

316L 不锈钢电化学着黑色研究

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摘要: **目的** 调整 316L 不锈钢表面组成结构, 改善表面性能, 获得表面着黑色最佳电化学工艺条件。**方法** 通过电化学方法在除油抛光活化的 316L 不锈钢表面发生阳极氧化, 研究了活化液浓度、阴阳极板面积比、电解液的硼酸用量、电化学氧化电流密度、终止电压、阳极氧化时间、氧化温度对着色膜颜色效果、结合力、重现性的影响; 研究了着黑色不锈钢与未着色不锈钢在酸碱盐水溶液体系中的表面腐蚀性能; 探讨了着色条件对着色膜性能的影响及着色机理。**结果** 磷酸活化液浓度对着色效果影响显著, 浓度越高活化的不锈钢板着黑色越纯正, 但膜层结合性变差; 着色液组成决定着着色膜颜色变化的范围。着色时间是影响着色膜颜色的主要因素, 随着着色时间的延长, 膜层颜色呈现青、黄、红、黑变化。温度是影响着色膜层与不锈钢基材结合紧密程度的主要因素, 25 °C 下形成的膜层与基体的结合最为紧密; 电极阴阳极面积比是影响着色膜均匀程度的主要因素, 阴阳极面积比为 1:1 时, 着色膜的一致性最好。**结论** 获得了 316L 不锈钢着纯正黑色膜层的最佳条件, 磷酸活化液浓度为 1.5 mol/L, 电解着色液组成为 30 g/L $K_2Cr_2O_7$ +20 g/L $MnSO_4 \cdot 4H_2O$ +40 g/L $(NH_4)_2SO_4$ +10 g/L H_3BO_3 , 阴阳极板对应面积比为 1:1, 着色温度为 25 °C, 着色电压为 2~4 V, 阳极电流密度 (D_A) 为 0.20 A/dm², 阳极氧化时间为 720 s。着黑色不锈钢膜层腐蚀性研究表明在含氯离子的中性水溶液环境中耐腐蚀性明显提高。

关键词: 电化学着色; 阳极氧化; 环保; 彩色不锈钢; 腐蚀曲线

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Electrochemical Black of 316L Stainless Steel

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ABSTRACT: The purpose of this study is to obtain the best electrochemical process conditions for surface blackening by adjusting the surface composition and structure of 316L stainless steel and improving the surface performance.

The electrochemical method was adjusted to oxide the surface of 316L stainless steel after degreasing, polishing and

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activation processes. The effects of the concentration of the activated solution, the area ratio of the anode and cathode plates, the amount of boric acid in the electrolyte, the current densities of the electrochemical oxidation, the termination voltages, the anodization time and the oxidation temperature on the coloring effect, binding force and reproducibility of the colored film were studied in detail; the surface corrosion resistance performance of the blackened stainless steel and the uncolored stainless steel in acid, alkali, and neutral salt solution systems were analyzed respectively; the effects of coloring conditions on the performance of the coloring film and the coloring mechanism were also discussed.

The results showed that the concentration of phosphoric acid activation solution had a significant impact on the coloring effect, the higher the concentration, the more pure the black color of the activated stainless steel plate would be, but the bonding force of the film with the substrate would become worse; the composition of the coloring liquid determined the ranges of color change of the coloring film; the coloring time was the main factor that would affect the color of the colored film, with the extension of the coloring time, the color of the film changes into blue, yellow, red, and black colors in series; the temperature was the main factor that would affect the bonding force of the color film layer with the stainless steel substrate. It is found that the film layer formed at 25 °C displayed the strongest bonded force with the substrate. The area ratio of the anode to cathode was the main factor that would affect the uniformity of the colored film, when the area ratio of the anode to cathode was 1 : 1, the formed colored film showed the most uniform film. The result shows that the best conditions for 316L stainless steel with pure black colored film are obtained, the concentration of phosphoric acid activated solution is 1.5 mol/L, the composition of the electrolytic coloring solution is $\text{K}_2\text{Cr}_2\text{O}_7$ 30 g/L, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ 20 g/L, $(\text{NH}_4)_2\text{SO}_4$ 40 g/L and H_3BO_3 10 g/L, the corresponding area ratio of the cathode to anode plate is 1 : 1, the coloring temperature is 25 °C, the coloring voltage is from 2.0 to 4.0 V, the anode current density (D_A) is 0.20 A/dm², and the anode oxidation time is about 720 s; the study on the corrosion resistance of the black stainless steel film showed that the corrosion resistance is significantly improved in a neutral aqueous solution containing chloride ions.

