Applied Materials and Interfaces*, 4(8), 4348–4356.
- Song, G., & Atrens, A. (1999). Corrosion mechanisms of magnesium alloys. *Advanced Engineering Materials*, 1(1), 11–13.
- Song, G., Atrens, A., & Dargusch, M. (1999). Influence of microstructure on the corrosion of diecast AZ91D. *Corrosion Science*, 41(2), 249–273.
- Song, J., Lu, Y., Huang, S., Liu, X., Wu, L., & Yu, W. (2013). A simple immersion approach for fabricating superhydrophobic Mg alloy surfaces. *Applied Surface Science*, 266, 445–450.
- Song, Y., Shan, D., Chen, R., Zhang, F., & Han, E. (2009). Biodegradable behaviors of AZ31 magnesium alloy in simulated body fluid. *Materials Science and Engineering C*, 29(3), 1039–1045.
- Staiger, M., Pietak, A., Huadmai, J., & Dias, G. (2006). Magnesium and its alloys as orthopedic biomaterials: a review. *Biomaterials*, 27(9), 1728–1734.
- Torrey, S., Campbell, A., & Cunliffe, D. (2006). Kinetic analysis of organosilane hydrolysis and condensation. *International Journal of Adhesives and Adhesion*, 26(1–2), 40–49.
- Unigovski, Y., & Gutman, E. (1999). Surface morphology of a die-cast Mg alloy. *Applied Surface Science*, 153(1), 47–52.
- Wagener, V., Killian, M., Turhan, C., & Virtanen, S. (2013). Albumin coating on magnesium via linker molecules-comparing different coating mechanisms. *Colloids and Surfaces B: Biointerfaces*, 103, 586–594.
- Wang, J., Li, D., Liu, Q., Yin, X., Zhang, Y., Jing, X., et al. (2010). Fabrication of hydrophobic surface with hierarchical structure on Mg alloy and its corrosion resistance. *Electrochimica Acta*, 55(22), 6897–6906.
- Wang, L., & Carrier, R. L. (2011). Biomimetic topography: bioinspired cell culture substrates and scaffolds. In A. George (Ed.), *Advances in biomimetics*, Chapter 21 (pp. 453–472), Intech Open.

- Wang, S., Guo, X., Xie, Y., Liu, L., Yang, H., Zhu, R., et al. (2012). Preparation of super-hydrophobic silica film on Mg-Nd-Zn-Zr magnesium alloy with enhanced corrosion resistance by combining micro-arc oxidation and sol-gel method. *Surface and Coatings Technology*, 213, 192–201.
- Wang, Y., Wang, W., Zhong, L., Wang, J., Jiang, Q., & Guo, X. (2010). Super-hydrophobic surface on pure magnesium substrate by wet chemical method. *Applied Surface Science*, 256(12), 3837–3840.
- Wang, Z., Li, Q., She, Z., Chen, F., & Li, L. (2012). Low-cost and large-scale fabrication method for an environmentally-friendly superhydrophobic coating on magnesium alloy. *Journal of Materials Chemistry*, 22(9), 4097–4105.
- Wang, Z., Li, Q., She, Z., Chen, F., Li, L., Zhang, X., et al. (2013). Facile and fast fabrication of superhydrophobic surface on magnesium alloy. *Applied Surface Science*, 271, 182–192.
- Waterman, J., Pietak, A., Birbilis, N., Woodfield, T., Dias, G., & Staiger, M. (2011). Corrosion resistance of biomimetic calcium phosphate coatings on magnesium due to varying pre-treatment time. *Materials Science and Engineering B*, 176(20), 1756–1760.
- Waterman, J., Birbilis, N., Dias, G., Woodfield, T., & Staiger, M. (2012). Improving in vitro corrosion resistance of biomimetic calcium phosphate coatings for Mg substrates using calcium hydroxide layer. *Corrosion Engineering Science and Technology*, 47(5), 340–345.
- Weng, L., & Webster, T. (2012). Nanostructured magnesium increases bone cell density. *Nanotechnology*, 23(48), 1–10.
- Weng, L., & Webster, T. (2013). Nanostructured magnesium has fewer detrimental effects on osteoblast function. *International Journal of Nanomedicine*, 8, 1773–1781.
- Witte, F., Hort, N., Vogt, C., Cohen, S., Kainer, K., Willumeit, R., et al. (2008). Degradable biomaterials based on magnesium corrosion. *Current Opinion in Solid State Materials Science*, 12(5–6), 63–72.
- Wong, H., Yeung, K., Lam, K., Tam, V., Chu, P., & Luk, K. (2010). A biodegradable polymer based coating to control the performance of magnesium alloy orthopaedic implants. *Biomaterials*, 31(8), 2084–2096.
- Wu, C., Wen, Z., Dai, C., Lu, Y., & Yang, F. (2010). Fabrication of calcium phosphate/chitosan coatings on AZ91D magnesium alloy with a novel method. *Surface and Coatings Technology*, 204(20), 3336–3347.
- Xin, C., Huo, K., Ju, T., Tang, G., & Chu, P. (2009). Corrosion products on biomedical magnesium alloys soaked in simulated body fluids. *Journal of materials research*, 24(8), 2711–2719.
- Xu, C., Wang, Q., Ban, H., & Xu, W. (2012a). Rapid deposition of hydroxyapatite on Mg-alloy by biomaterialization method. *Advanced Materials Research*, 413, 160–165.
- Xu, L., Zhang, E., & Yang, K. (2012b). Biocorrosion property and cytocompatibility of calcium phosphate coated Mg alloy. *Transactions of the Nonferrous Metals Society China*, 22(8), 2014–2020.
- Xu, W., Song, J., Sun, J., Lu, Y., & Yu, Z. (2011). Rapid fabrication of large-area, corrosion resistant superhydrophobic Mg alloy surfaces. *Applied Materials and Interfaces*, 3(11), 4404–4414.
- Yan, Y., Gao, N., & Barthlott, W. (2011). Mimicking natural superhydrophobic surfaces and grasping the wetting process: a review on recent progress in preparing superhydrophobic surfaces. *Advances in Colloid and Interface Science*, 169(2), 80–105.
- Yang, J., Cui, F., Yin, Q., Zhang, Y., Zhang, T., & Wang, X. (2009). Characterization and degradation study of calcium phosphate coating on magnesium alloy bone implant in vitro. *IEEE Transactions on Plasma Science*, 37(7), 1161–1168.

- Yang, J., Cui, F., & Lee, I. (2011). Surface modification of magnesium alloys for biomedical applications. *Annals of Biomedical Engineering*, 39(7), 1857–1871.
- Yang, L., & Zhang, E. (2009). Biocorrosion behaviour of magnesium alloy in different simulated fluids for biomedical application. *Materials Science and Engineering C*, 29(5), 1691–1696.
- Yanovska, A., Kuznetsov, V., Stanislavov, A., Danilchenko, S., & Sukhodub, L. (2012). Calcium-phosphate coatings obtained biomimetically on magnesium substrates under low magnetic field. *Applied Surface Science*, 258(22), 8577–8584.
- Yin, B., Fang, L., Hu, J., Tang, A.-Q., Wei, W.-H., & He, J. (2010). Preparation and properties of super-hydrophobic coating on magnesium alloy. *Applied Surface Science*, 257(5), 1666–1671.
- Zhang, J., Dai, C., Wei, J., & Wen, Z. (2012). Study on the bonding strength between calcium phosphate/chitosan composite coatings and a Mg alloy substrate. *Applied Surface Science*, 261, 276–286.
- Zhang, Y., Zhang, G., & Wei, M. (2008). Controlling the biodegradation rate of magnesium using biomimetic apatite coating. *Journal of Biomedical Materials Research B*, 89B(2), 408–414.

Surface modification by natural biopolymer coatings on magnesium alloys for biomedical applications

11

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11.1 Introduction

As a lightweight metal, magnesium possesses mechanical properties similar to natural bone. It is an essential element for human beings, with significant functional roles in biological systems. In addition, it easily degrades via corrosion in the electrolytic environment of the body. Therefore, magnesium and its alloys show promise as biocompatible, osteoconductive, cardiovascular, and degradable implants for load-bearing applications (Staiger, Pietak, Huadmai, & Dias, 2006). However, the high corrosion rate and accumulation of hydrogen gas upon degradation hinder its clinical application. Many surface modifications have been adopted to improve the biodegradation resistance of magnesium, such as ion implantation (Liu, Xin, Tian, & Chu, 2007a; Wan et al., 2008; Wang, Zeng, Wu, Yao, & Lai, 2007; Wu, Zeng, Yao, & Han, 2007), micro-arc oxidation (Gu et al., 2011; Zhang, Zhao, Wu, Wang, & Wu, 2007), and hydrothermal treatment (Gu, Zheng, Cheng, & Zheng, 2009a; Tomozawa & Hiromoto, 2011).

A great deal of polymers have been successfully adopted as surface coating modifications on magnesium alloys, including commonly used biodegradable synthetic polymers such as polylactic-co-glycolic acid (PLGA) (Li, Cao, Zhang, Zhang, & He, 2010), polycaprolactone (PCL) (Wong et al., 2010), and polylactic acid (PLA) (Chen et al., 2011). Some natural biopolymers, such as chitosan (Gu et al., 2009b), phytic acid (Ye, Zheng, Wang, Xi, & Li, 2012), and stearic acid (Ng, Wong, & Cheng, 2010) have been reported to be coated on the surface of magnesium alloys.

Natural biomaterial-based coatings are attractive for biomedical applications because they offer protection against corrosion and other functions, such as drug delivery and the ability to be functionalized with organic biomolecules (Hornberger, Virtanen, & Boccaccini, 2012). Compared to synthetic polymers, natural biomaterials exhibit excellent biocompatibility and bioactivity due to their extracellular cell matrix (ECM) components, which contain cell-specific domains such as the RGD (Arg-Gly-Asp) sequence (Tan & Marra, 2010). In addition, they are abundant in the biomass and are easily accessible from a range of sources, such as forest products, grasses, tunicates, crustacea, and stalks.

These natural materials have been shown to promote better healing at a faster rate and are expected to exhibit greater compatibility with humans. However, new concepts in implantable medical devices, especially tissue engineering derived from a combination of biomaterials, require temporal features that ensure the biomaterial biodegrades into nontoxic byproducts (Khor & Lim, 2003).

In this chapter, we review the surface modification of magnesium alloys by natural biopolymer coatings to improve the biocompatibility or corrosion properties of biodegradable magnesium and its alloys.

11.2 Phytic acid modification

11.2.1 Introduction to phytic acid

Phytic acid (myo-inositol hexaphosphoric acid $C_6H_{18}O_{24}P_6$) is a constituent of plants, which is composed of 1–5% by weight of edible legumes, cereals, oil seeds, pollens, and nut (Graf, Empson, & Eaton, 1987). Phytic acid (PA) has a strong ability to chelate multivalent metal ions, especially zinc, calcium, and iron, and, to a lesser extent, magnesium (Cheryan & Rackis, 1980). Figure 11.1 shows the structure of PA. Studies have shown its abilities to alter signal transduction, stimulate genes toward greater cell differentiation, act as an antioxidant as a food additive, and demonstrate anticancer properties (Ye et al., 2012).

11.2.2 Phytic acid coated on WE43 alloys

Ye et al. (2012) studied the *in vitro* corrosion and biocompatibility of PA-modified WE43 alloys as biomaterials. The conversion coatings were prepared by immersing the WE43 alloy into the phytic acid solutions with different pH values (pH 3, 5, 8 and 10) at 40 °C, with untreated WE43 alloy samples as controls.

In different pH conditions, one phytic acid can chelate with different numbers of magnesium ions using its 12 hydroxyl groups, resulting in different modification effects.

As shown in Figure 11.2, when the pH of the coating solution increased from 3 to 5, 8, and 10, the content of element P (at%) changed from 11.47% to 11.67%, 7.22%, and

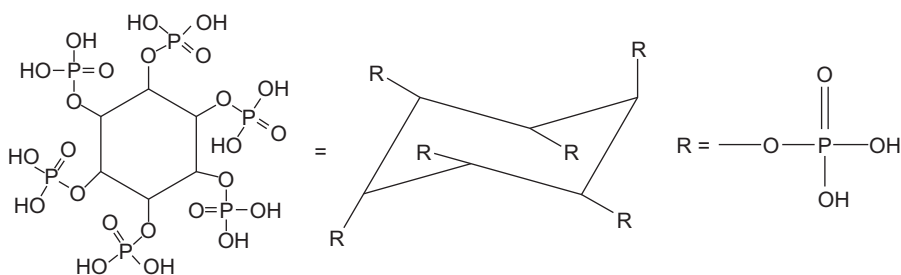


Figure 11.1 Structure of phytic acid.
Adapted from Ye et al. (2012).

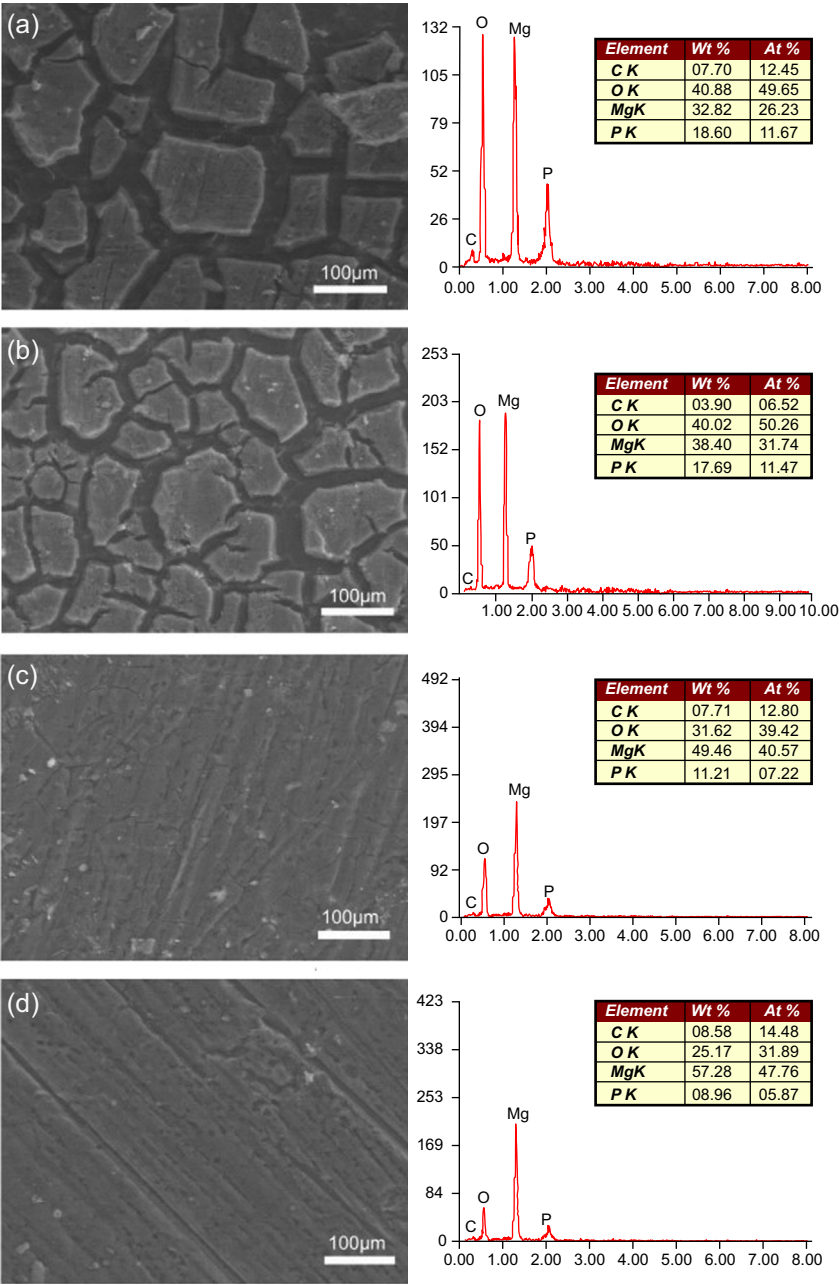
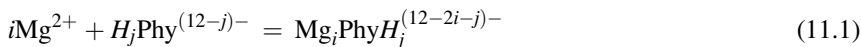


Figure 11.2 SEM micrographs and the EDS (Energy Dispersive Spectrometer) spectrum of the phytic acid-modified WE43 magnesium alloy with a solution of (a) pH 3, (b) pH 5, (c) pH 8, and (d) pH 10. Adapted from [Ye et al. \(2012\)](#).

5.87%, correspondingly. However, much narrower microcracks and smoother films were found, which suggested that less phytic acid but smoother and more compact films were coated on the sample surfaces as the pH value increased.

The reaction between PA and WE43 alloy can be demonstrated by the following equation (Crea, De Robertis, De Stefano, & Sammartano, 2006) and Figure 11.3(a):



in which Phy refers to phytic acid ion and i and j are the stoichiometric ratios.

In low pH environments, the matrix released more Mg^{2+} , which could produce more Phy–Mg chelate. However, Phy–Mg chelate was partly soluble in pH = 3 solution, so there would be less chelate complex on the surface of the WE43 Mg alloy than in the pH 5. At a high pH, the corrosion procedure was inhibited, so less Mg^{2+} could react with PA. Different from other conditions, the structure of PA was 1eq/5ax (Figure 11.3(b)) in pH 10; when the samples were put into SBF, the structure of PA changed to 1ax/5eq. (Here, ax is the axial bond between carbon and substituent that is projected vertically up or down on the carbon ring conformation, whereas eq is the equatorial band between a carbon and a substituent that extends out of a ring of carbons.) During this change, the chelate bond between Mg^{2+} with phosphate groups would break down, resulting in the migration of phytic acid to the SBF solution. Meanwhile, because the stability of Phy–Ca was

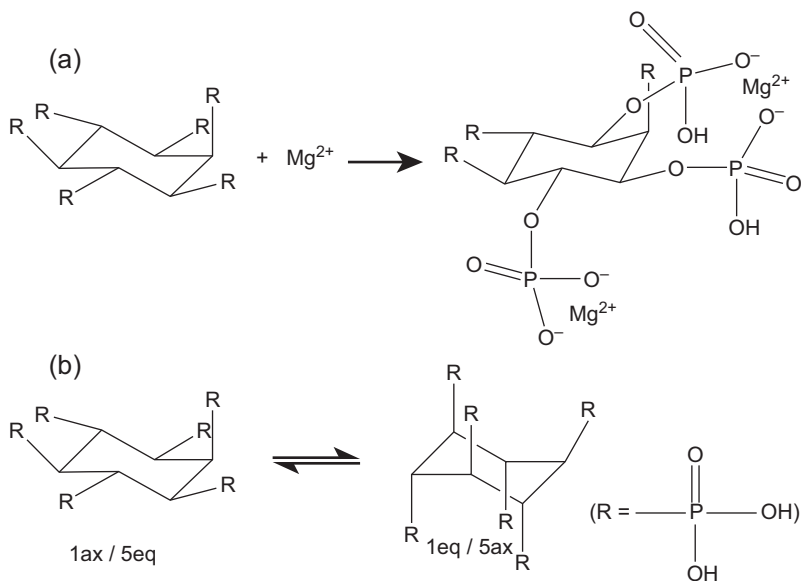


Figure 11.3 (a) The mechanism of the Phy–Mg complex formation. (b) The conformation of the phytic acid in different solution conditions.

Adapted from Ye et al. (2012).

higher than Phy-Mg and there were more Ca^{2+} than Mg^{2+} (2.5 mmol/L vs 1.5 mmol/L) in the SBF, the Phy after the bond cleavage would combine with calcium ions to form Ca-Phy chelate. The dissolve of Phy-Mg film accelerated Mg alloy corrosion.

The corrosion rate of PA-treated WE43 alloy samples follows the order: pH 5 < pH 3 < pH 8 < pH 10 in SBF solution, as indicated by the hydrogen evolution method (Figure 11.4) and potentiodynamic polarization parameters (Table 11.1).

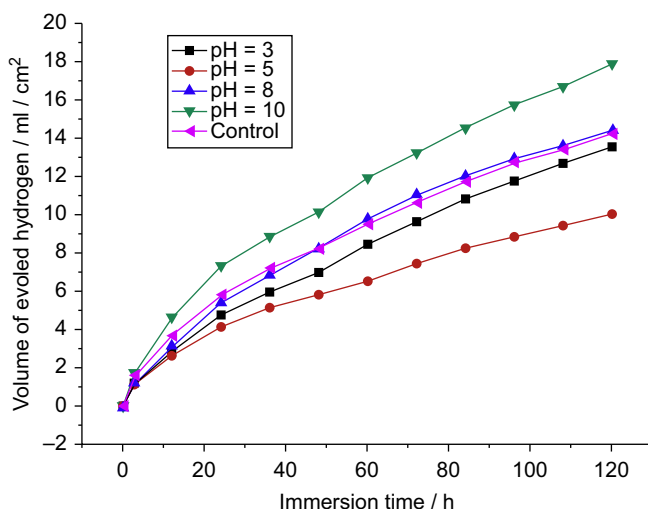


Figure 11.4 Hydrogen evolution volumes of the phytic acid-modified WE43 Mg with different pH and the control samples as a function of the immersion time in SBF.

Table 11.1 Potentiodynamic polarization parameters of the phytic acid-modified WE43 Mg samples and the control in SBF solutions at 37 °C

Coating condition	Corrosion potential: E_{corr} (V)	Corrosion current density: I_{corr} (A cm^{-2})
pH 3	-1.84	5.26×10^{-4}
pH 5	-1.79	8.08×10^{-4}
pH 8	-1.85	5.08×10^{-4}
pH 10	-2.08	3.07×10^{-3}
Control	-1.85	5.09×10^{-4}

As shown in Figure 11.5(a), all the modified groups exhibited better cell viabilities of L929 than the unmodified control after 1, 2, and 4 days of culture, and the hemolysis rate of PA-coated WE43 magnesium alloys were lower than 5% (Figure 11.5(b)), indicating that the modified WE43 magnesium alloy met the requirements of the hemolysis standard (ISO, 2006) for biomedical materials.

To conclude, the PA-treated WE43 alloys possess superior corrosion properties and biocompatibility compared with untreated WE43 alloy. The solution converted group

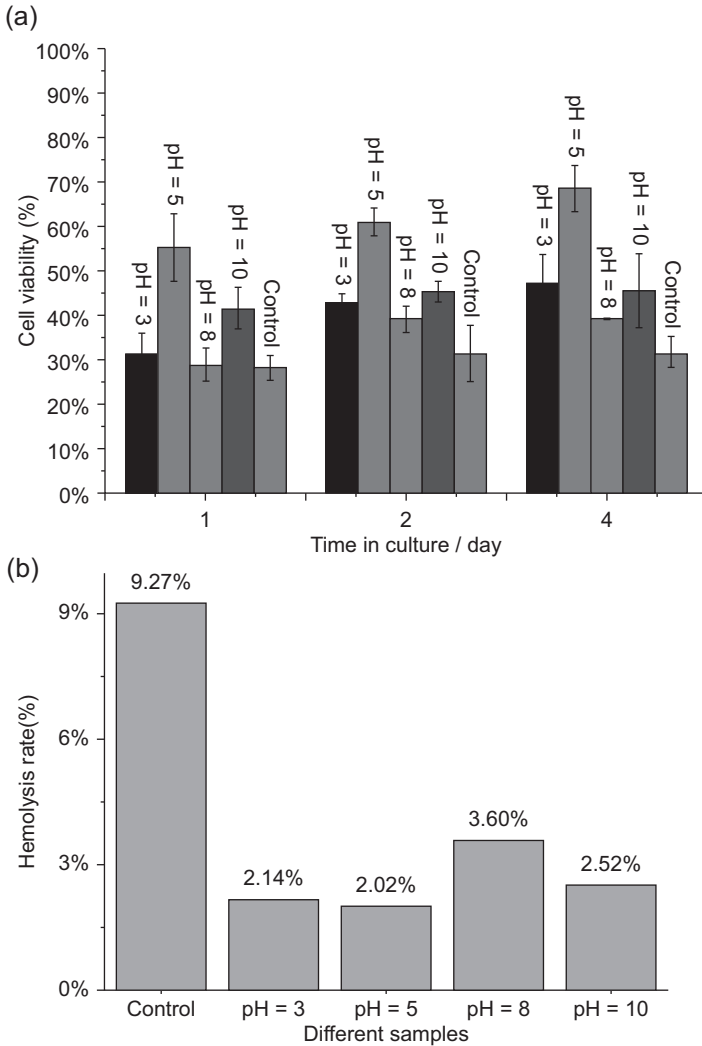


Figure 11.5 Biocompatibility. (a) L929 cell viability expressed as a percentage of the viability of cells in the control and phytic acid-modified WE43 Mg extraction solution after 1, 2, and 4 days of culture. (b) Hemolysis percentage of the WE43 Mg alloy and the phytic acid-modified WE43 Mg alloy.

with a pH of 5 displayed the best properties among the modified samples. Phytic acid modification is an industrial method to improve the corrosion property of metal alloys. This work successfully adopted the traditional method from industry to biomedical applications and achieved some ideal results.

11.3 Chitosan modification

11.3.1 Introduction to chitosan

Chitosan, the deacetylated product of chitin, is soluble in dilute acids such as acetic acid and formic acid. Commercially, chitin and chitosan can be obtained from shellfish sources, such as crabs and shrimp (Khor & Lim, 2003). The investigation on chitosan mainly focuses on its preparation with varied molecular weights and degrees of acetylation (DA) from chitin, the relationship between its solution properties and DA, and the preparation of derivatives and applications (Rinaudo, 2006).

Most of the naturally existing polysaccharides, such as cellulose, dextran, pectin, alginic acid, agar, agarose, and carrageenans, are neutral or acidic, whereas chitin and chitosan are examples of highly basic polysaccharides. Their unique properties include polyoxysalt ions and optical structural characteristics (Majeti, 2000). Meanwhile, chitosan is the only pseudonatural cationic polymer, and it could be used in many fields for its unique characters (flocculants for protein recovery, depollution, etc.). Being soluble in aqueous solutions, it is commonly used in different applications, such as solutions, gels, or films and fibers (Rinaudo, 2006). In addition, it has been used for the development of ocular bandage lenses (Rinaudo, 2006), the treatment of wastewater, as substratum for skin replacement (Ravi Kumar, 2000), and as a drug carrier.

11.3.2 Chitosan coating on Mg–1.4 wt% Ca alloys

Gu et al. (2009b) coated chitosan on the surface of extruded Mg–1.4 wt% Ca alloy for two main considerations: (1) the insolubility of chitosan in alkaline aqueous solutions may protect the Mg alloy substrate from corrosion; and (2) after being degraded by enzyme action and hydrolysis, the degradation products of chitosan are saccharides and glucosamines, which may be incorporated into glycoproteins or excreted as carbon dioxide gas during respiration.

Chitosan solutions were prepared with four types of chitosan (type 1: DD = 87%, $\eta = 15 \text{ mPa}\cdot\text{s}$, $M_w = 1.0 \times 10^4$; type 2: DD = 85%, $\eta = 200 \text{ mPa}\cdot\text{s}$, $M_w = 15 \times 10^4$; type 3: DD = 90%, $\eta = 370 \text{ mPa}\cdot\text{s}$, $M_w = 27 \times 10^4$; type 4: DD = 83%, $\eta = 725 \text{ mPa}\cdot\text{s}$, $M_w = 60 \times 10^4$) at one weight percentage in 0.2% acetic acid. Here DD, η , and M_w represented the degree of deacetylation, the intrinsic viscosity, and the molecular weight, respectively. After passivation in 10 g/L $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ and activation in 200 ml/L H_3PO_4 (85%) and 100 g/L NH_4HF_2 , magnesium alloy samples were dip-coated in chitosan solution with one, three, six, and nine cycles at a withdraw speed of 1 cm/min. Each time after coating, the samples would be evaporated at 60 °C for 20 min.

Chitosan coating prepared using type 3 chitosan after six cycles of dip coating showed the smoothest and flattest surfaces (Figure 11.6) among the four types. The surfaces after one, three, and nine cycles of type 3 chitosan coating showed the appearance of pores with different sizes, in comparison with the flat and compact surface of six cycles of type 3 chitosan coating.

The hydrogen evolution volume and the variation in the pH values were detected during an immersion test in SBF (Figure 11.7), which illustrated that six cycles of type 3 chitosan coating had the highest corrosion resistance. After 10 days of immersion, the surface of the uncoated Mg–Ca alloy sample suffered severe corrosion (Figure 11.8), while the surface of six cycles of type 3 chitosan coating sample presented a relatively smooth and regular morphology without any cracks.

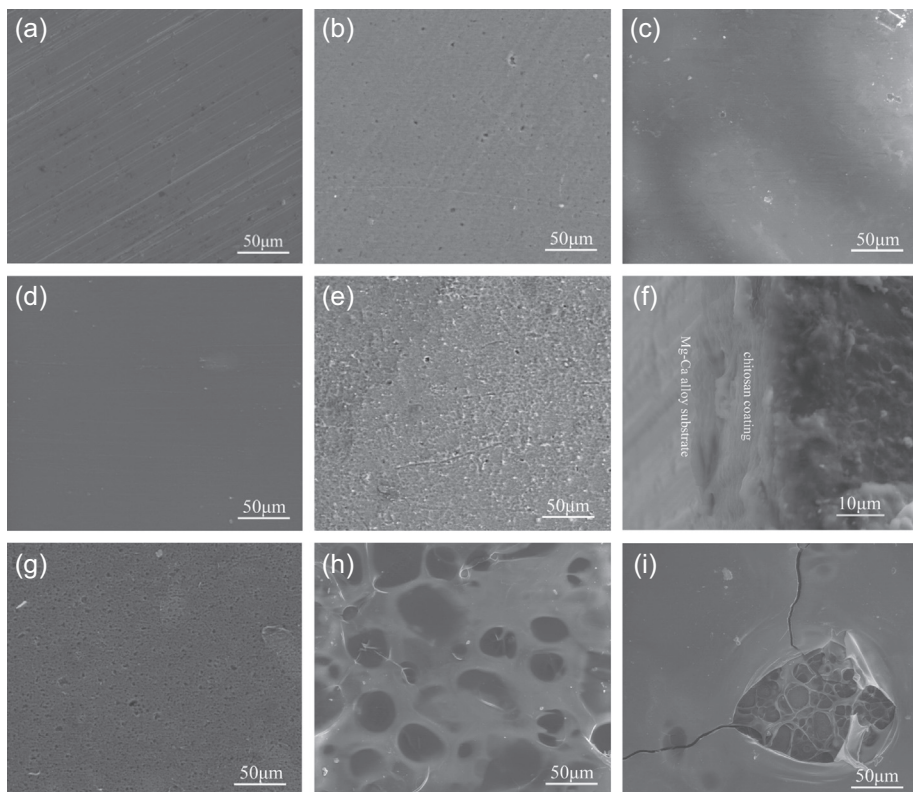


Figure 11.6 Plane-view SEM images of the surfaces of (a) uncoated Mg–Ca alloy and chitosan coatings with molecular weights of approximately (b) 1.0×10^4 , (c) 1.5×10^5 , (d) 2.7×10^5 , and (e) 6.0×10^5 for six cycles. (f) Cross-sectional SEM image of (d). Plane-view SEM images of the surfaces of the chitosan coatings with molecular weight of approximately 2.7×10^5 for (g) one cycle, (h) three cycles, and (i) nine cycles.

Adapted from Gu, Zheng, et al. (2009b).

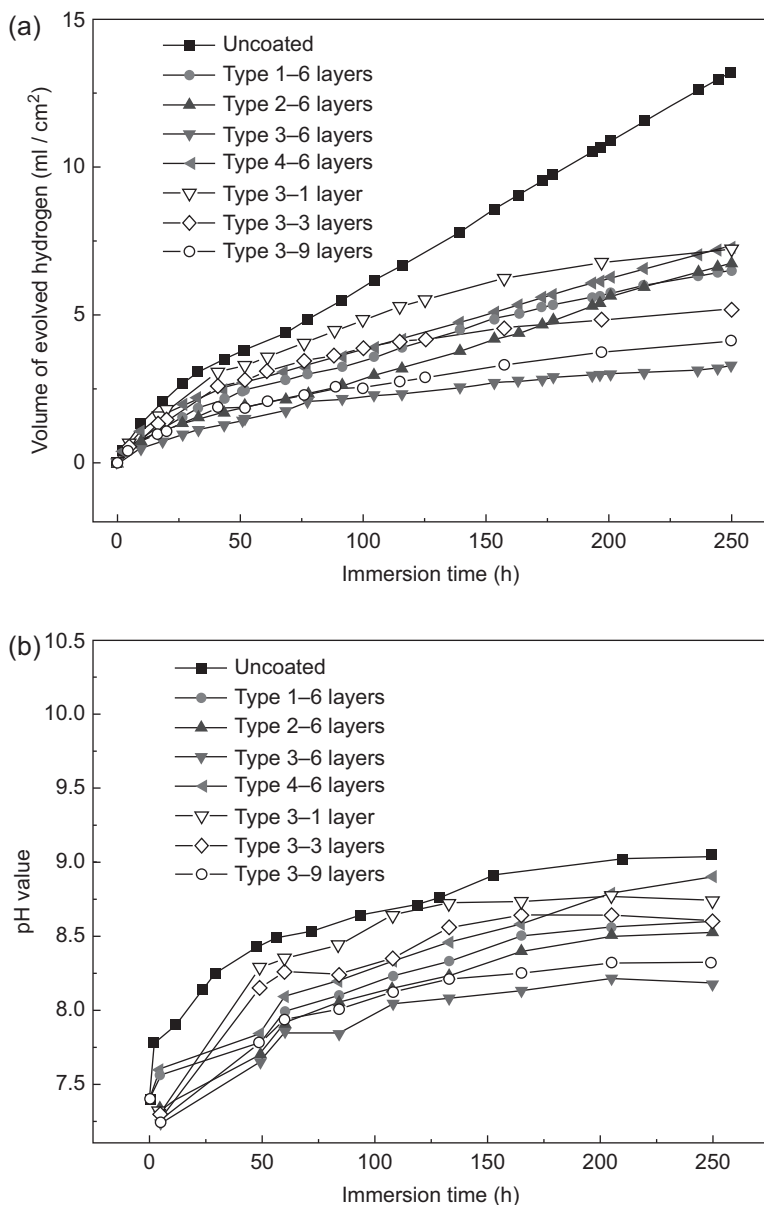


Figure 11.7 The hydrogen evolution volume (a) and the variation in the pH value of SBF (b) for samples coated by chitosan with different molecular weights (1.0×10^4 , 1.5×10^5 , 2.7×10^5 , and 6.0×10^5) and different cycles of chitosan coating with the same molecular weight ($\sim 2.7 \times 10^5$).

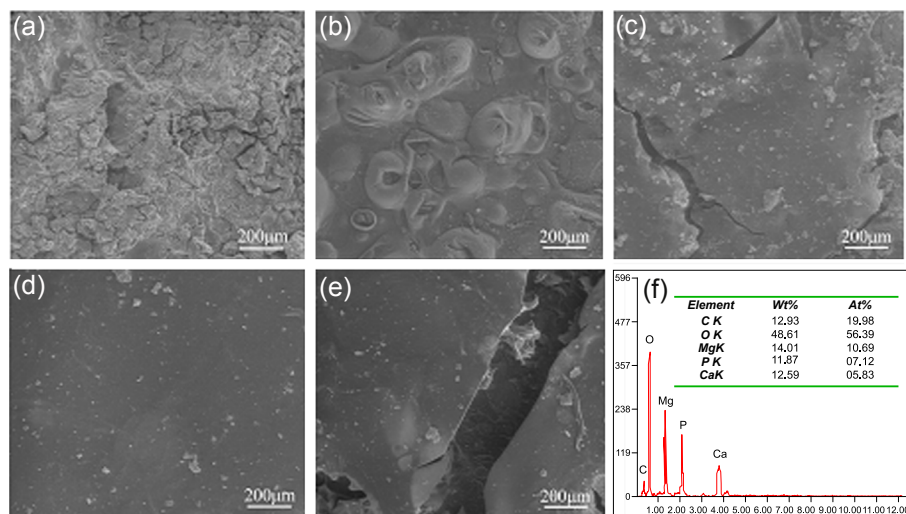


Figure 11.8 SEM images of the surfaces of chitosan coatings with a molecular weight of approximately 2.7×10^5 for (a) zero cycle (uncoated), (b) one cycle, (c) three cycles, (d) six cycles, and (e) nine cycles after immersion in SBF for 10 days. (f) Typical EDS spectra of the chitosan-coated Mg–Ca alloy after 10 days immersion in SBF.

Adapted from [Gu, et al. \(2009b\)](#).

Results showed that the dip coating of chitosan had effectively improved the biocorrosion resistance of the Mg–Ca alloy in the simulated body fluid, especially the coating with six cycles produced by 2.7×10^5 molecular weight chitosan.

In this work, a suitable type of chitosan and an appropriate dip-coating procedure are screened out as the best coating to improve the corrosion property of Mg–Ca alloy. However, the attachment force between the substrate and the chitosan coating has not been tested, and the morphology of the cross-section has been ignored. Apart from that, much more work to test the coating properties, such as biocompatibility, has to be done.

11.3.3 Phosphate/chitosan composite films by electrophoretic deposition

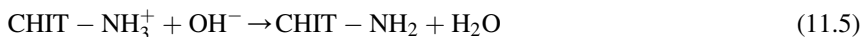
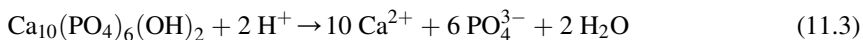
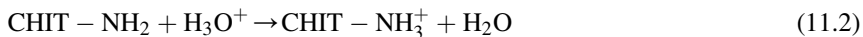
Hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) constitutes 65% of the mineral fraction of human bone and tooth, which is commonly used as coating of the implants due to its promotion of new bone ingrowth ([Petit, 1999](#)). However, the bonding strength between HA and magnesium alloy substrates does not meet the request. In order to improve the poor HA-Mg interfacial strength in EPD (Electrophoretic Deposition Fabrication) fabrication, calcium phosphate/chitosan composite films were fabricated on the surface of micro-arc oxidized (MAO)-AZ91D alloy through EPD followed by a conversion process of the coatings in phosphate-buffered saline (PBS) ([Wu, Wen, Dai,](#)

Lu, & Yang, 2010). The coating phases changed from HA/chitosan to $\text{Ca}(\text{OH})_2$ during EPD process and then transferred into HA immersed in PBS.

The degree of deacetylation of chitosan ($\text{Mw} = 200,000$) was about 85%. All the electrolytes were prepared by mixing an n-HA/ethanol suspension with an n-HA/chitosan—acetic acid aqueous solution, according to Table 11.2, where n-HA stands for stoichiometric HA for EPD precipitated through a wet chemical technique by Wu et al. (2010).

The coating conditions and composition of deposited coatings are shown in Table 11.3 and Figure 11.9. As the content of chitosan increased, the achievement ratio improved. This may be due to the reaction or electrostatic attraction between the charge of chitosan and the electrode, which is needed to prove. It revealed that flake-like crystals in different diameters were formed on the surface of samples. Also, with the increase of n-HA/chitosan—acetic acid aqueous solution, less flake-like crystals and more pores were produced, which is mainly caused by gas evolution in the deposited coatings.

As revealed by x-ray diffraction (XRD) patterns (Figure 11.10(a)), when the n-HA particles were dissolved into the chitosan—acetic acid aqueous solution, the intensities of HA peaks gradually decreased, while those of $\text{Ca}(\text{OH})_2$ gradually increased as the volume percentage of n-HA/chitosan—acetic acid aqueous solution increased in the electrolyte. Furthermore, the adhesion of the coatings to the substrate was enhanced gradually and the cracks in the layers became less. Chitosan reduced the surface energy of HA powders and stronger adhesion between the substrate and $\text{Ca}(\text{OH})_2$ could be produced, leading to dispersed particles and crack-free coatings. The reaction might occur as follows (Wu et al., 2010):



After immersion for 3, 10, and 15 days in PBS solution, HA and dicalcium phosphate dihydrate (DCPD $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) were converted from $\text{Ca}(\text{OH})_2$, as revealed by the XRD patterns (Figure 11.10(b) and (c)) of coatings. It is thought that $\text{Ca}(\text{OH})_2$ might be gradually converted to HA directly or experience a precursor phase (DCPD), as shown in Eqn (11.7–11.10). With the portion of $\text{Ca}(\text{OH})_2$ gradually increasing in the EPD layer, the appearance of the samples after conversion became more homogeneous and the size of the particles became smaller (Figure 11.11). This research successfully produced dense and uniform HA layers by converting HA/chitosan to $\text{Ca}(\text{OH})_2$ during EPD, and then transferred into HA in PBS. As the

Table 11.2 Compositions of six electrolytes for EPD (volume of electrolyte: 500 mL)

Electrolyte	n-HA/chitosan-acetic acid solution (ml)		n-HA/ethanol suspension (ml)		Volume percentage of n-HA/chitosan acetic acid solution (vol%)
	Weight of n-HA (g)	Volume of chitosan-acetic acid solution (ml)	Weight of n-HA (g)	Volume of chitosan-acetic acid solution (ml)	
E-I	0	0	2.5	500	0
E-II	0.5	100	2.0	400	20
E-III	1.0	200	1.5	300	40
E-IV	1.5	300	1.0	200	60
E-V	2.0	400	0.5	100	80
E-VI	2.5	500	0	0	100

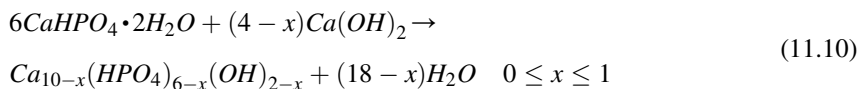
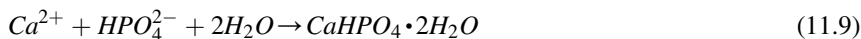
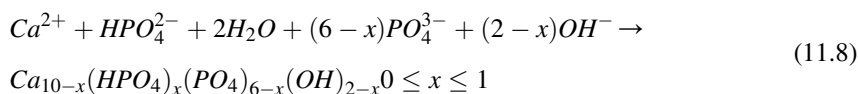
Adapted from [Wu et al. \(2010\)](#).

Table 11.3 Coating conditions and phase proportion after coating in different electrolytes

Deposit coatings	Conditions and phase (wt%) of deposited coatings					
	D-I	D-II	D-III	D-IV	D-V	D-VI
Electrolyte	E-I	E-II	E-III	E-IV	E-V	E-VI
Deposition current density (A/cm ²)	<0.01	<0.01	0.01	0.04	0.12	0.22
Coating condition	Thin	Detached	Poorly uniform	Uniform	Uniform	Uniform
Achievement ratio (%)	72	0	12	88	86	92
HA	100		67	45	35	0
Ca(OH) ₂	0		32	54	64	100

Adapted from [Wu et al. \(2010\)](#).

percentage of chitosan increased, the HA coating became more homogeneous, indicating higher biocompatibility.



EPD is a frequently used method in modification, and some electrochemical reaction may occur during the procedure. In this work, it is upset when bioactive HA particles are converted into unbioactive Ca(OH)₂ in EPD, which decreases the biocompatibility of the coatings, but the authors are sapiential to transform Ca(OH)₂ into HA by a subsequent immersion in PBS solution. Although the reaction procedure in the article is not definitive, especially the changes of chitosan in the formulas, it is an encourage work to apply a conversion thought transferring a bio-inert coating to a bio-mimetic or even bioactive surface by a low cost and easy method.

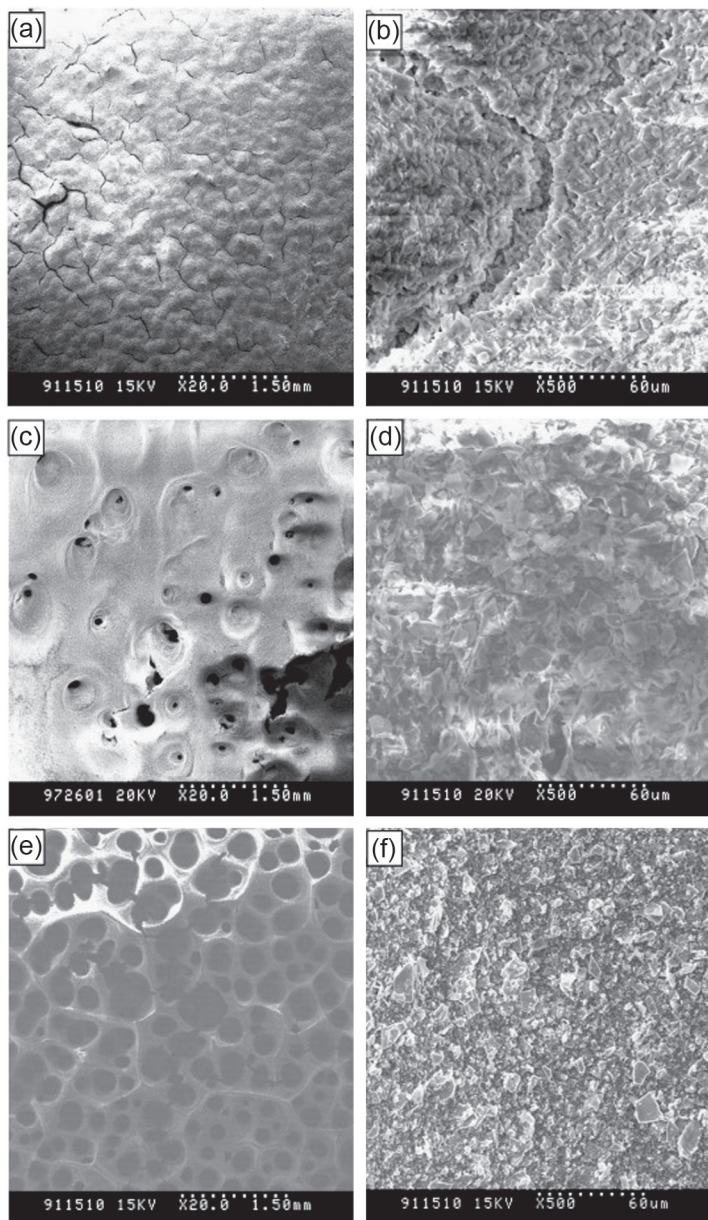


Figure 11.9 SEM images of the coatings prepared from five electrolytes on the MAO-AZ91D substrate by EPD. (a, b) D-I prepared from the E-I electrolyte. (c, d) D-III prepared from the E-III electrolyte. (e, f) D-IV prepared from the E-IV electrolyte. (g, h) D-V prepared from the E-V electrolyte. (i, j) D-VI prepared from the E-VI electrolyte.

Adapted from [Wu et al. \(2010\)](#).

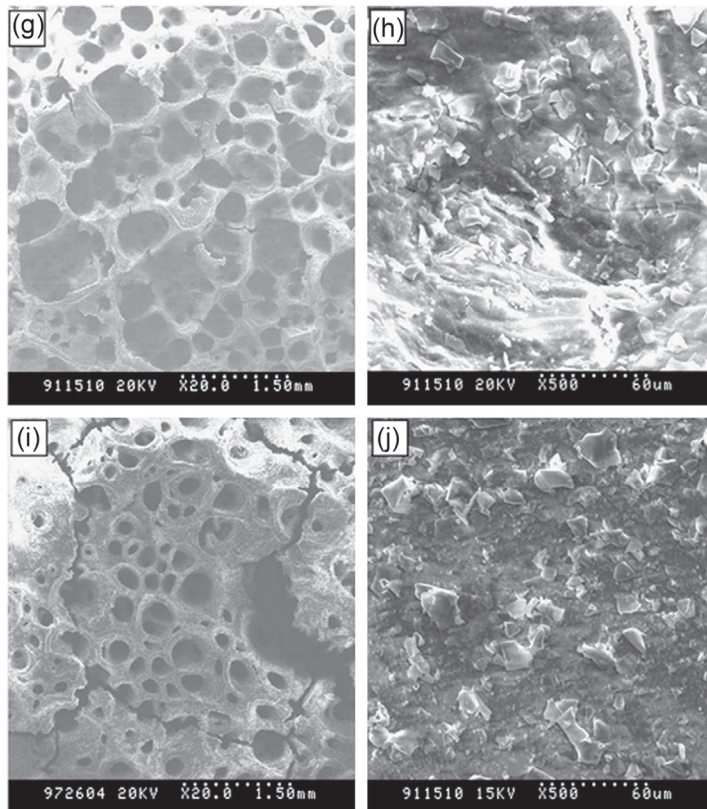


Figure 11.9 Continued.

