

doi: 10.11933/j.issn.1007-9289.20240323001

# 深海环境下环氧重防腐涂层的防护机理 和应用研究进展

王朴炎<sup>1</sup> 俞嘉辉<sup>1</sup> 臧显峰<sup>2</sup> 曹求洋<sup>3</sup>  
郭小平<sup>4</sup> 刘栓<sup>4</sup>

- (1. 宁波市电力设计院有限公司 宁波 315000;  
2. 广东蓝迪威工程技术有限公司 深圳 518107;  
3. 国网浙江省电力有限公司电力科学研究院 杭州 310010;  
4. 中国科学院宁波材料技术与工程研究所海洋关键材料重点实验室 宁波 315201)

**摘要:** 随着陆地矿产资源的日益枯竭, 开采深海中的矿产资源显得尤为紧迫和重要, 但深海采矿装备都会面临严重的海水腐蚀。涂装环氧重防腐涂料是深海环境中对海工装备最重要也是最普遍的防护手段, 阐明环氧重防腐涂层的防护机理和深海环境因素对涂层防护性能的影响具有重要意义。环氧重防腐涂层可通过物理屏蔽作用、缓蚀效应和电化学保护功能对深海装备进行长效防护。物理屏蔽效应是环氧涂层的基本功能, 可通过调整配方中的颜基比、颜料体积浓度和搭配不同的固化剂等方式来提高环氧涂层的物理阻隔性能。在环氧树脂中添加涂层缓蚀剂和电负性更负的颜料, 可与涂层本身物理屏蔽作用互为补充, 协同提升环氧涂层的防护性能。深海高压会加速水分子在环氧涂层中的渗透速率, 当水分子渗透涂层与金属基底接触后, 水分子会导致金属基底发生电化学腐蚀反应, 并降低环氧涂层在金属基底的附着力, 导致涂层剥落和涂层失效。海水温度和海水 pH 值对环氧涂层防护性能的影响较小。海水流速会加速环氧涂层的冲蚀磨损, 海生物污损对环氧涂层的影响有限。综述结果旨在阐明环氧重防腐涂层在深海环境下对金属的防护机理, 探讨深海环境因素对环氧重防腐涂层防腐性能的影响规律, 对深海环境用重防腐涂层内部结构调控和可控制备具有重要指导意义。综述相关研究现状不仅能指出现有研究的不足及未来研究的展开方向, 还能为开发更高抗腐蚀性、更好阻隔性和更长寿命的新型环氧重防腐涂层提供理论依据。

**关键词:** 深海环境; 重防腐涂层; 防腐机理; 失效

**中图分类号:** TG156; TB114

## Research Progress on the Protection Mechanism and Application of Epoxy Heavy-duty Anti-corrosion Coatings in Deep-sea Environments

WANG Puyan<sup>1</sup> YU Jiahui<sup>1</sup> ZANG Xianfeng<sup>2</sup> CAO Qiuyang<sup>3</sup>  
GUO Xiaoping<sup>4</sup> LIU Shuan<sup>4</sup>

- (1. Ningbo Electric Power Design Institute Co., Ltd., Ningbo 315000, China;  
2. Guangdong Landiwei Engineering Technology Co., Ltd., Shenzhen 518107, China;  
3. State Grid Zhejiang Electric Power Co., Ltd. Research Institute, Hangzhou 310010, China

**基金项目:** 国家重点研发计划 (2023YFC2809901); 宁波市电力设计院有限公司科技项目 (KJXM2022053); 变电站惰性气体泡沫灭火系统 (IGFS) 灭火关键技术研究及应用 (KJKY20230277)。

**Fund:** National Key R&D Program of China (2023YFC2809901); Technology Project of Ningbo Electric Power Design Institute Co., Ltd. (KJXM2022053); Research and Application of Key Technologies of Inert Gas foam Fire Extinguishing System (IGFS) in Substation (KJKY20230277)。

收稿日期: 2024-03-23; 修改日期: 2024-06-19; 接受日期: 2024-06-24; 上线日期: 2024-11-05。

Received March 23, 2024; Revised June 19, 2024; Accepted in revised form June 24, 2024; Available online November 5, 2024.

**引用格式:** 王朴炎, 俞嘉辉, 臧显峰, 等. 深海环境下环氧重防腐涂层的防护机理和应用研究进展[J]. 中国表面工程, 2024, 37(6): 135-145.

**Citation format:** WANG Puyan, YU Jiahui, ZANG Xianfeng, et al. Research progress on the protection mechanism and application of epoxy heavy-duty anti-corrosion coatings in deep-sea environments[J]. China Surface Engineering, 2024, 37(6): 135-145.

