

专题——液相等离子体电解-微弧氧化表面改性技术

锆微弧氧化表面处理技术研究进展

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摘 要: 锆及锆合金是重要的核结构材料和有潜力的生物医用材料, 但在实际应用中, 腐蚀、磨损易造成其失效, 而适当的表面改性是提高它们服役性能的有效手段。重点介绍了锆及锆合金微弧氧化 (MAO) 表面处理技术的研究现状, 讨论微弧氧化过程中电压电流特征及微弧放电机理, 总结电解液体系及电参数对锆微弧氧化膜生长及膜层性能的影响规律, 最后指出目前存在的问题和后续的研究方向。锆微弧氧化膜硬度高, 致密性好, 能大幅度提升基材的抗磨损和抗腐蚀性能。因此, 锆微弧氧化技术在核电及生物医学领域有着很好的应用前景。此外, 电解液中铝、硅元素进入微弧氧化膜后可以稳定膜层中高温氧化锆相 ($t\text{-ZrO}_2$), 避免膜层中应力集中和微裂纹的产生。用 P 和 Ca 元素修饰后的锆微弧氧化膜具有较好的生物活性、抗体液腐蚀和抗菌性能。

关键词: 锆; 微弧氧化; 耐磨性; 耐蚀性; 生物活性

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Advance in Microarc Oxidation Surface Treatment on Zr

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ABSTRACT: Zirconium and zirconium alloys are important nuclear structural materials and potential biomedical materials. Corrosion and wear may cause the failure of zirconium and zirconium alloys in application, but an appropriate surface modification is an effective means to improve their service performance. The work mainly introduced the research advance of microarc oxidation (MAO) surface treatment technology on zirconium and zirconium alloys. The voltage and current characteristics of MAO process and microarc discharge mechanism were discussed, and the influence of electrolyte and electrical parameters on the growth and performance of MAO films on zirconium alloys was summarized. Finally the short comings of the current research and the future research topics were also given. MAO film on Zr alloys had high hardness and good compactness, which could greatly enhance the wear and corrosion properties. Therefore, the MAO technology on Zr has a good application prospect in the fields of nuclear power and bio-medicine. Furthermore, the high temperature zirconia phase ($t\text{-ZrO}_2$) can be stabilized after the aluminum and silicon elements from the electrolyte entering into MAO film, so as to avoid the stress concentration and

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the generation of micro-cracks in the film. The modified MAO film on zirconium with P and Ca elements has better biological activity, anti-humoral corrosion and antibacterial properties.

KEY WORDS: zirconium; microarc oxidation; anti-friction; anti-corrosion; bioactivity

锆及锆合金具有较低的热中子吸收截面、良好的力学和抗腐蚀性能以及能够与核燃料相容等一系列优点,被广泛应用于裂变核能系统^[1-4]。在反应堆中,锆合金用作核燃料棒的包壳和格架等元件,其中包壳是防止核泄露的第一道防线。在反应堆运行过程中,包壳外侧受到高温高压循环冷却水的腐蚀(例如 360 °C/18.6 MPa, 硼锂水化学环境)。在高温高压循环冷却水的腐蚀下,锆合金易发生局部腐蚀、点状腐蚀和氢脆^[4-5]。其中,点状腐蚀一般为灰白色,深度可达几十微米,腐蚀产物积累形成较厚的白色氧化膜,会降低包壳材料的有效壁厚,从而导致包壳破裂,造成循环冷却水的放射性污染^[5-7]。另外,包壳与栅格间的微动磨损引起的破坏同样会造成循环冷却水的放射性污染^[8-9]。因此,提高锆合金的抗磨损和腐蚀性能对核电站安全运行是至关重要的。

除广泛应用于裂变核能系统外,锆也是一种潜在的生物医用材料。研究表明,V、Cu、Zn、Cd、Hg等元素的细胞毒性很大,但Zr、Sn、Ta、Pd、Mo等元素有较低的细胞毒性^[10]。于思荣^[11]也认为Ti、Nb、Zr、Sn、Mo、Ta和Fe是无细胞毒性或低细胞毒性元素,它们可以用来改善生物医用材料的力学性能、耐腐蚀性能和生物活性。此外,纯锆的弹性模量(92 GPa)比纯钛(100~110 GPa)更接近人体骨骼的弹性模量(15~30 GPa),能有效避免应力遮蔽(Stress shielding)造成的骨组织功能退化^[12],是牙科和骨科等植入体的良好候选材料。长期服役过程中体液腐蚀和磨损腐蚀会使锆植入体失效,因此增强锆植入体在体液中的耐蚀性和耐磨性有利于延长其服役寿命。

表面技术是改善锆及其合金磨损与腐蚀性能的有效方法^[13-22]。目前锆合金表面处理技术主要包括物理气相沉积^[13]、激光表面改性^[14]、热等静压技术^[15]、冷喷丸技术^[16]、超声冲击强化^[17]、离子注入^[18]、高压釜预膜^[19]、阳极氧化^[20]和微弧氧化^[21-22]。微弧氧化技术(MAO),又称为等离子体电解氧化(Plasma Electrolyte Oxidation),是一种在贵金属及其合金表面原位生长陶瓷膜的表面处理技术^[21-22]。近年来,锆微弧氧化技术开始得到关注^[23-41],并发现锆微弧氧化膜具有较高的耐磨、耐蚀性能^[23-34],且具有良好的生物活性^[35-41]。

本文分析了锆及锆合金微弧氧化过程,总结电解液体系和电参数对微弧氧化膜层生长及其性能的影响规律,介绍近些年锆微弧氧化技术在耐磨、耐蚀及生物活性方面取得的新进展,指出当前存在的问题和未来的研究方向。

1 文献检索概况

通过 Web of Science 数据库检索(检索词 microarc oxidation of zirconium, plasma electrolytic oxidation of zirconium)分析,锆微弧氧化研究领域发表论文和引文数量所占比例分布情况如图1所示。由图1可知,2003年以来锆微弧氧化技术的研究开始受到持续关注,2010年以后发表的论文数量和引文次数都明显增加。实际上,铝、镁、钛及其合金微弧氧化技术的研究已经比较深入和成熟^[42],但是锆及锆合金微弧氧化技术仍然处在探索阶段。

