

镁合金表面磷化/溶胶凝胶复合膜的制备及其耐蚀性

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摘要: 目的 结合磷化与溶胶凝胶工艺,在 AZ91 镁合金表面制备磷化/溶胶凝胶复合膜。方法 先对镁合金进行磷化处理,再多道涂覆 SiO₂ 溶胶凝胶层,通过正交试验结合电化学分析方法,优化溶胶凝胶层涂覆工艺,并分析磷化/溶胶凝胶复合膜的表面微观形貌和耐蚀性。结果 溶胶凝胶层的优化沉积工艺如下: TEOS,TEOH,H₂O,HCl 体积比为 28:20:10:0.35,凝胶温度 30℃,凝胶时间 5 min,涂覆 6 次。在优化条件下所制备的复合膜结合力好且光滑,有少许微裂纹,与镁合金基体和磷化膜样品相比,其腐蚀电流密度最小,电化学阻抗最大。结论 磷化/溶胶凝胶复合膜提高了镁合金的耐蚀性。

关键词: 镁合金; 磷化膜; 溶胶凝胶; 复合膜层; 耐蚀性

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Preparation and Corrosion Resistance of Phosphating Sol-Gel Composite Coatings on Magnesium Alloy

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ABSTRACT: **Objective** The composite coatings were prepared on AZ91 magnesium alloy using the phosphate and sol-gel process. **Methods** Magnesium alloy was phosphatized, then coated with multiple SiO₂ sol gel layers. Using the orthogonal experiment combined with electrochemical analysis method, we optimized the deposition process conditions of the sol gel film, and analyzed the surface microstructure and corrosion resistance of the composite coatings. **Results** The results showed that the optimized deposition process conditions of the sol gel film were as follows: volume ratio of sol formula (TEOS:TEOH:H₂O:HCl) 28:20:10:0.35, gel temperature 30℃, gel time 5 min, coating times 6. Under the optimal condition, the composite coating was smooth, with a few micro cracks and good binding force. Compared with the magnesium alloy substrate and phosphate coating, the corrosion current density of the composite coating was the lowest, and the electrochemical impedance was the largest. **Conclusion** The corrosion resistance of magnesium alloy was improved by phosphating sol-gel composite coating.

KEY WORDS: magnesium alloys; phosphate coating; sol-gel; composite coatings; corrosion resistance

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镁合金因其优异的性能被誉为 21 世纪理想的电子产品壳体和轻型车辆材料^[1-7],但耐蚀性差在某种程度上制约了其广泛应用,要想大规模应用于工业,必须进行表面处理。镁合金的表面处理通常采取化学转化膜法、阳极氧化、金属涂(镀)层、激光表面合金改性等^[8-12]。溶胶凝胶技术具有热处理温度低、流动性好等特点,常常与化学转化或阳极氧化等前处理技术相结合,在提高金属或合金的耐蚀性方面具有广阔的应用前景^[13]。工业上进行磷化处理的目的,是利用磷化膜对涂料的吸附能力来增强涂料与金属的结合力,因此磷化膜常作打底层^[14-15]。化学转化膜属于多孔材料,镁合金的磷化膜防护作用较小,涂溶胶可以起到封孔的作用,从而进一步提高镁合金的耐蚀性,拓展其应用空间。

为了提高 AZ91 镁合金的耐蚀性能,笔者拟在已有研究的基础上,先应用磷化工艺在镁合金表面制备磷化膜,再应用溶胶凝胶技术在磷化膜表面制备 SiO₂ 溶胶凝胶膜层,得到复合膜,并优化复合膜沉积工艺,分析其耐蚀性。

1 试验

1.1 磷化/溶胶凝胶复合膜制备

基材选用 AZ91 镁合金,其成分(以质量分数计)为:8.8% 铝,0.81% 锌,0.21% 锰,余量为镁。将镁合金加工成 20 mm×15 mm×3 mm 的试样,先依次用 240,360,600,1000 目的水磨砂纸打磨,再经除油液除油及热水、冷水冲洗,干燥后备用。除油液配方为 5 g/L NaOH + 1 g/L OP-10,在 60 ~ 70 ℃ 除油 1.5 ~ 2 min。试验过程中的用水均为蒸馏水。

