镁合金微弧氧化膜层性能优化研究进展

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摘要：镁合金是一类重要的工程材料，具有许多优良的物理、化学性能，在航空航天、交通运输、电子通信、生物医学和能源等领域具有广阔的应用前景。镁合金的应用受到其高化学活性的限制，需要进行表面处理，以避免腐蚀。在众多表面处理技术中，微弧氧化技术极大地改善了镁合金的综合性能。其中，工艺参数对膜层性能有着重要的影响。在分析微弧氧化膜层厚度、微观结构和相组成成因的基础上，结合国内外研究现状重点阐述了电解质、颗粒添加物、电参数（电流模式、电压、电流密度、占空比、频率和氧化时间）对膜层耐蚀性、耐磨性及生物学性能的影响，并由此引出调控导向性、陶瓷膜增韧、性能匹配优化及能源利用率等关键问题。此外，还探讨了研究者针对上述问题采取的解决方案，并分析了方案的合理性。最后，结合镁合金微弧氧化目前存在的问题对其未来发展进行了展望。

关键词：镁合金；微弧氧化；耐蚀性；耐磨性；生物学性能

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Research Progress on Performance Optimization of Micro-arc Oxidation Films on Magnesium Alloys

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ABSTRACT: Magnesium alloy is an important engineering material with many excellent physical and chemical properties, which has broad application prospects in the fields of aerospace, transportation, electronic communications, biomedicine, energy, etc. However, the application of magnesium alloy is limited by its high chemical activity, so surface treatment is required to avoid corrosion. Micro-arc oxidation (MAO) leads the working area from the Faraday area to the high-voltage discharge area,

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which overcomes the defects of anodic oxidation and greatly improves the overall properties of magnesium alloys. Based on the research status in China and abroad, the effects of electrolyte, particle additives and electrical parameters (current mode, voltage, current density, duty cycle, frequency and oxidation time) on the corrosion resistance, wear resistance and biological properties of the films were introduced emphatically. Then, key issues such as regulation orientation, ceramic film toughening, performance matching optimization and energy utilization were proposed. In addition, the solutions adopted by the researchers to the above problems were discussed, and the rationality was analyzed accordingly. Finally, in view of the existing problems, the future development of MAO technology of magnesium alloys was discussed.

MAO films are known for higher thickness, dense structure and ceramic phase, which usually shows excellent corrosion resistance and wear resistance compared to other types of films. However, due to the film-forming characteristics of MAO process, there is inevitably a certain porosity in the ceramic films. To increase film density, researchers have explored the use of nanoparticles in the electrolyte, which can be deposited onto the film by electrophoretic adsorption or electromigration under a strong electric field. In fact, ceramic films can be brittle and prone to fatigue and peel off during wear. To address this issue, increasing the toughness can enhance the energy absorption capacity of the films and prevent the rapid crack propagation. At present, there has been little research on the toughening of magnesium alloy ceramic films, which can be deepened in the future. Studies were also made to introduce a lubricating phase, such as graphite, to enhance anti-friction performance of the films. It has been found that the single factor experiment may not accurately capture the influence of process parameters on films, which is due to the interaction between variables. Therefore, the relationship between the process parameters and the film properties is nonlinear, and when a certain critical value is exceeded, the film properties will deteriorate. In addition, magnesium alloys are commonly used in biological applications, where there are also checks and balances between biological properties, such as degradation rates and bacterial inhibition. Therefore, optimizing the matching between properties is key to improving the overall performance of the films.

Due to the complexity of MAO process, there is no complete explanation of the film formation mechanism. Thus, basic research should be further strengthened to explore the thermodynamics and kinetics of film formation. In recent years, the research direction tends to solidify, and there is little research with substantial innovation. Therefore, it is urgent to establish a richer and more scientific research system on the basis of the previous work. Last but not least, energy consumption is also an important factor that can hardly be ignored in future industrialization. Reducing energy consumption without sacrificing the quality of the film will both reduce costs and uphold the concept of sustainable development.

KEY WORDS: magnesium alloy; micro-arc oxidation; corrosion resistance; wear resistance; biological properties

气候恶化和能源消耗使得材料轻量化的应用刻不容缓。镁合金作为较轻的工程金属材料，具有高比强度、高比刚度及出色的阻尼能力等优点[1]，而且镁在地壳和海洋中的储量较丰富，具有足够的潜力应用于各种工程领域[2]。然而，镁合金较低的耐蚀性和热稳定性成为限制其应用的最大瓶颈，通过适当的表面改性可以提高镁合金的服役性能，并由此衍生出热喷涂、气相沉积、阳极氧化和微弧氧化等一系列表面防护工艺[3]。其中，微弧氧化（MAO，Micro-arc Oxidation）又称等离子体电解氧化（PEO，Plasma Electrolytic Oxidation），广泛应用于轻合金的表面改性[4]。在微弧氧化过程中，等离子体放电反复击穿膜层，最终在高温高压作用下形成附着力强的陶瓷膜。该膜层具有良好的耐蚀性、耐磨性、热稳定性及生物学性能[5]，但脆性大，存在微孔及微裂纹，对基体的保护性能有待提高[6-7]。文中概述了工艺参数对镁合金微弧氧化膜层性能的影响，以期发现所存在的问题，并进一步对其优化。