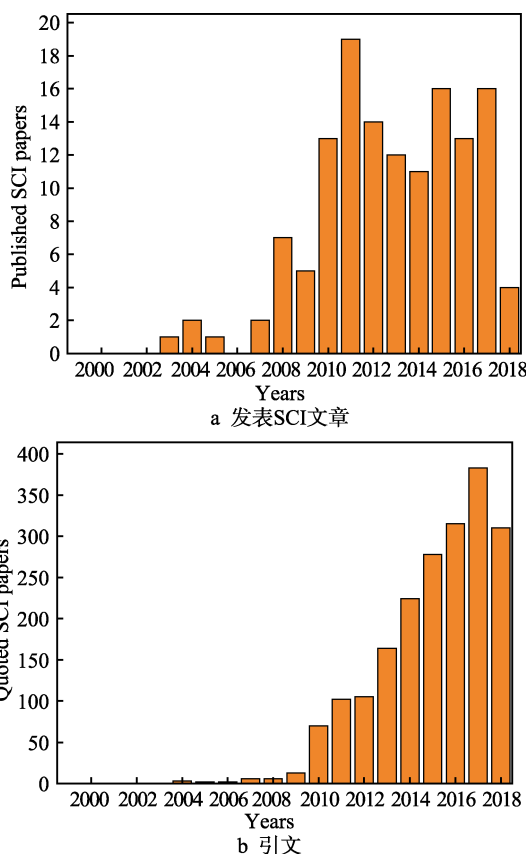


图1 锆微弧氧化领域发表SCI文章和引文的统计分析
Fig.1 Statistical analysis of published (a) and quoted (b) SCI papers in the field of microarc oxidation on zirconium

2 锆合金微弧氧化膜的制备

2.1 锆微弧氧化研究概况

表1列出了近年来文献中锆及锆合金微弧氧化的电解液成分、膜层相组成及其相关性能。该表显示,目前文献中主要报道了纯锆、Zr-2、Zr-4、Zr-1Nb、

表 1 锆及锆合金微弧氧化的电解液体系和膜层相结构
Tab.1 Electrolyte components and phase constituents of MAO coating on Zr and Zr alloys

Alloy	Nomial chemical composition	Electrolyte	Phase constituents of MAO Coating	Properties	References
Zr-2		Silicate & aluminate	77wt% t-ZrO ₂ , m-ZrO ₂	Anti-wear	[27]
Zr-2		Aluminate	t-ZrO ₂ , m-ZrO ₂ , γ -Al ₂ O ₃	Anti-wear	[43]
Pure Zr		Aluminate	t-ZrO ₂ , m-ZrO ₂ , α -Al ₂ O ₃	Anti-wear	[44]
Zr-2.5Nb		Silicate	m-ZrO ₂ , t-ZrO ₂ (little)	Anti-wear Anti-corrosion	[2, 34]
Zr-4	97.88% Zr, 1.58% Sn, 0.31% Fe, 0.1% Cr, 0.14% O, 0.015% C	CA + β -GP	t-ZrO ₂ , c-ZrO ₂ , m-ZrO ₂	Anti-wear	[45]
Zr-4		Silicate & aluminate	m-ZrO ₂ , t-ZrO ₂	Anti-wear	[46]
Zr-4	1.50% Sn, 0.20% Fe, 0.10% Cr, Ni < 0.007%, Zr bal.	Silicate	m-ZrO ₂ , t-ZrO ₂	Anti-corrosion	[47]
Zr-4		Silicate, phosphate, pyrophosphate	m-ZrO ₂ , t-ZrO ₂	Anti-corrosion	[48]
Pure Zr		Aluminate	t-ZrO ₂ , m-ZrO ₂ , α -Al ₂ O ₃	Anti-corrosion Anti-wear	[33]
Zr-2	Fe 0.19%, C 0.02%, Sn 1.31%, Hf < 0.01%, Cr 0.089%, Ni < 0.002% & Zr bal.	Silicate	m-ZrO ₂ , t-ZrO ₂	Anti-corrosion	[49]
Zr-1Nb		Silicate-phosphate	m-ZrO ₂ , t-ZrO ₂	Anti-corrosion	[30]
Pure Zr		(NH ₄) ₂ B ₄ O ₇ ·4H ₂ O	m-ZrO ₂	Anti-corrosion	[31]
Zr-4		Silicate, phosphate	m-ZrO ₂ , t-ZrO ₂	Anti-corrosion	[29]
Zr-4		Phosphate	m-ZrO ₂ , t-ZrO ₂	Anti-corrosion	[50]
Zr-2.5Nb		Aluminate	t-ZrO ₂ , m-ZrO ₂	Anti-corrosion	[51, 52]
Zirconium alloy	94.38wt.% Zr, 5.62wt.% rare earths	Silicate	m-ZrO ₂ , t-ZrO ₂ Amorphous Al ₂ O ₃	Anti-corrosion	[23]
Zr-1Nb		Phosphate	m-ZrO ₂ , t-ZrO ₂	Anti-corrosion	[24]
Zr-1Nb		Silicate(MAO)+ laser irradiation	m-ZrO ₂ , t-ZrO ₂	Anti-corrosion	[25]
Zirlo		Silicate	m-ZrO ₂ , t-ZrO ₂ , c-ZrO ₂	Anti-corrosion	[28]
Zr-2.5Nb		Silicate	m-ZrO ₂	Anti-corrosion	[53]
Pure Zr		CA+ β -GP	Ca-PSZ, m-ZrO ₂ , t-ZrO ₂ , c-ZrO ₂	Bio-activity	[35, 36]
Pure Zr		CA+GP	t-ZrO ₂ , c-ZrO ₂ , m-ZrO ₂	Bio-activity	[37]
Pure Zr		Phosphate	m-ZrO ₂ , t-ZrO ₂	Bio-activity	[38,40,54]
Pure Zr		CA+ β -GP	c-ZrO ₂ , Ca-PSZ, CaZrO ₃ , HAP	Bio-activity	[55-57]
Pure Zr		CA+ β -GP+HA, hydrothermal treatment	Ca-PSZ, CaZrO ₃	Bio-activity	[58]
Pure Zr		CA+ β -GP	c-ZrO ₂ , CaZrO ₃ , HAP	Bio-activity	[59]
Pure Zr		Silicate+CA+GP	t-ZrO ₂	Bio-activity	[60]
Pure Zr		Ca(OH) ₂ , (NH ₄) ₂ HPO ₄	c-ZrO ₂ , m-ZrO ₂	Bio-activity Anti-corrosion	[61]
Pure Zr		Silicate, phosphate silicate-phosphate	m-ZrO ₂ , t-ZrO ₂	Bio-activity Anti-corrosion	[39]
Pure Zr		(Silicate, phosphate, aluminate)+SiC	m-ZrO ₂ , t-ZrO ₂ , SiC	Anti-corrosion	[41]
ZrH _{1.8}		Phosphate	m-ZrO ₂ , t-ZrO ₂ , c-ZrO ₂	Anti-hydrogen	[62]
Pure Zr		Citric acid	m-ZrO ₂ , t-ZrO ₂	photocatalytic	[63]
Pure Zr		Boric acid, borax, E _u 2O ₃	m-ZrO ₂ , t-ZrO ₂	photocatalytic	[64]