This study provides a strategy to color the stainless steel plate into a series of colors under mild conditions by utilizing electrochemical process, and the colored film on the surface shows superior wearing resistance, corrosion resistance, and film contaces tightly with the stainless steel sbustrate.

KEY WORDS: electrochemical coloring; anodic oxidation; environmental protection; colored stainless steel; corrosion curve

彩色不锈钢作为一种优越的工程材料,自诞生以来,其表面着色技术得到快速发展^[1-3]。当今以铬酐-硫酸混合液为着色液的不锈钢化学着色法虽然已经实现了工业化,但操作温度高、能耗高,且铬污染环境^[4]等,制约了工艺发展。20 世纪末,化学浸渍法、电解着色法得到广泛应用^[5-8],在化学着色基础上,通过调整着色液组成,采用电化学阳极氧化技术进行电化学着色研究得到快速发展。邓妹皓等^[9]对 1Cr18Ni9Ti 不锈钢着银灰色研究表明,电解法获得的膜层更为细腻致密,耐腐蚀性更强;电化学着色法在低铬含量着色液和低着色温度下对不锈钢着黑色,获得较理想膜层^[10-11]。因此,简便快捷、经济适用、低能耗、低污染、高品质的电化学着色方法研究成为当今不锈钢着色研究的主要方向。

1 试验

1.1 不锈钢着色的预处理

本试验采用市售 316L 不锈钢,加工成 100 mm×20 mm×1 mm,试样预处理^[12-13]如下。

(1) 除油:采用含氢氧化钠 80 g/L、磷酸三钠

30 g/L、十二烷基硫酸钠 50 g/L 洗液,浸泡温度 45~60 °C,时间 600~1 200 s,清水冲淋 10~12 s,热风干燥 120~240 s。

(2) 抛光:按机械抛光、电解抛光顺序预处理试样。

①机械抛光:用 80#、100#砂纸将不锈钢试片逐级打磨,使其表面光滑平整。

②电解抛光:以不锈钢试片为阳极,石墨板作为阴极,阴阳极面积比 1 : 1。

电解抛光液配方如表 1 所示,工艺条件如表 2 所示。

(3) 酸洗活化:抛光表面活化对电解着色质量影响显著^[14-15],采用 0~2.1 mol/L 磷酸在 25 °C 浸泡 300~600 s 获得了良好活化效果。

表 1 电解抛光液配方

Tab.1 Fomulation of the aqueous electrolyte for polishing

Name	Phosphoric acid	Sulphuric acid	Glycerol	CrO ₃
Content	200 mL/L	280 mL/L	4 mL/L	25 g/L

表 2 电解抛光工艺条件

Tab.2 Process for electrolytic polishing

Name	Current	Temperature	Polishing time
Parameter	30 A/dm ²	50 °C	240 s

1.2 着色处理

(1)着色液组成: 在 $\text{K}_2\text{Cr}_2\text{O}_7$ 20~40 g/L+ $(\text{NH}_4)_2\text{SO}_4$ 20~50 g/L+ MnSO_4 10~20 g/L+ H_3BO_3 0~25 g/L 的着色液组成下进行了不同组成、极板面积比、温度、时间进行着色试验, 确定了最佳试样制备条件。

(2)着色条件: 温度 18~35 ℃, 时间 10~960 s, 不同阴阳极面积比例, 不同恒电流操作。

(3)电源: 采用 Maynuo M8811 型直流电源进行恒电流电化学着色^[16-18]试验, 研究着色时间、着色电流对着色的影响。电解着色槽同抛光设备。

1.3 着色膜层的耐蚀性能检测

运用 Solartron 公司 Solartron1287+1255B 电化学工作站, 选择 5 mV/s 稳态阳极极化方法, 在碱性、酸性、氯离子液体环境下对着色不锈钢进行耐蚀性检测^[19-20]。

