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中国腐蚀与防护学会
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锌铝镁镀层和纯锌镀层在典型大气环境中初期腐蚀行为研究

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摘要：目的 增加对不同大气环境中锌铝镁镀层钢腐蚀行为的了解，研究中国地区不同气候条件下 1 a 内锌铝镁镀层钢腐蚀产物的组成和腐蚀速率。**方法** 采用 SEM、GDS、XRD 研究了纯锌（GI）镀层材料和锌铝镁合金（ZM）镀层材料的结构，对比研究了 GI 镀层和 ZM 镀层在吐鲁番、江津、青岛以及万宁 4 个大气试验站的腐蚀试验。**结果** 万宁 GI 的腐蚀速率为 ZM 的 4.56 倍，江津 GI 的腐蚀速率为 ZM 的 3.76 倍，青岛 GI 的腐蚀速率为 ZM 的 2.84 倍，吐鲁番 GI 的腐蚀速率为 ZM 的 2.42 倍，对于 GI 镀层和 ZM 镀层，按腐蚀速率从大到小的顺序依次为万宁、青岛、江津、吐鲁番。江津和万宁 GI 镀层的自腐蚀电流密度较小，万宁 ZM 镀层的自腐蚀电流密度最小。锌的大气腐蚀速率主要受相对湿度、氯离子含量、SO_2含量等影响，主要通过影响腐蚀产物组成来影响锌的腐蚀速率。腐蚀产物的保护性受其化学组成、导电性、黏附性、致密性、溶解性、厚度、形态和亲水性等因素影响，不同的锈层结构对阴极氧还原的抑制作用不一样，高氯环境对 GI 的保护性腐蚀产物 $Zn_5(CO_3)_2(OH)_6$ 有较大的破坏性，在高碱性环境下，容易使腐蚀产物转变成疏松导电的 ZnO。在高氯环境中，由于镀层中 $MgZn_2$ 的阳极溶解，释放出可与 OH 反应的 Mg^{2+} 以形成氢氧化镁（$Mg(OH)_2$）。在 ZM 表面用 $Mg(OH)_2$ 代替氧化锌被认为可以降低阴极氧还原反应（ORR），具有缓冲阴极位置的 pH 值升高的作用，能使碱式碳酸锌变得稳定，显著提升耐腐蚀性。**结论** ZM 镀层材料在高盐高湿环境下能形成稳定的腐蚀产物，降低阴极氧还原速率，在典型大气环境下具有广阔的应用前景。

关键词： 镀锌板；大气腐蚀；腐蚀产物
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Study on Initial Corrosion Behavior of Zn-Al-Mg Coating and Pure Zinc Coating in Typical Atmospheric Environment

