

电镀锌钛/锆基无铬化学转化膜的制备与耐蚀性能

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摘要: 借助优化钛/锆基化学转化工艺,在碱性无氰镀锌层基体上获得了环保型的无铬转化膜,并与铬酸盐彩色钝化膜作对比. 中性盐雾试验、动电位极化和电化学阻抗谱测试结果表明:钛/锆基化学转化膜出现白锈时间为96 h,达到铬酸盐彩色钝化膜标准,且呈现出较低的腐蚀电流和较高的极化电阻,但钝化特性不如铬酸盐彩色钝化膜明显.

关键词: 镀锌; 无铬钝化; 钛/锆基; 盐雾试验; 耐蚀性能

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为抑制镀锌钢板在空气中尤其是潮湿环境中被腐蚀,通常需要在镀后再经过如铬酸盐钝化或磷化等表面处理以提高其耐蚀性能^[1-2]. 由于环保法规对六价铬和磷酸盐的严格限制,故开发无毒、高耐蚀性和低成本的钝化工艺迫在眉睫^[3-4]. 而至今有关环保型化学转化膜的品质尚难以全面取代传统的化学转化膜,尤其是耐蚀性能仍达不到工业应用要求^[5-6]. 钛/锆基化学转化膜对铝基材目前虽已有少量应用^[7-8],但有关镀锌层的防护方面却鲜有报道.

本文利用氟钛酸和氟锆酸,在碱性无氰电镀镀锌钢基体上得到一种无铬无磷的环保型钛/锆基化学转化膜,并以正交试验优化该工艺条件. 由中性盐雾试验(NSS)考察了该化学转化膜耐盐雾腐蚀性能,以动电位极化和电化学阻抗谱初步探索其耐蚀机理,并与铬酸盐彩色钝化膜的相关性能作对比分析.

1 实验

1.1 样品制备

采用ZB-80碱性无氰光亮镀锌工艺,在经过砂纸打磨和电解抛光的50 mm × 50 mm冷轧钢板上得到厚度为15~20 μm的光亮镀锌层.

然后,在镀锌层之上经过化学转化处理使形成钛/锆基化学转化膜. 工艺流程为:镀锌→纯水洗→化学转化处理(工艺配方见表3)→纯水洗→

室温干燥. 对比试验的铬酸盐彩色钝化工艺^[9]流程与之类似,但干燥步骤改为50℃、10 min.

1.2 耐蚀性能测试

中性盐雾腐蚀试验参照GB/T 10125-1997标准进行. 试样为50 mm × 50 mm镀锌冷轧钢板,分作3组(每组6块),分别为未经处理(A)、铬酸盐彩色钝化(B)和钛/锆基无铬化学转化处理(C),以松香/石蜡=1/1混合物封样,间隔8 h观察1次,以开始出现白色锈点平均时间作为耐蚀性评价标准.

电化学性能测试使用EG&GM 273电化学工作站,三电极体系. 待测样品为工作电极,测试面积0.582 cm²,辅助电极为大面积铂片电极,参比电极为232型饱和甘汞电极. 测试介质为5% (by mass) NaCl溶液(pH=7.0). 动电位极化曲线扫描速率为0.5 mV/s,电位区间为-250~500 mV(vs. OCP),采集数据以CorrView软件作拟合处理. 电化学阻抗谱测试频率范围10⁻²~10⁵ Hz,激励信号幅值为5 mV. 各实验均在室温下经静置10 min后测试.

2 结果与讨论

2.1 钛/锆基化学转化处理工艺

有关钛/锆基化学转化处理的反应机理,目前尚不十分清楚,但一般认为,该过程是由于在酸性

转化液中存在游离 F⁻等刻蚀组分,致使金属基体发生析氢腐蚀,伴随表面微区 pH 值上升,从而使钛、锆等金属离子在基体表面形成复合氧化物沉淀膜^[10]. 作者前期试验也发现,在钛/锆基化学转化处理溶液中,氟钛酸(H₂TiF₆)、氟锆酸(H₂ZrF₆)和氟化氢钠(NaHF₂) 3 种含氟成分对生成转化膜的耐蚀性能影响最为显著.

表 1 正交试验因素水平表

Tab. 1 Factor-level table of the orthogonal experiment			
Test	Factor		
	A	B	C
	H ₂ TiF ₆ (60% ,g/L)	H ₂ ZrF ₆ (45% ,g/L)	NaHF ₂ (g/L)
1	4	6	1.0
2	8	12	1.2
3	12	18	1.4

由表 2 可以看出,3 种因素对钛/锆基转化膜耐蚀性影响程度依次为:C > A > B. 最终的优选方案为 A₂B₁C₂,与试验方案 4 相对应. 表 3 列出据此确定的钛/锆基化学转化处理最佳工艺.