1.4 着色膜与基材结合力分析

采用市售辉柏嘉橡皮擦对着色试样表面整体进行 N 次反复擦拭, 考察结合力^[21]。

1.5 着色膜表面微观形貌分析

运用 Keyence 公司的 VHX-950F 数码显微系统, 观察不同色膜表面微观形貌, 探讨不同着色时间表面膜层颜色形成机理。

2 结果与讨论

2.1 活化液浓度对着黑色效果的影响

除油抛光后的不锈钢, 表面活化对着色膜性能影

响显著, 活化时间延长, 越有利于不锈钢表面深色形成^[22-23]。将不锈钢浸在稀磷酸或盐酸中, 可除去薄氧化层, 提高着色层的结合力和色彩均匀性^[24-25]。磷酸活化液浓度对着色效果的影响见表 3, 电解活化时间 720 s。活化阴阳极板面积均为 20 mm×20 mm。

由表 3 可知, 活化液的浓度直接影响着色膜层的颜色、结合强度。活化液浓度提高, 膜层颜色由黄色变化至纯黑色, 结合力增强, 随浓度继续提高, 黑色膜颜色掺杂, 膜层脱落。可认为活化液达 1.5 mol/L 时金属表面处于良好的活性状态, 不锈钢基体本身所含的金属原子在通电后会趋于更易失去电子成为离子, 在着色液和不锈钢基体之间的界面上, 与着色液中的离子共同生成均匀稳定着色膜, 膜层与基体的过渡结合很强, 膜层致密且耐摩擦而不脱落; 同试验条件下, 所得膜层颜色均匀, 膜层致密, 重现性好, 色泽光亮。

2.2 阴阳极面积比对着黑色效果的影响

在着色液组成 30 g/L $\text{K}_2\text{Cr}_2\text{O}_7$ +20 g/L $\text{MnSO}_4\cdot 4\text{H}_2\text{O}$ +40 g/L $(\text{NH}_4)_2\text{SO}_4$ + 10 g/L H_3BO_3 , 温度 25 ℃, 阳极电流密度 0.20 A/dm², 时间 720 s。改变阴阳极板面积比, 获得着色膜性能见表 4。

由表 4 可知, 不同的阴阳极面积比, 垂直于极板平面方向上产生的电力线强度分布不一致, 电化学着色膜颜色、致密性、重现性无明显影响, 着色膜最后都生成了纯黑色膜层, 不同之处在于结合强弱差别较大, 这说明阴阳极面积比的不同致使相应生成的膜层结合力也不同。当选择阴阳极面积比为 1 : 1 时, 着色膜层的结合力最好, 其原因是 2 个平行对应的面积大小相同的极板之间所产生的电力线分布是最均匀的, 因而膜层结合力的一致性也最好。

表 3 磷酸浓度对着黑色效果的影响 (着色时间: 720 s)
Tab.3 Effect of phosphoric acid concentration on blackening (coloring time: 720 s)

H_3PO_4 concentration/(mol·L ⁻¹)	Film color	Film coloring effect				Film adhesion
0	Light yellow	Uneven, loose reproducibility	film	and	poor	Extremely poor adhesion, decolorization by wiping once
0.3	Tan	Uniform, loose, dark reproducibility	film	and	poor	Very poor adhesion, decolorization by wiping 23 times
0.6	Bright black	Scattered spots, bright reproducibility		and	poor	Very poor adhesion, decolorization by wiping 52 times
0.9	Bright black	Uniform, dense, bright reproducibility	film	and	good	Poor adhesion, the film contains many bubbles
1.2	Bright black	Uniform, dense, bright reproducibility	film	and	good	Good adhesion, falling off partially by wiping 143 times
1.5	Bright black	Uniform, dense, bright reproducibility	film	and	good	Strong adhesion, falling off a little by wiping 285 times
1.8	Yellow black	Uniform, dense dark reproducibility	film	and	poor	Poor adhesion, decolorization by wiping 30 times
2.1	Black	Uneven, loose, dark reproducibility	film	and	poor	Very poor adhesion

