

Review



Improved In Vitro and In Vivo Corrosion Resistance of Mg and Mg Alloys by Plasma Ion Implantation and Deposition Techniques—A Mini-Review

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Abstract: Enhanced in vitro corrosion resistance, cytocompatibility, in vitro antibacterial activities, in vivo antibacterial activities, in vivo corrosion resistance and in vivo stimulation of bone formation on plasma-modified biodegradable Mg and its alloys are reviewed, where the plasma modification includes plasma ion implantation (PII), plasma immersion ion implantation (PIII), or plasma immersion ion implantation and deposition (PIII&D) techniques. PII, PIII, and PIII&D are useful surface modification techniques, which can alter the surface properties of the biomaterials while preventing the bulk properties, which is much desirable factor especially for Mg based biomaterials. At first, this paper reviews the improved corrosion resistance by the formation of protective passive surface layer containing Zr-O, Zr-N, N, Si, Al-O, Zn-Al, Cr-O, Ti-O, Ti-N, Fe, Y, Sr, P, Pr, Ce, Nd, Hf, Ta, or C on Mg or its alloys using PII, PIII, or PIII&D techniques. Then, this paper reviews the improved biological properties such as cytocompatibility, in vitro antibacterial activities, and in vivo antibacterial activities on plasma-modified Mg or its alloys. Finally, this paper reviews the improved in vivo corrosion resistance and in vivo stimulation of bone formation on plasma modified Mg alloys. This review suggests that PII, PIII, and PIII&D techniques are effective techniques to improve the in vitro and in vivo corrosion resistance of Mg and its alloys for the development of degradable bio-implants.

Keywords: magnesium and its alloys; plasma ion implantation; surface modification made by various oxidation techniques; corrosion resistance; improved metallic bio-implants

1. Introduction

Mg and its alloys are considered for the development of biodegradable metallic implants for cardiovascular stents [1–5], wound closing rivet for stomach trauma [6], and orthopedic implants [7]. Biodegradable metallic implants are considered much attention because they can eliminate the need for secondary surgeries after sufficiently healing the tissues. Mg and its alloys are given much attention as a biodegradable metallic implant because Mg alloys have specific densities almost similar to that of human bone, and they have a Young's modulus almost closer to that of human bone that can reduce the stress at the bone/implant interface [7]. Moreover, Mg-based materials are considered as a promising biodegradable biomaterial [8–24]. Mg is a vital element in the human body. It stimulates new bone growth. It takes part in human metabolic activities. It is a cofactor in many enzymes. It stabilizes the structure of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) [25]. Thus, Mg and its alloys have several kinds of advantages. However, the major obstacle of Mg and its alloys as biodegradable implants are their low corrosion resistance



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2 of 27

because of their high chemical activity in physiological environment. Mg corrodes too fast in physiological environment containing high chloride content, consequently the interfacial pH rises high and producing huge amount of hydrogen gas, resulting in loss of mechanical integrity prior to the healing of the tissues [7,26–29].

Various approaches including alloying, aging, and surface modification have been used to improve the corrosion resistance of Mg and its alloys. In vitro and/or in vivo degradation of various kinds of Mg alloys such as Mg-Zn [30], Mg-Ca [31], Mg-Sr [32], Mg-Cu [33], Mg-Al [33], Mg-Zn-Mn [34,35], Mg-RE [28], Mg-Al-Zn [28], Mg-Bi-Ca [36], Mg-Zn-Sr [37], and Mg-Nd-Zn-Zr[38] have been investigated. Sankara Narayanan's group [34] has compared the corrosion behavior of pure Mg and Mg-Zn-Mn alloy at different immersion time intervals for 92 h in Ringer's solution. They observed that Mg-Zn-Mn alloy exhibits lesser corrosion resistance than that of pure Mg in the earlier immersion time, while Mg-Zn-Mn alloy exhibits better corrosion resistance after 40 h of immersion, and then Mg-Zn-Mn alloy exhibits significant improvement in corrosion resistance after 92 h of immersion due to the formation of protective corrosion product on it. They further observed that the Mg-Zn-Mn alloy exhibits better corrosion resistance than pure Mg after 92 h of immersion because of the presence of Zn and Mn as alloying elements in Mg-Zn-Mn alloy. In addition, Jamesh et al. [26] have compared the corrosion behavior of ZK60 and WE43 Mg alloys at different immersion time intervals for 96 h in Ringer's solution and simulated body fluid (SBF). They observed that the corrosion resistance of WE43 Mg alloy increases with increase in immersion time interval and protective corrosion product is formed on a WE43 Mg alloy containing calcium phosphate bio-mineral, while the formation of pitting corrosion and localized damage are observed on a ZK60 Mg alloy. They further observed that the WE43 Mg alloy exhibits better corrosion resistance than ZK60 Mg alloy after immersion for 96 h in Ringer's solution and SBF, because WE43 Mg alloy contains Y and Nd as alloying elements while ZK60 Mg alloy contains Zn and Zr as alloying elements. Hagihara et al. [33] have compared the corrosion behavior of pure Mg, Mg-Al alloy, and Mg-Cu alloy with different crystal orientations in Hanks' balanced salt solution (HBSS). They observed that the Mg-Al alloy exhibits better corrosion resistance than pure Mg while the Mg-Cu alloy exhibits lesser corrosion resistance than pure Mg and the influence of crystal orientation on the corrosion resistance of pure Mg, Mg-Al alloy, and Mg-Cu follows the same trend, which is in the following order: $(0001) > (11\overline{2}0) > (1010) > (11\overline{2}3) > (1012)$. In addition, Wu et al. [39] observed the precipitation of β -phases (Mg₁₇Al₁₂) from the supersaturated α -phases and the β -phases distributed along grains or grain boundaries using aging treatment (heated at 440 °C for 24 h, quenched, heated again at 220 °C for 48 h, and quenched) on Mg-Al-Zn-Mn alloy and the aged Mg-Al-Zn-Mn alloy exhibits lesser corrosion resistance than untreated Mg-Al-Zn-Mn alloy in the initial stages of immersion time intervals but the aged Mg-Al-Zn-Mn alloy exhibits better corrosion resistance than the untreated Mg-Al-Zn-Mn alloy in the lateral stage of immersion time intervals (8 h to 30 h of immersion) in cell culture medium.

Surface modification is a useful approach to tailor the surface properties of the materials [40–44]. Sankara Narayanan's group [45] has fabricated dicalcium phosphate dihydrate (brushite, CaHPO₄·2H₂O) coating on pure Mg using electrodeposition method and subsequently the brushite coating is converted into calcium phosphate (hydroxyapatite (HA), Ca₁₀(PO₄)₆(OH)₂) after immersion in NaOH. The HA coated Mg exhibits better corrosion resistance than untreated Mg in SBF. Cordoba et al. [46] have fabricated silane/TiO₂ coating on AZ31 and ZE41 Mg alloys using sol-gel coating method and the silane/TiO₂ coated Mg alloys (AZ31 and ZE41) exhibit better corrosion resistance than the untreated Mg alloys (AZ31 and ZE41) in SBF. Sankara Narayanan's group [47] has prepared MgO-ZrO₂ composite coating on Mg using anodizing method, micro-arc oxidation (MAO) coating on Mg, anodizing followed by MAO coating on Mg, and MAO coating followed by anodizing on Mg. The corrosion resistances of coated and uncoated Mg are in the following order in HBSS: anodizing followed by MAO coating on Mg > MAO coating followed by anodizing on Mg > MAO coating on Mg > MAO coating followed by anodizing on Mg > MAO coating on Mg > MgO-ZrO₂ composite (using anodizing)

coating on Mg > uncoated Mg. Wong et al. [48] have fabricated porous polymeric membrane coating made up of polycaprolactone (PCL) and dichloromethane on AZ91 Mg alloy. The porous polymeric coated AZ91 Mg alloy exhibits better corrosion resistance (both in vitro and in vivo) than untreated AZ91 Mg alloy. Zhao et al. [49] observed enhanced corrosion resistance on Zr&O plasma-treated (contains oxides of Zr after Zr plasma ion implantation followed by O plasma immersion ion implantation) Mg alloys (Mg-Ca and Mg-Sr) than that of untreated Mg alloys in SBF, tryptic soy broth (TSB), and cell culture medium. Wu et al. [17] observed enhanced corrosion resistance on C_2H_2 plasma-treated Mg-Nd-Zn-Zr alloy than that of untreated Mg-Nd-Zn-Zr alloy in 0.9 wt% NaCl solution, where about 200 nm thick diamond-like carbon (DLC) film was formed on the surface of the Mg alloy after C_2H_2 plasma immersion ion implantation and deposition (PIII&D).