1　电解质对镁合金微弧氧化膜层性能的影响

电解质的组分和浓度会显著改变膜层的厚度、微观结构和相组成，表 1 列出了近年来的一些相关研究成果[8-17]。由于酸性电解液会污染环境，腐蚀基体，成膜效率较低，而碱性电解液可以有效规避这些问题，更易形成均匀优质的膜层，因此碱性电解液得到了更广泛的应用[18]。此外，镁合金在微弧氧化过程中作为阳极，电解液中的金属离子在电场作用下无法进入膜层，因而需要添加适量的螯合剂，以形成带负电的螯合物，使其能够参与成膜反应。目前尚未发现关于螯合剂种类对陶瓷膜性能影响的相关研究，后续可以进一步完善。

1.1　耐蚀性

电解液按主盐类型大致可分为硅酸盐、磷酸盐和

表 1 电解质对膜层性能的影响

Tab.1 Effect of electrolytes on the properties of film

Substrate	Base electrolyte	Additives	Results	Ref.
Mg-Li	10 g/L Na_2SiO_3, 3 g/L NaOH, 10 mL/L TEA	0.1 g/L $Ce(NO_3)_3$	Corrosion resistance is improved by three orders of magnitude	[8]
Mg-2Zn-1Ca-0.8Mn	Na_2HPO_4, NH_4HF_2, KOH, $C_3H_8O_3$, H_2O_2	$(CH_3COO)_2Ca$	The coatings exhibit better apatite inducing ability	[9]
AZ41	Na_2SiO_3, KOH	KF	The corrosion current density is nearly two orders of magnitude lower than PEO treatment without additives	[10]
LA103Z	8 g/L Na_2SiO_3, 0.5 g/L NaF	4 g/L KOH	The sample shows the best electrochemical behavior, which resulted in high corrosion resistance	[11]
Mg-8.5Li	15 g/L Na_2SiO_3, 2 g/L KOH, 4 g/L KF	5 g/L $(NaPO_3)_6$	With higher thickness, hardness, and wettability	[12]
Mg	0.07 mol/L KOH, 0.1 mol/L $Na_2SiO_3·9H_2O$	0.2 mol/L NaF	The breakdown voltage, spark density and intensity decrease.	[13]
AZ91	10 g/L $NaAlO_2$, 2 g/L KOH	5 g/L Na_3PO_4	Enhancing resistance against chemical and mechanical degradation	[14]
AZ80	Na_2SiO_3, NaF, HA	K_2TiF_6	Improving the bioactivity and long-time protective ability.	[15]
AZ31	Na_2SiO_3, NaOH, NaF, $C_3H_8O_3$、$KNaC_4H_4O_6·4H_2O$	0.4 g/L $CoSO_4$	Improving hardness, corrosion resistance and thermal shock resistance	[16]
AZ31	0.03 mol/L CaGP	0.2 mol/L NaOH	Prompting corrosion resistance and decreasing degradation rate	[17]

铝酸盐等体系。添加适量的主盐可以提高电解液的电导率、降低击穿电压、改善膜层质量，并与基体形成相应的稳定化合物，所以通过调控其组分和浓度可以有效提高膜层的耐蚀性。Ghasemi 等[19]分别在 3 种电解液体系中对镁合金进行了微弧氧化处理，发现除了存在 MgO 之外，3 个膜层中还分别形成了特定的 Mg_2SiO_4、$Mg_3(PO_4)_2$ 和 $MgAl_2O_4$ 相。相比之下，在硅酸盐中形成的膜层厚度最大、孔隙率最低，具有最低的腐蚀电流密度。由此可见，硅酸盐系具有理想的稳定性、成膜效率、放电特性及相组成。然而，单一电解液体系存在优化膜层综合性能的局限性，因此可以通过复合来实现各体系的优势互补。此外，电解质浓度对膜层耐蚀性也有显著影响，Toorani 等[20]研究发现，添加 $La(NO_3)_3$ 一方面降低了膜层的孔隙率，另一方面通过生成难溶的 $La(OH)_3$ 能够防止腐蚀剂的渗透，EIS（Electrochemical Impedance Spectroscopy）测试表明，膜层的阻抗随着浓度的增加而增加。电化学阻抗谱大多采用以下模型进行等效模拟（见图 1[21]），其中 R_s 为溶液电阻，R_p/CPE_p 和 R_c/CPE_c 分别为多孔层和阻挡层的电阻及其对应的恒相位元件。也有研究者采用其他等效电路，因为电极反应与电路元件并不一一对应，因此还需对电极反应进行深入研究。

传统的调控方法对膜层的致密化效果非常有限，而且调控过程的导向性并不十分明确。强烈的熔体喷发是造成膜层疏松多孔的根本原因，弱化熔体喷发可以有效增加阻挡层的厚度，从而实现膜层致密化。为此，Zhang 等[22]通过调节 KF 和 KOH 的浓度，控制 2

