

不同离子交换体对碳钢在有机涂层下腐蚀行为的影响

厦门大学化学化工学院(361005) 王周成 杜荣归 胡艳玲 林昌健 周绍民

[摘要] 为探讨在离子选择性涂层中离子交换体的不同对金属腐蚀行为的影响,用动电位扫描极化曲线和电化学交流阻抗技术研究了A3钢表面涂装含不同离子交换体的阴离子选择性和阳离子选择性有机涂层在3%NaCl溶液中的腐蚀和电化行为。实验结果表明,同一种涂层中不同离子交换体对碳钢的腐蚀行为有不同影响,可以通过选择具有缓蚀作用的交换离子来改善涂层的防蚀性能。在阴离子选择性涂层中交换离子为 MoO_4^{2-} 型时对碳钢的防蚀性能比交换离子为 SO_4^{2-} 型好,在阳离子选择性涂层中则交换离子为 Na^+ 型时比交换离子为 NH_4^+ 型好。

[关键词] 有机涂层; 腐蚀行为; A3钢; 离子交换体

[中图分类号] TG172.7

[文献标识码] A

[文章编号] 1001-1560(2001)10-0009-02

1 前言

离子选择性有机涂层是近年来依据金属钝化的双极性新概念^[1],在原理和技术上结合钝化膜和有机涂层的特点而发展起来的新型涂层。利用掺杂不同离子交换体可制备出阴离子选择性、阳离子选择性以及由阴、阳离子选择性构成的双极性有机涂层^[2]。多种电化学方法和表面分析技术的实验结果表明,离子选择性有机涂层的不同结构和组成对金属的腐蚀电化行为影响很大,双极性和阳离子选择性涂层的防蚀性能较好,而阴离子选择性涂层的防蚀性能较差^[3]。本文着重探讨在同一类型的离子选择性涂层中,离子交换体的不同对金属腐蚀行为的影响。

2 实验

2.1 材料制备

选用经离子交换处理过的 SO_4^{2-} 型和 MoO_4^{2-} 型阴离子交换树脂作为阴离子交换体,磷钼酸铵 $[(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}]$ 和 Na^+ 型阳离子交换树脂作为阳离子交换体,按固体分1:10(质量比)与酚醛清漆混合配制成离子选择性涂料。试样为A3钢,加工成圆柱状,经金相砂纸逐级打磨至光亮、无水乙醇除油后,分别涂装阴离子选择性和阳离子选择性涂料,涂层厚度为75~80 μm 。涂装试样在80 $^\circ\text{C}$ 烘干0.5h,取出在室温下存放备用,工作面积为1.0 cm^2 ,用环氧树脂封涂非工作面。

2.2 试验方法

采用EG&G PARC M352腐蚀测试系统测量涂装电极的极化曲线,动电位扫描速度为1 mV/s 。采用EG&G PARC M378电化学阻抗测试系统,配合5208锁相分析仪和273恒电位仪在腐蚀电位下测定电化学阻抗谱,频率范围0.01 Hz ~100 kHz ,激励信号取10 mV 。试验溶液为3%NaCl,以饱和甘汞电极为参比电极,铂片为辅助电极,实验在室温(约25 $^\circ\text{C}$)下进行。

3 结果与讨论

3.1 动电位扫描极化曲线

图1和图2是碳钢表面涂装含不同离子交换体的阴离子和阳离子选择性涂层在3%NaCl溶液中浸泡16天后的动电位扫描极化曲线,其腐蚀电位、腐蚀电流和极化电阻的数值见表1。