Notes: CA is calcium acetate, β -GP is β -glycerophosphate disodium salt pentahydrate, Ca-PSZ is CaO partially stabilized zirconia (Ca_{0.15}Zr_{0.85}O_{1.85}), HAP(HA) is Hydroxyapatite, YAT is Yttrium Acetate Tetrahydrate

Zr-2.5Nb、Zirlo 等合金的微弧氧化工艺, 重点研究微弧氧化膜的耐磨性(Anti-wear)、耐蚀性(Anti-corrosion)和生物活性(Bioactivity), 其中对生物活性的研究则主要集中在纯锆表面膜层。此外, 锆合金微弧氧化膜还具有光催化特性^[63-64], 但目前这方面的研究还较少。Wang 等人^[62]发现 $ZrH_{1.8}$ 表面也可以进行微弧氧化表面处理, 获得的氧化膜具有较好的抗氢渗透性能。这些都显示各种锆基材料都可以进行微弧氧化表面处理, 并具有相应特性。

2.2 锆微弧氧化的电压时间曲线

典型的锆微弧氧化电压-时间曲线如图 2 所示^[38,40]。同镁、铝和钛合金一样, 锆微弧氧化过程可以分为三个阶段: (1) 动态阶段(dynamic state), (2) 近稳态(near steady state), (3) 稳态(steady state)。需要注意的是, 在微弧氧化后期, 锆表面局部区域可能出现放电位置比较固定的大火花, 它会破坏已形成的氧化膜, 甚至造成基体烧蚀, 在实际处理过程中应尽量避免。

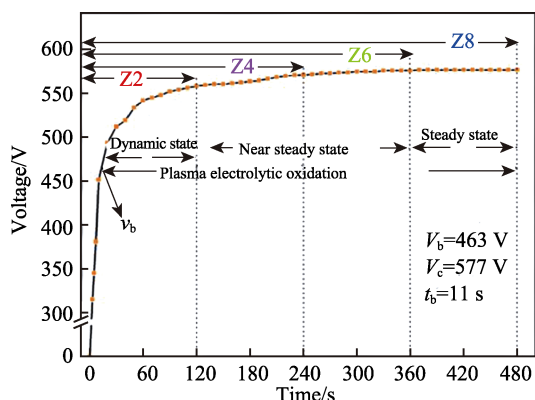
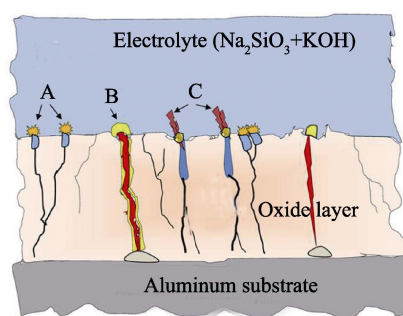


图 2 锆微弧氧化过程中的电压-时间曲线^[38]
Fig.2 Voltage-time response during MAO process for Zr^[38]

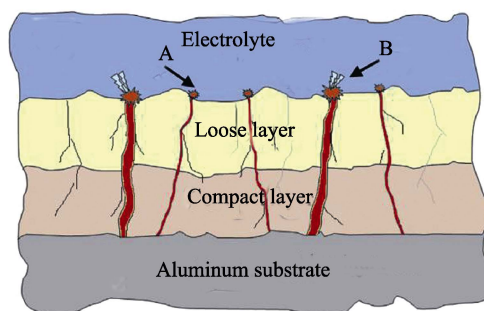
2.3 锆微弧氧化处理的等离子体放电模型

微弧氧化过程中, 当电压超过临界值就会发生锆表面氧化膜的介电击穿, 伴随有电弧和放电通道的形成。微弧氧化初期, 氧化膜较薄, 较低的击穿电压就能将其击穿, 形成较小的电火花并伴随轻微的爆鸣声。随着膜层厚度的增加, 电弧击穿膜层, 会形成较大的电火花并伴随强烈的爆鸣声。Hussein 等人^[65]利用光发射谱技术(Optical emission spectroscopy, OES)研究了铝合金微弧氧化过程中的等离子体放电行为, 认为它们可以分为三类: (1) 微弧氧化膜表面放电(Type A), (2) 微弧氧化膜与基体界面放电(Type B), (3) 微弧氧化膜表层下气孔放电(Type C), 放电模型如图 3a 所示。而 Liu 等人^[66]研究认为, 每个放电火花都应该击穿氧化膜并形成等离子体放电通道, 进而实现电子电流、离子电流和氧化膜溶解电流的导通。他们将放电现象分为两类, 即较弱的击穿微

弧氧化膜层放电(Type A)和较强的击穿微弧氧化膜层放电(Type B), 分别对应微弧氧化过程中的小放电火花和大放电火花, 其放电模型如图 3b 所示。通过示踪元素 Ti 的分布, 也直观地证实微弧氧化膜的击穿放电过程^[67-68]。Cheng^[69]借用图 3a 模型解释了 Zircaloy-2 合金微弧氧化膜的生长过程及其性能, 但 Wang^[50]对比了图 3 中的两种放电模型, 认为图 3b 模型更适理解锆微弧氧化过程中的等离子体放电现象、膜层结构和相组成。当然, 这些模型里提出的放电类型都是根据观察到的放电现象推测出来的, Type A、B、C 对应着不同放电位置和强弱。虽然对膜层击穿放电过程已有部分实验证据^[67-68], 但是还需要设计更多实验去验证和完善这些放电模型。



a 模型1^[65]



b 模型2^[66]

图 3 微弧氧化过程中的等离子体放电模型
Fig.3 Schematic illustration of the plasma discharge during MAO processes: (a) model 1^[65]; (b) model 2^[66]

2.4 锆微弧氧化电解液的组成及对膜层特性的影响

表 1 显示, 锆及锆合金微弧氧化电解液主要由硅酸盐、磷酸盐和铝酸盐等电解液体系组成, 这与其他金属微弧氧化电解液体系相似。国内外学者研究了电解液成分对锆合金微弧氧化膜生长和膜层组织性能的影响。Cheng 等人^[27,43]在硅酸钠电解液中对 Zircaloy-2 合金微弧氧化处理 30 min, 膜厚度增加到 56 μm , 但在铝酸钠电解液中快速生长 10 min 能够达到 32 μm , 随即外层脱落, Zr 离子溶解量增大, 膜层厚度不再增加。膜层分为三层, 即内部阻挡层(a barrier layer, 1 μm)、多孔中间层(a porous intermediate layer)和开裂外层(a cracked outer layer)。