#### 4. Key Laboratory of Advanced Marine Materials, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China)

**Abstract:** The increasing depletion of land mineral resources has made their exploration and utilization in deep sea particularly important and urgent. However, deep-sea mining equipment can not suffer from severe seawater corrosion. The application of epoxy heavy-duty anti-corrosion coatings is the most important and common protective measure for marine equipment in deep-sea environments. Therefore, clarification of the protective mechanism of heavy-duty epoxy anti-corrosion coatings and the influence of deep-sea environmental factors on protective performance is of great significance. Developed countries have begun to introduce advancements into deep-sea mining equipment to perform mining operations at different seawater depths. With the exploration and development of deep-sea resources in China and the proposal of the strategic goal “going to deep-sea oceans”, the country’s marine construction process has moved from near-shallow to deep sea. Although an increasing number of marine facilities have been developed for deep-sea exploration and extraction, they suffer serious corrosion damage due to the harsh environment in the deep sea. Galvanic, pitting, and uniform corrosion types are common and seriously threaten the structural safety and decrease the life of facilities because of their strong destructive effects. The failure of heavy-duty anticorrosion coatings in deep-sea environments seriously threatens the reliable operation and long-term service safety of deep-sea equipment. The deep-sea environment includes corrosion factors, such as static seawater pressure, alternating pressure, marine biofouling, as well as seawater temperature, pH, and flow rate. The protective effect of epoxy heavy-duty anticorrosion coatings on marine equipment varies in different deep-sea corrosive environments. Heavy-duty epoxy anti-corrosion coatings can provide long-term protection for deep-sea equipment through physical shielding, corrosion inhibition, and electrochemical protection. The physical shielding effect is the basic function of epoxy coatings and can be improved by adjusting the pigment-to-base ratio, pigment volume concentration, and a combination of different curing agents, to enhance the physical barrier performance of epoxy coatings. Adding corrosion inhibitors and more electronegative pigments to the epoxy resin can complement the physical shielding effect of the coating and synergistically enhance its protective performance. Deep-sea high pressure can accelerate the penetration rate of water molecules in epoxy coatings when water molecules penetrate the coating and come in contact with the metal substrate, thereby causing electrochemical corrosion reactions on the metal substrate, which reduces the adhesion of the epoxy coating on the metal substrate, leading to coating peeling and failure. The influence of seawater temperature and pH on the protective performance of the epoxy coatings is relatively small. The seawater flow rate accelerates the erosion and wear of the epoxy coatings, whereas the impact of marine biofouling on epoxy coatings is limited. This review aims to clarify the protective mechanism of heavy-duty epoxy anti-corrosion coatings on metals in deep-sea environments, by exploring the influence of deep-sea environmental factors on the anti-corrosion performance of heavy-duty epoxy anti-corrosion coatings, to provide important guidance for internal structure regulation and controllable preparation of the heavy-duty anti-corrosion coatings used in deep-sea environments. This review not only highlights the shortcomings of existing studies and future research directions but also provides a theoretical basis for the development of new epoxy heavy-duty anti-corrosion coatings with higher corrosion resistance, better barrier properties, and longer lives.

**Keywords:** deep-sea environment; heavy anti-corrosion coating; anti corrosion mechanism; failure

## 0 前言

海洋是地球上最广阔水体的总称,海洋面积占地表总表面积的 71%,海水平均深度约为 3 700 m<sup>[1-2]</sup>。其中 90%海域深度超过 1 000 m,深海海域面积约占地球总表面积的 65%,深海不仅蕴含着丰富的矿产资源,同时天然气、可燃冰和石油资源的储量巨大,深海已成为最具开发价值和利用潜力的战略空间<sup>[3-4]</sup>。美国(海军水文局、通用电气公

司和海军水下兵器站等)、日本(北九州试验点)、英国(BKL 合金有限公司)等发达国家早在 20 世纪 60 年代末已陆续开展各类材料的深海腐蚀和防污损试验研究,试验材料包括合金材料、碳钢、不锈钢、聚合物材料、橡胶和重防腐涂层材料(共计 2 万片样板),探究各类海洋工程材料在深海腐蚀环境下的电化学腐蚀特性和失效机制,为海底采矿车、深潜器、采油平台等海工装备的结构设计和腐蚀防护提供技术支持和理论指导<sup>[5-9]</sup>。

深海蕴藏着丰富的矿产资源。随着陆地矿产资

源的持续消耗和日益枯竭,发达国家,尤其是沿海发达国家和欧盟已经开始研制各种深海采矿设备和探测设备,并进行不同海水深度的采矿作业。深海矿产资源开发具有广阔的发展前景,对海洋经济的发展起着重要作用。但深海装备都面临着严重海水腐蚀难题,涂装重防腐涂层是减缓海工装备腐蚀最重要也是最普遍的防护技术。由于我国涂料技术研究起步晚,国内涂料原材料的生产厂家在关键树脂和固化剂合成、纯化和性能方面有待进一步提高,导致我国采油平台、海上风电、临海核电等高新技术领域重防腐技术和涂层主要依赖外资品牌。但随着我国生产力水平的提高和腐蚀防护技术的快速发展,现已逐步开展各类金属、合金、浮力材料和功能涂层在不同腐蚀环境(包括深海高压环境)下的耐蚀性能研究工作。王福会团队已成功搭建深海 6 000 m 原位电化学测试系统<sup>[10]</sup>,通过测试深海环境下压力-应力-流体交互作用并结合有限元模拟方法,构建深海有机防腐涂层的理论寿命预测模型,以期实现深海环境中对涂层服役寿命的预测。该团队同时采用电化学交流阻抗谱技术详细探究交变压力对纯环氧涂层在深海腐蚀环境下的失效行为,发现压力增大会导致海水轻松扩散到漆膜内部,使纯环氧涂层的吸水量增大,涂层电阻降低,涂层对碳钢板的防护性能逐渐减弱。邢少华<sup>[11]</sup>采用数值仿真和深海原位测试手段,对比研究深海腐蚀因子对低合金钢-不锈钢体系电偶腐蚀行为的影响规律,并建立了海水温度、溶解氧浓度和偶接电阻三因素影响电偶腐蚀速度的预测模型。方志刚研究员系统研究了深海压力对海水在环氧涂层中传输行为的影响<sup>[12]</sup>,发现深海高压增加了海水在涂层中的传输动力,引起涂层内部结构变化,并指出在深海环境下,提高涂层交联密度可提高涂层在金属基体上的附着力。