11.3.4 Phosphate/chitosan composite films by aerosol deposition

Highly dense and adherent HA–polymer composite coatings onto metallic substrates were difficult to fabricate by conventional low-temperature processes, such as electrochemical and EPD. [Hahn et al. \(2011\)](#) chose the aerosol deposition (AD) method to improve the properties of the coatings, which can deposit dense and well-adherent ceramic coatings on metal substrates at room temperature.

HA nanocrystalline powder (volumetric mean diameter of 15 nm) was heated at 1050 °C for 2 h. The chitosan powder (DD = 85%) was dry ball-milled for 12 h in a planetary mill using ZrO₂ balls and a jar. Thereafter, the HA–chitosan composite powders containing 5, 10, and 20 wt% of chitosan were prepared by a simple dry-powder mixing process and then used for coating by AD over the entire surface of hot-rolled AZ31 Mg alloy plates.

The coatings showed different microstructures depending on the amount of chitosan added ([Figure 11.12](#)). The rough surface with a network structure of HA coating became smoother, with the amount of chitosan increasing. In addition, the coatings

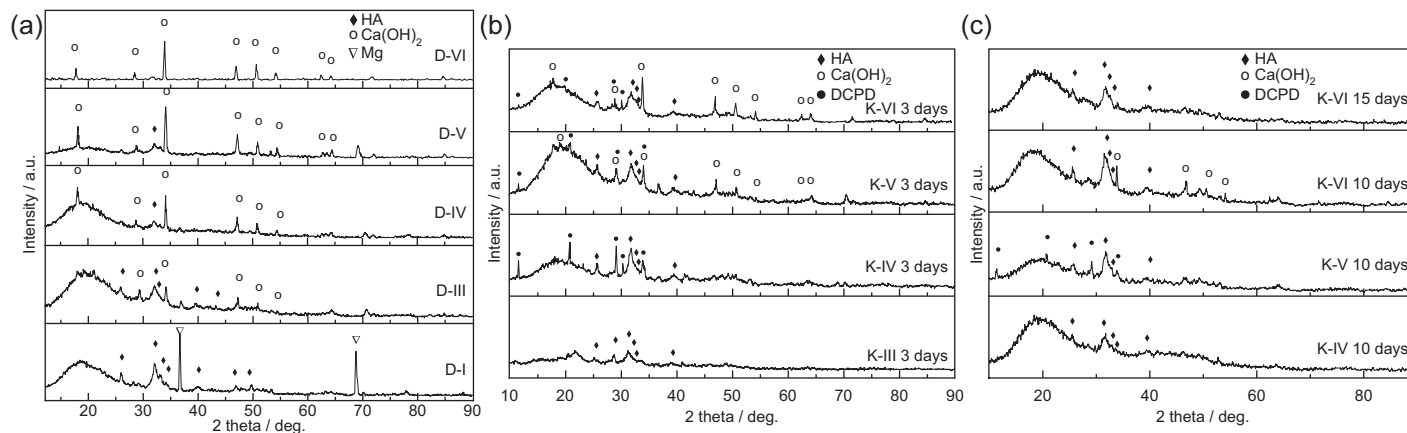


Figure 11.10 XRD patterns of the coatings (a) prepared from five electrolytes on the MAO-AZ91D Mg alloy substrate by EPD. (b) After immersion in PBS for 3 days. (c) After immersion in PBS for 10 and 15 days. D-I, K-I coatings were prepared from the E-I electrolyte; D-III, K-III coatings were prepared from the E-III electrolyte; D-IV, K-IV coatings were prepared from the E-IV electrolyte; D-V, K-V coatings were prepared from the E-V electrolyte; and D-VI, K-VI coatings were prepared from the E-VI electrolyte.

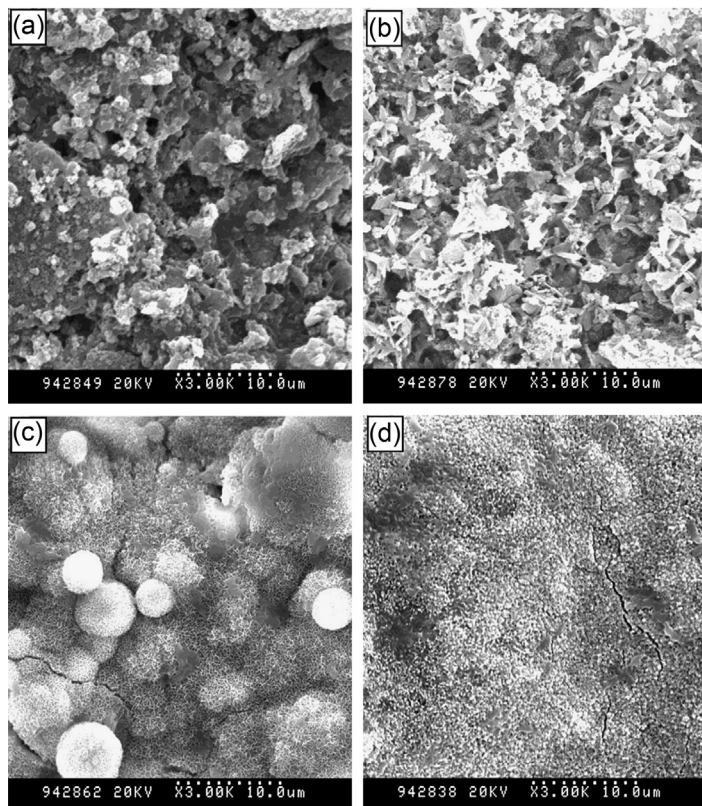


Figure 11.11 SEM images of four coatings after immersion into PBS for 3 days. (a) K-III converted from the D-III coatings. (b) K-IV converted from the D-IV samples. (c) K-V converted from the D-V coatings. (d) K-VI converted from the D-VI coatings. Adapted from [Wu et al. \(2010\)](#).

showed fairly dense cross-sectional microstructures ([Figure 11.12](#)) without obvious pores or cracks.

The adhesion strengths between the AD coatings and substrates were 27.7–24.6 MPa, which is higher than those of electrochemically deposited HA coatings and EPD HA coatings. The results of the protective property of the coatings investigated by electrochemical measurements at 37 °C in SBF are listed in [Table 11.4](#). It was found that the coating formed on the AZ31 alloy significantly promoted its resistance to corrosive degradation, even though the addition of chitosan slightly lowered the corrosion resistance of the HA coating.

The MC3T3-E1 preosteoblast cell line attached on the samples after 5 h of incubation was used to characterize the cell attachment behaviors on the HA–chitosan composite coatings. The field-emission gun (FEG) scanning electron microscopy (SEM) morphologies of the cells presented in [Figure 11.13](#) showed that more multiple filopodia of the cells were found to spread on the surface of the HA–chitosan composite

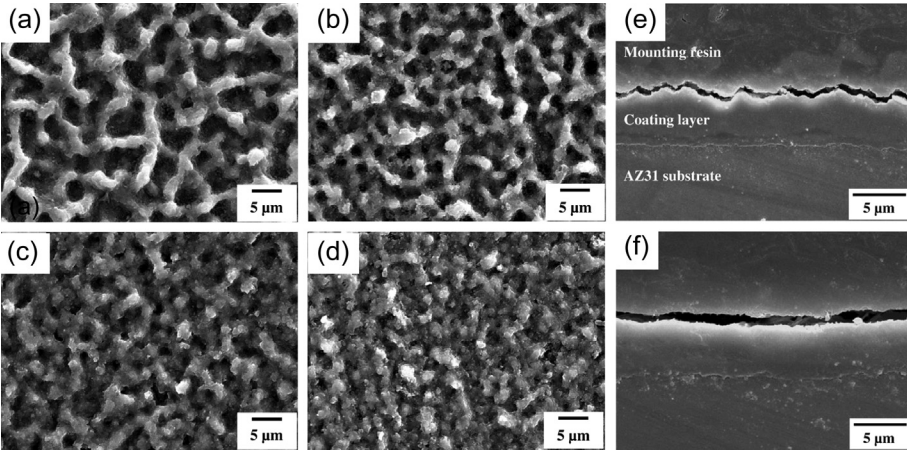


Figure 11.12 SEM micrographs of the surfaces of the (a) pure HA, (b) HA-5 wt% chitosan, (c) HA-10 wt% chitosan, and (d) HA-20 wt% chitosan composite coatings deposited on the AZ31 Mg alloy substrates. Cross-sectional SEM micrographs of (e) the pure HA and (f) HA-20 wt% chitosan composite coatings deposited on AZ31 Mg alloy substrates. Adapted from [Hahn et al. \(2011\)](#).

Table 11.4 Electrochemical corrosion parameters derived from potentiodynamic polarization

	Corrosion potential: E_{corr} (V)	Corrosion current density: I_{corr} (A/cm ²)
AZ31	−1.733	3.839×10^{-4}
HA	−1.569	4.765×10^{-6}
HA-5 wt% chitosan	−1.601	1.515×10^{-5}
HA-10 wt% chitosan	−1.581	3.144×10^{-5}
HA-20 wt% chitosan	−1.586	5.097×10^{-5}

Adapted from [Hahn et al. \(2011\)](#).

coating with increasing content of chitosan, implying that the biocompatibility was improved by the incorporation of chitosan.

This AD method used gas as a solvent to avoid an aqueous solution, which reduced the corrosion probability of the active magnesium substrate. Meanwhile, superior to the electrochemical deposition and the EPD coating method of HA/chitosan, this method does not require MAO preprocessing or later stage conversion, which makes it easier and lower in cost.

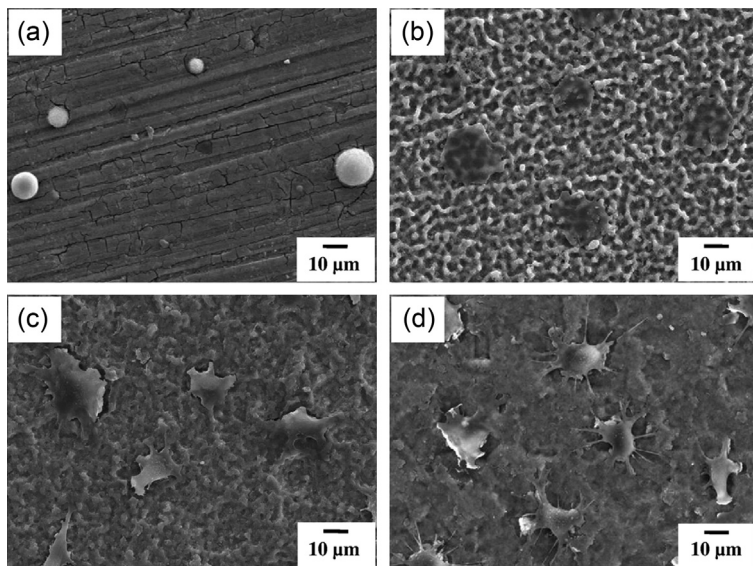


Figure 11.13 Filed-emission gun SEM micrographs of the MC3T3-E1 cells attached to the samples: (a) uncoated AZ31 substrate, (b) HA coating, and HA–chitosan composite coatings with (c) 5 wt% and (d) 20 wt% chitosan.

Adapted from [Hahn et al. \(2011\)](#).

11.4 Stearic acid modification

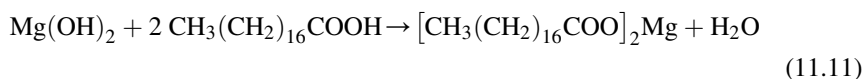
11.4.1 Introduction to stearic acid

Stearic acid, another name for octadecanoic acid $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$, is one of the most common fatty acids. It exists as a glycerol ester in most animal and plant fats ([Beare-Rogers, Dieffenbacher, & Holm, 2001](#)). Stearic acid is more abundant in animal fat (up to 30%) than vegetable fat (typically <5%). The important exceptions are cocoa butter and shea butter, in which the stearic acid content (as a triglyceride) is 28–45%. Unlike the other long-chain saturated fatty acids, stearic acid has no effect on lipoprotein cholesterol concentrations in men or women ([Yu, Derr, Etherton, & Kris-Etherton, 1995](#)). Results from the study by [Kelly et al. \(2001\)](#) indicate that stearic acid (19 g/day) in the diet has favorable effects on thrombotic and atherogenic risk factors in males; the authors recommend that the food industry consider enriching foods with stearic acid instead of palmitic acid and trans fatty acids. Thus, stearic acid is nontoxic and biocompatible with the human body. With a polar head group that can bind with metal cations and a nonpolar chain that confers solubility in organic solvents, stearic acid is commonly used in the production of detergents, soaps, and cosmetics, such as shampoos and shaving cream products.

11.4.2 Stearic acid coating on magnesium

A study by Ng et al. (2010) attempted to employ stearic acid (SA, $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$) as an organic coating for enhancing the corrosion resistance of Mg. The organic coating was prepared by a two-step process using hydrothermal treatment to form a $\text{Mg}(\text{OH})_2$ layer at 120°C for 24 h, then immersion in SA to form an organic coating. For comparison, three different coating conditions were used (Table 11.5). It was concluded that higher viscosity resulted in a thicker coating film.

After hydrothermal treatment, a loose layer of $\text{Mg}(\text{OH})_2$ was formed on the surface of Mg samples. When the samples were soaked in SA, the SA diffused easily into the hydroxide layer due to the open structure of the latter, and the reaction took place according to Eqn (11.11)



The schematic diagram of Figure 11.14 proposed the mechanism of formation and the structure of the coating. As the SA filled up the space between the hydroxide branches, it reacted with the $\text{Mg}(\text{OH})_2$ to form magnesium stearate (MgSt), which contributed to the strong adhesion of SA coating to the substrate.

Figure 11.15 showed different surface morphologies of the coating layers in different preparation conditions. The calibration curve was obtained from Fourier transform infrared spectroscopy for spectra of different mixtures of MgSt and SA using the peaks at 1702 cm^{-1} for SA and at 1573 cm^{-1} for MgSt. The ratios of MgSt to SA (by weight) were 49.7:50.3, 33.8:66.2, and 39.6:60.1 for SA1–Mg, SA2–Mg, and SA3–Mg, respectively. Among these samples, for the thickest coating layer ($230 \mu\text{m}$), the surface of SA2–Mg was relatively smooth and compact (Figure 11.15(a–c)). The differences in composition could be attributed to the different soaking temperatures, leading to different degrees of completion of the reaction and differences in viscosity as well.

Electrochemical measurements and long term immersion test were conducted in Hanks' solution. The results of electrochemical test (Table 11.5) showed that among the coated samples, where R_t ($R_t = R_{po} + R_p$) stands for the total corrosion resistance of a polymer-coated metal sample. R_{po} and R_p are the “pore resistance” of the coating and the polarization at the coating/substrate interface, respectively. SA2–Mg exhibited the best corrosion resistance due to its thicker and better quality film. After immersion in Hanks' solution (Figure 11.16) bare Mg corroded severely after 6 days of immersion. For SA1–Mg, the surface also underwent heavy corrosion attack after 6 days of immersion, consistent with the results of EIS (Electrochemical Impedance Spectroscopy) measurements. However, SA2–Mg still kept almost its original appearance, even after 80 days of immersion.

The variation of the corrosion resistance between SA2–Mg and bare Mg is given in Figure 11.17. In the initial period, the corrosion resistance of SA2-coated Mg was four orders of magnitude greater than bare Mg and gradually dropped to about 40 times in the long run, which facilitated the maintenance of mechanical strength of implants in the

Table 11.5 Summary of coating conditions and corrosion parameters

Sample designation	Viscosities of SA or SA solution (centipoise)	Coating thickness(μm)	Polarization test		Day 5 (pH 5.5)		Day 30 (pH 7.4)	
			E_{corr} (VSCE)	I_{corr} (A/cm^2)	E_{oc} (VSCE)	R_t ($\text{k}\Omega\text{cm}^2$)	E_{oc} (VSCE)	R_t ($\text{k}\Omega\text{cm}^2$)
Bare Mg	—	—	−1.80	0.25×10^{-3}	−1.94	0.03	−1.78	25
HT-Mg	—	170	−1.71	4.0×10^{-6}	Not tested	—	—	—
SA1-Mg	0.5	180	−1.49	0.12×10^{-6}	−1.86	0.7	—	—
SA2-Mg	5.2	230	−1.45	11.2×10^{-9}	−1.48	700	−1.54	107
SA3-Mg	2.3	210	−1.45	0.14×10^{-6}	−1.69	43	−1.62	102

R_t ($R_t = R_{\text{po}} + R_p$) is the total corrosion resistance of a polymer-coated metal sample. R_{po} and R_p are the pore resistance of the coating and the polarization resistance at the coating/substrate interface, respectively.

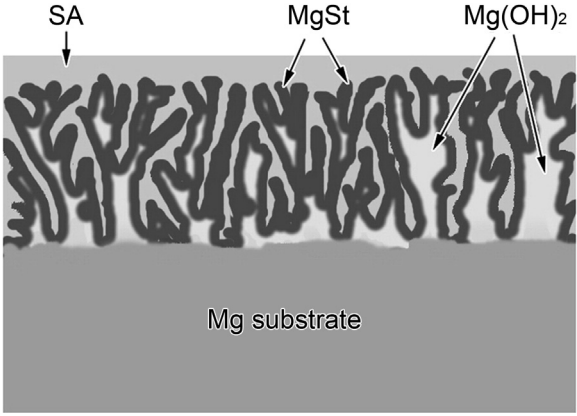


Figure 11.14 Schematic diagram showing the structure of organic coating on Mg. Adapted from Ng et al. (2010).

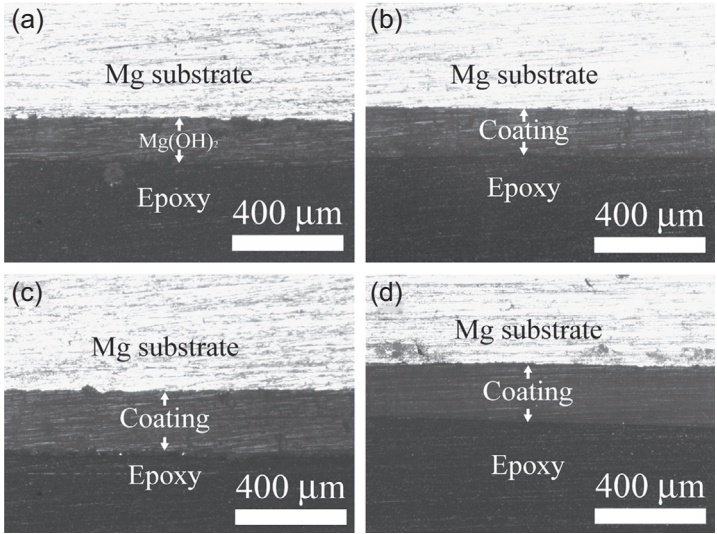


Figure 11.15 Optical micrographs showing the cross-section of different Mg samples (coating thickness shown in parentheses): (a) HT–Mg (170 μm), (b) SA1–Mg (180 μm), (c) SA2–Mg (230 μm), and (d) SA3–Mg (210 μm). Adapted from Ng et al. (2010).

bone healing period. Along with the degradation of the coating, apatite phases formed on the sample surface (Figure 11.18), showing the potential excellent biocompatibility.

To sum up, MgSt worked as a bridge between Mg substrates with SA, and the higher viscosities of SA could produce a thicker and more compact coating. The corrosion resistance had been significantly improved by SA-coated HT-Mg.

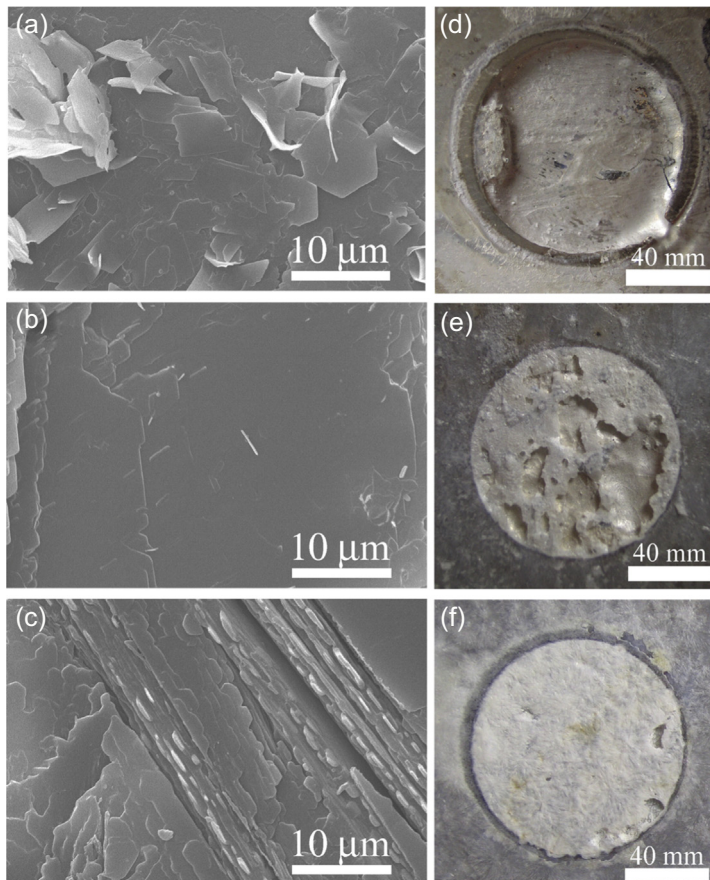


Figure 11.16 SEM micrographs showing the surface of (a) SA1–Mg, (b) SA2–Mg, and (c) SA3–Mg. Optical images showing surface appearance of samples after immersion in Hank’s solution: (d) Bare Mg (6 days), (e) SA1–Mg (6 days), and (f) SA2–Mg (80 days).

The results from the SA coating work are encouraging; however, some problems still exist. Like lard coating on the surface of metals, it is hard for cells to attach on the surface. Also, although MgSt provided a bridge between Mg and SA, a binding force is suspected.

11.5 Gelatin modification

11.5.1 Introduction to gelatin

Gelatin is a proteinaceous material derived from naturally existing collagen by controlled hydrolysis. It is a substance of great commercial importance and always contains large amounts of proline and hydroxyproline as well as glycine. It also exists in other residues, including polar amino acids, which tend to occur in positive and negative clusters at points along the tropocollagen rod surface (Clark & Ross-Murphy, 1987). Due to its numerous

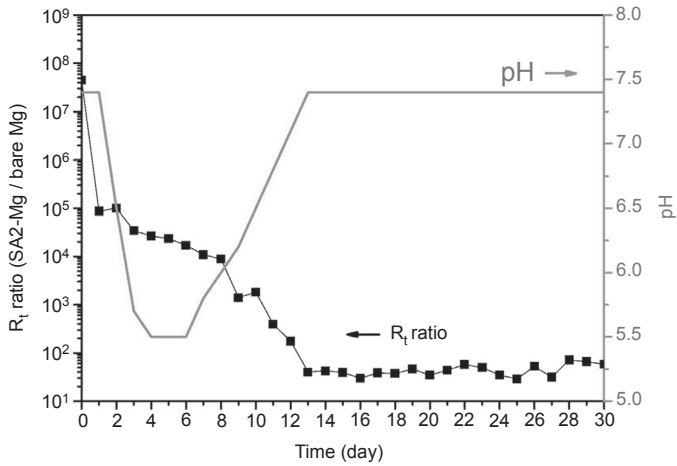


Figure 11.17 Corrosion resistance of SA-coated sample (SA2–Mg) relative to bare Mg in the immersion test.
Adapted from [Ng et al. \(2010\)](#).

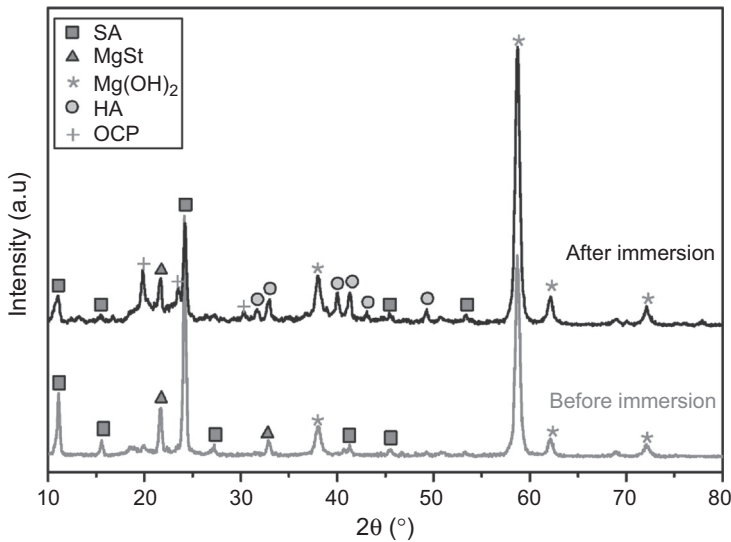


Figure 11.18 XRD patterns of SA2–Mg before and after immersion in Hanks' solution for 80 days.
Adapted from [Ng et al. \(2010\)](#).

advantages, such as its biological origin, biodegradability, and good biocompatibility, together with its commercial availability at a relatively low cost, gelatin has been widely used in biomedical applications. For example, it has long been used as a sealant for vascular prostheses, an artificial skin ([Ponticiello, Schinagl, Kadiyala, & Barry, 2000](#)), a carrier for drug delivery ([Tabata & Ikada, 1998](#)), and in regeneration therapy ([Ponticiello et al., 2000](#)), among others ([Zhang, Ouyang, Lim, Ramakrishna, & Huang, 2005](#)).

11.5.2 Gelatin coating on WE42 alloy

In the study by Xu, Lu, Guo, and Fang, (2010), a cross-linked gelatin with well-distributed PLGA nanoparticles composite coating on an MAO film of WE42, which could control drug release and biocorrosion of magnesium alloy stent materials, was prepared by sealing microcracks and holes on the surface of the MAO coating. An equal volume of gelatin solution (6%) was mixed with different concentrations of glutaraldehyde solution (1%, 2%, 3%) to form different degrees of cross-linked gelatin solution. Three milligrams of paclitaxel-loaded nanoparticles fabricated by a modified oil-in-water single-emulsion solvent evaporation/extraction technique were mixed and sonicated with 400 μl of cross-linked gelatin solution. After being dried at room temperature, the cross-linked gelatin/nanoparticle solution was dropped onto the surface of MAO film, and then the samples were dried at room temperature.

Figure 11.19 shows the surface morphologies of the MAO coating and cross-linked gelatin/nanoparticles composite coating on the MAO coating. Randomly distributed molten oxide flakes with pores and microcracks were observed on the MAO coating surface. After being modified by the cross-linked gelatin/nanosphere composite coating, most of the pores and microcracks of the MAO film could be overlaid, forming a smooth and uniform composite coating. This composite coating has higher stability and better binding capacity due to the physical interlocking between the cross-linked gelatin/nanosphere composite and MAO film.

Electrochemical tests were carried out in Hanks' solution by potentiodynamic polarization curves and EIS. As shown in Figure 11.20, the higher the concentration of glutaraldehyde, the higher the transfer resistance R_p of the samples. The R_p of WE42-MAO-composite coating was much higher than that of WE42-MAO ($R_p > 100 \text{ k}\Omega \text{ cm}^2$), which was already more than 30 times higher than the R_p of the bare WE42 ($3.5 \text{ k}\Omega \text{ cm}^2$). In addition, MAO-composite coated samples showed much lower corrosion current density than the sample with MAO coating and bare WE42 samples. These results indicated that the composite coating on WE42 served as an effective barrier against corrosive electrolyte, effectively improving the corrosion resistance of WE42.

An *in vitro* drug release test showed that a cross-linked gelatin/nanoparticles coating exhibited a nearly linear relationship with no significant burst releases

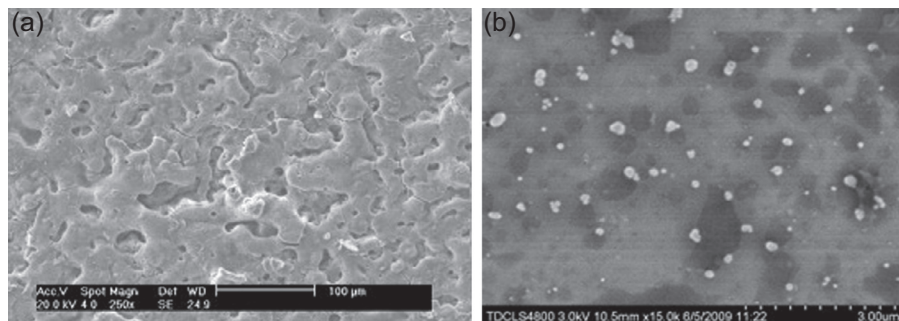


Figure 11.19 The SEM images of (a) surface morphologies of MAO coating and (b) cross-linked gelatin/nanoparticles composite coating on MAO coating.

(Figure 11.21). In addition, the release rate of paclitaxel decreased as the concentration of the glutaraldehyde increased. This suggests that highly cross-linked gelatin could more effectively decrease the diffusion of the paclitaxel and water by swelling of the gelatin and hinder the release of paclitaxel from the PLGA nanoparticles.

A cross-linked gelatin/nanosphere composite coated WE42-MAO has increased the corrosion resistance of WE42-MAO and controlled the drug release

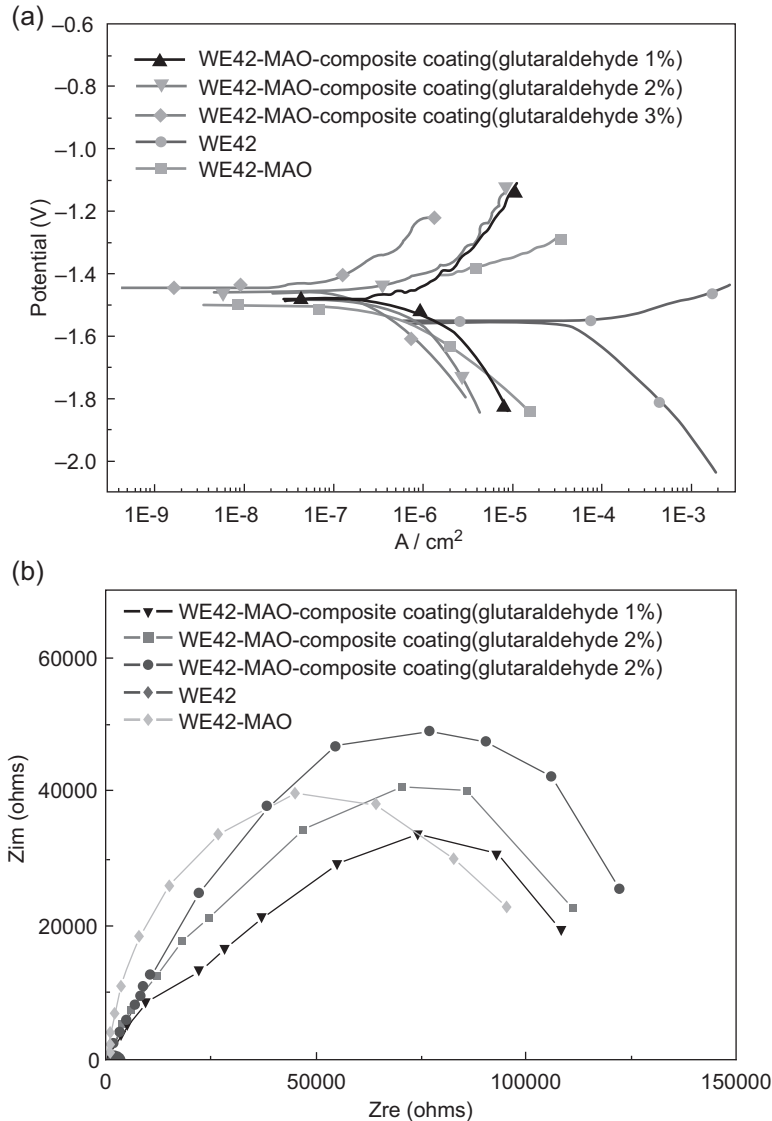


Figure 11.20 The electrochemical characteristics of MAO coating and cross-linked gelatin/nanoparticles coating on the MAO film in pH 7.4 Hanks' solution at 37 °C.

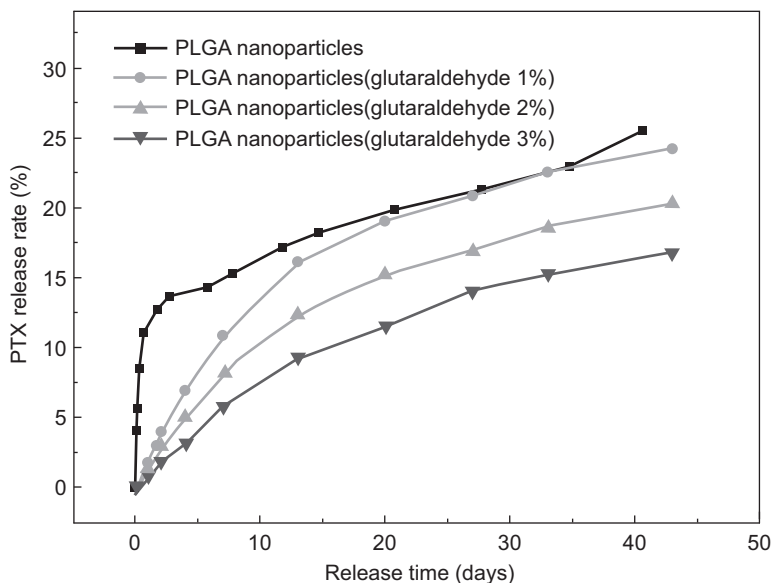


Figure 11.21 The *in vitro* release pattern of paclitaxel from different degrees of cross-linking gelatin/nanoparticles composite coating.

Adapted from [Xu et al. \(2010\)](#).

of paclitaxel-loaded PLGA nanoparticles effectively. The higher the cross-linking rate, the better the corrosion protective ability and drug-release control properties.

11.6 Bovine serum albumin modification

11.6.1 Introduction to stearic bovine serum albumin

Serum albumins are the most abundant proteins in the circulatory system of various organisms. As the major macromolecule related to the osmotic blood pressure, they play an important role in drug disposition and efficacy ([Kamat, 2005](#)). Many drugs and other bioactive small molecules bind reversibly to albumin and other serum components, which can be functionalized as carriers. The solubility of hydrophobic drugs in plasma can be increased by serum albumin, and their delivery to cells is modulated. Therefore, it is of great importance to study the interactions of drugs with this protein. The effectiveness of drugs depends on their binding ability ([Hu, Liu, Wang, Xiao, & Qu, 2004](#)).

11.6.2 Bovine serum albumin coating on magnesium

As reported by [Liu Xin, Tian, and Chu, \(2007b\)](#), the adsorbed bovine serum albumin (BSA) resulted in decreased cathodic current and enhanced corrosion resistance, which was ascribed to the blocking effect of the BSA-adsorbed layer, suggesting that the adsorbed BSA coverage layer can suppress the dissolution of magnesium alloys.

Killian et al. (Killian, Wagener, Schmuki, & Virtanen, 2010) managed to prepare an albumin-coated magnesium for comparatively smooth surfaces via silane coupling chemistry. They used 3-aminopropyltriethoxy silane (APTES) as a silane coupling agent and ascorbic acid (vitamin C) worked as a linker for the grafting of BSA on the surface of the Mg substrate. BSA (400 unit/mL) was attached from aqueous solution by soaking magnesium discs for 24 h at room temperature under stirring. The Mg samples steeped in albumin solution directly were used as controls.

Results of XPS and time-of-flight secondary ion mass spectrometry (ToF-SIMS) both showed an increased relative intensity of magnesium signals ($\text{Mg } 2p$; $m/z = 24$ u, Mg^+) as well as a decrease in amino acid signals ($\text{N } 1s$; $m/z = 110$ u, $\text{C}_5\text{H}_8\text{N}_3^+$, histidine) on the steeped sample compared with those of the pretreated magnesium surface (Figure 11.22(a) and (b)). This indicated a more homogeneous, dense coverage of the silane-coupled protein coating.

In Figure 11.23, the surface of the pretreated sample was smoother and contained fewer defects than the steeped one. Pretreatment in organic solutions had a suppressive effect on the formation of H_2 gas as a result of decreased availability of reactive sites. This has led to a more uniformly coated surface that is less prone to corrosion. After being soaked in SBF for 2.5 days, the surface of the steeped sample was not only rougher after immersion in SBF but also exhibited larger holes because of localized corrosion. Meanwhile, the hydrogen evolution decreased significantly from $0.12 \text{ mL/cm}^2/\text{d}$ for the polished sample to $0.075 \text{ mL/cm}^2/\text{d}$ after treatment with APTES (Figure 11.24), which also indicated that the albumin coatings attached via silane linkers on magnesium had higher corrosion resistance.

This procedure provides a simple and efficient way to attach proteins on the surface of magnesium alloys. Because the attachment was based on silane coupling chemistry on an OH-terminated surface, the approach should be applicable to a variety of proteins as well as to biocompatible magnesium alloys.

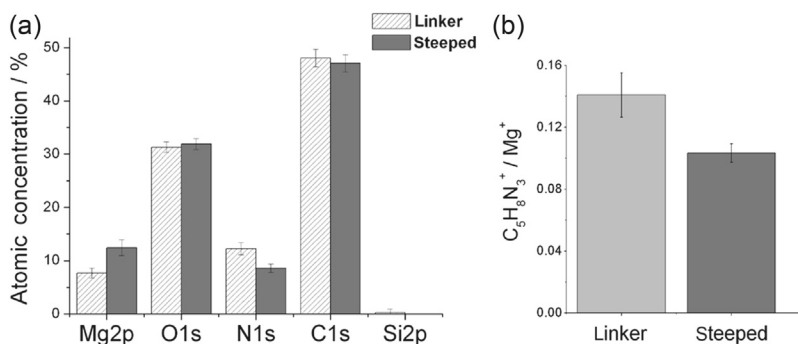


Figure 11.22 Comparison of albumin attached to pretreated Mg and Mg steeped in albumin solution. (a) XPS atomic percentages. (b) Time-of-flight secondary ion mass spectrometry (ToF-SIMS) ratio of histidine $\text{C}_5\text{H}_8\text{N}_3^+$ to magnesium Mg^+ .

Adapted from Killian et al. (2010).

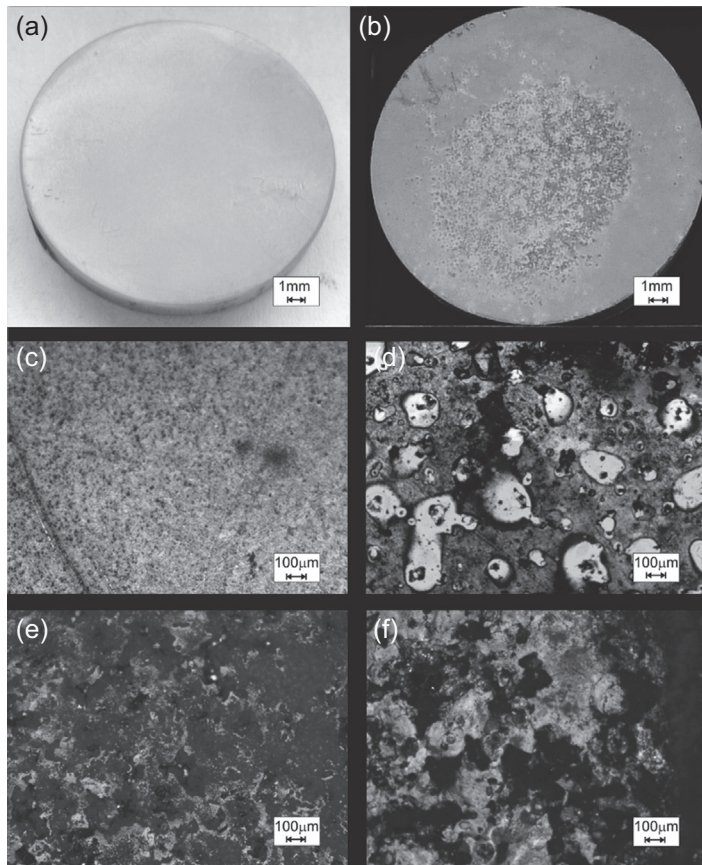


Figure 11.23 Optical images of (a) albumin attached via silane coupling on Mg and (b) Mg steeped in albumin solution. Light microscopy images of (c) albumin attached via silane coupling on Mg and (d) Mg steeped in albumin solution. Light microscopy images after 2.5 days of immersion in SBF for (e) albumin attached via silane coupling on Mg and (f) Mg steeped in albumin solution.

Adapted from Killian et al. (2010).

11.7 Future perspectives

After surface modification by some natural biopolymer or macromolecules, the corrosion property or biocompatibility of magnesium or its alloys have been greatly improved in these studies. However, literature reports about natural biopolymer modification magnesium alloys are limited. Because natural biopolymers are abundant, biocompatible, and bioactive, more potential applications of other kinds of natural biopolymers, such as alginate agar, hyaluronic acid, and cellulose, should be developed as coatings on magnesium alloys. Table 11.6 lists the commonly used natural biopolymers. These

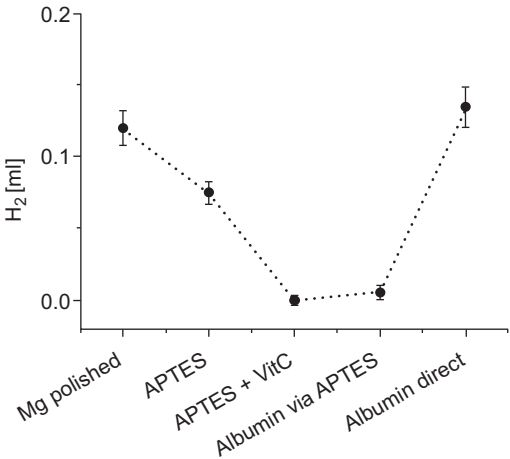


Figure 11.24 Hydrogen evolution measurements of all of the reaction stages after 24 h of immersion in SBF.
Adapted from Killian et al. (2010).

Table 11.6 Natural biopolymers used as biomaterials

Natural biopolymers	
Modified polysaccharides	Alginate agar/agarose
Cellulose	Hyaluronic acid
Starch	Chondroitin sulfate
Dextran	Fibroin
Chitin	Gelatin
Modified proteins	Chitosan
Collagen	Casein

biopolymers are widely used in biomedical fields, such as delivery systems, cell carriers, and scaffolds for tissue engineering.

As for the manufacturing procedures, most of the coating preparations use a two-step method to create a bond between layers. Firstly, MAO or hydrothermal treatment is used to form an interlayer to get stronger binding force. Secondly, natural biopolymer modification is performed by dipping or other methods. However, adhesion tests for polymer or composite coatings have rarely been performed.

In addition, natural biopolymer-based coatings have shown the capability to act as local drug delivery platforms. However, only a few studies have focused on this topic, indicating that the development of these coatings is in its infancy.

References

- Beare-Rogers, J., Dieffenbacher, A., & Holm, J. (2001). Lexicon of lipid nutrition (IUPAC technical report). *Pure and Applied Chemistry*, 73, 685–744.
- Chen, Y., Song, Y., Zhang, S., Li, J., Zhao, C., & Zhang, X. (2011). Interaction between a high purity magnesium surface and PCL and PLA coatings during dynamic degradation. *Biomedical Materials*, 6, 025005.
- Cheryan, M., & Rackis, J. J. (1980). Phytic acid interactions in food systems. *Critical Reviews in Food Science & Nutrition*, 13, 297–335.
- Clark, A. H., & Ross-Murphy, S. B. (1987). *Structural and mechanical properties of biopolymer gels*. *Biopolymers* (pp. 57–192). Berlin, Heidelberg: Springer.
- Crea, P., De Robertis, A., De Stefano, C., & Sammartano, S. (2006). Speciation of phytate ion in aqueous solution. Sequestration of magnesium and calcium by phytate at different temperatures and ionic strengths, in NaCl_{aq}. *Biophysical Chemistry*, 124, 18–26.
- Graf, E., Empson, K. L., & Eaton, J. W. (1987). Phytic acid. A natural antioxidant. *Journal of Biological Chemistry*, 262, 11647–11650.
- Gu, X., Li, N., Zhou, W., Zheng, Y., Zhao, X., Cai, Q., et al. (2011). Corrosion resistance and surface biocompatibility of a microarc oxidation coating on a Mg–Ca alloy. *Acta Biomaterialia*, 7, 1880–1889.
- Gu, X., Zheng, W., Cheng, Y., & Zheng, Y. (2009a). A study on alkaline heat treated Mg–Ca alloy for the control of the biocorrosion rate. *Acta Biomaterialia*, 5, 2790–2799.
- Gu, X., Zheng, Y., Lan, Q., Cheng, Y., Zhang, Z., Xi, T., et al. (2009b). Surface modification of an Mg–1Ca alloy to slow down its biocorrosion by chitosan. *Biomedical Materials*, 4, 044109.
- Hahn, B.-D., Park, D.-S., Choi, J.-J., Ryu, J., Yoon, W.-H., Choi, J.-H., et al. (2011). Aerosol deposition of hydroxyapatite–chitosan composite coatings on biodegradable magnesium alloy. *Surface and Coatings Technology*, 205, 3112–3118.
- Hornberger, H., Virtanen, S., & Boccaccini, A. R. (2012). Biomedical coatings on magnesium alloys – a review. *Acta Biomaterial*, 8, 2442–2455.
- Hu, Y.-J., Liu, Y., Wang, J.-B., Xiao, X.-H., & Qu, S.-S. (2004). Study of the interaction between monoammonium glycyrrhizinate and bovine serum albumin. *Journal of Pharmaceutical and Biomedical Analysis*, 36, 915–919.
- ISO, E., 10993–4. (2006). Biological evaluation of medical devices - Selection of tests for interactions with blood.
- Kamat, B. P. (2005). Study of the interaction between fluoroquinolones and bovine serum albumin. *Journal of pharmaceutical and biomedical analysis*, 39, 1046–1050.
- Kelly, F., Sinclair, A., Mann, N., Turner, A., Abedin, L., & Li, D. (2001). A stearic acid-rich diet improves thrombogenic and atherogenic risk factor profiles in healthy males. *European Journal of Clinical Nutrition*, 55, 88.
- Khor, E., & Lim, L. Y. (2003). Implantable applications of chitin and chitosan. *Biomaterials*, 24, 2339–2349.
- Killian, M. S., Wagener, V., Schmuki, P., & Virtanen, S. (2010). Functionalization of metallic magnesium with protein layers via linker molecules. *Langmuir*, 26, 12044–12048.
- Li, J., Cao, P., Zhang, X., Zhang, S., & He, Y. (2010). In vitro degradation and cell attachment of a PLGA coated biodegradable Mg–6Zn based alloy. *Journal of Materials Science*, 45, 6038–6045.
- Liu, C., Xin, Y., Tian, X., & Chu, P. K. (2007a). Corrosion behavior of AZ91 magnesium alloy treated by plasma immersion ion implantation and deposition in artificial physiological fluids. *Thin Solid Films*, 516, 422–427.