其他作者对 Zirlo 锆合金和纯锆进行微弧氧化放电处理, 制备的膜层也为多层结构^[28,33-34]。

在铝酸钠电解液中, 铝元素参与到微弧氧化放电过程中并形成氧化铝相掺杂, 高硬度氧化铝相的存在可以提高膜层的耐磨性能。纯锆在铝酸钠电解液中形成 $\text{Al}_2\text{O}_3\text{-ZrO}_2$ 复合膜, 证明了电解液中铝酸根离子参与微弧氧化放电过程。铝酸钠电解液浓度升高时, $\text{Al}_2\text{O}_3\text{-ZrO}_2$ 复合膜的厚度增加且具有更高的致密性, 相应的耐磨和耐蚀性能也得到改善^[33-44]。

对于裂变核能系统, 燃料棒包壳的服役环境要求锆合金表面防护涂层致密且不能太厚, 几十微米厚的微弧氧化膜并不适合锆合金包壳的防护。Zou 等人^[24]将 Zr-1Nb 置于磷酸钠电解液中进行微弧氧化放电, 膜层厚度约为 11~15 μm , 并且非常致密(见图 4), 外部疏松层很薄, 膜层主要为内部致密层, 可明显提高锆合金的耐腐蚀性能。Wang^[34]和 Chen^[2]等人在 Zr-2.5Nb 合金表面制备了厚度在 5~15 μm 之间的微弧氧化膜层, 膜层也具有较好的耐磨损和耐腐蚀性能。此外, 在乙酸钙和甘油磷酸酯盐溶液中对纯锆进行微弧氧化放电处理, 钙、磷元素的掺杂有利于提高微弧氧化膜的生物活性, 可用于生物医用领域^[35-37,56-59]。因此, 电解液成分对锆微弧氧化膜的生长和特性有重要影响, 应根据应用需求进行合理选择。

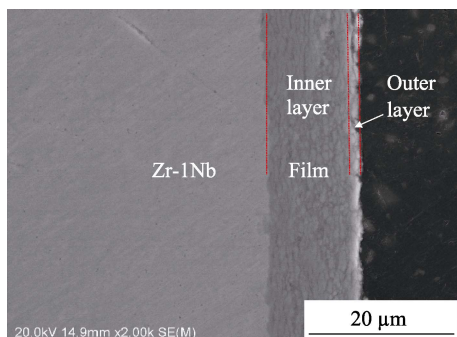


图 4 Zr-1Nb 合金微弧氧化膜截面形貌^[24]

Fig.4 Cross-sectional morphology of MAO coatings on Zr-1Nb^[24]

2.5 锆微弧氧化膜的相结构

表 1 显示, 锆微弧氧化膜主要由氧化锆相组成, 其典型的 XRD 图谱如图 5 所示。氧化锆有三种晶型^[70], 分别是立方氧化锆 (c-ZrO_2)、四方氧化锆 (t-ZrO_2) 和单斜氧化锆 (m-ZrO_2)。常温下 m-ZrO_2 是平衡相, 它在 1170 $^{\circ}\text{C}$ 以上转变为 t-ZrO_2 相, 在 2370 $^{\circ}\text{C}$ 以上 t-ZrO_2 相转变为 c-ZrO_2 相。从高温冷却时, 在 1000 $^{\circ}\text{C}$ 以下 t-ZrO_2 相会向 m-ZrO_2 相转变, 它属于马氏体相变, 相变过程伴随约 14% 的晶格切变和 3%~5% 的体积效应, 进而会在组织内部产生应力导致微裂纹的产生。因此, t-ZrO_2 相的存在可以减少膜层中微裂纹的产生并提高其性能。

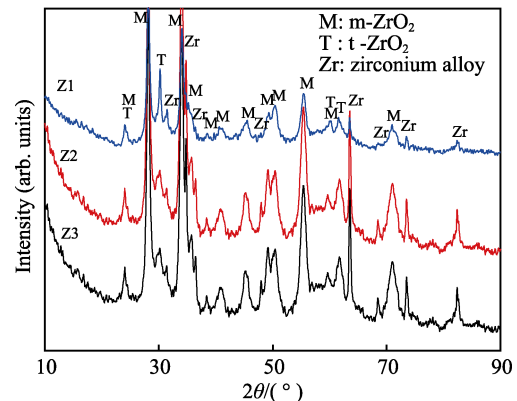


图 5 Zr-1Nb 微弧氧化膜的 XRD 图谱^[24]

Fig.5 XRD patterns of MAO coatings on Zr-1Nb alloys (Z1: +300 V/-50 V; Z2: +340 V/-50 V; Z3: +400V/-50 V)^[24]

在铝酸钠电解液中制备的锆微弧氧化膜主要由 t-ZrO_2 、 m-ZrO_2 和 Al_2O_3 相组成^[27,33,43,51-52], Al_2O_3 和 t-ZrO_2 相的含量随着铝酸钠电解液浓度的升高而增加^[33]。在 30 g/L 的铝酸钠电解液中微弧氧化处理 5 min, 其膜层中 t-ZrO_2 相含量可高达 93.6%^[51-52], 而 Al 主要分布在微弧氧化膜层的外部疏松层中, 内部致密层中的含量较少^[33]。此外, Wei 等人^[71]研究 Zr_3Al 合金在磷酸钠电解液中微弧氧化膜制备工艺, 发现其膜层也主要由 t-ZrO_2 相和少量的 Al_2O_3 相组成。这些研究表明, 锆微弧氧化膜中 Al_2O_3 相的存在可以起到稳定 t-ZrO_2 相的作用。这可能是因为 Al_2O_3 的弹性模量 (390 GPa) 大约是 ZrO_2 (207 GPa) 的 2 倍, 由于应力作用, 高弹性模量 Al_2O_3 分布在 ZrO_2 的周围可以阻止 t-ZrO_2 向 m-ZrO_2 的转变, 进而起到稳定 t-ZrO_2 相的作用^[33,52,72]。

实际上, 常温下 MgO 、 Y_2O_3 、 CaO 和 CeO_2 等氧化物的掺杂可以起到稳定 t-ZrO_2 相的作用^[27]。其稳定机制可以分为两大类: (1) 颗粒尺寸效应 (particle size effect), (2) 约束效应 (constraint effect)。此外, 电解液中的硅元素也有稳定锆微弧氧化膜里 t-ZrO_2 相的作用^[27,39,48,50]。对氧化硅-氧化锆材料的研究表明, 氧化硅也可以稳定 t-ZrO_2 相, 但超过一定晶粒尺寸的 t-ZrO_2 相就会向 m-ZrO_2 相转变^[73-74]。但是相关研究表明, 磷元素没有稳定 t-ZrO_2 相的作用^[43]。综上所述, 锆微弧氧化膜层中 t-ZrO_2 相的形成机制还需要进一步探索。但总体来说, 锆合金在硅酸盐和磷酸盐电解液生长的微弧氧化膜层主要由 m-ZrO_2 组成^[23-25,28-30], 而在铝酸盐中生长的膜层中 t-ZrO_2 相的含量会增加, 锆合金基体中 Al 含量较高时, 膜层中 t-ZrO_2 相含量也会增加。