Among various surface modifications, plasma surface modification techniques are useful (for various biomaterials) to achieve strong adhesion between the modified layer and coating [50,51] even in complicated cases, and also useful to enhance corrosion resistance, cytocompatibility, antimicrobial properties, covalent immobilization of protein molecules, and in vivo stimulation of bone formation [49,52–60]. In particular, plasma ion implantation (PII), plasma immersion ion implantation (PIII), and plasma immersion ion implantation and deposition (PIII&D) are useful surface modification techniques, where the techniques have the following advantages: (a) using this techniques, the surface properties (usually in nanometer) of the biomaterials can be altered while the preservation of bulk properties and especially in Mg based biomaterials is vitally important; (b) the surface modification using these techniques are solution free route, where chemical wastes will not be generated after plasma treatment. More recently, significant progress has been achieved by improving the corrosion resistance [38,49,52,54,61–77], cytocompatibility [49,54,63,70,76,77], antibacterial activities [49,63], and in vivo stimulation of bone formation [54,63] of Mg and its alloys using plasma modification techniques (PII/PIII&D). However, the reviews on enhanced corrosion resistance and biological properties of Mg and its alloys by plasma modification techniques (PII/PIII&D) have been scarcely reported. This paper reviews the improved corrosion resistance, cytocompatibility, antibacterial activities, and in vivo stimulation of bone formation of Mg and/or its alloys using plasma modification techniques (PII/PIII/PIII&D).

2. Plasma Ion Implantation (PII), Plasma Immersion Ion Implantation (PIII), and Plasma Immersion Ion Implantation and Deposition (PIII&D) Processes

Plasma ion implantation and deposition process have been elaborately described earlier [41,78]. Accordingly, conventional beam-line ion implantation also indicated as plasma ion implantation (PII) is a line-of sight process where energetic ions are bombarded into the surface layer of a substrate. As shown in Figure 1, the plasma immersion ion implantation (PIII) eliminates the line-of sight process and the PIII process involves the immersion of substrate in plasma and a high negative potential is applied for biasing the substrate. As a result, the substrate is surrounded by plasma sheath and acceleration of ions across the plasma sheath occurs normal to the surface of the substrate. Plasma immersion ion implantation and deposition (PIII&D) process is a hybrid process which combines plasma ion implantation and deposition. PIII&D involves the use of metal plasmas in the presence or absence of gas plasmas. High efficiency surface modification can be achieved by bombarding energetic ions generated from a cathodic arc plasma source and the plasma process can be tailored to obtain only implantation or only deposition or combined implantation and deposition.



Figure 1. Schematic diagram to illustrate the process of plasma immersion ion implantation (PIII).

3. Corrosion Resistance of Plasma Modified (PII, PIII, or PIII&D) Mg and/or Its Alloys 3.1. Zr Based or N Based Plasma Modification

Preparing thin Zr oxide surface layer can improve the corrosion resistance of Mg alloy. Chu's group [52] has observed enhanced corrosion resistance on zirconium (Zr) plasmatreated, and Zr&O plasma-treated ZK60 Mg alloy than that of untreated ZK60 Mg alloy in SBF, where the former contains 69 nm in thick Zr rich surface layer after Zr PII, and the later contains 80 nm in thick Zr rich surface layer (with O rich surface layer) after Zr PII followed by O PIII. Zr plasma-treated and Zr&O plasma-treated ZK60 Mg alloy exhibit lower icorr (Table 1), higher resistance, and lower capacitance than that of untreated ZK60 Mg alloy, where the corrosion resistances are in the following order: Zr&O plasma treated >Zr plasma treated > untreated ZK60 Mg alloy. The Zr or Zr&O plasma-treated Mg alloy contains Zr oxide surface layer with few nm in thick, where this thin surface passive layer can retard the charge transfer process for corrosion, and that can improve the corrosion resistance of ZK60 Mg alloy. Immersion tests disclose smaller surface damage after Zr or Zr&O plasma treatment initially and after 30 h immersion, while protective corrosion products including Mg(OH)₂, zirconium phosphate, $Ca_{10}(PO_4)_6(OH)_2$, and $Ca_3(PO_4)_2$ ·3H₂O are formed (Figures 2 and 3). Moreover, Zhao et al. [49] have observed enhanced corrosion resistance on Zr plasma-treated (Zr PII) Mg alloys (Mg-Ca and Mg-Sr) and Zr&O plasmatreated (Zr PII followed by O PIII) Mg alloys (Mg-Ca and Mg-Sr) than that of untreated Mg alloys in SBF, tryptic soy broth (TSB), and cell culture medium. In addition, Liu et al. [61] have observed improved corrosion resistance on Zr plasma-treated (Zr PIII&D) AZ91 Mg alloy than that of untreated AZ91 in Hank's simulated body fluid. Moreover, Ba et al. [79] have observed enhanced corrosion resistance on Zr plasma-treated Mg than that of pure Mg in SBF. In addition, Jia et al. [80] have observed improved corrosion resistance on Zr plasma-treated ZK60 Mg alloy than that of untreated ZK60 Mg alloy in SBF. Moreover, Liang et al. [81] have observed enhanced corrosion resistance on Zr&O plasma-treated (Zr&O PIII) ZK60 Mg alloy than that of untreated ZK60 Mg alloy in SBF and TSB.

(a)

Intensity (a.u.)

01

Depth: 500

Mg KLL





Ca LMM - Mg 1s

Figure 2. (a) XPS survey scan spectra and (**b**–**f**) High resolution XPS spectra (Mg 1s, Ca 2p, P 2p, Zn 2p, and Zr 3d) of the ZK60 Mg alloy after 30 h immersion in SBF (Reproduced with permission from Ref. [29]; Copyright 2014, Elsevier Ltd.).

Preparing thin Zr nitride along with Zr oxide surface layer can enhance the corrosion resistance of Mg alloys. Chu's group [62] has observed enhanced corrosion resistance on Zr&N plasma-treated (Zr PII followed by N PIII) WE43 Mg alloy than that of untreated WE43 Mg alloy in SBF and cell culture medium, where the plasma-treated Mg alloy contains 53 nm in thick Zr rich surface layer and 66 nm in thick N rich surface layer. Zr&N plasma-treated WE43 Mg alloy exhibits lower i_{corr}, higher resistance, and lower capacitance than that of untreated WE43 Mg alloy in both solution, where the corrosion resistance is more enhanced in cell culture medium than in SBF. Calcium phosphate $(Ca_{10}(PO_4)_6(OH)_2 \text{ and/or})$

Ca₃(PO₄)₂·3H₂O) is formed in the corrosion product of Zr&N plasma-treated and untreated WE43 Mg alloy after corrosion studies in SBF and cell culture medium. The formation of oxides and nitrides of Zr along with oxides of Y on the surface layer of Zr&N plasma-treated WE43 Mg alloy are observed, where this thin surface passive layer can diminish the charge transfer process for corrosion, and that can enhance the corrosion resistance of WE43 Mg alloy. Moreover, Cheng et al. [63] have observed enhanced corrosion resistance on Zr-N plasma-treated (contains about 80 nm of modified layer after Zr-N PIII) AZ91 Mg alloy (i_{corr}: 1.16×10^{-6} A/cm²) than that of untreated AZ91 (i_{corr}: 4.26×10^{-6} A/cm²) in 0.9% NaCl solution. Preparing nitrogen rich surface layer can enhance the corrosion resistance of Mg alloy. Li et al. [82] have observed that N⁺ plasma-treated AZ31 Mg alloy exhibits higher corrosion resistance than that of untreated AZ31 Mg alloy in Hank's solution. On the other hand, Wei et al. [83] have observed that NH₂⁺ plasma-treated AZ31 Mg alloy exhibits higher corrosion resistance on plasma-treated Mg alloy is ascribed to the formation protective surface layer comprising of oxides and amino group.



Figure 3. Schematic illustration of different stages of corrosion mechanism of untreated, Zr, Zr&O, and O plasma-treated ZK60 Mg alloy for 30 h immersion in SBF (Reproduced with permission from Ref. [29]; Copyright 2014, Elsevier Ltd.).