- Liu, C., Xin, Y., Tian, X., & Chu, P. K. (2007b). Degradation susceptibility of surgical magnesium alloy in artificial biological fluid containing albumin. *Journal of Materials Research*, 22, 1806–1814.
- Majeti, N. V. R. K. (2000). A review of chitin and chitosan applications. *Reactive & Functional Polymers*, 46, 1–27.
- Ng, W. F., Wong, M. H., & Cheng, F. T. (2010). Stearic acid coating on magnesium for enhancing corrosion resistance in Hanks' solution. *Surface and Coatings Technology*, 204, 1823–1830.
- Petit, R. (1999). The use of hydroxyapatite in orthopaedic surgery: a ten-year review. *European Journal of Orthopaedic Surgery & Traumatology*, 9, 71–74.
- Ponticciello, M. S., Schinagl, R. M., Kadiyala, S., & Barry, F. P. (2000). Gelatin-based resorbable sponge as a carrier matrix for human mesenchymal stem cells in cartilage regeneration therapy. *Journal of Biomedical Materials Research*, 52, 246–255.
- Ravi Kumar, M. N. (2000). A review of chitin and chitosan applications. *Reactive and Functional Polymers*, 46, 1–27.
- Rinaudo, M. (2006). Chitin and chitosan: properties and applications. *Progress in Polymer Science*, 31, 603–632.
- Staiger, M. P., Pietak, A. M., Huadmai, J., & Dias, G. (2006). Magnesium and its alloys as orthopedic biomaterials: a review. *Biomaterials*, 27, 1728–1734.
- Tabata, Y., & Ikada, Y. (1998). Protein release from gelatin matrices. *Advanced Drug Delivery Reviews*, 31, 287–301.
- Tan, H., & Marra, K. G. (2010). Injectable, biodegradable hydrogels for tissue engineering applications. *Materials*, 3, 1746–1767.
- Tomozawa, M., & Hiromoto, S. (2011). Microstructure of hydroxyapatite-and octacalcium phosphate-coatings formed on magnesium by a hydrothermal treatment at various pH values. *Acta Materialia*, 59, 355–363.
- Wan, Y., Xiong, G., Luo, H., He, F., Huang, Y., & Wang, Y. (2008). Influence of zinc ion implantation on surface nanomechanical performance and corrosion resistance of biomedical magnesium-calcium alloys. *Applied Surface Science*, 254, 5514–5516.
- Wang, X., Zeng, X., Wu, G., Yao, S., & Lai, Y. (2007). Effects of tantalum ion implantation on the corrosion behavior of AZ31 magnesium alloys. *Journal of Alloys and Compounds*, 437, 87–92.
- Wong, H. M., Yeung, K. W., Lam, K. O., Tam, V., Chu, P. K., Luk, K. D., et al. (2010). A biodegradable polymer-based coating to control the performance of magnesium alloy orthopaedic implants. *Biomaterials*, 31, 2084–2096.
- Wu, C., Wen, Z., Dai, C., Lu, Y., & Yang, F. (2010). Fabrication of calcium phosphate/chitosan coatings on AZ91D magnesium alloy with a novel method. *Surface and Coatings Technology*, 204, 3336–3347.
- Wu, G. S., Zeng, X. Q., Yao, S. S., & Han, H. B. (2007). Ion implanted AZ31 magnesium alloy. *Materials Science Forum*, 546–549, 551.
- Xu, X., Lu, P., Guo, M., & Fang, M. (2010). Cross-linked gelatin/nanoparticles composite coating on micro-arc oxidation film for corrosion and drug release. *Applied Surface Science*, 256, 2367–2371.
- Ye, C., Zheng, Y., Wang, S., Xi, T., & Li, Y. (2012). In vitro corrosion and biocompatibility study of phytic acid modified WE43 magnesium alloy. *Applied Surface Science*, 258, 3420–3427.
- Yu, S., Derr, J., Etherton, T. D., & Kris-Etherton, P. (1995). Plasma cholesterol-predictive equations demonstrate that stearic acid is neutral and monounsaturated fatty acids are hypocholesterolemic. *The American Journal of Clinical Nutrition*, 61, 1129–1139.

- Zhang, X., Zhao, Z., Wu, F., Wang, Y., & Wu, J. (2007). Corrosion and wear resistance of AZ91D magnesium alloy with and without microarc oxidation coating in Hank's solution. *Journal of Materials Science*, 42, 8523–8528.
- Zhang, Y., Ouyang, H., Lim, C. T., Ramakrishna, S., & Huang, Z. M. (2005). Electrospinning of gelatin fibers and gelatin/PCL composite fibrous scaffolds. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, 72, 156–165.

Surface modification of magnesium by functional polymer coatings for neural applications

12

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12.1 Introduction

In the last three decades the understanding and treatment of neurological injuries has improved dramatically. While nerves were once thought to have limited regenerative capacity, research has shown that if the postinjury environment can be closely controlled and protected, functional recovery of the central and peripheral nerves is possible. However, there are fundamental limits to nerve regeneration. To overcome these limits, researchers and clinicians intervene through the use of neural prosthetics and neural implants. The interfaces between biological tissues and medical devices require careful engineering but hold the promise to improve the quality of life for patients living with nerve loss or damage.

12.2 Current neural prosthetic devices and their material requirements

Neural prosthetics rely on the interface of biological tissues and conductive materials. The key component of this interface is the electrode. The main function of nerves is to conduct electrical impulses; therefore electrodes must be highly conductive, making metals the natural first choice of material. However, over the last few decades of neural prosthesis research it has become clear that there is much room for improvement in both electrode materials and electrode—neural tissue interfaces (Prutchi & Norris, 2005).

Various electrode configurations have been designed, and each is suited to a particular purpose. Electrodes of a neural prosthesis must be sensitive to electrical impulses as well as able to discriminate between different impulses so that the proper signals can be transduced and interpreted by the rest of the prosthetic machinery. Electrodes can be either invasive or noninvasive (surface) electrodes. Although invasive electrodes require surgical implantation, they also present various advantages over surface

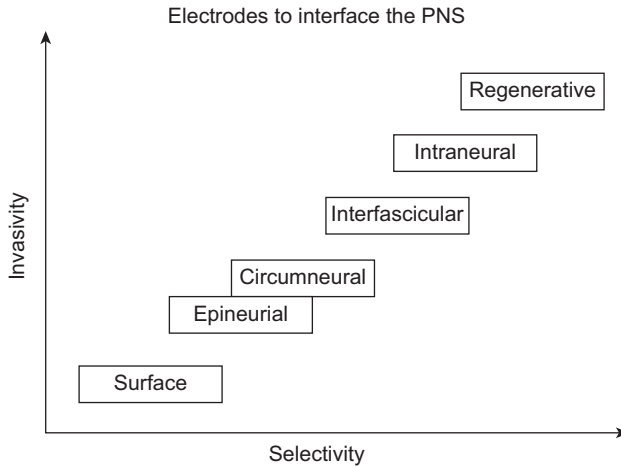


Figure 12.1 Schematic of the fundamental trade-off between invasiveness and selectivity, showing some key electrode types. Reproduced from Navarro et al. (2005).

electrodes such as increased sensitivity to signals and reduced power requirements to provide stimulation, which results in less damage due to electrochemical reactions at the electrode–tissue interface (Navarro et al., 2005). Invasive electrodes can be placed intermuscularly or directly into nerves, although the latter is generally considered more dangerous as there is greater risk of damaging the nerve (see Figure 12.1).

The goal of neural prosthesis is to provide a closed-loop system in which signals from the central nervous system can be detected and cause a desired motor response and in turn external signals from the environment can be encoded and sent to the brain in order to restore lost sensory information. To this end, “bidirectional” electrodes have been developed that can record signals as well as provide them.

Current electrodes come in a variety of configurations (see Figure 12.2) — from microarrays to cuff electrodes to regenerative electrodes — and the ideal material characteristics and requirements for each type vary with their design and application. Generally, invasive electrodes must be very stable so that the efficiency of the prosthetic does not deteriorate over time. The most important material properties for these types of electrodes are stability and biocompatibility. Biostability is the lack of reaction or breakdown of the material. Biocompatibility of a material is assessed using structural properties, such as the ability to match the mechanical properties of the surrounding environments, as well as surface properties. All permanent or semipermanent electrodes are considered to be foreign bodies; therefore, to be biocompatible the material must result in the minimal possible immune reaction, limited to mild response or fibrous encapsulation. Current metals used for electrodes were chosen for their low ohmic resistance (and therefore increased sensitivity) and include gold, platinum, platinum-iridium, tungsten, and tantalum. Cuff and epineural-type electrodes are placed adjacent to or surrounding nerves and allow for the monitoring and stimulation of greater portions of nerve axons. On the other hand, interfascicular or sieve

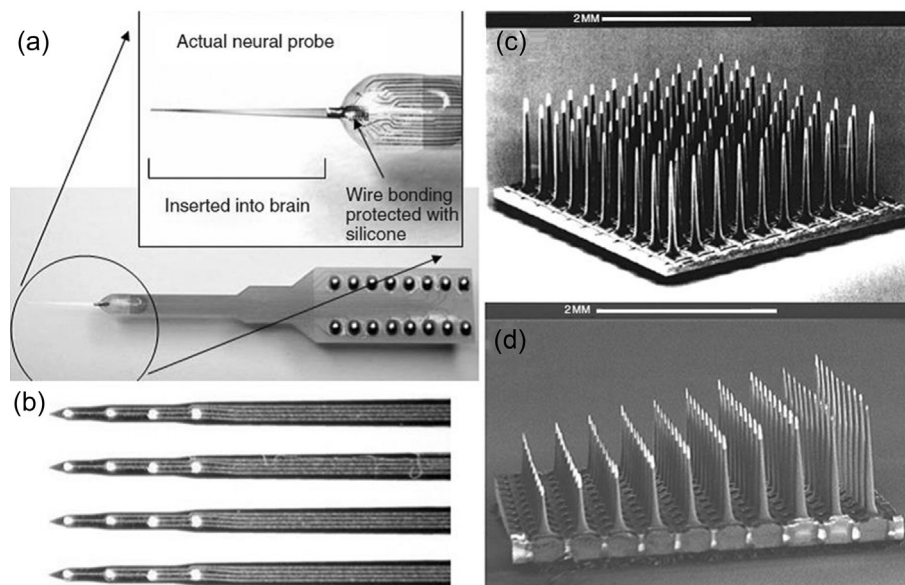


Figure 12.2 Electrode microarrays for neural applications.

Reproduced from [Navarro et al. \(2005\)](#).

electrodes are placed directly into nerves and generally offer more spatially specific control over stimulation and recruit smaller areas of the nerve.

One of the main issues with invasive electrodes is how to minimize tissue damage and irritation at the electrode–tissue interface. High charge density (C/m^2) at the interface causes irritation and attracts macrophages and fibroblasts to the site, resulting in chronic immune response, foreign-body reaction, and eventual biofouling ([Navarro et al., 2005](#)). The biological build-up on the electrode increases impedance at the interface, reducing signal sensitivity. One possible solution that many groups are looking at is the coating of electrodes in polymeric materials. Polymeric surfaces generally demonstrate higher cytocompatibility as well as superior biocompatibility when compared to metallic surfaces. In addition, polymers tend to integrate more readily with the host tissue and tend not to develop foreign body reactions and associated fibrous capsule formation, which may result in more sensitive reading over time. Finally, polymers have the potential to protect metal electrodes from corroding, extending their useful lifetime.

One specialized type of electrode, the regenerative electrode, is designed to provide electrical stimulation to the ends of a severed nerve while serving as a guide for these ends to rejoin as they regenerate. Regenerative electrodes are designed as “sieve” electrodes, with hundreds of “via holes” on the order of tens of microns in diameter. These electrodes are designed to be placed between the proximal and distal ends of severed peripheral nerves (see [Figure 12.3](#)). The electrodes provide therapeutic stimulation and the via holes allow the nerve to reconnect through the electrode. Current materials for regenerative sieve electrodes include silicon or polyimide sieve faces with embedded metallic or semiconducting microelectrode connections. The intimate contact between

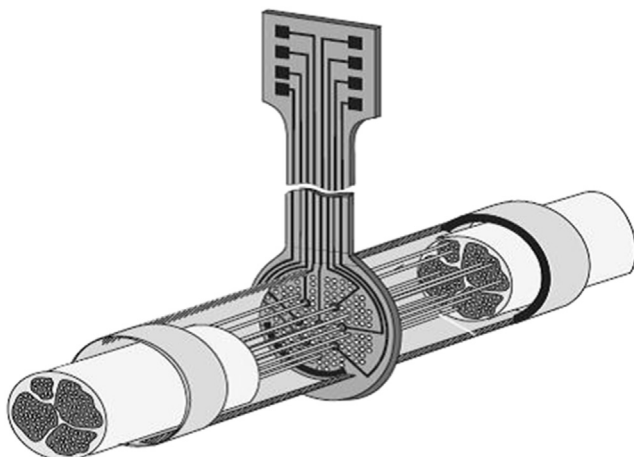


Figure 12.3 Schematic drawing of regenerative electrode.
From Navarro et al. (2005).

electrode and damaged nerve has been shown to enhance nerve regeneration in terms of number of regenerated neurons. However, there is evidence that permanent electrode implantation limits the amount of regeneration that can be achieved. Lago et al. found that when using a silicon electrode, the number of regenerated neurons peaked at 6 months and was reduced at later time points (9 and 12 months postimplantation). The group hypothesized that nerve fibers that were originally regenerated were lost or damaged after 6 months of implantation due to nerve compression from the stiff silicon sieve and proposed the use of thinner, more flexible polyimide that may provide improved outcomes (Lago, Ceballos, Rodriguez, Stieglitz, & Navarro, 2005).

A group from John's Hopkins University has been working on a regenerative electrode that is made from a tyrosine derived from a polycarbonate polymeric material that will be bioresorbable (Lewitus et al., 2011). In their conception, the wires are made from a bio-inert metallic material (iridium), and when the electrode dissolves, the wires are left embedded in the nerve. However, for other applications where long-term electrical interfacing is not necessary, incorporation of a bioresorbable metal such as magnesium would allow for the development of a fully biodegradable electrode.

12.3 Current state and desired material properties for nerve regenerative devices

In addition to electrodes, another common device for neural regeneration is the nerve guidance conduit (NGC). A NGC is an implant that serves as a channel connecting the proximal and distal ends of a severed nerve, providing a channel through which the nerve can regrow and reconnect properly. These implants differ from the regenerative electrode discussed in the previous section; they do not provide external electrical stimulation, nor can they record electrical impulses coming from nerves. Clinical

indications for the use of NGCs are when the gap between the distal and proximal ends of a transected nerve (classified clinically as a total lesion) is too great for the ends to be sutured together without significant tension. Guidance conduits are an attractive alternative to nerve grafting procedures—which are the current clinical gold standard—because they overcome limitations of traditional grafting procedures (Belkas, Shoichet, & Midha, 2004; Kehoe, Zhang, & Boyd, 2012; Nectow, Marra, & Kaplan, 2012). These limitations and disadvantages include

- lack of supply of allografts (grafts taken from other organisms of the same species);
- donor site morbidity, loss of function, or development of painful neuromas when using autografts (grafts taken from the patient); and
- size mismatch between the graft and the nerve to be repaired.

The design of nerve conduits as tubular implants is based on several aspects of the nerve regeneration process (see Figure 12.4). During the first stage of nerve regeneration, termed the fluid phase, nerve stumps secrete a protein-rich exudate that contains growth-promoting factors. Entubulation prevents this axoplasmonic fluid from diffusing away. During the next (matric) phase of regeneration, a new fibrin matrix is formed, and contact guidance with the inner diameter of the NGC ensures that the matrix is confined to the area between nerve stumps. This is important as it ensures that during the subsequent cell phase, migrating Schwann cells will be able to bridge the gap between nerve stumps. There is some evidence that when Schwann cells exist in high density, they are more resistant to apoptotic signals. Taken as a whole, the cylindrical NCG promises to provide regeneration that is faster and more complete, when made of an optimized biomaterial.

The ideal nerve guidance conduit would provide topographical, chemical, and electrical stimulation (Subramanian, Krishnan, & Sethuraman, 2009). The ideal material for a nerve guidance conduit would be biocompatible, immunologically inert, infection resistant, porous, electrically conducting, neuroconductive, neuroinductive, mechanically strong but flexible, strong enough to be easily suturable, and biodegradable (Subramanian et al., 2009). We have yet to find a material that possesses all of these qualities; therefore, it is likely that the ideal nerve conduit will be created from a composite of several materials with tunable properties.

Although the ideal material has yet to be designed, many acceptable nerve guidance devices can be found in the literature, and five such devices are approved for clinical use by the U.S. Food and Drug Administration (FDA). However, current NGCs are limited to bridging nerve defects that are 3 cm or less in length (Deal, Griffin, & Hogan, 2012; Kehoe et al., 2012), which is considered a critical-sized defect in humans (Mackinnon & Dellon, 1990). Materials for current devices are generally synthetic or natural biodegradable polymers.

12.4 Magnesium for neural applications

Magnesium has been researched as a material for biomedical implants for orthopedic and cardiovascular stent applications because it possesses a variety of characteristics that are desirable for implant applications. These include being lightweight and having

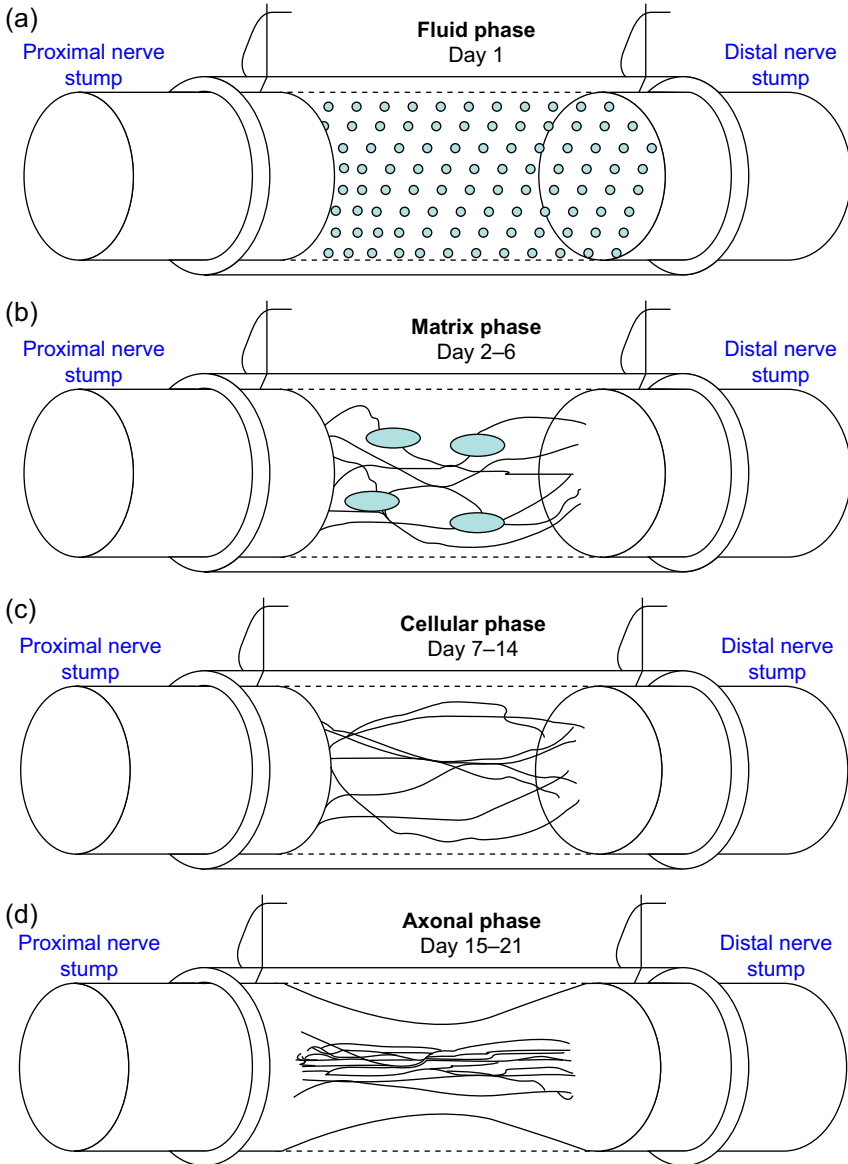


Figure 12.4 Schematic of nerve regeneration through a nerve guidance conduit. Reproduced from Kehoe et al. (2012).

mechanical properties that are more similar to bone than traditional metals (such as titanium) while being superior to other metals because it is biodegradable and well tolerated in the body (Pan et al., 2011; Volpe, 2013). In addition, magnesium is of particular interest in neural applications because of its interactions with neuron function. Magnesium has been used in clinical practice as a neuroprotective agent for many

decades. Magnesium ions are known to shut down the N-methyl-D-aspartate ion-gated channels of cells (Feria, Abad, Sanchez, & Abreu, 1993), making them more difficult to depolarize and therefore protecting cells against damage due to overstimulation. For this reason magnesium sulfate infusion is used clinically to treat eclampsia (Guerrera, Volpe, & Mao, 2009). There have also been several preclinical and clinical trials to investigate the effectiveness of magnesium sulfate treatment in improving outcomes following neuroexcitatory events such as acute cerebral ischemia (stroke), spinal lesion, and eclampsia. While preclinical data were promising, the results of clinical trials have been contradictory and the efficacy of treatment with magnesium salts for these applications in humans is not yet proven (Perlman, 2006).

Magnesium as a component of a composite material for neural applications is very appealing. Because it is a metal, magnesium can provide strength to a scaffold, while its biodegradation means that no additional surgeries will be necessary to remove the implant after it has served its purposes. In addition, magnesium is biocompatible and found naturally in the body and is even a necessary nutrient. Finally, there is mounting evidence that magnesium ion is beneficial to overstimulatory neural conditions. However, the degradation of bare magnesium in physiological environments occurs so rapidly that it limits its use even as a biodegradable material (Hornberger, Virtanen, & Boccaccini, 2012). In addition, natural magnesium degradation is a nonuniform and poorly predictable process that leaves behind highly alkaline degradation byproducts and hydrogen gas (Witte et al., 2008). Therefore, in order to use Mg for biomedical applications, including neural applications, its degradation rate must be controlled and the harmful degradation products eliminated, neutralized, or otherwise removed from the system.

Sebaa et al. introduced the idea of using magnesium and conductive polymers to create biodegradable electrodes and nerve guidance conduits for neural applications (Sebaa, Dhillon, & Liu, 2013).

12.5 Functional improvements to magnesium

In order to utilize magnesium as a viable biomaterial for neural applications, various improvements are necessary or desirable.

The most important improvement is to control the degradation rate through application of a corrosion resistant layer. The fundamental limitation faced by researchers proposing to utilize magnesium as a medical implant material is the metal's vigorous and unpredictable corrosion behavior (Hornberger et al. 2012). Pure magnesium corrodes within a few days, too rapidly to be of use even in biodegradable implant applications. Possible solutions to this problem include protective coatings to reduce and control corrosion and the use of magnesium alloys rather than pure magnesium. In addition, the degradation behavior is nonuniform, with a strong tendency toward localized corrosion and internal galvanic corrosion caused by interactions with impurities, secondary phases, or alloying elements (Song, Atrons, & Wu, 1998). Hydrogen gas formed in the corrosion reaction presents additional challenges. If gas formation is too rapid to be absorbed, it can damage tissues, the implant, or its remaining coating

material. However, choice of coating material and methodology has been reported to have less effect on the accumulation of gas in comparison to phases and microstructure of magnesium and the geometry of the implant. Finally, local increase in pH of the region surrounding the implant is a concern for medical applications.

Coatings to prevent corrosion of magnesium are best when they do not let Cl ions through, so the best coating materials are hydrophobic polymers (Conceicao, Scharnagl, Blawert, Dietzel, & Kainer, 2010; Zomorodian et al., 2013). Polylactic acid (PLGA) (Makadia & Siegel, 2011) and polyetherimide (PEI) (Conceicao et al., 2010) both fit these criteria.

For use as an electrode, it is necessary to optimize properties that affect the material–tissue interface including surface resistance, charge density, and wettability. Enhanced biocompatibility and biointegration can be achieved through the application of chemical cues and the creation of physiologically relevant topographical features on the magnesium surface. Finally, controlled release of drugs or neurotropic factors is an important functional improvement that could be made to magnesium.

12.6 Polymer coating

Polymers are an ideal coating material for invasive electrodes because polymeric coatings present a more biomimetic surface to the body. However, for a polymer coating to be suitable as a part of a degradable electrode system, it must not get in the way of either the signal transduction or degrading functions of the system, while still providing protection to the magnesium surface. These requirements narrow the possible classes of polymers to be used in this application significantly.

12.6.1 Conductive polymers

While polymeric materials generally behave as insulators, a few special classes of electrically conductive polymers have been pursued with increasing enthusiasm over the last three decades. These materials are especially well suited for next-generation biomaterials and “smart” material systems because they can transduce electronic signals.

Electrically active polymers (ECPs) consist of conjugated organic molecules and are able to conduct current through their system of conjugated π bonds (Wallace, Teasdale, Spinks, & Kane-Maguire, 2008). The most extensively researched of these polymers is polypyrrole (PPy), followed closely by polyaniline (PANi). Both of these polymers have been reported to be cytocompatible *in vitro*, as well as biocompatible *in vitro*. Durgam et al. (2010) created nerve guidance conduits of Ppy and implanted them in the severed sciatic nerves of mice. After 8 weeks of implantation there was no observable immune response at the implant site as determined by histological analysis (Durgam et al., 2010). The most promising ECPs for neural applications have been polythiophenes (PT), especially the PT derivative poly(3,4-ethylenedioxythiophene) (PEDOT). PEDOT is favored for the development of clinical devices because its oxidation states are more stable than those of other conductive polymers, and it does not lose conductivity after extended use. PEDOT has been successfully used as a coating on electrodes to improve long-term

performance and sensitivity to electrical signals as well as reduce damage to tissue at the electrode–nerve interface (Frost, Wei, Baghmanli, Cederna, & Urbanchek, 2012).

12.6.2 Biodegradable polymers

Biodegradable or bioresorbable polymers have also been extensively researched for biomaterials applications (Makadia & Siegel, 2011). Many of these materials are ideal for use in implants and invasive electrodes because they are well-characterized and have already been approved for use by the FDA. Many biodegradable polymers have already been used for neural applications such as peripheral nerve guidance conduits. Biodegradable polymers can be either natural or synthetic in origin. Natural biodegradable polymers include chitosan, collagen, chitin, alginate, and gelatin. The most popular biodegradable polymers for neural applications are polyglycolic acid (PLGA), PLA, and poly- ϵ -caprolactone (PCL).

12.6.3 Combination

One of the major drawbacks of traditional conductive polymers is that they are not biodegradable. However, there has been extensive research into engineering ECPs that can be naturally cleared from the body over time. One strategy is to create co-polymers with short lengths of ECPs connected by hydrolysable bonds to biodegradable polymers, such as polylactide (Huang et al., 2008). These co-polymers are bio-erodible because although the sections of ECP remain intact, the molecular weight of nondegradable sections is engineered to be low enough so that the lymphatic or circulatory systems can clear these sections of ECP away.

Another approach is the creation of oligothiophenes, a fully biodegradable PT derivative developed by Guimard, Sessler, and Schmidt (2009).

12.7 Coating methods

The main objective of these coating methods is to create a uniform polymeric coating with controllable pore size and strong adhesion to the underlying magnesium substrate. The general goal when coating magnesium for biomedical purposes is to protect the metal from corrosion and control its degradation rate. Magnesium is very reactive in aqueous environments. One way to slow the corrosion of magnesium is through the formation of a passivation layer. In fact, passivation at the surface of magnesium occurs naturally, forming MgO , $\text{Mg}(\text{OH})_2$, and carbonate layers on the surface. However, this passivation layer is unstable and quickly breaks down when exposed to physiological levels of Cl^- ions (Witte et al., 2008). Alternative protection methods through surface alteration include

- chemical conversion coatings;
- anodization; and
- plasma electrolytic anodization (PEO), also called micro arc oxidation (MAO) or anodic spark deposition (ASD).

These are all well studied and commonly used in industrial applications, and an excellent review on these methods was written by [Gray and Luan \(2002\)](#). While such methods may protect magnesium, the use of bare magnesium is not ideal for biomedical application in general, or neural application specifically. Instead, this chapter will concentrate on methods to apply polymeric coatings.

12.7.1 Pretreatment of magnesium surface

It should be noted that pretreatment through use of the surface-altering methods listed above has been found to improve the adhesion strength of subsequent polymeric coating ([Hornberger et al., 2012](#); [Ostrowski et al., 2013](#)). Some refer to the use of such pretreatment as a “two-step” coating method and application of coating to bare, unaltered Mg surfaces is a “one-step” method. No studies are currently published in which neural cells have been grown on Mg substrates coated through a two-step process, but it seems reasonable to assume that this method might increase surface roughness of this applied polymer coating. It has been reported that nano-rough gold surfaces cause high rates of cell death by necrosis in neurons ([Brunetti et al., 2010](#)). Therefore, the question remains whether the increase in adhesion strength achieved through pretreatments is an optimal strategy for creating neural biomaterials.

12.7.2 Dip-coating

Dip-coating is one of the most facile coating methods. It involves dissolving monomers in a solvent and then dipping the magnesium substrate. Coating thickness can be controlled by the viscosity of the monomer solution; the number of dipping cycles; and most importantly, the dipping rate. This type of coating can be used to apply thermoplastic polymers as well as polymers that need to be dissolved in organic solvents. Although this method is simple, it offers less exact control over coating thickness and uniformity. This method is well suited for thicker coatings, tens of microns to the sub-millimeter range. However, film thickness per dipping cycle varies widely with the viscosity of the dipping solution and rate of dipping. [Zomorodian et al. \(2013\)](#) reported films of less than 5 μm thickness (see [Figure 12.5](#)) when coating magnesium with PEI dispersed with nano-sized hydroxyapatite (HA). In addition, they showed that agglomeration of their nanoparticles resulted in defects in the uniformity of the coating, which can be seen in [Figure 12.5](#), panel C. Others have also reported difficulties in creating uniform, nonporous coatings through the dipping process ([Xu & Yamamoto, 2012](#)). In the field of neural biomaterials, this may not necessarily be a drawback, as a certain degree of porosity is desirable for many neural applications. However, being able to exert strict control over the features of polymer coatings on magnesium is important since the degradation of magnesium is highly unpredictable. Even with the reported defects, magnesium samples with the coating in the study were stable in DMEM solution for 3 months.

Application of polymer coatings onto magnesium substrates through a dipping process is the most reported method, most likely because it requires no special equipment. This method also has value as an experimental tool because thickness parameters can

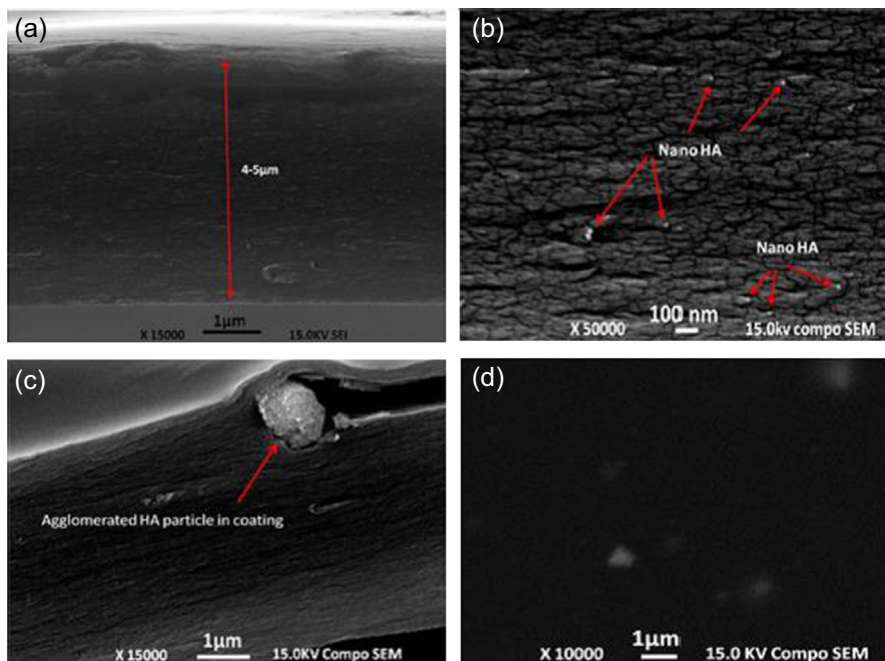


Figure 12.5 a) SEM image showing 4–5 μm coating achieved through dipping. (b) High-magnification image showing un-agglomerated nano HA. (c) Agglomerated HA and associated defect in surrounding polymer film. (d) Agglomerated HA particles as seen from the surface of the coated Mg substrate.

Reproduced from [Zomorodian et al. \(2013\)](#).

be easily changed by addition of dipping cycles or altering the speed of dipping. Such simple optimization methods could be especially valuable when designing neural guidance conduits, where wall thickness is a key parameter ([Kokai, Lin, Oyster, & Marra, 2009](#)).

12.7.3 Spin-coating

Spin-coating is an ideal method for applying a uniform thin coating onto a flat substrate. The substrate is secured to a spinning stage, and then the coating material is applied to the center of the substrate and allowed to spread evenly over the surface through centripetal acceleration forces.

Spin-coating is a good method for spreading uniform thin films of polymers that are extremely sticky or hydrophobic and suitable for coating flat, axi-symmetrical substrates. It is also a good research tool for screening potential coating materials because this method is compatible with a wide variety of coating materials including solvent-dissolved solutions, thermoplastics, and coatings that require additional processing such as curing or sintering. However, it is less effective for coating cylindrical or oddly shaped objects and may present edge effects if it is used to coat non-axi-symmetric shapes ([Boellaard, Pham, Sarro, & Burghartz, 2002](#), pp. 81–86). In addition, if the substrate to be coated has

any depressions of features, this method is not optimal as there is a tendency for polymer to collect in features, which results in nonuniform coating thickness (Boellaard et al., 2002, pp. 81–86). This has the potential to be a strong negative effect when coating conducting objects such as electrodes, where charge density at the surface must be closely controlled.

Altering the spinning speed changes the thickness and surface roughness of the resulting coatings. In addition, when using solvent casting methods, the choice of solvent may be important, as differences in vapor pressure of the solvent will result in different rates of vaporization speed and ultimately alter the morphology and characteristics of the resulting film (Kamanyi, Ngwa, Luo, & Grill, 2008).

12.7.4 Spray-coating

Spray-coating is similar to dip-coating, but requires additional equipment to create a continuous, controlled spray. Spray-coating is appropriate for polymeric material that can exist in a liquid or colloid form, which includes most of the popular synthetic biodegradable polymers. The coatings created by spraying are inherently porous in nature (Gray & Luan, 2002), which may be beneficial in neural applications, where a degree of porosity is ideal, as previously discussed. Jo et al. recently used spray-coating of PCL in combination with aerosol deposition of bioactive nanoparticles (Jo, Li, Kim, Kim, & Koh, 2013). This combination coating method allowed the researchers to create a flexible, uniform coating of biodegradable polymer to temper the corrosion processes of the magnesium substrate. Spray-coating is an excellent option when trying to coat objects that are three dimensional, nonsymmetrical, or with topographical features. Generally, spray-coating will result in a layer of more uniform thickness than can be achieved with spin-coating (Boellaard et al., 2002, pp. 81–86).

There are a variety of sub-technologies that come under the heading of spray-coating. The previous paragraph concentrated on the spraying of colloids, but there is also thermal spray-coating, which allows for the coating of a surface in any material that is meltable (Gray & Luan, 2002). Another variation is electrostatic spray-coating (Liu, Jiang, & Malshe, 2009). In this solvent-free process, powders of solid charged particles or atomized liquids are accelerated toward a surface by the application of an electrical field. For such a process to work, both the particles and the item to be coated must be conductive and able to carry charge. This process is advantageous in that it does not require solvents, which are often not biocompatible and need to be removed carefully, and it is more efficient, reducing the waste of coating material due to overspray, which is common with traditional spray techniques.

Wong et al. (2010) created what they called polymer membranes of PCL on magnesium through layers of spray-coating. As seen in Figure 12.6, pores of different sizes can be created by changing the concentration of PCL used in the spraying apparatus. Small implants covered in these membranes were implanted into the greater trochanter of rabbits for 2 months, and an interesting finding in this study was that no evidence of excessive hydrogen gas was found, which is very different from previous studies. Based on these findings, Wong et al. hypothesizes that implantation in different areas of the body as well as the protection provided by the coating limited the evolution of hydrogen gas to a level that was able to be absorbed easily into the body.

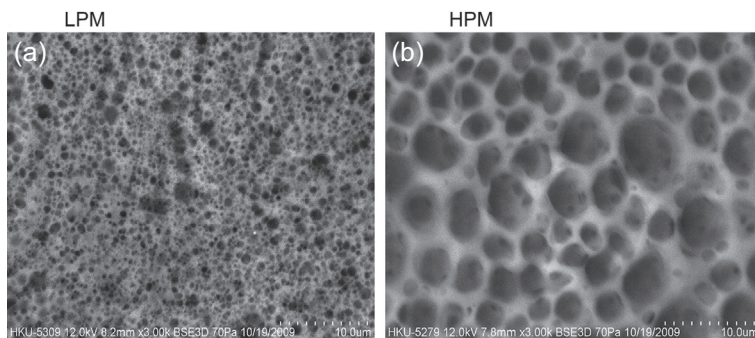


Figure 12.6 Porous membranes of PCL produced through spray-coating onto magnesium. The size and density of resulting pores was easily controlled by changing the density of PCL used in the spraying apparatus. LMP, low-porosity membrane; HPM, high-porosity membrane. PCL, poly- ϵ -caprolactone.

12.7.5 Electrospinning

In electrospinning, a liquid-phase polymer is released from a syringe into an electric field. The field disrupts the surface tension of the polymer, stretching the droplets until they form a thin, continuous stream from the syringe tip. The thin fibers are collected at a certain distance from the syringe tip where they are generated. Fibers produced through electrospinning can range from microns to nanometers in diameter and can be collected on a stationary plate, resulting in random alignment; or the collecting plate can be rotated, which will result in controlled alignment of fibers.

Electrospinning is the most promising coating method for supporting neural cell growth and adhesion (Aurand, Lampr, & Bjugstad, 2012; Subramanian et al., 2009), as it can be used to create highly porous scaffolds, such as the surface shown in Figure 12.7, which allow flow of nutrients and waste products. The interconnected network structure of the pores created from this method makes it more suitable than the isolated pores created through other methods such as salt-leaching. In addition,

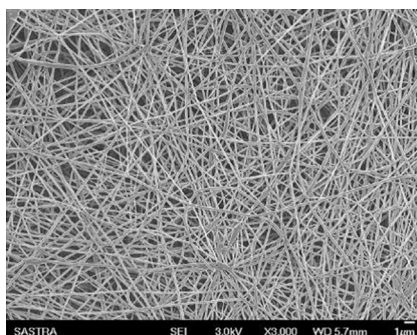


Figure 12.7 Example of an electrospun scaffold for neural tissue engineering, created from PLGA-PANi composite fibers.

Reproduced from Subramanian et al. (2009).

control of alignment of fibers creates micro and nano-patterning, and such anisotropic topographical cues have been shown to influence many factors of regeneration including neurite alignment, neurite outgrowth, formation of synaptic connections, and cell differentiation (Nectow et al., 2012). This method creates porous coatings, which might present a problem when coating magnesium substrates that need to be protected from premature degradation in the physiological environment. Possible solutions to that problem would be to use dual coating methods: one “inner coating” that is not as porous to protect the magnesium from corrosion followed by a second “outer coating” that supports active cellular adhesion, proliferation, and migration.

12.7.6 Electrophoretic deposition

Electrophoretic deposition is a two-step process by which the particles suspended in a colloid solution are collected onto a substrate. Deposition takes place in an electrochemical cell in which one of the electrodes is the substrate to be coated. When the potential is applied, the suspended coating particles are polarized and pulled toward the substrate (electrophoresis) to form a loose coating. The coating at this point is a powder agglomeration and must undergo additional processing such as sintering to secure the bonds between the particles and to the substrate (Vandeperre & Van der Beist, 1999). Polymers that can be used in electrophoretic deposition must be polarizable or possess the ability to sustain induced dipoles in order for the electrophoresis to take place. Advantages of this method include that it tends to produce uniform coatings on three-dimensional substrates, and the entire exposed surface is easily coated, making it simple to coat inner and outer surfaces of cylindrical objects (Boellaard et al., 2002, pp. 81–86).

12.7.7 Electrochemical deposition

Electrochemical deposition is similar to electrophoretic deposition in that it also takes place in an electrochemical cell, but in this case, a chemical bonding process occurs, as opposed to electrophoretic deposition. In electrochemical deposition, a monomer solution is loaded into an electrochemical cell and the magnesium substrate serves as one of the electrodes. When voltage is applied, the monomers undergo a chemical polymerization onto the magnesium. An example of the electrochemical cell used by Sebaa et al. (2013) is shown in Figure 12.8. Advantages of electrochemical deposition include its relatively low cost and improved interfacial bonding between the coating material and the substrate before heat treatment or sintering. However, the uniformity and morphology of the coating depends on the polymerization pattern or the polymer used. For example, PEDOT coating on magnesium substrates (see Figure 12.9) appeared particulate. Luo et al. explored direct electrodeposition of conductive polymer coating onto magnesium substrates using magnesium as a working electrode in the electrochemical cell and an ionic liquid solution (Luo & Cui, 2011). Sebaa et al. compared various electrochemical deposition parameters to produce films of uniform thickness and reduce the cost of the electrochemical deposition (Sebaa et al., 2013). The electrochemically deposited PEDOT on magnesium substrates was thoroughly characterized by Sebaa et al.

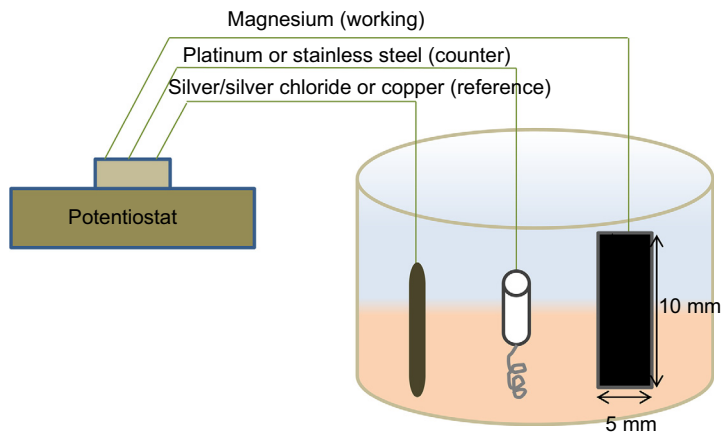


Figure 12.8 Schematic of electrochemical cell for the direct electrodeposition of conductive polymer onto magnesium working electrode.

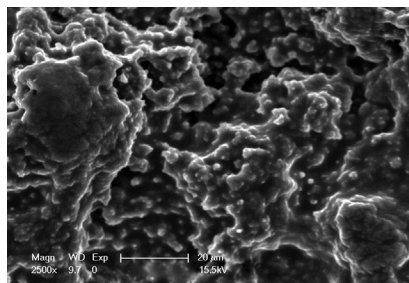


Figure 12.9 Representative image of morphology of PEDOT deposited on magnesium substrate by electrochemical deposition (Sebaa et al., 2013).

12.8 Evaluation of coating

Coating of the magnesium substrates will have an effect on the biological, chemical, and mechanical performance of the material. It is extremely important to evaluate how the coating changes the substrate properties, as well as the stability and strength of the coating itself. Despite this being crucial for proper evaluation of coatings and preclinical or clinical adoption of technologies, there is little consensus around which tests should be used.

12.8.1 Characterization of microstructure

The topography and surface roughness of objects plays an important role in determining cell adhesion properties and more specifically the neuroconductive and

neuroinductive abilities of materials *in vivo*. Many experimental NGCs have incorporated micropatterning in an attempt to provide directional growth cues for regenerating neuritis.

To evaluate structures and features at the submicron and nanometer scales, higher resolving power is needed than can be provided through optical microscopy. Therefore, characterizing micro- and nanostructure of polymeric coatings must be done through more sensitive methods such as electron microscopy, the most widely used of which is scanning electron microscopy (SEM). If the coating polymer is not conductive, it is necessary to prepare the samples with a sputter coat or to use an environmental SEM (ESEM), an excellent method for analyzing biological samples as it can look at “wet” and un-sputter-coated samples. However, the resolution of ESEM is usually not as good as that provided by a standard SEM set-up. Polymeric samples are delicate, and even sputter-coated samples may be damaged if the acceleration voltage used is too high.

12.8.2 Adhesion strength (ASTM tape test, ASTM microscratch test)

While many in the literature agreed that adhesion strength is essential for a good coating material, as [Hornberger et al. \(2012\)](#) and [Xu and Yamamoto \(2012\)](#) have previously pointed out, there is a dearth of concrete data being reported. Some authors give detailed mechanisms of how polymers and magnesium might interact ([Zomorodian et al., 2013](#)), but in most papers no physical testing results are reported. In addition, adhesion properties that are reported are often given for tests performed in dry conditions, which may or may not be relevant for neural and other biomedical applications.

The American Society for Testing and Materials (ASTM) is a valuable resource for information about accepted and proper testing of the mechanical properties of materials. Strong, uniform adhesion is desirable to create magnesium with stable coating and to predict its properties in living systems. Therefore, it is necessary to test the adhesion strength of the coating to the material. A simple test of adhesion strength is the tape test. In this test, a grid pattern is scored into the coating and then tape is applied to the scored grid and removed at a set angle and speed. Strength of adhesion is ranked on a five-point scale depending on the amount of coating that has detached from the underlying magnesium and become stuck to the tape instead. Examples of how to evaluate adhesion strength with the tape tests are shown in [Figure 12.10](#).

The microscratch and closely related nanoscratch tests are techniques from which one can glean a range of information, including coating material hardness, yield strength, and Young's modulus. This test is often done with a specialized piece of equipment, which can apply a constant and controlled force directed at an angle normal to the coating surface. This technique can be used to evaluate organic or inorganic thin film coatings (less than 5 μm in thickness for the microscratch test and less than 800 nm for the nanoscratch test).

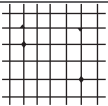
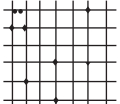
Classification	Surface appearance after tape test
5B	None
4B	
3B	
2B	
1B	
0B	Greater than 65%

Figure 12.10 ASTM 3359 tape test classifications.

Reproduced from [Sebaa et al. \(2013\)](#).

References

- Aurand, E. R., Lampr, K. J., & Bjugstad, K. B. (2012). Defining and designing polymers and hydrogels for neural tissue engineering. *Neuroscience Research*, 72(3), 199–213.
- Belkas, J. S., Shoichet, M. S., & Midha, R. (2004). Peripheral nerve regeneration through guidance tubes. *Neurological Research*, 26, 151–160.
- Boellaard, E., Pham, P. N., Sarro, P. M., & Burghartz, J. N. (2002). Spin, spray coating and electrodeposition of photoresist for MEMS structures - a comparison. In: *SAFE 2002 Proceedings of 5th Semiconductor Advances for Future Electronics Workshop* (pp. 81–86). Utrecht: STW Technology Foundation.
- Brunetti, V., Maiorano, G., Rizzello, L., Sorce, B., Sabella, S., Cingolani, R., et al. (2010). Neurons sense nanoscale roughness with nanometer sensitivity. *Proceedings of the National Academy of Sciences of the United States of America*, 107(14), 6264–6269. <http://dx.doi.org/10.1073/pnas.0914456107>.
- Conceicao, T. F., Scharnagl, N., Blawert, C., Dietzel, W., & Kainer, K. U. (2010). Corrosion protection of magnesium alloy AZ31 sheets by spin coating process with poly(ether imide) [PEI]. *Corrosion Science*, 52(6), 2066–2079. <http://dx.doi.org/10.1016/j.corsci.2010.02.027>.
- Deal, D. N., Griffin, J. W., & Hogan, M. V. (2012). Nerve conduits for nerve repair or reconstruction. *Journal of the American Academy of Orthopaedic Surgeons*, 20(2), 63–68.
- Durgam, H., Sapp, S., Deister, C., Khaing, Z., Chang, E., Luebben, S., et al. (2010). Novel degradable co-polymers of polypyrrole support cell proliferation and enhance neurite out-growth with electrical stimulation. *Journal of Biomaterials Science. Polymer Edition*, 21(10), 1265–1282. <http://dx.doi.org/10.1163/092050609X124817518063303046>.