深海是一个多因素耦合的复杂苛刻腐蚀环境,与浅海相比,深海具有高静压力、无光、低温、多沉积物和低溶解氧浓度等特点。由于深海环境中温度、盐度、交变压力、流速、溶解氧浓度和 pH 值等随着海水深度的变化而变化,深海服役装备面临着不同等级的腐蚀侵害。长效重防腐防护技术已成为深海装备工程应用必须攻克的共性关键技术<sup>[13-16]</sup>。由于环氧树脂的分子结构中含有活泼的环氧基团,可与不同类型的固化剂发生交联反应,形成多维网状结构的高聚物,是海洋重防腐涂层体系中常用的主要成膜物<sup>[17-20]</sup>。环氧涂层具有以下优点:

① 附着力强,对各类基材均有优良的黏结性,同时漆膜固化收缩率低;② 耐化学品性和耐原油性能优异,耐碱性尤其突出;③ 兼容性好,能同多种树脂、助剂互溶,填料在环氧树脂中的分散性好;④ 制得的环氧涂膜硬度高,兼具一定韧性,同时环氧树脂的相对分子质量不高,有利于配制成无溶剂和高固含涂料。环氧涂层成为最具代表性、用量最大的高性能深海重防腐涂料品种。因此,探究环氧重防腐涂层在深海高压环境下对海工装备的防护机理和失效演化机制,特别是深海高压加速水分子在环氧涂层中的渗透过程,对指导和优化环氧涂层的配方设计、发展高性能深海装备表面防护用涂料技术,具有重要的科学指导意义。

## 1 环氧重防腐涂层的深海防护机理

环氧重防腐涂层具有防腐性能优异、施工简单、性价比高等其他材料与防护技术无法比拟的优点,是深海装备腐蚀防护的优选防护技术。本文结合深海环境下腐蚀电化学的基本理论,阐明环氧重防腐涂层在深海环境中对基材的防护机制,主要包括物理屏蔽作用、缓蚀效应、电化学保护功能<sup>[21-26]</sup>三个方面,以期为发展高性能深海装备用环氧重防腐涂层提供理论指导。

### 1.1 物理屏蔽效应

环氧重防腐涂层可以有效阻隔金属基底与外界腐蚀环境因子(主要包括水分子、氧气、氯离子等)的直接接触而大大降低金属的腐蚀速度。金属发生电化学腐蚀需要水、氧和导电离子形成闭合回路。在深海高压浸没环境下,环氧重防腐涂层能阻止或抑制海水、溶解氧和电解质离子渗透漆膜,使腐蚀介质与金属物理隔离,从而有效抑制金属腐蚀原电池的形成并达到腐蚀防护目的。需要指出的是,任何有机涂层都是半透膜,都不能完全屏蔽腐蚀介质的渗入,随着涂层服役时间的延长,环氧涂层逐渐老化并产生一定孔隙,涂层表面的水分子通过吸附、扩散、溶渗作用逐步渗入涂层/金属基体界面,诱导金属发生电化学腐蚀反应。在持续深海高压环境下,深海高压会加速水分子在涂层内部的渗透速率。由于在环氧涂层/金属基体界面处水分子的渗入,环氧涂层湿附着力降低,加速环氧涂层从防护基体上剥落和失效。同时被防护金属基材与水分子接触后,会发生电化学腐蚀并产生腐蚀产物,腐蚀产物的聚集也会加速漆膜的剥离。因此,环氧重防腐涂层

的致密性和耐渗透性直接决定该涂层在深海高压环境下的服役寿命。

环氧树脂中添加二维层状微/纳米无机填料,可有效提高环氧涂层在深海腐蚀环境中的防护性能。研究表明<sup>[27-31]</sup>,在环氧树脂中添加二维层状材料为功能填料,具有以下优势:①二维层状材料能减小环氧树脂固化过程中漆膜的内应力,降低漆膜体积收缩率,提高环氧涂层在基材的附着力;②二维层状材料可以在环氧涂层中交错排列,形成“迷宫效应”,有效延长腐蚀介质在漆膜中的渗透路径,这对提高环氧重防腐涂料在深海高压海水中的物理屏蔽尤其重要;③二维层状材料的延展性和柔韧性能大幅度提高环氧固化漆膜的物理力学性能,这对提高环氧涂料在深海低温下的防开裂性和韧性十分重要;④二维层状材料可提高环氧重防腐涂料的抗阴极剥离性能<sup>[32]</sup>。常用二维微/纳米无机填料主要包括石墨烯<sup>[33]</sup>、氮化硼<sup>[34-35]</sup>、二硫化钼<sup>[36]</sup>等,添加到有机涂层中可显著提高漆膜的物理阻隔性能和综合防护性能。