表 2 L₉(3³)正交试验结果

Tab. 2 Results of the L ₉ (3 ³) orthogonal experiment				
Test	Factor			Emergence time of the white rust in NSS test/h
	A	B	C	
1	1	1	1	64
2	1	2	2	56
3	1	3	3	72
4	2	1	2	96
5	2	2	3	64
6	2	3	1	56
7	3	1	3	88
8	3	2	1	56
9	3	3	2	48
$\overline{K_1}$	64.000	82.667	58.667	
$\overline{K_2}$	72.000	58.667	66.667	
$\overline{K_3}$	64.000	58.667	74.667	
R	8.000	24.000	16.000	

表 3 钛/锆基化学转化处理最佳工艺
Tab. 3 Best technology of Ti/Zr based chemical conversion

	Technique parameter
H ₂ TiF ₆ (60% ,g/L)	8
H ₂ ZrF ₆ (45% ,g/L)	6
NaHF ₂ (g/L)	1.2
Additives	Suitable amount
pH	3.5 ~ 4.0
Temperature/℃	30 ~ 40
Processing time/s	60 ~ 90

2.2 中性盐雾试验

以上 3 组试样的中性盐雾试验结果如表 4 所列. 如表镀锌钢板的铬酸盐彩色钝化膜出现白锈的平均时间为101 h,而钛/锆基无铬化学转化膜为 96 h,与之接近,说明后者耐蚀性能已达到应用指标.

2.3 动电位极化曲线

由图1可以看出,经过处理的两种试样(2和

表4 未经处理和经过化学转化处理的镀锌层试样中性盐雾试验结果

Tab. 4 Results of NSS tests for the untreated and chemical converted zinc coatings

	Equal emergence time of the white rust in NSS test/h
Untreated	8
Chromate colour passivation	101
Ti/Zr based chemical conversion	96

3)的自腐蚀电流较未经处理(1)的均明显减小,说明镀锌层经过两种方法处理后均可大大降低其腐蚀速率. 此外,尽管钛/锆转化膜(3)的自腐蚀电位比铬酸盐钝化膜(2)略低,但其自腐蚀电流却更小,对此大致可以认为二者防护性能接近,与盐雾试验结果一致. 图中同时给出,不同处理的两种膜层(2和3)其极化曲线阳极和阴极分支均向低电流密度区移动,此外未经处理试样阳极分支呈现活性溶解趋势,而处理后极化曲线则呈现一定程度的钝化趋势. 表5为根据图1动电位极化曲线的拟合结果,由此可知后两者阳极分支的Tafel斜率 b_a 明显增大,尤其钛/锆基化学转化处理试样更甚;而处理后试样阴极分支的Tafel斜率 b_c 却比未经处理试样下降许多. 因此可见,经过两种化学转化处理后,该镀锌层腐蚀机制已有所转变,主要表现为阳极腐蚀抑制显著,阴极腐蚀则未能抑制,但总体上还是能够有效降低镀锌层的腐蚀速率.

2.4 电化学阻抗测试

图2和图3分别为试样于不同浸泡时间后的电化学阻抗图谱. 可以看出,两种经过处理试样的总阻抗 $|Z|$ 均比未经处理试样提高了10倍以上,而且钛/锆基化学转化膜的总阻抗接近于铬酸盐彩色钝化膜. 说明二者均能起到阻挡腐蚀介质的

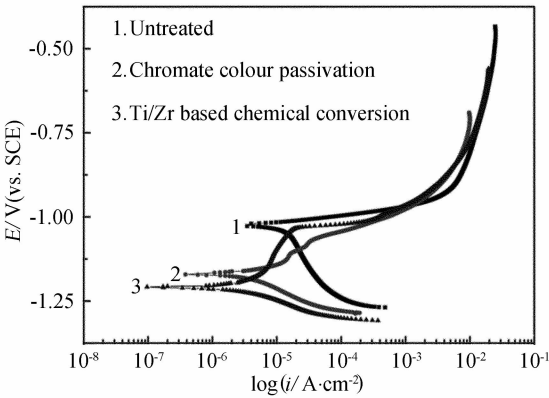


图1 未经处理和经过化学转化处理的镀锌层试样动电位极化曲线

Fig. 1 Potentiodynamic polarization curves of the untreated and chemical converted zinc coatings

作用,且阻挡能力相当. 另外,3种试样还表现出不同的腐蚀机制(图2):其中,未经处理试样呈现单一容抗弧,低频区域出现实部感抗收缩,这是典型的镀锌层活性溶解的腐蚀特征^[11-12];铬酸盐彩色钝化试样高频区出现容抗弧,可归因于该铬酸盐钝化膜的阻抗,而低频区出现的Warburg阻抗特征,意味着镀锌层腐蚀受扩散控制,可以认为该铬酸盐膜的钝化作用在腐蚀初期就表现出来;而经过钛/锆基化学转化处理后的试样,则同时显示为两个弧,其高频区的弧对应于该钛/锆基化学转化膜的阻抗,而低频区的弧则对应于镀锌层的电化学腐蚀,该过程只受电化学反应控制,扩散控制特征不明显,由此说明对钛/锆基化学转化膜,它刚接触腐蚀介质时只是起到物理阻挡作用,钝化机制未能体现出来.

