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金属有机框架材料在防腐涂层中的应用进展*

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摘要: 金属有机框架材料是由金属离子和有机配体自组装而成的多孔配位聚合物,具有大比表面积、结构功能可调、高孔隙率、高表面活性等优势,金属有机框架材料在金属防腐领域表现出巨大的应用潜力,然而还少有相关的研究综述,有必要对目前金属有机框架材料在金属表面防腐涂层领域的研究成果进行综述。系统总结近年来该领域的相关研究成果,以金属有机框架材料的自身特性和防腐机理为出发点,分类概述金属有机框架材料功能性填料在防腐涂层中的应用以及防腐转化膜材料的最新研究。相关研究结果表明:金属有机框架材料作防腐涂层的功能性填料或防腐转化膜能极大增强对金属的防腐保护,金属有机框架材料功能性填料可改善涂层的致密度与相容性,作为理想容器负载活性剂实现了涂层的自修复、腐蚀自预警等功能性;另外,直接在金属表面制备金属有机框架材料防腐转化膜实现了涂层的主动防护(物理阻隔效应)和被动防护(响应释放缓蚀剂),将金属有机框架材料应用在防腐涂层中增强了对金属的防护性能,延长了金属基体的使用寿命。讨论了金属有机框架材料在应用过程中存在的问题并提出可行的解决途径,对金属有机框架材料在金属防腐涂层领域的应用前景和发展方向进行展望。

关键词: 金属有机框架; 腐蚀防护; 防腐涂层; 填料; 转化膜

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Research Progress of Metal-organic Frameworks in Anti-corrosion Coatings

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Abstract: Metallic corrosion has been a major challenge worldwide for a long time. In addition to significant economic losses, there are concomitant risks of security loss and environmental pollution. Coating can be an economic and effective method to retard the corrosion of metals. However, a simple passive anticorrosion coating is difficult to achieve a long-term and effective anticorrosion effect. Once the coating is damaged, it fails, and even a more serious local corrosion occurs. In recent years, an intelligent self-healing anticorrosion coating has been proposed based on micro- and nanocontainers that can release functional substances such as corrosion inhibitors according to environmental changes, independently repair the damaged parts of the coating, restore the protective ability of the coating, and prolong the service life of the metal matrix. The metal-organic framework material is a porous coordination polymer composed of metal ions and organic ligands, which has a large specific surface area, tunable structure and function, high porosity, high surface activity, etc. Recent studies have shown that metal-organic framework materials have high application potentials in the field of metal anticorrosion. The reviews on the related studies are still rather scarce. It is necessary to review the current research results of metal-organic framework materials in the field of anticorrosion coatings on metal surfaces. This paper systematically summarizes the related research results in this field. Based on the characteristics and anticorrosion mechanism of metal-organic

