

医用镁合金微弧氧化工艺研究进展

冯宴荣¹, 周亮¹, 贾宏耀¹, 张祥¹, 赵李斌², 房大庆³

(1.长安大学 材料科学与工程学院, 西安 710064; 2.山西银光华盛镁业股份有限公司, 山西 运城 043800; 3.西安交通大学 金属材料强度国家重点实验室, 西安 710049)

摘要: 从火花放电方面归纳整理了镁合金微弧氧化膜层的形成机理, 并分析了膜层结构。在此基础上, 结合国内外研究现状, 阐述了预处理、电解质和添加剂以及电参数(电压、电流模式和脉冲频率)和封孔技术对镁合金微弧氧化膜层耐蚀性和生物相容性的影响。着重分析了电解质和添加剂的种类、浓度对膜层和生物性能的影响机制, 其中电解质包括碱性硅酸盐和磷酸盐电解液等, 添加剂包括甘油、氟化物、羟基磷灰石和纳米粒子等。研究发现, 碱性磷酸盐电解质的加入可以降低膜层腐蚀速率, 促进骨整合和细胞附着过程, 羟基磷灰石、Ca、P 等具有生物活性和对人体有益的粒子作为添加剂加入, 可以显著提高膜层的耐蚀性和生物相容性。最后, 基于研究现状, 对镁合金微弧氧化技术在生物医用方面的发展进行了展望。

关键词: 医用镁合金; 微弧氧化; 成膜机理; 耐蚀性; 生物相容

中图分类号: TG146.2 **文献标识码:** A **文章编号:** 1001-3660(2023)07-0011-14

DOI: 10.16490/j.cnki.issn.1001-3660.2023.07.002

Research Progress on Micro-arc Oxidation of Medical Magnesium Alloy

FENG Yan-rong¹, ZHOU Liang¹, JIA Hong-yao¹, ZHANG Xiang¹, ZHAO Li-bin², FANG Da-qing³

(1. School of Materials Science and Engineering, Chang'an University, Xi'an 710064, China;

2. Shanxi Yinguang Huasheng Magnesium Co., Ltd., Shanxi Yuncheng 043800, China;

3. State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China)

ABSTRACT: Magnesium alloy is a highly promising biodegradable metal material for biomedical use, with the advantages of density and elastic modulus similar to those of human bone, reducing the stress-shading effect of bone implants, avoiding osteoporosis and promoting new bone growth. In addition, magnesium alloy also has good machinability, castability and fracture toughness at high temperature, which is more advantageous than other materials for biomedical materials. However, the defects of magnesium alloy as an implant material are that its corrosion rate in body fluids is too fast. Therefore, degradation rate is not easy to control, and the mechanical properties of the implant are greatly reduced, which is not enough to support human bone healing. To address this issue, the surface treatment is necessary to achieve degradation control and improve mechanical

收稿日期: 2022-05-24; 修订日期: 2022-11-01

Received: 2022-05-24; Revised: 2022-11-01

基金项目: 陕西省重点研发计划项目(2021GY-244); 陕西省自然科学基金基础研究计划项目(2021JLM-41); 西安交通大学金属材料强度国家重点实验室开放课题(20202204)

Fund: Shaanxi Province Key Research and Development Program Project (2021GY-244); Shaanxi Province Natural Science Basic Research Program Project (2021JLM-41); State Key Laboratory of Strength of Metal Materials, Xi'an Jiaotong University Open Subjects (20202204)

作者简介: 冯宴荣(1998—), 女, 硕士研究生, 主要研究方向为镁合金表面处理技术。

Biography: FENG Yan-rong (1998-), Female, Postgraduate, Research focus: surface treatment technology of magnesium alloy.

通讯作者: 周亮(1983—), 男, 博士, 副教授, 主要研究方向为镁合金表面处理技术。

Corresponding author: ZHOU Liang (1983-), Male, Associate professor, Research focus: surface treatment technology of magnesium alloy.

引文格式: 冯宴荣, 周亮, 贾宏耀, 等. 医用镁合金微弧氧化工艺研究进展[J]. 表面技术, 2023, 52(7): 11-24.

FENG Yan-rong, ZHOU Liang, JIA Hong-yao, et al. Research Progress on Micro-arc Oxidation of Medical Magnesium Alloy[J]. Surface Technology, 2023, 52(7): 11-24.

properties, corrosion resistance, biocompatibility and antibacterial properties of magnesium alloys. Among the surface technologies, micro-arc oxidation has the advantages of simple pretreatment, uniform film formation, high bonding strength with matrix and enhanced biocompatibility of magnesium alloys.

Currently, there are few reviews on micro-arc oxidation technology of magnesium alloys. In this work, the formation mechanism and structure of micro-arc oxide film on magnesium alloy were summarized from the perspective of spark discharge theory. On this basis, from the classification of the affecting parameters of micro-arc oxidation, the effects of pretreatment, electrolyte, additives, electrical parameters (voltage, current mode and pulse frequency) and sealing technology on the corrosion resistance and biocompatibility of magnesium alloy micro-arc oxidation film were expounded combined with the research status in China and abroad. Thus, the research progress of micro-arc oxidation technology for medical magnesium alloys was introduced by studying the affecting parameters. Herein, the work mainly focused on the analysis of the type and concentration of electrolytes and additives on the membrane and biological properties of the mechanism, in which electrolytes included alkaline silicate and phosphate electrolyte and additives included glycerol, fluoride, hydroxyapatite and nanoparticles, etc. It was found that the addition of alkaline phosphate electrolyte could reduce the corrosion rate of the film and promote the process of bone integration and cell attachment. Besides, hydroxyapatite, Ca, P and other bioactive particles as additives could significantly improve the corrosion resistance and biocompatibility of the film. Last but not least, according to the further research, it was found that the affecting factors of process parameters on the micro-arc oxide film layer were not single linear. No matter the process parameters were lower than the minimum value or higher than the maximum value, the performance of the film would be damaged to some extent. From this perspective, it is necessary for researchers to strike an optimal balance between corrosion resistance and biocompatibility.

At present, compared with other surface technologies, there is a lack of comprehensive and profound explanation of its film formation mechanism due to the complexity of micro-arc oxidation. Therefore, it is urgent to establish a rich and scientific mechanism research system. Finally, in view of the existing problems, the application of micro-arc oxidation in medical magnesium alloys is prospected.

KEY WORDS: medical magnesium alloy; micro-arc oxidation; film formation mechanism; corrosion resistance; biocompatibility

近年来,金属材料和高分子材料已经成为医用骨植入材料的优先选择^[1-2]。常用人体植入材料的基本性质见表1。由表1可知,大多数金属材料的弹性模量与人骨相差大、匹配度低,同时在体内可降解性低,需二次手术移除,增加了患者的感染率和手术费用^[3-5]。高分子材料的力学性能差,在人体内降解时会释放延迟骨组织愈合的酸性物质,在临床应用中面临着很大的困难^[6-7]。与其他植入材料相比,镁合金植入体具有以下特点:储量丰富;物理性能优异,镁的密度(1.738 g/cm³)及镁合金的密度(1.75~1.85 g/cm³)小、弹性模量(41~45 GPa)和抗压屈服强度更符合植入人体材料的要求,可以减少“应力遮挡”的产生;生物相容性良好,镁离子在人体内大量存在,许多代谢反应和生物机制中镁离子均有参与;可降解性高,镁合金在人体内的可降解特性使患者避免二次手术的疼痛风险^[8-11]。基于以上优点,医用镁合金骨植入材料逐渐成为研究的热点,但镁合金在人体内的高腐蚀速率成为人们亟需攻克的难题。

针对镁合金高腐蚀速率的缺点,现有解决方法主要是对镁合金进行表面处理,提高镁合金的耐蚀性和生物相容性,使其在生物材料上的应用更加广泛。镁合金表面改性的方法一般有:阳极氧化、电沉积、激

光表面改性、溶胶-凝胶、浸涂、有机膜层和微弧氧化(Micro-arc Oxidation, MAO)等^[12-14]。其中MAO工艺由于具有预处理简单、能形成均匀膜层、与基体结合强度高和增强镁合金生物相容性等优点,因此广大学者对微弧氧化技术进行了深入的研究^[15]。对于生物医学应用而言,体液中Cl⁻的存在使得MAO膜层降解速度过快,且膜层成分选择不当,容易对人体产生危害,使得MAO膜层的生物相容性较差^[16],需要通过工艺手段将一些生物活性物质(如Ca、P等元素)引入到膜层中。因此,MAO工艺的改善在医用镁合金表面处理上拥有广阔的前景^[12]。

表1 常用植入体材料的基本性质对比
Tab.1 Comparison of basic properties of common implant materials

Materials	Density/ (g·cm ⁻³)	E/GPa	σ_b /MPa	Degradability
Mg alloys	1.85	41-45	290	Excellent
Titanium alloys	4.51	110-117	686-1 176	Poor
Stainless steel	7.70-8.00	189-205	520	Poor
PGA	1.52	1.22×10 ⁻²	110	Excellent

鉴于以上原因, 本文综述了 MAO 膜层的形成机理和结构, 并从预处理方法、电解液、电参数和后处理封孔技术这几个方面综述了医用镁合金微弧氧化膜层耐蚀性和生物相容性的研究现状, 同时也展望了医用镁合金微弧氧化的研究方向。

1 MAO 膜层形成机理和结构

微弧氧化又称为等离子体电解氧化 (Plasma Electrolytic Oxidation, PEO), 广泛地用于镁合金的表面改性^[17-19]。目前 MAO 过程主要被划分为阳极氧化、火花放电、微弧氧化和大弧放电 4 个阶段^[20-24]。

MAO 膜层的形成机理复杂, 主要包括化学、电化学和高温等离子体反应这 3 个方面的内容, 现在国内外并没有一个可以解释 MAO 膜层生长过程的合理模型。国内外学者主要是从火花放电方面研究了 MAO 膜层的形成机理, 对火花放电机理较为认可的有“电子雪崩”“Schottky 隧道”“微桥放电”“孔内放电”和“红色火花”等理论模型^[24-25]。“电子雪崩”的理论模型如图 1 所示。相关研究人员指出, “电子雪崩”总是在膜层较薄的位置进行, “电子雪崩”能够发生的主要动力是由于在放电时有大量热量发生^[15,26]。除此之外, 国内学者也探究了微弧氧化的放电机理。Chen 等^[15]认为, MAO 膜层是由电弧放电高温生成的金属氧化物堆积而成的, 并将一次