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ABSTRACT: The work aims to improve the understanding of corrosion behavior of Zn-Al-Mg coated steel in different atmospheric environments, and to study the composition and corrosion rate of corrosion products of Zn-Al-Mg coated steel in China area under different climatic conditions within 1 year. The structures of the GI coating and the ZM coating were studied by SEM, GDS and XRD, and the corrosion tests of the GI coating and the ZM coating in Turpan, Jiangjin, Qingdao and Wanning, were compared. There were no peaks of Mg and Al elements in the GI coating, but there were obvious Mg and Al elements in the ZM coating, which were evenly distributed in the coating. The surface of GI plate was a pure zinc coating, and there were a lot of binary eutectic phases composed of Zn and MgZn2 on ZM surfaces. The corrosion rate of Wanning GI was 4.56 times that of ZM, Jiangjin GI was 3.76 times that of ZM, Qingdao GI was 2.84 times that of ZM, and Turpan GI was ZM. The traditional electrochemical test adopted the solution system, which was equivalent to the corrosion of galvanized sheet in solution. The metal corrosion rate basically did not change with the thickness of the liquid film, and the diffusion of oxygen in it was slow, which became a control link of the test. In this paper, the flowing electrolyte solution was used for the test to increase the diffusion coefficient of oxygen in the electrolyte. For the GI coating, the self-corrosion current density in Jiangjin and Wanning was low, and for the ZM coating, the self-corrosion current density in Wanning, Hainan was the lowest. The atmospheric corrosion rate of zinc was mainly affected by relative humidity, chloride ion content, SO_2 content, etc., and the corrosion rate of zinc was mainly affected by the composition of corrosion products. The protection of corrosion products depended on its chemical composition, conductivity, adhesion, compactness, solubility, thickness, morphology and hydrophilicity. Different rust layers had different inhibition effects on cathodic oxygen reduction. $Zn_5(CO_3)_2(OH)_6$ had a good inhibition effect on oxygen reduction. The overall current density of the ZM coating was smaller than that of the GI coating, which was consistent with the atmospheric corrosion law. ZM material had obvious advantages in Wanning area with high salt and humidity, but less advantages in Turpan area with relatively mild corrosion environment. This was because different environments would affect the structure and properties of the corrosion products, and the structure and properties of the products would affect their corrosion resistance. The high chlorine environment had great damage to the protective corrosion of GI $Zn_5(CO_3)_2(OH)_6$, and it was easy to transform the corrosion products into loose and conductive ZnO in the high alkaline environment. In the high chlorine environment, Mg^{2+} ions which could react with OH were released due to anodic dissolution of $MgZn_2$ in the coating to form magnesium hydroxide ($Mg(OH)_2$). Replacing zinc oxide with $Mg(OH)_2$ on ZM surface was considered to reduce cathodic oxygen reduction reaction (ORR), buffer the increase of pH value at cathode position, stabilize basic zinc carbonate, and significantly improve corrosion resistance. The ZM coating material can form stable corrosion products and reduce cathodic oxygen reduction rate in a high-salt and high-humidity environment, and has a broad application prospect in a typical atmospheric environment.

KEY WORDS: galvanized sheet; atmospheric corrosion; corrosion products

与碳钢相比，镀锌板因其优异的腐蚀性能而在工业中得到了广泛应用。连续热镀锌（HDG）钢和电镀钢（EG）是主要产品。自 20 世纪 90 年代以来，含有镁和铝的镀层已在市场上商业化。最早开发的镀层，如 Zn-11Al-3Mg-0.2Si 和 Zn-6Al-3Mg，相对较厚，主要用于建筑行业。最近连续热浸锌铝镁已被引入市场。与热镀锌钢和电镀钢相比，这些镀层在盐雾和循环腐蚀试验中均显示出更好的腐蚀性能[1-4]，但大多数大气腐蚀研究都是在纯锌上进行的，而锌铝镁钢的数据较少。Persson 等[5]介绍了全球暴露计划中 HDG 上大气腐蚀和腐蚀产物形成的数据。在所有暴露条件下，锌镀层上的腐蚀都是局部的。腐蚀产物的组成和分布与阳极和阴极过程的分离有关，这会导致大气腐蚀过程中表面局部化学成分发生变化[6-7]。

尽管研究者们在加速腐蚀试验中对锌铝镁镀层的腐蚀行为进行了大量研究[8]，但关于这些新镀层长期现场性能的研究以及与热浸镀锌镀层的对比数据很少。相关研究表明，在海洋大气中暴露 6 个月后，锌铝镁的腐蚀速率约为纯锌板的一半，这归因于 Mg^{2+} 从镀层中溶解对腐蚀产物的贡献[9-10]。Schuerz 等[11]比较了锌铝镁和 HDG 在不同环境条件（包括海洋、农村和城市位置）下的腐蚀行为，研究发现，暴露 2 a 后，腐蚀速率的改善率为 2.4~3.3。Nishimura 等[12]在海上环境中研究了 2 种不同的锌铝镁合金镀层，研究表明，与 HDG 相比，合金镀层在耐腐蚀性方面得到了改善，但 ZnAlMg 镀层受到了共晶相的选择性局部腐蚀。

为了解锌铝镁镀层的大气腐蚀机理，对腐蚀产物成分进行了研究。现场暴露后腐蚀产物的特征表明，主要腐蚀产物与相同条件下暴露的热浸镀锌类似，以碱式碳酸锌为主[13-16]。其他研究表明，在盐雾试验和不同加速循环腐蚀试验后，除碱式碳酸锌和碱式氯化锌外，在锌铝镁镀层上还形成了含有 Zn 和 Al 的层状