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framework materials, this paper summarizes the research progress of metal-organic framework materials for metal surface coating from two aspects. One of them is the application of metal-organic framework materials as functional fillers in anticorrosion coatings, including epoxy, acrylic, polyhexylactone, polyvinyl butyraldehyde, polyvinylidene fluoride, and sol-gel coating. The other is the use of the metal-organic framework as the main body of a film layer in a metal anticorrosion coating. Relevant research results show that the metal-organic framework material can largely enhance the protection of metals against corrosion, as functional fillers or conversion films in anticorrosion coatings. Metal-organic framework functional fillers improve the denseness and compatibility of the coating, as ideal containers to load active agents and achieve self-healing, corrosion self-reporting, and other functions. In addition, a metal-organic framework anticorrosion conversion film can be prepared directly on the metal surface to achieve a passive protection (physical barrier effect) and active protection (response to the release of corrosion inhibitors) of the coating. The application of metal-organic framework materials in anticorrosion coatings enhances the corrosion resistance performance and extends the service life of the metal substrate. Although the metal-organic framework film layer and metal-organic framework anticorrosion coating are constantly studied and improved, there are still some technical and controllability problems. First, even though the metal-organic framework conversion film and metal-organic framework anticorrosion coating exhibit ideal corrosion resistances, it is impossible to prepare a metal-organic framework material on a large scale due to the cost and process. Second, different metal-organic framework materials, different metal-organic framework concentrations, different metal substrates, and different process parameters affect the corrosion resistance performance of the metal-organic framework anticorrosion coating. In addition, there are still challenges in maintaining the long-term corrosion resistance of a metal-organic framework material. Therefore, this paper introduces the application of metal-organic framework materials in anticorrosion coatings, and outlines the future development trend. First, the advantages of the metal-organic framework structure and composition should be fully studied. To further improve the loading efficiency of inhibitors, it is necessary to design multiple-response and release-controllable metal-organic framework nanocontainers. Second, the use of novel methods such as machine learning facilitates the screening of proper metal ions and ligands, preparation of metal-organic framework materials with excellent inhibition performances, and investigation on the relevance between the inhibition properties and metal-organic framework structures. With the design of the coating combined with metal-organic framework nanocontainers, properties such as multieffect, long-term effect, and intelligent anticorrosion can be achieved. Third, based on the full application of existing technical methods (in-situ growth, electrospinning, electrochemical deposition, etc.), numerous new methods to prepare a dense metal-organic framework anticorrosion conversion film with a strong adhesion will emerge.

Keywords: metal-organic framework; corrosion protection; anticorrosion coating; fillers; conversion film

0 前言

金属腐蚀一直是各国面临的主要挑战之一, 据统计, 工业发达国家每年由于腐蚀造成的损失占国民经济总产值的 2%~4%, 全世界每年因腐蚀造成的直接经济损失 7 000~10 000 亿美元, 远远超过水灾、火灾、风灾、地震等自然损失的总和^[1-2]。此外, 腐蚀问题还给人们生活带来了潜在的安全隐患以及环境污染^[3-4]。因此, 鉴于金属腐蚀问题的严重性, 研究者一直致力于尝试各种措施来减轻腐蚀的危害。涂层技术是延缓金属腐蚀的经济与有效手段, 通过物理屏障效应将腐蚀因子隔绝在外, 达到金属腐蚀防护的效果。然而, 随着金属材料面临日益严苛的服役条件, 单纯的被动防腐涂层难以达到长久、有效的防腐效果, 一旦涂层受损则会失效, 甚至发生更严重的局部腐蚀。近年来发展起来的基于微纳

米容器的智能自修复防腐涂层, 可根据环境变化释放缓蚀剂等功能性物质, 自主修复涂层受损处, 恢复涂层的防护能力, 延长金属基体的使用寿命。目前主要的微纳米容器包括有机大分子(如聚合物微胶囊^[5]、纳米纤维^[6]、壳聚糖^[7]、环糊精^[8]), 纳米碳材料(如碳纳米管^[9]、石墨烯^[10]), 介孔纳米颗粒(如二氧化硅^[11]、二氧化钛^[12]), 无机粘土(如多水高岭石^[13]、类水滑石^[14]、沸石^[15])等。

金属有机框架化合物是由多齿有机配体和金属离子或金属簇自组装而成的三维多孔材料, 与上述材料相比具有更加致密的周期性网络结构, 因而呈现高比表面积、高孔隙率、高活性等特性^[16], 已在气体存储^[17-19]、催化^[20-21]、抗菌^[22-24]等领域得到广泛研究与应用。最近几年, 金属有机框架材料已发展成为金属表面防腐涂层领域的研究热点。目前金属有机框架材料在防腐涂层中的研究主要有两种思路, 一是利用金属有机框架材料的多孔道、多活性

基团及可调粒径等特点负载缓蚀剂或其他功能性物质,作为防腐涂层的功能性填料;二是在金属表面直接制备金属有机框架材料防腐转化膜。图1为目前金属有机框架材料用于金属表面防腐涂层的示意图。

