工艺技术

钢材表面硅烷处理后的防腐蚀性能研究

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[摘 要] 采用硫酸铜点滴、线性极化、交流阻抗等试验对比研究了经硅烷偶联剂(SCA)和铬酸盐表面处理后冷轧板的耐蚀性能。结果表明,经硅烷偶联剂表面处理后不但提高了基材的防腐蚀性能,并且还提高了基材与涂层的结合力,明显增强了钢材的耐蚀性。SCA处理能够起到和铬酸盐钝化相同的防护效果,有望取代造成环境污染的铬酸盐钝化工艺。

[关键词] 硅烷偶联剂(SCA);铬酸盐;表面处理;冷轧钢板;耐蚀性
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0 前 言

磷化、铬酸盐钝化等工艺是应用非常广泛的表面处理技术,保护效果显著。但这些工艺严重污染环境,对人体健康有害,其应用已逐渐受到限制。现在腐蚀控制领域出现的"绿色"硅烷技术已引起越来越多的关注。硅烷偶联剂(SCA)广泛用于表面处理,如热塑性增强塑料的表面处理、填充物的表面处理、密封胶、树脂、混凝土、水交联性聚乙烯、树脂封装材料、胶粘剂等[1,2]。W. J. Van Ooij[3]对SCA在金属防腐预处理上的应用进行了研究,对SCA溶液最佳优化、成膜工艺、膜的性质及与涂层结合后的防腐作用做了详细的研究;徐溢[4,5]对成膜工艺及膜的性质的研究更为详细全面,开辟了其作为钢材表面预处理新的应用方向。硅烷技术具有环保、涂层结合力大等优点,有望取代传统的磷化和铬酸盐处理技术[6~11]。本工作通过硫酸铜点滴、线性极化、交流阻抗等试验,研究了经过SCA处理后基材的耐蚀性及其与涂层的结合力,考察了SCA表面预处理对钢材的防护效果,并与铬酸盐处理的样品进行了防腐蚀性能的比较。

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1 试 验

1.1 材料

硅烷处理溶液的配制:选用乙烯基硅烷偶联剂配制用于钢材表面处理的试验溶液,SCA∶乙醇∶水=1∶1∶1,用醋酸调节pH值为3.5～4.1。

试验钢板表面预处理:试验基材选用冷轧Q235钢,厚度0.8 mm,将试板表面用金相砂纸磨至800号,然后表面碱洗除油,清水漂洗,再用热空气吹干。

1.2 表面处理

试板采用以下7种处理方式:

试板A:空白样品,未处理。

试板B:在5%SCA溶液中浸泡15 s,然后氮气吹干,再继续浸入5%SCA溶液15 s,经氮气吹干,加热到100 ℃,保温30 min。

试板C:在铬酸盐溶液中浸泡1 min,吹干,60 ℃下烘干10 min。

试板D:与试板B采用同样的处理方法,只是试板未完全浸入溶液,还有一小部分为空白未处理区域。

试板E:空白未处理表面上直接喷涂(60±5)μm聚酯涂层。

试板F:在5%SCA溶液中浸泡15 s,然后氮气吹干,再继续浸入5%SCA溶液15 s,用氮气吹干,表面再

喷涂 (60 ±5) μm 聚酯涂层。

试板 G:在铬酸盐溶液中浸泡 1 min,吹干,60 ℃下烘干 10 min,表面再喷涂 (60 ±5) μm 聚酯涂层。

1.3 $CuSO_4$点滴试验

配制 4% $CuSO_4$溶液,对试板 C、D 进行点滴试验。点滴后观察记录 $CuSO_4$液滴颜色开始发生变化的时间。

1.4 线性极化测试

测试 A、B、C 3种无聚酯涂层试板的腐蚀速率,评价不同处理方式对提高基材耐蚀性的作用。试验溶液为 3% NaCl,温度为室温。测试前试板 B、C 浸入试验溶液中 2 h,试板 A 在放入试验溶液后立即进行测试。