表 4 阴阳极面积比对着黑色效果的影响 (着色时间: 720 s)
Tab.4 Effect of area ratio of cathode and anode on blackening (coloring time: 720 s)

$S_{\text{cathode}}/S_{\text{anode}}$	Color	Coloring effect	Film adhesion
0.5 : 1	Bright black	Uniform color, dense film, bright color and good reproducibility	Poor adhesion, falling off by wiping 52 times
1 : 1	Bright black	Uniform color, dense film, bright color and good reproducibility	Good adhesion, falling off by wiping 218 times
2 : 1	Bright black	Uniform color, dense film, bright color and good reproducibility	Slightly poor adhesion, falling off by wiping 135 times
3 : 1	Bright black	Uniform color, dense film, bright color and good reproducibility	Poor adhesion, falling off by wiping 135 times

2.3 硼酸用量对着黑色效果的影响

根据 2.2 节的着色条件, 调整硼酸用量, 获得着色膜性能如表 5 所示。

由表 5 可以得出, 硼酸用量低于 10 g/L 时, 膜与基材结合变差; 硼酸用量选取 10 g/L 时, 所得膜层的结合力强度最为理想; 硼酸用量过高, 着色液 pH 值愈低, 所得膜层表面会很粗糙, 甚至会出现膜层疏松

的现象。其原因是 pH 值愈低, 溶液中的 H^+ 浓度越高, 电解时大量析氢, 致使膜层内应力增大或不易形成稳定膜层。结果表明, 硼酸引入量对膜层的机械性能起着重要作用。

2.4 电流密度对着黑色效果的影响

根据 2.2 节的着色条件, 调整着色电流密度, 控制着色时间, 不同电流密度时的着色性能见表 6。

表 5 硼酸用量对着黑色效果的影响 (着色时间: 720 s)
Tab.5 Effect of boric acid dosage on blackening (coloring time: 720 s)

Dosage/(g·L ⁻¹)	color	Coloring effect	Film adhesion
0	Bright black	Uniform and dense film, bright and good reproducibility	Poor adhesion, dry cracks
6	Bright black	Uniform and dense film, bright and good reproducibility	Very poor adhesion, falling off by light wiping
10	Bright black	Uniform and dense film, bright and good reproducibility	Good bonding, falling off by wiping 123 times
14	Black	Uniform and dense film, dark and good reproducibility	Poor adhesion, falling off by wiping 35 times
18	Black	Uniform and dense film, dark and poor reproducibility	Very poor adhesion, falling off by wiping 8 times
24	Black	Uniform and dense film, dark and poor reproducibility	Very poor adhesion, falling off by wiping 8 times

表 6 电流密度对着色效果的影响
Tab.6 Effect of current density on blackening

Current density/(A·dm ⁻²)	Time/s	Color	Final voltage/V	Coloring effect	Film adhesion
0.002	360	Light yellow	1.47	Uniform, dense, bright and good reproducibility	Wiping 53 times without falling off, and color becomes lighter
0.008	330	Yellow	1.59	Uniform, dense, bright and good reproducibility	Wiping 55 times without falling off, and color becomes lighter
0.01	360	Dark yellow	1.70	Uniform, dense, bright and good reproducibility	Wiping 53 times without falling off, and color becomes lighter
0.08	360	Reddish brown	2.10	Uniform, dense, bright and good reproducibility	Wiping 60 times without falling off, and color becomes lighter
0.16	420	Red black	2.46	Uniform, dense, bright and good reproducibility	Wiping 60 times without falling off, and color becomes lighter
0.20	360	Black	2.55	Uniform, dense, bright and good reproducibility	Wiping 90 times without falling off, and color becomes lighter
0.24	390	Black	2.68	Uniform, dense, bright and good reproducibility	Wiping 90 times without falling off, and color becomes lighter
0.28	390	Black	2.70	Uniform, dense, bright and good reproducibility	Wiping 100 times without falling off, and color becomes lighter
0.32	390	Black	2.75	Uniform, dense, bright and good reproducibility	Wiping 100 times without falling off, and color becomes lighter
0.36	360	Black	2.80	Uniform, dense, bright and good reproducibility	Wiping 100 times without falling off, and color becomes lighter