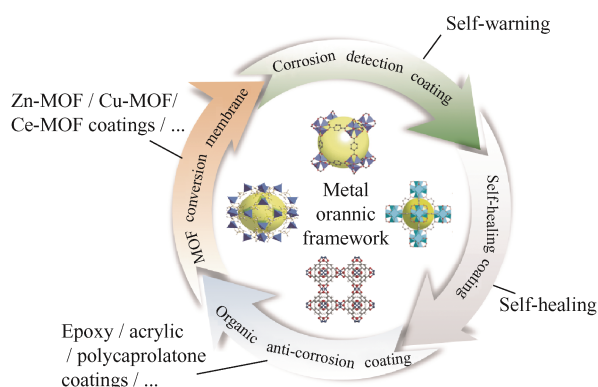


图1 金属有机框架材料用于金属表面防腐涂层示意图

Fig. 1 Schematic diagram of metal organic framework applied to anti-corrosion coatings on metals

本文以金属有机框架材料的自身特性和防腐机理为出发点,分为金属有机框架材料功能性填料在防腐涂层中的应用和金属有机框架材料防腐转化膜两大部分,综述近年来金属有机框架材料用于涂层防腐的研究进展,并分别讨论不同类型的金属有机框架材料对涂层防腐性能的影响。最后对金属有机框架材料在金属防腐涂层领域的应用前景和发展方向进行了展望。

1 金属有机框架填料在防腐涂层中的应用

目前,金属有机框架材料可作为功能性填料应用于多种防腐涂层中,主要包括环氧涂层^[25-48]、丙烯酸涂层^[49-50]、聚偏氟乙烯涂层^[51]、聚乙烯醇缩丁醛涂层^[52]、聚己内酯涂层^[53]和溶胶-凝胶涂层^[54-57]。上述研究报道普遍表明:未添加金属有机框架材料填料的涂层在固化过程中由于气体逸出或溶剂挥发,涂层普遍存在裂纹和针孔,对金属基体的防护性能不理想;添加金属有机框架材料填料的涂层有效改善了涂层的致密度与耐蚀性。金属有机框架材料作为理想的纳米容器可封装缓蚀剂、预警剂,避免活性功能剂与涂层间的强相互作用,保留了涂层的完整性;此外,金属有机框架纳米容器避免了活性功能剂短期内迁移和逸出,具有控制释放活性剂的优点,从而实现对金属表面涂层的自修复、腐蚀

自预警等功能特性。金属有机框架功能性填料在防腐涂层中兼具两方面的作用:一是智能防腐,金属有机框架材料可对某些环境因素变化产生响应(如pH、离子、水等),但由于金属有机框架材料在防腐领域的应用起步较晚,目前主要利用其pH响应性释放活性功能剂,实现涂层的自修复或自预警,且金属有机框架材料自身具有缓蚀作用,增强了涂层的主动防腐性能;二是化学键合,金属有机框架材料中的活性基团易与树脂或固化剂相互作用,与涂层具有良好的相容性,加上金属有机框架纳米粒子填充涂层的缺陷,有效提升了涂层的相容性,有利于填料分散,进而获得良好的综合性能,包括力学性能等。本文总结了不同金属有机框架材料用于防腐涂层的发展历程(图2),可以看到近年来,各类金属有机框架材料在防腐涂层中的研究受到了越来越广泛的关注。

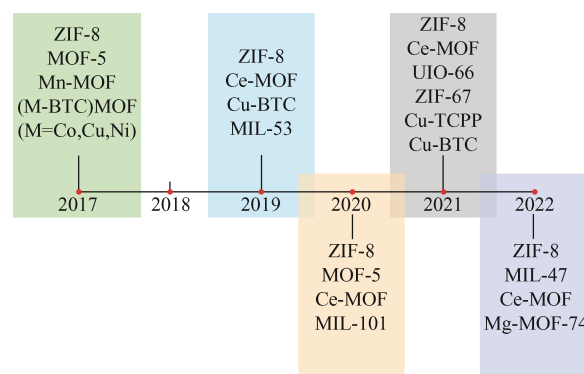


图2 不同金属有机框架材料用于防腐涂层的发展历程

Fig. 2 Development chart of different metal organic framework applied to anti-corrosion coatings