单独的微弧放电划分为电解、放电、氧化和冷却 4 个过程, 由此提出微区电弧放电模型, 如图 2 所示。

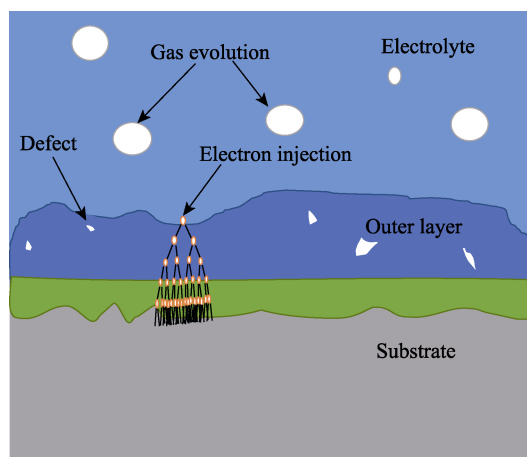


图 1 “电子雪崩”模型
Fig.1 Model of "electron avalanche"

众多学者认为, 微弧氧化膜层主要由 3 部分组成: 过渡层、致密层和疏松层^[23,27]。膜层结构主要由电解液和工艺参数决定。纯镁的微弧氧化膜层主要由 MgO 组成。一般情况下, 疏松层厚度大于致密层, 外层形貌均为多孔结构, 并分布着孔径不一的微孔和微裂纹^[19,21,28-30]。MAO 膜层表面及截面形貌如图 3 所示。

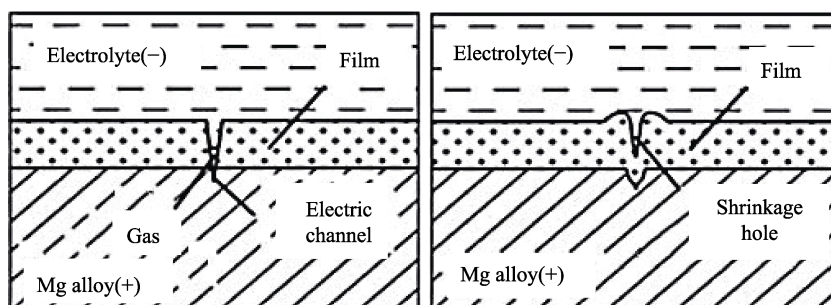


图 2 镁合金微弧氧化的微区微弧放电模型^[15]
Fig.2 Model of separate local arc discharge in magnesium alloy MAO process^[15]

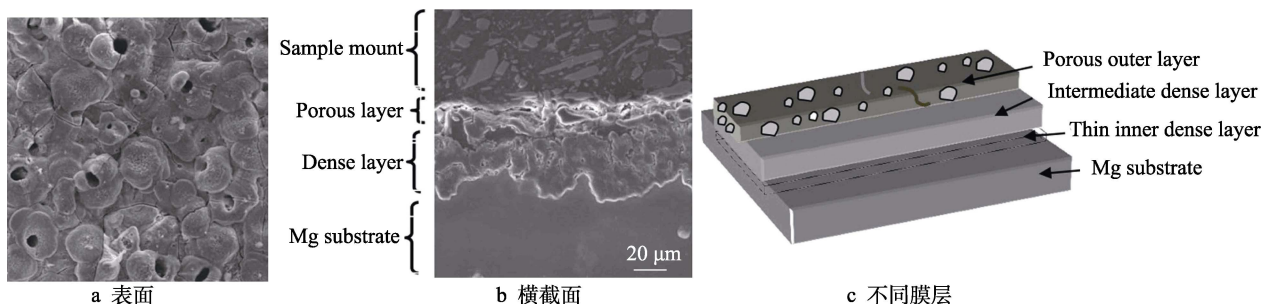


图 3 微弧氧化膜层表面、横截面和不同膜层的示意图^[26]
Fig.3 Schematic diagram of coating surface (a), cross section (b) and different layer (c) of MAO film^[26]

2 预处理对 MAO 膜层性能的影响

镁合金进行 MAO 处理虽然可以使合金的耐蚀性

有所提高, 但依旧无法避免在人体中由于体液腐蚀而快速降解的缺点。因此, 为了提高 MAO 膜层在人体环境内的耐蚀性, 需要对微弧氧化工艺进行必要的改善。

研究发现,在进行 MAO 前,对镁基体进行预处理可以改变表层的组织和微观结构,使 MAO 膜层与基体的结合强度更好,组织更致密,性能更佳^[31-32]。近年来,一些预处理技术如等通道角压 (ECAP)、热处理和激光表面处理技术等被应用于镁合金微弧氧化预处理,来提高 MAO 膜层的耐蚀性和生物相容性^[31-33]。由表 2 可知,Xiong 等^[34]在激光冲击强化 (LSP) 的预处理条件下,采用 MAO 工艺在 AZ80 镁合金表面制备了 LSP/MAO 复合生物膜层。研究发现,LSP/MAO 复合生物膜层提高了镁合金基体的耐蚀性和在体液中的力学性能,显著降低了植入体的腐蚀速率,并在骨愈合初期维持植入体完整的力学性能,所以经过 LSP/MAO 处理的镁合金更适合作为可

生物降解的骨科植入物。Ly 等^[35]通过在 ECAP 预处理下,对镁合金进行 MAO,制备了 ECAP/MAO 复合膜层。镁基体经 ECAP 处理后,制备的 MAO 膜层微孔尺寸大小明显小于铸态镁基体的 MAO 膜层,且 ECAP/MAO 膜层更加致密,提高了镁合金的耐蚀性和生物活性,如图 4 所示。Yan 等^[36]对 Mg-0.06Cu 合金固溶处理后,再进行 MAO 处理。在固溶处理的预处理条件下,MAO 膜层的腐蚀速率有所降低,合金表现出良好的抗菌能力,以及修复骨折和骨缺损的潜力。对基体进行预处理后,膜层与基体的结合更加紧密、不易剥落,同时 MAO 膜层的致密性有所提高,可有效防止腐蚀离子进入膜层内部,提高了镁合金的耐蚀性。

表 2 预处理对 MAO 膜层性能的影响
Tab.2 Effects of the pretreatment on properties of MAO film

Substrate	Pretreatment	Corrosion resistance	Biocompatibility
Mg-Gd-Y-Zn-Zr	Laser surface texturing	Improve the corrosion resistance of the matrix	
Mg-0.06Cu	Solution treatment	Improve the corrosion resistance of the matrix	Have high quality for killing the bacteria.
Mg-4.71Zn-0.6Ca	Equal channel angular pressing	Corrosion resistance is better than as-cast specimens	Improve the biological activity of the alloy
AZ80	Laser shock peening	Improve the corrosion resistance of the matrix	Suitable as a degradable bone implant
AZ31B	Ultrasonic shot peening	Improve the corrosion resistance of the matrix	

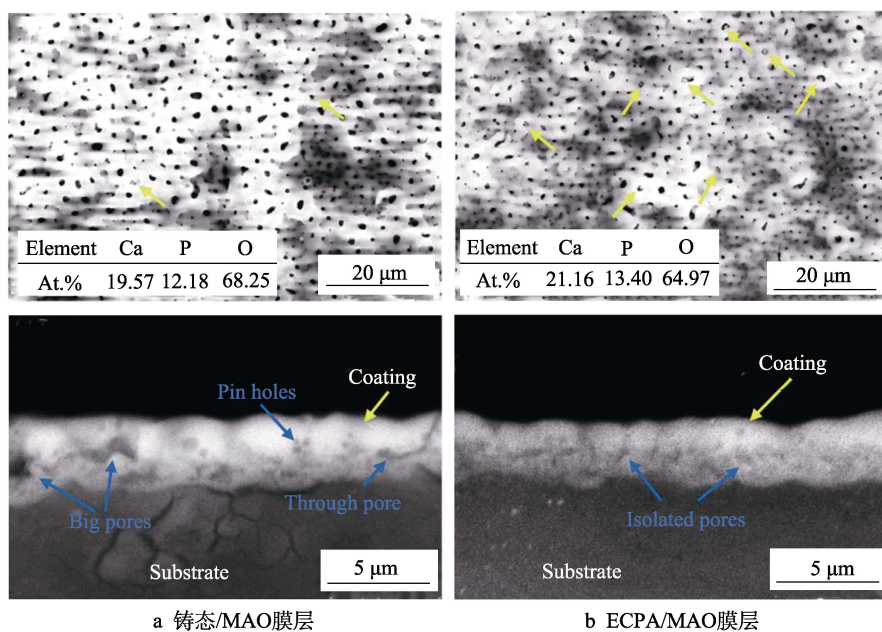


图 4 铸态/MAO 和 ECAP/MAO 膜层的表面形貌和横截面^[35]

Fig.4 Surface morphologies and cross section of as-cast/MAO (a) and ECAP/MAO films (b)^[35]

3 电解液对 MAO 膜层性能的影响

在微弧氧化过程中,电解液对成膜反应和放电特性有极大的影响。其中,电解液的组成和浓度对 MAO 膜层的相组成和性能起着决定作用,所以镁合金在进行 MAO 处理时,对电解液要进行合理的选择^[24]。本文主要从电解液和添加剂的种类和浓度这 2 个方