王玉琼和刘栓在水性环氧 E44 中添加分散性能良好的石墨烯,发现石墨烯在水性环氧树脂中具有较好的隔水效果。纯水性环氧涂层 E44 和添加 0.5wt.% 石墨烯-E44 涂层在浸泡初期的 Fick 扩散系数分别为  $5.56 \times 10^{-9}$  和  $1.61 \times 10^{-11} \text{ cm}^2 / \text{s}$ ,说明水性环氧中添加 0.5wt.% 石墨烯后,石墨烯可将水分子在纯环氧涂层中的渗透速率降低 300 倍以上。同时发现石墨烯可提高水性环氧涂层的耐盐雾性能,环

氧石墨烯涂层盐雾 200 h 后,其涂层表面完整,未出现明显腐蚀,划线处也没有腐蚀扩展<sup>[37]</sup>。石墨烯还能降低水性环氧涂层在干摩擦和海水摩擦环境下的摩擦因数和磨损率,在环氧树脂表面形成转移膜,抑制磨损裂纹的扩展,进而提高环氧涂层在海水环境中的抗冲蚀性能<sup>[38]</sup>。

物理屏蔽效应是环氧涂层的基本功能,在环氧涂层的配方设计中,可通过调整配方中的颜基比、颜料体积浓度和搭配不同的固化剂等方式,提高环氧涂层的物理阻隔性能。

## 1.2 缓蚀效应

当环氧重防腐涂层添加化学防腐蚀颜填料(缓蚀剂)时,在服役过程中缓蚀剂会从环氧漆膜中缓慢渗出,并与金属基底表面发生化学反应并形成钝化膜,从而抑制金属阳极氧化反应,提高金属的耐蚀性能。如环氧树脂中添加环氧磷酸酯、多聚磷酸锌、多聚磷酸铝、铬酸盐、聚苯胺等缓蚀剂,在长期服役过程中,缓蚀剂会吸附在金属基底表面形成钝化膜,提高金属的耐蚀性。赵海超研究员制备了大量苯胺低聚物类涂层缓蚀剂<sup>[39-41]</sup>,不仅可以作为石墨烯的高效分散剂,还能直接与环氧树脂复合,提高环氧涂层的防护性能。同时,为了提高缓蚀剂与环氧树脂的兼容性,将磷酸与双酚 A 环氧树脂反应制备环氧磷酸酯(图 1),发现在环氧树脂中仅添加 2wt.% 的环氧磷酸酯就可以有效提高环氧漆膜的涂层电阻和电荷转移电阻,进而提高环氧涂层的整体防护效果<sup>[42]</sup>。

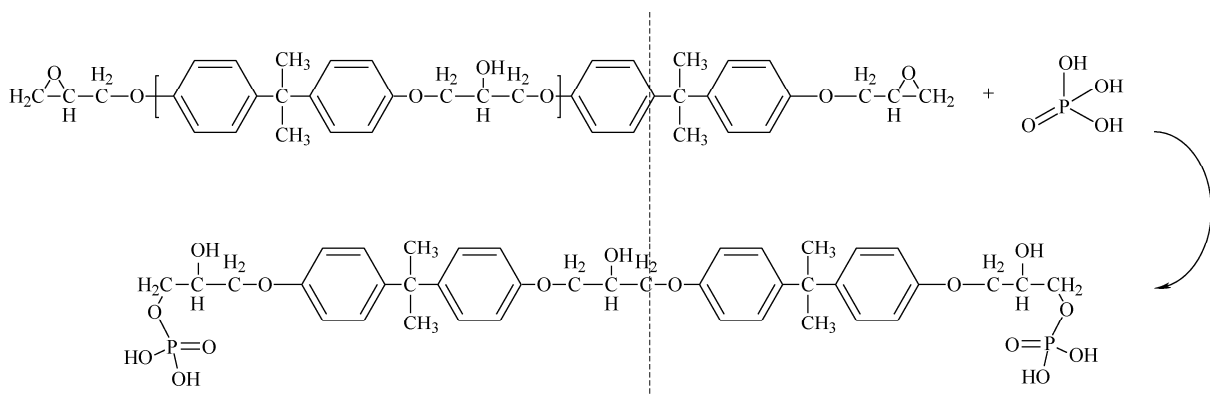


图 1 环氧磷酸酯的合成<sup>[42]</sup>

Fig. 1 Synthesis diagram of epoxy phosphate<sup>[42]</sup>

通过在环氧树脂中添加涂层缓蚀剂,可与涂层本身物理屏蔽作用互为补充,协同提升环氧涂层的防护性能。

## 1.3 电化学保护功能

环氧重防腐涂层中可添加电位比被保护金属电位更负的颜料,当腐蚀介质渗透涂层并与金属基底

发生电化学腐蚀时,被保护金属变成原电池的阴极,电位更负的颜料为阳极而优先腐蚀,从而对被保护金属基底产生电化学保护。对于应用最广泛的钢铁基材,环氧涂层添加大量电位比钢铁更负的颜料(主要是锌粉和铝粉),且颜料之间保持导电通路畅通,就可以有效抑制钢铁基底的腐蚀。环氧富锌涂料是