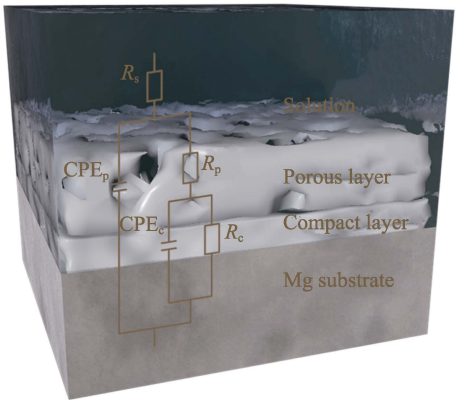


图 1 EIS 等效电路模型[21]

Fig.1 Equivalent electrical circuit model of EIS[21]

种不同介电性能产物的占比，使得高介电常数的物质限制自由发生的电子雪崩，抑制大范围的熔体喷发（见图 2），从而有序放电，最终形成致密的膜层。该方法进一步拓展了微弧氧化的研究思路，对后续发展具有重要的参考价值。

1.2 耐磨性

如前所述，电解质的组分和浓度会影响膜层的厚度、微观结构和相组成，从而导致膜层具有不同的耐磨性。在常用的碱性电解液体系中，硅酸盐系形成的膜层的耐磨性较高。Durdu 等[23]和 Pezzato 等[24]对比了硅酸钠和磷酸钠对陶瓷膜摩擦性能的影响，结果表明，在硅酸盐体系下膜层的磨损率较低，这归因于镁橄榄石（Mg_2SiO_4）的硬度高于镁尖晶石（$MgAl_2O_4$）的硬度。随着研究的深入，发现氟化物的加入可以降低膜

层的表面粗糙度，往复磨损测试显示含氟膜层的磨痕窄而浅（见图 3），具有最低的磨损率[25]。此外，Aktuğ 等[26]研究发现，所制备膜层的摩擦因数和磨损率均随着 $Na_2SiO_3·5H_2O$ 浓度的增加而增加。由此可见，通过调控电解质的组分和浓度，可以制备出高硬度、低粗糙度的膜层。由于陶瓷膜的脆性较大，在磨损过程中易发生疲劳剥落，因此提高陶瓷膜的韧性可以增强膜层的能量吸收能力，避免裂纹的快速扩展。目前，针对镁合金微弧氧化膜层的增韧研究还较少，可采取的方式大致分为第二相掺杂和原位增韧。相较于第二相掺杂，原位增韧可以确保各相之间的良好匹配[27]，在满足强度要求的同时，对韧性也有一定程度的提升。

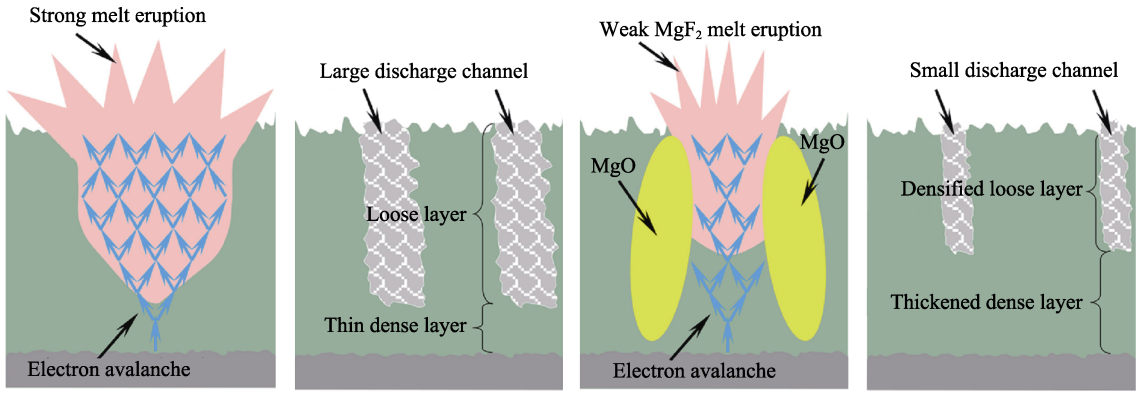


图 2　不同的放电模型[22]

Fig.2 Different discharge models[22]: a) electron avalanche under TD mode; b) loose PEO film; c) electron avalanche under OD mode; d) densified PEO film

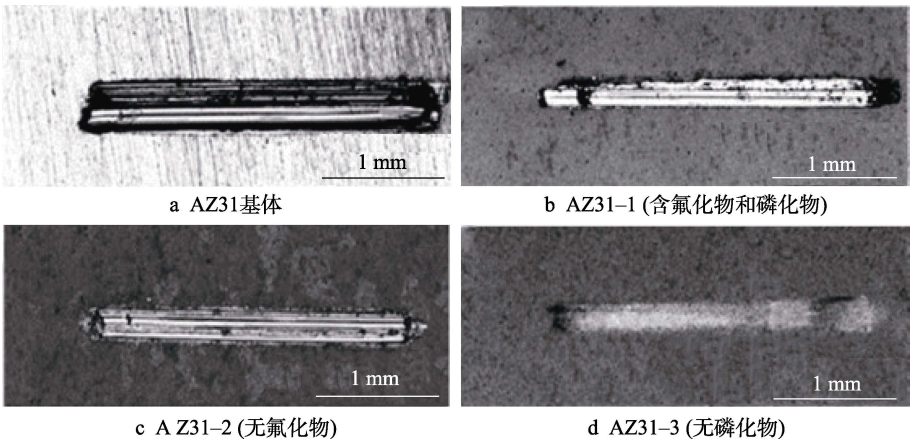


图 3　磨痕形貌的光学图像[25]