由表 6 可知, 着色时间一致时, 电流密度越小, 膜层越薄, 颜色越浅; 电流密度越大, 生成的膜层越厚, 颜色越深, 360~420 s 就表现出黑色; 电流密度在 0.28 A/dm² 左右时, 所得着色膜层的结合力最好; 电流密度由小到大增加时, 膜层颜色由青、浅黄、黄、黄红色、红棕到黑色变化, 电流密度影响了膜层的颜色、光泽以及结合强度; 电流密度过大时, 膜层疏松, 多孔易于脱

落, 应该是膜层形成太快所致。实际操作中在 0.20 A/dm² 恒电流密度下控制着色时间或控制终止电压(终止电压与着色时间呈一一对应关系)可获得相应着色膜。

2.5 温度对着黑色效果的影响

根据 2.2 节的着色条件, 研究了室温条件下温度波动对着色膜的影响, 结果见表 7。

表 7 温度对着黑色效果的影响 (着色时间: 720 s)
Tab.7 Effect of temperature on blackening (coloring time: 720 s)

Temperature/℃	color	Coloring effect	Film adhesion
18	Brown Black	Uneven, dark brown black, dense film	Poor adhesion, falling off by wiping 28 times
25	Bright black	Uniform, bright, dense film and good reproducibility	High bonding strength, falling off slightly after wiping 262 times
28	Bright black	Uniform, bright, dense film and good reproducibility	General adhesion, falling off by wiping 83 times
31	Bright black	Uniform, bright, dense film and good reproducibility	Poor adhesion, falling off by wiping 38 times
34	Black	Uniform, dense, dull film with poor reproducibility	Very poor adhesion, falling off by wiping 15 times

由表 7 可知, 控制温度在 25 ℃左右时, 着黑色效果最明显, 结合力强度最为理想; 温度升高, 膜层结合力变差。着色温度对氧化膜性能的影响较大, 当温度过高时, 生成膜脆性大, 易开裂。

2.6 时间对着色膜层颜色的影响

根据 2.2 节的着色条件, 不同着色终止时间, 膜层相关性能变化如表 8 所示。

表 8 时间对着色膜层颜色的影响
Tab.8 Effect of time on blackening

Time/s	Coloring effect
10	Cyan, transparent
28	Light yellow, transparent
40	Light red, transparent
60	Yellow circle around the center, orange in the middle
120	Light black links orange below the liquid level line, unevenly
180	Purplish red, light purplish red at the peripheral edge
240	Black at upper part, slightly purplish red at the lower edge
360	Black film
480	Black and smooth
720	Bright black and smooth
960	Bright black and smooth

由表 8 可知: 着色时间低于 40 s 获得纯亮的浅色膜层, 均匀一致; 着色时间在 40~480 s 之间, 着色膜层颜色一致性较差, 随时间延长颜色变化由液面向下总体呈现逐渐增黑且稳定下来的趋势, 该段内出现了红棕、棕褐色膜; 480~960 s 时间段内均匀黑亮膜层出现且稳定。40~480 s 之间出现杂色环及液面线附近较黑, 向下紫红, 可能是试验条件下液面线附

近电力线密度较高, 向下特别是极板最底边缘处电力线密度变小所致。总体上根据着色时间延长, 生成了比较稳定的青色-黄色-红色-血红色-棕褐色-黑色系列样品, 在 720 s 获得了理想黑色不锈钢膜。试验条件优化试制出的多种色彩着色不锈钢如图 1 所示。黑色膜层着色优化条件如表 9 所示。此方案生产着色膜色彩丰富, 可选品种多, 尤其黑色色膜更为漂亮美观。