- Feria, M., Abad, F., Sanchez, A., & Abreu, P. (1993). Magnesium sulphate injected subcutaneously suppresses autotomy in peripherally deafferented rats. *Pain*, 53(3), 287–293.
- Frost, C. M., Wei, B., Baghmanli, Z., Cedema, P. S., & Urbanchek, M. G. (2012). PEDOT electrochemical polymerization improves electrode fidelity and sensitivity. *Plastic and Reconstructive Surgery*, 129(4), 933–942. <http://dx.doi.org/10.1097/PRS.0b013e31824422bf00006534-201204000-00024>.
- Gray, J. E., & Luan, B. (2002). Protective coatings on magnesium and its alloys—a critical review. *Journal of Alloys and Compounds*, 336(1–2), 88–113.
- Guerrera, M. P., Volpe, S. L., & Mao, J. J. (2009). Therapeutic uses of magnesium. *American Family Physician*, 80(2), 157–162.
- Guimard, N. K. E., Sessler, J. L., & Schmidt, C. E. (2009). Towards a biocompatible, biodegradable copolymer incorporating electroactive oligothiophene units. *Macromolecules*, 42(2), 502–511.
- Hornberger, H., Virtanen, S., & Boccaccini, A. R. (2012). Biomedical coatings on magnesium alloys - a review. *Acta Biomaterialia*, 8(7), 2442–2455.
- Huang, L., Zhuang, X., Hu, J., Lang, L., Zhang, P., Wang, Y., et al. (2008). Synthesis of biodegradable and electroactive multiblock polylactide and aniline pentamer copolymer for tissue engineering applications. *Biomacromolecules*, 9(3), 850–858. <http://dx.doi.org/10.1021/bm7011828>.
- Jo, J. H., Li, Y., Kim, S. M., Kim, H. E., & Koh, Y. H. (2013). Hydroxyapatite/poly(epsilon-caprolactone) double coating on magnesium for enhanced corrosion resistance and coating flexibility. *Journal of Biomaterials Applications*, 28(4), 617–625. <http://dx.doi.org/10.1177/0885328212468921>.
- Kamanyi, A. E., Ngwa, W., Luo, W. L., & Grill, W. (2008). Effects of solvent vapor pressure and spin-coating speed on morphology of thin polymer blend films. *Proceedings of SPIE 6935, Health Monitoring of Structural and Biological Systems 2008*, 69351X. <http://dx.doi.org/10.1117/12.776274>.
- Kehoe, S., Zhang, X. F., & Boyd, D. (2012). FDA approved guidance conduits and wraps for peripheral nerve injury: a review of materials and efficacy. *Injury*, 43(5), 553–572.
- Kokai, L. E., Lin, Y. C., Oyster, N. M., & Marra, K. G. (2009). Diffusion of soluble factors through degradable polymer nerve guides: Controlling manufacturing parameters. *Acta Biomaterialia*, 5(7), 2540–2550.
- Lago, N., Ceballos, D., Rodriguez, F. J., Stieglitz, T., & Navarro, X. (2005). Long term assessment of axonal regeneration through polyimide regenerative electrodes to interface the peripheral nerve. *Biomaterials*, 26(14), 2021–2031.
- Lewitus, D., Vogelstein, R. J., Zhen, G., Choi, Y. S., Kohn, J., Harshbarger, S., et al. (2011). Designing tyrosine-derived polycarbonate polymers for biodegradable regenerative type neural interface capable of neural recording. *IEEE Transactions on Neural Systems and Rehabilitation Engineering: a Publication of the IEEE Engineering in Medicine and Biology Society*, 19(2), 204–212.
- Liu, H., Jiang, W., & Malshe, A. (2009). Coating for dental and orthopedic implants. *JOM*, 61(9), 67–69.
- Luo, X., & Cui, X. T. (2011). Electrochemical deposition of conducting polymer coatings on magnesium surfaces in ionic liquid. *Acta Biomaterialia*, 7(1), 441–446.
- Mackinnon, S., & Dellon, A. L. (1990). Clinical nerve reconstruction with a bioreprobable polyglycolic acid tube. *Plastic and Reconstructive Surgery*, 85(3), 419–424.
- Makadia, H. K., & Siegel, S. J. (2011). Poly lactic-co-glycolic acid (PLGA) as biodegradable controlled drug delivery carrier. *Polymers*, 3(3), 1377–1397.

- Navarro, X., Krueger, T. B., Lago, N., Micera, S., Stieglitz, T., & Dario, P. (2005). A critical review of interfaces with the peripheral nervous system for the control of neuroprostheses and hybrid bionic systems. *Journal of the Peripheral Nervous System : JPNS*, 10(3), 229–258.
- Nectow, A. R., Marra, K. G., & Kaplan, D. L. (2012). Biomaterials for the development of peripheral nerve guidance conduits. *Tissue Engineering. Part B Reviews*, 18(1), 40–50.
- Ostrowski, N., Lee, B., Enick, N., Carlson, B., Kunjukunju, S., Roy, A., et al. (2013). Corrosion protection and improved cytocompatibility of biodegradable polymeric layer-by-layer coatings on AZ31 magnesium alloys. *Acta Biomaterialia*, 9(10), 8704–8713.
- Pan, H. C., Sheu, M. L., Su, H. L., Chen, Y. J., Chen, C. J., Yang, D. Y., et al. (2011). Magnesium supplement promotes sciatic nerve regeneration and down-regulates inflammatory response. *Magnesium Research : Official Organ of the International Society for the Development of Research on Magnesium*, 24(2), 54–70.
- Perlman, J. M. (2006). Intervention strategies for neonatal hypoxic-ischemic cerebral injury. *Clinical Therapeutics*, 28(9), 1353–1365.
- Prutchi, D., & Norris, M. (2005). *Design and development of medical electronic instrumentation*. Hoboken, NJ: Wiley and Sons.
- Sebaa, M. A., Dhillon, S., & Liu, H. (2013). Electrochemical deposition and evaluation of electrically conductive polymer coating on biodegradable magnesium implants for neural applications. *Journal of Materials Science. Materials in Medicine*, 24(2), 307–316.
- Song, G., Atrons, A., & Wu, X. (1998). Corrosion behaviour of AZ21, AZ501 and AZ91 in sodium chloride. *Corrosion Science*, 40(10), 1769–1791.
- Subramanian, A., Krishnan, U. M., & Sethuraman, S. (2009). Development of biomaterial scaffold for nerve tissue engineering: biomaterial mediated neural regeneration. *Journal of Biomedical Science*, 16, 108.
- Vandeperre, L. J., & Van der Beist, O. O. (1999). Electrophoretic deposition of materials. *Annual Review of Materials Science*, 29(1), 327–352.
- Volpe, S. L. (2013). Magnesium in disease prevention and overall health. *Advances in Nutrition*, 4, 3785–3835.
- Wallace, G. G., Teasdale, P. R., Spinks, G. M., & Kane-Maguire, L. A. (2008). *Conductive electroactive polymers: intelligent polymer systems*. Boca Raton, FL: CRC press.
- Witte, F., Hort, N., Vogt, C., Cohen, S., Kainer, K. U., Willumeit, R., et al. (2008). Degradable biomaterials based on magnesium corrosion. *Current Opinion in Solid State & Materials Science*, 12(5–6), 63–72.
- Wong, H. M., Yeung, K. W., Lam, K. O., Tam, V., Chu, P. K., Luk, K. D., et al. (2010). A biodegradable polymer-based coating to control the performance of magnesium alloy orthopaedic implants. *Biomaterials*, 31(8), 2084–2096.
- Xu, L., & Yamamoto, A. (2012). Characteristics and cytocompatibility of biodegradable polymer film on magnesium by spin coating. *Colloids and Surfaces. B, Biointerfaces*, 93, 67–74.
- Zomorodian, A., Garcia, M. P., Moura e Silva, T., Fernandes, J. C., Fernandes, M. H., & Montemor, M. F. (2013). Corrosion resistance of a composite polymeric coating applied on biodegradable AZ31 magnesium alloy. *Acta Biomaterialia*, 9(10), 8660–8670.

Biodegradable polymeric coatings for surface modification of magnesium-based biomaterials

13

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13.1 Introduction

Metallic magnesium is an attractive material for load-bearing biodegradable mini-implant applications. Magnesium dissolves in the physiological environment, and the degradation product is non-toxic and can be harmlessly excreted in the urine (Witte et al., 2008; Zheng, Gu, & Witte, 2014). Favourably, magnesium is an essential element to human metabolism and is naturally found in bone tissues (Witte et al., 2008). The mechanical properties of magnesium are closer to those of the natural bone, which are highly advantageous, especially to minimise stress-shielding effect, which is an issue with non-degradable implant materials such as stainless steel and titanium alloys (Staiger, Pietak, Huadmai, & Dias, 2006). However, the degradation rate of pure magnesium is extremely high in physiological conditions, i.e. pH level (7.4–7.6) and high chloride concentration (Staiger et al., 2006; Witte et al., 2008). Hence, it is expected that magnesium implants will dissolve rapidly before the tissues completely heal.

In the last decade, a significant amount of work has been carried out to decrease the degradation rate of magnesium through alloying with elements such as aluminium, zinc, calcium and rare earths (Kannan, 2010; Kannan & Raman, 2008; Liu et al., 2011; Walter & Kannan, 2011; Witte et al., 2005, Witte et al., 2010). Indeed, magnesium alloys have shown improvement in degradation resistance; however, due to their inhomogeneous microstructures, these alloys are prone to localised degradation (Kannan, 2010). The localised attack leading to pits/trenches could potentially affect the mechanical integrity of magnesium alloy implants during service (Kannan & Singh Raman, 2008; Kannan, Singh Raman, Witte, Blawert, & Dietzel, 2011). Hence, it is critical to minimise the localised degradation of magnesium-based biodegradable biomaterials for maintaining the mechanical integrity of the implant at least during the initial stage of service.

A potential method for improving the initial general and localised degradation resistance of magnesium alloys without altering the bulk properties of the material is through biocompatible coatings. Certainly, the coating material has to be biocompatible and biodegradable but degrade at a slower rate than that of magnesium. In recent

years, surface modification techniques such as anodisation, alkaline and fluoride treatments, electrochemical deposition, plasma electrolytic oxidation and biodegradable polymer coatings on magnesium-based materials have been studied (Narayanan, Park, & Lee, 2014; Witte et al., 2008; Wu, Ibrahim, & Chu, 2013; Zheng et al., 2014). Compared with other techniques, biodegradable polymer coatings are attractive, since there are a number of biodegradable polymers available in the market for medical applications with good biocompatibility and a range of degradation rates.

13.2 Biodegradable polymers

Biodegradable polymers are polymeric materials that can degrade in physiological conditions and produce non-toxic products. Polylactic acid (PLA), polyglycolic acid (PGA), polycaprolactone (PCL) and polyhydroxybutyrate (PHB) are some of the biodegradable polymers (chemical structures shown in Figure 13.1), which are popular and have found applications in the medical and pharmaceutical industries (Peppas & Langer, 1994), such as encapsulating materials for drug delivery (Holland, Tighe, & Gould, 1986), cardiovascular stents (Ramcharitar & Serruys, 2008) and scaffold for tissue engineering (Freed et al., 1993). These biodegradable polymers undergo hydrolytic degradation with by-products excreted in the urine or converted into carbon dioxide and water via the citric acid cycle. The mechanical properties of these polymers are poor as compared to those of natural bone; hence, they are not suitable for load-bearing orthopaedic applications (Witte et al., 2008). However, these biodegradable polymers are very attractive for top-coatings on magnesium-based materials to control the initial

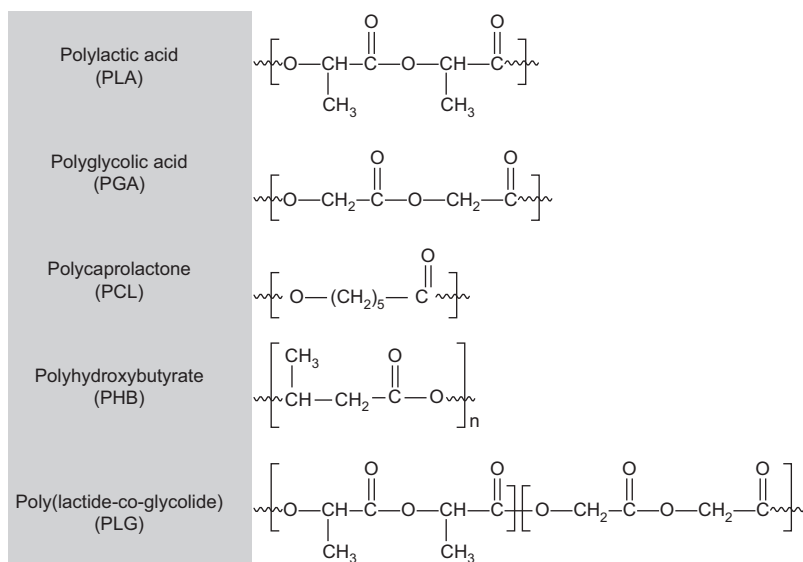


Figure 13.1 Chemical structures of biodegradable polymers.

degradation rate, since they possess a low and wide range of degradation rates based on their molecular weights. Further, the degradation rate of the polymers can be tailored, e.g. altering their crystallinity by low-temperature heat treatment (Nair & Laurencin, 2007).

Biodegradable polymers, especially aliphatic polyesters based on lactic and glycolic acids such as PLA and PGA, are researched extensively for biomedical applications. These two polymers are approved materials by U.S. Food and Drug Administration (FDA) for a number of clinical applications (Edlund & Albertsson, 2002). The degradation product of PLA is lactic acid, a human metabolic by-product, which breaks down into water and carbon dioxide via the citric acid cycle (Nair & Laurencin, 2007). Basically, PLA exists as two optical isomers, i.e. D and L. PLLA (L-lactide) is semi-crystalline (37% crystallinity) and possesses high tensile strength and low degradation rate (>2 years for complete absorption (Bergsma, de Bruijn, Rozema, Bos, & Boering, 1995; Daniels, Chang, Andriano, & Heller, 1990)). On the other hand, PDLA (DL-lactide) contains a random distribution of D-lactide and L-lactide and is an amorphous polymer. The higher degradation and lower tensile strength of PDLA as compared to PLLA make it attractive for drug delivery applications. PGA is a highly crystalline (45–55% crystallinity) polymer and it exhibits high tensile strength. PGA degrades at a faster rate than that of PLA, and in fact, it is reported that PGA will completely absorb in 4–6 months in the human body (Shalaby & Johnson, 1994).

A significant amount of work has been carried out on the co-polymers of lactide and glycolide, i.e. poly(lactide-co-glycolide) (PLG). A co-polymer of 50% glycolide and 50% DL-lactide degrades faster than the homo-polymers (Miller, Brady, & Cutright, 1977). Co-polymers of L-lactide with 25–70% glycolide are amorphous (Gilding & Reed, 1979). PLG (82/18) is used as suture anchors and as screws and plates for craniomaxillofacial repair (Pietrzak, Verstynen, & Sarver, 1997). PCL is another biodegradable polymer that is semi-crystalline and degrades slower than PLA. PCL has been used in drug delivery applications. The degradation rate of PCL is reported to be in the order of 2 years. However, it has been shown that the degradation rate of PCL can be increased by co-polymerisation with DL-lactide (Schindler et al., 1997). PHB is a highly crystalline and brittle biodegradable polymer. The degradation product of PHB is hydroxybutyric acid, which is a normal constituent of human blood.

13.3 Polymer degradation mechanisms

Understanding the degradation mechanism of biodegradable polymers is crucial for making the right selection in coating applications for biodegradable implants. The degradation mechanism of the biodegradable polymers will dictate the degradation rate, which plays an important role in the new tissue growth during the healing process. Ideally, the degradation rate of the polymer should be similar to, if not slightly less than, the rate of tissue formation such that the degradation of the polymer can be replaced by newly formed tissue.

Generally, biodegradable polymers undergo hydrolytic bond cleavage to form water-soluble degradation products (Griffith, 2000). Chemical hydrolysis is the main mechanism for the polymer degradation. The polymers contain hydrolysable bonds that make them susceptible to chemical degradation. Chemical degradation is generally mediated by water, enzymes and microorganisms. Mechanisms of chemical degradation are cleavage of cross-links between chains, side-chains and polymer backbone. Broadly, the degradation of a polymer material can proceed through two different mechanisms: (1) bulk degradation and (2) surface degradation. The sequence of degradation of bulk and surface degradation polymers is shown in Figure 13.2.

In bulk degradation polymers, the body fluid enters the polymer and causes hydrolytic degradation. The fluid penetrates the polymer at a higher rate as compared to the polymer conversion rate into water-soluble material, i.e. the uptake of the fluid will be faster than critical bond breaking. The polymer will contain some fluid before the degradation starts throughout the bulk of the polymer. Hence, the molecular weight decreases continuously during the degradation process (Zhang, Kuijer, Bulstra, Grijpma, & Feijen, 2006). Followed by fluid diffusion, the oligomers with acidic end-groups autocatalyse the hydrolysis reaction, and then the oligomers diffuse out of the polymer, resulting in a highly porous structure (Lewis, 1990). Hence, the degradation rate of bulk degradation polymers is not constant (Gopferich, 1996). Typically, hydrophilic polymers such as PLA and PGA undergo bulk degradation (Kohn & Langer, 1996). It has been reported that for bulk degradation polymers (PLA/PGA), the surface degradation rate is slower than that of the interior (Therin, Christel, Li, Garreau, & Vert, 1992). This has been attributed to the local acidic environment in the interior, which accelerates the hydrolysis of the ester linkages.

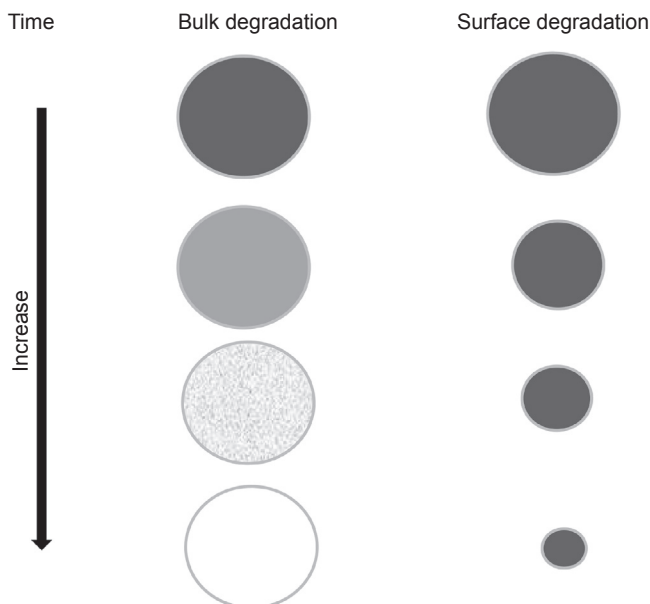


Figure 13.2 Degradation sequence of bulk and surface degradation polymers.

In surface degradation polymers, the degradation rate is constant and is directly proportional to the external surface area of the implant (Gopferich & Langer, 1993). In this case, the penetration rate of the fluid through the polymer is slower than the degradation rate of the polymer, i.e. the fluid penetration is limited by surface degradation. Surface degradation can also occur via enzymatic degradation. Cleavage of critical bonds is faster than fluid uptake for surface degrading polymers (Zhang et al., 2006). This would lead to a linear mass loss during the degradation process (Middleton & Tipton, 2000). The degradation precedes the interface between the polymer and the aqueous environment (Hofmann, Entrialgo-Castaño, Kratz, & Lendlein, 2009). Hence, a decrease in the molecular weight will not be significant during the degradation process (Zhang et al., 2006). Since the degradation occurs on the surface, thinning of the polymer implant occurs over time (Kohn & Langer, 1996). Hydrophobic polymers such as polycarbonates (PTMC — poly(1,3-trimethylene carbonate)), polyanhydrides and polyorthoesters (PHB — polyhydroxybutyrate) undergo surface degradation, where water intake is limited. Similar to bulk degradation polymers, acidic by-products are released in surface degradation polymers, but the release will be slower and hence we can expect a lower chance of inflammation as compared to bulk degradation polymers. Further, due to the difference in the degradation mechanism, the mechanical integrity of surface degradation polymers will be maintained over a longer period of time in comparison with bulk degradation polymers.

Parameters such as polymer composition, morphology of the material and functional groups have been identified to influence the polymer degradation (Li, Garreau, & Vert, 1990; Vert, Christel, Chabot, & Laray, 1984; Vert, Li, & Garreau, 1992). The chemical stability of the polymer backbone, crystallinity, molecular weight, nature of end-groups, fabrication process and hydrophobicity/hydrophilicity determines the degradation rate of the polymer. The swelling behaviour of the polymer, diffusion of oligomers and monomers and morphological changes can also affect the degradation process. In semi-crystalline polymers, the fluid penetrates the bulk of the polymer, attacking the chemical bonds in the amorphous phase first and then the crystalline phase, due to their difference in dissolution rates. Since the amorphous phase dissolves first, there will be a reduction in molecular weight but no loss in the physical properties initially. Middleton and Yarbrough (1999) reported that when the ester end-groups of poly(D,L-lactide-co-glycolide) (DLPLG) were replaced with covalently bonded monofunctional poly(ethylene glycol) (mPEG), the resulting polymer exhibited enhanced water uptake but without accelerating the degradation rate. They suggested that increase in water uptake will allow the acidic products to diffuse quicker from the interior. This is important because an acidic environment will not only accelerate the degradation (Athanasίου, Agrawal, Barber, & Bukhart, 1998; Athanasίου, Schmitz, & Agrawal, 1998) but may also lead to adverse tissue reactions (Suganuma & Alexandar, 1993). Athanasίου, Agrawal, et al. (1998) and Athanasίου, Schmitz, et al. (1998) found that DLPLG (50/50) implants with low porosity degrade faster than those with high porosity, which is attributed to the lower pH (interior) in the former than in the latter. In the high-porosity implant, the degradation products diffuse faster and hence the pH drop is not high as compared to low-porosity implants.

13.4 Polymer biocompatibility

For polymers to be used as coatings in implant applications, one of the main criteria is their biocompatibility. Biodegradation of the polymers should not cause any significant systemic or local reactions, i.e. the degradation products must not invoke an inflammatory or toxic response. The by-products must metabolise in the body after serving their purpose, leaving without any trace. There are many factors that may influence the biocompatibility of biodegradable implant materials. For example, the behavior of cells in contact with the substrate, and importantly the cell adhesion to the surface, may play an important role. Cell adhesion depends on the topography, chemistry and surface energy of the material (Zhang et al., 2008). The response of the body to the material can be related to the size and composition of the material as well as the material site. Importantly, the material site should be able to eliminate rapidly the degradation products so that there will be no inflammatory or toxic response.

Degradation of the polymers may alter their functionality and associated biological response. It has been reported that the rate of the polymer degradation affects cell vitality, cell growth and host response (Babensee, Anderson, McIntire, & Mikos, 1998). However, the majority of the work suggests that biodegradable polymers such as PLA and PGA are sufficiently biocompatible (Agrawal, Niederauer, Micallef, & Athanasiou, 1995). PLA hydrolyzes to lactic acid, which metabolises through the tricarboxylic acid cycle and is then excreted as carbon dioxide and water. On the other hand, PGA degrades by hydrolysis and esterases to glycolic acid, which can be excreted directly in urine or may react to form glycine and enters the tricarboxylic acid cycle. (Athanasiou, Agrawal, et al., 1998; Athanasiou, Schmitz, et al., 1998). Bergsma et al. (1995) carried out a study on patients who have received PLLA implants for zygomatic fractures. Their analysis showed that PLLA remained even after 3.3–5.7 years without causing any injury to the cell, which demonstrates the high biocompatibility of the polymer.

A considerable amount of work has been done on the biocompatibility of biodegradable polymer-coated magnesium-based materials. Li, Cao, Zhang, Zhang, and He (2010) examined the *in vitro* cell attachment on PLGA-coated magnesium alloy (Mg-6Zn). Their results indicated that the PLGA coating has the ability to improve cell adhesion and enhance subsequent cellular reactions. They observed that the osteoblast-like cells have been well spread on the coated alloy, whereas no obvious cell attachment was observed on the surface of uncoated alloy. The biocompatibility of PCL-coated magnesium alloy (AZ91) was studied by Wong et al. (2010). The authors reported better cytocompatibility of eGFP and SaOS-2 osteoblasts with the PCL-coated alloy as compared to that of the uncoated alloy. Based on *in vivo* micro-CT image analysis, it was suggested that PCL-coated magnesium alloy implants allowed sufficient time for bone healing and also promoted new bone growth. They found higher volumes of new bone formation on PCL-coated alloy in comparison with the uncoated alloy. Histological analysis indicated no inflammation, necrosis or hydrogen gas accumulation for the PCL-coated sample during the degradation process.

Xu and Yamamoto (2012a) coated amorphous PLLA and semi-crystalline PCL films on magnesium and studied their biocompatibility. They reported that SaOS-2

cells exhibited good attachment and high growth on both the polymer-coated samples. The number of cells on the polymer-coated samples increased with increase in incubation time. This indicates that cells could attach and proliferate on the polymer coatings. In the case of the uncoated magnesium, there was no noticeable increase in the number of cells in the whole incubation period. The authors compared the performance of PLLA with PCL films with a similar molecular weight and found that the number of cells on the PLLA film was higher than that of the PCL film. The effect of coating method on the biocompatibility of PLA coating on a magnesium alloy (AM50) was studied by [Abdal-hay, Barakat, and Lim \(2013\)](#). Dip-coating and electrospinning methods were used to coat PLA on the alloy. The cytocompatibility of the coated and the uncoated alloy was assessed using MC3T3-E1 osteoprogenitor cells. The authors found that the surface morphology played an important role in the biocompatibility, i.e. the nanofibre layer produced by the electrospinning method exhibited an excellent surface for cell adhesion, proliferation and differentiation due to its 3D structure.

The biocompatibility of a surface-degrading polymer, poly(1,3-trimethylene carbonate) (PTMC), coated magnesium alloy (Mg-Zn-Mn) was examined by [Wang et al. \(2013\)](#). It was reported that PTMC-coated alloy showed less hemolysis than the controls, i.e. under *in vitro* conditions fewer platelets were adherent and activated, and also fewer erythrocytes were attached on the PTMC-coated alloy. Importantly, they did not observe any excessive inflammation, necrosis and hydrogen gas accumulation for the PTMC-coated alloy. It was suggested that the neutral degradation products of the PTMC coating provided a mild environment and hence showed good hemocompatibility, including low hemolytic ratio and low coagulation.

Recently, hybrid coatings, i.e. ceramic-polymer, have also gained some interest for tailoring the degradation rate of magnesium-based materials. It is critical that these hybrid coatings also exhibit good biocompatibility for successful applications. [Guo, Cao, Lu, and Liu \(2011\)](#) examined the biocompatibility of a hybrid micro-arc oxidation (MAO)-PLLA coating on a magnesium alloy (WE42). PLLA was used as a top-coat and also to seal the microcracks/micropores on the surface of the MAO coating. Cytotoxicity testing revealed that the MAO-PLLA coating on the alloy had good cytocompatibility. In another study, [Abdal-hay, Amna, and Lim \(2013\)](#) developed nanoparticles containing hybrid coating (nano-hydroxyapatite(nHAP)-PCL) on a magnesium alloy (AM50). They found that the hybrid coating exhibited excellent biocompatibility as compared to the bare metal. It was suggested that the nHAP incorporated with PCL composite membranes may serve as an excellent 3-D platform for cell attachment, proliferation, migration and growth in bone tissue. A dense and well-adherent HAP-chitosan was coated on a magnesium alloy (AZ31) by [Hahn et al., \(2011\)](#). Biocompatibility studies of the hybrid coating showed that the pre-osteoblast MC3T3-E1 cells were poorly adherent, with a spherical morphology, on the bare alloy; however, on the coated alloy the cells were well attached and spread. They also found that the spreading of the cells having multiple filopodia on the surface of the composite coating was enhanced as compared with the HAP-only coating, which confirmed the better biocompatibility of the composite coating.

Overall, literature on the biodegradable polymers or ceramic-polymer coatings on magnesium-based materials suggests that the biocompatibility of the coated materials has improved and hence could be considered for implant applications.

13.5 Polymer coating performance

Owing to the inability to control the localised degradation of magnesium by alloying only, research focus on biocompatible coatings, including biodegradable polymers, has gained increased interest. [Chen et al. \(2011\)](#) coated PLA on pure magnesium using a dip-coating method. Interestingly, they observed bulging of the coating after a period of exposure time to simulated body fluid (SBF). They attributed this behaviour to the SBF penetration through the defects in the polymer which initiated degradation, i.e. magnesium hydroxide formation and consequent hydrogen evolution. Generally, the dip-coating method produces thick non-uniform coating and as a result the adhesion of the coating may not be good enough to withstand the degradation process. However, [Li et al. \(2010\)](#) reported excellent degradation resistance for a magnesium alloy (Mg-6Zn) coated with PLGA using a dip-coating method. The coated alloy showed a degradation rate at least two orders of magnitude lower than the bare alloy. Interestingly, they found that 2% PLGA coating, which produced a coating thickness of 33 μm , performed better than 4% PLGA coating with 72- μm coating thickness. The difference in the performance can be related to the thickness of the coating, which affects the adhesion strength.

Generally, porosity/defects in dip-coating are higher than with the spin-coating method, and hence one could expect better performance with spin-coated polymers. Recently, [Alabbasi, Liyanaarachchi, and Kannan \(2012\)](#) coated PLA using a spin-coating method on a magnesium alloy (AZ91) and studied its *in vitro* degradation behaviour. They reported that the degradation resistance of the alloy increased significantly with the increase in the coating thickness ([Figure 13.3](#)). For example, a 5- μm thick PLA coating exhibited more than two orders of magnitude higher polarisation resistance than that of the bare metal. As expected, higher coating thickness resulted in poor adhesion. They also found that the degradation resistance of the coated alloy decreased gradually with the increase in SBF exposure time ([Figure 13.4](#)).

[Wong et al. \(2010\)](#) coated PCL on a magnesium alloy (AZ91) using spray method and evaluated its degradation behaviour. The polymer coating not only reduced the degradation rate of the alloy but also maintained the bulk mechanical properties upon degradation. [Figure 13.5](#) shows the weight loss of the PCL coated and uncoated alloy. The total weight loss after 2 months of immersion was ~ 17 mg for uncoated alloy; however, it was much lower for the PCL-coated alloy. They reported that the porosity of the polymer influenced the degradation behaviour, e.g. a low-porosity film exhibited a total weight loss of 3.59 mg, whereas a high-porosity film showed higher weight loss (6.22 mg) after 2 months of immersion.

[Xu and Yamamoto \(2012a\)](#) studied the adhesion behaviour of PLLA- and PCL-coated (spin-coating) magnesium. They reported that the PLLA film exhibits better adhesion strength than the PCL film. Further, it was reported that for both PLLA

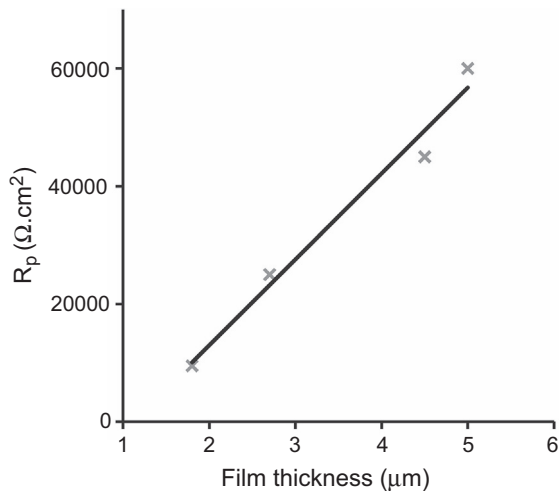


Figure 13.3 Polarisation resistance (R_p) of PLA-coated magnesium alloy (AZ91), with different coating thickness, after 2 h exposure to SBF.
From Alabbasi et al. (2012).

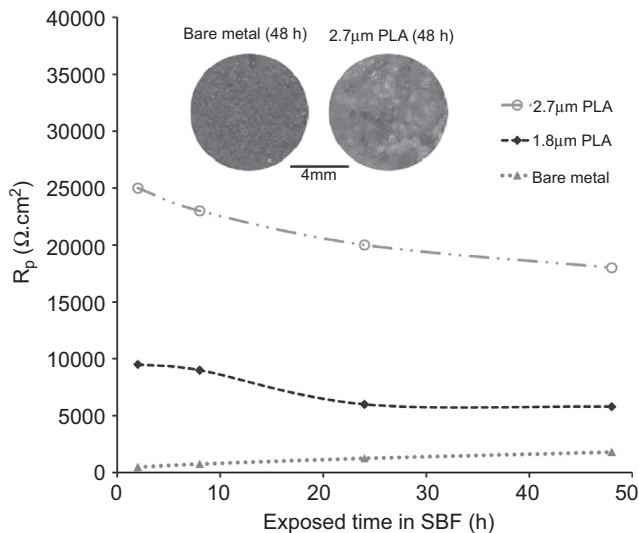


Figure 13.4 Polarisation resistance (R_p) of uncoated and PLA-coated magnesium alloy (AZ91) after different immersion periods in SBF.
From Alabbasi et al. (2012).

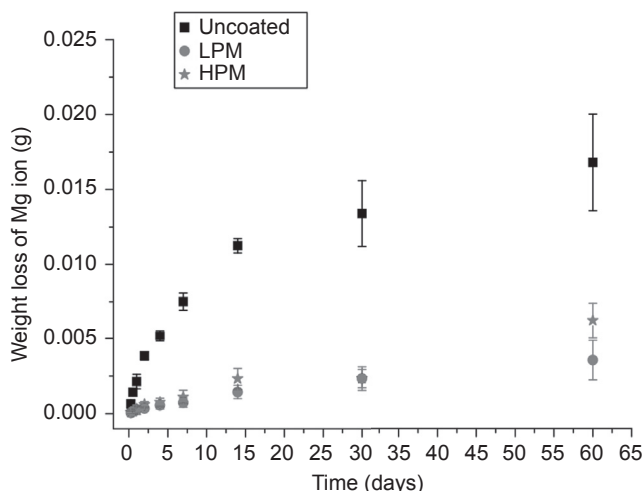


Figure 13.5 Weight loss of uncoated and PCL-coated magnesium alloy (AZ91) with different exposure periods. (LPM, low-porosity membrane; HPM, high-porosity membrane.)

From Wong et al. (2010).

and PCL, low molecular weight (LMW) film was thinner and exhibited better adhesion strength than high molecular weight (HMW) film. As shown in Figure 13.6, the highest adhesion strength was for PLLA (LMW) and the lowest was for PCL (HMW). Both the coatings, PLLA and PCL with LMW, exhibited higher adhesion strengths than those of HMW films. Interestingly, it was also noticed that PLLA coating showed higher adhesion strength compared to the PCL coating with similar molecular weight. However, the reason for such a difference was not reported. Following this study, Xu and Yamamoto (2012b) examined the degradation performance of PLLA- and PCL-coated magnesium. The release of Mg^{2+} was measured during the immersion period. The authors reported that all the polymer-coated magnesium exhibited significantly lower release of Mg^{2+} as compared to that of uncoated magnesium. They also noticed that there was no difference in the chemical composition of the corrosion layer between the polymer-coated and uncoated magnesium. However, the PLLA-coated magnesium showed relatively uniform degradation as compared to that of PCL-coated magnesium and uncoated magnesium. All the polymer-coated magnesium exhibited a significantly lower degradation rate as compared to that of uncoated magnesium. PLLA (HMW)-coated magnesium had the lowest corrosion rate of $1.63 \mu\text{m/day}$, and PCL(LMW)-coated magnesium showed the highest corrosion rate of $3.85 \mu\text{m/day}$ (Figure 13.7), and large pits were observed in PCL-coated magnesium. The authors found that the performance of the material was related to the adhesion strength, i.e. the higher the adhesion, the better the performance. Between PLLA and PCL coatings with similar film thickness and molecular weight, the adhesion strength of PLLA film was higher than that of PCL film, and as a result the former exhibited better performance than the latter.

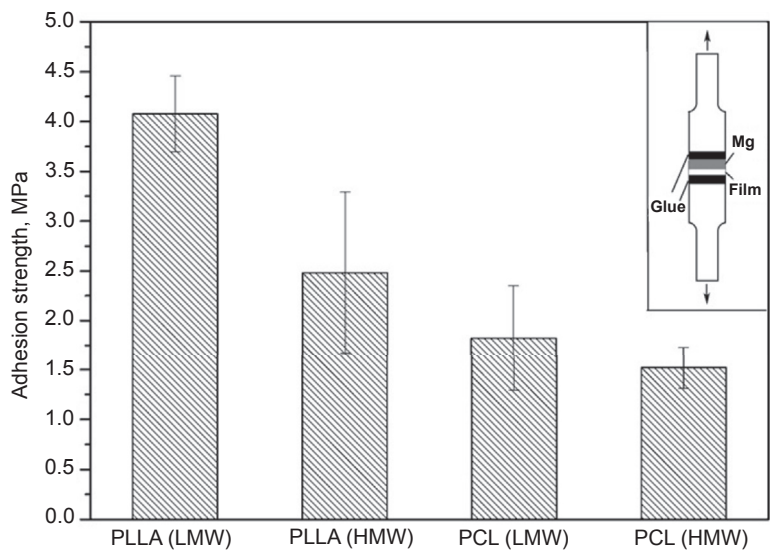


Figure 13.6 Adhesion strength of polymer coatings on magnesium metal.
From Xu & Yamamoto (2012a).

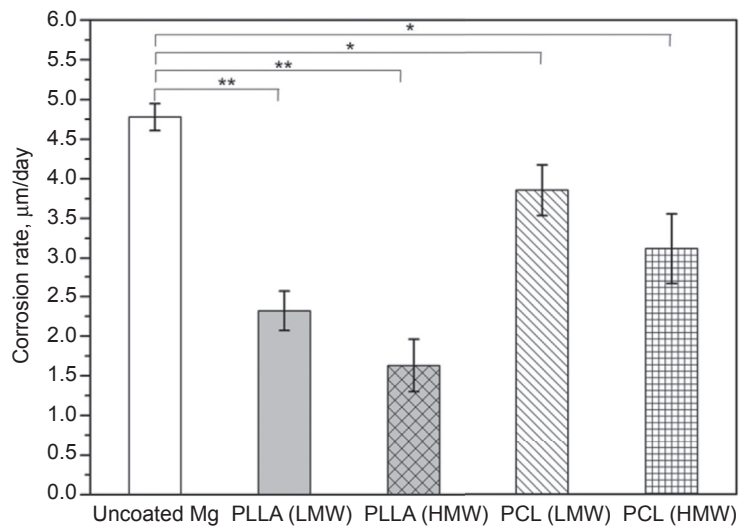
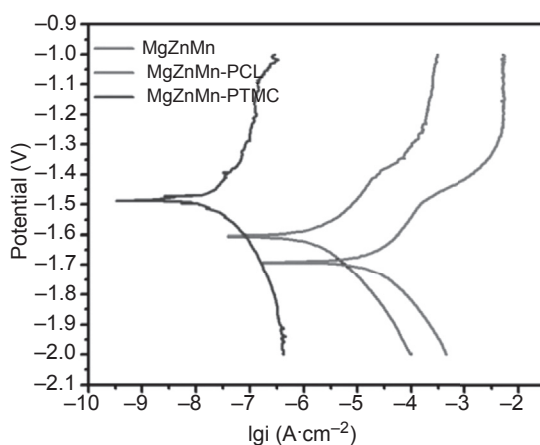


Figure 13.7 Corrosion rate of uncoated magnesium and magnesium coated with different polymers after 10-day immersion in cell culture conditions.
From Xu & Yamamoto (2012b).

A surface degradation polymer, poly(1,3-trimethylene carbonate) (PTMC), was coated on a magnesium alloy (Mg-Zn-Mn) using an evaporation method by Wang et al. (2013). The degradation test results suggested that the PTMC coating protected the alloy from degradation. The corrosion current density of the PTMC-coated alloy was reduced by three orders and one order of magnitude as compared to that of bare and PCL-coated magnesium alloy, respectively. It was suggested that the homogeneous surface degradation of the PTMC coating, i.e. exterior to interior (surface degradation behavior), and also its charge neutral degradation products, contributed to its excellent performance. As shown in Figure 13.8, the degradation rate of the PTMC-coated magnesium alloy was significantly lower than that of the uncoated and PCL-coated magnesium alloy. They observed that the PTMC-coated alloy exhibited the least increase of pH, Mg^{2+} release, and weight loss during the degradation, as compared to the uncoated and PCL-coated alloy. Interestingly, even after 30 days of testing, the pH value of PTMC-coated alloy solution remained at ~ 7.4 , whereas for the uncoated and PCL-coated alloy it increased sharply. Their post-degradation analysis revealed that the PTMC-coated alloy exhibited a smooth and homogeneous surface with the coating intact, whereas the PCL-coated alloy exhibited a number of areas of localised corrosion. They reported that PTMC on magnesium alloy was homogeneously thinned from the surface to the interior, which is a surface degradation mode, and hence advantageous for long-term degradation control of magnesium alloy.

Adbal-hay, Barakat, et al. (2013) investigated the performance of electrospinning coating of PLA on a magnesium alloy (AM50). They compared the electrospinning method with a dip-coating method of coating PLA on the alloy. It was reported that both the techniques significantly enhance the short-term degradation resistance of the alloy. The corrosion currents decreased by 87.5% and 78.09%, for dip-coated and electrospin-coated alloy, respectively, as compared to the bare alloy. However, under long-term testing the degradation resistance of the electrospinning-coated alloy was superior to that of dip-coated alloy, which was porous in nature (Figure 13.9). It was reported that in the dip-coating process, a thick layer could generate three polymer films: (1) a primer, to ensure good adhesion and protect the substrate; (2) an

Figure 13.8 Potentiodynamic polarisation curves of magnesium alloy (Mg-Zn-Mn) uncoated and coated with two different polymers. From Wang et al. (2013).



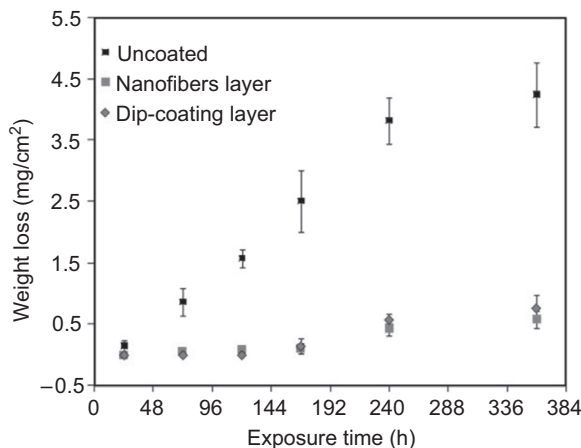


Figure 13.9 Weight loss of uncoated and polymer-coated (with different methods) magnesium alloy (AM50). From Abdal-hay, Barakat, et al. (2013).

intermediate film, impeding the transport of aggressive species; and (3) a top-coating film, on the substrate. With the electrospinning-coated alloy, in contrast, the polymer was deposited layer-by-layer on the substrates, and thereby a fully interconnected porous 3-D structure was generated. The authors suggested that the adhesion in electrospinning coating was via many points of interaction between the nonwoven polymer layer and magnesium substrate and hence did not produce any delamination or/and blistering on the polymer layer.

Based on the literature, it can be suggested that polymer-alone coating provides magnesium-based materials only short-term resistance to degradation. Under long-term testing, it appears that the coating fails due to fluid penetration. Compared to bulk degradation polymer, surface degradation polymer appears to be superior for these applications.

13.6 Hybrid coatings

Due to the long-term ineffectiveness of polymer-alone coatings in controlling the degradation of magnesium-based materials, hybrid coatings, i.e. a combination of ceramics and biodegradable polymers, have been investigated in recent years. The advantage of this type of coating is that the degradation properties of the base material can be tailored effectively to produce implant materials with specific properties. Typically, the material is coated with a ceramic and then a top-coat of polymer is applied. However, composite coatings have also been investigated.

Calcium phosphate (CaP) is a biocompatible ceramic, which is naturally present in bone. Although CaP coatings on magnesium-based materials have shown some improvement in terms of degradation resistance (Kannan, 2012a,b; Kannan & Orr, 2011; Kannan & Wallipa, 2012; Shadanbaz & Dias, 2011), one of the major issues is the porosity in the CaP coatings. However, the porosity in the CaP coating can be effectively sealed using biodegradable polymers for enhanced performance.

Oosterbeek, Seal, Seitz, and Hyland (2013) coated CaP and other bioceramics (A — MgCO_3 , Mg(OH)_2 and NaHCO_3 ; B — $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, $\text{Mg}(\text{H}_2\text{PO}_4)_2$ and CaCO_3) in combination with PLA on pure magnesium. They used an immersion method to coat the bioceramics on the metal and then coated PLA onto the bioceramic surface. The morphology of the two bioceramics was different, i.e. bioceramic A exhibited a thin, plate-like structure, and the bioceramic coating B was found to be a much thicker layer of elongated plate-like crystals. Interestingly, it was found that both the composite coatings exhibited poor adhesion strength as compared to PLA alone coating (Figure 13.10). The authors attributed this to the poor bonding between the bioceramic layer and the magnesium substrate. All of the coatings provided some resistance to degradation; however, the coatings blistered and cracked due to gas evolution, a by-product of magnesium degradation. A correlation was drawn between the maximum adhesion strength of the coating and the time taken for the cracking during the degradation tests (Figure 13.11). It was suggested that as gas accumulates within the blister, the pressure gradually increases, which leads to a gradually increasing stress between the coating and magnesium substrate, and hence a coating with lower adhesion strength will fail earlier.

Wang, Zhao, Chen, Li, and Zhang (2012) used an electrodeposition method to coat dicalcium phosphate dihydrate (DCPD) on a magnesium alloy (Mg-Zn) and then coated PCL by immersing the DCPD-coated sample in a 2 wt.% PCL chloroform solution. The corrosion current of the hybrid coating was one-third of the DCPD-coated alloy. Long-term tests also confirmed that the hybrid coating exhibited higher degradation resistance as compared to the alloy coated with DCPD alone. Similarly, Kannan and Liyanarachchi (2013) coated CaP on a magnesium alloy (AZ91) using the electrodeposition method and further coated PLA using a spin-coating method. Their electrochemical degradation test results showed that the hybrid coating enhanced the

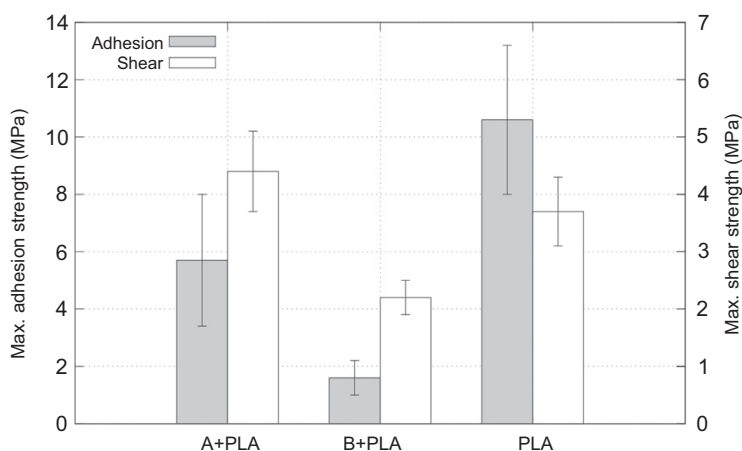


Figure 13.10 Maximum adhesion and shear strength of PLA and two composite coatings on pure magnesium.

From Oosterbeek et al. (2013).