Fig.3 Optical images of wear tracks[25]: a) AZ31 substrate; b) AZ31-1 (including fluoride and phosphorus); c) AZ31-2 (no fluoride); d) AZ31-3 (no phosphorus)

1.3　生物学性能

镁合金具有可降解性和生物相容性，但其生物活性较低。作为植入体，良好的生物活性更有利于硬组织和软组织的愈合。诸多研究表明，在电解液中引入钙、磷元素可以获得具有生物活性的物质。Baghdadabad 等[28]在电解液中加入 $Ca_2H_4P_2O_8$，发现膜层在模拟体液中浸泡后所产生的碳酸羟基磷灰石可以增加体内钙、磷离子的局部浓度，从而促进新骨的形成。然而，在生理环境下的高降解速率过早地降低了镁合金植入体的机械完整性，并且其腐蚀产物还会引起局部炎症。虽然陶瓷膜能够有效提高镁合金的耐蚀性，但其降解速率的减缓会导致其碱性的降低，从而削弱抗菌效果。为此，Chen 等[29]在镁合金表面制备了含银膜层，发现 Ag^+的释放会破坏细菌细胞壁，与酶的有机基团和巯基结合，导致正常细菌的功能紊乱。此外，膜层的多孔结构和粗糙表面为羟基磷灰石提供了合适的成核位点。由此可见，生物活性物质的生成、降解速率的降低及抑菌性的提高极大地推动了镁合金在生物医学领域的应用。

2　颗粒添加物对镁合金微弧氧化膜层性能的影响

由于镁的 P/B 比（Pilling-Bedworth ratio，氧化物与形成该氧化物所消耗金属的体积比）较小，以及微弧氧化工艺的成膜特性，陶瓷膜不可避免地存在一些

孔隙。为了弥补这一短板，近年来研究者通过添加纳米颗粒来改变电解液的 pH 值、电导率和黏度，从而影响膜层的形貌和性能，达到预期效果。表 2 列出了研究者在颗粒添加物方面所做的一些工作[30-39]，研究表明，颗粒浓度通常存在最佳值，当浓度超过这一水平时，膜层的性能会发生劣化。

表 2　颗粒添加物对膜层性能的影响

Tab.2 Effect of particles on the properties of film

Substrate	Particles	Results	Ref.
AZ31	2 g/L WO_3	Reducing the size and proportion of tiny defects	[30]
Mg	2 g/L CeO_2	The film has a self-sealing effect, which leads to a remarkable improvement in corrosion resistance	[31]
AZ31	2 g/L Si_3N_4	Exhibiting the best corrosion resistance, high hardness, good adhesion and low friction coefficient	[32]
Mg-Ca	4 g/L TiO_2	The hydrophobicity, corrosion resistance and hardness are improved	[33]
AZ91	ZrO_2	The densification of the film reduces the corrosion current density	[34]
Mg	HA	The film thickness and porosity decrease, but the corrosion resistance increases	[35]
MA8	4 g/L TiN	The microhardness increased, but the wear resistance decreased	[36]
AZ31	GO	Prevent corrosive medium from penetrating into the substrate	[37]
AM50	SiO_2	The abrasion resistance is improved, but the corrosion resistance is slightly reduced	[38]
AZ31	SiC	The friction coefficient is greatly reduced, showing excellent self-lubricating performance	[39]

2.1　耐蚀性

微孔和微裂纹大大降低了陶瓷膜的耐蚀性，因此降低膜层的孔隙率显得尤为重要。研究发现，纳米颗粒能够起到填充微孔及使膜层更加均匀致密等作用[40]。近年来，颗粒性质对膜层耐蚀性的影响机制受到广泛关注。Lu 等[41]研究了不同熔点颗粒对膜层微观结构和耐蚀性的影响，如图 4 所示。添加黏土后，膜层的腐蚀电流密度最低，这是由于黏土的反应性结合有助于形成致密的膜层。在反应过程中，颗粒对微孔起到了封闭作用，经过封孔的膜层阻止了破坏性离子向基体的渗透，从而提高了耐蚀性。由于离域 π 键的存在，因此过渡型晶体石墨具有较强的化学稳定性。朱鼎等[42]研究发现，在质量浓度为 0~5 g/L 时，石墨含量的增加会诱导放电通道的形成，抑制大弧放电，从而降低局部电火花的能量密度。石墨烯具有与石墨相似的化学性质，研究表明，添加适当浓度的石墨烯可以有效地改善陶瓷膜的微观结构，降低其腐蚀电位。然而，过高的浓度会导致电解液的电导率降低，击穿能量升高，微孔尺寸随之增大[43-44]。