1.5 交流阻抗测试

对涂有聚酯的 E、F、G 3种不同预处理样品进行交流阻抗测试。试验仪器为美国 PARASTAT2263,试验溶液为 3% NaCl,试验电位控制在自腐蚀电位。

1.6 马丘 (Machu)试验

测试前,将涂层样品表面划交叉线,然后分别浸入 1 000 mL 5% NaCl + 3% H_2O_2溶液,溶液温度保持在 37 ℃。24 h后,将试板取出并用胶带沿着划痕将剥落的涂层撕掉。测剥落层宽度来评价被测系统的涂层附着力,并比较其耐蚀性。

2 结果与讨论

2.1 $CuSO_4$点滴试验

对试板 A、B、C 进行 $CuSO_4$ 点滴试验发现,试板 A 浸泡时间少于 1 min 就发生变色,并且极快全部变色。试板 B、C 浸泡时间多于 6 min后,局部小区域出现变色。在显微镜下观察发现,液滴内局部出现细小颗粒状锈点,经过一段时间后才逐渐扩散到其他区域。说明极薄膜的存在起到了缓蚀作用。

试板 D 同一表面不同处理区域的对比试验可知,经过 3 min后,左边的 $CuSO_4$ 液滴,横垮 SCA 处理边界线的左侧已经出现红锈,颜色变深;液滴的右侧颜色很浅,颜色从左侧扩散。试板右边的 $CuSO_4$ 液滴依然是浅蓝色的 $CuSO_4$ 颜色,并未发生反应。说明经过 SCA 处理后提高了基材的耐蚀性。

SCA 处理提高耐蚀性的原因主要与 SCA 水解反应后与钢材表面作用成膜有关。SCA 可用 R_nSiX_{4-n}表示,其中 R 为不能水解的反应性有机官能团,X 为水解基团,如烷氧基、酰氧基、卤素等,遇水可分解为硅醇。

$$R_nSiX_{4-n} + (4-n)H_2O \rightarrow R_nSi(OH)X_{4-n} + (4-n)HX$$

硅醇缩合脱水生成低聚物,与无机金属底材表面以 Si-O-M 键相结合,形成网状结构的膜覆盖在底材表面[6]。这种以共价键为主要结合方式的膜阻碍了腐蚀的进行,提高了基体材料的耐腐蚀性能。

2.2 线性极化试验

在 (E_{corr} ±10) mV 电位范围内进行扫描,A、B、C 3种试板的极化曲线见图 1。从图 1 可以看出,经过 SCA 及铬酸盐处理的试板的 $\triangle E/\triangle I$ 斜率均高于裸板,经 SCA 处理后试板的 E_{corr}要比裸板的高 80 mV 左右,铬酸盐钝化的试板 E_{corr}要比裸板的高 30 mV 左右。说明经 SCA 处理后所形成的膜对腐蚀过程有一定的阻碍作用。从腐蚀学的观点来看,硅烷偶联剂所形成的 Si/Fe 体系能起到如下作用。

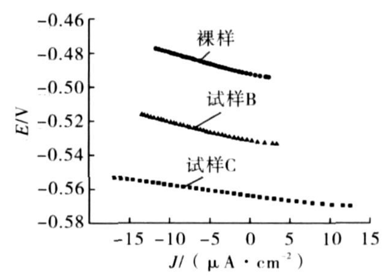

图 1 3种试板的极化曲线

首先,通过在钢板表面形成 FeOSi 共价键而使硅烷膜紧紧地钉扎在金属基体上,共价键的形成是通过 SiOH 基团及钢板表面 FeOH 基团的相互反应:

$$FeOH + SiOH \rightarrow FeOSi + H_2O$$

钢板表面形成的 FeOSi 键密度越大,金属基体和膜之间的作用力也越大。

其次,表面形成的 FeOSi 键本身并不稳定。当遇到大量水的时候,反应的平衡会向着左边的方向进行,由于表面 FeOSi 键的水解,表面的附着力将会降低,硅烷膜便失去了其保护作用。为了保证表面的附着力及膜的保护作用,必须阻止反应向左进行。一般而言,可以通过 SiOH 基团间的相互反应生成高度交叉的 SiOSi 网:

$$SiOH + SiOH \rightarrow SiOSi + H_2O$$

由于 SiOSi 本身就疏水性,当表面形成大量的 SiO-

Si基团时,硅烷 /Fe的疏水性很强。另外,高度交叉的SiOSi网之间的孔隙很小,阻碍了水的渗透[6],降低了钢材的腐蚀速率,提高了钢材的耐蚀性。

2.3 交流阻抗测试结果

分别对试板 D、E进行交流阻抗实验。在经 3% NaCl溶液浸泡 2,4 d及 50 d后分别测出其阻抗值,测试结果见图 2。

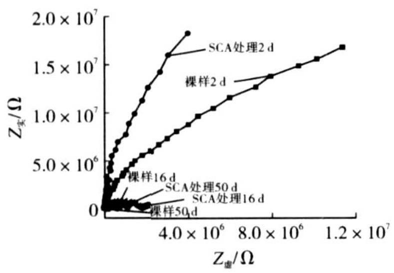

图 2 试样 D、E在 3%NaCl溶液浸泡后 Bode图

从图 2可以看出,浸泡 2d时,经过 SCA处理的钢板和未经过处理的冷轧板的阻抗值差别不大,此时水还没有渗透涂层,所测出的是涂层的阻抗值。随着浸泡时间的延长,阻抗值出现明显差别;浸泡 50 d后,当溶液已经渗透涂层到达钢板表面时,经过 SCA处理后涂聚脂的冷轧板,其阻抗值比表面直接涂聚脂的裸露钢板的阻抗值要高。说明经过 SCA处理后,不但提高了基材自身的耐蚀性,也提高了涂层的致密度,从而增强其抗渗水性,使材料耐蚀性得到明显提高,尤其是在涂层保护的后期。

2.4 Machu试验

Machu试验结果见图 3。从图 3可以看出,经过SCA和铬酸盐处理的试板涂聚脂后划痕腐蚀宽度要比直接涂聚脂的试板的宽度小的多,未经过处理而直接涂聚脂的试板表面的涂层已经被严重破坏并且翻卷起。

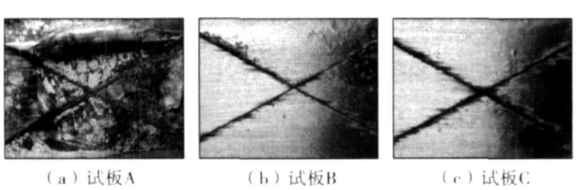

图 3 马丘试验结果

硅烷可与金属基体形成极强的 Me - O - Si键,而硅烷的有机部分又可与表面聚合物涂层系统形成化学键,硅氧烷键的形成可大大提高表面聚合物涂层与基体冷轧板的结合力[12],从而提高冷轧钢板耐腐蚀能力。

3 结 论

(1)冷轧钢板表面经过 SCA处理后,可形成致密的膜,明显提高了钢材的防腐蚀性能。

(2)在钢板表面形成致密 SCA膜后,表面涂覆涂料,涂层的阻抗值明显提高;并且与基体的结合力也大大提高,改善了钢板的抗腐蚀能力,能取得和传统的铬酸盐钝化处理相近的防腐蚀效果。

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was smooth, and the PTFE particles were tightly bonded with the nickel matrix and uniformly distributed in the coating. Moreover, the wear resistance of the composite coating increased with increasing content of nano-PTFE, while its friction coefficient decreased with increasing content of nano-PTFE.