将前处理后的镁合金试样置于磷化液中进行磷化处理,温度为 45 ~ 65 ℃,反应时间为 20 ~ 40 min。磷化液配方为:10 ~ 30 mL/L H₃PO₄,0.5 ~ 2 mL/L 二乙醇胺,2 ~ 5 g/L HNO₃,3 ~ 7 g/L ZnO,1 ~ 2 g/L NaF,1 ~ 3 g/L 酒石酸,3 ~ 5 g/L 3-硝基苯磺酸钠。之后,利用浸渍提拉法在磷化膜表面制备 SiO₂ 溶胶凝胶膜。SiO₂ 溶胶是将正硅酸乙酯、乙醇、蒸馏水按一定体积比混合^[16-17],加入盐酸作为催化剂而成。选择的提拉速度为 5 cm/min,提拉后,将样品放置在距离具有一定温度的水面上方 2 cm 处,于蒸汽中凝胶化一段时间,然后在干燥箱中升温至 80 ~ 100 ℃,保温 2 h 后,自然降温到室温,再进行二次涂覆,之后采

用同样条件进行干燥。浸渍提拉次数为 2 ~ 6 次,最后一次升温至 180 ℃ 固化 1.5 h,即在镁合金表面制得锌系磷化/SiO₂ 溶胶凝胶复合膜。

1.2 测试方法

采用 S-4800 型扫描电子显微镜观察磷化膜及复合膜的表面形貌。

采用 CHI860D 电化学工作站测试极化曲线和交流阻抗谱。测试时采用三电极体系:参比电极为饱和甘汞电极;辅助电极为铂电极;工作电极为待测样品电极,其有效暴露面积为 1 cm²,非工作面用 AB 胶密封。电解质溶液均采用 3.5% (质量分数) 的 NaCl 溶液。测定极化曲线的扫描电位范围为 -1.70 ~ -1.30 V,扫描速率 5 mV/s。交流阻抗在开路电位下测试,频率范围为 100 kHz ~ 0.1 Hz,扰动幅值为 5 mV。

2 结果与讨论

2.1 溶胶凝胶膜的沉积工艺优化

以凝胶化时间、凝胶化温度、涂覆次数和溶胶配方(见表 1)作为变量,以样品的腐蚀电流密度作为考核指标,采用 L₉(3⁴) 正交试验对 SiO₂ 溶胶凝胶膜沉积工艺进行优化。表 2 为因素水平表,表 3 为正交试验分析结果。

由表 3 数据可知,各因素的影响由大到小依次为

表 1 SiO₂ 溶胶配方
Tab.1 Formulations of SiO₂ sol

溶胶	成分(体积比)			
	正硅酸乙酯	无水乙醇	蒸馏水	盐酸(36% ~ 38%)
1	28	28	10	0.35
2	28	20	10	0.35
3	30	18	5	0.35

注:盐酸浓度以质量分数计。

表 2 L₉(3⁴) 正交试验表
Tab.2 Orthogonal experiment table of L₉(3⁴)

水平	因素			
	A 凝胶温度/℃	B 凝胶时间/min	C 涂覆次数	D 溶胶
1	30	5	2	1
2	50	15	4	2
3	70	40	6	3

表 3 $L_9(3^4)$ 正交试验方案及结果

Tab.3 Final results of orthogonal experiment of $L_9(3^4)$

试验号	A	B	C	D	腐蚀电流密度 / $(\mu\text{A}\cdot\text{cm}^{-2})$
1	1	1	1	1	11.17
2	1	2	2	2	6.29
3	1	3	3	3	6.06
4	2	1	2	3	6.35
5	2	2	3	1	12.07
6	2	3	1	2	7.07
7	3	1	3	2	4.85
8	3	2	1	3	28.47
9	3	3	2	1	16.80
K_1	23.52	22.37	46.71	40.04	
K_2	25.48	46.83	29.43	18.20	
K_3	50.12	29.93	22.98	40.88	
$K_1/3$	7.84	7.46	15.57	13.37	
$K_2/3$	8.49	15.61	9.81	6.07	
$K_3/3$	16.71	9.98	7.66	13.63	
R	8.87	8.15	7.91	7.56	

A>B>C>D。凝胶温度对腐蚀电流的影响最大,其次是凝胶时间和涂覆次数,溶胶配方的影响最小。分析可知,制备溶胶凝胶膜层的优化条件如下:溶胶配方为 $V(\text{TEOS}):V(\text{TEOH}):V(\text{H}_2\text{O}):V(\text{HCl})=28:20:10:0.35$,凝胶温度 $30\text{ }^\circ\text{C}$,凝胶时间 5 min ,涂覆 6 次。

2.2 镁合金基体、磷化膜与复合膜性能对比

2.2.1 耐蚀性能分析

采用优化的工艺条件于镁合金表面制备复合膜层,通过 Tafel 曲线和 EIS 图谱分析其耐蚀性,并与镁合金基体和单层磷化膜样品进行对比。由 Tafel 曲线(图 1)可以看出,单层磷化膜能够提高镁合金的腐蚀电位,这是由于磷化膜代替镁合金自然膜层作为与外界接触的表面,改变了界面接触层,进而改变了其在电解液中的腐蚀电位。磷化膜有裂缝且多孔,阳极极化时会形成比镁合金基体还小的阳极反应面,因而在其他条件相同时,腐蚀电流相对更小。复合膜的腐蚀电流比镁合金基体及磷化膜都低,说明 SiO_2 溶胶能够填充磷化膜层表面的孔洞,同时由于磷化膜的存在,复合膜与基体能够有效结合。由 EIS 图谱(图 2)也可以看出,与外界不同电位的物质组成微电池时,复合膜的抗破坏能力最强,磷化膜次之,镁合金基体