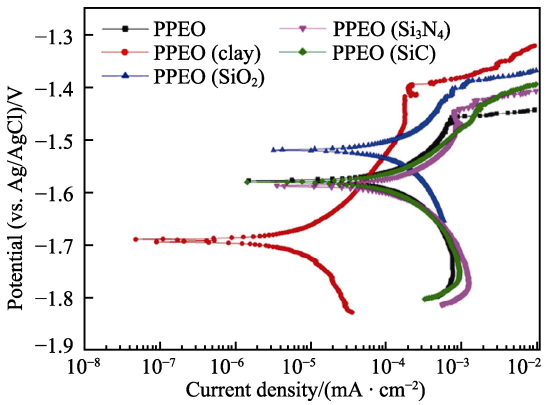


图 4　含不同颗粒微弧氧化膜层的极化曲线[41]

Fig.4 Polarization curves of the oxidation films with different particles[41]

颗粒的吸收过程在高温、高压放电条件下进行，颗粒的性质决定了颗粒本身的结合状态。如图 5 所示，颗粒的结合状态分为反应性结合和惰性结合，通常熔点较低或尺寸较小的颗粒更容易发生反应性结合[45]。然而，在电解液中颗粒的均匀分散是需要解决的难题。目前，通常利用外力来避免聚沉，例如在微弧氧化过程中辅以超声处理[46]。值得注意的是，在增加颗粒分散程度的同时，应避免超声处理对膜层造成损害。

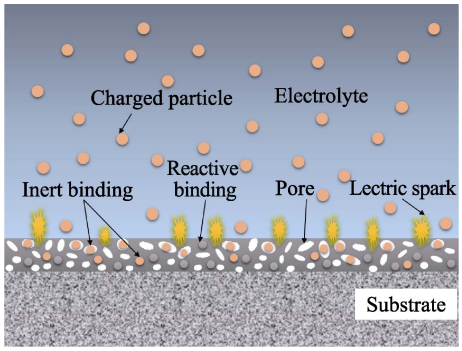


图 5　颗粒吸收模型示意图

Fig.5 Schematic diagram of particle absorption model

2.2　耐磨性

颗粒的添加降低了膜层的孔隙率，同时所形成的硬质相大大降低了膜层的磨损率。近年来，石墨、氧化石墨烯和二硫化钼等自润滑材料被广泛用于提高陶瓷膜的耐磨性。如图 6 所示，由于微弧氧化膜层表面粗糙，加之摩擦副与磨屑形成了三体磨料磨损，使得膜层具有较高的摩擦因数。在添加石墨后，膜层在磨损过程中形成了致密的低剪切转移层，因此其摩擦因数有所降低[47]。石墨含量对膜层耐磨性也有着显著影响，Gao 等[48]研究发现，含大量石墨的陶瓷膜具有

较好的耐磨性，而加入少量石墨的膜层由于润滑不足，使得其耐磨性并未得到显著提高。研究还发现，在电解液中引入氧化石墨烯，可以提高膜层的显微硬度，降低膜层的孔隙率、摩擦因数和磨损量[49]。由此可见，在陶瓷膜中引入固体润滑颗粒可以获得更好的耐磨性。

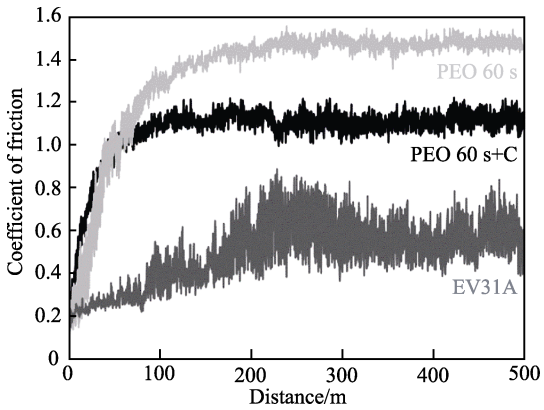


图 6　EV31A 镁合金及其微弧氧化试样的摩擦因数曲线[47]

Fig.6 Friction coefficient curve of EV31A magnesium alloy and its micro-arc oxidation sample[47]

固体润滑颗粒的减摩机理如图 7 所示，微弧氧化陶瓷膜较粗糙，初期的接触应力较大，磨损速度较快。磨球与初始表面之间的摩擦导致微凸体剥落，并填充微孔，从而使得磨损轨迹更加平滑[50]。摩擦副实际接触面积的增大及润滑相的增多导致其具有弹性接触的特点，因此磨损进入稳定阶段。随着磨损时间的延长，润滑物逐渐覆盖整个磨损轨道，进一步改善润滑条件，降低了磨损率[51]。

2.3　生物学性能

耐蚀性与抑菌性是一对矛盾体，二者的匹配度优化是镁合金用于植入体的关键。银、铜和锌等金属元素具有很强的抑菌能力[52]，它们通过破坏细菌表面的活性结构，使其因生理变化或活动受阻而死亡。Chen 等[53]研究了纳米 CuO 对镁合金微弧氧化膜层抑菌性和生物相容性的影响，抑菌试验结果表明（见图 8a），含铜膜层具有良好的抗菌效果，细胞毒性测试结果也表明该膜层具有较高的细胞存活率。从图 8b、c 可以看出，镁合金及其无铜膜层均表现出一定的抗菌能力，这主要归因于体外降解过程中局部的高 pH 值抑制了细菌的生长。相较于体外模拟，人体自身可将 pH 值缓冲至中性水平，因此在实际应用中很难依靠高碱性产生抗菌能力。由此可见，抑菌元素的加入突破了这一壁垒，使得膜层兼具耐蚀性和抑菌性。