面讨论电解液对 MAO 膜层耐蚀性和生物相容性的影响。

3.1 电解液

MAO 常用电解液主要为酸性电解液和碱性电解液两大类^[37]。酸性电解液对基体有较强的腐蚀性,同时对环境也存在一定的污染,所以在进行微弧氧化

时, 会优先选择碱性电解液。对医用镁合金进行 MAO 处理时, 由于硅酸盐和磷酸盐会提高膜层的生物相容性, 所以 MAO 常用电解液为碱性硅酸盐^[29,38-40]和磷酸盐^[38,40-44]电解液。在硅酸盐和磷酸盐中制备的膜层, 均有 MgO 的存在, 其余的相组成为 Mg_2SiO_4 和 $\text{Mg}_3(\text{PO}_4)_2$ 。磷酸盐的 MAO 终止电压高于硅酸盐, 所以在磷酸盐中制备的膜层厚度比在硅酸盐中制备的膜层厚度大, 并且磷酸盐膜层的致密层更厚。因此, 在磷酸盐电解液中制备的膜层, 耐蚀性更好, 且制备多孔状的 Ca-P 膜层会提高氧化膜层的生物相容性^[18,38,45]。Seyfoori 等^[38]在硅酸盐和磷酸盐电解液中对 AZ31 镁合金进行 MAO 处理后, 发现 2 种电解液均有利于提高镁合金的耐蚀性。磷酸盐膜中 MgF_2 相的存在, 可以抑制磷酸盐膜层在模拟体液中的快速降解, 且在磷酸盐电解液中制备的膜层具备膜层较厚、低亲水性和在 SBF 溶液中的腐蚀速率低等优点。综上所述, 磷酸盐膜层的耐蚀性更优异。由于磷酸盐膜层具有大的烧蚀坑结构, 可应用于骨科, 促进骨整合和细胞附着过程, 加速相邻组织的愈合, 因此磷酸盐膜层也具备更为优异的生物相容性。Jia 等^[40]在 3 种 KF 碱性电解液中对 Mg-1Ca 合金进行 MAO, 制备了 Si 膜层、P 膜层和 Si-P 膜层。经分析发现, 3 种膜

层均提高了镁合金的耐蚀性和细胞相容性, 其中磷酸盐的加入使膜层致密化, 降低了膜层的孔径和孔隙率, 所以 P 膜层的耐蚀性和细胞相容性均优于其他 2 种膜层。

不仅电解液种类会对膜层结构和性能产生影响, 电解液的浓度也显著影响 MAO 膜层性能^[41,43,46]。由表 3 可知, Pan 等^[41]在不同类型的磷酸盐电解液中对 Mg-Zn-Zr 合金进行 MAO 处理制备 Ca-P 膜层时发现, 虽然电解质不同, 但 Ca-P 膜层表面形貌均呈多孔状, 主要成分为 MgO 、 MgF_2 、 ZnO 、 ZnF_2 、 CaO 、 CaF_2 和 $\text{Ca}_3(\text{PO}_4)_2$ 。经分析发现, 在含有 $(\text{NaPO}_3)_6^-$ 的电解液中形成的 MAO 膜层厚度更厚、结合强度更高, 并且具有良好的生物相容性。Gu 等^[43]在质量浓度分别为 20、30、40 g/L 的 Na_3PO_4 电解液中, 对 AZ31 镁合金制备了 MAO 膜层。膜层的表面形貌如图 5 所示, 可以看出, 在电解质质量浓度为 30 g/L 时制备的 MAO 膜层形貌呈现出微孔均匀、孔隙率低和孔径小的特征, 并且在此浓度下膜层的电化学阻抗最高, 此时膜层的耐蚀性更高。在模拟体液中产生的腐蚀产物中, 形成了羟基磷灰石 (HA), 从而抑制了降解速度, 使得合金在人体内的力学性能和使用寿命均得以延长。

表 3 常见碱性电解液膜层性质对比
Tab.3 Comparison of properties of common alkaline electrolyte films

Substrate	MAO Electrolyte	Concentration	Corrosion resistance	Biocompatibility
AZ31	CaGP+NaOH	NaOH(0.05, 0.1, 0.2, 0.4 mol/L)	Best corrosion resistance (0.2 mol/L NaOH)	The degradation rate is slow and the bioactivity is good
AZ31B	$\text{Na}_2\text{SiO}_3+\text{KF}+\text{KOH}+\text{C}_3\text{H}_8\text{O}_3$		The corrosion resistance of the film is improved	
AZ31	Na_3PO_4	20, 30, 40 g/L	Best corrosion resistance (30 g/L)	Low degradation rate
Mg-Zn-Zr	$(\text{CH}_3\text{COO})_2\text{Ca} \cdot \text{H}_2\text{O} + \text{NH}_4\text{HF}_2 + \text{C}_3\text{H}_8\text{O}_3 + \text{H}_2\text{O}_2 + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} / \text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O} / (\text{NaPO}_3)_6$		Best corrosion resistance $[(\text{NaPO}_3)_6]$	The degradation rate is slow and the biocompatibility is good
AZ31	$\text{Na}_2\text{SiO}_3/\text{Na}_4\text{P}_2\text{O}_7+\text{KOH}+\text{NaF}$		The corrosion resistance of the film is improved	Phosphate film is the best biocompatible
Mg-1Ca	KF+Si-/P-/Si-P-		Phosphate film has the best corrosion resistance	Phosphate film is the best biocompatible

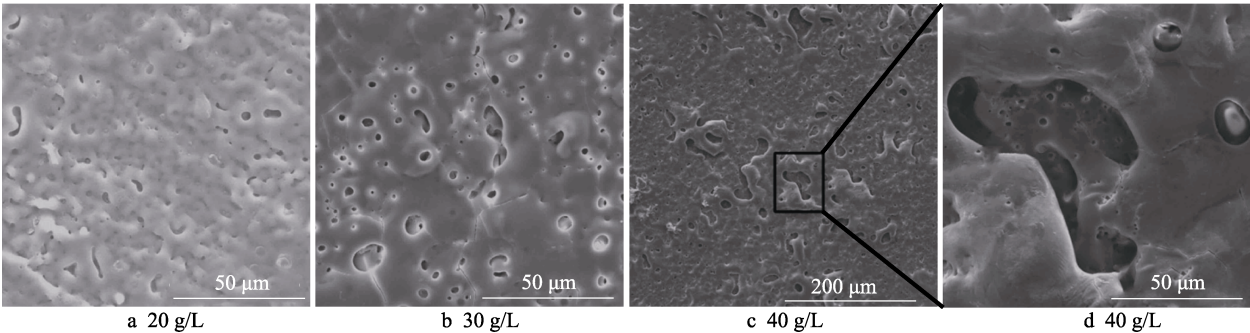


图 5 不同浓度的 Na_3PO_4 电解液下制备的 MAO 膜层表面形貌^[43]
Fig.5 Surface morphologies of the MAO films produced at various Na_3PO_4 electrolyte concentrations^[43]

在制备医用镁合金微弧氧化膜层时,其中电解液种类和浓度均对膜层的医用性能起到重要作用。综上所述,医用 MAO 膜层的电解液优先选择碱性电解液,可以降低膜层降解速率,提高 MAO 膜层的生物相容性。电解质浓度对膜层形貌也有显著影响,若浓度过低,导致参与反应的粒子减少,使得膜层不完整;浓度过高,导致大量电解液粒子参与反应,产生较大放电火花,使得膜层局部产生大孔。因此,在进行微弧氧化时,既要考虑电解液的种类,又要考虑合适的浓度,使得镁合金达到作为植入材料的最佳耐蚀性和生物相容性。

3.2 添加剂

为了改善 MAO 膜层的相组成、微观结构和性能,在电解液中通常会加入不同种类的添加剂^[47-48]。常用的添加剂为甘油($C_3H_8O_3$)、氟化物、HA 和纳米粒子等^[49-54]。电解液中添加剂的加入基本都会参与 MAO 中陶瓷膜层的生长过程,所以添加剂的种类对 MAO 膜层性能有明显的影响。不同的添加剂可以改变 MAO 过程中的火花放电现象,氟化物可以促进放电和加速反应,而 $C_3H_8O_3$ 等的引入有利于细化火花

和降低热反应,提高膜层的致密度和耐蚀性。由于 HA 是人体骨骼中的主要无机成分,可以参与人体代谢,促进骨修复,所以 HA 的加入可以形成生物活性膜层。Wu 等^[54]通过在添加和不添加 $C_3H_8O_3$ 的硅酸钠电解液中对 AZ91D 镁合金进行微弧氧化制备 MAO 膜层。在电解液中加入 $C_3H_8O_3$ 后, $C_3H_8O_3$ 分子替换了界面处的 H_2O 分子,提高了阳极和电解液界面负离子的单位面积吸附能力(如图 6 所示),使得膜层致密度高,也提高了 MAO 膜层的耐蚀性。Pan 等^[52]在硅酸盐电解液中加入 4 种添加剂(KF、 NH_4HF_2 、 $C_3H_8O_3$ 和 H_2O_2),并在 ZK60 镁合金基体上进行了 MAO 制备膜层。结果表明,在含 7 g/L NH_4HF_2 和 5 mL/L $C_3H_8O_3$ 的碱性电解液中,形成的膜层具有更高的耐蚀性。Ma 等^[51]在加入 2 g/L HA 粒子的碱性磷酸盐电解液中对 Mg-Zn-Ca 合金进行了 MAO 制备膜层。结果表明,HA 粒子参与了 MAO 过程,烧结相 $Ca_3(PO_4)_2$ 和 $Mg_3(PO_4)_2$ 与 HA 粒子结合,形成了生物活性膜层。通过试验证明,膜层的结合强度和耐蚀性均有提高,主要原因是烧结产物封闭了 MAO 膜层的部分气孔。

表 4 添加剂种类和浓度对 MAO 膜层性能的影响

Tab.4 Effects of the type and concentration of additives on properties of MAO film

Substrate	Additives	Concentration	Corrosion resistance	Biocompatibility
AZ91D	$C_3H_8O_3$		good corrosion resistance	
ZK60	KF, NH_4HF_2 , $C_3H_8O_3$, H_2O_2		good corrosion resistance (7 g/L NH_4HF_2 +5 mL/L $C_3H_8O_3$)	
Mg-Zn-Ca	HA	2 g/L	good corrosion resistance	Good biocompatibility
AZ91	TiO_2 Sol	5 vol.%, 10 vol.%	good corrosion resistance	
Mg-1Ca	Nano- TiO_2	0, 4, 8 g/L	The film has the best corrosion resistance (4 g/L)	
Mg-2Zn-1Gd-0.5Zr	Nano-CuO	1 g/L	good corrosion resistance	Improve the film resistance to degradation, good biocompatibility