最低。这可能是由于复合膜是由导电能力差的磷化膜盐及 SiO_2 氧化物相互结合形成,而磷化膜的耐蚀性主要由磷酸锌盐的组成和结构决定^[18-19]。综合考虑腐蚀电流密度和电化学阻抗,复合膜比磷化膜的耐蚀性更优越,最能提高镁合金的耐蚀性能。

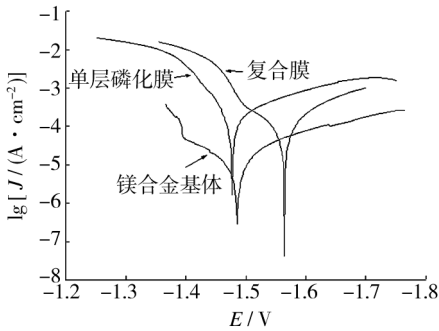


图 1 Tafel 曲线对比
Fig.1 Comparison of Tafel curves

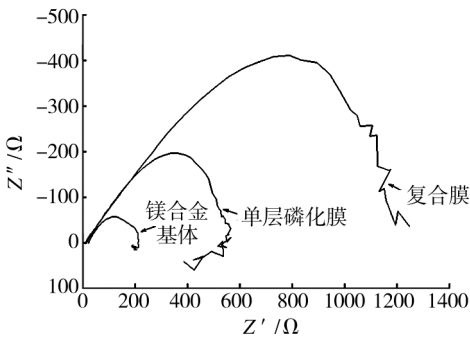


图 2 EIS 谱对比
Fig.2 Comparison of EIS curves

2.2.2 微观形貌分析

图 3 为镁合金表面磷化膜和复合膜的微观形貌对比。可以看出,磷化膜表面不平整,有孔隙;复合膜中的溶胶凝胶层大部分覆盖磷化层,但也存在裂纹。这是由于冲洗、干燥后的磷化膜是一种微显酸性的多孔磷酸锌盐,与 pH 为 3 左右的酸性硅溶胶作用时,会析出氢气泡,使复合膜表面产生小孔,影响硅溶胶覆盖的完整性、致密性,进而影响膜层的耐蚀性。此外,溶胶虽然具有粘性,但粘性较小,因为经干燥、固化后的凝胶本质上是以 $-\text{Si}-\text{O}-\text{Si}-$ 伸出的小键能 $\text{Si}-$ 键与磷酸锌以分子间作用力的形式结合起来的,不是经过化学或高能的物理变化结合,难以引起结合力强的质变^[20]。但在一定工艺条件下得到的复合膜层表面微观缺陷较磷化膜少,使得复合膜的防腐蚀性能比磷化膜好,这与 Tafel 曲线和 EIS 图谱的分析结果一致。

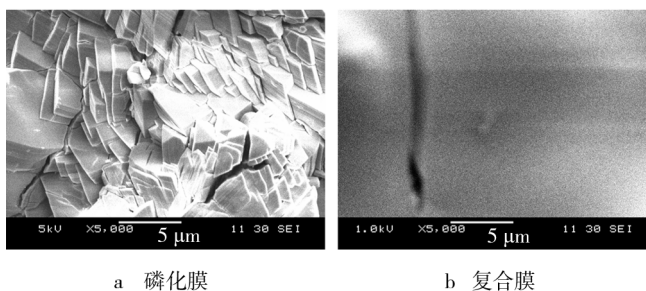


图3 镁合金表面膜层的微观形貌

Fig.3 Microstructure of the coatings on magnesium alloy

3 结论

1) 将磷化与溶胶凝胶技术相结合,先对镁合金进行磷化处理,再采用 SiO_2 溶胶封孔,可在镁合金表面制备出磷化/溶胶凝胶复合膜。

2) 溶胶凝胶层的优化沉积工艺如下:溶胶配方为 $V(\text{TEOS}) : V(\text{TEOH}) : V(\text{H}_2\text{O}) : V(\text{HCl}) = 28 : 20 : 10 : 0.35$,凝胶温度 30°C ,凝胶时间 5 min ,涂覆6次。在优化条件下所制备的复合膜表面平整,较为致密,有少许微裂纹,与基体的结合力良好,提高了镁合金的耐蚀性。

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