通常金属以离子的形式发挥抑菌作用（见图 9），在库仑力的作用下，金属离子吸附于带负电的细菌表面，阻碍了微生物的物质传输通道，抑制了肽聚糖的生成，进而导致细胞膜破裂及胞质外流。此外，金属离子还会与细胞内的基团结合，破坏酶蛋白分子的结构，引起催化效率的降低甚至丧失。金属离子还可能进一步产生活性氧自由基，并与 DNA 结合，导致其分子链被破坏[54]。

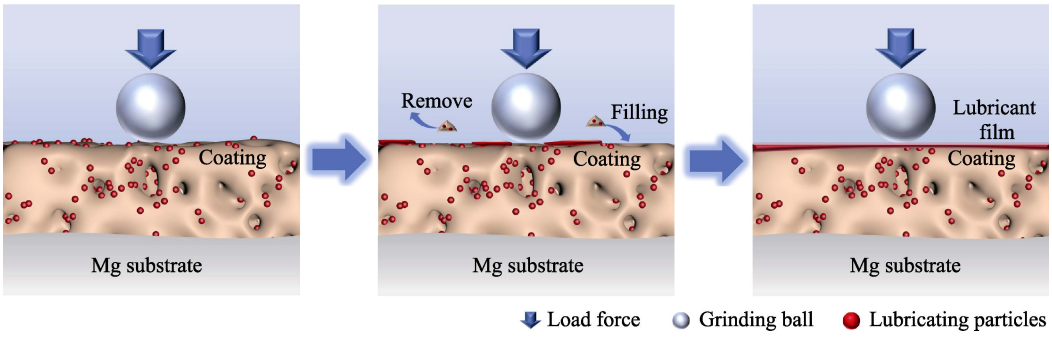
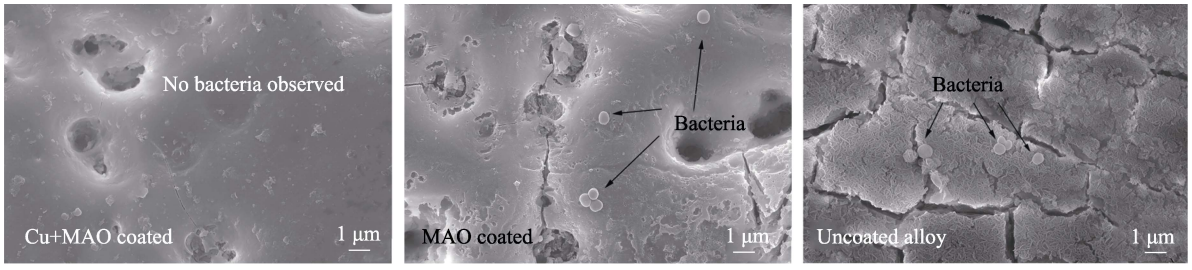


图 7　自润滑颗粒的减摩示意图

Fig.7 Schematic diagram of wear reduction of self-lubricating particles



a 含铜MAO膜层　　b MAO膜层　　c 基体合金

图 8　共培养 24 h 后不同试样表面金黄色葡萄球菌的 SEM 形貌[53]

Fig.8 SEM morphologies of S. aureus on surfaces of different samples after co-culture for 24 h[53]: a) MAO coated alloy; b) Cu + MAO coated alloy; c) uncoated alloy

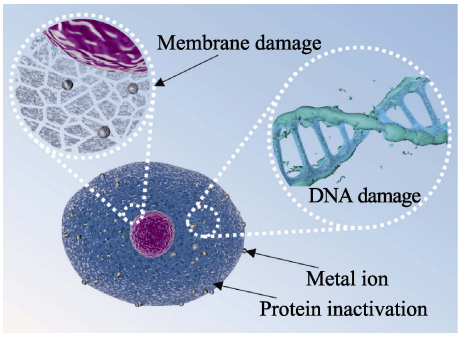


图 9　金属元素抑菌模型示意图[54]
Fig.9 Schematic diagram of metal element bacteriostatic model[54]

3　电参数对镁合金微弧氧化膜层性能的影响

这里概述了电参数对镁合金微弧氧化膜层表面形貌、孔隙率和厚度的影响，并结合研究现状分析了现存问题及其解决方案。微弧氧化电参数的种类繁多，可以利用试验设计法（DOE，Design of Experiment）对其进行优化，从而制备出高质量膜层。在多变量组合优化过程中，常用的方法有单因子实验[55]和正交实验[56-60]。由于变量间具有交互作用，因此采用正交实验更为合理。