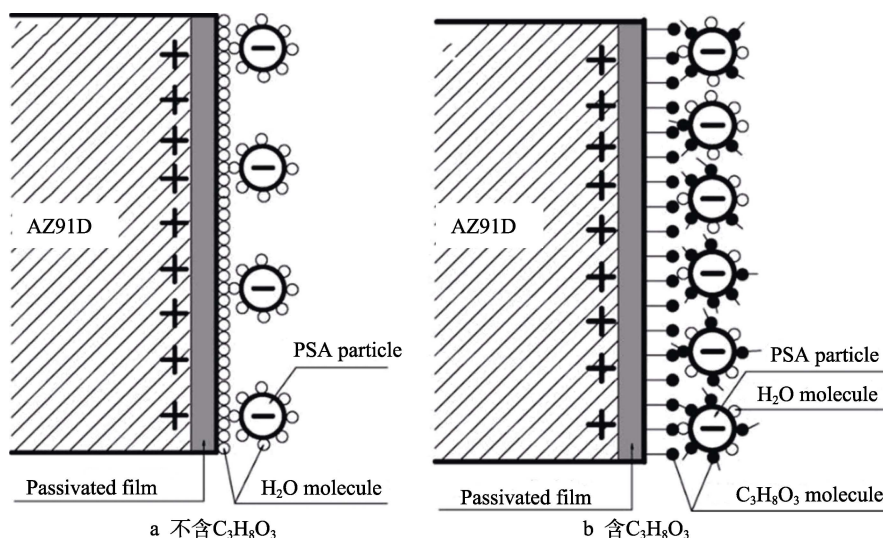


图 6 MAO 初级阶段 2 种不同电解液中阳极/电解液界面处颗粒分布^[54]

Fig.6 Schematic diagram of the particle distribution at anode/electrolyte interface in two different electrolyte at the primary stages of the MAO treatment^[54]: a) without $C_3H_8O_3$; b) with $C_3H_8O_3$

在电解液中加入添加剂时,膜层的耐蚀性与添加剂浓度不呈线性关系。当浓度达到合适值时,膜层的耐蚀性才会达到最佳。Wang 等^[53]在电解液中分别加入不同浓度的 TiO_2 纳米粒子对 AZ91 镁合金进行 MAO 制备氧化膜层。分析发现,在制备的膜层中会引入少量的 TiO_2 , 电解液中添加剂的体积分数为 5% 和 10% 时,膜层的耐蚀性比未添加 TiO_2 溶胶的膜层较高。将质量浓度分别为 0、4、8 g/L 的 TiO_2 纳米粒子加入到碱性铝酸盐电解液中,对 MAO 膜层的表面形貌和耐蚀性均有很大程度的提高^[49]。添加不同浓度 TiO_2 纳米粒子的 MAO 改性镁合金截面形貌如图 7 所示,对比图 7a、b 发现,在不含 TiO_2 纳米粒子和含有 8 g/L TiO_2 纳米粒子的电解液中,形成的膜层的微

观结构较为相似。与 MAO 8 g/L 的膜层相比,MAO 0 g/L 膜层外层的孔隙更多。从图 7c 可以明显地看到,在 TiO_2 纳米粒子质量浓度为 4 g/L 时,膜层表面的孔隙与其他样品相比,尺寸和数量明显变小,MAO 膜层具有高的致密度,此时膜层耐蚀性有很大程度的提高。电解液中含有较高浓度的添加剂时,致使大量添加剂粒子参与 MAO 反应,使得能量过高,容易产生大范围火花放电现象形成大弧,从而增加了膜层的缺陷密度,导致膜层的耐蚀性降低。综上所述,在电解液中的添加剂种类及其含量不仅会改变 MAO 中火花放电过程,也会影响膜层孔隙的尺寸和数量,以此改变膜层性能。考虑合金医用用途,可以选择 HA、Ca、P 等具有生物活性和对人体有益的粒子作为电解液添加剂。

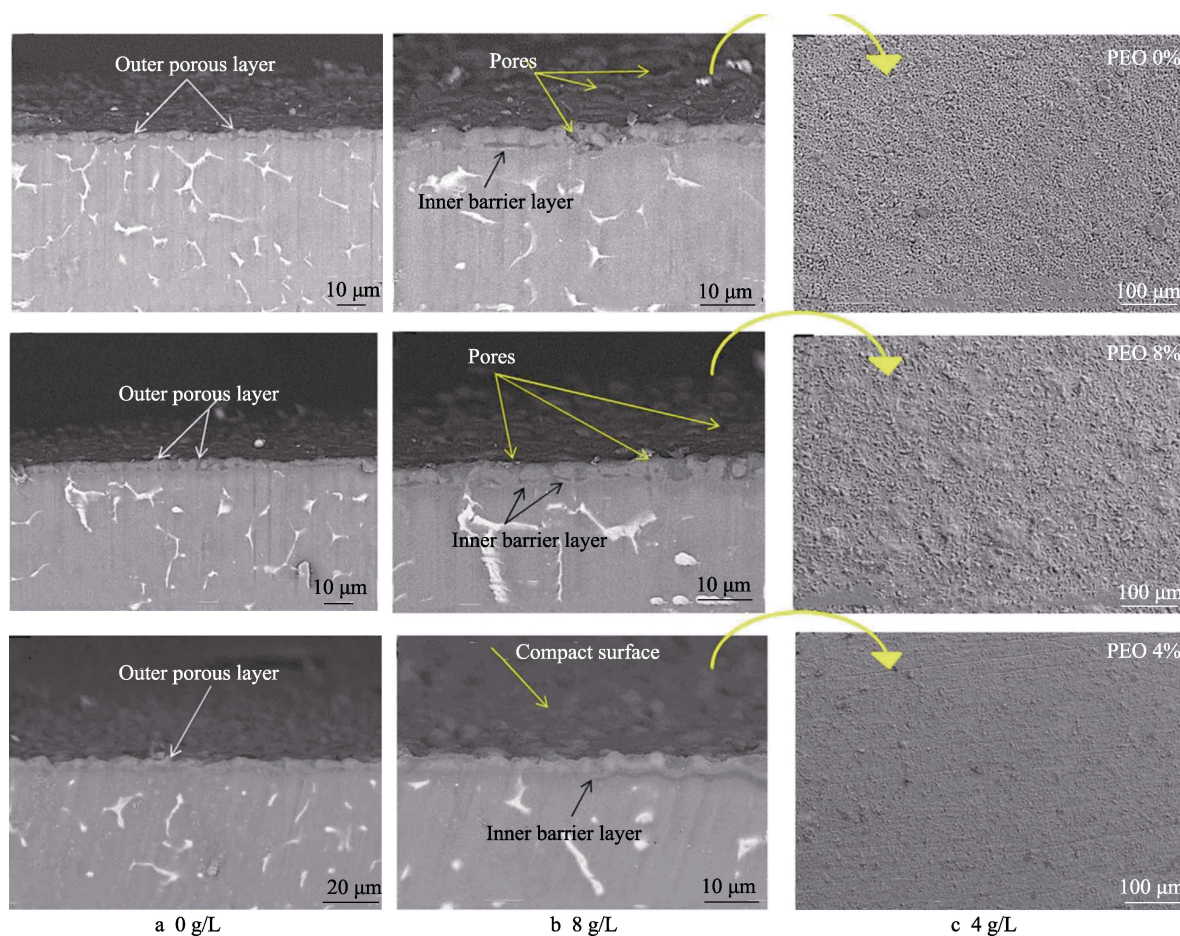


图 7 MAO 改性 Mg 合金的截面形貌^[49]

Fig.7 Cross section morphologies of MAO modified Mg alloys^[49]

4 电参数对 MAO 膜层性能的影响

微弧氧化电参数会改变 MAO 过程的放电特点,影响 MAO 膜层形貌,也进一步影响膜层的耐蚀性和生物相容性。本文主要从电压、电流和脉冲频率这 3 个方面讨论了电参数对医用镁合金 MAO 膜层性能的影响。

4.1 电压的影响

电压大小对 MAO 膜层的厚度、孔径大小和耐蚀性等有明显的影响^[20,55-63]。膜层的厚度、孔径大小与电压呈正比关系,膜层的耐蚀性则需要通过试验判定。Tang 等^[55]在含 NaOH 和 $\text{C}_3\text{H}_7\text{CaO}_6\text{P}$ 的碱性电解液中,分别用 250、300、350、400、450、500 V 的目标电压在 AZ31 镁合金表面制备含羟基磷灰石膜

层。在较高电压下,膜层的生长速度较快,微孔数量减少,但孔径变大。这主要归因于当阳极处于更强的电场时,会出现高能火花,击穿膜层时会有大量的熔融物喷出,导致孔径变大,同时伴有裂纹的产生。研究发现,在低于 400 V 的电压下形成的氧化膜层没有观察到裂纹,但在电压升高时,裂纹却分散出现。因此,在低于 400 V 的电压下制备的膜层耐蚀性最高。Dou 等^[62]采用两步微弧氧化工艺在 Mg-Zn-Ca 合金上沉积了含 Si-CaP 的膜层,研究了电压 350、400、450 V 对膜层形貌和性能的影响。不同电压下,MAO 膜层的表面形貌和相应的 EDS 分析如图 8 所示。可以发现,随着电压的增加,表面上的微孔减少,表面变得更加致密。从 EDS 结果分析发现,两步 MAO

法使电解液中的 Ca、P 元素成功结合到膜层中。模拟体液中的电化学测试证明,与基体相比,CSB-400 V 膜层表现出了最佳的耐蚀性,主要归因于相对光滑的表面、致密且厚的膜层。由此可见,电压大小对 MAO 膜层的形貌和性能的影响较大。MAO 中击穿电压和大弧电压的大小对膜层孔隙率和孔径大小也有着极大的影响。其中,击穿电压是由电解液的浓度和电导率决定的,不同类型的电解液对应的击穿电压值不同,均需通过实验获得最佳击穿电压值,以得到最佳膜层形貌和性能。MAO 过程中产生大弧电压时,局部表面会散发大量的能量和熔融物,导致更大的孔径和不均匀的表面形貌形成,从而使得膜层的耐蚀性降低。