据图2和图3,浸泡10 h后,未经处理样品的 $|Z|$ 急剧下降,而经过处理的两种样品 $|Z|$ 却未有明显变化,说明膜层完好无破损(与宏观观察一致),仍能起到很好的阻挡作用. 此时铬酸盐钝化膜仍呈现出明显的扩散控制特征,钝化作用继续

表5 图1动电位极化曲线拟合结果

Tab. 5 Fitting results of the potentiodynamic polarization curves in Fig. 1

	$I_{\text{corr}}/\mu\text{A} \cdot \text{cm}^{-2}$	$E_{\text{corr}}/\text{mV}$	$R_p/\mu \cdot \text{cm}^{-2}$	b_a/mV	b_c/mV
Untreated	22.01	-1028	978	54.49	981.2
Chromate colour passivation	7.857	-1171	3320	95.67	92.58
Ti/Zr based chemical conversion	5.025	-1208	5121	349.8	85.36

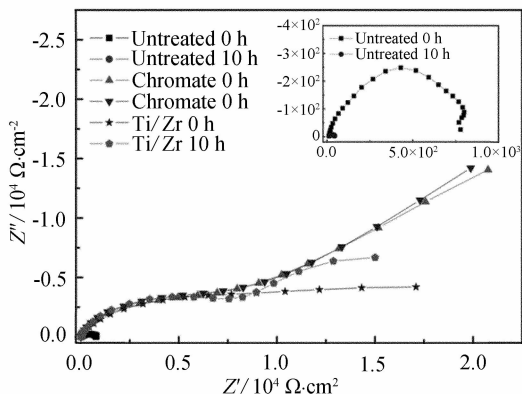


图2 未经处理和经过化学转化处理的镀锌层试样于不同浸泡时间的 Nyquist 图谱

Fig. 2 EIS Nyquist plots of the untreated and chemical converted zinc coatings with different immersion time

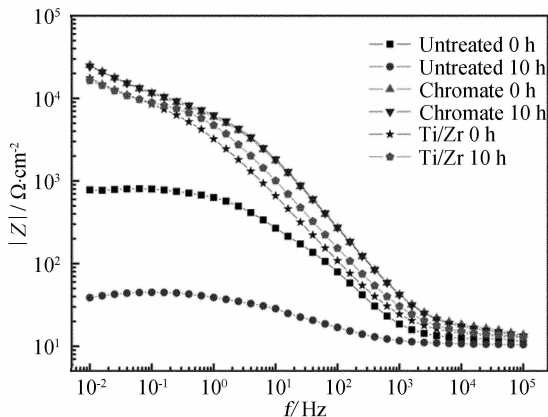


图3 未经处理和经过化学转化处理的镀锌层试样于不同浸泡时间的 Bode 图谱

Fig. 3 EIS Bode plots of the untreated and chemical converted zinc coatings with different immersion time

发挥作用。而钛/锆基化学转化膜的阻抗特征变化较为明显,出现了明显的第2个弧,且其半径明显高于腐蚀初期。这说明随着腐蚀的进行,钛/锆基化学转化膜的防护作用愈加显现,使镀锌层的腐蚀电阻逐渐增加,从而促进钛/锆基化学转化膜的总阻抗 $|Z|$ 仍与铬酸盐钝化膜相互接近,比较之下防护性能并不差。

3 结 论

本文应用钛/锆基化学转化处理工艺,在碱性无氰电镀镀锌钢基体上获得了环保型的无铬化学转化膜,中性盐雾试验出现白锈时间为96 h,达到铬酸盐彩色钝化膜标准。钛/锆基无铬化学转化膜呈

现出了较低的自腐蚀电流和较高的极化电阻,其防护能力接近于铬酸盐彩色钝化膜。

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Study on Preparing Technology and Corrosion Resistance of Ti/Zr Based Chromium-free Chemical Conversion Coating on Zinc Electroplating Layer

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Abstract: In this paper, we obtained environmental-friendly chromium-free chemical conversion coating on the non-cyanide alkaline zinc electroplating layer by employing the optimized Ti/Zr based conversion technique. At the same time, the performances of the Ti/Zr based conversion coating were compared with chromate colour passivation coating. The corrosion resistances of the conversion coatings were investigated by using neutral salt spray (NSS) test, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The results showed that the white rust appeared after 96 hours when the NSS test was performed on the Ti/Zr based conversion coating, which was close to the corrosion resistance rating of chromate colour passivation coating. Compared with the chromate passivation coating, the Ti/Zr based conversion coating showed lower corrosion current and higher polarization resistance. However, the passivation characteristic of the former was less evident than the latter.

Key words: zinc electroplating; chromium-free chemical conversion; Ti/Zr based; salt spray test; corrosion resistance