Key words: electro-spraying plating; Ni-based composite coating; nano-PTFE; friction; wear behavior

Influence of Energy Parameters on Adhesion of Black Micro-Arc-Oxidation Ceramic Film

ZHONG Tao-sheng[1,2], JIANG Bai-ling[3], YI Mao-zhong[2] (1. School of Applied Sciences, Jiangxi University of Technology, Ganzhou 341000, China; 2. State Key Laboratory for Powder Metallurgy, Central South University, Changsha 410083, China; 3. School of Material Science and Engineering, Xi'an University of Technology, Xi'an 710048, China). *Cailiao Baohu* 2008, 41 (04), 18 ~ 20 (Ch). An MAO-240/750 micro-arc-oxidation equipment was performed to prepare black micro-arc-oxidation (MAO) ceramic film on ADC12 aluminum alloy substrate. The adhesion of the ceramic film to the Al alloy substrate was evaluated using adhering-tearing test of adhesive tape and metallorgraphic residue stress test, while the effects of energy parameters including temperature, duty cycle and voltage on the adhesion of the black MAΘ ceramic film were investigated. It was found that the higher the temperature, the better the adhesion between the ceramic film and substrate, which could be related to the temperature-dependent ionization degree of the electrolyte. Moreover, the adhesive strength of the ceramic film increased with duty cycle and voltage, but the film would experience ablation at an excessively high voltage. Besides, the adhesion of the ceramic film was also correlated with the thickness of the dense layer, and the film with a thicker dense layer had better adhesive strength. In general, it could be suitable for engineering application if the energy parameters such as temperature, duty cycle and voltage were adjusted as 45 ℃, 18% and 600 V.

Key words: energy parameter; micro-arc-oxidation; adhesion; temperature; vottage; duty cycle

Structure and Properties of Epoxy Resin Modified by Nano-SiO_2

LI Chao-yang, QIU Da-jian, XIE Guo-xian, XIAO Xiang-ding, NI Xiao-xue (Wuhan Research Institute of Materials Protection, Wuhan 430030, China). *Cailiao Baohu* 2008, 41 (04), 21 ~ 23 (Ch). Nano-SiO_2 as a modifying agent was dispersed and chemically bonded with epoxy resin matrix by high-shearing-strength sand milling in the presence of catalyst. The properties and structure of the modified epoxy resin were studied using a tensile tester, scanning electron microscope, and micro-infrared spectrometer. The results indicate that Si – O – C bond was formed after chemical modification of epoxy resin by nano-SiO_2, which contributed to greatly increase the toughness, the tensile strength and elongation at break of the epoxy resin, while the corrosion resistance of the epoxy resin was improved, to a certain degree as well after the chemical modification.

Key words: epoxy resin; elongation modify; nano-SiO_2

Corrosion Resistance of Cold-Rolled Steel Sheet Surface Modified by Silane Coupling Agent and Chromate Passivation

CHEN Shan[1], CHEN Ren-lin[2], CHEN Xue-qun[1], LI Guo-ming[1] (Department of Chemistry & Material, Navy Engineering University, Wuhan 430033, China; 2. Ma'anshan Iron & Steel Co., Ma'anshan 243000, China). *Cailiao Baohu* 2008, 41 (04), 24 ~ 26 (Ch). The corrosion-resistance of cold-rolled steel sheet treated with silane coupling agent (SCA) and chromate passivation was evaluated using $CuSO_4$ dropping test, linear polarization test, and electrochemical impedance spectroscopy (EIS). It was found that the steel sheet after surface modification with SCA had improved corrosion resistance, and the modifying coating had strong adhesion to the steel substrate. Moreover, the steel sheet modified by SCA had corrosion protection performance comparable to that of chromate passivation coating. Thus it could be feasible to use SCA modification to replace conventional chromate passivation process so as to avoid environmental pollution by Cr.

Key words: silane coupling agent (SCA); chromate passivation; surface treatment; cold-rolled steel sheet; corrosion resistance

Preparation of Composite Resin Coating on Aluminum Alloy and Corrosion Resistance of the Coating