发射光谱计算表明, 微弧氧化过程中等离子体放电区的瞬时电子温度高达 3000~12 000 K^[66,75-76]。这使锆合金首先氧化为高温相 c-ZrO_2 , 由于周围电解液的温度较低 (300 K), 随之发生 ZrO_2 晶型之间的转变。因为微弧氧化膜外层和周围低温电解液接触, 冷却速度较快, 致使较多的 t-ZrO_2 相存留在外层膜中,

而膜层内部冷却速度较慢,较多的 $t\text{-ZrO}_2$ 相转变为 $m\text{-ZrO}_2$ 相^[23]。由于应力和体积效应的存在,微裂纹等缺陷会伴随晶型转变而产生。因此,高温相 $t\text{-ZrO}_2$ 的存在,可减少应力和体积效应带来的缺陷,能提高膜层的耐磨、耐蚀性能^[2,77]。

3 锆微弧氧化膜的性能

3.1 锆微弧氧化膜的耐磨性能

锆微弧氧化膜物相以 ZrO_2 为主,硬度较高,这预示着膜层具有较高的耐磨性能。实际上,锆微弧氧化膜的耐磨性能同膜层特性(如相组成、厚度、微观结构)和磨损条件(摩擦副、荷载、环境及摩擦时间)等多种因素密切相关。表1列出了纯锆、Zr-2、Zr-4和Zr-2.5Nb微弧氧化膜摩擦性能的论文^[2,27,33,35,43-46]。通常较厚的微弧氧化膜比薄膜的耐磨性好^[43],然而Cheng等人^[43]在铝酸盐电解液中生成的Zr-2合金微弧氧化膜层,厚膜的中间存在一条20 μm 的间隙,导致其耐磨性能较差,可见微弧氧化膜显微结构对耐磨性能有较大的影响。

Cheng等人^[27,43]对比了Zr-2在硅酸盐、磷酸盐和铝酸盐电解液中形成微弧氧化膜的摩擦学特性,认为在铝酸盐电解液中生长的微弧氧化膜致密,硬度高,耐磨性能好。Yan等人^[33,44]研究发现,纯锆表面的 $\text{Al}_2\text{O}_3/\text{ZrO}_2$ 复合膜层硬度高达1630 HV,在油润滑条件下摩擦系数仅为0.115(荷载200~1000 N),耐磨性能优异。笔者对比研究了Zirlo锆合金及其微弧氧化膜的磨损性能,它们同钢球对磨条件下的磨损率如图6所示^[78]。微弧氧化膜在3.0 N荷载下的磨损率为 $4.59 \times 10^{-6} \text{ mm}^3/(\text{N} \cdot \text{m})$,大约是相同磨损条件下Zirlo合金基体磨损率的1/60。此外,去除微弧氧化膜表面疏松层后,其磨损率还可以进一步下降。因此,微弧氧化表面处理可以显著提高锆合金的抗磨损性能,且内部致密层对膜层耐磨性的提高至关重要。

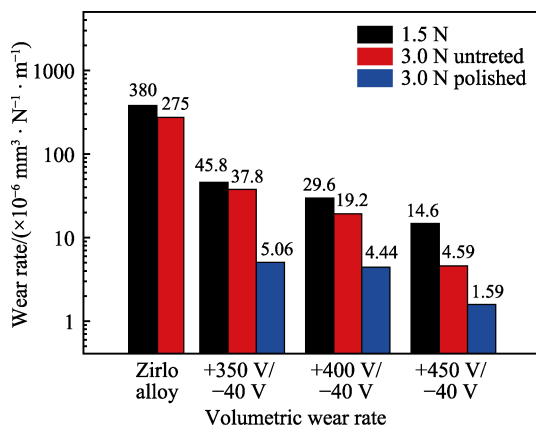


图6 Zirlo 锆合金及其微弧氧化膜在不同荷载条件下的磨损率^[78]

Fig.6 Volumetric wear rates of bare Zirlo alloy and MAO coatings under different loads^[78]

前面提到,铝和硅氧化物的存在能够稳定膜层中高温氧化锆相($t\text{-ZrO}_2$),减少相变引起的应力集中和微裂纹,提高锆微弧氧化膜致密性,从而提高其耐磨性能^[27]。另外,在铝酸盐电解液中生成的锆合金微弧氧化膜含有一些硬度很高的氧化铝相^[43],也有利于进一步提高膜层的耐磨性能。

3.2 锆微弧氧化膜的耐腐蚀性能

锆合金腐蚀是影响核反应堆安全运行的主要问题之一,其腐蚀类型包括均匀腐蚀、点状腐蚀、吸氢腐蚀和辐照损伤。一方面,腐蚀会使锆合金包壳的有效壁厚减薄,从而影响到核燃料元件的使用寿命;另一方面,腐蚀过程释放出来的氢被锆合金部分吸收形成氢化锆析出相,引起锆合金氢脆。表2总结了不同牌号锆合金及其微弧氧化膜在酸、碱、盐等不同腐蚀液中的抗腐蚀性能。微弧氧化表面处理可以大幅度降低(1—5个数量级)锆及锆合金的腐蚀电流,提高它们的耐腐蚀性能。

Cheng^[47-49]分析Zr-2、Zr-4合金在硅酸盐电解液中制备的微弧氧化膜结构及其耐腐性能,认为膜层的耐腐性由其内部很薄(0.2~0.5 μm)的阻挡层所决定。Farrakhov^[30]研究直流、单极性脉冲和双极性脉冲模式下Zr-1Nb合金微弧氧化膜在常温LiOH腐蚀液中的耐腐性能,发现单极性脉冲和双极性脉冲微弧氧化膜层的耐腐性能好于直流模式的膜层。对比双极性模式制备的膜层,单极性脉冲模式制备的膜层的耐腐性能更好,负向脉冲导致电解液中 Na^+ 和 K^+ 进入膜层,造成膜层抗腐性能下降。但是Zou等人^[24]采用双极性脉冲电源在Zr-1Nb表面生长的微弧氧化膜也非常致密(见图4),耐腐性能同样很好。因此锆合金微弧氧化膜的抗腐性能除受电源波形影响外,还同电解液成分和电参数密切相关。