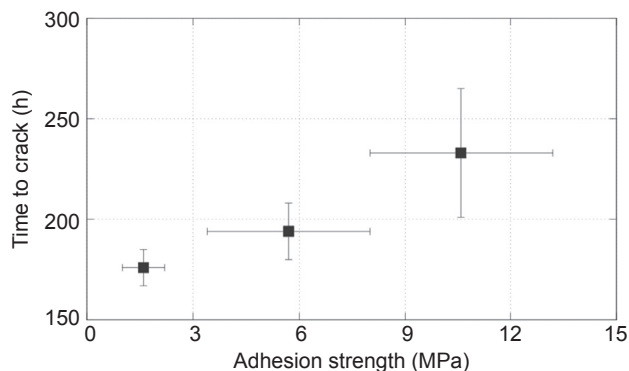


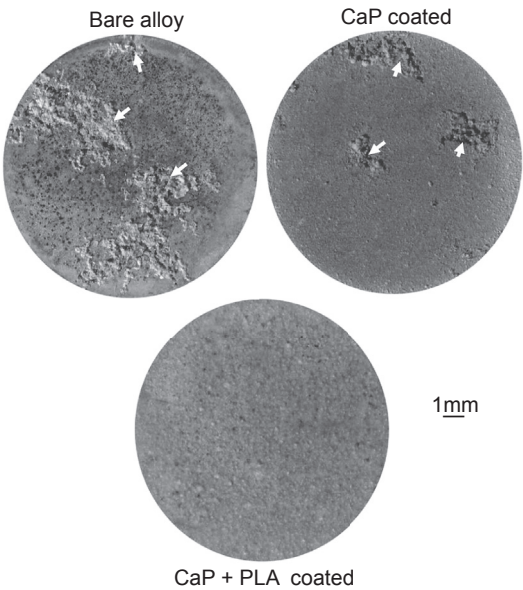
Figure 13.11 Correlation between adhesion strength of a polymer coating and time taken for the coating to crack.

From Oosterbeek et al. (2013).

degradation resistance of the alloy by more than two orders of magnitude as compared to the bare alloy and one order of magnitude higher than that of the CaP-coated alloy, after 1 h exposure in simulated body fluid (SBF). Long-term (48 h) experimental results also confirmed that the hybrid coating performed better than the bare alloy and the CaP-coated alloy. Importantly, the hybrid coating improved the localised degradation resistance of the alloy significantly, which is critical for better in-service mechanical integrity. The R_p of the alloy with hybrid coating decreased with increase in SBF exposure period; however, the R_p was appreciably high even after 48 h exposure to SBF. While the bare alloy and CaP-coated alloy exhibited patches of localised degradation, there was no evidence of localised attack on the alloy with the hybrid coating (Figure 13.12).

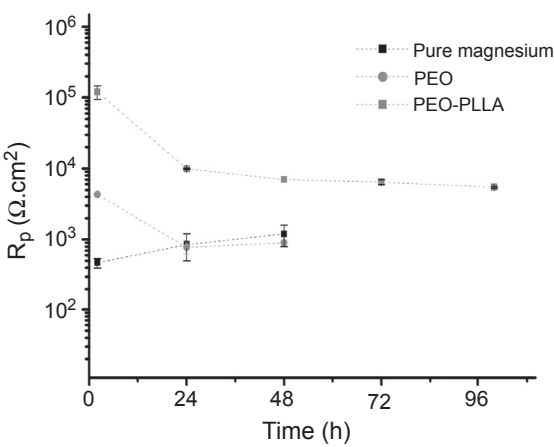
Plasma electrolytic oxidation (PEO), also called micro-arc oxidation (MAO), is a relatively new technique to produce a hard ceramic coating on metallic materials such as magnesium and titanium alloys (Alabbasi, Kannan, Walter, Stomer, & Blawert, 2013; Sreekanth & Rameshbabu, 2011; Tang, Yu, Luo, & Wang, 2012). A major drawback of this technique is that it produces a coating with a large number of pores. Research has been carried out to reduce the porosity of the coating for enhanced performance. Recently, Narayanan et al. (2014) have published a comprehensive review article on MAO coating for magnesium-based biomaterials. Guo et al. (2011) developed a composite micro-arc oxidation (MAO)-PLLA on a magnesium alloy (WE42) and examined its degradation behaviour. It was reported that the PLLA coating effectively sealed the microcracks and micropores on the surface of the MAO coating by physical interlocking to interfere with the corrosion ions. The MAO-PLLA coated alloy exhibited lower i_{corr} than the alloy with MAO-alone coating or the bare alloy. The hybrid coating on the alloy served as an effective barrier against the corrosive electrolyte. The authors suggested that the PLLA sealing layer was connected with the outer layer by physical interlocking and by penetrating into most of the pores and microcracks. Recently, Alabbasi, Mehjabeen, Kannan, Ye, and Blawert (2014) produced a porous silicate-based PEO layer on pure magnesium and then attempted to seal the pores using PLLA. The

Figure 13.12 Photographs of uncoated and CaP-PLA-coated magnesium alloy (AZ91) after immersion in SBF for 48 h. From Kannan & Liyanaarachchi (2013).



PEO coating was developed using a pulsed constant current method, and PLLA was coated using a two-step spin-coating method. Electrochemical test results showed that the polarisation resistance of the PEO-PLLA-coated magnesium was close to two orders of magnitude higher than that of the PEO-coated magnesium. The polarisation resistance of the PEO-PLLA-coated magnesium decreased with increase in exposure time; however, it was higher even after 100 h, i.e. 6 times higher than that of the PEO-coated magnesium after 48 h exposure (Figure 13.13). There was also no evidence

Figure 13.13 Polarisation resistance of uncoated, PEO-coated and PEO-PLLA-coated magnesium in SBF. From Alabbasi et al. (2014).



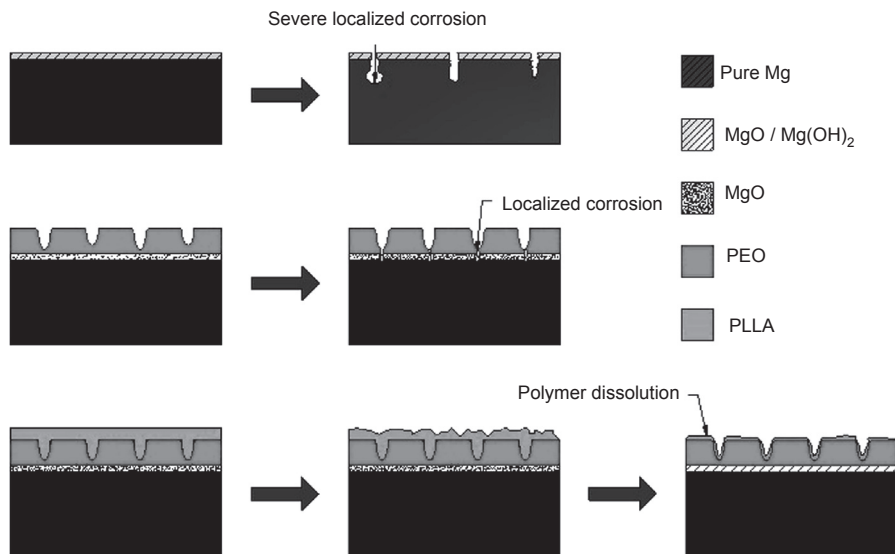


Figure 13.14 A schematic representation of the degradation mechanism of PEO-PLLA-coated magnesium as compared to uncoated and PEO-only coated magnesium. From [Alabbasi et al. \(2014\)](#).

of localised degradation attack on the PEO-PLLA-coated magnesium. A schematic representation of the degradation mechanism of the hybrid coating in comparison with uncoated and PEO-only coated magnesium was presented by the authors ([Figure 13.14](#)).

A few researchers have also investigated the performance of bioceramic dispersed polymer coatings on magnesium-based materials. [Abdal-hay, Amna, et al. \(2013\)](#) produced a coating of PCL containing nano-hydroxyapatite (nHAP) on a magnesium alloy (AM50). They used a dip-coating method to form this composite coating (nHAP-PCL). The degradation results showed that both the PCL and nHAP/PCL composites showed improvement in the degradation resistance as compared to the bare metal in SBF. Under long-term testing, the composite coatings exhibited more uniform and superior resistance to degradation attack than PCL. The composite coatings displayed better mechanical integrity than the bare metal. Both the coated samples did not show any significant weight loss during the initial immersion time, which suggests that these coatings can provide protection during the initial service period. The tensile strength of the coated and uncoated samples decreased by $\sim 13\%$ and 34% , respectively, in comparison to unexposed magnesium alloy. [Hahn et al. \(2011\)](#) deposited HAP-chitosan using aerosol deposition method on a magnesium alloy (AZ31). The produced coatings were dense and well-adherent to the alloy. The coatings exhibited high adhesion strength, i.e. 24.6–27.7 MPa, and improved the degradation resistance as compared to the bare alloy.

A recent study by [Abdal-hay, Dewidar, Lim, and Lim \(2014\)](#) reported the performance of Ti-O thin films and PLA on a magnesium alloy (AM50). The authors used the EB-PVD method for coating Ti-O film, followed by dip-coating with PLA.

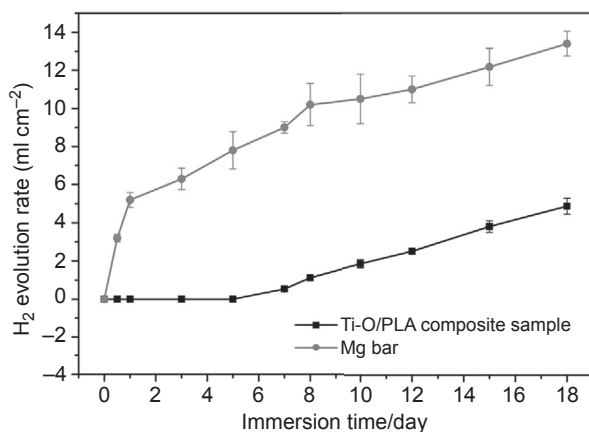


Figure 13.15 Hydrogen evolution rate of uncoated and Ti-O/PLA-coated magnesium alloy (AM50) with different immersion periods.

From [Abdal-hay et al. \(2014\)](#).

It was found that the use of the composite coating layer decreased the hydrogen evolution rate ([Figure 13.15](#)), which led the authors to suggest that this method may be useful for magnesium-based implants during the initial stages of healing, since this limits the formation of hydrogen gas around the host tissue.

It is evident from the literature that hybrid coatings have significantly improved the general and localised degradation resistance of magnesium-based materials. The research in the area of biodegradable magnesium-based materials for the next few years will be primarily focused on hybrid coatings. However, it is important to understand the degradation tendency of the hard ceramics, i.e. PEO/MAO coatings, after the bone healing process. *In vivo* studies should be carried out on these coated implants for successful orthopaedic implant applications.

13.7 Conclusions

Biodegradable polymer coatings have proven to be beneficial for enhancing the degradation resistance of magnesium-based materials for biodegradable mini-implant applications. However, polymer coating alone might not solve the problem, since body fluid can permeate through the polymer coatings, especially in bulk degradation polymers. In this regard, surface degradation polymers could be more effective than bulk degradation polymers. However, poor adhesive strength of polymer-alone coatings has also been reported for the poor long-term performance. On the other hand, hybrid coatings, i.e. combinations of ceramics and polymers, have shown promising results and hence could potentially delay the localised degradation of magnesium-based implants during the initial service period, which is critical for better mechanical integrity particularly in load-bearing orthopaedic implant applications.

References

- Abdal-hay, A., Amna, T., & Lim, J. K. (2013). Biocorrosion and osteoconductivity of PCL/nHAP composite porous film-based coating on magnesium alloy. *Solid State Sciences*, 18, 131–140.
- Abdal-hay, A., Barakat, N. A. M., & Lim, J. K. (2013). Influence of electrospinning and dip-coating techniques on the degradation and cytocompatibility of Mg-based alloy. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 420, 37–45.
- Abdal-hay, A., Dewidar, M., Lim, J., & Lim, J. K. (2014). Enhanced biocorrosion resistance of surface modified magnesium alloys using inorganic/organic composite layer for biomedical applications. *Ceramics International*, 40, 2237–2247.
- Agrawal, C. M., Niederauer, G. G., Micallef, D. M., & Athanasiou, K. A. (1995). The use of PLA-PGA polymers in orthopedics. In D. L. Wise, D. J. Trantolo, D. E. Altobelli, M. J. Yaszemski, J. D. Greser & E. R. Schwartz (Eds.), *Encyclopedic handbook of biomaterials and bioengineering Part A. Materials* (Vol. 2, pp. 1055–1089). New York, NY: Marcel Dekker.
- Alabbasi, A., Kannan, M. B., Walter, R., Stomer, M., & Blawert, C. (2013). Performance of pulsed constant current silicate-based PEO coating on pure magnesium in simulated body fluid. *Materials Letters*, 106, 18–21.
- Alabbasi, A., Liyanaarachchi, S., & Kannan, M. B. (2012). Polylactic acid coating on a biodegradable magnesium alloy: an in vitro degradation study by electrochemical impedance spectroscopy. *Thin Solid Films*, 520, 6841–6844.
- Alabbasi, A., Mehjabeen, A., Kannan, M. B., Ye, Q., & Blawert, C. (2014). Biodegradable polymer for sealing porous PEO layer on pure magnesium: an in vitro degradation study. *Applied Surface Science*, 301, 463–467.
- Athanasiou, K. A., Agrawal, C. E., Barber, F. A., & Burkhart, S. S. (1998). Orthopaedic applications for PLA-PGA biodegradable polymers. *Arthroscopy: The Journal of Arthroscopic and Related Surgery*, 14, 726–737.
- Athanasiou, K. A., Schmitz, J. B., & Agrawal, C. M. (1998). The effects of porosity on degradation of PLA-PGA implants. *Tissue Engineering*, 4, 53–63.
- Babensee, J. E., Anderson, J. M., McIntire, L. V., & Mikos, A. G. (1998). Host response to tissue engineered devices. *Advanced Drug Delivery Reviews*, 33, 111–139.
- Bergsma, J. E., de Bruijn, W. C., Rozema, F. R., Bos, R. R. M., & Boering, G. (1995). Late degradation tissue response to poly(L-lactide) bone plates and screws. *Biomaterials*, 25–31.
- Chen, Y., Song, Y., Zhang, S., Li, J., Zha, C., & Zhang, X. (2011). Interaction between a high purity magnesium surface and PCL and PLA coatings during dynamic degradation. *Biomedical Materials*, 6, 025005.
- Daniels, A. U., Chang, M. K. O., Andriano, K. P., & Heller, J. (1990). Mechanical properties of biodegradable polymers and composites proposed for internal fixation of bone. *Journal of Applied Biomaterials*, 1, 57–78.
- Edlund, U., & Albertsson, A. (2002). Degradable polymer microspheres for controlled drug delivery. *Advances in Polymer Science*, 157, 67–112.
- Freed, L. E., Marquis, J. C., Nohria, A., Emmanuel, J., Mikos, A. G., & Langer, R. S. (1993). Neocartilage formation in vitro and in vivo using cells cultured on synthetic biodegradable polymers. *Journal of Biomedical Materials Research Part A*, 27, 11–23.
- Gilding, D. K., & Reed, A. M. (1979). Biodegradable polymers for use in surgery polyglycolic/poly(lactic acid) homo and copolymers. *Polymer*, 20, 1459–1464.

- Gopferich, A. (1996). Mechanisms of polymer degradation and erosion. *Biomaterials*, 17, 103–114.
- Gopferich, A., & Langer, R. (1993). Modeling of polymer erosion. *Macromolecules*, 26, 4105–4112.
- Griffith, L. G. (2000). Polymeric biomaterials. *Acta Materialia*, 48, 263–277.
- Guo, M., Cao, L., Lu, P., & Liu, Y. (2011). Anticorrosion and cytocompatibility behaviour of MAO/PLLA modified magnesium alloys WE42. *Journal of Materials Science: Materials in Medicine*, 22, 1735–1740.
- Hahn, B.-D., Park, D.-S., Choi, J.-J., Ryu, J., Yoon, W.-H., Choi, J.-H., et al. (2011). Aerosol deposition of hydroxyapatite-chitosan composite coatings on biodegradable magnesium alloy. *Surface & Coatings Technology*, 205, 3112–3118.
- Hofmann, D., Entrialgo-Castaño, M., Kratz, K., & Lendlein, A. (2009). Knowledge-based approach towards hydrolytic degradation of polymer-based biomaterials. *Advanced Materials*, 21, 3237–3245.
- Holland, S. J., Tighe, B. J., & Gould, P. L. (1986). Polymers for biodegradable medical devices. *Journal of Controlled Release*, 4, 155–180.
- Kannan, M. B. (2010). Influence of microstructure on the in-vitro degradation behaviour of magnesium alloys. *Materials Letters*, 64, 739–742.
- Kannan, M. B. (2012a). Improving the packing density of calcium phosphate coating on a magnesium alloy for enhanced degradation resistance. *Journal of Biomedical Materials Research Part A*, 101A, 1248–1254.
- Kannan, M. B. (2012b). Enhancing the performance of calcium phosphate coating on a magnesium alloy for bioimplant applications. *Materials Letters*, 76, 109–112.
- Kannan, M. B., & Liyanaarachchi, S. (2013). Hybrid coating on a magnesium alloy for minimizing the localized degradation for load-bearing biodegradable mini-implant applications. *Materials Chemistry and Physics*, 142, 350–354.
- Kannan, M. B., & Orr, L. (2011). In vitro mechanical integrity of hydroxyapatite coated magnesium alloy. *Biomedical Materials*, 6, 045003.
- Kannan, M. B., & Raman, R. (2008). In vitro degradation and mechanical integrity of calcium-containing magnesium alloys in modified-simulated body fluid. *Biomaterials*, 29, 2306–2314.
- Kannan, M. B., & Singh Raman, R. K. (2008). Evaluation of stress corrosion cracking behavior of AZ91 alloy in modified-simulated body fluid for orthopedic implant application. *Scripta Materialia*, 59, 175–178.
- Kannan, M. B., Singh Raman, R. K., Witte, F., Blawert, C., & Dietzel, W. (2011). Influence of circumferential notch and fatigue crack on the mechanical integrity of biodegradable magnesium-based alloy in simulated body fluid. *Journal of Biomedical Materials Research, Part B*, 96B, 303–309.
- Kannan, M. B., & Wallipa, O. (2012). Potentiostatic pulse-deposition of calcium phosphate on magnesium alloy for temporary implant applications-An in vitro corrosion study. *Materials Science and Engineering: C*, 33, 675–679.
- Kohn, J., & Langer, R. (1996). Bioresorbable and bioerodible materials. In B. D. Ratner, A. S. Holman, F. J. Schoen & J. E. Lemons (Eds.), *Biomaterials Science* (pp. 164–172). New York, NY: Academic Press.
- Lewis, D. H. (1990). Biodegradable polymers as drug delivery systems, controlled release of bioactive agents from lactide/glycolide polymers. In M. Chasin & R. Langer (Eds.), *Biodegradable polymers as drug delivery systems* (pp. 1–43). New York, NY: Dekker M.

- Li, J. N., Cao, P., Zhang, X. N., Zhang, S. X., & He, Y. H. (2010). In vitro degradation and cell attachment of a PLGA coated biodegradable Mg-6Zn based alloy. *Journal of Materials Science*, 45, 6038–6045.
- Li, S. M., Garreau, H., & Vert, M. (1990). Structure-property relationships in the case of the degradation of massive aliphatic poly-(α -hydroxy acids) in aqueous media, part 1: poly(DL-lactic acid). *Journal of Materials Science: Materials in Medicine*, 1, 123–130.
- Liu, C. L., Jiang, J., Wang, M., Wang, Y. J., Chu, P. K., & Huang, W. J. (2011). In vitro degradation and biocompatibility of WE43, ZK60, and AZ91 biodegradable magnesium alloys. *Advanced Materials Research*, 287, 2008–2014.
- Middleton, J. C., & Tipton, A. J. (2000). Synthetic biodegradable polymers as orthopaedic devices. *Biomaterials*, 21, 2335–2346.
- Middleton, J. C., & Yarbrough, J. C. (1999). The effect of PEG end groups on the degradation of a 75/25 poly(DL-lactide-co-glycolide). *Transactions of the Society for Biomaterials 25th Annual Meeting*, 22, 535.
- Miller, R. A., Brady, J. M., & Cutright, D. E. (1977). Degradation rates of oral resorbable implants (polylactates and polyglycolates): rate modification with changes in PLA/PGA copolymer ratios. *Journal of Biomedical Materials Research Part A*, 11, 711–719.
- Nair, L. S., & Laurencin, C. T. (2007). Biodegradable polymers as biomaterials. *Progress in Polymer Science*, 32, 762–798.
- Narayanan, T. S. N. S., Park, S. I., & Lee, M. H. (2014). Strategies to improve the corrosion resistance of microarc oxidation (MAO) coated magnesium alloys for degradable implants: prospects and challenges. *Progress in Materials Science*, 60, 1–71.
- Oosterbeek, R. N., Seal, C. K., Seitz, J.-M., & Hyland, M. M. (2013). Polymer-bioceramic composite coatings on magnesium for biomaterial applications. *Surface & Coatings Technology*, 236, 420–428.
- Peppas, N. A., & Langer, R. S. (1994). New challenges in biomaterials. *Science*, 264, 1065–1067.
- Pietrzak, W. S., Verstynen, B. S., & Sarver, D. R. (1997). Bioabsorbable fixation devices: status for the Craniomaxillofacial surgeon. *Journal of Craniofacial Surgery*, 2, 92–96.
- Ramcharitar, S., & Serruys, P. (2008). Fully biodegradable coronary stents: progress to date. *American Journal of Cardiovascular Drugs*, 8, 305–314.
- Schindler, A., Jeffcoat, R., Kimmel, G. L., Pitt, C. G., Wall, M. E., & Zwiedinger, R. (1997). Biodegradable polymers for sustained drug delivery. *Contemporary Topics in Polymer Science*, 2, 251–289.
- Shadanbaz, S., & Dias, G. (2011). Calcium phosphate coatings on magnesium alloys for biomedical applications: a review. *Acta Biomaterialia*, 8, 20–30.
- Shalaby, S. W., & Johnson, R. A. (1994). Synthetic absorbable polyesters. In S. W. Shalaby (Ed.), *Biomedical polymers. Designed to degrade systems* (pp. 1–34). New York, NY: Hanser.
- Sreekanth, D., & Rameshbabu, N. (2011). Development and characterization of MgO/hydroxyapatite composite coating on AZ31 magnesium alloy by plasma electrolytic oxidation coupled with electrophoretic deposition. *Materials Letters*, 68, 439–442.
- Staiger, M., Pietak, A., Huadmai, J., & Dias, G. (2006). Magnesium and its alloys as orthopedic biomaterials: a review. *Biomaterials*, 27, 1728–1734.
- Suganuma, J., & Alexandar, H. (1993). Biological response of intramedullary bone to poly(L-lactic acid). *Journal of Applied Biomaterials*, 4, 13–27.
- Tang, H., Yu, D., Luo, Y., & Wang, F. (2012). Preparation and characterization of HA microflowers coating on AZ31 magnesium alloy by micro-arc oxidation and a solution treatment. *Applied Surface Science*, 264, 816–822.

- Therin, M., Christel, P., Li, S., Garreau, H., & Vert, M. (1992). In vivo degradation of massive poly(alpha hydroxy acids): validation of in vitro findings. *Biomaterials*, 13, 594–600.
- Vert, M., Christel, P., Chabot, F., & Leray, J. (1984). In G. W. Hastings & P. Ducheyne (Eds.), *Macromolecular materials* (pp. 119–142). Boca Raton, FL: CRC Press.
- Vert, M., Li, S., & Garreau, H. (1992). New insights on the degradation of bioresorbable polymeric devices base on latic and glycolic acids. *Clinical Materials*, 10, 3–8.
- Walter, R., & Kannan, M. B. (2011). In-vitro degradation behaviour of WE54 magnesium alloy in simulated body fluid. *Materials Letters*, 65, 748–750.
- Wang, J., He, Y., Maitz, M. F., Collins, B., Xiong, K., Guo, L., et al. (2013). A surface-eroding poly(1,3-trimethylene carbonate) coating for fully biodegradable magnesium-based stent applications: toward better biofunction, biodegradation and biocompatibility. *Acta Biomaterialia*, 9, 8678–8689.
- Wang, H., Zhao, C., Chen, Y., Li, J., & Zhang, X. (2012). Electrochemical property and in vitro degradation of DCPD-PCL composite coating on the biodegradable Mg-Zn alloy. *Materials Letters*, 68, 435–438.
- Witte, F., Fischer, J., Nellesen, J., Vogt, C., Vogt, J., Donath, T., et al. (2010). In vivo corrosion and corrosion protection of magnesium alloy LAE442. *Acta Biomaterialia*, 6, 1792–1799.
- Witte, F., Hort, N., Vogt, C., Cohen, S., Kainer, K., Willumeit, R., et al. (2008). Degradable biomaterials based on magnesium corrosion. *Current Opinion in Solid State and Materials Science*, 12, 63–72.
- Witte, F., Kaese, V., Haferkamp, H., Switzer, E., Meyer-Lindenberg, A., Wirth, C. J., et al. (2005). In vivo corrosion of four magnesium alloys and the associated bone response. *Biomaterials*, 26, 3557–3563.
- Wong, H. M., Yeung, K. W. K., Lam, K. O., Tam, V., Chu, P. K., Luk, K. D. K., et al. (2010). A biodegradable polymer-based coating to control the performance of magnesium alloy orthopaedic implants. *Biomaterials*, 31, 2084–2096.
- Wu, G., Ibrahim, J. M., & Chu, P. K. (2013). Surface design of biodegradable magnesium alloys – a review. *Surface and Coatings Technology*, 233, 2–12.
- Xu, L., & Yamamoto, A. (2012a). Characteristics and cytocompatibility of biodegradable polymer film on magnesium by spin coating. *Colloids and Surfaces B: Biointerfaces*, 93, 67–74.
- Xu, L., & Yamamoto, A. (2012b). In vitro degradation of biodegradable polymer-coated magnesium under cell culture condition. *Applied Surface Science*, 258, 6353–6358.
- Zhang, Z., Kuijjer, R., Bulstra, S. K., Grijpma, D. W., & Feijen, J. (2006). The in vivo and in vitro degradation behavior of poly(trimethylene carbonate). *Biomaterials*, 27, 1741–1748.
- Zhang, Y., Venugopal, J. R., El-Turki, A., Ramakrishna, S., Su, B., & Lim, C. T. (2008). Electrospun biomimetic nanocomposite nanofibers of hydroxyapatite/chitosan for bone tissue engineering. *Biomaterials*, 29, 4314–4322.
- Zheng, Y. F., Gu, X. N., & Witte, F. (2014). Biodegradable metals. *Materials Science and Engineering R*, 77, 1–34.

Cold-spray coatings on magnesium and its alloys

14

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14.1 Introduction

The high strength-to-weight ratio of magnesium (Mg) alloys has attracted increasing interest in almost all areas where weight reduction is critical, because replacement of heavy metals, such as steels and even titanium and aluminum, with lighter Mg alloys can significantly reduce the weight. However, wider application of Mg alloys has been limited due to the poor wear and corrosion resistance (An *et al.*, 2007; Song & Atrens, 2007; Song, Atrens, & Dargusch, 1998), particularly for outdoor applications, where exposure to a harsh environment is unavoidable. In addition, in recent years magnesium and its alloys have attracted attention for biomedical applications, because they are biocompatible and have mechanical properties close to those of human bones. The implants made of Mg alloys have potential to function as osteoconductive and biodegradable substitutes in load-bearing applications in the field of hard-tissue engineering. However, the effects of corrosion and degradation in the physiological environment of the human body have prevented their actual applications to date.

One of the most effective approaches to overcoming these limitations of Mg alloys is surface treatment, which can provide Mg alloys with sufficient protection from both wear and corrosion without altering the bulk microstructure and properties of the substrate (Champagne, 2008; Deforce, Eden, & Pickering, 2009; Spencer & Zhang, 2008, 2009; Villafuerte & Zheng, 2007). Although there are a large number of surface treatment techniques available for Mg alloys (Gray & Luan, 2002), such as conversion coating, electroplating, physical/chemical vapour deposition, anodizing and thermal spray, cold spray (CS) is an emerging coating technology that enables deposition of dense, high-quality coatings, showing promise for applications to surface coating of thermally sensitive substrates, such as aluminum and magnesium alloys (Bae, Xiong, Kumar, Kang, & Lee, 2008). For example, it has been demonstrated that cold-spray coatings of oxidation-sensitive materials such as MCrAlY (Stoltenhoff, Kreye, & Richter, 2002), Ti (Segall, Papyrin, Conway, & Shapiro, 1998) and Cu (Kang & Kang, 2003) show similar oxygen contents with their respective powder feedstock. Ajdelsztajn and co-workers (Ajdelsztajn, Jodoin, Richer, Sansoucy, & Lavernia, 2006) have also successfully produced Fe-based amorphous coatings using cold spraying.

Due to the low operation temperature, CS surface coating is produced through severe plastic deformation of particles at solid state (Dzhurinskiy, Maeva, Leshchinsky, & Maev, 2012; Han, Birbilis, Spencer, Zhang, & Muddle, 2010; Moy, Cairney, Ranzi, Jahedi, & Ringer, 2010). Compared with the thermal-spray technologies, such as plasma spray (PS), twin wire-arc spray (TWA) and high-velocity oxygen-fuel spray (HVOF), which involve either partially or fully melting particles during deposition, CS has the advantage in minimizing the thermal defects, such as oxidation, porosity and phase transformation (Sova, Kosarev, Papyrin, & Smurov, 2010; Wang, Birbilis, Huang, & Zhang, 2013; Cizek, Kovarik, Siegl, Khor, & Dlouhy, 2013; Kang, Won, Bae, HA, & Lee, 2012; Kang, Park, Bae, & Lee, 2012; Rolland et al., 2011). Therefore, CS is particularly suitable for coating and substrate materials that are sensitive to heat or oxidation, for example, aluminum and magnesium. In this chapter, the current research progress in cold-spray coating on Mg alloys is reviewed.

14.2 Current challenges of magnesium applications

14.2.1 Poor corrosion and wear resistance

One of the main challenges in the use of magnesium alloys, particularly for outdoor applications, is their poor corrosion resistance. Due to a lower electrode potential among the engineering materials, magnesium and its alloys are extremely susceptible to galvanic corrosion (Song & Atrens, 1999), which can cause severe pitting, resulting in decreased mechanical stability and an unattractive appearance. The major step for improving the corrosion resistance of magnesium alloys was the introduction of high-purity alloys. But this adds significant extra costs. Alloying can improve the general corrosion behaviour, but it does not change galvanic corrosion problems if magnesium is in contact with another metal and an electrolyte. In addition, Mg alloys are relatively soft, which leads to low wear resistance. Although the addition of high alloying elements may improve the wear behaviour, it not only adds more cost but also increases the overall weight of components, losing the advantage of this type of alloy. Therefore, surface treatment is a more effective approach to overcoming these drawbacks (Champagne, 2008; Deforce et al., 2009; Spencer & Zhang, 2008, 2009; Villafuerte & Zheng, 2007).

14.2.2 Available surface treatment techniques for magnesium alloys

The currently available surface treatment techniques for Mg alloys include electrochemical plating (Brown, 1994; Dennis, Wan, & Wake, 1985; Zhu, Li, & Shan, 2006), conversion coatings (Gonzalez-Nunez et al., 1995; Gonzalez-Nunez, Skeldon, Thompson, & Karimzadeh, 1999; Montemor, Simoes, & Carmezim, 2007; Rudd, Breslin, & Mansfeld, 2000), anodizing (Barton, 1998; Sharma, Uma Rani, & Giri, 1997) and organic coatings such as polymer-based paints (Mori, Hirahara, Oishi, &

Kumagai, 2000). One of the major issues associated with electroplating is the use of toxic chemicals, such as chromium compounds, cyanide compounds and fluoride compounds, in both the pre-treatment and plating processes. Environmental contamination is of concern. In addition, it is also a challenge to produce uniform, dense and pore-free coating on Mg alloy substrate using electroplating because of the narrow window for operating conditions and the difference in the surface chemistry of various magnesium alloys. Conversion coating is currently widely used in industry. However, as it uses chromate, environmental contamination is also a major concern not only during the coating process but also during service, as the coating contains leachable hexavalent chromium. A number of chromate-free conversion coating techniques are being developed, but all of them are still in their infancy. Similar to electrochemical plating, the difference in surface chemistry of various magnesium alloys represents another challenge in development of uniform, pore-free coatings. In addition, conversion coatings do not provide adequate corrosion and wear protection from harsh service conditions when used alone.

Anodizing is a commercially used surface coating technique for magnesium alloys. This process is technologically more complex than electroplating or conversion coating but is less sensitive to the type of alloy being coated. The coating produced by anodizing is porous ceramic like -coating. This type of coating has good paint-adhesion characteristics and excellent wear and abrasion resistance. However, without proper sealing of the pores, the coating is not adequate to protect substrate from corrosion attack. Furthermore, anodizing coating is generally brittle ceramic, insulating material and is not appropriate for load-bearing applications or applications where electrical conductivity is required. In many service environments involving mechanical wear, such coatings offer unsatisfactory performance. Recently, metal powder coating has been considered as an option for surface protection of light metals (Karthikeyan, 2006). Such coating may be tailored to improve corrosion resistance, wear resistance, surface electrical and thermal conductivity (Stoltenhoff, Borchers, Gartner, & Kreye, 2006) or as an inter-layer to bond two incompatible materials.

Another commercially used coating process is thermal spray, which is suitable for hard-facing and repair of worn surfaces (Hardwicke & Lau, 2013). High-strength metals or even ceramic powders can be used as coating materials and deposited on metal substrate. Two of the most popular thermal-spray techniques are plasma arc (PA) powder spray and high-velocity oxygen-fuel (HVOF) powder spray (Ibrahim & Berndt, 2007). Both offer good integrity and bond strength as compared to other thermal-spray processes. The PA spray process uses coating materials in the form of powders, which are heated and melted in a plasma heat source that is capable of producing an extremely high-temperature plasma. After spraying of the coating materials in liquid form on the substrate, liquid materials solidify on the substrate, producing a protective coating. The major advantage of the PA process is that oxidation and decomposition of materials during spraying is minimized because the high gas velocity produced by the plasma results in a short residence time for the powder in the thermal environment. The plasma process also provides a controlled atmosphere for melting and transport of the coating material, limiting oxidation. The HVOF process uses fuel combustion through a nozzle to create a supersonic stream

of high-temperature gas. Entrained in this gas is a mixture of powder and process gas, leading to full or partial melting of the powder (Richer, Yandouzi, Beauvais, & Jodoin, 2010). The gas stream with entrained liquid droplets is accelerated toward the substrate, and the coating solidifies immediately upon impact with the substrate. The major drawback of thermal spray, including both PA and HVOF processes, is the high residual stress in the coatings due to the shrinkage during rapid solidification on the substrate (cold substrate absorbs heat rapidly once the hot liquid is sprayed on it), phase transformations and oxidization of the material during the subsequent cooling. In addition, as the high-temperature liquid is involved in thermal spray, it is not really suitable for low melting temperature and thermal-sensitive metals, such as Al, Mg and Ti alloys.

As the most recent coating technology, CS has the potential to overcome the problems associated with currently available ones. Because of the low thermal influence, CS has been used to deposit thermal-sensitive materials such as nanocrystalline and amorphous materials (Ajdelsztajn et al., 2006; Richer, Jodoin, & Ajdelsztajn, 2006), as well as oxygen-sensitive materials such as aluminium and titanium (Kim, Watanabe, Mitsuishi, Iakoubovskii, & Kuroda, 2009; Wang, Spencer, Birbilis, & Zhang, 2010). Therefore, cold spraying is one of the optimal surface treatment processes to coat high-quality metal and metal-based composite coatings on magnesium alloys, without significant alerting the microstructure and properties of and the substrates.

14.3 Applications of cold-spray coatings on magnesium alloys

14.3.1 Corrosion protection coatings

Aluminium is one of the popular spray materials used in the CS process due to the light weight, good ductility and good corrosion resistance compared to Mg alloys. Cold-sprayed Al coatings on Mg alloy substrate performed as well as cast bulk Al in terms of corrosion behaviour. Spencer and Zhang's work (Spencer and Zhang, 2008) showed that porosity within the cold-sprayed Al coatings on Mg alloy substrates dramatically accelerates the corrosion rate when immersed in a 5% NaCl water solution due to galvanic coupling. Therefore, it is very critical to control the porosity in CS coatings. It is known that addition of hard ceramic particles into cold-sprayed coatings not only improves the hardness and wear resistance but also increases the density of the coatings (Irissou, Legoux, Arsenault, & Moreau, 2007). Coatings with improved density can accordingly improve corrosion resistance due to reduced porosity, provided there is no galvanic coupling between the ceramic particles and the coating matrix material. The corrosion behaviour of cold-sprayed pure Al and 6061 aluminium alloy-based Al_2O_3 particle-reinforced composite coatings on AZ91E substrates was investigated by means of salt spray testing and electrochemical testing (Spencer, Fabijanic, & Zhang, 2009). The optical microstructure of the 6061Al coatings with various fractions of Al_2O_3 on an AZ91E

substrate is shown in Figure 14.1. Although 1–1.5% porosity can be observed within the 6061Al coating, composite coatings with Al_2O_3 show dense and uniform distribution.

The coatings' responses to linear polarization are shown in Figure 14.2, plotted with respect to the standard hydrogen electrode potential. It can be seen that the volume fraction of Al_2O_3 has no obvious effect on the polarization behaviour. The corrosion current density is roughly the same in each case, as is the pitting potential, where the behaviour transitions from passive to stable pitting; the passivation potential range and the potential above which pitting occurs are indicated in the figure. Of interest is the 'noise' in the passive region of the polarization curves, which is interpreted physically as the formation of metastable pits that are subsequently repassivated. It is generally considered that post-spray heat treatment can further improve the corrosion resistance of CS coatings because the formation of a diffusion layer during heat treatment process increases the bond strength at interface, making delamination more difficult. In addition, the heat treatment process also relaxes the residual stress that built up at the coating interface during spraying, again making delamination more unlikely. However, comparing the coating's responses to polarization as shown in Figure 14.2(b) with those in Figure 14.2(a), post-spray heat treatment at 400 °C for 2 h did not change the corrosion behaviours of the CS coatings.

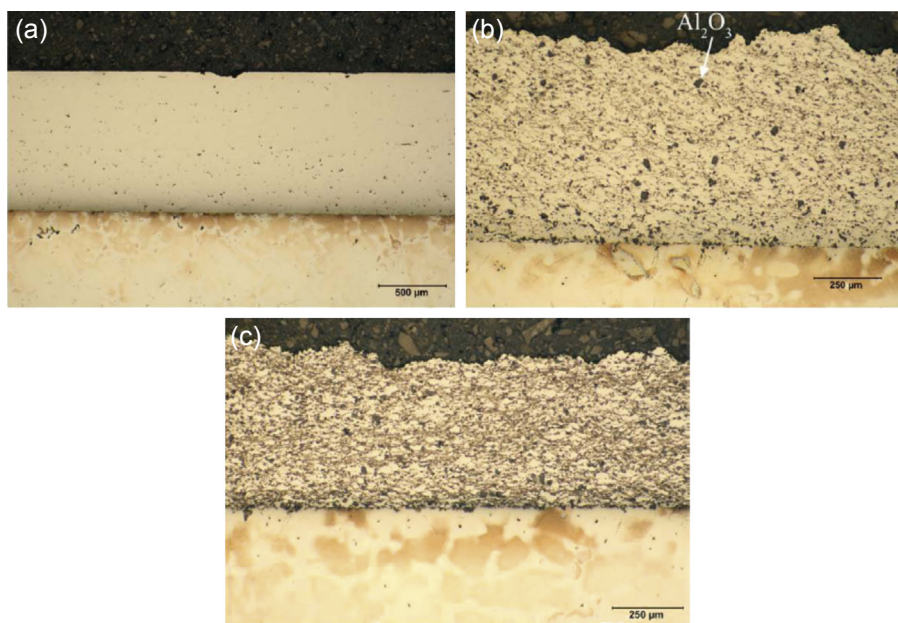


Figure 14.1 (a) Optical micrograph of CS 6061Al coating on an AZ91 substrate. (b) Optical micrograph of CS 6061Al–25% Al_2O_3 coating on an AZ91 substrate. The black phase is the Al_2O_3 . (c) Optical micrograph of CS 6061Al–75% Al_2O_3 coating on an AZ91 substrate. The black phase is the Al_2O_3 .

From Ref. [Spencer et al. \(2009\)](#).

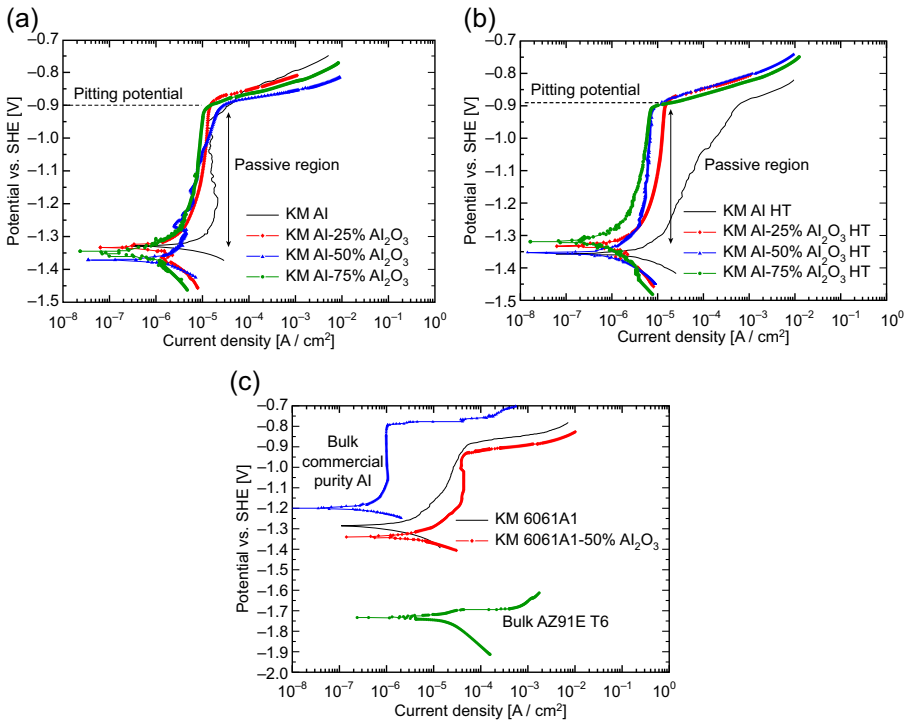


Figure 14.2 (a) Linear polarization behaviour of Al coatings, as sprayed. (b) Linear polarization behaviour of Al coatings, after a heat treatment of 400 °C for 2 h. (c) Linear polarization behaviour of 6061Al coatings as sprayed, compared to bulk Al and AZ91E T6. Ref. [Spencer et al. \(2009\)](#).

Furthermore, a comparison of the polarization response of the coatings with bulk commercial purity Al and the AZ91E substrate material, as shown in [Figure 14.2\(c\)](#), indicates that the polarization behaviours of the CS coatings are similar to those of bulk commercial purity Al but are much better than that of the T6 AZ91E alloy.

As one of the most common stainless metals, stainless steel coating is naturally considered as an effective approach to protecting the Mg alloy substrate from corrosion. Fortunately, cold spray is a powerful tool for producing such coating. Similarly to the Al alloy coatings, control of the coating porosity is the key determinant of the behaviour of the coating. The effect of porosity and thickness of CS 316L stainless steel coatings (on T6 AZ91E alloy substrate) on corrosion behaviour was investigated by Spencer and co-workers through incorporating the mixture of fine and coarse particles ([Spencer & Zhang, 2011](#)). The coatings sprayed with $-22\text{ }\mu\text{m}$ stainless steel powder were used as the reference case, and the average porosity was measured to be $\sim 4\text{ vol. \%}$. The anodic polarization behaviour of the coatings of different thickness is shown in [Figure 14.3](#). The behaviour of the coatings is compared to that of the

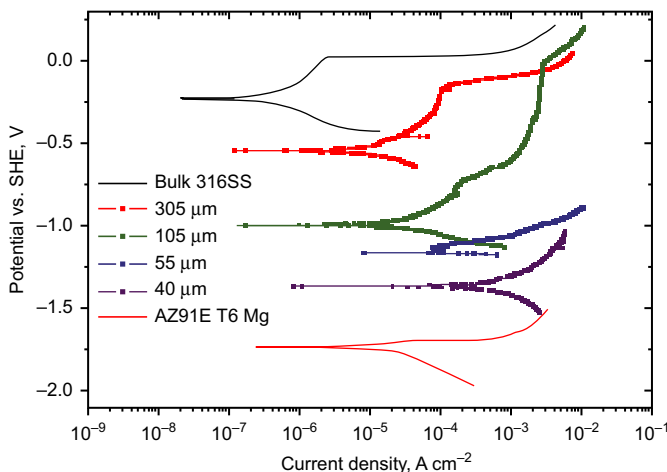


Figure 14.3 Anodic polarization behaviour of 316SS cold-spray coatings of different thickness, compared to bulk type 316SS and AZ91E T6 substrate material. Coatings were sprayed using $-22\ \mu\text{m}$ powder.

Ref. [Spencer & Zhang \(2011\)](#).

substrate material and to that of bulk 316L stainless steel. The curves follow a trend from behaviour dominated by the substrate, gradually approaching the behaviour of bulk stainless steel as the coating thickness increases. The coating with a thickness of $105\ \mu\text{m}$ marks a transition from non-passivation, through a series of different mixed potentials, to passivation behaviour at a thickness of $305\ \mu\text{m}$. In cases where a coating is not fully dense or subject to localized attack, this could be a useful means of determining the critical thickness necessary to avoid the formation of interconnected porosity from the coating surface to the substrate via localized attack.

[Figure 14.4](#) shows secondary electron micrographs of the cross-sections of CS stainless steel coatings on pure Mg produced using different particle sizes. The coating cold-sprayed with $-22\ \mu\text{m}$ particle size shows a significant level of porosity ($\sim 4\%$ in volume) throughout the coating. While the coating sprayed using a $-10\ \mu\text{m}$ particle size is almost fully dense through the bulk, it contains a porous region just below the topmost surface, as shown in [Figure 14.5\(a\)](#). When sprayed using $-5\ \mu\text{m}$ powder, the porosity is significantly reduced, as illustrated in [Figure 14.5\(b\)](#). The coatings sprayed using 50% volume fraction $-22\ \mu\text{m}$ powder and 50% $-5\ \mu\text{m}$ powder have a heterogeneous structure. There are discontinuous regions of porosity concentrated in the region between successive layers, while the material within the layers is nearly fully dense. Finally, the coating sprayed using a 50/50 vol. % mixture of the $-10\ \mu\text{m}$ and $-5\ \mu\text{m}$ powders shown in [Figure 14.4e](#) has a uniformly high density.

