环保型多功能磷化液的磷化性能

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[摘 要] 工业常用的磷化液存在高能耗、工艺复杂、污染环境等缺点。以磷酸、氧化锌、成膜助剂铝盐和阴离子表面活性剂与非离子表面活性剂复配的表面活性剂为主要原料，以钼酸铵为磷化促进剂，研制了多功能钢铁磷化液，常温下具有除油、除锈、磷化、钝化等多重功能，在Q235钢上形成了均匀、连续，厚度约为 5 μm的磷化膜。考察了磷化膜耐 NaCl溶液和硫酸铜点滴腐蚀性能。结果表明：磷化膜在 3% NaCl溶液中，(20±2) ℃浸泡 1 h不生锈，取出洗净吹干后 13 h无锈蚀；耐硫酸铜点滴时间 3 min以上，磷化膜干燥后，存放在相对湿度不大于 70%，无腐蚀气体的室内，60 d无锈蚀。

[关键词] 中低温磷化；除油；除锈；钝化；耐蚀性能
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0 前 言

磷化被广泛应用于汽车、轮船、军工、电器、机械等金属件的涂装前表面预处理。传统的中、高温磷化要先对金属进行除油、除锈，磷化后再进行水洗和钝化处理，工艺复杂、耗能高、对环境有污染。因此，常温、低温磷化已成为研究的热点[1]。常温多功能磷化体系所含亚硝酸盐、铬酸盐、氟化物、镍离子等对人体有害和污染环境[2~7]。本工作制备了常温下集除油、除锈、磷化、钝化于一步，且不含亚硝酸盐、铬酸盐、氟化物、镍离子等环境污染物的环保型多功能磷化液，研究了磷化液的成分对磷化膜耐蚀性的影响，以期为这类磷化液的制备提供理论依据。

1 试 验

1.1 基材及磷化液的制备

基材为 Q235冷轧钢板，尺寸为 4 mm × 3 mm，用蒸馏水冲洗掉表面的灰尘，烘干。

(1)磷化液的组成 环保型常温磷化液的组成：35.0 g/L ZnO，5.0 g/L 成膜助剂铝盐 M，0.4 g/L $(NH_4)_2MoO_4$，250 g/L H_3PO_4，5.0 g/L DJ_1(由十二烷基苯磺酸钠和 OP-10表面活性剂复配的表面活性剂)，5.0 g/L DJ_2(由柠檬酸和酒石酸复配的金属离子配位剂)。

(2)磷化液的配制 室温下将氧化锌(分析纯)放入烧杯中，加入少许自来水，搅拌均匀。将磷酸(85%)缓慢加入氧化锌中，并搅拌至氧化锌完全反应，然后加入成膜助剂 M，并不断搅拌至其完全溶解，过滤得主磷化液；将钼酸铵(分析纯)和其他磷化助剂分别溶于水，然后加入到主磷化液中；将复配表面活性剂加入 40 ℃的热水中，待完全溶解后加入到主磷化液中。

(3)磷化处理 在 18~25 ℃下，将清洗、烘干的试片磷化 15 min，再将试片从磷化液中取出，在空气中自然晾干 12 h以上。

1.2 测试分析

(1)膜外观检验 直观观察磷化膜表面颜色和附着情况，即是否存有残余空白或锈渍，是否为均匀、连续、致密的晶体膜。

(2)耐蚀性检测 耐 3% NaCl溶液腐蚀：将磷化试样浸渍在质量分数 3% NaCl的溶液中，温度为(20±2) ℃，1 h后取出，洗净吹干，记录出现第一个肉眼可见的腐蚀现象所需的最短时间。耐 $CuSO_4$点滴腐蚀：溶液由 41 g/L $CuSO_4 \cdot 5H_2O$，35 g/L $NaCl$，13 mL/L 0.1 mol/L HCl组成，温度为 15~25 ℃；磷化膜表面滴 1滴检验溶液，启动秒表，观察溶液从天蓝色变为淡红色的时间。磷化膜的防锈期按照 GB/T 12612-2005规定测定。