随着 NaAlO_2 电解液浓度的升高(5~30 g/L), $\text{Al}_2\text{O}_3/\text{ZrO}_2$ 复合膜层在0.2 mol LiOH腐蚀液中的耐蚀性也得到提高^[51-52]。但在浓度基本一样的 NaAlO_2 电解液里(0.2~0.35 mol)制备的 $\text{Al}_2\text{O}_3/\text{ZrO}_2$ 复合膜层在3.5%NaCl腐蚀液中的耐蚀性,却随 NaAlO_2 浓度的升高呈现出先升高后下降的规律^[33]。此外,在 Na_2SiO_3 和 Na_3PO_4 电解液中制备Zr-4合金微弧氧化膜,在0.1 mol LiOH的常温腐蚀液中长期浸泡(100 d)测试发现,在 Na_2SiO_3 电解液中形成的微弧氧化膜更加致密,可以长时间保护Zr-4合金免受LiOH腐蚀液的侵蚀^[29]。综上所述,锆微弧氧化膜的耐腐性能不仅和电解液的选取有关,也和腐蚀液的选取密切相关。

双极性模式不同正向电压条件下形成的Zr-1Nb合金微弧氧化膜的电化学腐蚀行为表明,在0.5 mol LiOH腐蚀液中膜层的耐腐性能随着正向电压的升高而升高(见图7)^[24]。此外,电源频率和负向电压对锆合金微弧氧化膜耐腐性能也有影响^[34,50]。在论文中报道的实验条件下,膜层耐腐性能随着电源频率的升高而升高,随着负向电压升高呈现出先升高后下降的趋势。

表 2 锆及锆合金微弧氧化膜的耐腐蚀性能
Tab.2 Anti-corrosion properties of MAO film on Zr and Zr alloys

Substrate	Electrolyte systems	Thickness/ μm	Corrosion solution	Proterties	Refer-ences
Zr-4	30 g/L $\text{Na}_2\text{SiO}_3\cdot 5\text{H}_2\text{O}$ +4.88 g/L KOH	1.0~1.9 (30 s), 1.6~2.4(60 s)	6 mol HNO_3	I_{corr} : decreases 2 orders of magnitude	[47]
Zr-4	10 g/L $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$ +10 g/L $\text{Na}_4\text{P}_2\text{O}_7\cdot 10\text{H}_2\text{O}$	29.7 \pm 3.0 (10 min)	3.5% NaCl	I_{corr} : decreases 2 orders of magnitude	[48]
Zr-2	8 g/L $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$ +1 g/L KOH	\geq 20(10 min)	0.5 mol NaCl	I_{corr} : decreases 2 orders of magnitude	[49]
Zr-1Nb	1 g/L KOH+2 g/L Na_2SiO_3 +2 g/L $\text{Na}_4\text{P}_2\text{O}_7$	4.8(10 min)	1 mol LiOH	I_{corr} : one fifth of I_{corr} for uncoated Zr, impedance value improves 2 orders of magnitude	[30]
Zr-4	10 g/L Na_2SiO_3 +3 g/L KOH	5(20 min)	0.1 mol LiOH	I_{corr} : decreases 4 orders of magnitude	[29]
Zr-4	10 g/L $\text{Na}_3\text{P}_3\text{O}_{10}$ +2 g/L NaOH+other additive	6.7~7.6(5 min)	1200 mg/L H_3BO_3 +2 mg/L LiOH	Impedance value improves 2 orders of magnitude	[50]
AZ91D	3 g/L K_2ZrF_6		3.5% NaCl	I_{corr} : decreases 2 orders of magnitude	[79]
Pure Zr	0.3 mol NaAlO ₂	70(30 min)	3.5% NaCl	I_{corr} : decreases 4 orders of magnitude	[33]
Zr-2.5Nb	30 g/L NaAlO ₂	38~60(10 min)	0.2 mol LiOH	I_{corr} : decreases 3 orders of magnitude	[51]
Zr-2.5Nb	25 g/L NaAlO ₂	12.7~20.6(5 min)	0.2 mol LiOH	I_{corr} : decreases 2 orders of magnitude	[52]
Zirconium alloy	6~10 g/L Na_2SiO_3 +1 g/L KOH	25(10 min), 70(25 min)	3.5% NaCl	I_{corr} : decreases 2 orders of magnitude	[23]
Zr-1Nb	2 g/L Na_3PO_4 with additive	11~15(15 min)	0.5 mol LiOH	I_{corr} : decreases 3 orders of magnitude	[24]
Zr-1Nb	4 g/L Na_2SiO_3 +1 g/L KOH +excimer laser	8.6(15 min), 6.3(after laser)	360 $^{\circ}\text{C}$ /18.6 MPa/0.01 mol/L LiOH	94 Days, lower weight gain than uncoated Zr-1Nb	[25]
Zirlo	30 g/L $\text{Na}_2\text{SiO}_3\cdot 5\text{H}_2\text{O}$ +2.8 g/L KOH	100 \pm 10 (3600 s)	0.1 mol H_2SO_4	Impedance value improves 1 orders of magnitude	[28]
Zr-2.5Nb	14 g/L Na_2SiO_3	30	500 $^{\circ}\text{C}$ and 25 MPa H_2O	400 h, 1.5 times less weight gain than uncoated Zr-1Nb	[53]
Zr-2.5Nb	8 g/L Na_2SiO_3 + 0.8 g/L KOH	5~6(\leq 4 min)	0.2 mol LiOH, 25 $^{\circ}\text{C}$ 300 $^{\circ}\text{C}$ +10 MPa in 0.05 mol LiOH	I_{corr} : decreases 3 orders of magnitude 30 Days, lower weight gain than uncoated Zr-2.5Nb	[2]
Zr-2.5Nb	8 g/L $\text{Na}_2\text{SiO}_3\cdot 5\text{H}_2\text{O}$ +0.8 g/L KOH	15(5 min)	8% NaCl	I_{corr} : decreases 3 orders of magnitude	[34]
Pure Zr	5 g/L $\text{Na}_3\text{PO}_4\cdot 12\text{H}_2\text{O}$ +4 g/L SiC	7 \pm 0.5(6 min)	0.1 mol LiOH	I_{corr} : decreases 5 orders of magnitude	[41]
Pure Zr	5 g/L $\text{Na}_3\text{PO}_4\cdot 12\text{H}_2\text{O}$	12(6 min)	SBF*	Higher Open circuit potential I_{corr} : decreases 3 orders of magnitude No pitting corrosion	[38]
Pure Zr	5 g/L $\text{Na}_3\text{PO}_4\cdot 12\text{H}_2\text{O}$ +5 g/L $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$ +3 g/L+KOH	6.9 \pm 0.8(6 min)	SBF*	Higher Open circuit potential I_{corr} : decreases 2 orders of magnitude superior pitting corrosion resistance	[39]
Pure Zr	5g/L $\text{Na}_3\text{PO}_4\cdot 12\text{H}_2\text{O}$	12.5 \pm 0.8(6 min)	SBF*	I_{corr} : decreases 4 orders of magnitude superior pitting corrosion resistance	[40]
Pure Zr	$\text{Na}_3\text{PO}_4\cdot 12\text{H}_2\text{O}$ +Ca(OH) ₂ , (NH ₄) ₂ HPO ₄ with additive	75 \pm 5(6 min)	SBF*	I_{corr} : decreases 2 orders of magnitude superior pitting corrosion resistance	[61]