1.1 有机防腐涂层

常用的有机防腐涂层有环氧、丙烯酸、聚己内酯、聚乙烯醇缩丁醛等涂层,普遍具有较好的耐腐蚀性、防水性、便于施工等优点,并且可在很宽的温度和湿度范围内使用,大大延长了金属基体的使用寿命。然而涂层基体有一定的亲水性,导致外界污染物能够缓慢透过涂层,形成与基材的直接接触,从而逐步失去防腐作用。目前,金属有机框架材料作为功能性填料应用在有机防腐涂层中有效改善了传统涂层存在的问题,研究表明^[25-48],大多数金属有机框架材料与有机、无机材料表现出良好的相容性,添加金属有机框架材料的防腐涂层改善了涂层的物理阻隔效应、耐蚀性能、力学性能、长期保护能力等,表现出良好的应用前景。MOTAMEDI等^[38]采用一锅共沉淀法制备出以2-甲基咪唑为配体的

Ce-IM 粉末, 将其均匀分散在环氧涂层中合成具有较好防腐性能和热力学性能的环氧复合涂层。试样经划痕盐雾试验 24 d 后, 仅出现少量腐蚀产物, 无明显的涂层脱落, 表明 Ce-IM 基防腐涂层对碳钢有良好的保护作用, 而不含 Ce-IM 材料的划痕试样表面出现严重的涂层脱落。Ce-IM 填料在环氧涂层中的防腐作用主要归结于三个方面: 一是 Ce-IM 响应释放的 Ce^{3+} 和咪唑分子具有缓蚀作用, 在金属表面形成保护层; 二是涂层可将腐蚀介质与基体隔开, 并为金属提供有效保护; 三是 Ce-IM 与环氧基体发生开环反应, 且 Ce-IM 填充了涂层的孔洞, 有效改善了涂层的致密性和交联密度。此外, 金属有机框架材料在丙烯酸、聚己内酯、聚乙烯醇缩丁醛等聚合物涂层中的应用也取得了一定进展^[49-53]。YIN 等^[51]在镁合金表面制备了以 1H, 1H, 2H, 2H-全氟癸基三乙氧基硅烷改性的聚偏氟乙烯 (PVDF) 和双金属氢氧化物 (LDH) 复合涂层, 添加 ZIF-8 的复合涂层兼具良好的耐蚀性、超疏水性和机械磨损性, 测得腐蚀电位 (E_{corr}) 为 $-1\ 617\ \text{mV}$, 腐蚀电流密度 (I_{corr}) 为 $2.26\ \mu\text{A} \cdot \text{cm}^{-2}$ (相比镁合金降低约 3 个数量级), 电荷转移电阻 (R_{ct}) 为 $66\ \text{k}\Omega / \text{cm}^2$, 缓蚀率 (η) 达到 99.95%, 在 3.5 wt.% NaCl 溶液中浸泡 7 d 后, 仍保持较好的耐蚀性。金属有机框架基涂层除了应用于工业防腐领域, 目前在生物医疗领域也受到了越来越多的关注与研究。ZHENG 等^[53]报道了一种由聚己内酯 (PCL) 和叶酸 (FA) 修饰的 HKUST-1 复合涂层, 改性后的涂层兼具三方面的特性: 一是良好的致密性, 金属有机框架通过氢键均匀分布在 PCL 涂层中; 二是优良的耐蚀性, 试验测得含复合涂层的镁合金 R_{ct} 为 $244\ \text{M}\Omega / \text{cm}^2$, I_{corr} 为 $164\ \text{nA} \cdot \text{cm}^{-2}$ (相比基体降低约 5 个数量级); 三是良好的生物相容性, PCL 无毒, 具有生物可降解性, 且释放的 Cu^{2+} 能促进成骨细胞的增殖和分化, 促进了镁合金在可降解植入体的应用。