Plasma Treatment	Substrate	Corrosion Medium	i _{corr} (µA cm ⁻²)	E _{corr} (V vs. SCE)	References
Untreated	ZK60	SBF	409	-1654	[52]
Zr PII	ZK60	SBF	70	-1569	[52]
Zr PII + O PIII	ZK60	SBF	11	-1571	[52]
Untreated	Mg-Ca	SBF	230	-1.92	[49]
Zr PII	Mg-Ca	SBF	120	-1.6	[49]
Zr PII + O PIII	Mg-Ca	SBF	26	-1.78	[49]
Untreated	Mg-Sr	SBF	1000	-1.79	[49]
Zr PII	Mg-Sr	SBF	250	-1.6	[49]
Zr PII + O PIII	Mg-Sr	SBF	170	-1.68	[49]
Untreated	Mg-Ca	Tryptic Soy Broth	280	-1.91	[49]
Zr PII	Mg-Ca	Tryptic Soy Broth	49	-1.51	[49]
Zr PII + O PIII	Mg-Ca	Tryptic Soy Broth	41	-1.66	[49]
Untreated	Mg-Sr	Tryptic Soy Broth	430	-1.81	[49]
Zr PII	Mg-Sr	Tryptic Soy Broth	42	-1.45	[49]
Zr PII + O PIII	Mg-Sr	Tryptic Soy Broth	40	-1.63	[49]
Untreated	Mg-Ca	Cell culture medium	15	-1.76	[49]
Zr PII	Mg-Ca	Cell culture medium	6.4	-1.48	[49]
Zr PII + O PIII	Mg-Ca	Cell culture medium	4.6	-1.63	[49]
Untreated	Mg-Sr	Cell culture medium	23	-1.56	[49]
Zr PII	Mg-Sr	Cell culture medium	5	-1.44	[49]
Zr PII + O PIII	Mg-Sr	Cell culture medium	4	-1.45	[49]
Untreated	Mg	SBF	52.6	-1.7	[79]
Zr PII	Mg	SBF	19.9	-1.43	[79]
Untreated	ZK60	SBF with glucose	22.68	-1.577	[80]
Zr PII	ZK60	SBF with glucose	4.416	-1.629	[80]
Untreated	ZK60	SBF	740	~-1.7	[81]
Zr PIII + O PIII	ZK60	SBF	102	~-1.62	[81]
Untreated	ZK60	Tryptic Soy Broth	142	~-1.49	[81]
Zr PIII + O PIII	ZK60	Tryptic Soy Broth	19.3	~-1.51	[81]
Untreated	WE43	SBF	368	-1.997	[62]
Zr PII + N PIII	WE43	SBF	29.8	-1.82	[62]
Untreated	WE43	Cell culture medium	36.6	-1.78	[62]
Zr PII + N PIII	WE43	Cell culture medium	0.51	-1.517	[62]
Untreated	AZ91	0.9% NaCl	4.26	-1.49	[63]
Zr-N PIII	AZ91	0.9% NaCl	1.16	-1.3	[63]
Untreated	AZ91	DMEM	10.8	-1.57	[63]
Zr-N PIII	AZ91	DMEM	0.392	-1.32	[63]
Untreated	AZ31	Hank's solution	869.72	-1.03	[83]
NH2 ⁺ II	AZ31	Hank's solution	125.23	-1.01	[83]

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SCE: Saturated Calomel Electrode; PII: Plasma Ion Implantation; PIII: Plasma immersion ion implantation; SBF: Simulated Body Fluid; DMEM: Dulbecco's modified Eagle's medium; II: Ion Implantation.

3.2. Si, Al Based, Zn Based, Zn&Al, or Cr Based Plasma Modification

Preparing thin Si oxide surface layer can enhance the corrosion resistance of Mg alloy. Chu's group [64] has observed enhanced corrosion resistance on Si plasma-treated (contains Si rich surface layer after Si PII) WE43 Mg alloy than that of untreated WE43 Mg alloy in SBF. Si plasma-treated WE43 Mg alloy exhibits lower i_{corr} (Table 2), higher resistance, and lower capacitance than untreated WE43 Mg alloy, and the Si plasma-treated WE43 Mg alloy exhibits higher phase angle maximum (-60° at 180 Hz) than that of untreated WE43 Mg alloy (-26° at 202 Hz) indicating that Si plasma-treated WE43 Mg alloy exhibits better corrosion resistance than that of untreated WE43 Mg alloy in SBF. The Si plasma-treated Mg alloy contains Si oxide surface layer with few nm in thick, where this thin surface passive layer can hinder the charge transfer process for corrosion, and that can enhance the corrosion resistance of WE43 Mg alloy.

Plasma Treatment	Substrate	Corrosion Medium	i _{corr} (μA cm ⁻²)	E _{corr} (V vs. SCE)	References
Untreated	WE43	SBF	642	-1.972	[64]
Si PII	WE43	SBF	27	-1.895	[64]
Untreated	Mg	SBF	394.2	~-1.98	[67]
Al PII	Mg	SBF	33.66	~-1.76	[67]
Untreated	AZ31	SBF	230.4	~-1.68	[67]
Al PII	AZ31	SBF	28.27	~-1.55	[67]
Untreated	AZ91	SBF	150.1	~-1.70	[67]
Al PII	AZ91	SBF	58.24	~-1.47	[67]
Untreated	WE43	SBF	602.5	-1.972	[65]
Al PII + O PIII	WE43	SBF	44.68	-1.586	[65]
Untreated	Mg-Nd-Zn-Zr	SBF	434.1	-1.987	[66]
Cr PII + O PIII	Mg-Nd-Zn-Zr	SBF	38.32	-1.592	[66]
Al PII + O PIII	Mg-Nd-Zn-Zr	SBF	152.7	-1.637	[66]
Untreated	Mg	SBF	173.8	-1.998	[84]
Zn PII	Mg	SBF	1147	-1.517	[84]
Untreated	Mg-1Ca	SBF	248.1	-1.92	[85]
Zn II&D	Mg-1Ca	SBF	321.8	-1.58	[85]'
Untreated	Mg	SBF	359	-1.976	[68]
Zn PII + Al PII	Mg	SBF	22.7	-1.8125	[68]
Untreated	Mg	SBF	168	-1.98	[69]
Cr PII + O PIII	Mg	SBF	58.9	-1.63	[69]
Untreated	Mg	SBF	395.4	-2.00	[70]
Cr PII + O PIII	Mg	SBF	38.04	-1.57	[70]

Table 2. E_{corr} and i_{corr} of the untreated, and Si/Al based/Zn based/Zn&Al/Cr based plasma-treated Mg/Mg alloys.

SCE: saturated calomel electrode; PII: Plasma Ion Implantation; PIII: Plasma immersion ion implantation; SBF: Simulated Body Fluid; II&D: Ion Implantation and Deposition.

Preparing thin Al oxide surface layer can enhance the corrosion resistance of Pure Mg and Mg alloy. Wu et al. [67] have observed enhanced corrosion resistance (exhibits lower icorr) on Al plasma-treated (Al PII) pure Mg, AZ31 Mg alloy, and AZ91 Mg alloy than that of untreated pure Mg, AZ31 Mg alloy, and AZ91 Mg alloy in SBF, respectively. The Al plasmatreated pure Mg and Mg alloy contains Al oxide surface layer with few nm in thick, where this thin surface passive layer can retard the charge transfer process for corrosion, and that can enhance the corrosion resistance of pure Mg and Mg alloy. Moreover, Zhao et al. [65] have observed enhanced corrosion resistance on Al&O plasma-treated (Al PII followed by O PIII) WE43 Mg alloy than that of untreated WE43 Mg alloy in SBF, where the plasmatreated WE43 Mg alloy exhibits lower i_{corr}, higher resistance, and lower capacitance than that of untreated WE43 Mg alloy. In addition, Wu et al. [66] have observed enhanced corrosion resistance on Al&O plasma-treated (Al PII followed by O PIII) Mg-Nd-Zn-Zr alloy than that of untreated Mg-Nd-Zn-Zr alloy in SBF. In addition, Liu et al. [61] have observed enhanced corrosion resistance on Al plasma-treated (contains Al rich surface layer after Al PIII&D) AZ91 Mg alloy than that of untreated AZ91 in Hank's simulated body fluid. Moreover, Wong et al. [54] have observed enhanced corrosion resistance on Al-O plasma-treated AZ91 Mg alloy (contains Al and O rich surface layer for about 250 nm after Al-O PIII&D) than that of untreated AZ91 in SBF.