(3)磷化膜膜厚检测 利用 MIKROTEST Ⅳ型全自动磁性测厚仪测试磷化膜的厚度，每个试样检测 5个点，取平均值。

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2 结果与讨论

2.1 磷化膜的性能

磷化液为无色透明液体, pH值为 1.4,轻重锈均可去除,除油性良好,形成的磷化膜为灰色。磷化膜硫酸铜点滴时间大于 200 s,在 3% NaCl溶液中(20±2) ℃浸泡 1 h不生锈,取出洗净吹干后 13 h无锈蚀,符合 GB/T 6807-2001规定的技术指标。干燥后的磷化膜存放在相对湿度不大于 70%,无腐蚀气体的室温条件下,60 d无锈蚀,远超过 GB/T 12612-2005规定的不少于 7 d的标准。

2.2 DJ_1 对磷化膜的影响

多功能磷化液中添加表面活性剂,主要作用有 2个,一是除去金属件表面的油污;二是利用其润湿作用降低磷化液与金属件表面的界面张力,使磷化液易于与金属件表面充分接触,有利于最终生成磷化膜。多功能磷化液具有除油、除锈、磷化、钝化一次完成的功能,故酸性很强($pH < 1.5$),且含氧化剂和高浓度无机盐,所以,磷化液中所用表面活性剂应具有:在水中有较好的溶解性,具有良好的耐硬水能力;化学稳定性好,在无机盐、酸和氧化剂中稳定。

表面活性剂的浓度太小,基材上的油污不能被完全除净,使之不能完全与磷化液接触,难以生成磷化膜,导致磷化膜不均匀,耐蚀性低。复配表面活性剂的浓度太大,过多的表面活性剂分子可以在金属表面形成一层憎水基团朝外的类似油膜,阻止金属表面与磷化液直接接触,导致基体表面不能形成致密的磷化膜,磷化后的试片表面出现黄色的锈渍,耐蚀性降低。当复配表面活性剂浓度适量时,才能形成均匀的灰色磷化膜,耐蚀性才较好。复配表面活性剂 DJ_1的浓度对磷化膜耐蚀性能的影响见图 1。

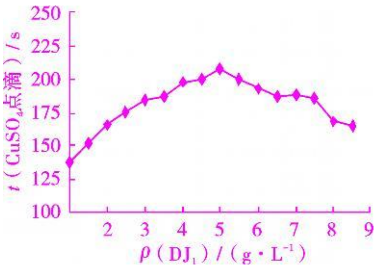

图 1 复配表面活性剂 DJ_1的浓度对磷化膜耐蚀性的影响

由图 1可见:磷化膜的耐蚀性能随复配表面活性剂 DJ_1浓度的增大呈现先增强后减弱的趋势,这一结果与理论分析一致;当复配表面活性剂的浓度为 5 g/L左右时,磷化膜的耐蚀性最好,硫酸铜点滴时间达到 200 s以上。

2.3 ZnO对磷化膜的影响

在锌系磷化液中锌离子是成膜的主要成分,对磷化膜的形成起着决定性的作用, ZnO含量对磷化膜的外观和耐蚀性都有影响。ZnO含量对磷化膜耐蚀性的影响见图 2。由图 2可见:当 ZnO的浓度较低时,磷化膜的耐蚀性随 ZnO浓度的增大而增强,当 ZnO的浓度为 37 g/L时,磷化膜的耐蚀性最好,硫酸铜点滴时间大于 200 s,ZnO的浓度大于 38 g/L之后,磷化膜的耐蚀性随 ZnO浓度的增加显著降低。这是因为 ZnO与磷酸反应,生成磷酸盐,是基本的成膜物质,形成锌铁系磷化膜的主要成分为 $Zn_2Fe(PO_4)_2 \cdot 4H_2O$, $Zn_3(PO_4)_2 \cdot 4H_2O$[8]。ZnO含量过少,磷化液中锌离子含量低,不能有效形成磷化膜,导致膜薄、疏松、磷化速度慢;ZnO含量过高,则锌离子含量过高,磷化膜的生长速率快,形成的晶粒粗大,结合力差,从而导致膜层薄且不够致密,ZnO浓度对磷化膜厚度的影响见图 3。只有当锌离子浓度达到某一范围,使金属件-溶液界面上锌离子浓度足够与磷化液中其他成分共同作用以适当的速度形成磷酸盐沉淀,才能生成致密的磷化膜。