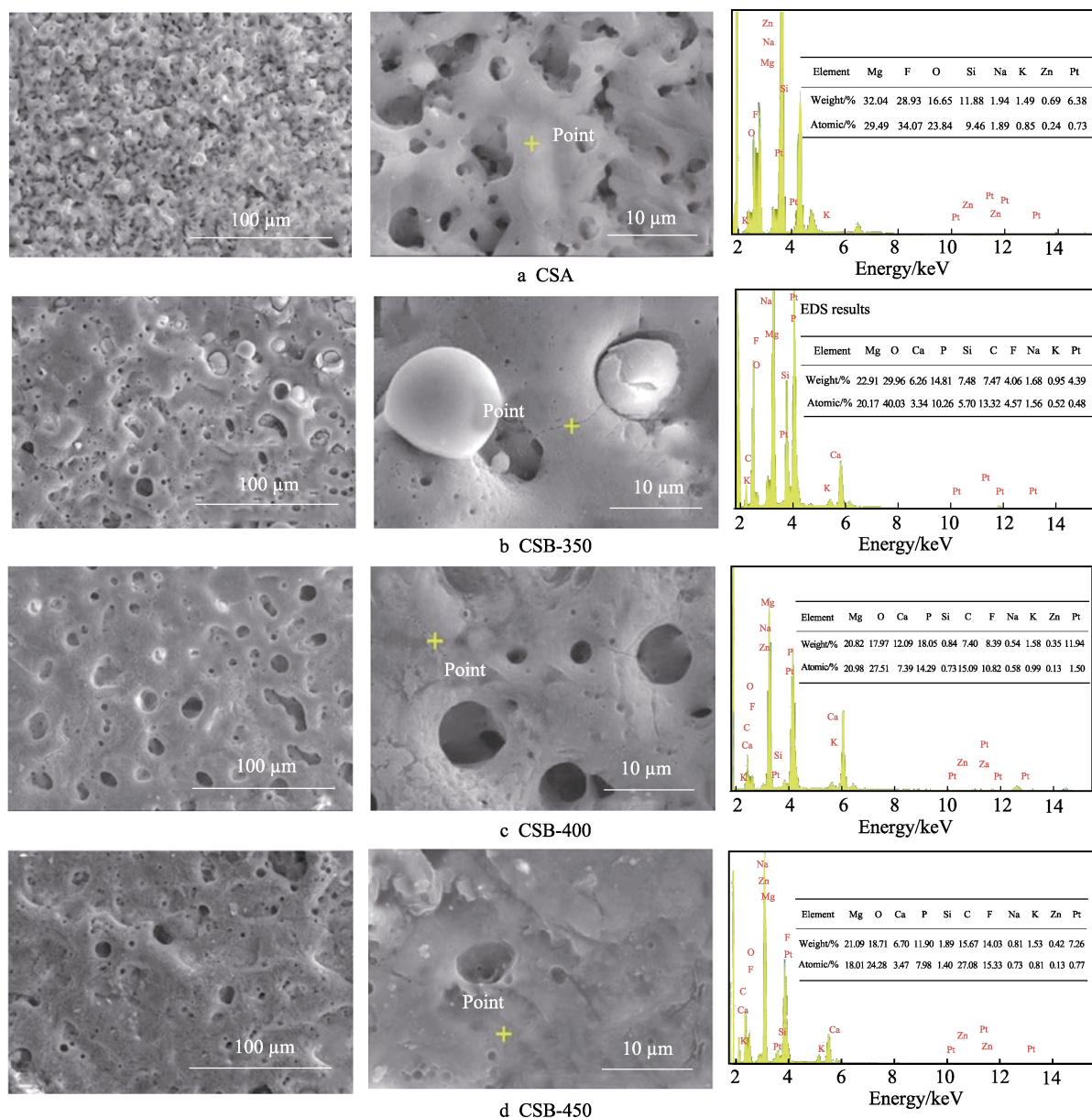


图 8 经一步和两步工艺产生的 MAO 膜层表面和 EDS 分析^[62]
Fig.8 Surface morphology and EDS analysis of MAO films produced by first step and two-step process^[62]

4.2 电流模式

MAO 过程中的放电火花导致微孔的形成, 不同的电流模式产生不同的放电火花, 从而影响 MAO 膜层的表面形貌, 进而影响膜层的耐蚀性。电流模式一般分为单极、双极和混合模式 (单极与双极结合), 用不同的电流模式进行 MAO 得到的氧化膜层性能为混合模式>双极>单极。混合模式中, 先单极、后双极模式优于先双极、后单极模式^[35,64-65]。单极模式获得 MAO 膜时, 会出现强烈的火花放电, 使试样表面产生高温, 导致部分 MAO 膜层重熔, 大孔变得更大或被覆盖, MAO 膜层厚度减小。在双极模式下, 阴极组分降低火花放电强度, 并为氧化物冷却提供了足够时间, 使得膜层更厚, 平均孔径比前者更大。在混合模式下进行 MAO 时, 施加电流模式的顺序对膜层的形态和耐蚀性有显著的影响。先单极后双极的混合模式下 MAO 膜层的表面和横截面形貌如图 9 所示。由图 9a 可以得出, 在最初的 15 min (单极模式), 强度波动较高, 第 2 个 15 min 由于双极模式的放电能量低, 总强度波动较小。由图 9b、c 可以得出, 在先单极后双极的混合模式下, 由于最初施加的单极电流模式, 强火花放电使得具有较小孔隙薄膜层的形成, 之后的双极模式减弱了放电火花, 喷射出的氧化物被电解液快速固化而没有重熔, 获得了膜层较厚和孔隙率相对较低的 MAO 膜层, 双极电流模式修复了单极模式造成的损坏, 并产生具有最小缺陷的致密膜层^[64]。Ly 等^[65]采用不同电流模式的微弧氧化技术在 Mg-Zn-Ca 合金表面制备了 MAO 膜层。实验结果表明, 经 MAO 处理后, 明显提高了 Mg-Zn-Ca 合金的耐蚀性, 混合模式制备的 MAO 膜层的耐蚀性优于单极和双极模式, 同时也使得 Mg-Zn-Ca 合金具有作为骨修复和植入材料的潜力。

4.3 脉冲频率

电压的输出方式由电源模式决定。电源模式一般分为直流、交流和脉冲模式。由于在微弧氧化过程中

使用脉冲电源有利于正、负脉冲周期和宽度的调整, 其工艺过程可得到有效控制, 同时在脉冲模式下制备的膜层质量更为优异, 且电能利用率更高, 所以 MAO 常用的电源模式为脉冲电源^[17,23,66-72]。脉冲电源中需要调整的主要参数为脉冲频率, 脉冲频率指的是单个脉冲的作用时间长短。调整脉冲频率时, 对 MAO 膜层的形貌和粗糙度会产生较为明显的影响, 从而影响膜层的耐蚀性。在频率参数较低时, 单个脉冲作用时间较长, 此时由于微弧放电时间增加, 使得放电能量增大, 微孔半径增大, 致使膜层厚度和结合强度降低, 粗糙度增加。在频率参数较高时, 脉冲作用时间短, 此时微弧放电时间减少, 脉冲能量小, 但放电次数频繁, 致使微孔尺寸减小、密度增加和膜层粗糙度降低。脉冲频率增加与降低对膜层的厚度并无显著影响, 但膜层中致密层比例随脉冲频率的线性增加, 相应地, 膜层的耐蚀性得以提升。Gu 等^[17]在不同脉冲频率下对 AZ31 镁合金进行了微弧氧化, 研究了不同微弧氧化膜层在 SBF 中的腐蚀行为。采用脉冲直流模式, 以恒定的脉冲比, 分别在 30、500、1 000、3 000 Hz 等 4 种不同的脉冲频率下沉积微弧氧化膜, 膜层的平均孔径和平均裂纹尺寸随脉冲频率的增加而减小。由图 10 可以看出, AZ31 基体和沉积 MAO 膜层的 AZ31 合金分别在 SBF 中浸泡 7 d 后, 3 000 Hz 样品与其他频率下形成的膜层样品相比, 腐蚀速率最慢, 即耐蚀性更好。这是因为在 3 000 Hz 下形成具有孔隙率低、孔径小的光滑表面, 所以频率为 3 000 Hz 的样品表现出最好的耐蚀性。

电参数的调整会改变微弧氧化膜层的结构和形貌, 对膜层的性能有很大影响。电压、电流模式和脉冲频率的调控会使得膜层结构更加致密, 降低了镁合金微弧氧化膜层在模拟体液中的降解速率, 从而提高膜层的耐蚀性。大多数学者对电参数的研究只是研究单一参数对膜层结构和性能的改善, 并没有大量研究同时调控电压、电流和频率参数对膜层形成有何影响。

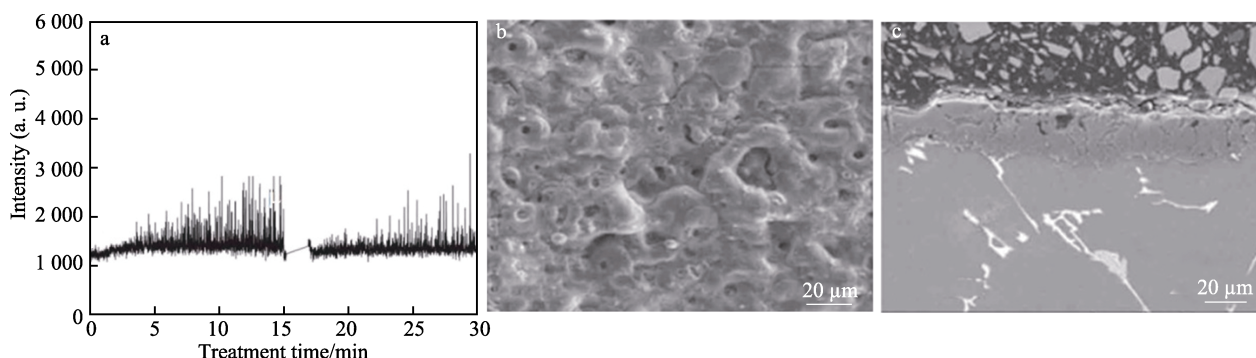


图 9 (a) 单极+双极混合模式下 MAO 期间 Mg 383.3 nm 发射线强度的典型变化,

(b) MAO 膜层表面形貌的 SEM 形貌, (c) MAO 膜层横截面背散射电子模式的 SEM 形貌^[64]

Fig.9 (a) Typical time variation of the Mg 383.3 nm emission line intensity during the MAO process, (b) SEM images showing surface morphology of the MAO film and (c) SEM images using back-scattered electron mode of cross section of MAO film^[64]

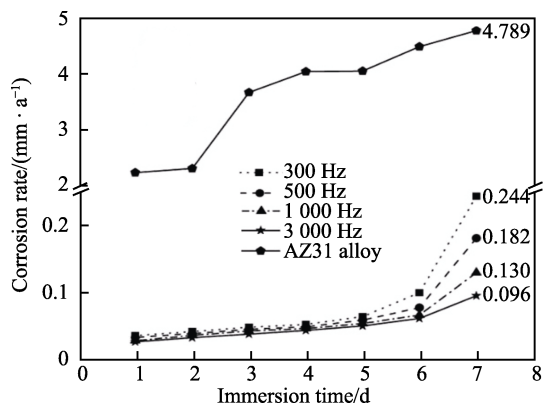


图 10 浸泡在 SBF 中 MAO 膜层和 AZ31 基体的腐蚀速率^[17]