目前应用最多的具有电化学保护功能的底漆涂料, 所选锌粉主要为球状锌粉和片状锌粉, 球状锌粉粒径优选  $5\sim 10\ \mu\text{m}$ , 而片状锌粉的厚度为  $0.1\sim 0.2\ \mu\text{m}$ 。片状锌粉可以在涂层中形成平行搭接、交叠排列的体系, 提高复合涂层的抗沉降性和屏蔽性能。球状锌粉具有优异的分散性能并形成良好的导电通路, 一般采用片状锌粉和球状锌粉复配, 综合利用二者优势。

为了提高环氧底漆中锌粉的牺牲阳极效果, 研究人员尝试在富锌底漆中添加少量石墨烯、铝粉等导电功能填料, 将石墨烯与锌粉桥接产生“锌激活”效应, 可以提高富锌底漆的耐盐雾性能、耐水性和附着力。图2是环氧石墨烯锌底漆防腐机理示意图, 在环氧富锌底漆中添加石墨烯后, 一方面石墨烯的二维层状结构可以提高漆膜的致密性; 另一方面, 石墨烯优异的导电性能将锌粉颗粒桥接成片, 提高锌粉的电子传输能力, 单道环氧石墨烯锌底漆的耐盐雾性能可达  $3\ 000\ \text{h}^{[43]}$ 。图3是中国科学院宁波材料技术与工程研究所刘栓将自制环氧石墨烯锌底漆与市售环氧富锌底漆在  $3.5\text{wt.}\% \text{ NaCl}$  溶液中浸泡不同时间的交流阻抗谱。由试验结果可知, 对于相同漆膜  $50\ \mu\text{m}$  厚度的环氧石墨烯锌涂层与市售环氧富锌涂层, 在  $3.5\text{wt.}\% \text{ NaCl}$  溶液中浸泡 20 d 后, 二者之间的防护性能差异显著。环氧石墨烯锌涂层的低频阻抗模值高达  $10\ \text{G}\Omega \cdot \text{cm}^2$ , 而市售环氧富锌涂层的模值仅为  $10\ \text{M}\Omega \cdot \text{cm}^2$ 。继续浸泡 30 d 后, 市售环氧富锌涂层几乎失去了防护效果。同时, 长期加速试验中, 在  $3.5\text{wt.}\% \text{ NaCl}$  溶液浸泡 45 d 内, 石墨烯涂层的防护性能没有明显降低, 仍具有良好的防护效果。因此环氧石墨烯锌涂层可以明显提高环氧涂层的防护效果, 有望作为新型防护底漆应用到海洋工程装备的防护实践中。

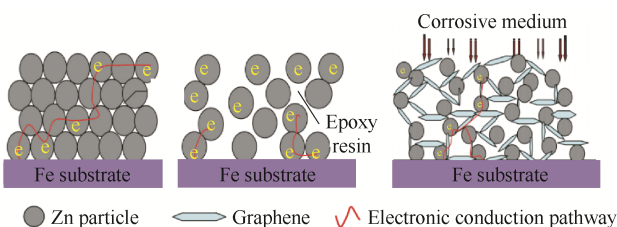
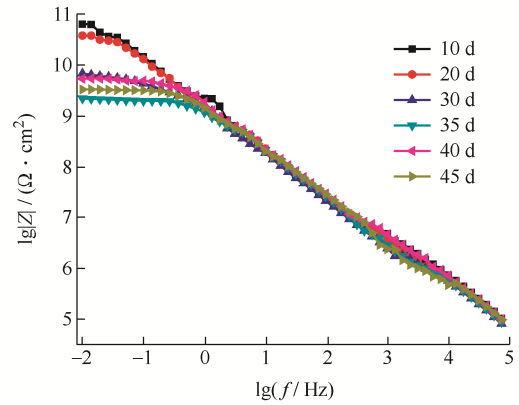
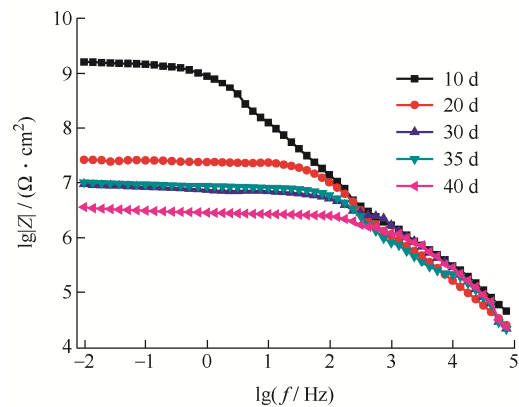