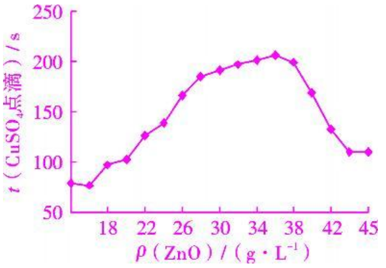

图 2 ZnO浓度对磷化膜耐蚀性能的影响

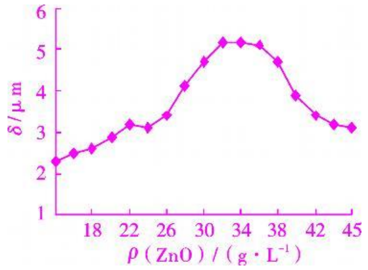

图 3 ZnO浓度对膜厚的影响

2.4 $(NH_4)_2MoO_4$对磷化膜的影响

$(NH_4)_2MoO_4$是较为理想的常温磷化促进剂,并有钝化作用。钼酸盐与磷酸盐能转化为以 P(Ⅴ)为中心原子,钼酸酐为配位体的磷钼杂多酸离子,

$[PMo_{12}O_{40}]^{3-}$或$[PMo_{12}O_{42}]^{7-}$等[8]。杂多酸及其盐是高效的多电子氧化剂，可获得多个电子而不破坏其多阴离子的结构。磷钼杂多酸的氧化性比钼酸盐强得多[10]，极易氧化其他物质，使磷化液中的Fe^{2+}快速被氧化为Fe^{3+}，常温下形成磷化膜；同时当杂多酸根离子吸附在沉积膜上，可与磷化液中的金属离子作用形成杂多酸盐膜，补充磷酸盐膜的不致密性，促进成膜过程和金属的钝化。钼酸盐虽然具有显著的氧化加速和缓蚀成膜的双重作用，但其浓度并非越高越好，钼酸铵过量时，磷化过程中会产生大量的“杂多蓝”，使溶液变蓝色，且磷化膜的质量下降。

图 4为钼酸铵含量对磷化膜耐蚀性的影响。由图 4可以看出：在低浓度时，随着$(NH_4)_2MoO_4$浓度的不断增加，磷化膜耐硫酸铜点滴时间呈上升趋势，在$(NH_4)_2MoO_4$浓度在 0.35~0.55 g/L之间，磷化膜的耐蚀性最好；随着钼酸铵浓度的进一步增加，硫酸铜点滴时间开始下降，这是由于过量的钼酸盐会使钢铁表面发生钝化而得不到理想的磷化膜。

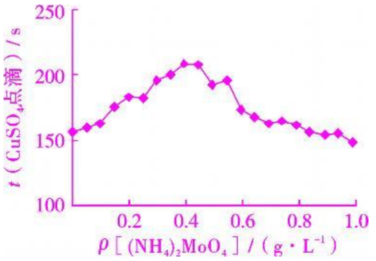

图 4 $(NH_4)_2MoO_4$浓度对磷化膜耐蚀性的影响

2.5 DJ_2对磷化膜的影响

在磷化过程中基体金属铁被氧化成Fe^{3+}，当溶液中Fe^{3+}浓度足够大时，磷化液中便产生沉渣。柠檬酸和酒石酸都是多齿配体，可与许多金属离子形成可溶性的螯合物离子。在磷化中柠檬酸和酒石酸可与Fe^{3+}，Zn^{2+}形成可溶性配合物，从而减少渣垢的形成，控制沉渣生成量，延长磷化液寿命；另一方面，柠檬酸、酒石酸能与磷酸协同作用，可增大阴极极化，使钢铁表面晶界充分暴露，有效活性点增多，有利于快速生成晶核细密、均匀的磷化膜，减少孔隙率，降低膜重，提高膜与基体的结合力[2]。