3.1　耐蚀性

微弧氧化的电流模式大体分为直流电、交流电和脉冲电流，脉冲电流又分为单脉冲和双脉冲[61]。由于脉冲电流能够更好地控制能量输入，因而受到广泛应用。与单脉冲相比，双脉冲可以控制或降低膜层与基体界面强放电产生的温度峰值，从而改善等离子体温度分布和膜层质量。研究发现，由于双脉冲生成膜层的孔隙率较低，因此通常具有较高的极化电阻[62-63]。事实上，占空比的增大会增加电火花的能量密度和膜层熔融的可能性。田溪梅等[64]研究发现，较高的占空比会增加孔隙率，减小膜层厚度。此外，脉冲频率对孔隙特征也有着显著影响。Zhang 等[65]研究发现，随着频率的增加，膜层的孔径和孔隙率减小，而孔间距和孔圆度增大，低孔隙率和良好的连续性提高了膜层的耐蚀性。由此可见，为了在实际生产中制备出高质量膜层，应尽量选择双脉冲模式、较低的占空比及较高的频率。

除了脉冲电流、占空比和脉冲频率的影响外，电压和电流密度的升高往往会引起成膜效率的增大、膜层的增厚及物相结构的转化。Zhang 等[66]和 Bai 等[67]研究发现，膜层的厚度、粗糙度和孔径均随着电压的增大而增大，导致其耐蚀性先增加后降低。大多数研究表明，电流密度对膜层的影响具有相同特性[68]。在恒压模式下，初始阶段会产生大量的自由电子，容易引起电化学极化，从而造成过多的自耗。在恒流模式下，能量的提供与消耗始终保持相对平衡的状态，这有望提高能源利用率。

氧化时间对膜层耐蚀性的影响类似于电压，在厚度、粗糙度和孔径的综合作用下存在最佳值。随着微弧氧化时间的延长，熔体在微孔周围积聚，可以在一定程度上覆盖微孔。在此过程中，电火花能量升高，移动速度减缓，会导致膜层的粗糙度和孔径增大。Liu 等[69]探讨了氧化时间（10、20、30、40 min）对膜层耐蚀性的影响，发现在氧化时间为 30 min 时形成的膜层阻抗最大，其腐蚀电流密度约比基体的腐蚀电流密度低 4 个数量级。换言之，氧化时间对膜层耐蚀性的影响同样存在一个临界值。

3.2　耐磨性

Hussein 等[70]提出了 3 类等离子体放电模型（见图 10），A 型和 C 型由氧化物与电解液界面处的气体放电引起，分别发生在表面附近及深孔中；B 型由膜层击穿引起，具有强烈的微放电，起源于金属与氧化物界面。大多数研究表明，单脉冲以 B 型放电为主，导致微孔等结构缺陷的发生；双脉冲通过减弱等离子体强放电来改善膜层形貌，使其具有更理想的粗糙度和硬度。此外，Hussein 等[71]研究了 2 种脉冲应用顺序对陶瓷膜耐磨性的影响，发现摩擦因数取决于表面粗糙度。磨损测试结果表明，在先单脉冲后双脉冲的混合模式下制备的膜层光滑、硬度高，磨损率最小。

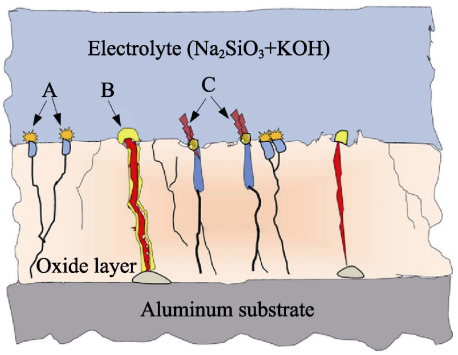


图 10　微弧氧化放电模型示意图[70]
Fig.10 Schematic diagram of the discharge models for the MAO process[70]

放电强度的减弱大大降低了膜层的粗糙度和孔隙率，通过精确调整脉冲频率，可以显著改善膜层的耐磨性。Zou 等[72]研究发现，随着脉冲频率的增加，膜层结构变得更加均匀、致密，这是由高频下局部放电次数减少及放电强度减弱所致。从电解液角度分析，频率的增大会导致水合离子在短距离内往复迁移，使得分散系更加稳定。特别是对于含有纳米颗粒的介稳体系，高频更容易避免颗粒的聚沉，使其在膜层中均匀分布。

目前，大多数研究从结构的角度讨论电流密度对膜层耐磨性的影响，但该方法相对较单一。Zhuang 等[73]另辟蹊径，研究了电流密度对膜层中硬质相含量的影响，发现它随着电流密度的增加而增加。磨损测试表明，相较于基体宽而深的磨痕，在 10 A/dm^2 下形成的磨痕窄而浅，这与其致密的结构和相对较高的 ZrO_2 含量有关。虽然在 20 A/dm^2 下形成的膜层也含有大量硬质相，但其孔隙率和粗糙度的增加降低了膜层的耐磨性。由此可见，高能电场的增强会使膜层产生更多的硬质相，同时膜层结构也会随之劣化。

