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抗菌耐蚀性功能复合镀层 (Ag)-Ni/Cr 的开发研究

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摘要: 通过正交试验法, 在优化电镀工艺条件基础上, 开发并研制了一种新型金属表面功能材料 (Ag)-Ni/Cr 复合镀层, 并分别利用菌落计数法和交流阻抗法比较镀层抗菌和耐蚀性能。研究表明, 该镀层具有抗菌性和耐蚀性兼顾的特点, 极具广阔的应用前景。

关键词: 正交试验; 菌落计数法; 交流阻抗; 抗菌性; 耐蚀性

中图分类号: TQ 153; O 646

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微生物容易引起材质损伤^[1,2], 尤其在建筑、医疗、食品、卫生等领域, 由微生物引起的腐蚀、感染、食物中毒等现象甚为严重^[3]。现今, 已有的各种抗菌方法在其实际应用中还存在着各自的缺点, 简要说明如表 1 所列:

表 1 各种抗菌方法及其缺点

Tab 1 Various antibacterial methods and their shortcomings

Various antibacterial methods	Shortcomings
Addition of organic antibacterial agents ^[4] (typical agents such as antibiotics, etc.)	Antibacterial agents easier to be left over the foods and microbe easier to gain high level resistance to these agents
Addition of inorganic antibacterial agents ^[5] (antibiotic metals such as Ag, Cu, Zn, Cd, etc. contained)	Lower safety, lower stability and higher costs
Electrochemical treatment	Higher limitation due to the electrode reaction involved

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近几年来, 抗菌性金属表面功能材料, 尤其是具有抗菌作用的电镀层, 因为不存在有机, 无机抗菌剂的缺点(见表 1), 而且价格低, 可使用面广, 制作工艺简单, 逐渐显示出广阔的应用前景^[4]。但目前有关这方面的报道为数不多, 特别是那些涉及抗菌性和耐蚀性兼顾的镀层的开发研究尚处于初步阶段。本文通过正交试验法, 在优化电镀工艺条件基础上, 开发并制备了一种新型的抗菌耐蚀性复合镀层(Ag)-Ni/Cr。

1 实验和讨论

采用正交实验法选定影响镀层性能的 3 个主要因素及每因素 3 个水平构成 $L_9(3^4)$ 正交表。各主要因素, 即电镀(Ag)-Ni 复合镀层的电流密度(I)和电镀时间(t_1), 电镀 Cr 时间(t_2)及相应水平变数如表 3 所列。

1.1 (Ag)-Ni/Cr 复合镀层的制备方法

(Ag)-Ni/Cr 镀层的制备关键步骤乃系(Ag)-Ni 复合镀层的电镀。本文采用布砂法^[6], 阴极为面积 $2\text{ cm} \times 2\text{ cm}$ 的 Cu 片, 经 2[#], 4[#] 金相纸打磨, 绒布抛光后, 在 10% 硫酸中浸泡 2~3 min, 再于 $3\text{ g} \cdot \text{L}^{-1}\text{NaOH} + 5.6\text{ g} \cdot \text{L}^{-1}\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} + 31.3\text{ g} \cdot \text{L}^{-1}\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ 的混合液中电解脱脂; 阳极为面积 $3\text{ cm} \times 3\text{ cm}$ 的 Pt 片, 背面用胶粘剂施以绝缘, 酸洗、水洗后使用; 抗菌剂为纯度 99% 的 200 目 Ag 粉(上海化学试剂公司), 经活化后加入镀液中; 用 ZF-5 恒电位仪控制电流; 通电前先经 81-2 型恒温磁力搅拌器(上海司乐仪器厂)搅拌约 1 min, 电镀条件如表 2 所列。

表 2 (Ag)-Ni/Cr 复合镀层镀液组成及电镀条件

Tab. 2 Bath composition and electroplating technique conditions for the (Ag)-Ni/Cr composite plating

	(Ag)-Ni composite plating		Cr plating	
Bath composition	NiSO ₄ · 6H ₂ O	250.0 g · L ⁻¹	H ₂ CrO ₄	250.0 g · L ⁻¹
	NiCl ₂ · 6H ₂ O	55.0 g · L ⁻¹	NaSiF ₆	10.0 g · L ⁻¹
	H ₃ BO ₃	35.0 g · L ⁻¹	H ₂ SO ₄	1.0 g · L ⁻¹
	Brightener	40.0 g · L ⁻¹		
	Ag powder(200 orders)	4.0 g · L ⁻¹		
Temperature	50~60		40	
Current density	See also Tab. 3		10 A · dm ⁻²	
Plating time	See also Tab. 3		See also Tab. 3	
pH	4.0~4.4			

1.2 镀层性能的测试方法

1) 抗菌性测试 金黄色葡萄球菌(革兰氏阳性菌)^[7], 牛肉膏蛋白胨培养基, 采用生物测试方法, 即平板菌落计数法, 测得抗菌率^[8,9]。

2) 耐蚀性测定 采用三电极体系, 辅助电极为 Pt 电极, 参比电极为 Ag/AgCl 电极, 工作

电极于 $50 \pm 5 \text{ g} \cdot \text{L}^{-1} \text{NaCl}$ 溶液中经浸泡 3 h 后由 CHI 660A 系列电化学分析仪/工作站(上海辰华仪器公司)进行交流阻抗谱测量, 电解液为 $50 \pm 5 \text{ g} \cdot \text{L}^{-1} \text{NaCl}$ 溶液

1.3 Ag 粉的活化

实验装置如图 1 所示, 烧杯中盛有少量检验液, 将 Ag 粉分散在铺于漏斗中的滤纸上, 不断加入活化液, 待烧杯中检验物出现活化标志物时, 立即用蒸馏水清洗滤纸上 Ag 粉, 直至杯中该标志物不再产生, 移走烧杯, 换用电镀槽, 滴加少量镀液润湿 Ag 粉后, 捅破滤纸, 活化 Ag 粉即随镀液流入电镀槽