图 5为DJ_2的用量对磷化膜耐蚀性的影响。由图 5可见，磷化膜的耐蚀性随DJ_2的增加先增强后下降，这是因为DJ_2用量太少时，与Fe^{3+}，Zn^{2+}形成的可溶性配合物较少，磷化液中Fe^{3+}，Zn^{2+}含量较高，形成的磷化膜不够致密；用量过多，由于柠檬酸和酒石酸的强配位能力，使成膜金属离子减少，晶粒生成困难，磷化膜疏松多孔，膜的耐蚀性能降低，同时酸度升高，成膜速度减慢，DJ_2用量为 5 g/L时磷化膜的质量最好。

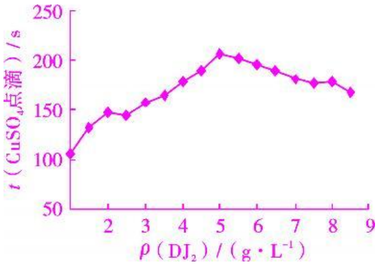

图 5 DJ_2的用量对磷化膜耐蚀性的影响

3 结论

(1)研制的磷化液在常温(15~25 ℃)下，对钢铁材料可一次性完成除油、除锈、磷化、钝化处理。磷化液不含亚硝酸根、铬酸盐、镍离子、氟化物等污染环境的物质。

(2)磷化后能在钢铁材料表面形成均匀致密的磷化膜，膜的耐蚀性良好，硫酸铜点滴时间大于 3 min，膜厚约 5 μm，磷化干燥后在相对湿度不大于 70%，无腐蚀气体的室温条件下 60 d无锈蚀。

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[编校：王 宇]

coating were investigated. It was found that the uniformity and color of the anodizing coating were dependent on the concentration of phosphoric acid, and the film-formation rate and potential range corresponding to the color of the coating were dependent on the concentration of sodium gluconate. Potential had influence on the thickness and color of the coating, and the current density greatly influenced the deposition rate of the coating. The optimized electrolyte was suggested to consist of 100 mL/L phosphoric acid and 20 g/L sodium gluconate, while the optimized anodizing temperature and time were suggested as 25 ℃ and 60 s. The substrate after pickling allowed more even coloring, while the anodizing coloring coatings after sealing were denser and had better anti-pollution capability.

Key words: anodic oxidation; TA2 pure titanium; quality of coating; coloring; sealing

Effect of Electrolyte Temperature on Performance of Hard Anodic Oxidation Coating of Hard Aluminum Alloy

PANG Guo-xing, LI Zhong-lei, CHEN Zhi-yong, HUANG Sheng-zhou (Department of Material Engineering, North China Institute of Astronautic Engineering, Langfang 065000, China). *Cailiao Baohu* 2011, 44(04), 41~42(Ch). The mixed solution of sulfuric acid and oxalic acid was used to conduct hard anodic oxidation of hard Al alloy. The effect of electrolyte temperature on the thickness, hardness and corrosion resistance of the hard anodic oxidation coating was investigated. It was found that the thickness and hardness of the hard anodic oxidation coating initially increased but then decreased with elevating electrolyte temperature. The hard anodic oxidation coating obtained at an electrolyte temperature of 15 ℃ had the maximum thickness and hardness. Sealing with potassium dichromate contributed to increasing corrosion resistance of the hard anodic oxidation coating, and electrolyte temperature also influenced the corrosion resistance of the coating sealed with potassium dichromate.