2.7 黑色膜层的微观结构及显色机理

经过 0~720 s 电化学着色获得着系列色泽的不锈钢膜层, 其光学微观形貌如图 2 所示。相较于光滑的不锈钢基体微观形貌(图 2a), 着色后的不锈钢膜层(图 2b—d)表面生成了许多类似“粒子”状颜色较深的微观凸起, 且随电化学氧化时间延长, 粒子颜色由浅到深, 粒子分布密度由低到高, 且粒子粒径在微米级别以下, 这说明电化学着色过程中在不锈钢电极表面生成了由氧化物粒子组成的薄膜, 随着微粒数增加, 吸光性增强, 从而使着色膜的颜色逐步从浅黄色向黑色过渡。

2.8 着色膜的耐蚀性

着黑色不锈钢与未着色不锈钢在 3%碳酸钠溶液中的腐蚀曲线见图 3, 在 10%冰乙酸溶液中的腐蚀曲线见图 4, 在 3%氯化钠溶液中的腐蚀曲线见图 5。

由图 3 可知: 在 0~0.82 V 之间, 黑色不锈钢膜层和未着色不锈钢表面氧化膜结构稳定, 在 3%碳酸钠溶液中均未发生表面溶解; 在 0.82 V 之后, 未着色不锈钢氧化膜和黑色不锈钢的着色膜开始溶解, 但着色膜的腐蚀电流密度增加明显慢于未着色膜, 表明着色膜层抗氧化腐蚀能力高于未着色不锈钢。

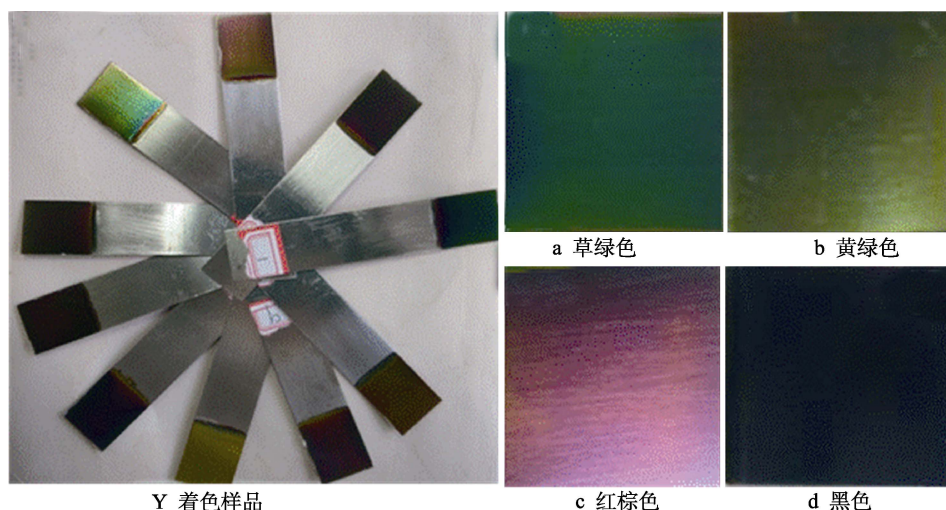


图 1 着色试样及彩色膜图案

Fig.1 Colored sample and color film pattern (Y-coloring sample, a-grass green, b-yellowish green c-reddish brown, d-black)

表 9 黑色膜主要着色技术指标
Tab.9 Main technical indicators of black film

Project	Name/ Parameter
Composition of coloring solution	$K_2Cr_2O_7$ 30 g/L+ $MnSO_4 \cdot 4H_2O$ 20 g/L+ $(NH_4)_2SO_4$ 40 g/L+ H_3BO_3 10 g/L
Coloring voltage	2~4 V
Current density	0.20 A/dm ²
Coloring time	720 s