Notes: the electrolyte composition, thickness, treatment time and corrosion resistance in the table correspond to the optimal values in the literature
SBF*: simulated body fluid (pH=7.4, 37 $^{\circ}\text{C}$)

目前对锆微弧氧化膜耐腐蚀机理的研究主要集中在膜层的厚度、致密性及孔隙率等结构特征方面，然而笔者通过测量 Zirlo 锆合金微弧氧化膜在不同腐蚀液中（包含核电站冷却液）的表面电荷情况，评估了锆合金及其微弧氧化膜表层 Zeta 电位与腐蚀行为

的关系^[80]。图 8 显示 Zirlo 锆合金微弧氧化在硼酸氢氧化锂混合溶液中的表面 Zeta 电位变化情况。从膜层-腐蚀液界面电荷与腐蚀液中离子间的相互作用出发，认为膜层界面聚集的电荷对锆合金微弧氧化膜的腐蚀行为具有十分重要的影响。

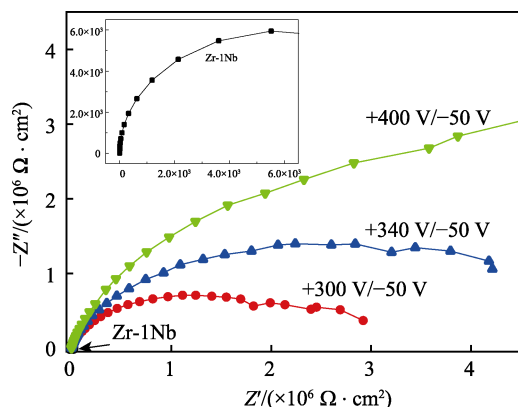


图7 Zr-1Nb 合金微弧氧化膜在 0.5 mol LiOH 中的 Nyquist 图^[24]

Fig.7 Nyquist plots of MAO film on Zr-1Nb in 0.5 mol LiOH solution^[24]

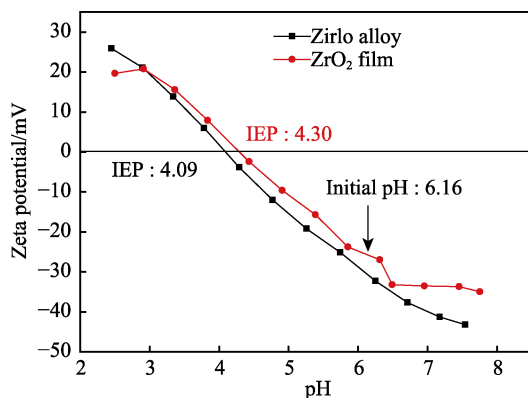


图8 Zirlo 合金及其微弧氧化膜在 1500 ppm B^{3+} +2.3 ppm Li^+ 溶液中的 Zeta 电位^[80]

Fig.8 Zeta potentials of bare and MAO-coated Zirlo alloy as a function of pH in 1500 ppm B^{3+} and 2.3 ppm Li^+ mixed solution^[80]

前面对锆微弧氧化膜腐蚀性能的评估都是在常温常压水环境下进行的,考虑到核电是锆合金的主要应用领域,评估微弧氧化处理的锆合金在高温高压极端环境中的腐蚀行为是十分必要的,但目前这方面的研究还较少。Chen^[2]和 Hui^[53]等人利用挂片方式研究 Zr-2.5Nb 合金微弧氧化膜分别在 300 °C/10 MPa 和 500 °C/25 MPa 高温高压水环境中的腐蚀特性,发现微弧氧化处理的锆合金具有较低的腐蚀增重和较好的耐高温腐蚀性能。

多种表面技术复合处理可以进一步提高锆合金微弧氧化膜抗高温高压水腐蚀的性能。Yang 等人^[25]通过激光处理 Zr-1Nb 锆合金微弧氧化膜表面,剥落外部疏松层并使表层重熔,进一步提高膜层的致密性。经过 94 d 高压釜 (360 °C/18.6 MPa, 0.01 mol LiOH) 腐蚀测试后,复合处理膜层截面形貌如图 9 所示,可以清晰地看到微弧氧化膜外部有一层致密的激光重熔层。该重熔层有利于阻挡锂、氢和氧的扩散,进一步提高微弧氧化膜的耐高温水腐蚀性能。

高温高压水环境条件下微弧氧化膜优异的耐腐

蚀性能可以提高锆合金元件的服役安全性,但太厚的微弧氧化膜会造成锆合金强度和传热性能的下降^[2,24],威胁到核电站的安全运行。因此,在锆合金表面制备一层较薄的致密微弧氧化膜在核电应用领域具有较好的前景。

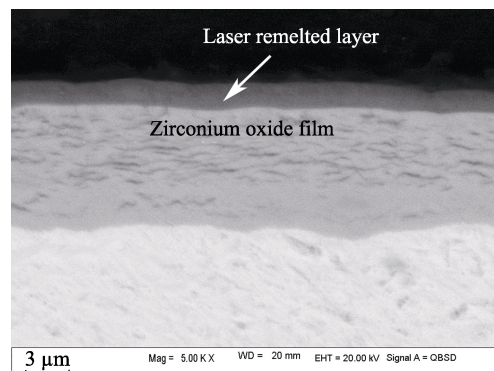


图9 高温高压腐蚀测试后的 Zr-1Nb 合金微弧氧化+激光复合处理膜层截面形貌^[25]

Fig.9 Cross-sectional morphology of the MAO + laser complex treated Zr-1Nb alloy after the autoclave corrosion test^[25]

另外,锆作为植入体在生物医学方面也有着广泛的应用价值,因此评估锆及其微弧氧化膜层在人体内部环境中的腐蚀行为是必要的。Sandhyarani 等人^[38-40,61]在纯锆表面制备微弧氧化膜,并在人体模拟液 (SBF) 中评估其耐腐蚀性能。相比纯锆基体,微弧氧化膜覆盖的基体具有更高的开路电位,更低 (低 2—4 个数量级) 的腐蚀电流和优异的抗点蚀特性 (表 2),有利于减少锆植入体的腐蚀和腐蚀产物对人体的危害。