图2 环氧石墨烯锌底漆防腐机理  
Fig. 2 Anti-corrosion mechanism of epoxy graphene zinc primer

通过在环氧树脂中添加电负性更负的颜料, 可增强环氧涂层的电化学保护功能, 延长环氧涂层的服役寿命。



(a) Epoxy graphene zinc primer



(b) Epoxy zinc rich primer

图3 环氧石墨烯锌底漆与环氧富锌底漆在  $3.5\text{wt.}\% \text{ NaCl}$  溶液中浸泡不同时间的交流阻抗谱图  
(涂层厚度为  $50\ \mu\text{m}$ )

Fig. 3 EIS spectra of epoxy graphene zinc primer and epoxy zinc rich primer immersed in  $3.5\text{wt.}\% \text{ NaCl}$  solution after different times (coating thickness is  $50\ \mu\text{m}$ )

## 2 深海环境因素对环氧重防腐涂层防护性能的影响机制

### 2.1 海水静态压力和交变压力

深海静态压力和交变压力都会加速环氧重防腐涂层的腐蚀失效。与常压相比, 深海静水压力会加快海水向漆膜内部渗透速度, 导致涂层吸水率增大, 涂层/金属界面的电荷转移电阻变小。在深海交变压力下, 高压会加快腐蚀介质的渗透过程, 交变压力会导致环氧涂层内部填料与环氧树脂的结合程度降低, 在涂层表面和内部形成微小孔隙。在静水压力和交变压力综合作用下, 涂层吸水率随时间延长而逐渐增大, 导致涂层附着力逐渐下降, 涂层防护性能减弱。

刘斌博士<sup>[44]</sup>提出了涂层在深海环境中的两种失效模型: 渗透失效模型和力学失效模型。其中渗



透失效模型主要依据是深海高压增大了海水在涂层中的渗透量和渗透速度,使涂层提前丧失对金属的防护效果。力学失效模型主要依据是深海交变应力导致涂层内部的微观结构和力学性能发生变化,使涂层附着力和柔韧性快速降低,导致涂层脱落进而失去防护效果。刘栓采用改性环氧树脂为主要成膜物质<sup>[45]</sup>,添加古马隆树脂、硅烷偶联剂和功能填料,制备一种深海防护用高固体份环氧防腐涂料(体积固体份为85%),对比研究该环氧涂层在常压模拟海水环境和超深海高压环境(3 600 m)下对铝合金的防护性能,并采用电子扫描电镜分别对涂层/铝合金体系的截面和平面进行微区拍照表征。发现高固体份环氧防腐涂层在常压海水中浸泡35 d后,高固体份环氧涂层截面无明显缺陷(图4a),涂层平面处的颜填料比较均匀、致密(图4b);而在3 600 m模拟海水溶液浸泡35 d后,高固体份环氧涂层截面处颜填料疏松,填料与环氧树脂结合不紧密(图4c),在涂层平面处可观察到微小孔隙(图4d),主要原因是在深海高压下环氧涂层中的颜填料与环氧树脂容易脱附,海水沿颜填料缝隙渗透环氧涂层内部,导致涂层/碳钢基体界面处发生电化学腐蚀。因此提高环氧树脂在金属基底上的湿附着力和致密性,是延长环氧涂层在深海环境下防护寿命的关键因素。

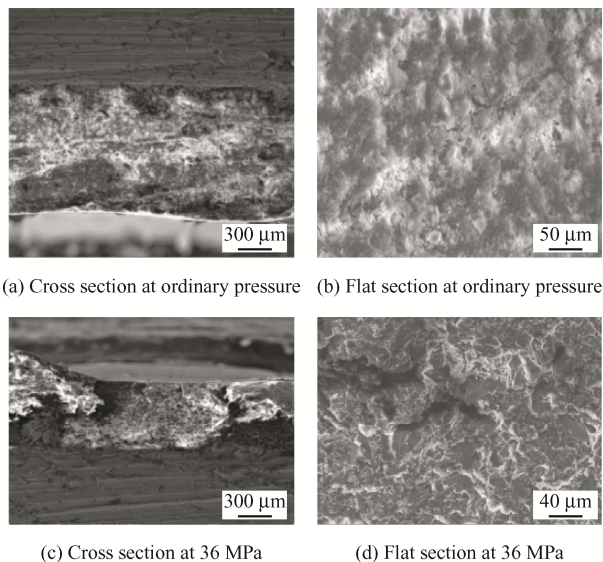


图4 高固体涂层/铝合金体系在常压和36 MPa模拟海水溶液中浸泡35 d后的SEM照片<sup>[45]</sup>

Fig. 4 SEM images of high solid coating/aluminum alloy system soaked in atmospheric pressure and 36 MPa simulated seawater solution after 35 d<sup>[45]</sup>