At the same thickness, anodic polarization behaviour of these coatings is shown in [Figure 14.6](#). The coating cold-sprayed using the $-22\ \mu\text{m}$ powder has the lowest noble potential and the highest corrosion current density. Reducing the powder size to $-10\ \mu\text{m}$ significantly lowers the current density. Coatings sprayed with a mixture

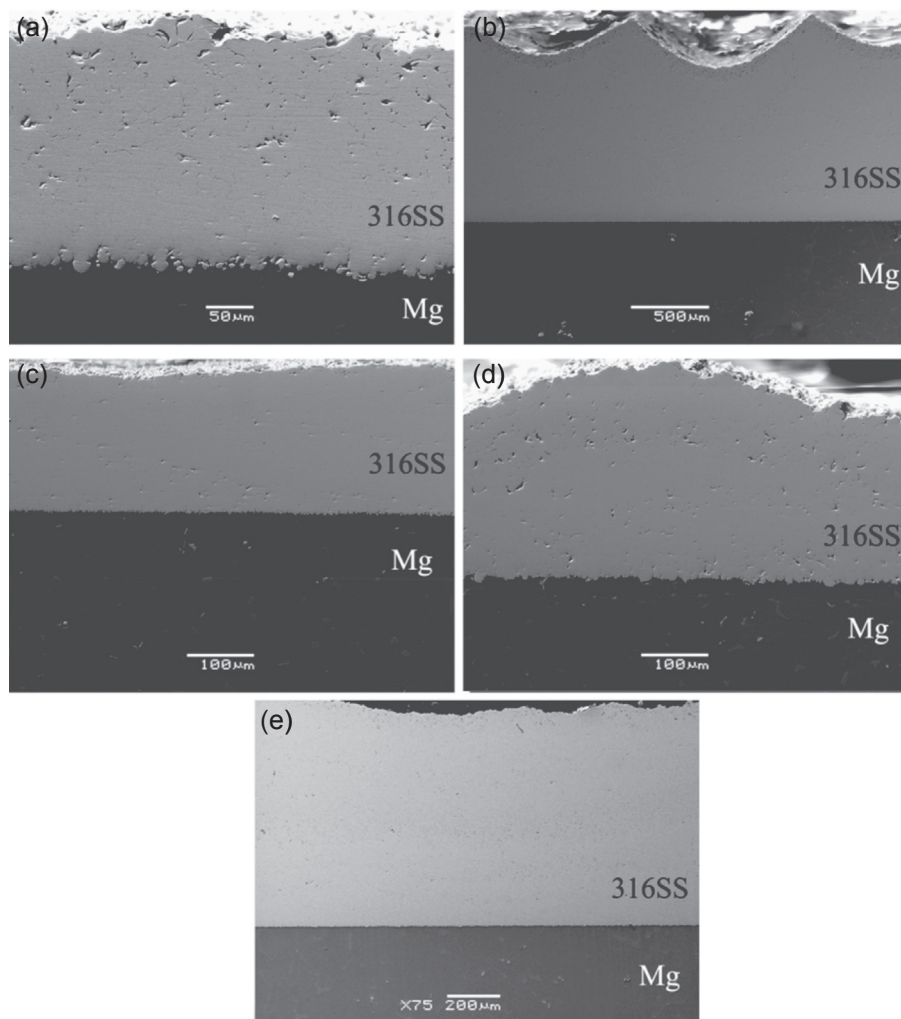


Figure 14.4 Secondary electron micrographs of 316L stainless steel coatings sprayed using (a) $-22\ \mu\text{m}$ powder; (b) $-10\ \mu\text{m}$ powder; (c) $-5\ \mu\text{m}$ powder; (d) a mixture of 50% $-5\ \mu\text{m}$ and 50% $-22\ \mu\text{m}$ powders and (e) a mixture of 50% $-5\ \mu\text{m}$ and 50% $-10\ \mu\text{m}$ powders. From Ref. [Spencer & Zhang \(2011\)](#).

of $-22\ \mu\text{m}$ powder and $-10\ \mu\text{m}$ powder exhibit corrosion behaviour closest to that of the bulk stainless steel. In addition to the effect of porosity, the polarization behaviour also depends on the quality of interparticle bonding. Coatings with higher interparticle bonding normally correspond to less localized attack ([Spencer & Zhang, 2011](#)). As a summary, [Spencer & Zhang \(2011\)](#) considered that cold-sprayed coating produced using the $(-22\ \mu\text{m} \pm 10\ \mu\text{m})$ powder mixture has corrosion resistance that is close to the bulk 316L stainless steel.

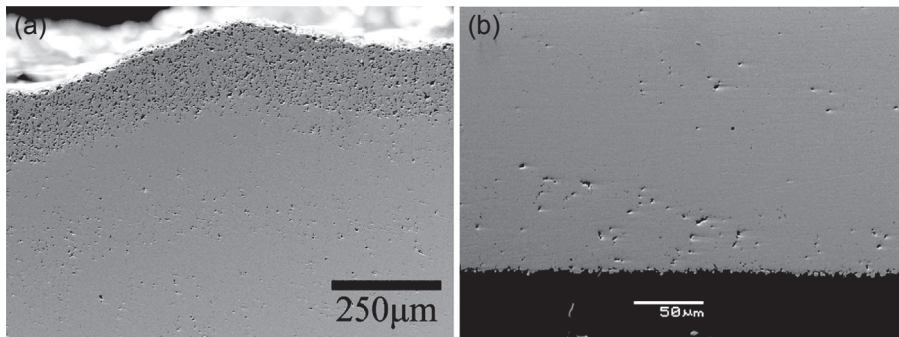


Figure 14.5 High-magnification images of coating porosity in coatings sprayed (a) using $-10\ \mu\text{m}$ powder and (b) using $-5\ \mu\text{m}$ powder.

From Ref. [Spencer & Zhang \(2011\)](#).

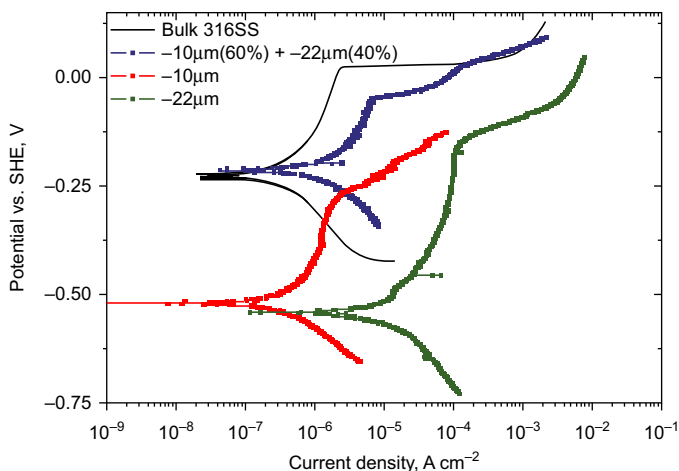


Figure 14.6 Anodic polarization behaviour of 316SS cold-spray coatings using different powder particles sizes.

From Ref. [Spencer & Zhang \(2011\)](#).

14.3.2 Wear protection coatings

During cold-spray deposition, the high kinetic energy of particles results in significant plastic strain through impact, which produces substantial work hardening. As a result, in most cases cold-sprayed coatings are expected to have a significantly higher hardness than the equivalent annealed bulk material ([Borchers, Gartner, Stoltenhoff, Assadi, & Kreye, 2003](#); [Klinkov, Kosarev, & Rein, 2005](#); [Stoltenhoff et al., 2002](#)). [Figure 14.7](#) shows the micro-hardness of the cold-spray coatings as a function of Al_2O_3 content ([Spencer et al., 2009](#)). With increasing Al_2O_3 additions in the Al and 6061Al coatings, micro-hardness increases slightly for both the as-sprayed and heat-treated coatings. The decrease in hardness after post-spray heat treatment is attributed

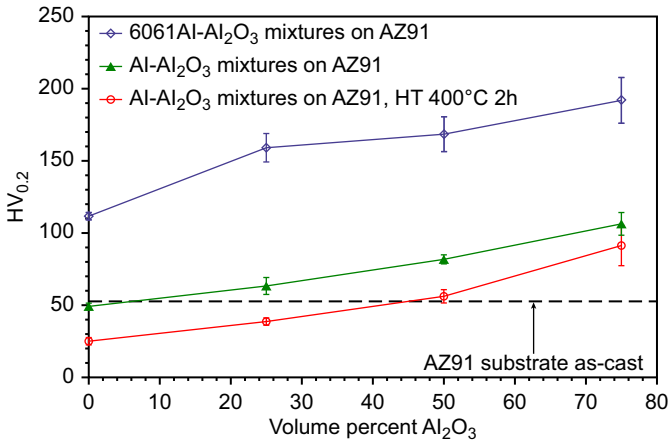


Figure 14.7 Vickers microhardness of cold spray as a function of Al₂O₃ content. From Ref. [Spencer et al. \(2009\)](#).

to the annealing effect of impact-induced cold work in the coating. Unlike microhardness, increasing the Al₂O₃ addition level has significant effect on the wear resistance, as shown in [Figure 14.8](#). The wear rate of the Al–25% Al₂O₃ and 50% Al₂O₃ composite coatings is reduced by roughly two decades compared with the pure Al coating. The latter has a very close wear rate to the bulk T6 AZ91E alloy, the 356.0 Al alloy and the Al–12 wt.% Si alloy under the same testing conditions. With the addition of 75% Al₂O₃ the wear rate decreases by over five decades.

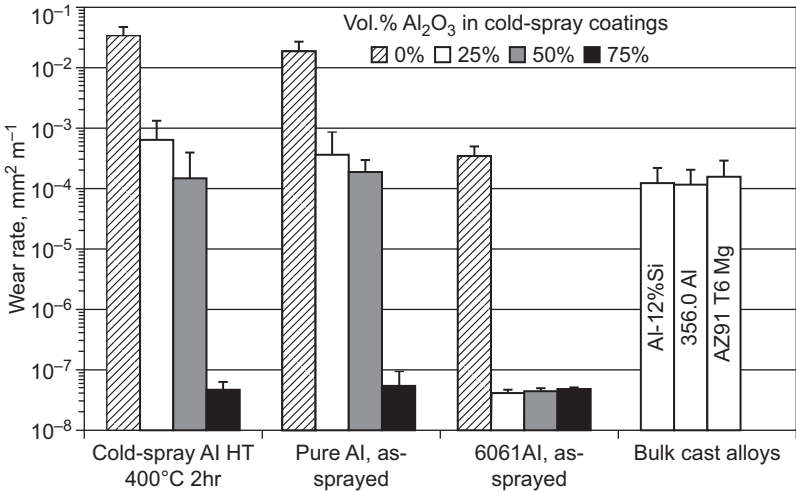


Figure 14.8 Wear volume per unit wear distance of coatings compared to bulk alloys. Ref. [Spencer et al. \(2009\)](#).

Spencer and co-workers also investigated the worn surface of the cold-sprayed coatings (Spencer et al., 2009). Typical wear tracks observed in scanning electron microscopy from the cold-sprayed pure Al and Al–Al₂O₃ composite coatings are shown in Figure 14.9. The smeared appearance of the worn surface of CS pure Al coating characterizes adhesive wear, with profiles showing evidence of ploughing and extrusion of the worn material outside the wear track. The wear track from the Al–50% Al₂O₃ cold-sprayed composite coating is shown in Figure 14.9(b). In addition to the adhesive wear feature that is similar to that of pure Al coating, there is also some evidence of abrasive wear. The worn surface of the Al–75% Al₂O₃ coating as shown in Figure 14.9(c) is characterized by regular markings and lack of smearing, which are characteristic of abrasive wear. This indicates that a transition from adhesive to abrasive wear occurred with increasing Al₂O₃ additions in the cold-spray coatings. This transition is also reflected by a significant reduction in wear rate of the coatings. When 6061Al was used as the matrix material, a similar transition in wear behaviour with increase in the Al₂O₃ content was also observed, but this transition occurred at 25 vol.% Al₂O₃ in the source powder (~12% deposited). Furthermore, increasing the Al₂O₃ content did not lead to any further drop in the wear rate in the 6061Al

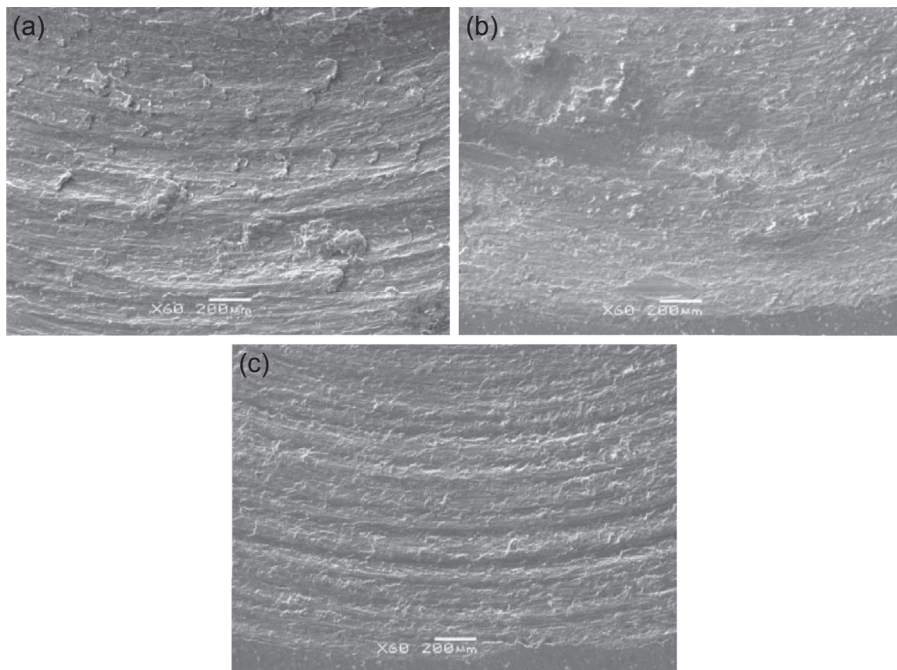


Figure 14.9 (a) SEM micrograph of the wear track on a cold-sprayed Al coating. (b) SEM micrograph of the wear track on a cold-sprayed Al–50% Al₂O₃ coating. (c) SEM micrograph of the wear track on a cold-sprayed Al–75% Al₂O₃ coating. From Ref. Spencer et al. (2009).

coatings, as shown in [Figure 14.8](#). This implies that the higher strength of 6061Al coatings enables a transition from adhesive to abrasive wear with a smaller fraction of Al_2O_3 . Thus, to achieve the same wear resistance, less volume fraction of reinforcement is required in cold-sprayed composite coatings.

14.3.3 Functional coating for biomedical applications

The good biocompatibility and similar mechanical properties of Mg alloys to human bones are attractive for biomedical applications. The density of magnesium is 1.74 g/cm^3 , which is slightly lower than natural bone ($1.8\text{--}2.1 \text{ g/cm}^3$). The elastic modulus of pure Mg is 45 GPa, which is compatible to the elastic modulus of human bone, which varies from 40 to 57 GPa ([Feng & Han, 2010](#); [Razavi, Fathi, & Meratian, 2010](#)). Hence, applications of Mg to hard-tissue engineering would greatly reduce the possibility of stress shielding, preventing bone resorption. It is particularly promising in development of biodegradable orthopaedic implants ([Li, Gao, & Wang, 2004](#)). However, the major disadvantage of Mg alloys is the high corrosion rate in the human body, which becomes the bottleneck problem limiting the medical application of Mg-based implants due to the electrolytic aqueous environment of the chloride-rich body fluid (pH ranges between 7.4 and 7.6). There are also two serious consequences of the rapid corrosion rate of Mg implants. The first is the rapid evolution of subcutaneous hydrogen gas bubbles, which are produced at too high a rate for the surrounding tissues to handle ([Wen et al., 2001](#)). These bubbles usually appear within the first week after surgery and can easily be treated by drawing off the gas using a subcutaneous needle. The second consequence of the high corrosion rate is the loss of mechanical integrity of the Mg implant being used in the load-bearing application. The rapid decrease in mechanical properties resulting from exposure to the body fluid environment means that the implant is unable to provide the necessary support for the healing bone tissue. Generally, the implant would be expected to maintain its mechanical integrity for 12 to 18 weeks while the healing process takes place and then slowly degrade while natural bone tissues replace the implant ([Witte et al., 2005](#)). As a consequence, surface modifications and treatments can play the critical role in governing the degradation rate of the implant made of Mg alloys.

Numerous surface modification techniques, such as chemical conversion coatings ([Yang, Cui, & Lee, 2011](#)), anodization ([Hiromoto et al., 2008](#)) and thermal-spray coatings ([Zeng, Dietzel, Witte, Hort, & Blawert, 2008](#)), have been developed to change the surface characteristics of magnesium alloys as biomaterials. Compared to other technologies, cold spray can produce dense and thick metallic or composite coatings on magnesium alloys at low temperatures, as discussed above. However, the disadvantage of using an Al coating on the AZ91D Mg alloy substrate for a possible biomedical implant application is the negative effect of Al^{3+} ions being released into the surrounding tissues during subsequent corrosion. To the authors' knowledge, there is little information on evaluation of cold-sprayed coatings for biomedical applications. [Qiu, Zhang, and Grondahl \(2013\)](#) produced Ti and Ti–HA composite coatings on Ti substrate using cold-spray technology. During the deposition Al powders were incorporated as porogen, which were consequently removed through alkaline leaching.

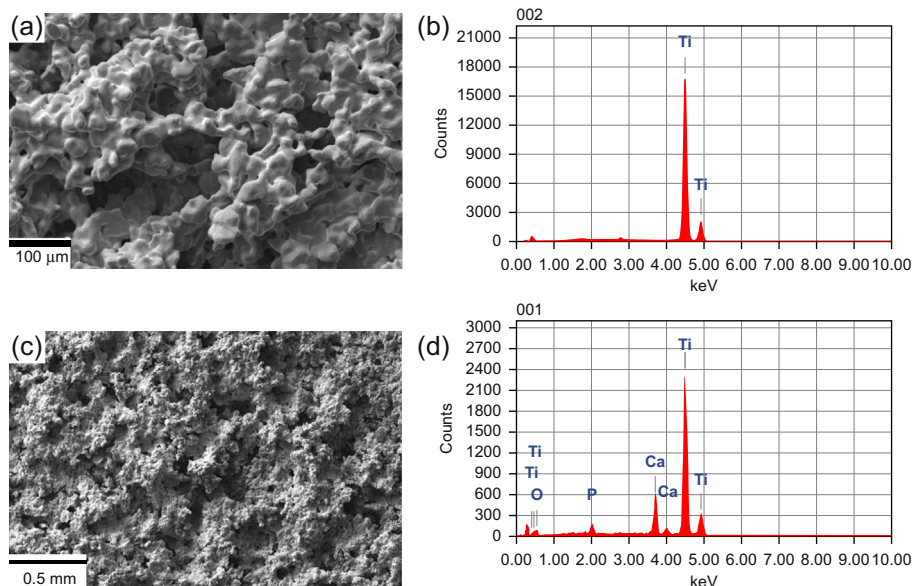


Figure 14.10 Porous coatings. (a) Surface profile of HA-free porous coating in SEM. (b) EDX spectrum from the coating surface of (a). (c) Surface profile of HA-CR-10 porous coating in SEM. (d) EDX spectrum from the coating surface of (c).
From Ref. [Qiu et al. \(2013\)](#).

Figure 14.10 shows the secondary electron images and EDX (energy dispersive X-ray diffraction) spectrum collected from the coating surface. The structure is composed of fused Ti particles of approximately 30 μm and clearly displays a porous morphology. The pore size ranges from 50 to 150 μm and the macroporosity is approximately 50% for pure Ti coatings (**Figure 14.10a**) and 60% for Ti-HA (HA-CR-10) composite coating (**Figure 14.10c**).

The elemental mapping of Ti, Ca, P and O on the coating surface is shown in **Figure 14.11**. It can be clearly seen that the Ca, P and O areas are overlapped, indicating the presence of HA particles embedded in the coating. Importantly, it can be observed from the elemental maps that the HA particles are uniformly distributed across the sample surface.

The surface morphology and the chemical composition of the HA-free and HA-containing coatings before and after 2 weeks' immersion in SBF was evaluated by [Qiu et al. \(2013\)](#) in SEM/EDX. The HA-free coating displayed no noticeable morphological or topological change after immersion in SBF. In contrast, the surface morphology of the HA-containing sample changed from large smooth fused particles before SBF immersion (**Figure 14.12a**) to large amounts of clusters of a fine precipitate after immersion (**Figure 14.12b**). The elemental mapping of these fine precipitate clusters (arrowed in the figure) in a local area of the HA-containing coating after SBF immersion is also shown in **Figure 14.12**. It can be clearly seen that the precipitate clusters are overlapped with high concentration regions of Ca, P and O. The efficiency

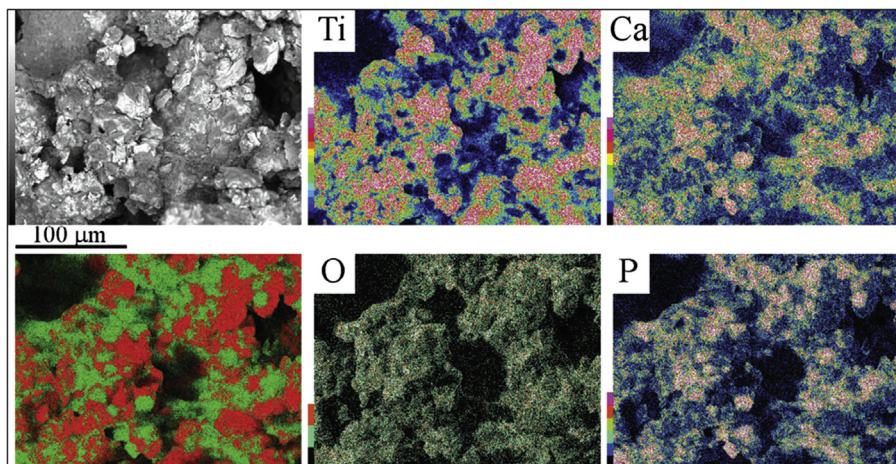


Figure 14.11 Elemental mapping on the coating surface of an HA-CR-10 as-annealed. Top left: back scatter electron image. Bottom left: overlapped map with Ti (red) and Ca (green). (Ti), (Ca), (O) and (P) show individual elemental maps for elements indicated.

Ref. [Qiu et al. \(2013\)](#).

of Ca^{2+} mineralization (decrease in Ca^{2+} concentration of SBF after 2 weeks' immersion per volume of the coating) of different coatings is summarized in [Figure 14.13](#). It was found that all HA-containing coatings exhibited an order of magnitude higher efficiency than the HA-free coating. This is consistent with the SEM observations. In addition, the efficiency of the HA-containing coatings increased significantly ($p < 0.01$) when changing the HA content from 5 to 10 vol. % and displayed an efficiency proportional to the vol. % in the feedstock powder. These findings suggest that the HA particles are exposed to the coating surface of the HA/Ti skeleton where they can act as nucleation sites.

It is important to evaluate if the coatings release any constituents that are cytotoxic to cells responsible for bone remodelling. In [Figure 14.14](#), TCP (tissue culture plastic) showed significantly higher cell viability at both time-points (0 and 48 h). However, viable cells were detected on all surfaces after 48 h at similar levels. This indicates that the coating samples are not cytotoxic. However, longer-term *in vitro* and *in vivo* studies are needed to further test the biocompatibility of the coatings and their effect on all the cell types present in the wound site.

14.4 Bonding mechanism of cold-sprayed coatings on magnesium and its alloys

Another major concern of surface coating is the adhesive strength between coating and substrate, which is controlled by the actual bonding mechanisms. Because the nature of cold spray is a process of powder particle consolidation, there are two types of

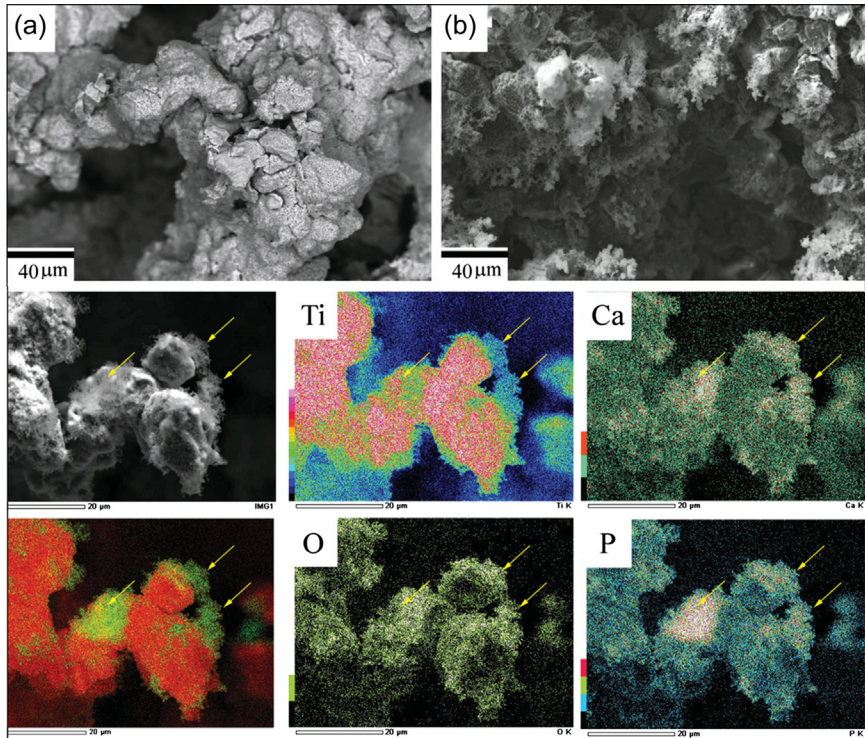


Figure 14.12 The surface morphology of HA-CR-10 porous coating in SEM (a) before and (b) after 2-week immersion in SBF. Middle left: secondary electron image of a local area in (b) with mineral nodules formed in SBF arrowed; bottom left: overlapped map of mineral nodules with Ti (red) and Ca (green). (Ti), (Ca), (O) and (P) show individual elemental maps for elements indicated of mineral nodules.

From Ref. [Qiu et al. \(2013\)](#).

interface existing in cold-sprayed coatings. One is the bonding between particles within the coating and another is the bonding between the coating and the substrate.

14.4.1 Bonding between particles within the coating

Aluminium is one of the popular spray materials in cold-spray processes due to the light weight and good ductility. A number of studies ([Balani, Agarwal, Seal, & Karthikeyan, 2005](#); [Borchers, Gartner, Stoltenhoff, Assadi, & Kreye, 2004](#); [Choi et al., 2007](#); [Van Steenkiste & Smith, 2004](#); [Van Steenkiste, Smith, & Teets, 2002](#); [Wang, Birbilis, & Zhang, 2011](#)) have been dedicated to revealing the microstructure of cold-sprayed aluminium coatings. Wang and Zhang ([Wang et al., 2011](#)) investigated the interfacial structure between particles within the CS pure Al coating. [Figure 14.15a](#) shows a backscattered electron image on the etched cross-section of Al deposition on Mg substrate. The spherical Al particles were elongated splats with clear particle boundaries, revealing severely plastic deformation. Some porosity

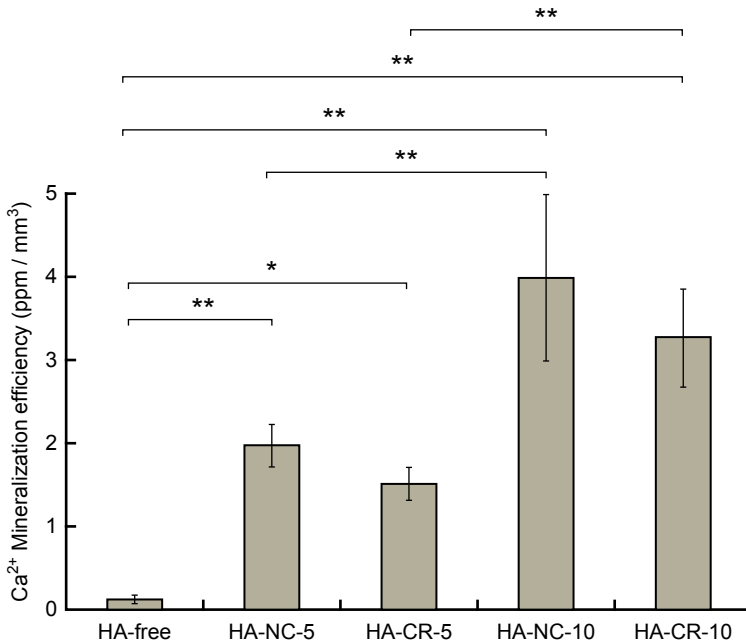


Figure 14.13 The efficiency of Ca^{2+} mineralization of different porous coating samples after 2-week immersion in SBF relative to coating volume. Statistical significance was evaluated with Tukey's multiple comparison tests. ** $p < 0.01$. * $p < 0.05$. Ref. Qiu et al. (2013).

can be observed within the coating, and this seems to be exaggerated by the attack of etching. Image analysis of the unetched samples shows the porosity within 1.5 vol.% (Wang et al., 2010). Figure 14.15b shows a typical TEM micrograph of the interface between Al particles within the coating. Severe plastic deformation resulting from the impact between particles led to microstructure variation near the particle boundary, which can be characterized in terms of the following features. In region A, the tangled structure with interlaced thin strips of material is observed. Thus the particle boundaries are mechanically interlocked to each other. These strips can be explained from the melt jetting due to the adiabatic shear instability on the surface of particles by high-velocity impact. Therefore, the extent of mechanical interlocking depends on the particle size and velocity, which influence the surface contact area and kinetic energy generated during the impact process. In region B, the lamellar microbands (MBs) presented with elongated sub-micron grains are observed. The formation of MBs resulted from the crystallographic slip on a dominant slip system and then propagated through multiple- or cross-slip events because of stress concentration, accompanied with the produce of a large amount of dislocations between the slip planes.

Figure 14.16a shows the details of the lamellar structure at the particle interface (which correspond to region B in Figure 14.15b). The elongated sub-micron grains within the MBs contain dislocation cells that are separated by dense dislocation walls

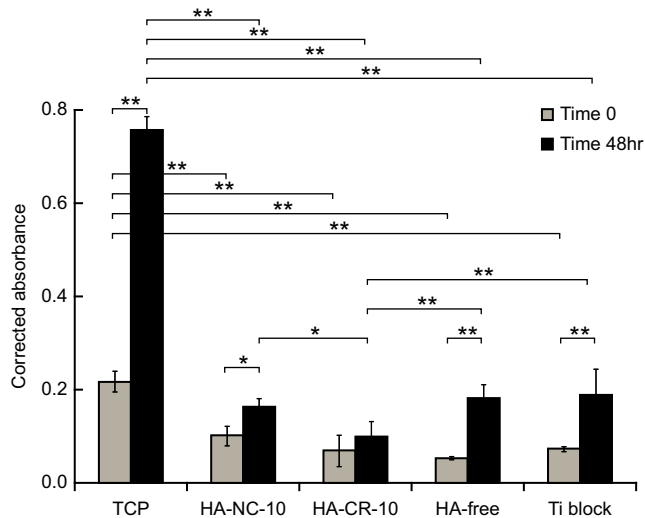


Figure 14.14 Absorbance of MTT reagent for selected coating samples at the zero and 48-h time points. Pure Ti and TCP served as control samples. Statistical significance was evaluated with Tukey's multiple comparison tests. ** $p < 0.01$. * $p < 0.05$. Ref. [Qiu et al. \(2013\)](#).

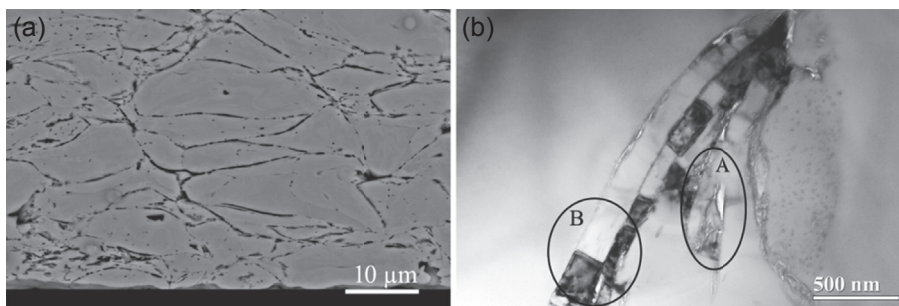


Figure 14.15 (a) Backscatter SEM micrograph of the etched cross-section. (b) TEM micrograph of the particle boundary. From Ref. [Wang et al. \(2011\)](#).

(DDWs). After annihilation of the DDWs, subgrains with clear boundaries can be found in the circled area. Inside, these subgrains are almost free of dislocations. In addition, dislocation arrays (DAs) piling up at subgrain boundaries are also observed. It is believed that the dislocation arrays were formed during subsequent deformation after the formation of the subgrains. The grain refinement effect on the particle boundaries can be further confirmed by the microstructure with associated selected area diffraction pattern, as shown in [Figure 14.16b](#). The mechanism of grain refinement related to CS is similar to that in SMAT (surface mechanical attrition treatment) process ([Wu et al., 2002](#)). The formation of dislocation tangles and high-density

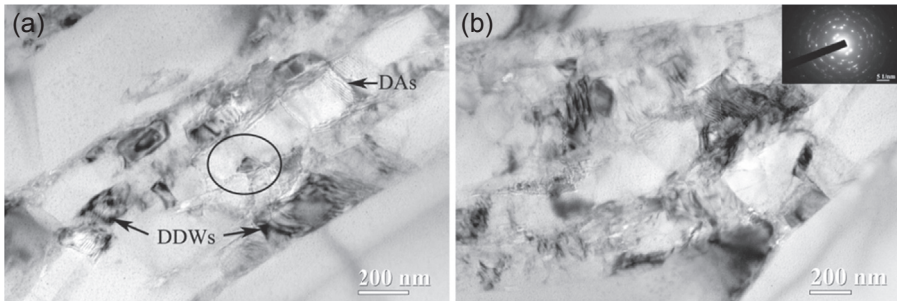


Figure 14.16 TEM micrographs of (a) elongated microbands with dense dislocation walls, dislocation arrays and newly formed subgrain and (b) refined sub-micron grains with selected area diffraction pattern.

From Ref. Wang et al. (2011).

dislocation walls within the coarse grains occur via severe plastic deformation at high strain rate, dividing grains into smaller ones separated by dislocations walls. The rotation of subgrains to accommodate further deformation leads to the formation of highly misoriented sub-micrometer scaled grains.

14.4.2 Bonding between coating and substrate

The deposition of CS coatings begins with collisions between particles and substrate surface. Upon impact with substrate, particles undergo severe plastic deformation and become flattened splats (King, Zahiri, & Jahedi, 2008, 2009). Localized deformation characteristics that concentrate at the outer layer of particles are revealed through microstructure analysis along the particle boundaries in cold-sprayed aluminium coatings (Kang, Park, et al., 2012; Wang et al., 2011). On the other hand, the particle impact also has a significant penning effect on the surface of substrate and induces the subsequent deformation of substrate surface. Through observing the interfacial microstructure, previous studies have revealed intimate contact between cold-sprayed coatings and substrate (Price, Shipway, McCartney, Calla, & Zhang, 2007), and along the interface there is also mixing of coating and substrate materials due to the jetting of materials resulting from the impact of particles, which accounts for the mechanical interlocking (Hussain, McCartney, Shipway, & Zhang, 2009; Schmidt, Gartner, Assadi, & Kreye, 2006). Therefore, the interfacial reaction between particles and substrate plays an important role in facilitating successful adhesion of coating materials.

14.4.2.1 Deformation at particle–substrate interface

Wang and co-workers (Wang, Birbilis, & Zhang, 2014) used a fast sweep-spray method to deposit individual Al particles on the surface of Mg substrate. Thus, the interfacial structure between individual particles and the substrate can be investigated in TEM (Wang, Qiu, Xiong, Birbilis, & Zhang, 2014). Figure 14.17a shows how a

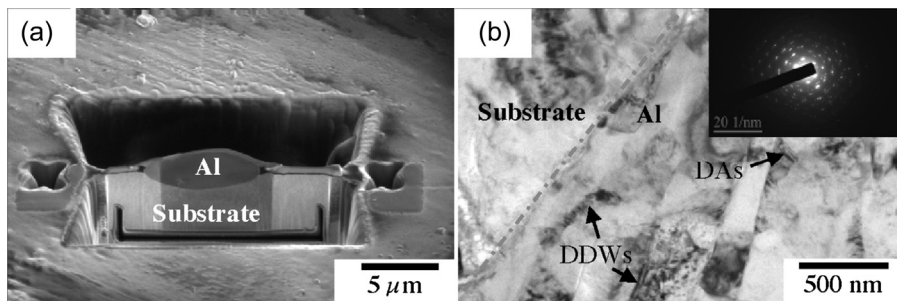


Figure 14.17 (a) TEM membrane prepared by focused ion beam (FIB) milling. (b) Typical conventional TEM microstructure along the interface (indicated by the red dashed line) of cold-sprayed Al and the AZ91 substrate; the insert diffraction pattern is from the Al side adjacent to the interface.

From Ref. Wang, Qiu, et al. (2014).

TEM specimen containing deformed Al particles and the Mg substrate was prepared using focused ion beam (FIB) milling. A typical TEM micrograph showing the microstructure across the particle–substrate interface (indicated by the red dashed line) is shown in Figure 14.17b. On the Al side, severe plastic deformation resulted in the formation of micro-bands that contain dense dislocation walls (DDWs) and dislocation arrays (DAs). The insert selected area diffraction pattern taken from the adjacent area to the interface indicates the formation of sub-grains in the localized area. The grain refinement mechanism is attributed to dislocation movements (double slip and/or cross-slip) that divide coarse grains into smaller ones (Canova, Fressengeas, Molinari, & Kocs, 1988; Chang, Kelly, Shi, & Zhang, 2012).

14.4.2.2 High-resolution TEM observation of the interfacial structure between Al coating and Mg substrate

When a spherical Al particle impacts on the substrate, the first contact point between the centre of the particle and the substrate surface underwent normal compressive strain. As the strain increased, the contact area was enlarged along the direction that is normal to the impact direction. Therefore, with the increase of radial distance from the central contact region, the tangential (shear) force dominates in the contact area (Stronge, 2000). Thus, the contact area of the Al particle and the Mg substrate after CS is divided into two regions, as shown in Figure 14.18. The compression region is at the central contact area and the shear region (or intermixing zone) is at the peripheral area.

At the central contact area of the particle–substrate, the compressive stress results in the surface deformation of the substrate, which contains two distinct regions, as marked in Figure 14.19a. Region I is close to the interface, and the corresponding selected area diffraction pattern (Figure 14.19b) indicates the formation of refined grains. Region II is further from the interface, with much less plastic deformation, and the selected area diffraction pattern (Figure 14.19c) shows no appreciable grain refinement. To reveal the details of bonding structure at the central area of the particle/substrate interface, Figure 14.19d shows a typical HRTEM image taken

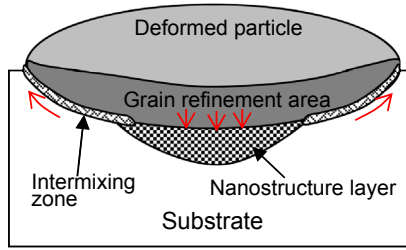


Figure 14.18 Schematic illustration of microstructure characteristics of deformed Al particle onto Mg alloy substrate.

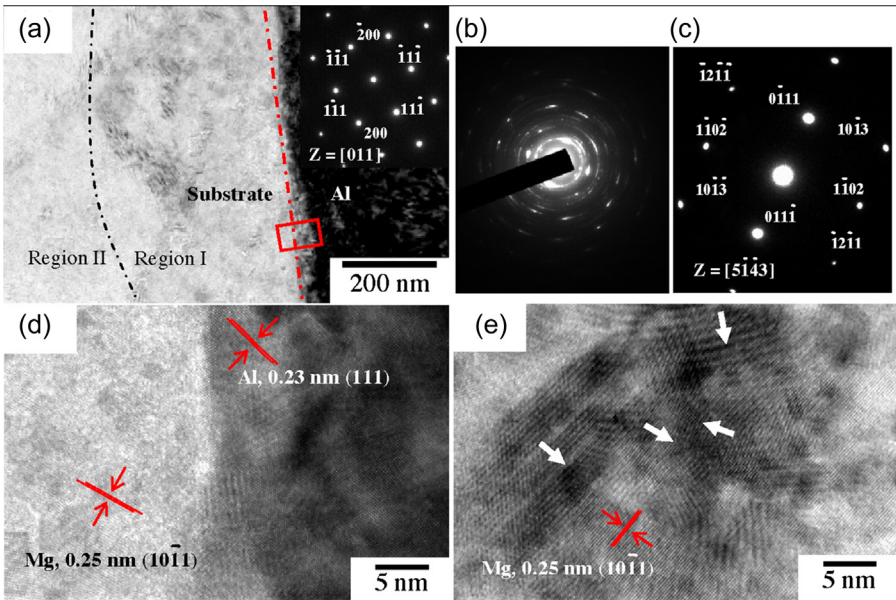


Figure 14.19 (a) Microstructure at the central region of the particle/substrate interface (indicated by the red dashed line). The insert diffraction pattern is from the recrystallized Al grain. Selected area diffraction patterns (b) and (c) are taken from Regions I and II in (a) marked by the black dashed line. (d) HRTEM image of the red boxed region in (a). (e) HRTEM image of the nanocrystalline in Region I. From Ref. [Wang and Qiu et al. \(2014\)](#).

from the area specified by the red rectangle in [Figure 14.19a](#). Since there was almost no relative movement between the particle and the substrate during the impact, a less disrupted intimate lattice matching between the Al particle and the Mg substrate across the interface was observed, indicating the formation of atomic (metallurgical) bonding. The HRTEM image of the refined grain in Region I is characterized in [Figure 14.19e](#). Typical deformation features of distorted lattice planes (pointed by white arrows) can be observed. TEM examination revealed that this nanostructured region in the

substrate was right underneath the centre of the deformed Al particle with depth of $\sim 300\text{--}500\text{ nm}$, and the radial dimension close to the interface was $\sim 100\text{--}250\text{ nm}$. The different deformation behaviour between an Al particle and AZ91 substrate at high strain rate is attributed to their distinct crystal structure and stacking fault energy (SFE). Since Al is a typical FCC metal with 12 slip systems and a high SFE of 200 mJ/mm^2 (Borchers et al., 2004), the formation of dense dislocation walls (DDWs) and dislocation arrays (DAs) is responsible for the grain refinement. Mg has an HCP crystal structure with only three slip systems and a lower SFE of 78 mJ/mm^2 (Sun, Shi, Zhang, & Lu, 2008), indicating that the deformation and accumulation of a high density of dislocations is more difficult. Thus, twinning and dynamic recrystallization is considered to dominate the deformation process and grain refinement of Mg (Sun, Shi, Zhang, & Lu, 2007). This is similar to the refinement phenomenon occurring during surface mechanical attrition treatment (SMAT), which is a surface nanocrystallization technique based on the impact of hard balls on the substrate surface (Sun et al., 2008; Tong, Tao, Wang, Lu, & Lu, 2003).

Wang, Qiu, et al. (2014) also verified that the shear stress governs the deformation of metal in the peripheral region. Figure 14.20a is a typical HRTEM image taken at this interface. An intermixing zone containing both particle and substrate metal is observed along the interface, as marked by the two red dashed lines.

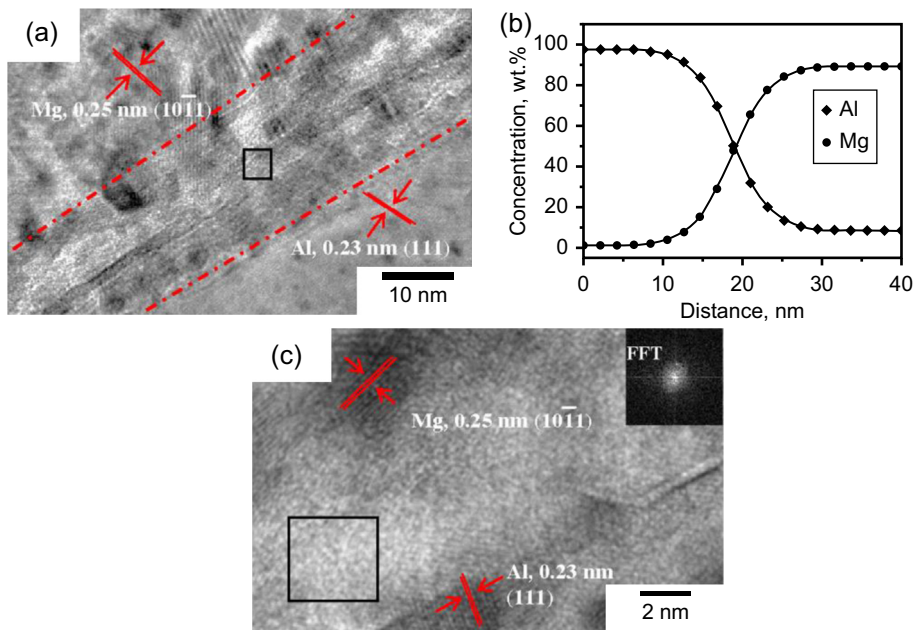


Figure 14.20 (a) Typical HRTEM image at the periphery region of particle/substrate interface. (b) EDX results showing the elemental distribution across the interface. (c) Enlarged HRTEM image of the boxed area in (a). The insert is a selected area FFT pattern. From Ref. Wang and Qiu et al. (2014).

zone (Figure 14.20b) verifies the co-existence of Al and Mg. The width of such mixing zones is ~ 20 nm, which is consistent with the microstructural observation in Figure 14.20a. Previous FEM results (Schmidt et al., 2006) suggested that the temperature rising at the interface due to the friction could be substantial upon high-speed impact during cold spray; therefore there is a possibility of atomic diffusion across the interface. The diffusion distance d can be calculated based on the relation $d \approx \sqrt{Dt}$, where D is the diffusion coefficient and t is the diffusion time. The inter-diffusion coefficient between Al and Mg at a solid state is in the order of 10^{-16} to 10^{-13} m²/s at 250–600 °C (Fujita, Horita, & Langdon, 2002). Considering a typical impact time of ~ 50 ns (Assadi, Gartner, Stoltenhoff, & Kreye, 2003), the calculated distance is less than 0.1 nm. Therefore, the ~ 20 nm width intermixing zone cannot be rationalized through atomic inter-diffusion alone. In addition, in Wang and Qiu's work (Wang, Qiu, et al., 2014), no traces of melting, such as flow features or diffuse boundaries, were observed. Thus, the intermixing zone did not result from metal melting and re-solidification. It is reasonable to consider that the disruption of the lattice arrangement induced by the severe shear plastic deformation at high strain rate in the peripheral region may have created a high concentration of vacancies and interstitials within an extremely short time (Ovid'ko, 1993), contributing to the formation of atomic intermixing within the outmost layers of the particles and the substrate. Another possible reason for such an intermixing zone is attributed to the formation of interfacial rolls-up and vortices resulting from interfacial instability under high-velocity particle impact (Grujicic, Saylor, Beasley, Derosset, & Helfrich, 2003). Figure 14.20c is an enlarged HRTEM image of the rectangular region identified in Figure 14.20a. The FFT pattern of the selected area marked by the rectangle in Figure 14.20c shows a diffuse halo rather than lattice fringes, indicating the inclusion of a small amorphous zone with a radius of ~ 3 nm surrounded by random Al and Mg lattices. Molecular dynamic (MD) simulations (Szulfarska, Nakano, & Vashishta, 2005) have predicted that in severe plastically deformed materials when applied strain within a finite region is over a critical level, mechanically driven structural disordering can be triggered as an accommodation mechanism to release the extremely high local stress and mediate plasticity. A rapid increase in the interface area is, therefore, beneficial for amorphization (Perepezko & Hebert, 2002). Xiong et al. (Xiong, Kang, Bae, Yoon, & Lee, 2008; Xiong, Xiong, Yoon, Bae, & Lee, 2011) also reported the formation of an amorphous zone at the interface of cold-sprayed Al/Al in a similar size, which corresponds with this observation. Therefore, it appears that dynamic amorphization may be necessary to accommodate the rapid intermixing of materials at high-strain rate shear deformation.

14.5 Future work and potential industrial application of cold-spray coatings on magnesium alloys

In summary, taking advantage of low-temperature operation process, cold-spray technology can produce dense metallic or metal-based composite coatings with high bonding strength to the magnesium alloy substrate. Bonding along the interfaces of

particle–particle and particle–substrate is attributed to severe plastic deformation induced by high-energy impact. Providing the comprehensive understanding of bonding mechanisms of cold-sprayed coatings, a wide range of coating materials can be developed to widen the applications of magnesium alloys to automotive, aerospace and biomedical industries. The ability of cold spray in surface modification of magnesium alloys provides the opportunity to design a specific coating to overcome the problems, such as corrosion and wear. For biomedical applications, further *in vitro* and *in vivo* experimental studies are required to evaluate the long-term reactions of cold-sprayed coatings with human bones and tissues.