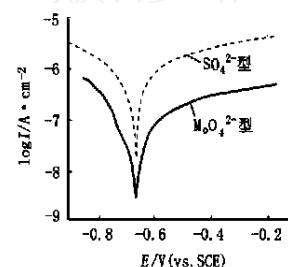


图1 A3钢涂装含不同类型阴离子交换体的酚醛涂层在3%NaCl溶液中的动电位扫描极化曲线

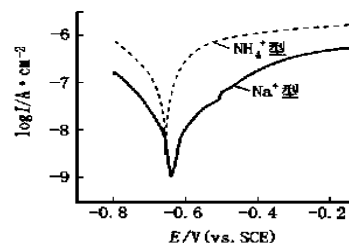


图2 A3钢涂装含不同类型阳离子交换体的酚醛涂层在3%NaCl溶液中的动电位扫描极化曲线

表1 A3钢涂装含不同离子交换体的酚醛涂层在3%NaCl溶液浸泡16d后的腐蚀数据

交换离子	MoO_4^{2-}	SO_4^{2-}	Na^+	NH_4^+
$E_{\text{corr}}(\text{V})$	-0.646	-0.650	-0.612	-0.638
$I_{\text{corr}}(\text{A}/\text{cm}^2)$	1.8×10^{-8}	7.2×10^{-7}	5.1×10^{-9}	3.2×10^{-8}
$R_p(\text{cm}^2)$	9.4×10^5	6.7×10^4	3.5×10^6	5.6×10^5

[收稿日期] 2001-04-25

由表 1 可见,在阴离子选择性涂层中,阴离子交换体为 MoO_4^{2-} 型时腐蚀电流比 SO_4^{2-} 型时小 1 个数量级,而在阳离子选择性涂层中阳离子交换体为 NH_4^+ 型腐蚀电流比 Na^+ 型时大近 1 个数量级,这表明在同一种类型的离子选择性涂层中,不同离子交换体对碳钢防锈性能的影响是不一样的。这可以认为是由于不同交换离子对碳钢的腐蚀行为有不同的影响所致。有些离子对碳钢在介质中的腐蚀具有缓蚀作用,当碳钢在涂层破损的情况下发生局部腐蚀时,具有缓蚀性的离子能抑制局部腐蚀的发生或减缓腐蚀,而有些离子则对碳钢的局部腐蚀有促进作用。

MoO_4^{2-} 是常用的缓蚀性阴离子^[4],Robitaille 的研究结果表明^[5],在钢管冷却水系统中,含 10~20 mg/L 的 MoO_4^{2-} 就能起到有效的缓蚀作用,尤其是在含有高浓度 Cl^- 的水质中。而 Music 等人对钢在水和 $(\text{NH}_4)_2\text{SO}_4$ 溶液中腐蚀行为的研究结果则表明^[6], NH_4^+ 对碳钢具有强腐蚀性,对碳钢的局部腐蚀过程有促进作用。尽管阴离子选择性涂层对金属的保护效果比较差^[2-3],但可以通过选择具有缓蚀作用的离子交换体来改善其防锈性能;同样地,虽然阳离子选择性涂层对金属的保护效果比较好,但如果离子交换体选择不当,也可能降低其防锈性能。

3.2 电化学交流阻抗谱

为了进一步说明不同离子交换体对 A3 钢腐蚀行为的影响,对这 4 种涂装钢样进行电化学交流阻抗谱测量。

图 3 和图 4 分别是碳钢表面涂装上述 4 种离子选择性涂层在 3%NaCl 溶液中浸泡 16 天的电化学交流阻抗 Nyquist 图。从图 3 和图 4 可看出,碳钢表面涂装阴离子选择性涂层的 Nyquist 图呈现 Warburg 阻抗特征,而涂装阳离子选择性涂层的 Nyquist 图呈现双容抗弧特征,二者的等效电路见文献[7]。由各自等效电路经数据拟合计算得到的元件参数值见表 2。