此外, 金属有机框架材料在有机-无机杂化涂层中也表现出良好的耐蚀性^[54-57]。LI 等^[56]将金属有机框架材料应用到溶胶-凝胶法制备的杂化涂层中, 使复合涂层兼具良好的耐蚀性和致密性。涂层中的主要功能填料—Mg-MOF-74 粉末通过水热法制备; 将此填料分散在硅烷溶胶中制备 Mg-MOF-74 复合涂层, 极化曲线测得复合涂层的 E_{corr} 为 $-1\ 330\ \text{mV}$ (相比镁合金提升 $121\ \text{mV}$), I_{corr} 为 $1.176\ \mu\text{A} \cdot \text{cm}^{-2}$ (相比镁合金降低约 1 个数量级), 由于 Mg-MOF-74 的

—OH 与硅烷水解生成的 Si-OH 发生脱水缩合反应, 改善了涂层的交联密度和耐蚀性。

1.2 自修复涂层

自修复涂层是指在极少或无需外界干预的情况下, 能够修复涂层损伤并恢复性能的涂层, 其中最常见类型是用纳米容器封装修复剂的外援型自修复涂层。金属有机框架材料是理想的纳米容器, 将其封装缓蚀剂后添加到防腐涂层, 可赋予涂层自修复性能。金属有机框架材料比常用的几种纳米容器 (如水滑石、埃洛石纳米管、介孔二氧化硅) 有更显著的优势: 一方面是负载过程简单, 便于设计金属有机框架材料结构前封装缓蚀剂; 另一方面是负载量较高, 金属有机框架材料的大比表面积和高孔隙率有利于更多缓蚀剂分子的负载。金属有机框架材料在自修复涂层中具有以下两方面的作用机理: 一是部分金属有机框架纳米容器在水、氧、pH 值、离子等触发条件下裂解释放具有缓蚀作用的稀土金属或咪唑等配体, 在金属表面形成吸附膜, 或再次聚合成金属有机框架网络^[58]; 二是负载缓蚀剂的金属有机框架纳米容器可赋予防腐涂层自修复性能, 缓蚀剂通过氢键或化学键与金属有机框架材料结合, 不仅避免了缓蚀剂分解造成的浪费, 而且金属发生腐蚀时金属有机框架材料响应释放的缓蚀剂可以渗透到涂层缺陷处, 抑制在金属基体暴露处发生的电化学反应^[59]。

截至目前, 金属有机框架基涂层的自修复性主要来源于金属有机框架材料自身的缓蚀作用或金属有机框架材料释放的缓蚀剂^[25-69]。比如, XIAO 等^[31]采用一锅共沉淀法合成了掺杂铈基金属有机框架材料 (Ce-IM) 的 ZIF-8 纳米粒子, 将该复合纳米材料应用于环氧树脂中, 使铝合金兼具优良、长久的耐蚀性能和自修复性能。当 Ce-IM / ZIF-8 添加量为 1 wt.% 的复合涂层耐蚀性最好, 老化试验前测得 Z 为 $100\ \text{G}\Omega / \text{cm}^2$, 经过 6 个周期 (720 h) 的老化试验后, 阻抗仍保持在 $220\ \text{M}\Omega \cdot \text{cm}^2$, 划痕试样表面在 60 d 的盐雾试验后无明显水泡和锈蚀点, 证实了金属有机框架纳米粉末的加入显著提高了涂层自愈合能力。其原因分为以下两个方面: 一是复合纳米粒子分解释放的 Ce^{3+} 、 Ce^{4+} 、 Zn^{2+} 离子和 2-甲基咪唑分子具有自修复性, 在缺陷区域形成沉积层, 有效抑制铝合金的腐蚀; 二是复合涂层的物理屏蔽效应, 有效阻挡腐蚀因子 (Cl^- 、 H_2O 、 O_2) 的侵入。MOHAMMADPOUR 等^[54]通过采用电辅助沉积在镍铁二元合金表面制备了掺杂 Cu-BTC 的硅溶胶凝