## 2.2 海水温度和海水 pH 值

海水温度会随着海水深度的增加而降低。500 m 深处的海水温度不到 10 °C, 2 000 m 深处的海水温

度约 2 °C, 5 000 m 深处的海水温度约 1 °C<sup>[46]</sup>。在不同海水深度或海域,一方面水温升高,分子热运动加快会增加海水的导电性能,同时溶解氧的扩散速度增大,会加速金属腐蚀速率;另一方面温度升高,海水中的溶氧量减少,在一定程度上也抑制了金属的吸氧腐蚀。海水温度对环氧涂层的耐久性影响有限,主要是因为环氧重防腐涂层本身耐温性较好,海水温度对漆膜本身的物化特性影响较小<sup>[47-48]</sup>。海水温度的微小变化不会降低环氧重防腐涂层的自身阻隔性能和防护效果。

全海域深度的海水酸碱度在 pH 7.6~pH 8.2。由于环氧涂层本身耐化学品性和耐酸碱性能优异,深海海水 pH 值对漆膜的防护性能影响可忽略不计。但是当水分子渗透环氧漆膜,与金属基底发生电化学腐蚀后,吸氧反应会在局部微区形成强碱环境,导致漆膜与基材之间的湿附着力降低,加速环氧涂层的剥落。

## 2.3 海水流速和海生物污损

随着海域或季风气候影响,海洋表面产生洋流效应会导致上层海水流速变化较大。但在深海环境下洋流效应要比海面小得多,海水流速对环氧重防腐涂层/金属体系的耐久性影响主要取决于环氧涂料自身的特性。但在海底环境中,海水中掺杂的泥沙会对环氧涂层表面形成持续冲刷腐蚀,因此选择韧性好、具有一定抗冲蚀能力的环氧涂层,具有更优异的深海防护性能。

海洋污损生物指能够附着、栖息、定殖在各种海洋工程设施上,造成经济损失或危害的动物、植物和微生物的总称<sup>[49]</sup>。目前已报道的海洋污损生物超过 4 000 种,我国各海域记录在案的主要污损生物高达 2 000 多种,包括黏附微生物(如细菌、真菌和厌氧菌等)、海生植物(如藻类、硅藻、浒苔、水云等)和海生动物(如藤壶、苔藓虫、牡蛎、水螅类、石灰虫、海鞘、花筒螅等)<sup>[50-52]</sup>。海生动物是造成海洋污损的主体生物,但是植物、细菌等黏附微生物在材料表面快速分泌黏液,形成一层黏膜,为大型海生动物提供了营养和附着载体,在海工构筑物表面共同形成了小型生态系统。海洋污损生物的多样性决定了海洋生物污损的复杂性。

但在深海环境下,由于缺乏光合作用,海生物污损主要以软体类动物污损为主。相对于浅海区,深海区的嗜氧、厌氧细菌等微生物的附着对材料的腐蚀作用更为显著。微生物附着生长在环氧涂层表面,形成特定的生物膜,该膜层将改变涂层/海水

界面环境的物理化学特性, 以硫酸盐还原菌和铁氧细菌为代表的微生物新陈代谢会产生大量腐蚀性硫化氢, 从而造成严重的局部腐蚀<sup>[53]</sup>。目前环氧涂层在深海环境下的生物污损研究处于起步阶段, 后续需要腐蚀科研工作者长期深入研究深海环境下海生物污损对环氧重防腐涂层的影响机制。

### 3 环氧重防腐涂层在深海海工装备的最新研究进展

深海蕴含着丰富的石油资源和矿产资源, 目前已探明具有开发前景的深海矿产资源包括多金属结核、富钴结壳、多金属硫化物等, 其中锰、镍、钴等金属的储量远高于陆地储量<sup>[54-56]</sup>。世界各国都在积极探索深海矿产资源的开采, 尽管海底矿产资源储量巨大、品位高, 但开采难度极大, 主要是由于深海海底地形复杂、压力高、低温、无光照, 同时存在海浪、洋流、内波等复杂海洋环境条件, 对作业设备提出了极高的安全性要求, 深海装备的腐蚀防护难题已经成为制约深海采矿的重要因素。美国、日本、英国等国家早已开展各类深海装备材料的耐腐蚀和防污损试验, 探究各类海洋工程材料在深海腐蚀环境中的腐蚀机理和失效演化过程<sup>[57-58]</sup>。

以美国、日本为主的发达国家针对深海装备腐蚀防护前期已开展大量试验研究, 对涂料性能测试尤其是耐海水压力性能评价十分重视。通过查阅各国海军深海装备上涂料品种可以发现, 环氧重防腐涂料是应用范围最广的深海装备防护涂料。高固体份和高膜厚是深海装备防护涂料的共同特点。涂层越厚, 海水渗透速率越小, 高固体份涂料不仅可以减少溶剂挥发, 增加漆膜厚度, 还具有优异的耐海水性和耐化学品性, 使漆膜能够抑制海水渗透, 具有良好的耐蚀性和长效使用寿命<sup>[59-60]</sup>。