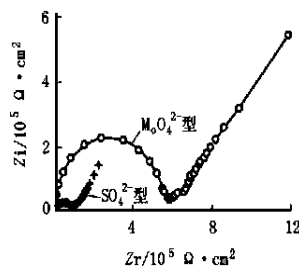


图 3 A3 钢涂装含不同类型阴离子交换体的酚醛涂层在 3%NaCl 溶液中的电化学阻抗谱

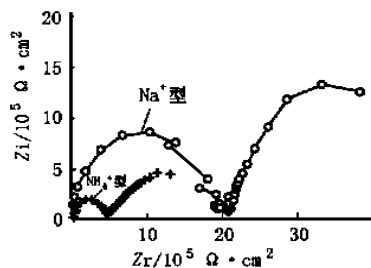


图 4 A3 钢涂装含不同类型阳离子交换体的酚醛涂层在 3%NaCl 溶液中的电化学阻抗谱

表 2 A3 钢涂装含不同离子交换体的酚醛涂层在 3%NaCl 溶液浸泡 16 天后的交流阻抗参数

交换离子	MoO_4^{2-}	SO_4^{2-}	Na^+	NH_4^+
Cc (pF/cm ²)	168	284	142	201
Rp (Ω·cm ²)	5.45×10^5	8.72×10^4	—	—
Zw (Ω·cm ²)	1.38×10^6	4.29×10^5	—	—
Rc (Ω·cm ²)	—	—	1.97×10^6	4.41×10^5
Rt (Ω·cm ²)	—	—	7.21×10^6	3.98×10^6
Cd (μF/cm ²)	—	—	7.64	8.77

从表 2 可见,在阴离子选择性涂层中阴离子交换体为 MoO_4^{2-} 型时的涂层电阻比 SO_4^{2-} 型时大近 1 个数量级,而在阳离子选择性涂层中阳离子交换体为 NH_4^+ 型的涂层电阻比 Na^+ 型时小近 1 个数量级。这表明阴离子选择性涂层中离子交换体为 MoO_4^{2-} 型时对碳钢的防锈性能比 SO_4^{2-} 型好,而阳离子选择性涂层中则离子交换体为 Na^+ 型时对碳钢的防锈性能比 NH_4^+ 型好,这与动电位扫描极化曲线的测量结果相一致。

4 结论

在同一种类型的离子选择性涂层中,不同离子交换体对碳钢的腐蚀行为有不同影响,可以通过选择具有缓蚀作用的交换离子来改善涂层的防锈性能。在阴离子选择性涂层中 MoO_4^{2-} 型对碳钢的防锈性能比 SO_4^{2-} 型好,在阳离子选择性涂层中 Na^+ 型比 NH_4^+ 型好。

[参 考 文 献]

- [1] Sato N. Toward a more fundamental understanding of corrosion process[J]. Corrosion, 1989, 45(5): 354~368
- [2] 王周成,张瀛洲,周绍民等. A3 钢在离子选择性涂层下的腐蚀电化学行为[J]. 厦门大学学报(自然科学版), 1997, 17(2): 388~393
- [3] 王周成,张瀛洲,周绍民等. 离子选择性酚醛涂层对碳钢防锈性能的研究[J]. 材料保护, 1998, 31(1): 1~4
- [4] 利建强,周德瑞,徐海涛. 钼酸钠抑制 GCY15 钢点蚀机理的研究[J]. 中国腐蚀与防护学报, 1986, 6(1): 15~21
- [5] Robitaille D R. Sodium molybdate as a corrosion inhibitor in cooling tower water[J]. Materials Performance, 1976, 15(11): 4~44
- [6] Music S. Formation of rust during the corrosion of steel in water and $(\text{NH}_4)_2\text{SO}_4$ solutions [J]. Croatia Chemica Acta, 1995, 68(2): 315~323
- [7] 张鉴清,孙国庆,曹楚南. 评价有机涂层防锈性能的 EIS 数据处理[J]. 腐蚀科学与防护技术, 1994, 6(4): 318

(责任编辑 张 帆)

长沙市化工研究所帐号变更启事

因银行帐号升位,现我所帐号已变更如下,敬请留意。

开户行:工行东支

帐 号:1901009009014428884

长沙市化工研究所

Contents & Abstracts

Friction - Reducing Internal Coating Technology for the West - East Gas Transmission Pipeline

HU Shi - xin, DONG Xu, DU Hong - qiang (China Petroleum Pipeline Engineering Corporation, Langfang, P. R. China 065000). *Cailiao Baohu* 2001, 34(10), 01 ~ 04 (Ch). The West - East Gas Transmission Project is from Xinjiang province to Shanghai city in China. The pipeline is about 4 000 kms long. In order to reduce friction and increase transmission efficiency, internal coating technology will be firstly used in China. The necessity, feasibility and maneuverability of friction - reducing internal coating technology was discussed.