Preparing thin Zn surface layer can deteriorate the corrosion resistance of Pure Mg possibly due to galvanic effect. Wu et al. [84] have observed diminish in corrosion resistance on Zn plasma-treated (contains Zn rich surface layer after Zn PII) pure Mg than that of untreated Mg in SBF possibly due to galvanic effect between metallic Zn and Mg. On the other hand, preparing Zn deposition layer on Zn ion implanted layer can diminish the galvanic effect. Liu et al. [85] have observed a comparable corrosion current density on Zn plasma-treated Mg-1Ca alloy (Zn ion implantation and deposition; i_{corr} : 321.8 µA cm⁻²) than that of untreated Mg-1Ca alloy (i_{corr} : 248.1 µA cm⁻²) in SBF, while the plasma-treated

Mg alloy (E_{corr} : -1.58 V) exhibits higher corrosion potential than that of untreated Mg alloy (E_{corr} : -1.92 V), where the positive shift in the potential can be attributed to the formation of ZnO as a passive layer. However, preparing thin Al surface layer over the Zn layer can enhance the corrosion resistance of Pure Mg. Xu et al. [68] have observed enhanced corrosion resistance on Zn&Al plasma-treated (Zn PII followed by Al PII) pure Mg than that of untreated Mg in SBF. The enhance corrosion resistance of the Zn&Al plasma-treated pure Mg is attributed to the formation of more compact hybrid oxide film along with the formation of the β -Mg₁₇Al₁₂ phase, where the hybrid oxide film is composed of three-layer surface film containing an inner metallic magnesium rich layer, a middle layer alloyed with metallic Zn, Al and Mg, and an outer layer of Mg oxide/Al oxide. The thin surface passive layer on Zn&Al plasma-treated pure Mg can diminish the charge transfer process for corrosion, and that can improve the corrosion resistance of pure Mg.

Preparing thin Cr oxide surface layer can enhance the corrosion resistance of Pure Mg and Mg alloy. Xu et al. [69] have observed diminish in corrosion resistance on Cr plasmatreated (Cr PII) pure Mg than that of untreated Mg in SBF, possibly due to the galvanic effect between metallic Cr and Mg. On the other hand, enhanced corrosion resistance is observed on Cr&O plasma-treated (Cr PII followed by O PIII) pure Mg than that of untreated Mg in SBF. The Cr&O plasma-treated pure Mg contains Cr and O rich surface layer with few nm in thick, where this thin surface passive layer can hinder the charge transfer process for corrosion, and that can enhance the corrosion resistance of pure Mg. Moreover, Cr&O plasma-treated (Cr PII followed by O PIII) pure Mg at different voltages (Cr PII at 15, 20, and 40 kV) exhibits higher corrosion resistance than that of untreated pure Mg in SBF, where the corrosion resistance are in the following order: 15 kV > 20 kV > 40 kV [70]. In addition, Cr&O plasma-treated (Cr PII followed by O PIII) Mg-Nd-Zn-Zr alloy exhibits higher corrosion resistance than that of untreated Mg in SBF.

3.3. Ti Based, Ni, Ti&Ni, Fe, Mn, Ag, Y, Sr, Ca, P, or Pr Plasma Modification

Preparing thin Ti oxide surface layer can enhance the corrosion resistance of the Mg alloy. Zhao et al. [71] have observed enhanced corrosion resistance on Ti plasma-treated (Ti PII) and Ti&O plasma-treated (Ti PII followed by O PIII) WE43 Mg alloys than that of untreated WE43 Mg alloy in SBF, where the former contains 64 nm in thick Ti rich surface layer, and the later contains 104 nm in thick Ti rich surface layer (with O rich surface layer), while the corrosion resistances are in the following order: Ti&O plasma treated > Ti plasma treated > untreated WE43 Mg alloy. The Ti plasma-treated or Ti&O plasma-treated Mg alloy contains Ti oxide surface layer with few nm in thick, where this thin surface passive layer can retard the charge transfer process for corrosion, and that can improve the corrosion resistance of Mg alloy. Moreover, Chen et al. [72] have observed enhanced corrosion resistance on Ti plasma-treated (Ti PII) AZ31 Mg alloy than that of untreated AZ31 in 3.5% NaCl solution. In addition, Liu et al. [61] have observed enhanced corrosion resistance on Ti plasma-treated (Ti PIII&D) AZ91 Mg alloy than that of untreated AZ91 in Hank's simulated body fluid.

Preparing thin Ti nitride along with Ti oxide surface layer can enhance the corrosion resistance of Mg alloy. Liu et al. [73] have observed enhanced corrosion resistance on Ti-N plasma-treated (Ti PII followed by N PIII) AZ31 Mg alloy (i_{corr} : $1.5 \pm 0.5 \times 10^{-3}$ A/cm²; Table 3) than that of untreated AZ31 (i_{corr} : $112 \pm 0.5 \times 10^{-3}$ A/cm²) in 0.56 M NaCl solution, where the plasma-treated modified layer contains MgO, TiO₂ and TiN along with Ti and Mg. The formation of oxides and nitrides of Ti on the surface layer of Ti&N plasma-treated AZ31 Mg alloy is observed, where this thin surface passive layer can diminish the charge transfer process for corrosion, and that can enhance the corrosion resistance of AZ31 Mg alloy. In addition, Dai et al. [86] have observed diminish in the corrosion resistance on Ni plasma-treated as well as on Ti&Ni plasma-treated AM60 Mg alloys than that of untreated AM60 Mg alloy in 3.5% NaCl solution, possibly due to the galvanic effect.

Preparing Fe rich surface layer by implantation can diminish the corrosion resistance of Mg alloy possibly due to galvanic effect. Liu et al. [87] have observed accelerated

corrosion on the Fe plasma-treated (Fe PII) Mg-1Ca alloy than that of the untreated Mg-1Ca alloy in Hank's solution possibly due to the galvanic effect between Fe and Mg. On the other hand, preparing Fe deposition layer on Fe ion implanted layer can enhance the corrosion resistance. Zheng et al. [88] have observed enhanced corrosion resistance on Fe plasma-treated (after Fe ion implantation and deposition) ZK60 Mg alloy than that of untreated ZK60 in Hank's solution. They have observed the formation of α -Fe thin film on surface of the Fe plasma-treated ZK60 Mg alloy (Figure 4a), where this surface passive layer can retard the charge transfer process for corrosion, and that can enhance the corrosion resistance of ZK60 Mg alloy (Figure 4b). Moreover, Zheng et al. [89] have observed enhanced corrosion resistance on theFe&O plasma-treated ZK60 Mg alloy (Fe&O ion implantation and deposition) than that of the untreated ZK60 Mg alloy in Hank's solution, where the improvement in corrosion resistance on plasma-treated Mg alloy is attributed to the formation of the protective passive layer comprising FeO/Fe-rich oxide (in the outer deposition zone) along with anFe&Mg mixture (in the inner implanted zone).



Figure 4. (a) Glancing Angle XRD patterns of Fe plasma-treated ZK60 Mg alloy, and (b) Potentiodynamic polarization curves of Fe plasma-treated and untreated ZK60 Mg alloy in Hank's solution (Reproduced with permission from Ref. [52]; Copyright 2014, Chinese Materials Research Society and Elsevier B.V.).

Preparing thin Mn rich surface layer can alter the corrosion behavior of Mg. Dong et al. [90] have observed diminish in corrosion resistance on Mn plasma-treated Mg than that of untreated Mg in the initial stage (after 20 minutes) possibly due to the galvanic effect between Mn and Mg, whereas the Mn plasma-treated Mg exhibits higher corrosion resistance than that of untreated Mg after 72 h in Hank's solution possibly due to the formation of protective corrosion products including calcium phosphate along with a small amount of Mn oxide.

Table 3. E_{corr} and i_{corr} of the untreated and Ti based/Fe based/Ag/Y/Sr/Ca/P/Pr plasma-treated Mg/Mg alloys.