3.3 锆微弧氧化膜的生物相容性

锆的弹性模量是 92 GPa, 低于钛的弹性模量 100~110 GPa, 更接近人体骨骼的弹性模量 (10~30 GPa), 可降低应力遮蔽效应 (Stress shielding effect)^[36,56]。此外,锆具有良好的化学稳定性、较高的弯曲强度和断裂韧性、较低的细胞毒性、优异的耐腐蚀性和生物相容性,因此锆是一种用作骨科和牙科的植入体材料^[36]。锆植入体在人体内很容易形成一层薄的钝化膜 (2~5 nm), 该钝化膜由于其生物活性低,很难与生物组织间形成有效连接。此外,这层钝化膜在植入体长期服役过程中磨损脱落会引起植入体失效^[38-40],因此有必要提高锆的表面生物活性及强度。相关研究表明^[38-40,54-59,61],经过修饰的微弧氧化膜层表面疏松多孔可以提高它与生物组织间的结合力,增强其生物活性。微弧氧化膜较厚且强度高、不易脱落,可提高植入体的使用寿命。

表 1 显示,目前主要采用醋酸钙 (CA)、甘油磷酸酯二钠 (β -GP) 电解液制备含 Ca、P 元素的锆微弧氧化膜。Ca、P 等元素参与微弧氧化膜的生长过程,形成晶态或非晶态羟基磷灰石 (HA),或作为后续羟基磷灰石的形核中心,从而提高了膜层的生物活

性^[60]。在模拟体液中羟基磷灰石的形成，不仅与钙、磷元素作为形核中心有关，还与其表面聚集的电荷相关。钙、磷元素的加入，使膜表面在模拟体液中呈现负电性，吸引模拟体液中的 Ca^{2+} ，进而吸引 PO_4^{2-} ，促进羟基磷灰石的形成^[81]。

骨质羟基磷灰石及成骨细胞能够在锆微弧氧化膜表面着陆、繁殖和生长，膜层具有较好的生物活性。表 3 给出部分文献中关于纯锆微弧氧化膜的生物相容性方面的研究。Yan^[35]和 Han^[36]等人研究了不同电压下锆微弧氧化膜的生物活性，发现在模拟体液中浸泡一段时间后，微弧氧化膜被骨质羟基磷灰石覆盖且

成骨细胞能够在其表面着陆、繁殖和生长，表明锆微弧氧化膜具有良好的生物活性。在电解液中添加羟基磷灰石纳米棒（HA nanarods）进行微弧氧化放电，膜层也有很好的生物活性^[58]。此外，占空比、电解液浓度、电流密度和处理时间对微弧氧化膜层生物活性也有一定的影响^[54,56-57]。Durdu 等人^[55,59]在纯锆微弧氧化膜层表面利用物理气相沉积制备 Zn 和 Ag 薄膜，在模拟体液中浸泡一段时间后，在 Zn 或 Ag 薄膜表面骨质羟基磷灰石层更加均匀和致密，且二者都具有良好的抗菌性能。因此，复合处理也是提高微弧氧化膜生物活性的有效手段之一。

表 3 纯锆微弧氧化膜的生物相容性
Tab.3 Biocompatibility of MAO film on pure Zr

Substrate	Electrolyte systems	Variable	Immersion solution	Proterties	Refer-ences
Pure Zr	0.2 mol CA, 0.02 mol β -GP	300~500 V, 5 min	SBF, 3 Days	Covered by the apatite	[35]
Pure Zr	0.2 mol CA, 0.02 mol β -GP	400~500 V, 5 min	SBF, 10 Days	Bond like apatite forming ability increases with voltages, Osteoblasts attach, proliferate and grow in good state	[36]
Pure Zr	0.1 mol K_3PO_4 +KOH(0.001, 0.005, 0.1 mol)	Duty cycle, elec-trolyte concentra-tion	SBF	Excellent corrosion resistance in SBF solution, good biocompatibility for 3T3 and MG63 cells	[54]
Pure Zr	0.25 mol CA, 0.06 mol β -GP	MAO+Zn film (TE)	SBF, 10 Days	Good bone like apatite layer on Zn-MAO than MAO, but lower bacteria adhesion	[55]
Pure Zr	CA, β -GP	Current density	SBF, 28 Days	Covered uniformly by the apatite, bacteria adhesion to surfaces decreased with increasing current density	[56]
Pure Zr	0.25 mol CA, 0.06 mol β -GP	Treatment time	SBF, 28 Days	Apatite forming ability on PEO surface enhanced with increasing treatment time, cell viability, attachment, growth on PEO film	[57]
Pure Zr	0.2 mol CA, 0.02 mol β -GP+HA (nanorods)	450 V, 5 min+ hydrothermal treatment	SBF, 3 Days	good hydrophilicity and apatite inducing ability	[58]
Pure Zr	0.25 mol CA, 0.06 mol β -GP	MAO+Ag film(TE)	SBF, 10 Days	Good bone like apatite layer on Ag-MAO than MAO, but lower bacteria adhesion	[59]

4 结论与展望

锆及锆合金微弧氧化膜具有良好的耐磨、耐腐蚀性能，经过修饰后的微弧氧化膜层具有优异的生物活性、低细胞毒性、抗菌性等特性，在核电、化工和生物医学材料方面具有广阔的应用前景。但是相对目前已被广泛研究的铝、镁、钛微弧氧化技术，锆及锆合金微弧氧化工艺、机理、性能和应用的探索还远未成熟，在下面几个方面值得进一步探索。

（1）当前对锆微弧氧化机理的认识大都借鉴于铝、镁、钛合金微弧氧化放电机制，前者的独特之处还需要深入研究。

（2）各种牌号的铝、镁、钛合金微弧氧化工艺和性能都有大量论文发表，而合金元素对锆微弧氧化膜生长过程影响的认识还不够清晰，仍然需要大量数据的

积累。

（3）目前锆及锆合金微弧氧化技术的研究主要集中在氧化工艺探索以及膜层的耐磨、耐腐蚀和生物活性等特性，但对膜层的热防护、热控、介电绝缘、催化等性能评估还有待开展。

（4）在核电应用方面，针对包壳与栅格间在高温高压水环境中的微动磨损，受试验条件限制还几乎没有研究。另外，对高温高压极端环境下腐蚀特性还需要深入探索。设计新型试验装置，开展高温高压水环境中摩擦和腐蚀性能的原位评估也是值得期待的研究方向。

（5）在生物医用方面，进行活体试验是锆微弧氧化技术得到实际应用前必须要开展的工作。此外，开展锆复合膜层的生物医学研究也是有价值的研究方向。

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