An Investigation of Metal Construction Anti - corrosion on Middle Route South - North Water Transfer Projection

LI Lan, ZENG De - long (Changjiang Water Resource Commission Designing Institute, Wuhan, P. R. China 430010). *Cailiao Baohu* 2001, 34(10), 05 ~ 06 (Ch). On Changjiang valley comprehensive utilization programming South - North Water Transfer Projection is a fundamental scheme, that water was transferred into the Chinese north lack water area from three lines, which are changjiang upper reaches (west route), middle reaches (middle route) and lower reaches (east route). And this projection is also the requirements of optimizing resource disposition, reasonable using water resource, cleaning water environment enhancing economic and social development of our country. The general disposition and metal construction engineering amount of middle - route engineering of South - North Water Transfer Projection were explained emphasistically. The natural environment conditions of middle route engineering's water source area and transmission water area were reviewed. The basic demand of metal construction anticorrosion measure and service life were proposed.

Improvement of Corrosion Resistance of Titanium in Acidic Chloride Solution by Ion - Implantation of Mo⁺ or Zr⁺

LI Guo - xi et al (College of Chemistry and Chemical Engineering, Hunan University, Changsha, P. R. China 410082). *Cailiao Baohu* 2001, 34(10), 07 ~ 08 (Ch). The corrosion behavior of titanium ion - implanted with Mo⁺ or Zr⁺ by using multiple energy was investigated in 25% MgCl₂ + 5% NaCl + 1.6% HCl solution at 70 °C. The result shows that after the ion - implantation of Mo⁺ or Zr⁺ corrosion potential of titanium is markedly increased and after initial stage of corrosion its variation with time attains to minimum, titanium changes into a self - passivation state from active dissolution. The ion - implantation of Mo⁺ or Zr⁺ can improve obviously the corrosion resistance in acidic chloride solution; the effect of ion implantation of Mo⁺ is better than that of Zr⁺. The high corrosion resistance of titanium by ion - implanted with Mo⁺ or Zr⁺ is attributed to formation of an intact and compact passivation film of titanium and Mo (or Zr) on the surface of sample.

The Effect of Ion Exchangers on the Corrosion Behavior of Carbon Steel Under Organic Coatings

WANG Zhou - cheng, DU Rong - gui, HU Yan - ling et al (College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, P. R. China 361005). *Cailiao Baohu* 2001, 34(10), 09 ~ 10 (Ch). In order to study the effect of different ion exchangers on the corrosion behavior of metal under ion - selective organic coatings potentiodynamic and electrochemical impedance spectroscopy (EIS) techniques were employed to investigate the corrosion and electrochemical behavior of A3 steel covered with anion - selective and cation selective - organic coatings in 3% NaCl solution. The results show that the different ion exchangers in the same ion - selective organic coating have different effect on the corrosion behavior of carbon steel. MoO₄²⁻ - type anion exchanger has better anti - corrosion performance than SO₄²⁻ - type anion exchanger in anion - selective organic coating, whereas NH₄⁺ - type cation exchanger has better anti - corrosion performance than NH₄⁺ - type cation exchanger in cation - selective organic coating. Hence the anti - corrosion performance of ion - selective organic coating can be improved by choosing the ion exchanger possessing inhibitory effect.

A New Tin Acidic Electroplating Brightener and Its Feature

LUO Xu - yan et al (The Institute of the Southern Metallurgy, Ganzhou, P. R. China, 341000). *Cailiao Baohu* 2001, 34(10), 11 ~ 12 (Ch). A schiff's base as an electroplating tin brightener was synthesized with an aliphatic aldehyde and an amine. The schiff's base and its coordinate compound with tin (II) were characterized by IR and UV spectroscopy. The results indicated that there are bigger difference between the schiff's base and the coordinate compound with tin(II) their V_{c=N} absorbed band appear respectively at 1 630.01 cm⁻¹ and 16 261.63 cm⁻¹. The peak location shifts ~ 4 cm⁻¹ towards lower wave band, the absorbed peak intensity is attenuated; at the

same time, the coordinate compound appears a absorbed peak at 455.38 cm⁻¹. it belongs to V_{Sn-N}. The absorbance peak at 273.6 nm disappears from the coordinate compound UV spectroscopy, but the absorbed peak intensity became strongly sharp. The stability of the schiff's base in an acidic electroplating solution is determined by UV spectrophotometry which indicated that the schiff's base is improved at lower temperature and in presence of tin(II) in the solution. It is enough stable for the schiff's base in the acidic solution to use as an electroplating tin(II) brightener.