Plasma Treatment	Substrate	Corrosion Medium	i _{corr} (µA cm ⁻²)	E _{corr} (V vs. SCE)	References
Untreated	WE43	SBF	327	~-1.98	[71]
Ti PII + O PIII	WE43	SBF	14.4	~-1.8	[71]
Untreated	AZ31	0.56 M NaCl	0.112	-1460	[73]
TiN	AZ31	0.56 M NaCl	0.0015	-850	[73]
Untreated	ZK60	Hank's solution	105.8	-1.493	[89]
Fe&O II&D	ZK60	Hank's solution	1.25	-1.066	[89]
Untreated	ZK60	Hank's solution	119	-1.528	[88]
Fe II&D	ZK60	Hank's solution	1.363	-1.295	[88]
Untreated	Mg-Ca	Hank's solution	92.58	-1.81	[87]
Fe PII	Mg-Ca	Hank's solution	235.23	-1.56	[87]
Ag PII	Mg-Ca	Hank's solution	524.93	-1.55	[87]
Y PII	Mg-Ca	Hank's solution	30.65	-1.60	[87]
Untreated	Mg	SBF with glucose	52.6	-1.694	[91]
Sr PII	Mg	SBF with glucose	25.1	-1.582	[91]
Untreated	Mg	SBF	161.66	-1.820	[92]
Ca PII	Mg	SBF	100	-1.825	[92]
Untreated	Mg	SBF with glucose	67.601	-1.657	[93]
P PII	Mg	SBF with glucose	54.955	-1.598	[93]
Untreated	Mg	artificial hand sweat	132.2	-1.985	[74]
Pr PII	Mg	artificial hand sweat	79.62	-1.881	[74]
Untreated	AZ80	artificial hand sweat	354.1	-1.653	[74]
Pr PII	AZ80	artificial hand sweat	11.12	-1.488	[74]

SCE: saturated calomel electrode; PII: Plasma Ion Implantation; PIII: Plasma immersion ion implantation; SBF: Simulated Body Fluid; II&D: Ion Implantation and Deposition.

Preparing an Ag rich surface layer by implantation can diminish the corrosion resistance of the Mg alloy possibly due to the galvanic effect. Liu et al. [87] have observed accelerated corrosion on an Ag plasma-treated (contains Ag rich surface layer after Ag PII) Mg-1Ca alloy than that of an untreated Mg-1Ca alloy in Hank's solution, possibly due to the galvanic effect between Ag and Mg (Type I in Figure 5).

Preparing thin Y oxide surface layer can enhance the corrosion resistance of Mg alloy. Liu et al. [87] have observed enhanced corrosion resistance on Y plasma-treated (contains Y rich surface layer after Y PII) Mg-1Ca alloys (0.69 ± 0.18 mm/year) than that of untreated Mg-1Ca alloys (2.10 ± 0.21 mm/year) in Hank's solution. The Y plasma-treated Mg alloy contains a Y oxide surface layer with a few nm in thickness, where this thin surface passive layer can diminish the charge transfer process for corrosion, and that can improve the corrosion resistance of Mg alloy. They proposed the schematic illustration to demonstrate the corrosion mechanism of plasma ion-implanted Mg alloys, where the formation of a compact passive protective oxide layer in Y plasma-treated Mg alloy improves its corrosion resistance (Type II in Figure 5), whereas the formation of non-protective layer (mainly metallic) in Ag or Fe plasma-treated Mg alloys accelerates its corrosion resistance (Type I in Figure 5). In addition, Jia et al. [91] have observed enhanced corrosion resistance on Sr plasma-treated Mg than that of pure Mg in SBF. The Sr plasma-treated Mg contains Sr oxide surface layer with about 30 nm in thick, where this thin surface passive layer can retard the charge transfer process for corrosion, and that can enhance the corrosion resistance of Mg. On the other hand, Somasundaram et al. [92] have observed only a slight improvement in corrosion resistance on Ca ion implanted Mg than that of pure Mg in SBF. In addition, Asdi et al. [93] have observed improvement in corrosion resistance on P ion implanted Mg than that of pure Mg in SBF, where the improvement in corrosion resistance on the ion implanted Mg is attributed to the formation of about 120 nm in thick passive layer comprising of PO along with MgO.



Figure 5. Schematic illustration of the degradation of plasma ion implanted Mg alloys in simulated physiological fluids (Reproduced with permission from Ref. [51]; Copyright 2015, Elsevier B.V.).

Preparing a thin Pr oxide surface layer can enhance the corrosion resistance of pure Mg and Mg alloy. Wang et al. [74] have observed enhanced corrosion resistance on Pr plasma-treated (Pr PII) pure Mg and AZ80 Mg alloy than that of untreated samples (pure Mg and AZ80 Mg alloy) in artificial hand sweat solution. The Pr plasma-treated pure Mg and Mg alloy contain Pr oxide surface layer with few nm in thick, where this thin surface passive layer can retard the charge transfer process for corrosion, and that can improve the corrosion resistance of pure Mg and Mg alloy.

3.4. Ce, Nd, Hf, Ta, H₂O or Hydroxyl Plasma Modification

Preparing thin Ce oxide surface layer can enhance the corrosion resistance of pure Mg and Mg alloy. Wang et al. [94] have observed enhanced corrosion resistance on Ce plasma-treated (Ce PII) AZ31 Mg alloy than that of untreated AZ31 in 3.5 wt.% NaCl solution saturated with Mg(OH)₂. Moreover, Wu et al. [75] have observed enhanced corrosion resistance on Ce plasma-treated (Ce PII) pure Mg than that of untreated pure Mg in Ringer's solution, artificial hand sweat solution, and complete cell culture medium. The Ce plasma-treated pure Mg and Mg alloy contain Ce oxide surface layer with few nm in thick, where this thin surface passive layer can diminish the charge transfer process for corrosion, and that can enhance the corrosion resistance of pure Mg and Mg alloy.

Preparing thin Nd oxide surface layer can enhance the corrosion resistance of Mg alloy. Jin et al. [76] have observed enhanced corrosion resistance on Nd plasma-treated (Nd PII) WE43 Mg alloy than that of untreated WE43 Mg alloy in SBF and cell culture medium. The Nd plasma-treated Mg alloy contains Nd oxide surface layer with few nm in thick, where this thin surface passive layer can hinder the charge transfer process for corrosion, and that can improve the corrosion resistance of Mg alloy.

Preparing thin Hf oxide surface layer can enhance the corrosion resistance of Mg alloy. Jin et al. [77] have observed enhanced corrosion resistance (exhibits lower i_{corr} (Table 4),

and higher resistance, Figure 6) on Hf plasma-treated (Hf PII) WE43 Mg alloy than that of untreated WE43 Mg alloy in SBF. The Hf plasma-treated Mg alloy contains Hf oxide surface layer with a few nm in thickness, where this thin surface passive layer can retard the charge transfer process for corrosion, and that can enhance the corrosion resistance of Mg alloy.



Figure 6. (a) Potentiodynamic polarization curves and (b) Nyquist plots with their corresponding equivalent circuits of Hf plasma-treated and untreated WE43 Mg alloy in SBF (Reproduced with permission from Ref. [48]; Copyright 2016, Elsevier B.V.).

Preparing thin Ta oxide surface layer can enhance the corrosion resistance of Mg alloy. Wang et al. [95] have observed enhanced corrosion resistance on Ta plasma-treated (Ta PII) AZ31 Mg alloy than that of untreated AZ31 in 3.5 wt.% NaCl solution saturated with Mg(OH)₂. The Ta plasma-treated Mg alloy contains Ta oxide surface layer with few nm in thick, where this thin surface passive layer can retard the charge transfer process for corrosion, and that can enhance the corrosion resistance of Mg alloy.

Increasing the surface oxide layer can enhance the corrosion resistance of Mg alloy. Tian et al. [96] have observed enhanced corrosion resistance on H₂O plasma-treated (H₂O PIII and oxidation) AZ31B Mg alloy than that of untreated AZ31B in 3 wt.% NaCl solution. The plasma-treated Mg alloy contains increased surface oxide layer with a few nm in thickness, where this thin surface passive layer can diminish the charge transfer process for corrosion, and that can enhance the corrosion resistance of Mg alloy. Moreover, Wei et al. [97] have observed enhanced corrosion resistance on OH⁻ plasma-treated ZK60 Mg alloy in Hank's solution, where the improvement in the corrosion resistance on the plasma-treated Mg alloy is attributed to the formation of passive surface layer comprising of (Mg(OH)₂/MgO).

Table 4. Ecorr and icorr of the untreated and Ce/Nd/Hf/Ta/hydroxyl plasma-treated Mg/Mg alloys.