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4 种典型热镀锌板表面钝化膜耐腐蚀性能研究

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摘要：目的 分析 4 种热镀锌板钝化膜体系成分，考察不同钝化膜的耐腐蚀性及防腐机理。**方法** 通过 SEM、XPS、GDS、红外光谱、润湿角，分析了 4 种钝化膜的微观结构和化学成分。通过电化学、中性盐雾、循环盐雾试验，验证了镀锌板钝化膜的耐腐蚀性。**结果** 耐指纹膜、自润滑膜、全无铬钝化的主体均含 Si 和 O，膜厚约 1 μm，耐指纹膜中还含有 Sn 和 P，自润滑膜和全无铬钝化中含有较多的 P 和 Sn，三价铬钝化膜主要含有 Si、O、Cr、C、P，膜厚仅为 0.05 μm。4 种钝化膜的成分分布与光整坑有较强的对应关系，光整坑中成膜较厚，光整坑外部出现明显的 Zn 元素强度，说明该处钝化膜较薄，三价铬具有最优的疏水性，全无铬和耐指纹也具有较好的疏水性，自润滑板疏水性较差，三价铬钝化的自腐蚀电流密度为 0.97 μA/cm^2，全无铬、自润滑、耐指纹的自腐蚀电流密度依次为 1.6、2.3、2.6 μA/cm^2。全无铬中树脂交联密度较高，三价铬钝化存在致密的氧化物膜，疏水性较好，对去极化剂的阻隔能力也更强，电荷在界面转移阻力较大，而耐指纹板和自润滑板存在部分孔隙，所以其平面耐腐蚀性稍差。在循环腐蚀过程中，由于存在干湿交替，高盐环境对钝化膜的持续攻击时间较短，故 4 种钝化膜在循环腐蚀过程中平面处的耐腐蚀性均优于中性盐雾环境中，盐雾结果与电化学结果有较好的一致性。**结论** 不同表面膜耐腐蚀性有一定区别，三价铬和全无铬具有较优的耐平面腐蚀性和划叉腐蚀性。

关键词：无铬钝化；三价铬钝化；划叉；耐蚀性

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Corrosion Resistance of Passivation Films on Four Typical Hot-dip Galvanized Plates

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ABSTRACT: The work aims to analyze the composition of four passivation films for hot-dip galvanized plates, and investigate the corrosion resistance and corrosion protection mechanism of different passivation films. The microstructure and chemical composition of four passivation films were analyzed by SEM, XPS, GDS, IR and wetting angle. The corrosion resistance of the

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精密与超精密加工 Precision and Ultra-precision Machining

表面功能化 Surface Functionalization

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passivation film of a galvanized plate was verified by electrochemical, neutral salt spray and cyclic salt spray tests. The fingerprint resistant film, self-lubricating film and total chromium-free passivation all contained Si and O, and the film thickness was about 1 μm. The fingerprint resistant film also contained Sn and P, while the self-lubricating film and total chromium-free passivation film contained more P and Sn. The trivalent chromium passivation film mainly contained Si, O, Cr, C and P, and the film thickness was only 0.05 μm. There was a strong correspondence between the composition distribution of the four passivation films and the smooth pit. The combination forms of Si in the four passivation films mainly existed in the form of Si—O—Si(102.4 eV) and Si—C(102.8 eV) and there was also Si—O—Zn(100.7 eV) in chromium-free, fingerprint-resistant and trivalent chromium. The Si—O—Si bond was the hydrolysis of silane coupling agent in passivation solution to form silanol. The hydrolysis-condensation rate was affected by silane concentration, pH value and solvent type, etc. The Si—O—Si bond in chromium-free passivation was obviously more than that in other passivation films, which might be due to the fact that the type and concentration of silane in chromium-free passivation solution were different from others, and it was hydrolyzed into more silanol in passivation solution. After curing into a film, its cross-linking density was higher and the film was denser. The Si—O—Zn bond proved that partially hydrolyzed silanol formed with zinc coating. The film thickness in the smooth pit was thick, and the apparent Zn element intensity appeared outside the smooth pit, which indicated that the passivation film here was thin, trivalent chromium had the best hydrophobicity, all chromium-free and fingerprint-resistant had better hydrophobicity, and the self-lubricating plate had poor hydrophobicity. The self-corrosion current density of trivalent chromium passivation was 0.97 μA/cm^2, and all chromium-free, self-lubricating and fingerprint-resistant were 1.6, 2.3, 2.6 μA/cm^2 in turn. All-chromium-free resin had higher cross-linking density, dense oxide film in trivalent chromium passivation, better hydrophobicity, stronger barrier ability to depolarizer, and greater resistance to charge transfer at interface, while fingerprint resistant plate and self-lubricating plate had some pores, so their plane corrosion resistance was slightly poor. In the cyclic corrosion process, due to the alternation of wet and dry, the sustained attack time of passivation film in high-salt environment was short, so the corrosion resistance of the four passivation films in the cyclic corrosion process was better than that in neutral salt spray environment, and the salt spray results were in good agreement with the electrochemical results. The corrosion resistance of different surface films is different. Trivalent chromium and total chromium-free film have better plane corrosion resistance and cross corrosion resistance.