3.3　生物学性能

镁钙合金体系是一种新型的可降解生物材料，但在生理环境下其降解速率过快。如前所述，在降解过程中局部 pH 值的升高会导致炎症、血栓和细胞毒性，因此必须控制降解速率，以改善其生物相容性。Tang 等[74]在电解液中加入甘油磷酸钙，形成了含 HA（Hydroxyapatite）的陶瓷膜，研究发现，Ca^{2+}能与部分水解的甘油结合，并稳定存在于溶液中，与 PO_4^{3-} 在电场作用下参与成膜反应。X 射线衍射分析显示，其衍射峰随着电压的升高而增强，表明电压越高越有益于羟基磷灰石的形成。浸泡试验表明，在 450 V 下生成膜层的析氢速率和 pH 值的变化最小。在析氢速率测试方面，容积法通过记录滴定管中不同时间的液位来评估释放的氢气量（见图 11a[75]）。受到检测周期的限制，该方法不适用于耐蚀材料，且部分氢气会附着在漏斗和滴管的内壁，导致测量值偏低。为了避免出现上述缺陷，Fajardo 等[76]提出一种用于实时收集氢气的重力法（见图 11b[75]），该方法通过氢气产生的浮力来降低集气瓶的重力，从而表征析氢速率。

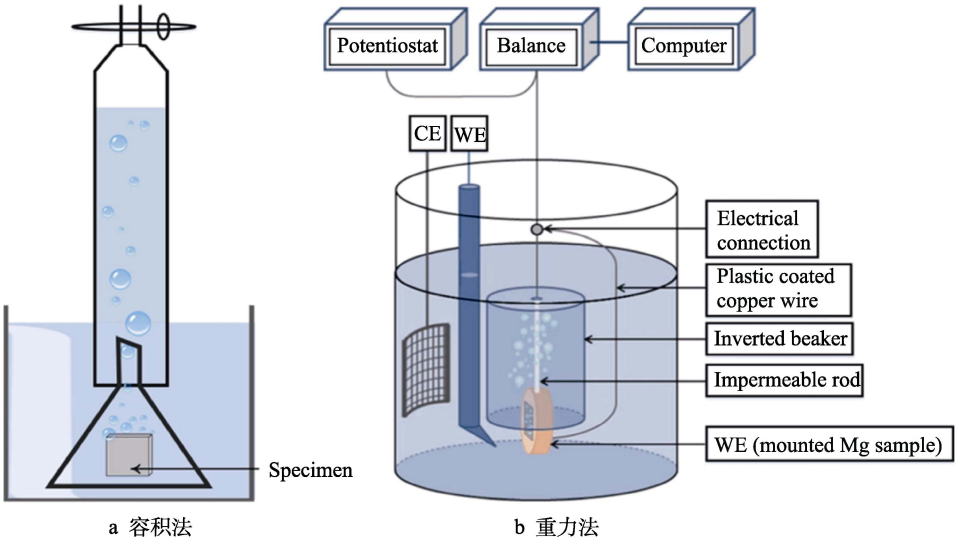


图 11　氢气收集实验装置示意图[75]

Fig.11 Schematic of the experimental setups for hydrogen gas collection[75]: a) volumetric method; b) gravimetric method

众所周知，羟基磷灰石具有良好的生物相容性和生物活性。Tang 等[77]采用不同的氧化时间在镁合金上原位合成了含 HA 的膜层，结果表明，随着氧化时间的延长，击穿能量和放电强度增大，反应通道内温度升高，这有利于 HA 的形成。此外，Lin 等[78]在膜层中引入纳米羟基磷灰石，研究发现，随着氧化时间的延长，膜层增厚，电压随之升高，在单位时间内从基体中释放的 Mg^{2+}增多，成膜速率加快。同时，在强电场的作用下，更多的负电纳米颗粒参与反应，导致其在膜层中的含量增加。上述方法为制备含羟基磷灰石陶瓷膜的 2 种典型方法，以添加颗粒的方式更容易将其引入膜层，但膜层的均匀性和稳定性较低。相比之下，原位生长膜层的附着力更强、组分更均匀、稳定性更高。然而，受限于复杂的反应过程，难以精确控制预期的产物类型。

4　结语

在实现绿色低碳经济转型的大背景下，镁合金无论作为结构材料还是功能材料都具有强大的生命力。文中基于电解质、颗粒添加物和电参数等因素对镁合金微弧氧化陶瓷膜的影响，围绕陶瓷膜的耐蚀性、耐磨性和生物学性能展开了讨论。综上所述，尽管微弧氧化处理增强了镁合金的耐蚀性、耐磨性和生物学性能，但目前仍存在一些问题，未来的研究应注意以下几个方面。

1）工艺参数对镁合金微弧氧化膜层的性能影响显著，但大多数研究只针对单一变量，未来研究多变量的交互作用同样具有价值。

2）由于微弧氧化过程的复杂性，成膜机理始终

难以解决，因此应进一步加强基础研究，探索成膜的热力学和动力学过程。

3）近年来，研究模式趋于固化，具有实质性的创新研究较少，因此迫切需要在以往工作的基础上建立更加丰富、科学的研究体系。

4）能耗是未来产业化不可忽视的因素，在不牺牲膜层质量的前提下降低能耗，既降低成本，又符合可持续发展的理念。

随着镁合金微弧氧化的深入研究，其应用会涉及更广泛的领域。

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