Plasma Treatment	Substrate	Corrosion Medium	i_{corr} (µA cm ⁻²)	E _{corr} (V vs. SCE)	References
Untreated	AZ31	3.5% NaCl saturated with Mg(OH) ₂	29.1	-1.45	[94]
Ce PII	AZ31	3.5% NaCl saturated with Mg(OH) ₂	3.5% NaCl saturated with Mg(OH) ₂ 2.81		[94]
Untreated	Mg	artificial hand sweat	106.1	-1.878	[75]
Ce PII	Mg	artificial hand sweat	39.9	-1.789	[75]
Untreated	Mg	Ringer's solution	41.8	-1.748	[75]
Ce PII	Mg	Ringer's solution	26.8	-1.514	[75]
Untreated	Mg	Cell culture medium	20.4	-1.731	[75]
Ce PII	Mg	Cell culture medium	5.2	-1.552	[75]
Untreated	WE43	SBF	555.7	-1.992	[76]
Nd PII	WE43	SBF	11.9	-1.740	[76]
Untreated	WE43	Cell culture medium	2.55	-1.705	[76]
Nd PII	WE43	Cell culture medium	0.5	-1.560	[76]
Untreated	WE43	SBF	625.7	~-1.9	[77]
Hf PII	WE43	SBF	40	~-1.75	[77]
Untreated	AZ31	3.5% NaCl saturated with Mg(OH) ₂	15	-1.43	[95]
Ta PII	AZ31	3.5% NaCl saturated with Mg(OH) ₂	3.9	-1.25	[95]
Untreated	ZK60	Hank's solution	312.26	-1.57967	[97]
OH- II	ZK60	Hank's solution	70.79	-1.60067	[97]

SCE: saturated calomel electrode; PII: Plasma Ion Implantation; SBF: Simulated Body Fluid; II: Ion Implantation.

3.5. C Based Plasma Modification

Preparing amorphous thin C containing surface layer can enhance the corrosion resistance of pure Mg. Xu et al. [98] have observed enhanced corrosion resistance on C plasma-treated (C PII) pure Mg than that of untreated pure Mg in SBF and cell culture medium, where the C plasma-treated Mg (26.3 μ A cm⁻²; Table 5) exhibits lower corrosion current density than that of untreated pure Mg (258 μ A cm⁻²) in SBF, while the C plasma-treated Mg (1.88 μ A cm⁻²) exhibits lower corrosion current density than that of untreated pure Mg (258 μ A cm⁻²) in SBF, while the C plasma-treated Mg (65.2 μ A cm⁻²) exhibits lower corrosion current density than that of untreated pure Mg (65.2 μ A cm⁻²) in cell culture medium. The C plasma-treated pure Mg contains amorphous graphite surface layer with 58 nm in thick, where this thin surface passive layer can hinder the charge transfer process for corrosion, and that can enhance the corrosion resistance of pure Mg. On the other hand, Yu et al. [99] have observed enhanced corrosion resistance on the C plasma-treated AM60 Mg alloy than that of the untreated AM60 Mg alloy in 3.5% NaCl, where the improvement in corrosion resistance of the plasma-treated Mg alloy is attributed to the formation of about a 250 nm thick C rich passive surface layer comprising an Mg₂C₃ phase.

Preparing thin C containing surface layer with increased surface oxide layer can enhance the corrosion resistance of Mg alloy. Xu et al. [100] have observed enhanced

corrosion resistance on CO_2 plasma-treated (CO_2 PIII) AZ31 Mg alloy than that of untreated AZ31 in SBF and cell culture medium. The CO_2 plasma-treated AZ31 Mg alloy contains graphite surface layer along with increase in surface oxide layer (Mg and Al oxide), where this thin surface passive layer can diminish the charge transfer process for corrosion, and that can improve the corrosion resistance of AZ31 Mg alloy.

Preparing thin diamond-like carbon (DLC) film on the surface can enhance the corrosion resistance of Mg alloy. Wu et al. [38] have observed enhanced corrosion resistance on the C_2H_2 plasma-treated (C_2H_2 PIII&D) Mg-Nd-Zn-Zr alloy than that of the untreated Mg-Nd-Zn-Zr alloy in 0.9 wt% NaCl solution. The C₂H₂ plasma-treated Mg alloy contains about a 200 nm thick DLC film on the surface, where this thin surface passive layer can hinder the charge transfer process for corrosion, and that can improve the corrosion resistance of the Mg alloy. The C_2H_2 plasma-treated Mg-Nd-Zn-Zr alloy exhibits lesser surface damage than that of untreated Mg-Nd-Zn-Zr alloy after 24 h immersion in 0.9 wt% NaCl solution. Moreover the cross sectional images observed at different locations of untreated Mg-Nd-Zn-Zr alloys (Figure 7a,b) and C₂H₂ plasma-treated Mg-Nd-Zn-Zr alloys (Figure 7c,d) after 24 h immersion in 0.9 wt% NaCl solution revealed that the C_2H_2 plasma-treated Mg-Nd-Zn-Zr alloy exhibits lesser corrosion with the existence of a carbon film (top inset of Figure 7c) and small corrosion pits (indicated using arrows in Figure 7d) after 24 h of corrosion, while the untreated Mg-Nd-Zn-Zr alloy exhibits higher corrosion with the existence of a thicker corrosion product with larger pits (Figure 7b) indicating that the C_2H_2 plasma-treated Mg-Nd-Zn-Zr alloy exhibits better corrosion resistance than untreated Mg-Nd-Zn-Zr alloys. Moreover, Feng et al. [101] have observed enhanced corrosion resistance on C_2H_2 plasma-treated (C_2H_2 PIII&D) AZ31 Mg alloys than that of untreated AZ31 Mg alloys in a Lysogeny broth medium, where the plasma-treated surface contains about a 200 nm thick DLC film. In addition, Yekehtaz et al. [102] have observed enhanced corrosion resistance on $CH_4\&C_2H_2$ plasma-treated Mg (contains DLC film on the surface after CH₄ PIII followed by C₂H₂ PIII&D) than that of CH₄ plasma-treated Mg and untreated Mg in a slightly acidic acetate buffer solution, where the corrosion resistances are in the following order: $CH_4\&C_2H_2$ plasma-treated Mg > CH_4 plasma-treated Mg > untreated Mg. On the other hand, Wei et al. [103] have observed that the COOH⁺ plasma-treated ZK60 Mg alloy exhibits higher corrosion resistance than that of the untreated ZK60 Mg alloy in Hank's solution, where the improvement is ascribed to the smooth passive surface layer comprising carbonate, and oxide/hydroxide.

Plasma Treatment	Substrate	Corrosion Medium	i _{corr} (µA cm ^{−2})	E _{corr} (V vs. SCE)	References
Untreated	Mg	SBF	258	-1.98	[98]
C PII	Mg	SBF	26.3	-1.94	[98]
Untreated	Mg	DMEM	65.2	-1.98	[98]
C PII	Mg	DMEM	1.88	-1.71	[98]
Untreated	AM60	3.5% NaCl	50.6	-1.48	[99]
C PII	AM60	3.5% NaCl	20.1	-1.35	[99]
Untreated	AZ31	SBF	561	~-1.77	[100]
CO ₂ PIII	AZ31	SBF	260	~-1.73	[100]
Untreated	AZ31	DMEM	241	-1.72	[100]
CO ₂ PIII	AZ31	DMEM	3.66	-1.62	[100]
Untreated	AZ31	Lysogeny broth medium	317	~-1.49	[101]
C ₂ H ₂ PIII&D	AZ31	Lysogeny broth medium	65.3	~-1.65	[101]
Untreated	ZK60	Hank's solution	291.94	-1.585	[103]
COOH+ II	ZK60	Hank's solution	33.245	-1.601	[103]

Table 5. E_{corr} and i_{corr} of the untreated and C based plasma-treated Mg/Mg alloys.

SCE: saturated calomel electrode; PII: Plasma Ion Implantation; PIII: Plasma immersion ion implantation; PIII&D: Plasma Immersion Ion Implantation and Deposition; SBF: Simulated Body Fluid; DMEM: Dulbecco's modified Eagle's medium; II: Ion Implantation.



Figure 7. Cross sectional images (Inset: its corresponding EDS map) observed at different locations of (**a**,**b**) untreated Mg-Nd-Zn-Zr alloy and (**c**,**d**) C_2H_2 plasma-treated Mg-Nd-Zn-Zr alloy after 24 h immersion in 0.9 wt% NaCl solution. Top inset of the figure (**c**) depicts the existence of carbon film after 24 h corrosion in NaCl solution. The existence of small corrosion pits is indicated using arrows in figure (**d**) (Reproduced with permission from Ref. [17]; Copyright 2013, Elsevier Ltd.).