Key words: hard anodic oxidation; electrolyte temperature; hard aluminum alloy; thickness; hardness; corrosion resistance

Effect of Heat Treatment on Microstructure and Corrosion Resistance of Electrodeposited Nickel-Tungsten Alloy Coating

CHEN Yi-sheng[1], ZHANG Xue-hui[1], CHEN Hao[1], LI Jin-hui[1], PENG Chao[2] (1. School of Material Science and Chemical Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China; 2. Hunan Nonferrous Metals Company Ltd., Academia Sinica, Changsha 410219, China). *Cailiao Baohu* 2011, 44(04), 43~45(Ch). Direct current electrodeposited Ni-W alloy coating was heat treated so as to increase its microhardness and corrosion resistance. The effects of heat treatment temperature and time on the microstructure, hardness and corrosion resistance of the coating were investigated. It was found that heat treatment within a proper range of temperature and time contributed to significantly increased hardness and corrosion resistance of the coating. The coating heat treated at 500 ℃ for 1 h had the best comprehensive properties, possessing microhardness as much as 1 010.44 HV and good corrosion resistance in 3.5% NaCl solution.

Key words: Ni-W alloy coating; electrodeposition; heat treatment; microstructure; hardness; corrosion resistance

Review of Critical Velocity in Cold Spraying and Its Factors

BU Heng-yong[a,b], LU Chen[a] (a. National Engineering Research Center of Light Alloy Net Forming; b. Key State Laboratory of Metal Matrix Composite, Shanghai Jiaotong University, Shanghai 200240, China). *Cailiao Baohu* 2011, 44(04), 46~49(Ch). A review was provided of methods for simulated calculation and practical evaluation of particle velocity and critical velocity in cold spraying. The factors influencing the critical velocity in cold spraying were analyzed. It was pointed out that improving the performance of the cold-sprayed coatings based on proper use of numerical simulation methods in relation to the physical nature of the particles and substrates to design nozzle geometric structure and optimize the coating preparation parameters was one of the major research directions in cold spraying.

Key words: cold spraying; critical velocity; particle velocity; factor

Current Status of Study and Development Trend of Electroless Plating for Plastics

LIU Lei, LIANG Xiao-ping, YAN Gui-long (School of Materials Science and Engineering, Cultivation Base of Province-Ministry Jointly Constructed State Key Laboratory of Hollow Fiber Membrane Material and Process, Tianjin Polytechnic University, Tianjin 300160, China). *Cailiao Baohu* 2011, 44(04), 50~54(Ch). A review was provided of the current status and development trend of electroless plating for plastics in relation to pre-treatment of surface, activation and metal deposition. It was pointed out that plastics possessing the advantages such as portability and easy molding had been widely used, but their poor wear resistance, corrosion resistance and weather resistance had limited their use and service life. It was feasible to significantly improve the surface properties and increase the service life of plastics by making use of electroless plating.

Key words: electroless plating; plastics; pre-treatment of surface; activation; metal deposition

Antioxidation Function of Glass Lubricating Paint for Titanium Alloy Forging

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Key words: protective and lubricating paint; Ti alloy; high-temperature forging; borosilicate-based glass powder; antioxidation

Phosphating Performance of Environmentally Friendly Multifunctional Phosphating Solution

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Key words: moderate and low temperature phosphating; degreasing; rust-removing; passivating; corrosion resistance

Corrosion Resistance of Electroless Ni-Fe-P Coating

ZHANG Yun-xia (School of Continuing Education, Liaoning Shihua University, Fushun 113001, China). *Cailiao Baohu* 2011, 44(04), 61~63(Ch). Electroless Ni-Fe-P coating was prepared by introducing $FeSO_4$ into electroless Ni-P plating bath. The surface morphology and composition of electroless Ni-P and Ni-Fe-P coatings were observed using a scanning electron microscope. The dynamic potential polarization curves and electrochemical impedance spectra of both coatings in 3.5% NaCl solution were tested by