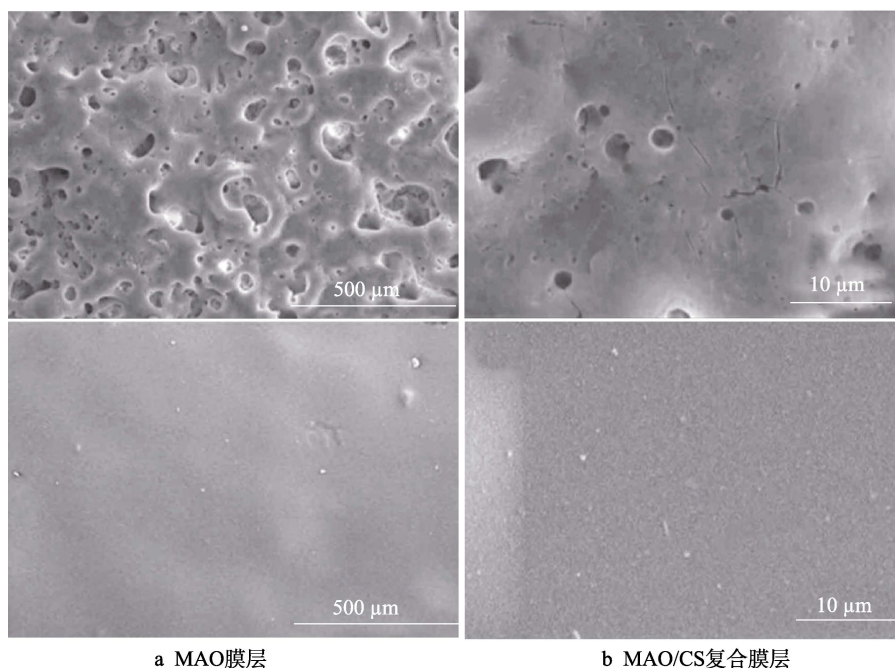
Fig.10 Corrosion rates of MAO films and uncoated AZ31 alloy after immersion in the SBF^[17]

5 封孔材料对膜层的影响

镁合金在人体中的降解速度很快,虽然 MAO 膜层的存在对耐蚀性稍有提高,但由于膜层表面微孔的存在,膜层的耐蚀性仍受到限制。为了进一步提高材料性能,改善 MAO 膜层表面形貌显得尤为重要。封孔技术是一种广泛使用的 MAO 膜层后处理方法,可以进一步减少膜层微孔缺陷,增强膜层的耐蚀性和生物相容性^[30,73]。可用于封孔工艺的材料主要有无机物封孔^[74]和有机物封孔^[68,71,75-76]两大类,制备复合膜层时,可以选择 HA、姜黄素 (Cur) 和壳聚糖 (CS) 等生物材料制备出更符合医用的膜层。

壳聚糖 (CS) 具有生物降解性和细胞亲和性、

封闭微孔等优点,被广泛应用于 MAO 生物复合膜层。Dou 等^[75]对 Mg-Zn-Ca 合金采用微弧氧化和浸渍法成功制备了 MAO/CS 复合膜层,如图 11 所示。图 11a 为 MAO 膜层的典型形貌特征,可发现膜层表面存在微孔和微裂纹。在膜层表面沉积 CS 层后,表面孔隙率降低,封闭了 MAO 膜层上的微孔 (见图 11b)。MAO/CS 复合膜层使得 MAO 膜层的多孔特征得到改善,使得镁合金的耐蚀性得到提高。体外浸泡试验表明,MAO/CS 复合膜层的生物相容性更好,能促进细胞增殖和分化,所以通过浸渍法得到的复合 MAO/CS 膜层具备较为优异的生物相容性。Yu 等^[76]在 Mg-4Li-Ca 合金表面制备微弧氧化/壳聚糖膜层时发现,微弧氧化复合膜层的耐蚀性和生物相容性均优于单一膜层。Guo 等^[77]在 AZ31B 合金表面采用微弧氧化和水热法成功制备了 MAO/HA 的生物活性复合膜层。MAO 层中存在 Mg_2SiO_4 和 CaSiO_3 相,由于电解液在放电过程中的快速冷却作用, Ca 和 P 可以与氧结合,形成非晶态 Ca^{2+} 、 HPO_4^{2-} 和 PO_4^{3-} 。在水热处理过程中,非晶态的存在促进 CaP 化合物的沉积,形成了 $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (也称为 HA)。制备的水热层密封孔效应使 MAO 膜层的耐腐蚀性得到明显改善,并通过沉积钙和磷化合物提高了生物相容性。因此,通过对 MAO 膜层的封孔后处理,可以添加具有良好生物相容性的材料,采用浸渍法、溶胶-凝胶法和水热法等制备生物复合膜层。复合膜层的存在,消除了 MAO 膜层表面的大孔和微裂纹等缺陷,在很大程度上提高了镁合金的耐蚀性,而具有生物活性材料的添加可以提高合金的生物相容性。



a MAO膜层

b MAO/CS复合膜层

图 11 MAO 膜层和 MAO/CS 复合膜层的表面形貌^[75]

Fig.11 Surface morphologies of (a) MAO film and (b) MAO/CS film^[75]

6 结语

作为医用骨植入物的主要材料, 镁合金具有很大的优势。经过微弧氧化处理的镁合金, 其耐蚀性和生物相容性能均得到提高。但镁合金在生物医用方面的很多问题还没有解决, 如降低降解速率、提高耐蚀性和延长在人体中的机械支撑等问题。在以后的研究过程中, 镁合金微弧氧化研究可以从以下几个方面出发。

1) MAO 工艺中的电参数(电压、电流和脉冲频率)如何影响阴离子、负电粒子与成膜机理和膜层微观结构的研究甚少, 且现有的 MAO 膜层腐蚀机理并不完整、成熟。

2) 镁合金微弧氧化预处理可以影响 MAO 膜层的组织与结构, 可以将纳米技术和 3D 打印技术等一些新型的表面技术与微弧氧化工艺结合, 使 MAO 膜层与基体的结合更加紧密, 降低膜层孔隙率, 提高膜层的耐蚀性。

3) 镁合金 MAO 过程中对大弧电压的起因和影响因素研究过少, 未来对大弧电压可以进行着重研究。

4) 在医用镁合金进行临床应用之前, 必须充分了解其降解机理和副作用。镁合金 MAO 膜层中包含的添加剂和复合膜层必须在短期和长期均满足生物相容性和生物安全性。

5) 作为医用骨植入物, 镁合金应保持足够的机械支撑至少 3 个月, 以避免骨植入物降解而导致二次骨折。但是现在对镁合金 MAO 膜层力学性能与膜层组织和结构之间的联系研究不够深入, 应从骨植入体所需的力学性能进行研究。

参考文献:

- [1] 颜廷亭, 谭丽丽, 熊党生, 等. 医用镁金属材料的研究进展[J]. 材料导报, 2008, 22(1): 110-112.
YAN Ting-ting, TAN Li-li, XIONG Dang-sheng, et al. Research Progress in Magnesium-Based Metals for Medical Applications[J]. Materials Review, 2008, 22(1): 110-112.
- [2] 潘尧坤. 生物医用可降解 Mg-Zn-Ca-Si 合金制备及其表面微弧氧化改性[D]. 济南: 山东大学, 2015.
PAN Yao-kun. Preparation and Micro-Arc Oxidation of Biodegradable Mg-Zn-Ca-Si Magnesium Alloys for Biomedical Applications[D]. Jinan: Shandong University, 2015.
- [3] 李涛, 张海龙, 何勇, 等. 生物医用镁合金研究进展[J]. 功能材料, 2013, 44(20): 2913-2918.
LI Tao, ZHANG Hai-long, HE Yong, et al. Research Progress in Biomedical Magnesium Alloys[J]. Journal of Functional Materials, 2013, 44(20): 2913-2918.
- [4] NIINOMI M. Mechanical Biocompatibilities of Titanium Alloys for Biomedical Applications[J]. Journal of the Mechanical Behavior of Biomedical Materials, 2008, 1(1): 30-42.
- [5] 胡欣, 魏强, 李长义, 等. 医用钛合金生物学及机械性能评述[J]. 材料导报, 2009, 23(19): 57-60.
HU Xin, WEI Qiang, LI Chang-yi, et al. Biological and Mechanical Properties of Biomedical Titanium Alloys[J]. Materials Review, 2009, 23(19): 57-60.
- [6] CHEN Jun-xiu, TAN Li-li, YU Xiao-ming, et al. Mechanical Properties of Magnesium Alloys for Medical Application: A Review[J]. Journal of the Mechanical Behavior of Biomedical Materials, 2018, 87: 68-79.
- [7] REZWAN K, CHEN Q Z, BLAKER J J, et al. Biodegradable and Bioactive Porous Polymer/Inorganic Composite Scaffolds for Bone Tissue Engineering[J]. Biomaterials, 2006, 27(18): 3413-3431.
- [8] BOMMALA V K, KRISHNA M G, RAO C T. Magnesium Matrix Composites for Biomedical Applications: A Review[J]. Journal of Magnesium and Alloys, 2019, 7(1): 72-79.
- [9] LI Nan, ZHENG Yu-feng. Novel Magnesium Alloys Developed for Biomedical Application: A Review[J]. Journal of Materials Science & Technology, 2013, 29(6): 489-502.
- [10] STAIGER M P, PIETAK A M, HUADMAI J, et al. Magnesium and Its Alloys as Orthopedic Biomaterials: A Review[J]. Biomaterials, 2006, 27(9): 1728-1734.
- [11] WITTE F. The History of Biodegradable Magnesium Implants: A Review[J]. Acta Biomaterialia, 2010, 6(5): 1680-1692.
- [12] WU Wei-wei, WANG Zi-yuan, ZANG Si-tian, et al. Research Progress on Surface Treatments of Biodegradable Mg Alloys: A Review[J]. ACS Omega, 2020, 5(2): 941-947.
- [13] 窦金河. 医用镁合金表面可降解复合膜层的制备及其耐蚀性的研究[D]. 济南: 山东大学, 2018.
DOU Jin-he. Preparation and Corrosion Resistance of Degradable Composite Coating on Magnesium Alloy for Orthopedics[D]. Jinan: Shandong University, 2018.
- [14] YIN Zheng-zheng, QI Wei-chen, ZENG Rong-chang, et al. Advances in Coatings on Biodegradable Magnesium Alloys[J]. Journal of Magnesium and Alloys, 2020, 8(1): 42-65.
- [15] 陈明. 镁合金微弧氧化微区电弧放电机理及电源特性的研究[D]. 兰州: 兰州理工大学, 2010.
CHEN Ming. Research on the Local Arc Discharge Mechanism and the Characteristics of Power Supply in Micro-Arc Oxidation of Magnesium Alloy[D]. Lanzhou: Lanzhou University of Technology, 2010.
- [16] 唐洋洋, 李林波, 王超, 等. 镁合金微弧氧化复合膜研究进展[J]. 表面技术, 2022, 51(4): 66-76.
TANG Yang-yang, LI Lin-bo, WANG Chao, et al. Research Progress of Micro-Arc Oxidation Composite Films