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References

- Ajdelsztajn, L., Jodoin, B., Richer, P., Sansoucy, E., & Lavernia, E. J. (2006). Cold gas dynamic spraying of iron-base amorphous alloy. *The Journal of Thermal Spray Technology*, 15, 495–500.
- An, J., Li, R. G., Chen, C. M., Xu, Y., Chen, X., Guo, Z. X., et al. (2007). Comparative studies on wear behaviour between as cast AZ91 and Mg97Zn1Y2 magnesium alloys. *Journal of Materials Science and Technology*, 23, 1208–1214.
- Assadi, H., Gartner, F., Stoltenhoff, T., & Kreye, H. (2003). Bonding mechanism in cold gas spraying. *Acta Materialia*, 51, 4379–4394.
- Bae, G., Xiong, Y., Kumar, S., Kang, K., & Lee, C. (2008). General aspects of interface bonding in kinetic sprayed coatings. *Acta Materialia*, 56, 4858–4868.
- Balani, K., Agarwal, A., Seal, S., & Karthikeyan, J. (2005). Transmission electron microscopy of cold sprayed 1100 aluminum coating. *Scripta Materialia*, 53, 845–850.
- Barton, T. F. (1998). *Anodization of magnesium and magnesium based alloys*. USA patent application 595,354.
- Borchers, C., Gartner, F., Stoltenhoff, T., Assadi, H., & Kreye, H. (2003). Microstructural and macroscopic properties of cold sprayed copper coatings. *Journal of Applied Physics*, 93, 10064–10070.
- Borchers, C., Gartner, F., Stoltenhoff, T., Assadi, H., & Kreye, H. (2004). Microstructural bonding features of cold sprayed face centered cubic metals. *Journal of Applied Physics*, 96, 4288–4292.
- Brown, L. (1994). UK company leads the way in magnesium plating. *Finish*, 18, 22–23.
- Canova, G. R., Fressengeas, C., Molinari, A., & Kocs, U. F. (1988). Effect of rate sensitivity on slip system activity and lattice rotation. *Acta Metallurgica*, 36, 1961–1970.
- Champagne, V. K. (2008). The repair of magnesium rotorcraft components by cold spray. *Journal of Failure Analysis and Prevention*, 8, 164–175.
- Chang, H. W., Kelly, P. M., Shi, Y. N., & Zhang, M. X. (2012). Thermal stability of nanocrystallized surface produced by surface mechanical attrition treatment in aluminum alloys. *Surface and Coatings Technology*, 206, 3970–3980.

- Choi, W. B., Li, L., Luzin, V., Neiser, R., Gnaupel-herold, T., Prask, H. J., et al. (2007). Integrated characterization of cold sprayed aluminum coatings. *Acta Materialia*, 55, 857–866.
- Cizek, J., Kovarik, O., Siegl, J., Khor, K. A., & Dlouhy, I. (2013). Influence of plasma and cold spray deposited Ti Layers on high-cycle fatigue properties of Ti6Al4V substrates. *Surface and Coatings Technology*, 217, 23–33.
- Deforce, B., Eden, T. J., & Pickering, H. W. (2009). Cold-sprayed aluminum coatings for magnesium aircraft components. *Materials Performance*, 48, 40–44.
- Dennis, J. K., Wan, M. K. Y. Y., & Wake, S. (1985). Plating on magnesium alloy die castings - the role of fluoride and pH. *Transactions of the Institute of Metal Finishing*, 63, 81–84.
- Dzhurinskiy, D., Maeva, E., Leshchinsky, E., & Maev, R. (2012). Corrosion protection of light alloys using low pressure cold spray. *The Journal of Thermal Spray Technology*, 1–10.
- Feng, A., & Han, Y. (2010). The microstructure, mechanical and corrosion properties of calcium polyphosphate reinforced ZK60A magnesium alloy composites. *The Journal of Alloys and Compounds*, 504, 585–593.
- Fujita, T., Horita, Z., & Langdon, T. G. (2002). Characteristics of diffusion in Al-Mg alloys with ultrafine grain sizes. *Philosophical Magazine A*, 82, 2249–2262.
- Gonzalez-Nunez, M. A., Nunez-Lopez, C. A., Skeldon, P., Thompson, G. E., Karimzadeh, H., Lyon, P., et al. (1995). A non-chromate conversion coating for magnesium alloys and magnesium-based metal matrix composites. *Corrosion Science*, 37, 1763–1772.
- Gonzalez-Nunez, M. A., Skeldon, P., Thompson, G. E., & Karimzadeh, H. (1999). Kinetics of the development of a nonchromate conversion coating for magnesium alloys and magnesium-based metal matrix composites. *Corrosion*, 55, 1136–1143.
- Gray, J. E., & Luan, B. (2002). Protective coatings on magnesium and its alloys - a critical review. *The Journal of Alloys and Compounds*, 336, 88–113.
- Grujicic, M., Saylor, J. R., Beasley, D. E., Derosset, W. S., & Helfritsch, D. (2003). Computational analysis of the interfacial bonding between feed-powder particles and the substrate in the cold-gas dynamic-spray process. *Applied Surface Science*, 219, 211–227.
- Han, Y. K., Biribilis, N., Spencer, K., Zhang, M. X., & Muddle, B. C. (2010). Investigation of Cu coatings deposited by kinetic metallization. *Materials Characterization*, 61, 1167–1186.
- Hardwicke, C., & Lau, Y.-C. (2013). Advances in thermal spray coatings for gas turbines and energy generation: a review. *The Journal of Thermal Spray Technology*, 1–13.
- Hiromoto, S., Shishido, T., Yamamoto, A., Maruyama, N., Somekawa, H., & Mukai, T. (2008). Precipitation control of calcium phosphate on pure magnesium by anodization. *Corrosion Science*, 50, 2906–2913.
- Hussain, T., McCartney, D., Shipway, P., & Zhang, D. (2009). Bonding mechanisms in cold spraying: the contributions of metallurgical and mechanical components. *The Journal of Thermal Spray Technology*, 18, 364–379.
- Ibrahim, A., & Berndt, C. C. (2007). Fatigue and deformation of HVOF sprayed WC-Co coatings and hard chrome plating. *Materials Science and Engineering A*, 456, 114–119.
- Irissou, E., Legoux, J.-G., Arsenault, B., & Moreau, C. (2007). Investigation of al-Al₂O₃ cold spray coating formation and properties. *The Journal of Thermal Spray Technology*, 16, 661–668.
- Kang, H.-K., & Kang, S. B. (2003). Tungsten/copper composite deposits produced by a cold spray. *Scripta Materialia*, 49, 1169–1174.
- Kang, K., Park, H., Bae, G., & Lee, C. (2012). Microstructure and texture of Al coating during kinetic spraying and heat treatment. *The Journal of Materials Science*, 47, 4053–4061.
- Kang, K., Won, J., Bae, G., HA, S., & Lee, C. (2012). Interfacial bonding and microstructural evolution of Al in kinetic spraying. *The Journal of Materials Science*, 47, 4649–4659.

- Karthikeyan, J. (2006). Evolution of cold spray technology. *Advanced Materials and Processes*, 164, 12–13.
- Kim, K., Watanabe, M., Mitsuishi, K., Iakoubovskii, K., & Kuroda, S. (2009). Impact bonding and rebounding between kinetically sprayed titanium particle and steel substrate revealed by high-resolution electron microscopy. *Journal of Physics D: Applied Physics*, 42, 5.
- King, P. C., Zahiri, S. H., & Jahedi, M. (2008). Focused ion beam micro-dissection of cold-sprayed particles. *Acta Materialia*, 56, 5617–5626.
- King, P. C., Zahiri, S. H., & Jahedi, M. (2009). Microstructural development in cold sprayed copper. In *Proceedings of the International Thermal Spray Conference, Las Vegas, NV* (pp. 243–248).
- Klinkov, S. V., Kosarev, V. F., & Rein, M. (2005). Cold spray deposition: significance of particle impact phenomena. *Aerospace Science and Technology*, 9, 582–591.
- Li, L., Gao, J., & Wang, Y. (2004). Evaluation of cyto-toxicity and corrosion behavior of alkali-heat-treated magnesium in simulated body fluid. *Surface and Coatings Technology*, 185, 92–98.
- Montemor, M. F., Simoes, A. M., & Carmezim, M. J. (2007). Characterization of rare-earth conversion films formed on the AZ31 magnesium alloy and its relation with corrosion protection. *Applied Surface Science*, 253, 6922–6931.
- Mori, K., Hirahara, H., Oishi, Y., & Kumagai, N. (2000). Polymer plating of 2-dioctylamino-1,3,5-triazine-4,6-dithiol to magnesium alloys. *Electrochemical and Solid-State Letters*, 3, 546–549.
- Moy, C. K. S., Cairney, J., Ranzi, G., Jahedi, M., & Ringer, S. P. (2010). Investigating the microstructure and composition of cold gas-dynamic spray (CGDS) Ti powder deposited on Al 6063 substrate. *Surface and Coatings Technology*, 204, 3739–3749.
- Ovid'ko, I. A. (1993). Dislocations, amorphization and plastic deformation in quasi-crystalline materials. *Materials Science and Engineering A*, 163, 67–72.
- Perepezko, J., & Hebert, R. (2002). Amorphous aluminum alloys—synthesis and stability. *Journal of the Minerals, Metals and Materials Society*, 54, 34–39.
- Price, T., Shipway, P., McCartney, D., Calla, E., & Zhang, D. (2007). A method for characterizing the degree of inter-particle bond formation in cold sprayed coatings. *The Journal of Thermal Spray Technology*, 16, 566–570.
- Qiu, D., Zhang, M., & Grondahl, L. (2013). A novel composite porous coating approach for bioactive titanium-based orthopedic implants. *Journal of Biomedical Materials Research Part A*, 101, 862–872.
- Razavi, M., Fathi, M. H., & Meratian, M. (2010). Microstructure, mechanical properties and bio-corrosion evaluation of biodegradable AZ91-FA nanocomposites for biomedical applications. *Materials Science and Engineering: A*, 527, 6938–6944.
- Richer, P., Jodoin, B., & Ajdelsztajn, L. (2006). Substrate roughness and thickness effects on cold spray nanocrystalline Al–Mg coatings. *The Journal of Thermal Spray Technology*, 15, 246–254.
- Richer, P., Yandouzi, M., Beauvais, L., & Jodoin, B. (2010). Oxidation behaviour of CoNiCrAlY bond coats produced by plasma, HVOF and cold gas dynamic spraying. *Surface and Coatings Technology*, 204, 3962–3974.
- Rolland, G., Sallamand, P., Guipont, V., Jeandin, M., Boller, E., & Bourda, C. (2011). Laser-induced damage in cold-sprayed composite coatings. *Surface and Coatings Technology*, 205, 4915–4927.
- Rudd, A. L., Breslin, C. B., & Mansfeld, F. (2000). The corrosion protection afforded by rare earth conversion coatings applied to magnesium. *Corrosion Science*, 42, 275–288.

- Schmidt, T., Gartner, F., Assadi, H., & Kreye, H. (2006). Development of a generalized parameter window for cold spray deposition. *Acta Materialia*, 54, 729–742.
- Segall, A. E., Papyrin, A. N., Conway, J. C. J., & Shapiro, D. (1998). A cold gas spray process for enhancing titanium. *Journal of Metals*, 50, 52–54.
- Sharma, A. K., Uma Rani, R., & Giri, K. (1997). Studies on amortization of magnesium alloy for thermal control applications. *Metal Finishing*, 95, 43–51.
- Song, G. L., & Atrens, A. (1999). Corrosion mechanisms of magnesium alloys. *Advanced Engineering Materials*, 1, 11–33.
- Song, G. L., & Atrens, A. (2007). Recent insights into the mechanism of magnesium corrosion and research suggestions. *Advanced Engineering Materials*, 9, 177–183.
- Song, G. L., Atrens, A., & Dargusch, M. (1998). Influence of microstructure on the corrosion of diecast AZ91D. *Corrosion Science*, 41, 249–273.
- Sova, A., Kosarev, V., Papyrin, A., & Smurov, I. (2010). Effect of ceramic particle velocity on cold spray deposition of metal-ceramic coatings. *The Journal of Thermal Spray Technology*, 20, 285–291.
- Spencer, K., Fabijanic, D. M., & Zhang, M. X. (2009). The use of Al-Al₂O₃ cold spray coatings to improve the surface properties of magnesium alloys. *Surface and Coatings Technology*, 204, 336–344.
- Spencer, K., & Zhang, M.-X. (2008). The emergence of cold spray as a tool for surface modification. *Key Engineering Materials*, 384, 61–74.
- Spencer, K., & Zhang, M.-X. (2009). Heat treatment of cold spray coatings to form protective intermetallic layers. *Scripta Materialia*, 61, 44–47.
- Spencer, K., & Zhang, M.-X. (2011). Optimisation of stainless steel cold spray coatings using mixed particle size distributions. *Surface and Coatings Technology*, 205, 5135–5140.
- Stoltenhoff, T., Borchers, C., Gartner, F., & Kreye, H. (2006). Microstructures and key properties of cold-sprayed and thermally sprayed copper coatings. *Surface and Coatings Technology*, 200, 4947–4960.
- Stoltenhoff, T., Kreye, H., & Richter, H. (2002). An analysis of the cold spray process and its coatings. *The Journal of Thermal Spray Technology*, 11, 542–550.
- Stronge, W. J. (2000). *Impact mechanics*. New York, NY: Cambridge University.
- Sun, H. Q., Shi, Y. N., Zhang, M. X., & Lu, K. (2007). Plastic strain-induced grain refinement in the nanometer scale in a Mg alloy. *Acta Materialia*, 55, 975–982.
- Sun, H. Q., Shi, Y. N., Zhang, M. X., & Lu, K. (2008). Surface alloying of an Mg alloy subjected to surface mechanical attrition treatment. *Surface and Coatings Technology*, 202, 3947–3953.
- Szlufarska, I., Nakano, A., & Vashishta, P. (2005). A crossover in the mechanical response of nanocrystalline ceramics. *Science*, 309, 911–914.
- Tong, W. P., Tao, N. R., Wang, Z. B., Lu, J., & Lu, K. (2003). Nitriding iron at lower temperatures. *Science*, 299, 686–688.
- Van Steenkiste, T. H., & Smith, J. R. (2004). Evaluation of coatings produced via kinetic and cold spray processes. *The Journal of Thermal Spray Technology*, 13, 274–282.
- Van Steenkiste, T. H., Smith, J. R., & Teets, R. E. (2002). Aluminum coatings via kinetic spray with relatively large powder particles. *Surface and Coatings Technology*, 154, 237–252.
- Villafuerte, J., & Zheng, W. (2007). Corrosion protection of magnesium alloys by cold spray. *Advanced Materials & Processes*, 165, 53–54.
- Wang, Q., Biribilis, N., Huang, H., & Zhang, M.-X. (2013). Microstructure characterization and nanomechanics of cold sprayed pure Al and Al-Al₂O₃ composite coatings. *Surface and Coatings Technology*, 232(0), 216–223.
- Wang, Q., Biribilis, N., & Zhang, M.-X. (2011). Interfacial structure between particles in an aluminum deposit produced by cold spray. *Materials Letters*, 65, 1576–1578.

- Wang, Q., Birbilis, N., & Zhang, M.-X. (2014). Process optimisation of cold spray Al coating on AZ91 alloy. *Surface Engineering*, 30, 323–328.
- Wang, Q., Qiu, D., Xiong, Y., Birbilis, N., & Zhang, M.-X. (2014). High resolution microstructure characterization of the interface between cold sprayed Al coating and Mg alloy substrate. *Applied Surface Science*, 289, 366–369.
- Wang, Q., Spencer, K., Birbilis, N., & Zhang, M.-X. (2010). The influence of ceramic particles on bond strength of cold spray composite coatings on AZ91 alloy substrate. *Surface and Coatings Technology*, 205, 50–56.
- Wen, C. E., Mabuchi, M., Yamada, Y., Shimojima, K., Chino, Y., & Asahina, T. (2001). Processing of biocompatible porous Ti and Mg. *Scripta Materialia*, 45, 1147–1153.
- Witte, F., Kaese, V., Haferkamp, H., Switzer, E., Meyer-Lindenberg, A., Wirth, C. J., et al. (2005). In vivo corrosion of four magnesium alloys and the associated bone response. *Biomater*, 26, 3557–3563.
- Wu, X., Tao, N., Hong, Y., Xu, B., Lu, J., & Lu, K. (2002). Microstructure and evolution of mechanically-induced ultrafine grain in surface layer of AL-alloy subjected to USSP. *Acta Materialia*, 50, 2075–2084.
- Xiong, Y., Kang, K., Bae, G., Yoon, S., & Lee, C. (2008). Dynamic amorphization and recrystallization of metals in kinetic spray process. *Applied Physics Letters*, 92, 194101–194103.
- Xiong, Y., Xiong, X., Yoon, S., Bae, G., & Lee, C. (2011). Dependence of bonding mechanisms of cold sprayed coatings on strain-rate-induced non-equilibrium phase transformation. *The Journal of Thermal Spray Technology*, 20, 860–865.
- Yang, J., Cui, F., & Lee, I. (2011). Surface modifications of magnesium alloys for biomedical applications. *Annals of Biomedical Engineering*, 39, 1857–1871.
- Zeng, R., Dietzel, W., Witte, F., Hort, N., & Blawert, C. (2008). Progress and challenge for magnesium alloys as biomaterials. *Advanced Engineering Materials*, 10, B3–B14.
- Zhu, L., Li, W., & Shan, D. (2006). Effects of low temperature thermal treatment on zinc and/or tin plated coatings of AZ91D magnesium alloy. *Surface and Coatings Technology*, 201, 2768–2775.

Biocompatible strontium-phosphate and manganese-phosphate conversion coatings for magnesium and its alloys

15

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15.1 Introduction

Magnesium (Mg)-based alloys are promising biomaterial candidates, in particular for load-bearing orthopaedic implants, owing to their high mechanical strength, light weight and similar density and elastic modulus to bone, which can minimise the stress shielding effect (Staiger, Pietak, Huadmai, & Dias, 2006; Zeng, Dietzel, Witte, Hort, & Blawert, 2008). In addition, Mg implants degrade *in vivo* and the degradable products, containing beneficial Mg (II) cations, are eventually excreted with urine (Dziuba et al., 2013; Hermawan, Dubé, & Mantovani, 2010). This eliminates the need for a secondary surgery to remove the implant after fractures are healed and also avoids interface loosening and associated inflammation (Xu, Yu, Zhang, Pan, & Yang, 2007), which is a substantial advantage over other commodity metallic biomaterials, such as cobalt-chromium-molybdenum (Co-Cr-Mo) alloys, titanium (Ti) and its alloys and stainless steel 316L alloy (Kirkland, Lespagnol, Birbilis, & Staiger, 2010; Kirkland, Birbilis, & Staiger, 2012).

It is acknowledged that Mg (II) cations assist the growth of new bone tissues and shorten the fracture recovery process (Rude, 1998). Mg is, however, highly reactive (both chemically and electrochemically), and degrades rapidly upon exposure to neutral aqueous electrolytes including media containing chloride (Cl⁻) ions, such as human body fluid. The rapid degradation rate of Mg implants in the physiological system (pH 7.4–7.6, 37 °C) can lead to accumulation of subcutaneous hydrogen (H₂) gas, which at high levels can cause separation of tissue and tissue layers (Meyer-Lindenberg, Windhugen, & Witte, 2004; Song, 2007; Witte et al., 2005, 2006). Moreover, the high degradation rate is most deleterious in the period immediately following implantation (Wang, Wei, Gao, Hu, & Zhang, 2008). The excessive Mg (II) cations may lead to hyper-magnesemia (Rude & Singer, 1981), and the high pH deviation from the balanced neutral value in the human body inhibits the growth of osteoblasts and damages osteoclasts (Remennik, Bartsch, Willbold, Witte, &

Shechtman, 2011). Hence, an efficient control of the initial degradation is of paramount importance (Brar, Ball, Berglund, Allen, & Manuel, 2013; Kirkland et al., 2010).

Approaches for control of the degradation phase of the implant are necessarily focused on bulk alloying, which is a parallel stream of study to surface coatings (Guo, Xu, Zhao, & Han, 2012; Kirkland et al., 2010; Peng, Huang, Zhou, Hort, & Kainer, 2010; Staiger et al., 2006). However, it is a challenge to avoid sacrificing mechanical strength for low corrosion rate of Mg alloys. As such, ideal protective coatings could retard degradation of Mg for a certain period of time but degrade along with the bulk of Mg during the late stage of its intended lifetime. As such, coatings are targeted for the stifling of the rapid initial corrosion of Mg implants, restricting any early pH changes or gas bubble formation during the acceptance phase of the implant. For orthopaedic applications, protective coatings must be non-toxic/biocompatible and bioactive. Applying hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), a well-known bioactive material with close chemical and structural resemblance to human bones and teeth, onto metallic implants, including Mg, is a practical option for moderating the biodegradation process (Chen, Birbilis, & Abbott, 2011; Cortés, López, & Mantovani, 2007; Kunjukunju et al., 2013; Wang, Wei, & Gao, 2009; Wang et al., 2013). Such a coating category has been identified to enhance biological fixation of the implant to the hard tissues (LeGeros, 2002; Yang, Kim, & Ong, 2005) and facilitate functional implant deployment without weakening the intrinsic mechanical properties (Hiromoto & Yamamoto, 2009; Meng et al., 2011; Song, Shan, & Han, 2008; Wen et al., 2009).

Nevertheless, HA layers prepared by means of physical deposition, such as plasma spray, present low adhesion strength and low crystallinity, leading to potential delamination of the coatings and failure of biological fixation (Manso, Jiménez, Morant, Herrero, & Martínez-Duart, 2000). Meanwhile, such deposition processes are not applicable to the implants with irregular shapes, owing to their line-of-sight characteristic. To address these limitations, chemical/wet coating technology has been extensively adopted to fabricate HA coatings, in particular, for Mg-based biomaterials (Chen et al., 2011; Hiromoto & Yamamoto, 2009; Wen et al., 2009). It is noted, however, that the presence of a vast amount of Mg (II) cations, which are generated by immersion of bulk Mg with any aqueous coating solution, inhibits the formation of an HA conversion coating of high purity. Dicalcium phosphate dihydrogen (DCPD) is one of the most common impurities, which plays an inhibitor role in ossification (Friedman, Constantino, & Jones, 1991; Shindo, Constantino, & Friedman, 1993). In order to therefore promote a more viable coating, subsequent post-treatment in alkaline solution is required to transform DCPD to the more desirable HA, which can give rise to concerns in terms of both production cost and safety (Chen et al., 2011). Thus, engineering of a load-bearing Mg-based implant system with satisfactory mechanical properties, well-controllable biodegradation rate, desirable bioactivity and biocompatibility remains essential.

In the past decade, some beneficial trace elements in the human body, which are essential for health, such as Mg, calcium (Ca), zinc (Zn), iron (Fe), strontium (Sr) and manganese (Mn) have been introduced into the surface of Ti-based implants to

improve bone fracture healing in the form of divalent cations (Bracci et al., 2009; Park, Park, & Suh, 2007; Zreiqat et al., 2002). A summary of some typical trace metallic elements found in the human body can be seen in Table 15.1.

Strontium was identified as beneficial in enhancing bioactivity and biocompatibility. Sr (II) cations depress bone resorption, develop bone mechanical properties, enhance replication of preosteoblastic cells and stimulate bone formation, thus eventually preventing bone loss (Buehler, Chappuis, Saffar, Tsouderos, & Vignery, 2001). It has been hypothesised that the presence of Sr (II) cations at the interface between implant and bone will ensure the longevity of a joint prosthesis (Oliveira, Reis, & Li, 2007). Sr cations have the same physiological and chemical behaviours as Ca (II), the major component of bone, and can be embedded into the mineral structure of bone by ionic substitution for Ca (Blake, Zivanovic, & Mcewan, 1986a,b). Sr may replace lattice sites of Ca in HA and form a continuous solid-solution (Sr.x-HA, x is a fraction of substitution) up to full substitution (Sr-HA) with higher solubility, more regular shape and stronger mechanical properties (Christoffersen, Christoffersen, Kolthoff, & Bärenholdt, 1997; Grynpsas & Marie 1990).

There are intensive studies on the *in vitro* (Zhang et al., 2011) and *in vivo* (Li et al., 2010; Wong et al., 2004) behaviours, cytotoxicity (Guo, Xu, Zhao, & Han, 2005) and bone formation mechanism (Ni et al., 2006) of Sr.x-HA cements and ceramics. Sr.x-HA coatings have also been implemented onto metallic implants, in particular Ti, for improved bone formation. A biomimetic method was applied to deposit Sr.x-HA coating on Ti (Oliveira et al., 2007). It was found that the fraction of Sr in the HA coating depends on the concentration of Sr (II) cations in the coating solution; however, the presence of Sr cations also mitigates the overall coating thickness. Porous Sr.x-HA films have also been plasma sprayed onto Ti-6Al-4V alloy (Xue et al., 2007) and demonstrated satisfactory mechanical properties and *in vitro* bioactivity. Capuccini et al. (2008) employed pulsed laser to deposit an Sr-HA coating on Ti and discovered that the presence of Sr in the coating reinforces the positive influence of HA on osteointegration and bone regeneration, whilst concomitantly reducing bone resorption. A series of Sr-HA coatings with varying ratio of Sr and Ca were prepared via micro-arc treatment to elucidate the effects of Sr content on osteointegration (Chung & Long, 2011). It was revealed that the fully Sr-substituted HA plays the most profound role in promoting osteoblast differentiation and inhibiting osteoclast differentiation, which is beneficial for anti-osteoporosis purposes.

Furthermore, well-ordered Sr titanate (SrTiO₃) nanotubes, formed on the surface of Ti implants by hydrothermal treatment, were reported to significantly enhance their osteointegration and increase the torque for removal (Park et al., 2010; Xin, Jiang, Huo, Hu, & Chu, 2009). This was attributed to the enhanced osteoblast differentiation and new bone apposition in both cortical and cancellous bone (Park et al., 2010). Though the beneficial effects of Sr on bone regeneration are clear, to date there are few studies exploring the effect of Sr-coated Mg-based biomaterials either on inhibiting biodegradation or osteointegration except for the latest work carried out by Chen et al. (Chen et al., 2014; Ke, Pohl, Biribilis, & Chen, 2014), where a

Table 15.1 Summary of some essential trace elements in the human body

Element	Atomic number/group	Major biological functions	Fraction of mass in human body	Daily tolerable (upper) intake level for adults (Hunt and Nielsen, 2009)
Mg (II)	12/II	Essential to basic nuclei acid chemistry of life and to all cells of all known living organisms. Required by enzymes for their catalytic action.	5×10^{-4}	30 mg (infant)—420 mg (male adult)
V	23/V	May improve glucose control in people with type 2 diabetes in the form of vanadyl sulfate.	2.6×10^{-7}	6–18 µg
Cr (III)	24/VI	Necessary to maintain blood sugar level.	2.4×10^{-8}	50–200 µg
Mn (II)	25/XII	Helps formation of enzymes. Antioxidant.	1.7×10^{-7}	2.5–5 mg ^a
Fe (II)	26/VIII	Carries O ₂ from lung to other organs. Part of many enzymes essential for growth, healing, immune function and synthesis of DNA.	6×10^{-5}	10–20 mg/kg
Co	27/IX	Key component of vitamin B ₁₂ .	2.1×10^{-8}	10–20 µg
Sr (II)	28/II	Similar to Ca. Aids bone growth, increases bone density.	4.6×10^{-6}	600 mg
Cu (II)	29/XI	Antioxidant. Stimulator for energy production and formation of bone, connective tissues and red blood cells.	1×10^{-6}	1.0–3.0 mg ^a
Zn (II)	30/XII	Promotes immune function and helps clot blood.	3.2×10^{-5}	150 mg for up to 12 months
Mo	42/XI	Activates enzymes and enables normal cell function.	1.3×10^{-7}	0.12–0.24 mg
Sn	50/XIV	Antioxidant along with vitamin E.	1.9×10^{-7}	800 mg

^aDaily required amount for adults.

biocompatible Sr phosphate (SrPO_4) conversion coating was fabricated through a simple wet-chemical conversion technique to significantly restrict the initial degradation of Mg.

There are also a number of emerging studies focusing on Mn phosphate (MnPO_4) conversion coatings to reduce the corrosion process in Mg alloys, in spite of being expected to be more stable and corrosion resistant than their Zn, Fe and Ca peers. Han et al. (Han, Zhou, Shan, & Ke, 2003) and Zhou et al. (Zhou, Shan, Han, & Ke, 2008; Zhou, Tang, Zhao, Wu, & Han, 2011) reported a manganese hydrogen phosphate (MnHPO_4) conversion coating for AZ31D and AZ91D alloys and proposed a mechanism of coating formation. Cui et al. also investigated the growing process of an MnHPO_4 conversion coating on AZ31 but presented an alternative coating growth mechanism (Cui, Zhou, Lin, Luo, & Gong, 2012). Though these existing reports indicate that the MnHPO_4 conversion coatings have a desirable corrosion resistance, the immersion/coating time, up to 30 min, is far from the minimum requirement for industrial applications. Chen et al. (Chen, Zhou, Abbott, Easton, & Biribilis, 2013) developed a double-layered $\text{MnPO}_4\text{-Mg}(\text{OH})_2$ conversion coating to improve corrosion resistance for Mg alloy AZ91D. It was found that the high processing temperature (80 °C) and mild acidity (pH 4.0) are favourable to the coating with a complete surface coverage and the best protectiveness against corrosion. However, none of these MnPO_4 coatings has been used in biomedical applications, which might be limited due to safety concerns regarding the excessive Mn ions released due to the biodegradation of MnPO_4 layers.

Mn (II) cations are another essential trace element in the human body and play a beneficial role in promoting ligand-binding affinity of integrins and activating cell adhesion at low concentration (Armulik, Svineng, Wennerberg, Fässler, & Johansson, 2000). It is expected, therefore, that incorporation of Mn in the coatings on metallic implants could promote the interaction with host bone tissues. But the daily overdosed intake of Mn leads to some toxic effects, such as neurodegenerative damage. However, there is little research investigating the correlation between the release rate of Mn ions from the surface into biological medium and their cytotoxicity. In contrast, similar research has been intensively conducted on Mn (II) cation-doped ceramic coatings, such as titanium oxide (TiO_2), HA, TCP, etc., but inconsistent results have been obtained by different researchers. It was assumed that low concentrations of Mn are acceptable when being incorporated into a thin film of TiO_2 . Park, Kim, and Jang (2011) developed a hydrothermally prepared Mn- TiO_2 film, which releases 1.6 ppm Mn (II) ions on the first day of incubation and retards osteoblast differentiation, compared with wet-ground Ti; thus an in-depth investigation of cytotoxicity of Mn (II) ion containing film was suggested. Similarly, a low concentration of Mn (II) ions (0.55 and 1.6 ppm, prepared by dissolving MnCl_2 into Dulbecco's Modified Eagle's Medium (DMEM)) does not present any detrimental influence on the proliferation and spreading of osteoblastic MG-63 cells, whilst higher concentrations (5.5 and 27.5 ppm) display an evidently cytotoxic impact (Bornhorst, Ebert, Hartwig, Michalke, & Schwerdtle, 2010; Lüthen et al., 2007). Byzova et al. proposed a high level of Mn ions in culture medium, i.e. 54.9 ppm, which facilitates adhesion of rat UMR 106 osteoblastic cells via markedly increasing activation of $\alpha_v\beta_3$ integrins (Byzova, Kim, Midura, & Plow, 2000).

Bracci et al. stated that Mn ions hinder the precipitation of highly crystalline HA and lead to formation of amorphous Mn-doped CaPO_4 that is supposed to have a higher solubility in aqueous solution and a greater amount of Mn (II) ions released into the incubation medium, though no such data were disclosed. Such a high content of Mn in CaPO_4 coating demonstrates a greater promotion of osteoblast differentiation and mineralisation, compared with the incorporation of divalent Sr and Mg cations (Bracci et al., 2009). Beneficial impacts on osteoblast proliferation, activation of their metabolism and differentiation have also been demonstrated (Bigi et al., 2005; György et al. 2004). Addition of divalent Mn ions into HA not only alters its morphology but also reduces its crystallinity, which is favourable for adsorption and disappearance during bone remodeling (Mayer, Cuisinier, Gdalya, & Popov, 2008; Sopyan, Ramesh, Nawawi, Tampieri, & Sprio, 2011).

15.2 Development of SrPO_4 coatings

Rapid degradation of Mg biomaterials at the initial stage of post-implantation must be controlled for a number of reasons, as discussed above. Applying protective coating is a promising technique for achieving this goal. Compared with CaPO_4 coating, so far, publication on SrPO_4 coating is still very limited, although divalent Sr cations have approved beneficial influence on promoting bone fracture healing. This section will introduce preparation, characterisation and evaluation of degradation of a novel biocompatible SrPO_4 conversion coating developed lately by Chen et al. (Chen et al., 2014; Ke et al., 2014). The advantages and limitations of such coating and its potential applications and future development will be discussed in details.

15.2.1 *How SrPO_4 coatings are prepared and inhibit initial biodegradation of Mg*

Metal phosphate coating is one of the important surface conversion techniques and has been commercially exploited on conventional metals, such as Zn, Fe and steel to improve their lifespan in corrosive environments. Normally, it is conducted in an acidic phosphate bath at room or elevated temperatures. Mg has a relatively negative redox potential and dissolves quickly in acidic solutions. Thus, a protective phosphate conversion coating is readily applied onto Mg surface as a barrier to insulate the underlying metal from corrosive medium. A number of metal-phosphate conversion coatings have been reported in the past decades.

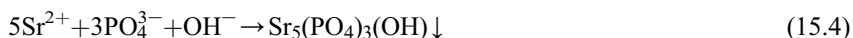
Similarly, SrPO_4 can also be generated via such wet-chemical conversion coating processes (Chen et al., 2014; Ke et al., 2014). Briefly, Mg specimens with a clean surface are immersed into a heated and acidic bath (pH 3.0 adjusted by HNO_3) containing 0.1 M Sr and 0.06 M $\text{NH}_4\text{H}_2\text{PO}_4$ for 5 min. The formation mechanism can be described as follows.

Upon contact with the acidic coating solution (pH 3.0), the Mg coupon dissolves (aggressively) and releases a massive amount of Mg (II) cations, alkaline hydroxyl

(OH[−]) anions and H₂ gas, as the following reactions occur (Chen et al. 2011, 2013):



In acidic conditions, the above reactions take place at a high rate, and in the vicinity of the Mg surface, accumulation of OH[−] ions can abruptly increase the pH (with prolonged time, the bulk pH will rise, however that is not relevant during the timescale of coating) (Chen et al., 2011, 2013). A local surface pH increase leads to the formation and precipitation of Mg(OH)₂ first and then SrPO₄ coating over the substrate according to (Ke et al., 2014):



In regard to the competition between Mg and Sr divalent cations to combine PO₄^{3−} ions to form precipitates, it is known that at similar conditions (pH, T, t and concentration of PO₄^{3−} ions), the stable complex formation is much more likely to be SrPO₄ rather than MgPO₄. Concomitantly, solubility of SrPO₄ in an aqueous system reduces with increasing pH. As such, SrPO₄ precipitates as the primary component of the coating, with a small fraction of MgPO₄.

The final SrPO₄ coating presents a compact structure consisting of numerous prismatic crystalline particles (Figure 15.1(a) and (b)). The inset graph of EDX in Figure 15.1(b) reveals the presence of elements of O, Sr, P and Mg. No H₂ gas was detected during the first 5 days of exposure to minimum essential medium (MEM). Corrosion products emerged on the flat side of the individual SrPO₄ prismatic granules after 5 days' immersion (Figure 15.1c). A small fraction of the whole coating dissolved after 14 days' immersion (indicated by an arrow in Figure 15.1(d)), implying a remarkably slower degradation. A small amount of Sr²⁺ ions were released from the SrPO₄ coating after 5 days' immersion at a rate of 2.8 ± 0.4 mg/L/day, which then gradually decreases to 0.5 ± 0.1 mg/L/day at the end of the 14 days' immersion (Figure 15.2(a)). The potentiodynamic polarisation curve of the SrPO₄ coating demonstrates an impressive passivation on the anodic kinetics, in which not only is the corrosion current density minimised but also no evident breakdown point is observed (Figure 15.2(b)). The restrictive effect on anodic kinetics leads to more noble open-circuit potential (*E*_{corr}), compared with uncoated Mg controls, indicating that the coating provided satisfactory protection against corrosion. Overall, the degradation of Mg has been significantly restricted, in particular, over the initial immersion period in MEM (14 days). SrPO₄ coating, prepared by a similar process, also shows outstanding corrosion resistance on Mg alloys, for instance, die-cast AZ91D. After exposure to a salt spray chamber for 72 h, the alloy surface covered by SrPO₄ presents perfect protection, with no identified corrosion spots, in contrast to other conversion coatings (Figure 15.3).

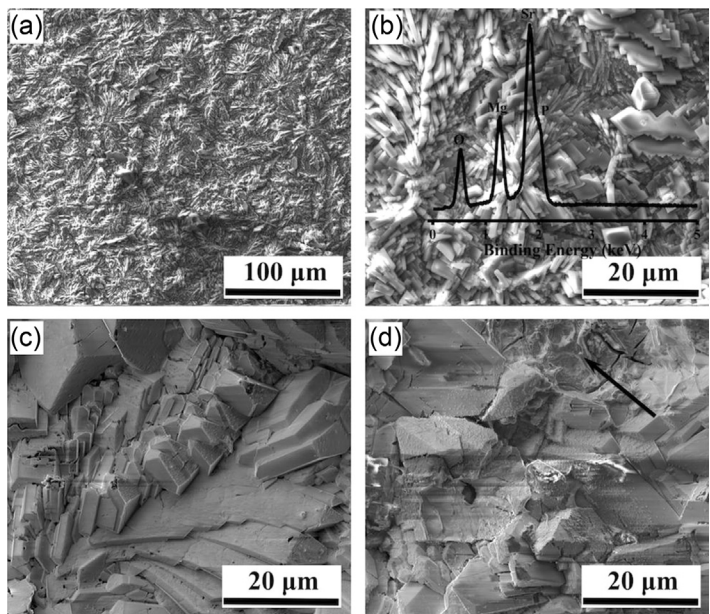


Figure 15.1 Micrographs of (a, b) as-prepared SrPO_4 coatings (inset: EDX spectrum). (c) SrPO_4 after 5 days' and (d) 14 days' immersion in MEM at 37 °C, 5% CO_2 . The corrosion products emerged on the surface of individual particles and a small fraction of the coating was peeled off after 14 days, as indicated by the black arrow.

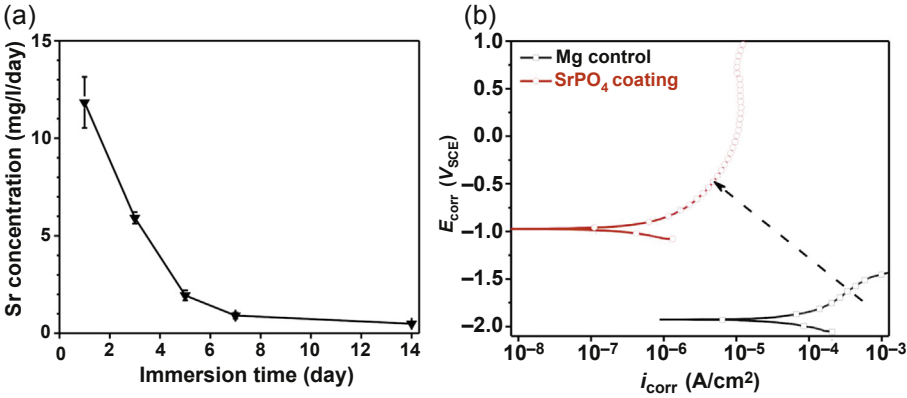


Figure 15.2 (a) The concentration of the Sr (II) cations released from SrPO_4 coating with immersion time in MEM, measured by ICP-MS. (b) Potentiodynamic polarisation curves of bare Mg and SrPO_4 -coated Mg in 0.1 M NaCl electrolyte. The evident restriction on anodic kinetics of Mg by means of SrPO_4 coating is indicated via the black arrow.

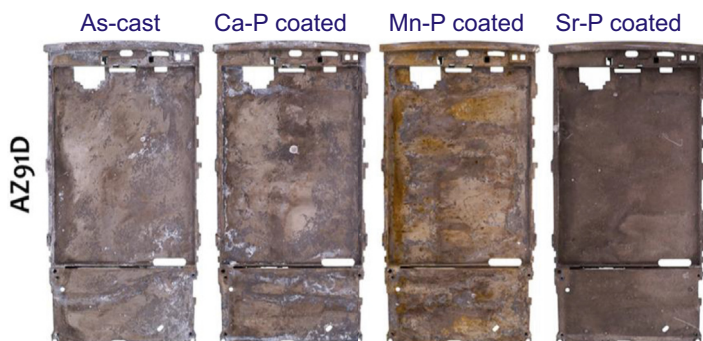


Figure 15.3 Photographs of die-cast AZ91D mobile-phone chase component and CaPO_4 , MnPO_4 and SrPO_4 coatings after exposure to salt spray for 72 h. The salt spray evaluation was carried out according to the ASTM B117 industrial standards. No corrosion spots can be identified on the surface covered by highly protective SrPO_4 .

15.2.2 Advantages and disadvantages over other coating technologies

The chemical conversion coating technique has been extensively applied onto conventional metallic materials for corrosion protection due to a number of outstanding advantages over other existing coating methods. This wet-coating skill, in general, generates a layer uniformly covering the surface of components even with irregular shapes, such as porous, hollow and screwed structures, which is not possible for some line-of-sight techniques, such as plasma spray, RF sputtering, chemical/physical evaporation deposition, etc. Chemical conversion coatings are more adhesive due to the presence of chemical bonds and an intermediate layer between the coating and underlying metal. Most importantly, this technique is easy to operate, processing time is short, raw chemicals used for bath solution are cheap and no specific equipment or conditions are required, which is favourable for industrial manufacturing. One critical limitation associated with chemical conversion coatings is their relatively low toughness/wear resistance and durability, which leads to defects and damage, which decreases the protectiveness, which relies heavily on the integrity of a coating.

Despite the fact that there are massive methods for preparation of biocompatible HA coatings, few of them have been transferred from laboratories to production, which is mainly due to the diverse materials needed in the preparation, complicated and expensive processes, and phase impurities in the crystal structure. The method for preparing SrPO_4 conversion coating, however, is cost-effective, easy to operate and has low impact on the environment. The final SrPO_4 product provides higher protection against degradation than HA. The released divalent Sr cations during the degradation process depress bone resorption, develop bone mechanical properties, enhance replication of preosteoblastic cells and stimulate bone formation, thus eventually preventing bone loss (Buehler et al., 2001). Although the clinical use of ever-approved Sr-containing drugs, i.e. Sr-ranelate, has been suspended by the European Pharmacovigilance Risk Assessment Committee (PRAC) owing to the adverse effects

on blood clots and skin health, there is no conclusion on whether this is associated with Sr ions. It has been hypothesised that the presence of Sr at the interface between an implant and bone will ensure the longevity of a joint prosthesis (Oliveira et al., 2007). In contrast, there are disputes on the tolerable release rate of Sr (II) cations from surface/implants. This issue must be tackled prior to clinical application of such techniques.

15.3 Development of MnPO_4 coatings

MnPO_4 conversion coatings have been developed to provide corrosion and wear protection for Mg alloys in the past decades. However, little research work has been carried out to exploit their biomedical applications, regardless what the underlying metals are, which might be attributed to the safety concerns of the presence of multi-valent Mn (VII and V) cations in addition to divalent Mn cations. On the contrary, divalent Mn cations were doped into a number of ceramic films, such as HA, TCP and TiO_2 , to facilitate reactions between implant and bone tissues by promoting ligand-binding affinity of integrins and activating cell adhesion. In the following sections, preparation of some MnPO_4 coatings will be reviewed and their performance in corrosion protection will be introduced. Their merits and demerits, potential applications and future development will be discussed.

15.3.1 *How MnPO_4 coatings are prepared and retard corrosion of Mg alloys*

Chemical conversion techniques have been extensively applied to manufacture MnPO_4 compounds on the Mg alloy surface. The properties of the resultant coatings can be modified through tailoring processing parameters, such as bath concentration, pH, temperature, time duration, etc. A typical MnPO_4 bath was proposed via Chen et al. (Chen et al., 2013), containing 0.01 M manganese nitrate ($\text{Mn}(\text{NO}_3)_2$), 0.01 M ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$). Nitric acid (HNO_3) or ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$) was utilised to adjust pH values (2.0–6.0). Similar coating solutions (containing Mn-nitrate-phosphate) have also been adopted by other researchers for corrosion protection purposes (Huan et al., 2012; Zhou et al., 2008, 2011). The coating process was thus conducted by immersing pre-cleaned AZ91D specimens into the coating solution varying from room temperature to 80 °C for 5 min. It was revealed that a MnPO_4 layer with full surface coverage and premium corrosion protectiveness was obtained at a condition of mild pH (4.0) and high processing temperature (80 °C) (Figure 15.4), which is attributed to the formation of a stable $\text{Mg}(\text{OH})_2$ - MnPO_4 double layer based on the thermodynamic equilibrium calculation (Figure 15.5) (Chen et al., 2013).

The overall coating formation process is also schematically depicted in Figure 15.6. Briefly, the formation process of the double-layered coating includes three primary phases, i.e. substrate dissolution, intermediate $\text{Mg}(\text{OH})_2$ film deposition and final

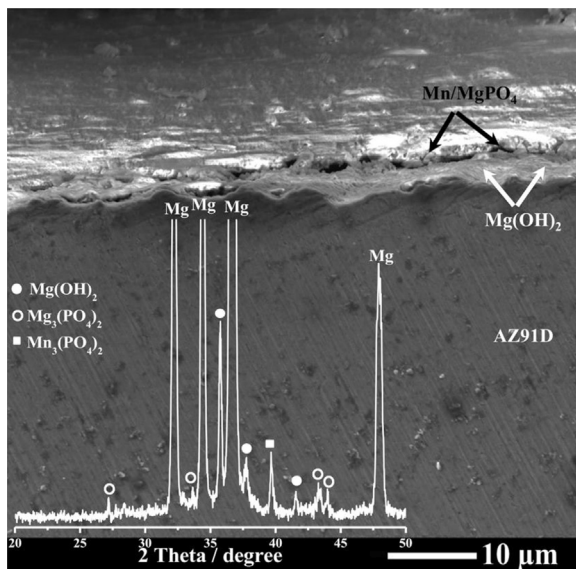


Figure 15.4 Cross-sectional micrograph and XRD spectrum of the AZ91D surface, which was treated at pH4-80 °C in 0.01 M $\text{Mn}(\text{NO}_3)_2\text{-NH}_4\text{H}_2\text{PO}_4$ solution, suggesting the existence of a $\text{Mg}(\text{OH})_2\text{-(Mg/Mn)}_3(\text{PO}_4)_2$ double layer coating. Modified from [Chen et al. \(2013\)](#).

$(\text{Mg/Mn})_3(\text{PO}_4)_2$ co-precipitation. Mg components are placed in the prepared acidic MnPO_4 bath, Mg dissolves and massive OH^- ions are released, locally raising the pH in the vicinity of the metal surface ([Figure 15.6](#)). The excess of the depleted Mg^{2+} and OH^- ions, compared to the small fraction of Mn^{2+} and PO_4^{3-} in the bath, would precipitate immediately in the form of $\text{Mg}(\text{OH})_2$ on metal surface as an intermediate film, followed by growth of MnPO_4 deposits. The presence of $\text{Mg}(\text{OH})_2$ as an intermediate layer could mitigate the interface shear strength by ‘melting’ the dissimilar coating compounds into an integrate film and increasing the coating adhesion. The presence of $\text{Mg}(\text{OH})_2$ with loose structure (pores) on Mg surface can provide more favourable sites to facilitate the hetero-nucleation of phosphate crystalline deposits.

To further investigate the chemical state of the coating elements, XPS survey scans, high-resolution elemental analysis and depth profiling were conducted on AZ91D treated for 5 min at 80 °C, pH 4.0, as depicted in [Figure 15.7](#). The survey scan displays the existence of Mg, O, P and Mn at the surface. O atomic concentration reduces (62.8–7.8 at%) and the Mg content increases (26.9–61.9 at%) with the depth of the coating. Meanwhile, Mn and P signals were detected mainly from the outer region of the coating. Mn and P concentrations decrease gradually from 3.4 to 6.6 to 0.9 and 2.4 at%, respectively. The high-resolution scans further identify the presence of inner $\text{Mg}(\text{OH})_2$ and outer $(\text{Mg/Mn})_3(\text{PO}_4)_2$ films.