由图 4 可知：在 0~0.85 V 之间，着色不锈钢膜层和未着色不锈钢氧化膜层电流密度随极化电压变

化相同，两者均未受 10% 冰乙酸溶液的影响；在 0.85~1.12 V 之间，着色不锈钢膜电流密度随极化电压增加，表明着色不锈钢腐蚀溶解快而未着色不锈钢腐蚀溶解慢；在 1.12~1.42 V 之间，着色不锈钢膜层沉积速度大于溶解速度，产生了短暂的钝化，结构变得更加稳定；而未着色不锈钢氧化膜的腐蚀作用并未减弱，还继续缓缓增加；在 1.42 V 之后，着色不锈钢的腐蚀溶解增加，自腐蚀电位发生正移，相比于未着色不锈钢自腐蚀电流密度下降，这表明在 1.42 V 之后，着色不锈钢的耐腐蚀性能优于未着色不锈钢的耐腐蚀性能。

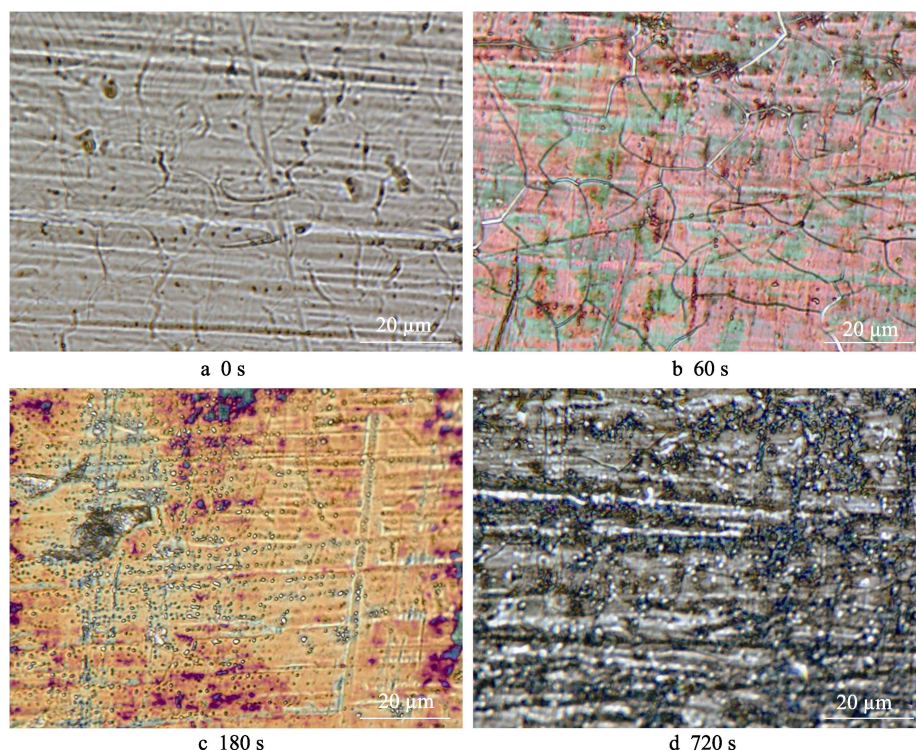


图 2 不同着色时间下不锈钢表面的微观形貌

Fig.2 Microscopic morphology of stainless steel surface under different coloring time

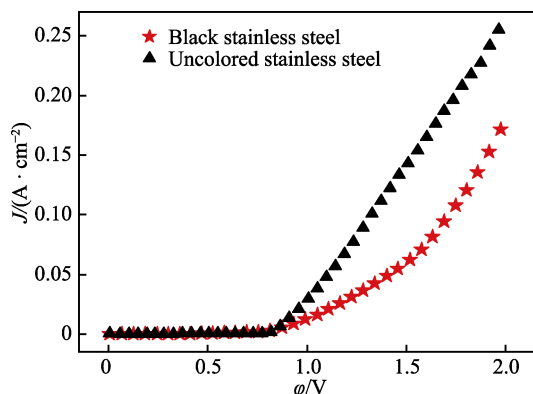


图 3 着黑色不锈钢与未着色不锈钢在 3% 碳酸钠溶液中的腐蚀曲线

Fig.3 Corrosion curves of black stainless steel and uncolored stainless steel in 3% sodium carbonate solution respectively