- for Magnesium Alloys[J]. *Surface Technology*, 2022, 51(4): 66-76.
- [17] GU Yan-hong, CHEN Cheng-fu, BANDOPADHYAY S, et al. Corrosion Mechanism and Model of Pulsed DC Microarc Oxidation Treated AZ31 Alloy in Simulated Body Fluid[J]. *Applied Surface Science*, 2012, 258(16): 6116-6126.
- [18] ZHANG Lei, ZHANG Jun-qing, CHEN Cheng-fu, et al. Advances in Microarc Oxidation Coated AZ31 Mg Alloys for Biomedical Applications[J]. *Corrosion Science*, 2015, 91: 7-28.
- [19] 王兴平. 镁、镁合金微弧氧化膜微观结构及耐蚀性的对比研究[D]. 兰州: 兰州理工大学, 2018.
WANG Xing-ping. Comparison of Microstructure and Corrosion Resistance of Micro-Arc Oxidation Coatings Formed on Magnesium and Magnesium Alloys[D]. Lanzhou: Lanzhou University of Technology, 2018.
- [20] 杨东东. 镁合金微弧氧化生物医用陶瓷层的结构与性能研究[D]. 哈尔滨: 哈尔滨工业大学, 2007.
YANG Dong-dong. Structure and Properties of Modified Layers Used in Biology and Medical Applications by Microarc Oxidation on Magnesium Alloy[D]. Harbin: Harbin Institute of Technology, 2007.
- [21] BARATI DARBAND G, ALIOFKHAZRAEI M, HAMG-HALAM P, et al. Plasma Electrolytic Oxidation of Magnesium and Its Alloys: Mechanism, Properties and Applications[J]. *Journal of Magnesium and Alloys*, 2017, 5(1): 74-132.
- [22] CHEN Wei-wei, WANG Ze-xin, SUN Lei, et al. Research of Growth Mechanism of Ceramic Coatings Fabricated by Micro-Arc Oxidation on Magnesium Alloys at High Current Mode[J]. *Journal of Magnesium and Alloys*, 2015, 3(3): 253-257.
- [23] 董海荣. AZ91D 镁合金微弧氧化膜生长过程及机理的研究[D]. 兰州: 兰州理工大学, 2015.
DONG Hai-rong. Growth and Mechanism of Micro-Arc Oxidation Coatings on Magnesium Alloys[D]. Lanzhou: Lanzhou University of Technology, 2015.
- [24] 吴雄飞. 基于回归正交设计研究电解液对 AM60B 微弧氧化膜的影响[D]. 兰州: 兰州理工大学, 2020.
WU Xiong-fei. Study on the Effect of Electrolyte on AM60B Micro-Arc Oxidation Coatings Based on Regression Orthogonal Experimental Design[D]. Lanzhou: Lanzhou University of Technology, 2020.
- [25] VIJH A K. Sparking Voltages and Side Reactions during Anodization of Valve Metals in Terms of Electron Tunneling[J]. *Corrosion Science*, 1971, 11(6): 411-417.
- [26] 李新义. 微弧氧化/颗粒复合膜层生长机理与关键制备技术研究[D]. 北京: 北京科技大学, 2020.
LI Xin-yi. Study on the Growth Mechanism of Micro-Arc Oxidation/Particle Composite Film and Its Key Technology[D]. Beijing: University of Science and Technology Beijing, 2020.
- [27] 丁兆勇, 牛宗伟, 夏汝岩, 等. 镁合金表面微弧氧化技术研究进展与展望[J]. *机械工程师*, 2018(12): 14-15.
DING Zhao-yong, NIU Zong-wei, XIA Ru-yan, et al. Research Progress and Prospect of Micro-Arc Oxidation Technology for Magnesium Alloy Surface[J]. *Mechanical Engineer*, 2018(12): 14-15.
- [28] DING Zi-you, CUI Lan-yue, CHEN Xiao-bo, et al. *In Vitro* Corrosion of Micro-Arc Oxidation Coating on Mg-1Li-1Ca Alloy—The Influence of Intermetallic Compound Mg_2Ca [J]. *Journal of Alloys and Compounds*, 2018, 764: 250-260.
- [29] YU Hui-jun, DONG Qing, DOU Jin-he, et al. Structure and *in Vitro* Bioactivity of Ceramic Coatings on Magnesium Alloys by Microarc Oxidation[J]. *Applied Surface Science*, 2016, 388: 114-119.
- [30] 刘朋, 刘群峰, 黄德群, 等. 微弧氧化膜封孔技术研究进展[J]. *表面技术*, 2019, 48(7): 61-71.
LIU Peng, LIU Qun-feng, HUANG De-qun, et al. Research Progress of Pore Sealing Technology for Micro-Arc Oxidation Films[J]. *Surface Technology*, 2019, 48(7): 61-71.
- [31] LI Yu-hang, GUAN Ying-chun, ZHANG Zhen, et al. Enhanced Bond Strength for Micro-Arc Oxidation Coating on Magnesium Alloy via Laser Surface Microstructuring[J]. *Applied Surface Science*, 2019, 478: 866-871.
- [32] 张超, 牛宗伟, 姚知深, 等. 硝酸铈浸渍超声喷丸对镁合金微弧氧化的影响[J]. *电镀与涂饰*, 2019, 38(4): 161-165.
ZHANG Chao, NIU Zong-wei, YAO Zhi-shen, et al. Effect of Ultrasonic Shot Peening in Cerium Nitrate Solution on Micro-Arc Oxidation of Magnesium Alloy[J]. *Electroplating & Finishing*, 2019, 38(4): 161-165.
- [33] WANG Ye, LU Dan-hua, WU Guo-long, et al. Effect of Laser Surface Remelting Pretreatment with Different Energy Density on MAO Bioceramic Coating[J]. *Surface and Coatings Technology*, 2020, 393: 125815.
- [34] XIONG Ying, HU Qiang, SONG Ren-guo, et al. LSP/MAO Composite Bio-Coating on AZ80 Magnesium Alloy for Biomedical Application[J]. *Materials Science and Engineering: C*, 2017, 75: 1299-1304.
- [35] LY X, YANG Sen, NGUYEN T. Effect of Equal Channel Angular Pressing as the Pretreatment on Microstructure and Corrosion Behavior of Micro-Arc Oxidation (MAO) Composite Coating on Biodegradable Mg-Zn-Ca Alloy[J]. *Surface and Coatings Technology*, 2020, 395: 125923.
- [36] YAN Xu-dong, ZHAO Ming-chun, YANG Yi, et al. Improvement of Biodegradable and Antibacterial Properties by Solution Treatment and Micro-Arc Oxidation (MAO) of a Magnesium Alloy with a Trace of Copper[J]. *Corrosion Science*, 2019, 156: 125-138.
- [37] 姜伟, 王桂香. 镁合金微弧氧化工艺的研究进展[J]. *电镀与环保*, 2010, 30(4): 1-4.
JIANG Wei, WANG Gui-xiang. Recent Progress of Microarc Oxidation Process for Magnesium Alloy[J]. *Electroplating & Pollution Control*, 2010, 30(4): 1-4.