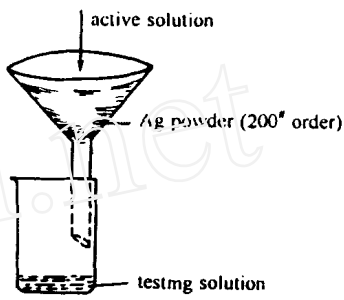


图 1 Ag 粉活化实验装置

1.4 正交试验结果与讨论

表 3 列出电镀(Ag)-Ni/Cr 复合镀层的正交试验结果, 其抗菌率的计算如式: 抗菌率= 样品原液中细菌数/空白原液中细菌数 $\times 100\%$. 表 3 中, 序号为 8, 1, 6 等 3 样品, 其电镀 Cr 实验时间指为 0, 此乃表示 Cu 基体表面仅镀一层(Ag)-Ni 复合镀层, 没有 Cr 镀层 以上三者都给出了较高的抗菌率, 这可能是由于表面无 Cr 镀层, 使 Ag 较易析出而提高了镀层的抗菌作用 图 2 示出表 3 中各序号(Ag)-Ni/Cr 镀层的交流阻抗谱, 据此计算得到电极反应电阻, 同时列于表 3, 如表可见 3, 9, 5, 4 号样品的反应电阻是其余样品的 6~ 10 倍, 比不锈钢的耐蚀性还要好.

Fig 1 Experimental equipment used to the activation of Ag powders

表 3 (Ag)-Ni/Cr 复合镀层电镀方案 $L_9(3^4)$ 正交表及相应测试结果

Tab 3 Operating plan based on the orthogonal table $L_9(3^4)$ and corresponding test results for (Ag)-Ni/Cr composite plating

Operating plan				Results	
	$I(\text{A} \cdot \text{dm}^{-2})$	$t_1(\text{Ag)-Ni plating})/\text{min}$	$t_2(\text{Cr plating})/\text{min}$	Antibacterial rate/%	R_r/ohm
1	3.5	30	0	94.36	720
2	3.5	35	0.5	83.76	—
3	3.5	40	1	83.83	5400
4	4.0	30	0.5	92.38	3400
5	4.0	35	1	79.68	3800
6	4.0	40	0	90.14	640
7	4.5	30	1	82.21	—
8	4.5	35	0	95.66	540
9	4.5	40	0.5	85.61	4400

Note: “—” indicates that R_r could not be clearly explicated from Fig. 2

综合表 3 与图 2, 考虑 Ag-Ni/Cr 复合镀层的抗菌和耐蚀性 一目了然, 8 和 1 号样品的抗

菌率最高,但耐蚀性较差,甚至劣于不锈钢,而4号样品的抗菌率虽没8和1号的高,但也达到>90%,由此当推该复合镀层的性能效果最佳 相应的电镀工艺条件为:

Ag 粉(200 目)含量4.0 g/L,复合电镀时,温度为50~60℃,pH 4.1~4.4,电流密度(I)=4.0 A·dm⁻²,施镀时间(t_1)=0.5 min,电镀Cr时温度40℃,电流密度100 A·dm⁻²,施镀时间(t_2)=0.5 min

3 结 论

通过正交试验法,得到

(Ag)-Ni/Cr 理想复合镀层电镀工艺中,采用布砂法可使镀层中Ag粒含量大为增加;较之传统活化Ag方法(即用各种浓度的HCl溶液)自制的活化剂以及有效的活化方法,可使原先无明显抗菌作用的Ag粉(200 目)具有抗革兰氏阳性菌(如金黄色葡萄球菌)达到90%的抗菌率

新开发的(Ag)-Ni/Cr 复合镀层是一种兼有抗菌性及耐蚀性的金属表面功能材料,具有广阔的应用前景

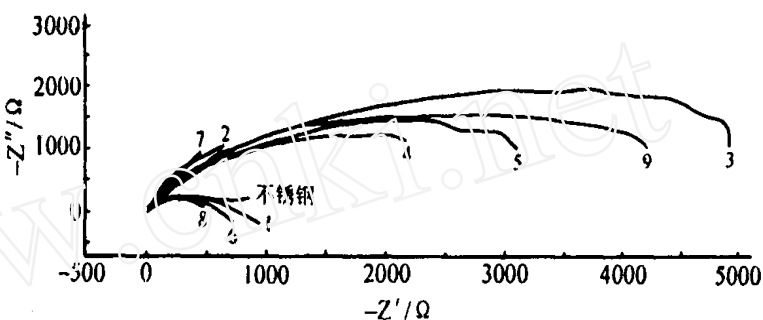


图2 各Ag-Ni/Cr镀层及不锈钢的交流阻抗谱比较(图中曲线序列同表3)

Fig 2 Comparison of the AC impedance spectra for various Ag-Ni/Cr composite coatings and stainless steel (the curves number same as Tab 3)

Development and Study of the (Ag)-Ni/Cr Composite Plating with Antibacterial Properties and Corrosion Resistance

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Abstract: The 3-factor and 3-level orthogonal experiment was designed and through the comparison of the different films' antibacterial properties measured by bacterial colony counting and the corrosion resistance studied with the AC impedance method. The optimal plating conditions of the (Ag)-Ni/Cr composite plating, a novel functional plating, were de-

tem ined

The results have indicated that the (Ag)-Ni/Cr composite plating is characterized by both antibacterial and corrosion resisting properties and has its wide applied prospect

Key words: Orthogonal experiment, Bacterial colony counting, The AC impedance, Antibacterial

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