KEY WORDS: chromium-free passivation; trivalent chromium passivation; cross; corrosion resistance

热浸镀锌钢价格低廉，性能优异，被广泛应用于汽车、家电、集装箱、建材、交通、能源等领域[1-3]。但在高温高湿环境下，热镀锌钢容易腐蚀，形成白锈。因此，热浸镀锌钢通常要进行钝化处理。铬酸盐钝化是最常用的商业处理方法。然而，传统的六价铬钝化技术毒性大，对环境有害，因此在世界范围内被禁用[4-6]。目前的钝化工艺主要包括三价铬钝化和无铬钝化。

无铬钝化工艺可分为 3 类：钼酸盐钝化、稀土盐钝化和有机硅烷钝化。等同于六价铬钝化防腐效果的单一无铬钝化工艺仍然难以实现[7-8]。三价铬钝化的效果和六价铬类似，毒性只有六价铬的 1%，然而，三价铬会被氧化成六价铬，因此铬污染的问题仍未解决[9-12]。钼酸盐毒性低，因此被认为是有效的替代铬酸盐，但单一钼酸盐钝化膜的耐腐蚀性不足[13-17]。稀土盐具有更好的耐腐蚀性，比钼酸盐更安全，但稀土离子的缓慢沉积使钝化过程耗时且成本高昂[18-22]。相比之下，有机硅烷成本低，无毒，易于合成，便于后续处理。因此，近年来，有机硅烷钝化已成为替代铬酸盐钝化的理想选择[23-26]。

近几十年来，镀锌层无铬钝化技术的研究主要集中在热镀锌钢带上。为此，几种经典的有机化学品，包括树脂、硅烷和蜡乳液已被用作钝化膜的主要成膜物质。已添加少量无机成分，如钼酸盐、锆或钒钛的氧酸盐和纳米 SiO_2 溶胶，作为缓蚀剂，以提高膜的性能[27]。耐指纹板是在镀锌钢板上直接涂覆一层有机薄膜而制成的高附加值产品，以优良的耐指纹性、导电性和耐蚀性而被广泛应用于电子及电器行业，特别是电脑、影音设备等产品。基于用户端差异化的需求，为了提升材料冲压性能，自润滑钝化液也在近几年得到了广泛的应用。此前关于热镀锌板钝化膜研究的论文较多，但是并没有将几种典型热镀锌板钝化膜进行对比研究。

本文选取了热镀锌板表面常用的三价铬、全无铬、自润滑、耐指纹钝化板。通过 SEM、XPS、GDS、红外光谱、润湿角分析了 4 种钝化膜的微观结构和化学成分。通过电化学、中性盐雾、循环盐雾试验验证了镀锌板钝化膜的耐腐蚀性，进而得出不同钝化膜的防腐机理，为镀锌板表面钝化产品的选用提供理论指导。

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