- [38] SEYFOORI A, MIRDAMADI S, KHAVANDI A, et al. Biodegradation Behavior of Micro-Arc Oxidized AZ31 Magnesium Alloys Formed in Two Different Electrolytes[J]. *Applied Surface Science*, 2012, 261: 92-100.
- [39] TANG Yu-ming, ZHAO Xu-hui, JIANG Kui-sheng, et al. The Influences of Duty Cycle on the Bonding Strength of AZ31B Magnesium Alloy by Microarc Oxidation Treatment[J]. *Surface and Coatings Technology*, 2010, 205(6): 1789-1792.
- [40] JIA Z J, LI M, LIU Q, et al. Micro-Arc Oxidization of a Novel Mg-1Ca Alloy in Three Alkaline KF Electrolytes: Corrosion Resistance and Cytotoxicity[J]. *Applied Surface Science*, 2014, 292: 1030-1039.
- [41] PAN Y K, CHEN C Z, WANG D G, et al. Effects of Phosphates on Microstructure and Bioactivity of Micro-Arc Oxidized Calcium Phosphate Coatings on Mg-Zn-Zr Magnesium Alloy[J]. *Colloids and Surfaces B: Biointerfaces*, 2013, 109: 1-9.
- [42] TANG Hui, GAO Yang. Preparation and Characterization of Hydroxyapatite Containing Coating on AZ31 Magnesium Alloy by Micro-Arc Oxidation[J]. *Journal of Alloys and Compounds*, 2016, 688: 699-708.
- [43] GU Yan-hong, BANDOPADHYAY S, CHEN Cheng-fu, et al. Long-Term Corrosion Inhibition Mechanism of Microarc Oxidation Coated AZ31 Mg Alloys for Biomedical Applications[J]. *Materials & Design*, 2013, 46: 66-75.
- [44] CHEN Jun-xiu, ZHANG Yi, IBRAHIM M, et al. *In Vitro* Degradation and Antibacterial Property of a Copper-Containing Micro-Arc Oxidation Coating on Mg-2Zn-1Gd-0.5Zr Alloy[J]. *Colloids and Surfaces B: Biointerfaces*, 2019, 179: 77-86.
- [45] 安凌云, 马颖, 王占营, 等. 微弧氧化工艺参数研究概况与展望[J]. *热加工工艺*, 2020, 49(8): 1-8.
AN Ling-yun, MA Ying, WANG Zhan-ying, et al. Research Situation and Prospect of Micro-Arc Oxidation Process Parameters[J]. *Hot Working Technology*, 2020, 49(8): 1-8.
- [46] CHU Cheng-lin, HAN Xiao, BAI Jing, et al. Surface Modification of Biomedical Magnesium Alloy Wires by Micro-Arc Oxidation[J]. *Transactions of Nonferrous Metals Society of China*, 2014, 24(4): 1058-1064.
- [47] 张璇, 邵忠财. 镁合金微弧氧化电解液组成对膜性能的影响[J]. *电镀与精饰*, 2011, 33(4): 18-21.
ZHANG Xuan, SHAO Zhong-cai. Effect of Magnesium Alloy Micro-Arc Oxidation Electrolyte Composition on Coating Properties[J]. *Plating & Finishing*, 2011, 33(4): 18-21.
- [48] 付景国, 刘建, 朱新河, 等. 微纳米颗粒在制备微弧氧化复合膜层中的影响研究现状[J]. *热加工工艺*, 2020, 49(2): 12-19.
FU Jing-guo, LIU Jian, ZHU Xin-he, et al. Research Status of Influence of Micro-Nano Particles in Preparation of Micro-Arc Oxidation Composite Layer[J]. *Hot Working Technology*, 2020, 49(2): 12-19.
- [49] DAROONPARVAR M, YAJID M A M, YUSOF N M, et al. Preparation and Corrosion Resistance of a Nanocomposite Plasma Electrolytic Oxidation Coating on Mg-1%Ca Alloy Formed in Aluminate Electrolyte Containing Titania Nano-Additives[J]. *Journal of Alloys and Compounds*, 2016, 688: 841-857.
- [50] FARSHID S, KHARAZIHA M. Micro and Nano-Enabled Approaches to Improve the Performance of Plasma Electrolytic Oxidation Coated Magnesium Alloys[J]. *Journal of Magnesium and Alloys*, 2021, 9(5): 1487-1504.
- [51] MA Xun, ZHU Shi-jie, WANG Li-guo, et al. Synthesis and Properties of a Bio-Composite Coating Formed on Magnesium Alloy by One-Step Method of Micro-Arc Oxidation[J]. *Journal of Alloys and Compounds*, 2014, 590: 247-253.
- [52] PAN Y K, CHEN C Z, WANG D G, et al. Influence of Additives on Microstructure and Property of Microarc Oxidized Mg-Si-O Coatings[J]. *Ceramics International*, 2012, 38(7): 5527-5533.
- [53] WANG Y M, WANG F H, XU M J, et al. Microstructure and Corrosion Behavior of Coated AZ91 Alloy by Microarc Oxidation for Biomedical Application[J]. *Applied Surface Science*, 2009, 255(22): 9124-9131.
- [54] WU Di, LIU Xiang-dong, LU Kai, et al. 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[J]. *Applied Surface Science*, 2009, 255(16): 7115-7120.
- [55] TANG Hui, HAN Yu, WU Tao, et al. Synthesis and Properties of Hydroxyapatite-Containing Coating on AZ31 Magnesium Alloy by Micro-Arc Oxidation[J]. *Applied Surface Science*, 2017, 400: 391-404.
- [56] GU X N, LI N, ZHOU W R, et al. Corrosion Resistance and Surface Biocompatibility of a Microarc Oxidation Coating on a Mg-Ca Alloy[J]. *Acta Biomaterialia*, 2011, 7(4): 1880-1889.
- [57] 马颖, 梁志龙, 安凌云, 等. 不同电压下制备等厚微弧氧化膜层的能耗及膜层的耐蚀性[J]. *兰州理工大学学报*, 2020, 46(4): 6-9.
MA Ying, LIANG Zhi-long, AN Ling-yun, et al. Energy Consumption and Corrosion Resistance of MAO Coatings with Same Thicknesses Fabricated under Different Voltages[J]. *Journal of Lanzhou University of Technology*, 2020, 46(4): 6-9.
- [58] LI Ying, LU Fang, LI Hong-long, et al. Corrosion Mechanism of Micro-Arc Oxidation Treated Biocompatible AZ31 Magnesium Alloy in Simulated Body Fluid[J]. *Progress in Natural Science: Materials International*, 2014, 24(5): 516-522.
- [59] QIAN Bing-yu, MIAO Wei, QIU Min, et al. Influence of Voltage on the Corrosion and Wear Resistance of Micro-Arc Oxidation Coating on Mg-8Li-2Ca Alloy[J]. *Acta Metallurgica Sinica (English Letters)*, 2019, 32(2):

- 194-204.
- [60] 孙乐, 马颖, 安凌云, 等. 高低电压下不同厚度微弧氧化膜抗蚀电化学响应对比研究[D]. 表面技术, 2021, 50(1): 366-374.
- SUN Le, MA Ying, AN Ling-yun, et al. Comparative Study on Anti-Corrosion Electrochemical Response of Micro-Arc Oxidation Coating with Different Thicknesses Under High and Low Voltage[D]. Surface Technology, 2021, 50(1): 366-374.
- [61] WANG Y M, GUO J W, SHAO Z K, et al. A Metasilicate-Based Ceramic Coating Formed on Magnesium Alloy by Microarc Oxidation and Its Corrosion in Simulated Body Fluid[J]. Surface and Coatings Technology, 2013, 219: 8-14.
- [62] DOU Jin-he, WANG Chun-yan, GU Guo-chao, et al. Formation of Silicon-Calcium-Phosphate-Containing Coating on Mg-Zn-Ca Alloy by a Two-Step Micro-Arc Oxidation Technique[J]. Materials Letters, 2018, 212: 37-40.
- [63] DOU Jin-he, YU Hui-jun, CHEN Chuan-zhong, et al. Formation of Calcium Phosphate Coating on Mg-Zn-Ca Alloy by Micro-Arc Oxidation Technique[J]. Materials Letters, 2016, 164: 575-578.
- [64] HUSSEIN R O, NORTHWOOD D O, NIE X. The Influence of Pulse Timing and Current Mode on the Microstructure and Corrosion Behaviour of a Plasma Electrolytic Oxidation (PEO) Coated AM60B Magnesium Alloy[J]. Journal of Alloys and Compounds, 2012, 541: 41-48.
- [65] LY X N, YANG S. Influence of Current Mode on Microstructure and Corrosion Behavior of Micro-Arc Oxidation (MAO) Biodegradable Mg-Zn-Ca Alloy in Hank's Solution[J]. Surface and Coatings Technology, 2019, 358: 331-339.
- [66] 彭飞. 不同电源模式下的镁合金微弧氧化工艺研究[D]. 兰州: 兰州理工大学, 2012.
- PENG Fei. Technical Study on Micro-Arc Oxidation of Magnesium Alloy with Different Power Supply Modes[D]. Lanzhou: Lanzhou University of Technology, 2012.
- [67] 刘金忠. 不同电源模式下电参数对 AM60B 微弧氧化膜的影响[D]. 兰州: 兰州理工大学, 2019.
- LIU Jin-zhong. Effects of Electrical Parameters on Micro-Arc Oxidation Coatings on AM60B under Different Power Supply Modes[D]. Lanzhou: Lanzhou University of Technology, 2019.
- [68] LIU Si-qin, QI Yu-ming, PENG Zhen-jun, et al. A Chemical-Free Sealing Method for Micro-Arc Oxidation Coatings on AZ31 Mg Alloy[J]. Surface and Coatings Technology, 2021, 406: 126655.
- [69] WANG Ping, LI Jian-ping, GUO Yong-chun, et al. Growth Process and Corrosion Resistance of Ceramic Coatings of Micro-Arc Oxidation on Mg-Gd-Y Magnesium Alloys[J]. Journal of Rare Earths, 2010, 28(5): 798-802.
- [70] WANG Ping, LIU Dao-xin, LI Jian-ping, et al. Growth Process and Corrosion Resistance of Micro-Arc Oxidation Coating on Mg-Zn-Gd Magnesium Alloys[J]. Transactions of Nonferrous Metals Society of China, 2010, 20(11): 2198-2203.
- [71] WANG Yan-qi, WANG Xiao-jun, ZHANG Tao, et al. Role of β Phase during Microarc Oxidation of Mg Alloy AZ91D and Corrosion Resistance of the Oxidation Coating[J]. Journal of Materials Science & Technology, 2013, 29(12): 1129-1133.
- [72] WANG Shu-yan, XIA Yong-ping. Microarc Oxidation Coating Fabricated on AZ91D Mg Alloy in an Optimized Dual Electrolyte[J]. Transactions of Nonferrous Metals Society of China, 2013, 23(2): 412-419.
- [73] 张慧杰, 向午渊, 杨胜, 等. 有色金属表面微弧氧化膜层封孔技术研究进展[J]. 材料保护, 2021, 54(1): 154-161.
- ZHANG Hui-jie, XIANG Wu-yuan, YANG Sheng, et al. Research Progress of Micro-Arc Oxidation Coating Sealing Technology in Non-Ferrous Metal Surface Treatment[J]. Materials Protection, 2021, 54(1): 154-161.
- [74] YANG Wei, WANG Ai-ying, JIANG Bai-ling. Corrosion Resistance of Composite Coating on Magnesium Alloy Using Combined Microarc Oxidation and Inorganic Sealing[J]. Transactions of Nonferrous Metals Society of China, 2012, 22: s760-s763.
- [75] DOU Jin-he, WANG Jing, LU Yu-peng, et al. Bioactive MAO/CS Composite Coatings on Mg-Zn-Ca Alloy for Orthopedic Applications[J]. Progress in Organic Coatings, 2021, 152: 106112.
- [76] YU Chi, CUI Lan-yue, ZHOU Yong-feng, et al. Self-Degradation of Micro-Arc Oxidation/Chitosan Composite Coating on Mg-4Li-1Ca Alloy[J]. Surface and Coatings Technology, 2018, 344: 1-11.
- [77] GUO J W, SUN S Y, WANG Y M, et al. Hydrothermal Biomimetic Modification of Microarc Oxidized Magnesium Alloy for Enhanced Corrosion Resistance and Deposition Behaviors in SBF[J]. Surface and Coatings Technology, 2015, 269: 183-190.

责任编辑: 刘世忠