4. Biological Properties of Plasma Modified (PII, PIII, or PIII&D) Mg and/or Mg Alloys

4.1. In Vitro Cytocompatibility of Plasma Modified Mg and Mg Alloys

Preparing thin Zr oxide surface layer can enhance the cytocompatibility of Mg alloy. Zhao et al. [49] observed enhanced cell viability (after 72 h incubation), cell proliferation (using BrdU incorporation after 1 day and 3 days), and cell adhesion (MC3T3-E1 preosteoblasts after cultured for 5 h) on Zr plasma-treated and Zr&O plasma-treated Mg alloys (Mg-Ca and Mg-Sr) than that of untreated corresponding Mg alloys. The Zr plasmatreated and Zr&O plasma-treated Mg alloys (Mg-Ca and Mg-Sr) exhibit good MC3T3-E1 pre-osteoblasts attachment and cell spreading and the attached cells on Zr&O plasmatreated Mg alloys (Mg-Ca and Mg-Sr) exhibit apparent filopodia, flattened membranes, and ordered F-actin, whereas the attached pre-osteoblasts are not able to spread well on untreated Mg alloys (Mg-Ca and Mg-Sr) as shown in Figure 8. Zr plasma-treated and Zr&O plasma-treated Mg alloys (Mg-Ca and Mg-Sr) contains Zr oxides surface layer that possibly enhances their corrosion resistance and that possibly enhances their cell viability, cell proliferation, and cell adhesion. These indicate that Zr plasma-treated and Zr&O plasma-treated Mg alloys (Mg-Ca and Mg-Sr) exhibit better cytocompatibility than that of untreated corresponding Mg alloys. Moreover, Liang et al. [81] have observed good cytocompatibility on Zr&O plasma-treated (Zr&O PIII) ZK60 Mg alloys. Preparing thin Zr nitride along with Zr oxide surface layer can enhance the cytocompatibility of Mg alloy. Cheng et al. [63] observed enhanced cell viability (after incubated for 1, 3, and 7 days), cell adhesion (using MG63 osteoblasts after incubated for 1 and 3 days), and alkaline phosphatase (ALP) activity (using MG63 osteoblasts after incubated for 7 and 14 days) on Zr-N plasma-treated AZ91 Mg alloy than that of untreated AZ91 Mg alloy. Zr-N plasmatreated AZ91 Mg alloy contains surface layer with Zr oxides and nitrides that possibly

enhance its corrosion resistance and that possibly enhance its cell viability, cell adhesion, and ALP activity. These indicate that Zr-N plasma-treated AZ91 Mg alloy exhibits better cytocompatibility than that of untreated AZ91 Mg alloy. Preparing nitrogen rich surface layer can maintain the cytocompatibility of Mg alloys. Li et al. [82] have performed the cytotoxicity test using NIH-3T3 mouse fibroblasts after cultured for 2 days, where the N⁺ plasma-treated AZ31 Mg alloy almost retains the cytocompatibility of AZ31 Mg alloy. On the other hand, Wei et al. [83] have performed the cytotoxicity test using MC3T3-E1 cells after cultured for 3 days, where the NH_2^+ plasma-treated AZ31 Mg alloy exhibits higher cytocompatibility than that of untreated AZ31 Mg alloy. Preparing thin Al oxide surface layer can enhance the cytocompatibility of Mg alloy. Wong et al. [54] observed enhanced cell adhesion (after cultured for 1 day and 3 days) on Al-O plasma-treated AZ91 Mg alloy than that of untreated AZ91 Mg alloy. Al-O plasma-treated AZ91 Mg alloy contains surface layer with Al oxides that possibly enhances its corrosion resistance and that possibly enhances its cell adhesion. These indicate that Al-O plasma-treated AZ91 Mg alloy exhibits better cytocompatibility than that of untreated AZ91 Mg alloy. Preparing Zn deposition layer on Zn ion implanted layer can enhance the cytocompatibility of Mg alloy. Liu et al. [85] have observed improved cytocompatibility of MC3T3-E1 cells on the Zn plasma-treated Mg-1Ca alloy (Zn ion implantation and deposition) than that of the untreated Mg alloy possibly due to the formation of ZnO layer on the surface. Preparing thin Cr oxide surface layer can enhance the cytocompatibility of Mg. Xu et al. [70] observed enhanced cell viability (after incubated for 1, 3, and 7 days), and cell adhesion (using MC3T3-E1 pre-osteoblasts after cultured for 1 day and 3 days) on Cr&O plasma-treated Mg than that of untreated pure Mg. Cr&O plasma-treated Mg contains surface layer with Cr oxides that possibly enhance its corrosion resistance and that possibly enhance its cell viability, and cell adhesion. These indicate that Cr&O plasma-treated Mg exhibits better cytocompatibility than that of untreated pure Mg. Preparing thin Nd oxide surface layer can enhance the cytocompatibility of Mg alloy. Jin et al. [76] observed enhanced cell viability (at higher concentration after incubated for 1 day and 3 days), and cell adhesion (using MC3T3-E1 pre-osteoblasts after cultured for 5 h) on Nd plasma-treated WE43 Mg alloy than that of untreated WE43 Mg alloy. Nd plasma-treated WE43 Mg alloy contains surface layer with Nd oxides that possibly enhance its corrosion resistance and that possibly enhance its cell viability, and cell adhesion. These indicate that Nd plasmatreated WE43 Mg alloy exhibits better cytocompatibility than that of untreated WE43 Mg alloy. Preparing thin Hf oxide surface layer can enhance the cytocompatibility of Mg alloy. Jin et al. [77] observed enhanced cell viability (after incubated for 1 day and 3 days), and cell adhesion (using MC3T3-E1 pre-osteoblasts after cultured for 5 h) on Hf plasma-treated WE43 Mg alloy than that of untreated WE43 Mg alloy. Hf plasma-treated WE43 Mg alloy contains surface layer with Hf oxides that possibly enhance its corrosion resistance and that possibly enhance its cell viability, and cell adhesion. These indicate that Hf plasma-treated WE43 Mg alloy exhibits better cytocompatibility than that of untreated WE43 Mg alloy. Preparing thin oxide/hydroxide surface layer can enhance the cytocompatibility of Mg alloy. Wei et al. [97] have performed the cytotoxicity test using MC3T3-E1 cells after cultured for 3 days, where the OH⁻ plasma-treated ZK60 Mg alloy exhibits higher cytocompatibility than that of untreated ZK60 Mg alloy. Preparing thin carbonate surface layer can enhance the cytocompatibility of Mg alloy. Wei et al. [103] have performed the cytotoxicity test using MC3T3-E1 cells after cultured for 3 days, where the COOH⁺ plasma-treated ZK60 Mg alloy exhibits higher cytocompatibility than that of untreated ZK60 Mg alloy.



Figure 8. Fluorescent microscopic images of MC3T3-E1 pre-osteoblasts after culturing for 5 h on (a) untreated Mg-Ca, (b) Zr plasma-treated Mg-Ca, (c) Zr&O plasma-treated Mg-Ca, (d) untreated Mg-Sr, (e) Zr plasma-treated Mg-Sr, and (f) Zr&O plasma-treated Mg-Sr (Reproduced with permission from Ref. [26]; Copyright 2013, Acta Materialia Inc. and Elsevier Ltd.).

4.2. In Vitro and In Vivo Antibacterial Activities of Plasma Modified Mg Alloys

Preparing thin Zr oxide surface layer can enhance the antibacterial activities of Mg alloy. Zhao et al. [49] observed significantly lesser numbers of live bacteria (*Staphylococcus aureus*) on Zr plasma-treated and Zr&O plasma-treated Mg alloys (Mg-Ca and Mg-Sr) than that of untreated corresponding Mg alloys, as shown in Figure 9. Zr plasma-treated and Zr&O plasma-treated Mg alloys (Mg-Ca and Mg-Sr) contain Zr oxides surface layer that possibly enhance their antibacterial activities. This indicates that Zr plasma-treated and Zr&O plasma-treated Mg alloys (Mg-Ca and Mg-Sr) exhibit better antibacterial activities than that of untreated corresponding Mg alloys. Moreover, Liang et al. [81] have conducted in vitro and in vivo antibacterial tests, where Zr&O plasma-treated (Zr&O PIII) ZK60 Mg alloy exhibits higher antibacterial activities than that of untreated ZK60 Mg alloy. The improved antibacterial activities on Zr&O plasma-treated ZK60 Mg alloy are ascribed to the improved surface hydrophobicity, diminished surface roughness, and large concentration of oxygen vacancies in the ZrO₂-containing surface layer, where the smooth and hydrophobic surface retard the bacterial adhesion. Preparing thin Zr nitride along with Zr oxide surface layer can enhance the antibacterial activities of Mg alloy. Cheng et al. [63] observed lesser numbers of live bacteria (Staphylococcus aureus) on Zr-N plasma-treated AZ91 Mg alloy than that of untreated AZ91 Mg alloy. Zr-N plasma-treated AZ91 Mg alloy contains surface layer with Zr oxides and nitrides that possibly enhance its antibacterial activities. This indicates that Zr-N plasma-treated AZ91 Mg alloy exhibits better antibacterial activities than that of untreated AZ91 Mg alloy.