The growth of a crystalline product on Mg coupons drastically reduces the electrical conductivity of the surface and acts as a barrier to isolate the corrosive electrolyte from the substrate. Since corrosion relies on the flow of electrons between the anode and cathode that exist on a heterogeneous surface like AZ91D, decreases in the electrical conductivity, and separation between metal and electrolyte, will significantly restrict

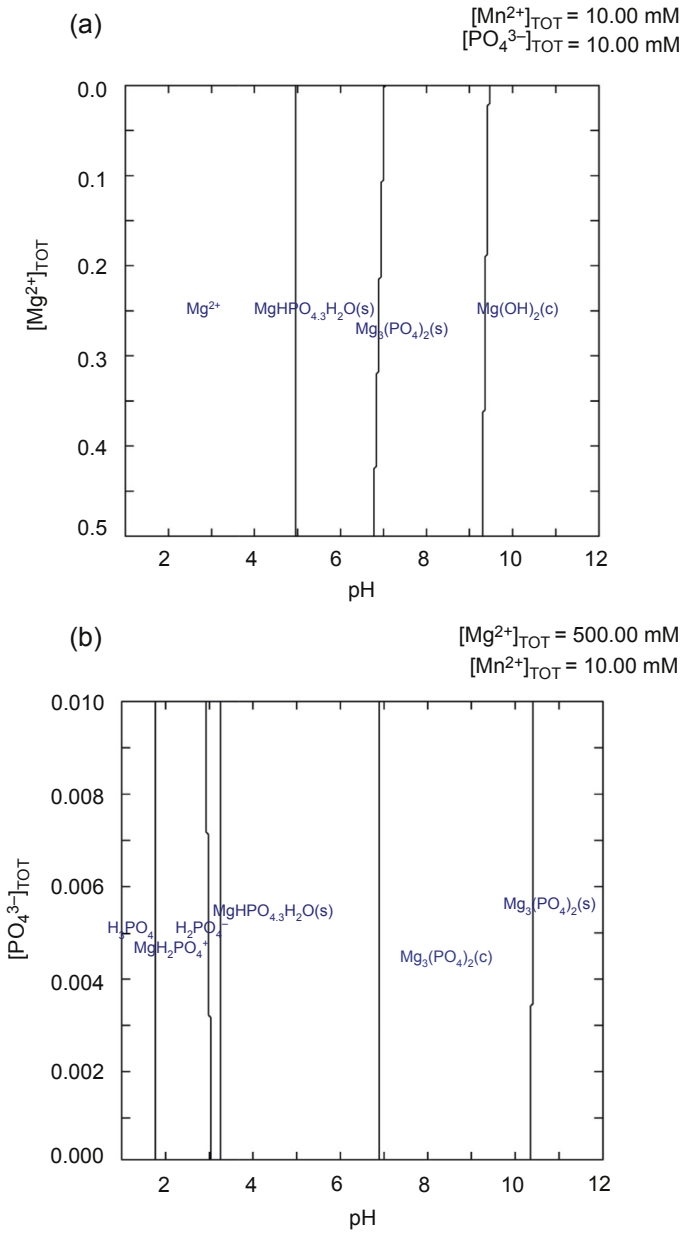


Figure 15.5 Thermo-equilibrium predominance area diagram for the Mn^{2+} , Mg^{2+} and PO_4^{3-} ions calculated using the MEDUSA software package (a and b). It can be seen that $\text{Mg}(\text{OH})_2$ (exists as intermediate layer) is the dominate deposition when bath pH is high, and then MgPO_4 and MnPO_4 precipitate orderly along with pH decrease (outer layer).

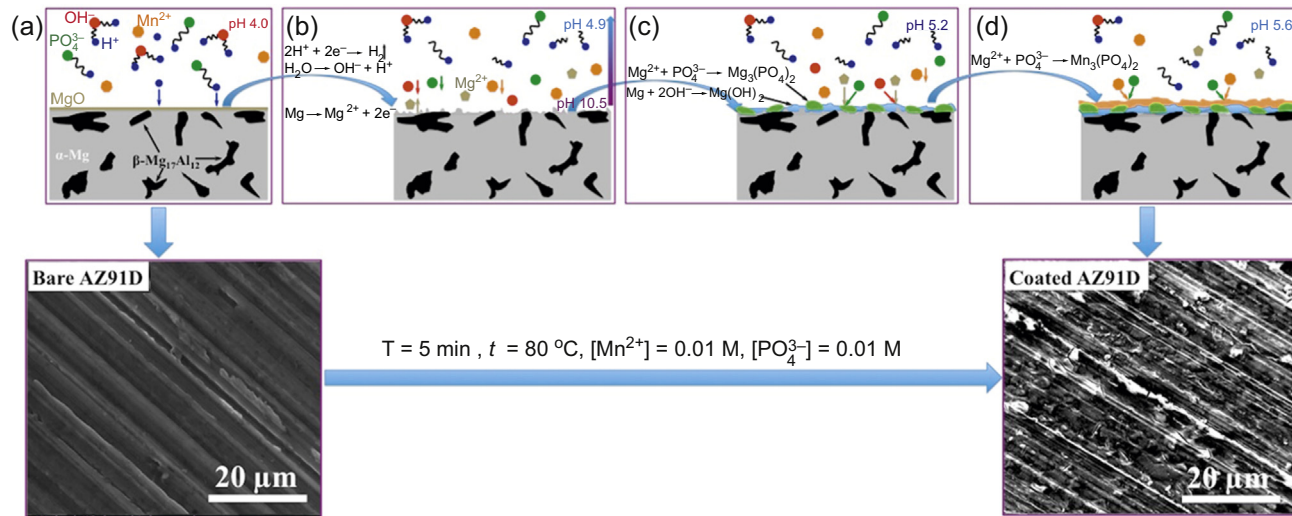


Figure 15.6 Schematic presentation of the formation process of MnPO_4 coating on Mg alloy AZ91D.

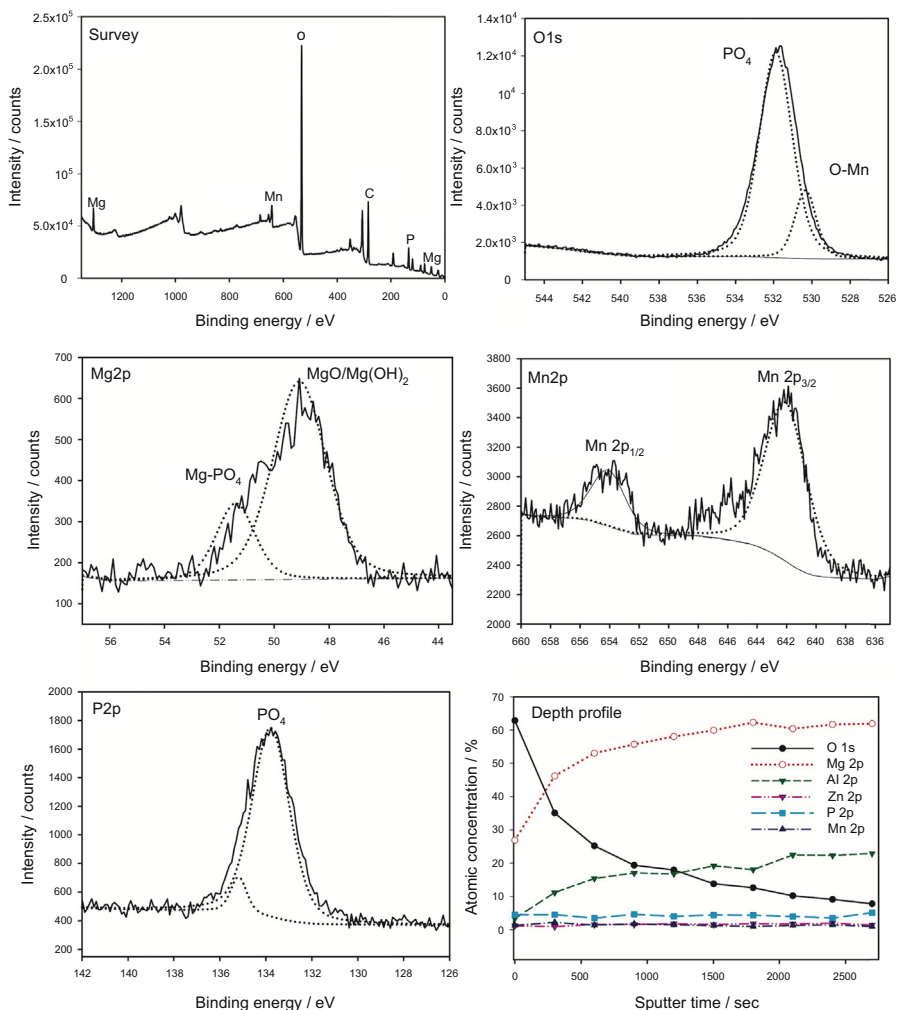


Figure 15.7 XPS analysis of the MgPO₄ conversion coating, survey, high resolution of O1s, Mg2p, Mn2p, P2p, and depth profile of the coating formed after 5 min of immersion at pH4-80 °C, revealing the existence of elements of O, Mg, P and Mn, and their distribution over the coating system.

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the corrosion kinetics. It was noted that the cathodic reactions were profoundly inhibited by the MnPO₄ coating, attributed to the formation of intermediate insoluble Mg(OH)₂, which acts as an inhibitor of oxygen and consequent cathodic kinetics, similar to that of chromate coatings on Al alloys as Kendig and Buchheit presented ([Kendig & Buchheit, 2003](#)). A breakdown potential point and pseudo-passivation region are evident in all anodic branches, revealing that the anodic dissolution reaction has also been retarded ([Figure 15.8\(a\) and \(b\)](#)).

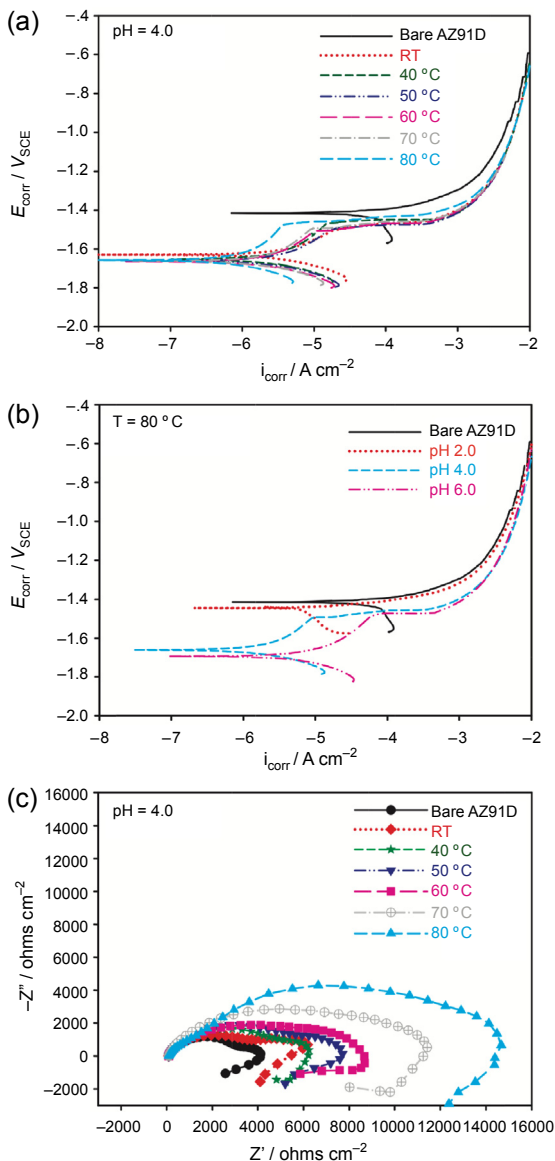


Figure 15.8 Potentiodynamic polarisation curves of various AZ91D obtained in 0.1 M NaCl at a sweep rate of 1 mV/s (a, b). Nyquist plots of the various AZ91D obtained in 0.1 M NaCl with a frequency range from 100 kHz to 10 mHz (c, d). (e) 3D plot of the corrosion current density i_{corr} (z axis) against treating temperature (x axis) and pH (y axis). (f) The equivalent circuit used for analysis of the EIS data of various AZ91D. (R_s , solution resistance. R_c , resistance and constant-phase element of a film on the sample surface. R_{ct} , Q , Q_{dl} , the charge transfer resistance of a coating, constant phase element of the charge transfer and charge transfer capacitance of a double layer, respectively. W , Warburg element accounting the diffusion of species.) Reprinted from [Chen et al. \(2013\)](#), with permission.

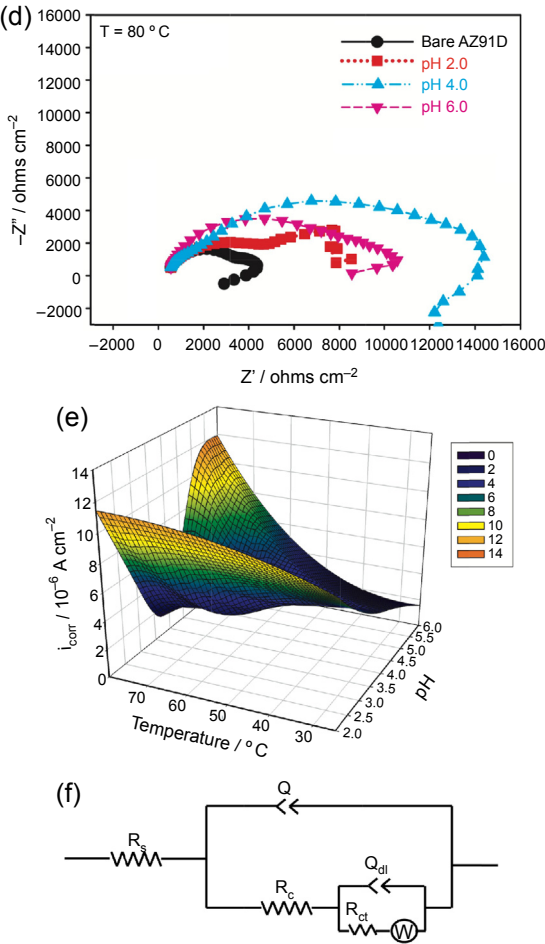


Figure 15.8 Continued.

In terms of EIS characterisation (Figure 15.8(c) and (d)), only one capacitive loop and a significant increase in diameter of the capacitive loop were observed for the MnPO_4 coatings, correlating with a passive nature (Forsyth et al., 2009). The EIS data were simulated using the equivalent circuit presented in Figure 15.8(f) (EC-Lab package, version 10.2). The parameters R_s (the solution resistance), Q (constant phase element representing a non-ideal capacitance related to the coating), R_c (the coating resistance), Q_{dl} (constant phase element representing a non-ideal capacitance related to the double layer), R_{ct} (the charge transfer resistance) and W (representing the Warburg element, which represents the diffusion of species) calculated. This equivalent circuit was chosen due to being the most simple representation of a filmed surface that can accommodate local breakdown/defects. Long-term salt spray evaluation (Figure 15.9) demonstrated that the optimal MnPO_4 conversion coating, generated

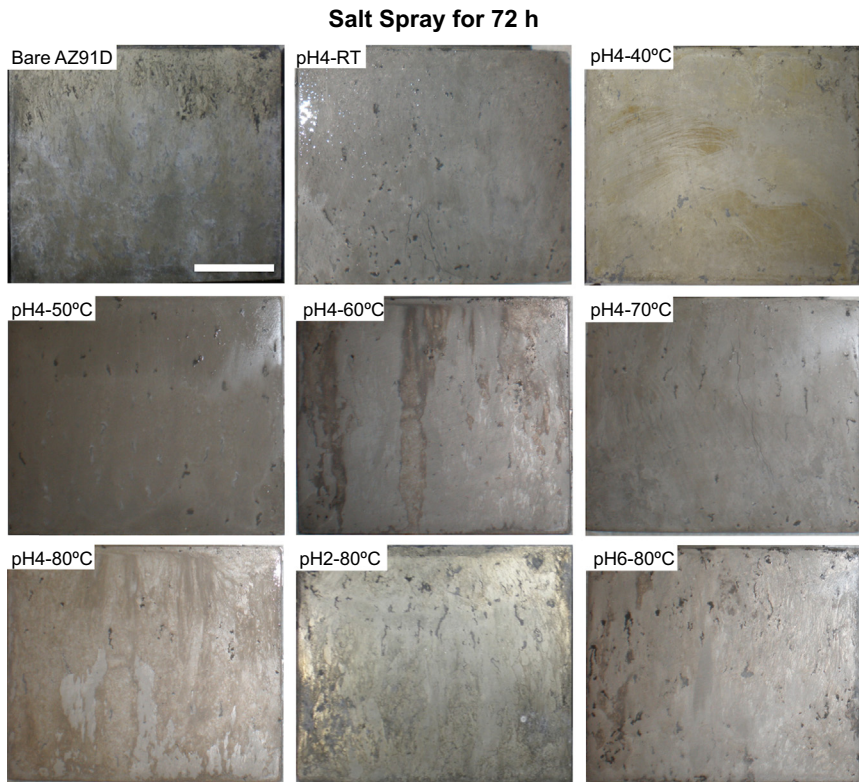


Figure 15.9 Various AZ91D alloys after salt spray for 48 h according to ASTM B117 standard. (Scale bar, 20 cm.)

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at the mild pH and high temperature, offered a corrosion protection similar to that of the DOW chromate conversion coating ([Ger, Yang, Sung, Hwu, & Liu, 2004](#); [Yang, Tsai, Huang, & Lin, 2012](#)).

15.3.2 Advantages and disadvantages over other coating technologies

MnPO_4 possesses some unique advantages and disadvantages over other current coating technologies. Bracci et al. stated that Mn ions hinder precipitation of highly crystalline HA and lead to formation of amorphous Mn-CaPO_4 that is supposed to have a higher solubility in aqueous solution and a greater amount of Mn ions are released into the incubation medium, though no such data has been disclosed. Such a high content of Mn in the CaPO_4 coating demonstrates a greater promotion of osteoblast differentiation and mineralisation, compared with incorporation of Sr and Mg ([Bracci et al., 2009](#)). Beneficial impacts on osteoblast proliferation, activation of their

metabolism and differentiation have also been demonstrated (Bigi et al., 2005; György et al., 2004). Addition of divalent Mn ions into HA not only alters its morphology but also reduces its crystallinity, which is favourable for adsorption and disappearance during bone remodeling (Mayer et al., 2008; Sopyan et al., 2011).

Apart from Ca, a major component of bone, Mn is one of the trace elements, and thus it is critical to determine the tolerable level of daily intake when MnPO_4 is used as a coating on an implant. The research results associated with this aspect originated from Mn-doped coatings and are not consistent, as discussed in the introduction section. Thus, it is an urgent task to undertake relevant investigations of acceptable release rates of Mn (II) cations from implants into the human body. The characteristic cracked structure of MnPO_4 conversion coating is an issue, as these cracks may be vulnerable sites for corrosive medium to penetrate and initiate galvanic corrosion, which would incur cracking, which will jeopardise the desirable mechanical properties.

15.4 Applications and future development

Biocompatible SrPO_4 -based conversion coatings are one of the promising candidates to protect Mg orthopaedic implants from rapid *in vivo* degradation and promote bone fracture recovery. The newly developed SrPO_4 coating degrades slowly at the initial stage of immersion in MEM and thus effectively prolongs the lifespan of the underlying Mg as supporting materials with desirable mechanical properties. Meanwhile, degradation products of SrPO_4 contain Sr cations, which promote cell growth and new tissue formation. Therefore, SrPO_4 plays a dual role that is favourable from a biomaterial perspective. Such coatings have a promising future to control the degradation rate of Mg implants and achieve a faster healing process. In addition to its biomedical functions, its superior protectiveness against corrosion and low cost of production may make it applicable where conventional steel and Al components are deemed to be replaced by light-weight Mg, such as transportation, electronic and household appliances. A good example for such industrial applications of SrPO_4 conversion coating can be seen in Figure 15.3, which demonstrates the outstanding corrosion protection of SrPO_4 on a mobile phone chassis made of die-cast Mg alloy AZ91D. After exposure to salt spray for 72 h, no evident corrosion spots emerge on the surface covered by SrPO_4 , compared with bare AZ91D, CaPO_4 and MnPO_4 coatings.

The research works on biocompatible Sr-based coatings are still rare compared with other divalent metal-phosphate coatings. Chen and his colleagues' work has identified the way forward, but intensive and in-depth exploration is desired to pave a way for clinical trials. For instance, the tolerable level of Sr cations releasing into the human body has not yet been identified. *In vitro* cell culture trials are necessary and should be expanded to cover more cell categories to obtain reliable results on cytotoxicity. Afterwards, *in vivo* implantation should be conducted to evaluate the biocompatibility and bioactivity of SrPO_4 coatings in real biomedical scenarios. In terms of biodegradation of SrPO_4 -coated Mg, only some preliminary investigations have been performed by Chen et al.; thus, in-depth, systematic and long-term evaluations are still needed.

MnPO₄-based conversion coatings could play a positive role in bone formation and new tissue growth over Mg implant surfaces as long as their degradation process can be controlled at a biocompatible level; however, more data are required and current data are unsatisfactory. Currently, MnPO₄ coatings have been specifically used to reduce the corrosion rate of Mg engineering components rather than for the biomedical field. A few Mn-doped ceramic coatings, such as HA, TCP and TiO₂, have been attempted, to perform its beneficial function to activate cell proliferation and growth. But there are disputes about what is the maximum amount of Mn ions released from implant that can be safely consumed by the human body. *In vitro* and *in vivo* investigations are necessary prior to performing clinical trials.

In addition to biological considerations, some other characteristic aspects are also essential when the end-users make the decision on whether or not to adapt a new coating technology for Mg-based implant materials. Wear resistance is critical when the coating is applied onto a component that will be subject to continuous abrasion or impact. The influence of wear debris on the surrounding tissues should also be monitored. High bonding strength between coating and implant is desirable to achieve satisfactory bone-implant integration, in particular in the early post-implantation period. Since cells are sensitive to surface features ranging from the nanoscale to the mesoscale, a key coating design criterion will be to provide appropriate topography to facilitate cell differentiation even without the requirement for an appropriate surface chemistry.

15.5 General discussion

It is of significant importance to reduce the high biodegradation rate of Mg-based implant materials to get full fracture recovery prior to the degradation of their mechanical strength. Thus, a large number of biocompatible and protective coatings have been developed to address this challenge. Of these, Sr- and Mn-based coatings have emerged as new candidate materials for Ti implants in the past few years, although little work relevant to Mg biomaterials has been reported. One of the major reasons may be the toxicity concern regarding release of excessive Sr and Mn ions, which are nominally trace elements in the human body. Nowadays, even the tolerable threshold of daily intake of such elements, in particular the long-term safety, is still not certain. It is therefore important to carry out further *in vitro* and *in vivo* trials regarding biocompatibility of Sr- and Mn-based protective coatings prior to commercialisation or clinical assessments, given their superior performance in biodegradation reduction for Mg alloys.

The SrPO₄ conversion coating described herein is differentiated from others in the bio-literature, as the corrosion protection herein is high (even very high in respect to coatings for non-bio or structural Mg alloys). Three key factors — the high crystallinity, 100% surface coverage and defect-free morphology — lead to the superior performance. Meanwhile, the high crystallinity imparts a low solubility and long-time stability to the SrPO₄ coating, which degrades slowly when immersed in

Table 15.2 Summary of the details of SrPO₄ and MnPO₄ coatings (Chen et al., 2013, 2014)

	SrPO ₄	MnPO ₄	Methodology
Colour	Light grey	Dark grey	Vision inspection
Uniformity	Homogenous	Homogenous	SEM observation
Chemical composition	Mg(OH) ₂ , MgHPO ₄ , Mg ₃ (PO ₄) ₂ and Sr apatite	Mg(OH) ₂ and (Mn/Mg) ₃ (PO ₄) ₂	XRD and XPS
Adhesion	23.5 ± 2.8 MPa	19.4 ± 3.1 MPa	Modified ASTM C-633 (Chen et al. (2014))
Thickness	1.9 ± 0.2 µm	1.1 ± 0.3 µm	SEM cross-sectional observation
Roughness	8.5 ± 0.6 µm	12.3 ± 1.9 µm	3D profilometry

biological environments. The details of the SrPO₄ and MnPO₄ coatings developed by Chen et al. have been listed in Table 15.2.

The highly protective coating can delay the initial burst of degradation products of Mg implants on exposure to the human body, which is often a concern in biomedical applications. Excessive release of corrosion products, including fragments of coating substances, will incur an adverse effect on the surrounding cells. The results presented by Chen et al. (2014) also demonstrate that the SrPO₄ coating promotes the proliferation of hMSC, thus providing a potential solution to avoid delayed or non-uniform fracture. This is important in the context of biodegradable Mg, as rapid initial *in vivo* degradation results in serious physiological effects. Long-term biocompatibility investigation of the coating material after the entire degradation process is essential to clarify how it would perform after biomedical implantation. The preliminary data set presented herein is encouraging, and future work will aim to assess the biocompatible mechanism of the SrPO₄ conversion coatings using *in vivo* animal models.

MnPO₄ coatings have been investigated for decades to perform a protective function on iron, steel, Zn and now Mg alloys. But none of these coatings has ever been used for biomedical applications, because highly toxic Mn (VII) and Mn (III) are common impurities in the coatings. As a result, biocompatible ceramic coatings have been doped with Mn (II) cations only to facilitate reaction between implant and bone tissue via promoting ligand-binding affinity of integrins and activating cell adhesion. Whilst the MnPO₄ coating described in this chapter was designed for the general purpose of corrosion protection, it is worth conducting *in vitro* and *in vivo* trials on biocompatibility since there were no present toxic impurities.

Phosphatation is an endothermic reaction; thus, coating procedures conducted at low temperature do not provide sufficient energy to generate phosphates satisfactorily.

Under such circumstances, the phosphating rate is either slow or does not take place at all. Consequently, long immersion times, up to a few days, may be required to give rise to a complete phosphate film — with extremely thin coatings being undesirable for corrosion resistance. In contrast, high processing temperatures can offer enough activation energy and eventually accelerate the phosphating rate. A thick phosphate film can be achieved in a relatively short time and render corrosion resistance to Mg substrates.

Bath pH is another crucial impact that significantly influences MnPO_4 coating morphology and thickness. A low pH (2.0) bath results in a coating with higher Mn and P content and greater thickness but evident network structure. The characteristic network structure of MnPO_4 -based conversion coatings can be correlated to the hydrogen evolution process rather than dehydration effects. Corrosive medium will readily penetrate this thick barrier coating and contact the substrate through the defect sites in the network structure and eventually deteriorate corrosion resistance. On the contrary, higher pH (6.0) induces a rough but thin coating with a lower Mn and P weight fraction. This can be attributed to the low acidity that inhibits the dissolution of Mg substrate and consequently moderates the nuclei formation rate of MnPO_4 coating. Thus, processing parameters have a profound influence on the final coating properties and should be optimised carefully.

15.6 Summary

SrPO_4 - and MnPO_4 -based conversion coatings are emerging technologies for the modification of the morphology and composition of the surface of Mg implant materials for tailoring the biodegradation/corrosion rate. Chemical conversion coating is the simplest technique to achieve stable, compact and corrosion-resistant coatings. However, processing parameters, such as bath pH and concentration, temperature and time, need to be optimised for premium coating properties. In the present chapter, it was attempted to review the recent developments and highlight the important issues associated with Sr- and Mn-based conversion coatings. Reported research on biocompatible Sr and Mn coatings for Mg alloys is limited. Little work so far has been focused on their *in vitro* or *in vivo* performance, in particular for long-term biocompatibility.

CaPO_4 conversion coatings have been fabricated to reduce corrosion of Mg components in some commercial applications, including orthopaedic implants. Of these, HA plays a superior role in corrosion inhibition owing to its high crystallinity (low solubility) and stability compared to its counterparts, such as DCPD and TCP. However, according to the complex equilibrium states of CaPO_4 components, it is difficult to achieve HA coatings without impurities, which will deteriorate its protective function for Mg alloys. Thus, SrPO_4 is proposed to replace HA owing to its similar chemical nature to Ca. The results demonstrate that the SrPO_4 coating, fabricated via a simple chemical conversion process, provides superior protection for Mg against biodegradation following initial immersion in MEM.

MnPO₄ conversion coatings can be produced by a simple immersion method, also capable of imparting corrosion resistance to the Mg alloy AZ91D. A coating formation mechanism was proposed with the aid of thermodynamic equilibrium calculations. Upon exposure to the coating bath, the matrix Mg dissolves, releases Mg (II), H₂ gas and OH⁻ ions and increases pH in the vicinity of the solid–liquid interface. The pH increase facilitates the formation of a thin Mg(OH)₂ intermediate layer on the substrate. Finally, a top coating in the form of (Mg/Mn)₃(PO₄)₂ is produced due to their decreasing solubility along with decreasing pH, as predicted from the thermodynamic equilibrium diagram, which is confirmed by XPS characterisation. Calculations could provide a theoretical rationalisation to engineering protective coating formation for AZ91D.

The effect of coating growth parameters, pH and temperature on coating morphology and subsequent corrosion resistance is also crucial. The pH is a key factor in determining coating thickness and characteristics. To avoid detrimental cracks to corrosion resistance, the mild acidity (pH 4.0) is adopted to obtain a more compact MnPO₄ conversion coating with premium protection. The processing temperature also has an influence on the coating formation, albeit much smaller than pH. Due to its exothermic characteristic, the phosphating reaction rate heavily depends on the energy imparted by the heating process. In general, the higher the temperature, the quicker the phosphating process. Overall, the instant growth of a dense and thin Mg(OH)₂ intermediate layer and complete coverage by an (Mg/Mn)₃(PO₄)₂ top layer at pH4, 80 °C exhibits the best corrosion resistance in corrosive environments. With respect to the salt spray evaluation, the proposed MnPO₄ surface film outperformed chromate conversion coatings.

References

- Armulik, A., Svineng, G., Wennerberg, K., Fässler, R., & Johansson, S. (2000). Expression of integrin subunit $\beta 1B$ in integrin $\beta 1$ -deficient GD25 cells does not interfere with $\alpha V\beta 3$ functions. *Experimental Cell Research*, 254(1), 55–63.
- Bigi, A., Bracci, B., Cuisinier, F., Elkaim, R., Fini, M., Mayer, I., Mihailescu, I. N., Socol, G., Sturba, L., & Torricelli, P. (2005). Human osteoblast response to pulsed laser deposited calcium phosphate coatings. *Biomaterials*, 26(15), 2381–2389.
- Blake, G. M., Zivanovic, M. A., & Mcewan, A. J. (1986a). Sr-89 strontium kinetics in disseminated carcinoma of the prostate. *European Journal of Nuclear Medicine*, 12(9), 447–454.
- Blake, G. M., Zivanovic, M. A., & Mcewan, A. J. (1986b). Sr-89 therapy strontium kinetics in metastatic bone disease. *Journal of Nuclear Medicine*, 27, 1030–1035.
- Bornhorst, J., Ebert, F., Hartwig, A., Michalke, B., & Schwerdtle, T. (2010). Manganese inhibits poly(ADP-ribosylation) in human cells: a possible mechanism behind manganese-induced toxicity? *Journal of Environmental Monitor*, 12, 2062–2069.
- Bracci, B., Torricelli, P., Panzavolta, S., Boanini, E., Giardino, R., & Bigi, A. (2009). Effect of Mg²⁺, Sr²⁺, and Mn²⁺ on the chemico-physical and in vitro biological properties of calcium phosphate biomimetic coatings. *Journal of Inorganic Biochemistry*, 103(12), 1666–1674.
- Brar, H. S., Ball, J. P., Berglund, I. S., Allen, J. B., & Manuel, M. V. (2013). A study of a biodegradable Mg-3Sc-3Y alloy and the effect of self-passivation on the in vitro degradation. *Acta Biomaterialia*, 9(2), 5331–5340.

- Buehler, J., Chappuis, P., Saffar, J. L., Tsouderos, Y., & Vignery, A. (2001). Strontium ranelate inhibits bone resorption while maintaining bone formation in alveolar bone in monkeys (*Macaca fascicularis*). *Bone*, 29(2), 176–179.
- Byzova, T. V., Kim, W., Midura, R. J., & Plow, E. F. (2000). Activation of integrin α_3 regulates cell adhesion and migration to bone sialoprotein. *Experimental Cell Research*, 254, 299–308.
- Capuccini, C., Torricelli, P., Sima, F., Boanini, E., Ristoscu, C., Bracci, B., Socol, G., Fini, M., Mihailescu, I. N., & Bigi, A. (2008). Strontium-substituted hydroxyapatite coatings synthesized by pulsed-laser deposition: In vitro osteoblast and osteoclast response. *Biomaterials*, 4(6), 1885–1893.
- Chen, X.-B., Birbilis, N., & Abbott, T. B. (2011). A simple route towards a hydroxyapatite-Mg(OH)₂ conversion coating for magnesium. *Corrosion Science*, 53(6), 2263–2268.
- Chen, X.-B., Nisbet, D. R., Li, R. W., Smith, P. N., Abbott, T. B., Easton, M. A., Zhang, D. H., & Birbilis, N. (2014). Controlling initial biodegradation of magnesium by a biocompatible strontium phosphate conversion coating. *Acta Biomaterialia*, 10(3), 1463–1474.
- Chen, X.-B., Zhou, X., Abbott, T. B., Easton, M. A., & Birbilis, N. (2013). Double-layered manganese phosphate conversion coating on magnesium alloy AZ91D: Insights into coating formation, growth and corrosion resistance. *Surface and Coatings Technology*, 217, 147–155.
- Christoffersen, J., Christoffersen, M. R., Kolthoff, N., & Bärenholdt, O. (1997). Effects of strontium ions on growth and dissolution of hydroxyapatite and on bone mineral detection. *Bone*, 20(1), 47–54.
- Chung, C.-J., & Long, H.-Y. (2011). Systematic strontium substitution in hydroxyapatite coatings on titanium via micro-arc treatment and their osteoblast/osteoclast responses. *Acta Biomaterialia*, 7(11), 4081–4087.
- Cortés, D. A., López, H. Y., & Mantovani, D. (2007). Spontaneous and biomimetic apatite formation on pure magnesium. *Materials Science Forum*, 539–543, 589–597.
- Cui, X.-J., Zhou, J.-X., Lin, X.-Z., Luo, H., & Gong, M. (2012). Growing process and formation mechanism of manganese phosphate conversion film of magnesium alloy AZ31. *The Chinese Journal of Nonferrous Metals*, 22(1), 15–21.
- Dziuba, D., Meyer-Lindenberg, A., Seitz, J. M., Waizy, H., Angrisani, N., & Reifenrath, J. (2013). Long-term in vivo degradation behaviour and biocompatibility of the magnesium alloy ZEK100 for use as a biodegradable bone implant. *Acta Biomaterialia*, 9(10), 8548–8560.
- Forsyth, M., Neil, W. C., Howlett, P. C., Macfarlane, D. R., Hinton, B. R. W., Rocher, N., Kemp, T. F., & Smith, M. E. (2009). New insights into the fundamental chemical nature of ionic liquid film formation on magnesium alloy surfaces. *ACS Applied Materials and Interfaces*, 1(5), 1045–1052.
- Friedman, C. D., Constantino, P. D., & Jones, K. (1991). Hydroxyapatite cement. II. Obliteration and reconstruction of the cat frontal sinus. *Archives of Otolaryngology Head & Neck Surgery*, 117(4), 385–389.
- Ger, M. D., Yang, K. H., Sung, Y., Hwu, W. H., Liu, Y. C. (2004). Method for treating magnesium alloy by chemical conversion. US patent 6755918.
- Grynepas, M. D., & Marie, P. J. (1990). Effects of low doses of strontium on bone quality and quantity in rats. *Bone*, 11(5), 313–319.
- Gu, X. N., Xie, X. H., Li, N., Zheng, Y. F., & Qin, L. (2012). In vitro and in vivo studies on a Mg-Sr binary alloy system developed as a new kind of biodegradable metal. *Acta Biomaterialia*, 8(6), 2360–2374.

- Guo, D. G., Xu, K. W., Zhao, X. Y., & Han, Y. (2005). Development of a strontium-containing hydroxyapatite bone cement. *Biomaterials*, 26(19), 4073–4083.
- György, E., Toricelli, P., Socol, G., Iliescu, M., Mayer, I., Mihailescu, I. N., Bigi, A., & Werckman, J. (2004). Biocompatible Mn^{2+} -doped carbonated hydroxyapatite thin films grown by pulsed laser deposition. *Journal of Biomedical Materials Research Part A*, 71A(2), 353–358.
- Han, E. H., Zhou, W. Q., Shan, D. Y., & Ke, W. (2003). Corrosion and protection of magnesium alloy AZ31D by a new conversion coating. *Materials Science Forum*, 419–422, 879–882.
- Hermawan, H., Dubé, D., & Mantovani, D. (2010). Developments in metallic biodegradable stents. *Acta Biomaterialia*, 6(5), 1693–1697.
- Hiromoto, S., & Yamamoto, A. (2009). High corrosion resistance of magnesium coated with hydroxyapatite directly synthesized in an aqueous solution. *Electrochimica Acta*, 54(27), 7085–7093.
- Huan, Z., Leeflang, S., Zhou, J., Zhai, W., Chang, J., & Duszczek, J. (2012). In vitro degradation behavior and bioactivity of magnesium-Bioglass® composites for orthopedic applications. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, 100B(2), 437–446.
- Hunt, C. D., & Nielsen, F. H. (2009). Nutritional aspects of minerals in bovine and human milks. In P. L. H. McSweeney & P. F. Fox (Eds.), *Advanced Dairy Chemistry Vol. 3: Lactose, Water, Salts and Minor Constituents* (3rd ed., pp. 391–456). New York, NY: Springer.
- Ke, C., Pohl, K., Birbilis, N., Chen, X.-B. (2014). Protective strontium phosphate coatings for magnesium biomaterials accepted by a special issue on biodegradable materials of *Journal of Materials Science and Technology*, 30(5), 521–526.
- Kendig, M. W., & Buchheit, R. G. (2003). Corrosion inhibition of aluminum and aluminum alloys by soluble chromates, chromate coatings, and chromate-free coatings. *Corrosion*, 59, 379–400.
- Kirkland, N. T., Birbilis, N., & Staiger, M. P. (2012). Assessing the corrosion of biodegradable magnesium implants: a critical review of current methodologies and their limitations. *Acta Biomaterialia*, 8(3), 925–936.
- Kirkland, N. T., Lespagnol, J., Birbilis, N., & Staiger, M. P. (2010). A survey of bio-corrosion rates of magnesium alloys. *Corrosion Science*, 52(2), 287–291.
- Kunjukunju, S., Roy, A., Ramanathan, M., Lee, B., Candiello, J. E., & Kumta, P. N. (2013). A layer-by-layer approach to natural polymer-derived bioactive coatings on magnesium alloys. *Acta Biomaterialia*, 9(10), 8690–8703.
- LeGeros, R. Z. (2002). Properties of osteoconductive biomaterials: calcium phosphates. *Clinical Orthopaedics and Related Research*, 395, 81–98.
- Li, Y. F., Li, Q., Zhu, S. S., Luo, E., Li, J. H., Feng, G., Liao, Y. M., & Hu, J. (2010). The effect of strontium-substituted hydroxyapatite coating on implant fixation in ovariectomized rats. *Biomaterials*, 31(34), 9006–9014.
- Lüthen, F., Bulnheim, U., Müller, P. D., Rychly, J., Jesswein, H., & Nebe, J. G. B. (2007). Influence of manganese ions on cellular behavior of human osteoblasts in vitro. *Biomolecular Engineering*, 24(5), 531–536.
- Manso, M., Jiménez, C., Morant, C., Herrero, P., & Martínez-Duart, J. M. (2000). Electrodeposition of hydroxyapatite coatings in basic conditions. *Biomaterials*, 21(17), 1755–1761.
- Mayer, I., Cuisinier, F. J. G., Gdalya, S., & Popov, I. (2008). TEM study of the morphology of Mn^{2+} -doped calcium hydroxyapatite and β -tricalcium phosphate. *Journal of Inorganic Biochemistry*, 102(2), 311–317.
- Meng, E.-C., Guan, S.-K., Wang, H.-X., Wang, L.-G., Zhu, S.-J., Hu, J.-H., Ren, C.-X., Gao, J.-H., & Feng, Y.-S. (2011). Effect of electrodeposition modes on surface

- characteristics and corrosion properties of fluorine-doped hydroxyapatite coatings on Mg-Zn-Ca alloy. *Applied Surface Science*, 257(11), 4811–4816.
- Meyer-Lindenberg, A., Windhugen, H., Witte F. (2004). Medical implant for the human or animal body. US patent 2004/0241036.
- Ni, G. X., Lu, W. W., Xu, B., Chiu, K. Y., Yang, C., Li, Z. Y., Lam, W. M., & Luk, K. D. K. (2006). Interfacial behaviour of strontium-containing hydroxyapatite cement with cancellous and cortical bone. *Biomaterials*, 27(29), 5127–5133.
- Oliveira, A. L., Reis, R. L., & Li, P. (2007). Strontium-substituted apatite coating grown on Ti6Al4V substrate through biomimetic synthesis. *Journal of Biomedical Materials Research: Applied Biomaterials*, 83B(1), 258–265.
- Park, J.-W., Kim, Y.-J., & Jang, J.-H. (2011). Surface characteristics and in vitro biocompatibility of a manganese-containing titanium oxide surface. *Applied Surface Science*, 258(2), 977–985.
- Park, J.-W., Park, K.-B., & Suh, J.-Y. (2007). Effects of calcium ion incorporation on bone healing of Ti6Al4V alloy implants in rabbit tibiae. *Biomaterials*, 28(22), 3306–3313.
- Park, L., Kim, H., Kim, Y., Jang, J., Song, H., & Hanawa, T. (2010). Osteoblast response and osseointegration of a strontium-incorporated Ti-6Al-4V alloy implant. *Acta Biomaterialia*, 6(7), 2843–2851.
- Peng, Q. M., Huang, Y. D., Zhou, L., Hort, N., & Kainer, K. U. (2010). Preparation and properties of high purity Mg-Y biomaterials. *Biomaterials*, 31(3), 398–403.
- Remennik, S., Bartsch, I., Willbold, E., Witte, F., & Shechtman, D. (2011). New, fast corroding high ductility Mg-Bi-Ca and Mg-Bi-Si alloys, with no clinically observable gas formation in bone implants. *Materials Science and Engineering: B*, 176(20), 1653–1659.
- Rude, R. K. (1998). Magnesium deficiency: a heterogeneous cause of disease in humans. *Journal of Bone and Mineral Research*, 13(4), 749–758.
- Rude, R. K., & Singer, F. R. (1981). Magnesium deficiency and excess. *Annual Review of Medicine*, 32, 245–259.
- Shindo, M. L., Constantino, P. D., & Friedman, C. D. (1993). Facial skeletal augmentation using hydroxyapatite cement. *Archives of Otolaryngology Head & Neck Surgery*, 119(2), 185–189.
- Song, G. L. (2007). Control of biodegradation of biocompatible magnesium alloys. *Corrosion Science*, 49(4), 1696–1701.
- Song, Y.-W., Shan, D.-Y., & Han, E.-H. (2008). High corrosion resistance of electroless composite plating coatings on AZ91D magnesium alloys. *Electrochimica Acta*, 53(5), 2135–2143.
- Sopyan, I., Ramesh, S., Nawawi, N. A., Tampieri, A., & Sprio, S. (2011). Effects of manganese doping on properties of sol–gel derived biphasic calcium phosphate ceramics. *Ceramics International*, 37(8), 3703–3715.
- Staiger, M. P., Pietak, A. M., Huadmai, J., & Dias, G. (2006). Magnesium and its alloys as orthopedic biomaterials: a review. *Biomaterials*, 27(9), 1728–1734.
- Wang, J., He, Y., Maitz, M. F., Collins, B., Xiong, K., Guo, L., Yun, Y., Wan, G., & Huang, N. (2013). A surface-eroding poly(1,3-trimethylene carbonate) coating for fully biodegradable magnesium-based stent applications: toward better biofunction, biodegradation and biocompatibility. *Acta Biomaterialia*, 9(10), 8678–8689.
- Wang, Y., Wei, M., & Gao, J. (2009). Improve corrosion resistance of magnesium in simulated body fluid by dicalcium phosphate dihydrate coating. *Materials Science and Engineering: C*, 29(4), 1311–1316.

- Wang, Y., Wei, M., Gao, J., Hu, J., & Zhang, Y. (2008). Corrosion process of pure magnesium in simulated body fluid. *Materials Letters*, 62(14), 2181–2184.
- Wen, C. L., Guan, S. K., Peng, L., Ren, C. X., Wang, X., & Hu, Z. H. (2009). Characterization and degradation behavior of AZ31 alloy surface modified by bone-like hydroxyapatite for implant applications. *Applied Surface Science*, 255(13–14), 6433–6438.
- Witte, F., Fischer, J., Nellesen, J., Crostack, H.-A., Kaese, V., Pisch, A., Beckmann, F., & Windhagen, H. (2006). In vitro and in vivo corrosion measurements of magnesium alloys. *Biomaterials*, 27(7), 1013–1018.
- Witte, F., Kaese, V., Haferkamp, H., Switzer, E., Meyer-Lindenberg, A., Wirth, C. J., & Windhagen, H. (2005). In vivo corrosion of four magnesium alloys and the associated bone response. *Biomaterials*, 26(17), 3557–3563.
- Wong, C. T., Lu, W. W., Chan, W. K., Cheung, K. M. C., Luk, K. D. K., Lu, D. S., Rabie, A. B. M., Deng, L. F., & Leong, J. C. Y. (2004). In vivo cancellous bone remodeling on a strontium containing hydroxyapatite (Sr-HA) bioactive cement. *Journal of Biomedical Materials Research*, 68A(3), 513–521.
- Xin, Y. C., Jiang, J., Huo, K. F., Hu, T., & Chu, P. K. (2009). Bioactive SrTiO₃ nanotube arrays: strontium delivery platform on Ti-based osteoporotic bone implants. *ACS Nano*, 3, 3228–3234.
- Xu, L., Yu, G., Zhang, E., Pan, F., & Yang, K. (2007). In vivo corrosion behavior of Mg-Mn-Zn alloy for bone implant application. *Journal of Biomedical Materials Research Part A*, 83A(3), 703–711.
- Xue, W. C., Hosick, H. L., Bandyopadhyay, A., Bose, S., Ding, C. X., Luk, K. D. K., Cheung, K. M. C., & Lu, W. W. (2007). Preparation and cell-materials interactions of plasma sprayed strontium-containing hydroxyapatite coating. *Surface and Coatings Technology*, 201(8), 4685–4693.
- Yang, Y. Z., Kim, K.-H., & Ong, J. L. (2005). A review on calcium phosphate coatings produced using a sputtering process—an alternative to plasma spraying. *Biomaterials*, 26(3), 327–337.
- Yang, Y. C., Tsai, C. Y., Huang, Y. H., & Lin, C. S. (2012). Formation mechanism and properties of titanate conversion coating on AZ31 magnesium alloy. *Journal of the Electrochemical Society*, 159(5), C226–C232.
- Zeng, R., Dietzel, W., Witte, F., Hort, N., & Blawert, C. (2008). Progress and challenge for magnesium alloys as biomaterials. *Advanced Engineering Materials*, 10(8), B3–B14.
- Zhang, W. B., Shen, Y. H., Pan, H. B., Lin, K. L., Liu, X. G., Darvell, B. W., Lu, W. W., Chang, J., Deng, L. F., Wang, D. P., & others. (2011). Effects of strontium in modified biomaterials. *Acta Biomaterialia*, 7(2), 800–808.
- Zhou, W. Q., Shan, D. Y., Han, E. H., & Ke, W. (2008). Structure and formation mechanism of phosphate conversion coating on die-cast AZ91D magnesium alloy. *Corrosion Science*, 50(2), 329–337.
- Zhou, W. Q., Tang, W., Zhao, Q., Wu, S. W., & Han, E. H. (2011). Influence of additive on structure and corrosion resistance of manganese phosphate film on AZ91 magnesium alloy. *Materials Science Forum*, 686, 176–180.
- Zreiqat, H., Howlett, C. R., Zannettino, A., Evans, P., Schulze-Tanzil, G., Knabe, C., & Shakibaei, M. (2002). Mechanisms of magnesium-stimulated adhesion of osteoblastic cells to commonly used orthopaedic implants. *Journal of Biomedical Materials Research*, 62(2), 175–184.

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