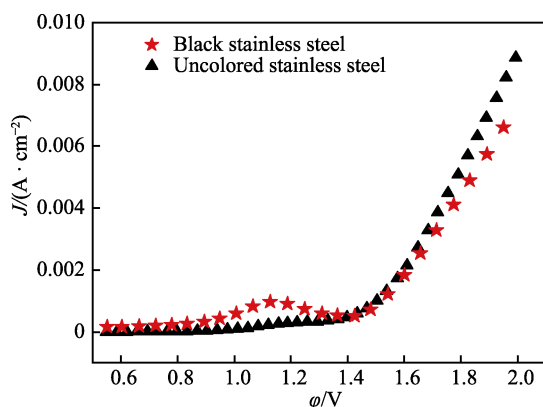


图 4 着黑色不锈钢和未着色不锈钢在 10% 冰乙酸溶液中的腐蚀曲线

Fig.4 Corrosion curves of black stainless steel and uncolored stainless steel in 10% glacial acetic acid solution respectively

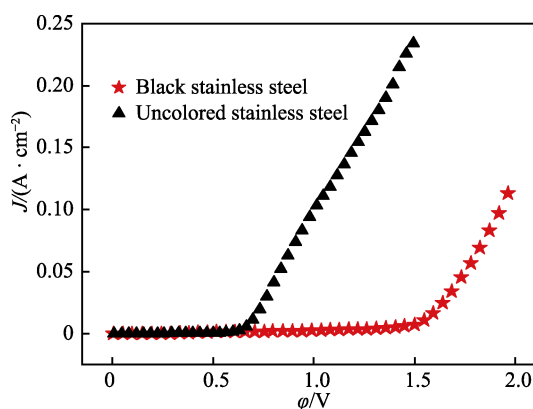


图 5 着黑色不锈钢和未着色不锈钢在 3% 氯化钠溶液中的腐蚀曲线

Fig.5 Corrosion curves of black stainless steel and uncolored stainless steel in 3% NaCl solution respectively

由图 5 可知: 在 0~0.6 V 之间, 未着色不锈钢和着色不锈钢在 3% 氯化钠溶液中电流密度值接近 0.00 A/cm^2 , 说明 2 种膜层均具有良好的耐腐蚀性;

极化电位高于 0.6 V 后, 未着色不锈钢的腐蚀曲线陡升而黑色不锈钢的电流密度几乎不变, 表明黑色不锈钢膜的耐腐蚀性强于未着色不锈钢; 在极化电位高于 1.5 V 后, 着黑色不锈钢的腐蚀曲线陡升, 说明黑色不锈钢腐蚀作用开始加剧。比较黑色不锈钢的自腐蚀电位与未着色不锈钢的自腐蚀电位明显正移了 0.9 V, 表明黑色不锈钢在 3% 氯化钠溶液中比未着色不锈钢具有更优越的耐腐蚀性能。

3 结论

1) 活化液 H_3PO_4 浓度显著影响膜层结合强度, 当活化液为 1.5 mol/L 磷酸时, 所得膜层的结合力最好, 同时颜色均匀、致密、色泽光亮。

2) 最佳着黑色液配方以及工艺参数: $\text{K}_2\text{Cr}_2\text{O}_7$ 30 g/L+ $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ 20 g/L+ $(\text{NH}_4)_2\text{SO}_4$ 40 g/L+ H_3BO_3 10 g/L。操作条件: 温度 25°C , 电压 2~4 V, 阳极电流密度 (D_A) 0.20 A/dm^2 , 时间 720 s。

3) 在恒电流密度 0.20 A/dm^2 时, 720 s 时着黑色膜层的综合质量指标最理想; 着色温度在 25°C 左右时, 黑色膜层致密, 结合力强度最为理想。选择平行对应面积比 1:1 的阴阳极板时, 着色膜层最均匀, 颜色纯正。

4) 黑色氧化膜层提高了 316L 不锈钢试片在碱性、酸性条件下的耐腐蚀性, 显著改善了氯离子环境下的耐腐蚀性。

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