Figure 9. Fluorescent microscopic images of plasma treated and untreated Mg alloys after 30 min of Staphylococcus aureus bacterial culture: (a) untreated Mg-Ca, (b) Zr plasma treated Mg-Ca, (c) Zr&O plasma treated Mg-Ca, (d) untreated Mg-Sr, (e) Zr plasma treated Mg-Sr, and (f) Zr&O plasma treated Mg-Sr (Reproduced with permission from Ref. [26]; Copyright 2013, Acta Materialia Inc. and Elsevier Ltd.).

4.3. In Vivo Stimulation of Bone Formation of Plasma Modified Mg Alloys

Preparing thin Al oxide surface layer can stimulate the new bone formation and improve the in vivo corrosion resistance of Mg alloy. Wong et al. [54] observed better in vivo stimulation of bone formation and in vivo corrosion resistance on Al-O plasmatreated AZ91 Mg alloy than that of untreated AZ91 Mg alloy after in vivo animal studies for a period of 2 months. To monitor the in vivo corrosion behavior, they have performed micro-computed tomography (CT), which shows the newly generated bone around the implants and the corrosion morphology of the implants. The micro-computed tomography 3D reconstruction models evaluation after 2 months post-operation revealed that the newly formed bone around the implant on Al-O plasma-treated AZ91 Mg alloy (7.11 mm³) is higher than that of untreated AZ91 Mg alloy (1.06 mm³). The Al-O plasma-treated AZ91 Mg alloy exhibits about 46% increase in bone volume while untreated AZ91 Mg alloy exhibits more than 54% bone resorption after 1 week of post-operation. In addition, the Al-O plasmatreated AZ91 Mg alloy exhibits about 138% increase in bone volume than that of untreated AZ91 Mg alloy after 2 months of post-operation (Figure 10). Moreover, the Al-O plasmatreated AZ91 Mg alloy (99%) exhibits lesser implant volume reduction than that of untreated AZ91 Mg alloy (97%) after 4 weeks of post-operation. In addition, the Al-O plasma-treated AZ91 Mg alloy (98%) exhibits further lesser implant volume reduction than that of untreated AZ91 Mg alloy (93%) after 2 months of post-operation; Al-O plasma-treated AZ91 Mg alloy contains surface layer with Al oxides that possibly enhance its in vivo corrosion resistance suggesting slower degradation rate than that of untreated, and that possibly exhibits higher new bone formation, much higher percentage changes in the bone volume, and lesser percentage changes in the implant volume reduction after 2 month of in vivo animal studies on Al-O plasma-treated AZ91 Mg alloy than that of untreated AZ91. These indicate that Al-Oplasma-treated AZ91 Mg alloy exhibits better in vivo stimulation of bone formation and in vivo corrosion resistance than that of untreated AZ91 Mg alloy. Preparing thin Zr nitride along with Zr oxide surface layer can stimulate the new bone formation and improve the in vivo corrosion resistance of Mg alloy. Cheng et al. [63] have conducted micro-computed tomography until 12 weeks to monitor the in vivo corrosion resistance on the implants and new bone formation around the implants. They have observed higher new bone

formation, higher percentage changes in the bone volume, and lesser percentage changes in the implant volume reduction after 12 weeks in vivo animal studies on Zr-N plasma-treated AZ91 Mg alloy than that of untreated AZ91 (Figure 11). These indicate that Zr-N plasmatreated AZ91 Mg alloy exhibits better in vivo stimulation of bone formation than that of untreated AZ91 Mg alloy. The Zr-N plasma-treated AZ91 Mg alloy contains surface layer with Zr oxides and nitrides that possibly enhance its corrosion resistance and that possibly enhance its in vivo stimulation of bone formation and in vivo corrosion resistance. Thus, enhanced in vitro/in vivo corrosion resistance, cytocompatibility, antibacterial activities, and in vivo stimulation of bone formation are observed on plasma-treated Mg or Mg alloys (Figure 12), where the plasma treatment includes plasma ion implantation (PII), plasma immersion ion implantation (PIII), or plasma immersion ion implantation and deposition (PIII&D) techniques.



Figure 10. Micro-computed tomography reconstructed images of the lateral epicondyle having (a) untreated AZ91 Mg alloy, and (b) Al-O plasma treated AZ91 Mg alloy after immediate surgery and 1, 2, 3, 4, and 8 weeks of post operation. Yellow arrow indicates the progressive new bone formation through the time intervals. (c) The bone volume changes (in %) around the Al-O plasma treated AZ91 Mg alloy and untreated AZ91 Mg alloy after immediate surgery and 1, 2, 3, 4, and 8 weeks of post operation, where the Al-O plasma treated AZ91 Mg alloy exhibits about 46 % increase in bone volume while untreated AZ91 Mg alloy exhibits more than 54 % bone resorption after 1 week of post-operation (Reproduced with permission from Ref. [31]; Copyright 2013, Elsevier Ltd.).



Figure 11. Micro-CT characterization of surrounding bones and implants volume. (**a**) 2D Micro-CT after surgery for 1, 4, 8, and 12 weeks, where the new bone formation is indicated by the red arrows, and 3D reconstruction models depicting the implants (in gray color) and bone (in pink color) response after surgery for 12 weeks [34]. (**b**) Bone volume changes around the implants after immediate surgery, and 4, 8, and 12 weeks of post-operation [34], and (**c**) Implant volume changes after immediate surgery, and 4, 8, and 12 weeks of post-operation; Error bars indicate mean \pm SD for n = 4, where * represents a significant difference between un-treated and Zr-N- plasma treated AZ91 Mg alloy (*p* < 0.05) (Reproduced with permission from Ref. [34]; Copyright 2016, Elsevier B.V.).



Figure 12. Schematic diagram illustrate the potential applications of plasma treated biodegradable Mg or Mg alloys, where the plasma treatment includes plasma ion implantation (PII), plasma immersion ion implantation (PIII), or plasma immersion ion implantation and deposition (PIII&D) techniques.

5. Summary and Outlook

Degradable metallic implants are potential candidates for bio-implants. Hence, Mg and its alloys are much attracted but their rapid degradation prevents their use. The improvement of in vitro corrosion resistance, in vivo corrosion resistance, cytocompatibility, in vitro antibacterial activities, in vivo antibacterial activities, and in vivo stimulation of bone formation on Mg or its alloys by plasma techniques have been reviewed, where the plasma techniques include plasma ion implantation (PIII), plasma immersion ion implantation (PIII), and plasma immersion ion implantation and deposition (PIII&D) techniques.

The following conclusions have been drawn:

- (a) The in vitro corrosion resistance is improved on the plasma-treated Mg or its alloys possibly due to the formation of passive protective layer comprising of Zr-O [81], Zr-N [62], N [82], Si [64], Al-O [54], Zn-Al [68], Cr-O [69], Ti-O [71], Ti-N [73], Fe [88], Y [87], Sr [91], P [93], Pr [74], Ce [75], Nd [76], Hf [77], Ta [95], or C [98].
- (b) The in vivo corrosion resistance and in vivo stimulation of bone formation are improved on the plasma-treated Mg alloys possibly due to the formation of suitable surface layer comprising of Al-O [54], or Zr-N [63], where the surface layer not only control the release of Mg but also stimulate the bone formation.
- (c) The antibacterial activities are improved on the plasma-treated Mg alloys possibly due to the formation of suitable surface layer consisting of Zr-O [49,81], or Zr-N [63], where the surface layer not only control the degradation of Mg but also retard the bacterial adhesion.
- (d) The cytocompatibility is improved on the plasma-treated Mg or Mg alloys possibly due to the formation of suitable surface layer comprising of Zr-O [49], Zr-N [63], N [83], Al-O [54], Zn [85], Cr-O [70], Nd [76], or Hf [77], where the surface layer not only control the release of Mg but also enhance the cell growth and adhesion.

The essential factors governing the performance of Mg or Mg alloys by using plasma treatment should be considered in future research:

- 1. The in vivo corrosion resistance, in vivo stimulation of bone formation, and in vivo antibacterial activities are improved on the plasmatreated Mg alloys. However, the studies on these aspects are very limited [54,63,81]. Therefore, additional progresses are obviously needed by using suitable plasma treatment on Mg and Mg alloys.
- 2. Surface modification of Mg and Mg alloys using other surface modification techniques followed by plasma treatment can tune the corrosion and biological properties. Nevertheless, the studies on these aspects are very limited [104–110]. Hence, additional efforts are obviously needed by combining other suitable surface modification with plasma treatment.

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