WANG Yun-fang[1], WANG-Hong[2] (1. Department of Chemistry, Xianyang Normal University, Xianyang 712000, China; 2. School of Materials, Northwestern Polytechnical University, Shanxi 712000, China). *Cailiao Baohu* 2008, 41 (04), 27 ~ 30 (Ch). Primary γ-glycidoxypropyltrimentoxysilane (GPS) and bisphenol A (BPA) were used to prepare nanoscale GPS-BPA composite coating on aluminum alloy via sol-gel process. The optimized mole ratio of GPS to BPA in the composite coating was determined by dynamic polarization. The chemical features of the composite resins on AA2024-T3 alloy surface before and after cross-linking by means of reflective absorbance infrared spectrometry, while the distribution of the inorganic phase in the cross-linked composite coating was analyzed using a scanning electron microscope. Moreover, the corrosion resistance of the composite coating was evaluated using salt-spray test (SST) and electrochemical impedance spectroscopy (EIS). The results show that the inorganic phase was uniformly dispersed in the coating and had a grit size of 45 ~ 80 nm. When the molar ratio of GPS to BPA was 1/1, the composite coating showed the best corrosion resistance. Moreover, there existed a certain amount of residue epoxy ethyl group in the cured composite coating, and covalent bond network was formed at the coating-substrate interface. Besides, the composite coating showed no obvious sign of corrosion after salt-spraying test, but the coating-substrate interface was corroded after being etched in 0.5% NaCl solution for 24 h.

Key words: composite coating; corrosion resistance; aluminum alloy; GPS; BPA

Corrosion Resistance of Arc-Sprayed Pseudo Zn-Al Alloy Coating

LI Bing-zhong[1], WANG Chang-hui[2], DONG Zhi-hong[1], MA Bao-sheng[2], ZHANG San-ping[1], LI Peng[1] (1. Wuhan Research Institute of Materials Protection, Wuhan 430030, China; 2. No. 2 Pipe-Casting Plant, Xinxing Group Co. Ltd., Handan 056300, China). *Cailiao Baohu* 2008, 41 (04), 31 ~ 32 (Ch). A twin-wire arc-spraying system was performed to prepare pseudo Zn-Al alloy coating so as to improve the corrosion resistance and realize long-term protection of the steel substrate. The adhesion to substrate and corrosion resistance of the pseudo Zn-Al alloy coating were investigated using neutral salt-spraying test and scanning electron microscopy, using Zn and Al coating for a comparison. It was found that the arc sprayed pseudo Zn-Al alloy coating had better corrosion resistance and adhesion to substrate than the Zn-15%Al alloy coating.

Key words: pseudo Zn-Al alloy; arc-spraying; adhesion; corrosion resistance

Effect of Zn^{2+} as a Stabilizer on the Stability of Electroless Nickel Plating Bath

CHEN Zhi-dong[1,2], LIU Qi-fa[1], WANG Wen-chang[1], KONG Yong[1], DONG Ru-lin[1], Mitsuzaki Naotoshi[2] (1. Department of Chemistry & Chemical Engineering, Jiangsu Polytechnic University, Changzhou 213164, China; 2. Changzhou JPU Qualtec Co. Ltd., Changzhou 213164, China). *Cailiao Baohu* 2008, 41 (04), 33 ~ 35 (Ch). Trace Zn^{2+} was added to the plating bath for electroless Ni-P plating as a stabilizer so as to keep the stability of the plating bath. The effect of Zn^{2+} on the stability of the electroless Ni-P plating bath was investigated, while the deposition rate and morphology of the Ni-P coating were investigated. It was found that Zn^{2+} contributed to improve the stability of the electroless Ni-P plating bath and the appearance quality of the Ni-P coating.

Key words: electroless plating; Zn^{2+}; stability; Ni-P alloy

Preparation and Properties of Self-Assembled Monolayer for Pretreatment of Metal Surface

LI Zhi-lin[1], ZHANG Qiao-yun[1], CHEN Ze-min[2], ZHANG Wei-fang[2] (1. College of Chemistry and Environmental Science, Hebei University, Baoding 071002, China; 2. Department of Chemistry and Materials Science, Langfang Teachers College, Langfang 065000, China). *Cailiao Baohu* 2008, 41 (04), 36 ~ 37 (Ch). Silane coupling agents, degreasing agent, and poly-epoxy succinic acid were used to prepare self-assembled monolayer on metal surface, aiming at replacing conventional phosphating and chromating processes for the pretreatment of metals. The optimized processing parameters gained by orthogonal tests for the prepara-