Study on the Corrosion - Resistance of Uranium After Reacted with CO

YANG Jiang - rong, ZOU Jue - sheng (China Academy of Engineering Mianyang P. R. China 621900). *Cailiao Baohu* 2001, 34(10), 13 ~ 14 (Ch). In order to develop the corrosion resistance of metallic uranium, carbon monoxide (CO) was used to react with fresh uranium in a sealed vessel at different conditions, the effect of CO on uranium was investigated using the weight gain method and the electrochemical measurement to evaluate the oxidation resistance of uranium in dry air at 70 °C and the electrochemical corrosion resistance in solution of 14 mmol/L Cl⁻ respectively. The result indicated that the oxidation resistance in dry air at 70 °C is improved after reaction of uranium with CO, and its oxidation rate is 25% ~ 60% lower than that of fresh uranium at initial stage of oxidation; The electrochemical measurement demonstrated the electrochemical corrosion resistance in solution of 14 mmol/L Cl⁻ is also enhanced. In addition, corrosion resistance of uranium increases as the dose of CO increases in the experimental range.

Study of the Corrosion Resistance of Automobile Shock Absorber Connecting Rod

TANG Fei - ran et al (College of Mechanical Engineering, Shanghai Jiaotong University, Shanghai, P. R. China 200030). *Cailiao Baohu* 2001, 34(10), 15 ~ 16 (Ch). This paper discussed the mechanism and the influence of pitting on the corrosion resistance of shock absorber connecting rod by electrochemical corrosion experimentation on the shock absorber connecting rod with two different plating process. The composition of the electrodeposits was observed and analyzed by metallography and SEM before and after corrosion. It was proved that the defects of the connecting rod coating is the main reason that weakens the corrosion resistance. By decreasing the current density in plating process, the width and depth of cracks of the electrodeposits are reduced and the corrosion resistance of the electrodeposits improves.

Investigation in Microstructure and Properties of Hot - Dip Aluminized Layer of Q235 Steel

DING Yi, WEI Wu - ji, ZHOU Yong - zhang (Department of Materials Science and Engineering, Nanjing University of Chemical Technology, P. R. China 210009). *Cailiao Baohu* 2001, 34(10), 17 ~ 18 (Ch). This paper investigated the microstructure of hot - dip aluminized layer on Q235 steel. The properties of oxidation and hot - corrosion resistance were tested. EDS analyses showed that the hot - dip aluminized layer consist of pure aluminum and phase (Fe₂Al₅). But after annealing the aluminizing layer is composed of phase (Fe₂Al₅), phase (FeAl₂), phase (FeAl), phase (Fe₃Al) and a solid solution. High temperature oxidation and hot - corrosion tests showed that the anti - oxidation properties of aluminized Q235 steel and 1Cr8Ni9Ti stainless steel are in the same level, but the former hot - corrosion resistance is superior to the latter remarkably.

Review of the Progress in Surface Treatments for Magnesium Alloys

YAO Mei - yi, ZHOU Bang - xin (Institute of Material, Shanghai University Shanghai, P. R. China 200072). *Cailiao Baohu* 2001, 34(10), 19 ~ 21 (Ch). Surface treatment processes for magnesium alloys including cleaning, chemical passivation, anodic oxidation and sealing with organic coating were reviewed. Several new methods for non - chromate chemical passivation and anodizing process being introduced in this paper might reduce the cost and environmental pollution. Chemical passivation treatments mainly contain a phosphate - permanganate treatment, a fluorozirconate treatment and a condensed phosphate treatment. The formed coatings show equivalent performance to the standard chrome pickle and play a good base coating for sealing application. The anodizing solution comprises an aqueous soluble hydroxide, fluoride and silicate. This coating possesses better abrasion and corrosion resistance than those obtained by the early DOW17 and HAE treatments, and it's a complex coating being composed of SiO₂, MgO, MgF₂. In addition, this anodizing coating is also an excellent base coating for sealing application.

Erosion Resistance of Materials

KANG Jin - xing, ZHAO Wen - zhen, ZHU Jin - hua (State Key Laboratory, for Mechanical Behavior of Material, Xi'an Jiaotong University Xi'an, P. R. China