美国海军部海上系统司令部批准 INTERGARD143 高固体份环氧涂料作为深海装备维修保养涂料, 高固体份环氧涂层具有致密性好和交联密度高等优势, 可以显著提高海工装备的防护性能<sup>[59]</sup>。俄罗斯海军深海装备主要采用以 E-51 液态环氧树脂制备的厚浆型高固体涂料(干膜厚度超过 1 000  $\mu\text{m}$ )<sup>[61]</sup>。英国海军的深海装备接触水部位采用的是体积固体含量大于 82% 的环氧高固体份防腐涂料配套, 一般涂装两道, 防腐层总厚度为 300  $\mu\text{m}$ <sup>[62]</sup>。德制 209 级深海装备防腐蚀涂料配套采用高固体份环氧涂料(体积固含为 81%), 干膜厚度达 550  $\mu\text{m}$ , 所设计的深海装备涂料配套使用海域与

中国南海情况类似, 设计使用寿命 10 年。中国科学院宁波材料技术与工程研究所王立平课题组为深海装备开发的高固体环氧重防腐涂层, 采用低表面处理底漆(100  $\mu\text{m}$ ) + 高固体环氧石墨烯面漆(400  $\mu\text{m}$ ) 进行配套, 在 2 000 m 东海海域服役两年后, 漆膜完整, 无任何腐蚀迹象。同时该课题组为海上风电钢管桩开发的高固体环氧石墨烯厚浆涂层体系, 一次成膜厚度可达 500  $\mu\text{m}$ , 极限成膜厚度可达 1 000  $\mu\text{m}$ , 设计防护寿命为 25 年, 已经在国电浙江象山海上风电场进行大规模工程应用(图 5), 目前服役一年, 综合防护性能良好。



图 5 高固体环氧石墨烯厚浆涂层在钢管桩上的涂装照片

Fig. 5 Coating photo of high solid graphene modified epoxy coating coated on steel pipe piles

总体来说, 国内环氧重防腐涂层在深海海工装备的规模应用还处于起步阶段, 环氧涂层的长效服役性能需要持续监测和评估。随着深海大洋战略的稳步开展, 对深海装备防护技术的要求随之提高<sup>[63-66]</sup>。腐蚀防护工作者可通过对环氧树脂及固化剂的化学改性, 特种环氧树脂的高分子合成, 并与各类功能填料(包括二维片层材料、自修复填料、柔性填料)进行复配, 优化涂料配方体系等手段来综合提升环氧涂层的深海防护性能<sup>[67-68]</sup>。

### 4 结论与展望

环氧重防腐涂层作为深海装备最常用的防护材料, 环氧涂层的可靠性和服役寿命对深海装备的安全可靠运行至关重要。与浅海相比, 环氧重防腐涂层在深海环境下的腐蚀失效主要受海水交变压力和高压海水渗透的影响。高压使海水在环氧涂层中的渗透速度加快, 导致环氧涂层/基材界面处的结合力快速下降, 水和腐蚀产物在涂层/金属界面处聚集, 最终导致环氧涂层剥离并失效。本文从环氧重防腐涂层的深海防护机理、深海环境因素对环氧重

防腐涂层防护性能的影响机制和环氧重防腐涂层在深海海工装备的最新研究进展三方面概述近年来国内外的最新研究成果:

(1) 环氧重防腐涂层在深海环境中可通过物理屏蔽作用、缓蚀效应和电化学保护功能对深海装备进行长效防护。物理屏蔽效应是环氧涂层的基本功能,可通过调整配方中的颜基比、颜料体积浓度和搭配不同的固化剂等方式,来提高环氧涂层的物理阻隔性能。在环氧树脂中添加涂层缓蚀剂和电负性更负的颜料,可与涂层本身物理屏蔽作用互为补充,协同提升环氧涂层的防护性能。

(2) 深海静态压力和交变压力都会加速环氧重防腐涂层的腐蚀失效。海水温度和海水 pH 值对环氧涂层防护性能的影响较小。海水流速会加速环氧涂层的冲蚀磨损,海生物污损对环氧涂层的影响有限。

(3) 国内环氧重防腐涂层在深海海工装备的规模应用还处于起步阶段,环氧涂层的长效服役性能需要持续监测和评估。

基于以上总结,为推动环氧重防腐涂层在海工装备的大规模工程应用,对提高环氧重防腐涂层的性能做出以下展望:

(1) 提高环氧重防腐涂层的物理阻隔性能。尤其是提高环氧树脂在金属基底上的湿附着力和致密性,是延长环氧涂层在深海环境下防护寿命的关键指标。

(2) 提高环氧重防腐涂层的综合防护性能。通过对环氧树脂及固化剂的化学改性,特种环氧树脂的高分子合成,并与各类功能填料(包括二维片层材料、自修复填料、柔性填料)进行复配,优化涂料配方体系,最终综合提升环氧涂层的深海防护性能。

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作者简介: 王朴炎, 男, 1992 年出生, 工程师。主要研究方向为金属腐蚀与防护。

E-mail: 692972506@qq.com

刘栓(通信作者), 男, 1986 年出生, 博士, 高级工程师, 硕士研究生导师。主要研究方向为海洋腐蚀与防护。

E-mail: liushuan@nimte.ac.cn