胶复合涂层, 其中 Cu-BTC 原位负载的 2-氨基苯并噻唑 (2-ABT) 使涂层具有更持久的耐蚀性, 负载率约为 10%, 试验测得复合涂层的 E_{corr} 为 -259.8 mV (相比基体提升 85.7 mV), I_{corr} 为 $1.93 \mu\text{A} \cdot \text{cm}^{-2}$ (相比基体降低约 1 个数量级), η 为 97.53%, 表现出良好的耐蚀性。此外, 添加与未添加 2-ABT 的涂层在 1 d 前参数保持一致, 但随着时间推移, 两种涂层耐蚀性差异越来越大, 一方面是由于 2-ABT 的胺基与二氧化硅膜层的羟基之间形成氢键, 金属表面可与 2-ABT 芳环中的硫、氮和 π 电子相互作用, 有效提高涂层的致密度; 另一方面是 Cu-BTC 随腐蚀响应缓慢释放具有自修复性的 2-ABT, 化学吸附在金属表面形成保护层。

1.3 腐蚀预警涂层

腐蚀预警涂层是一种依靠单一活性成分实现自主预警的涂层^[70], 能够对涂层破损及基底金属的早期腐蚀做出及时检测。金属有机框架材料可以作为腐蚀预警剂的载体, 实现涂层的腐蚀预警指示, 其作用机理是金属有机框架纳米容器在水、氧、pH 值、离子等条件下破裂释放腐蚀预警剂, 产生明显的荧光或颜色变化实现涂层腐蚀的自动检测。

WANG 等^[71]报道了一种荧光比色传感的环氧涂层, 实现铜合金的早期腐蚀检测。他们通过酰基化和席夫碱反应两步合成腐蚀预警剂罗丹明 B 衍生物 (RHS), 用 ZIF-8 包封活性探针 RHS 实现涂层的腐蚀自预警 (图 3)。试验结果表明制备的涂层在无破损的前提下可进行早期腐蚀检测, 检测灵敏度明显优于未添加金属有机框架的 RHS 涂层, 主要是由于 ZIF-8 作为纳米容器降低了 RHS 的浓度, 腐蚀检测机理是 RHS 对 Cu^{2+} 有高灵敏度和特异性, 在腐蚀过程中 RHS 与释放的 Cu^{2+} 反应后从螺旋内酰胺转变为开环酰胺结构, 从而检测到腐蚀产生的红色荧光信号。尽管金属有机框架材料用于涂层的腐蚀检测取得了一定进展, 然而, 仅实现腐蚀传感功能的涂层缺少主动防护性能, 对金属往往表现出不理想的防护效果。因此, LIU 等^[72]构建了具有高效腐蚀传感和主动防护功能的智能防腐系统, 合成了以聚乙二醇-单宁酸为外壳, ZIF-7 作为核心的纳米传感器, 添加纳米传感器的环氧涂层兼具三重功能: 一是抗渗性, 致密均匀的涂层在早期可防止电解液的侵入; 二是腐蚀检测性, 当发生腐蚀时, 纳米传感器解离释放单宁酸, 单宁酸可快速捕捉铁离子变为紫色; 三是自愈合性, ZIF-7 响应释放的苯并咪唑配体具有缓蚀性, 在金属表面形成不溶性保护膜。

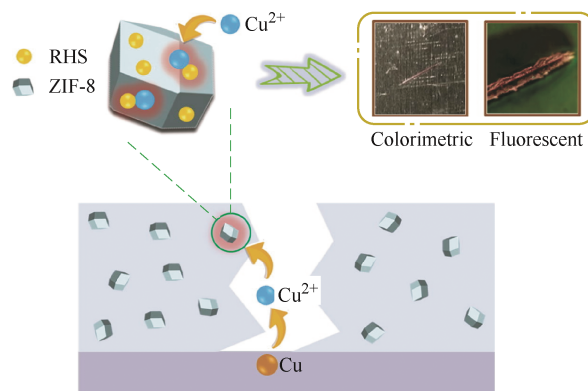


图3 智能涂层的腐蚀自预警^[71]

Fig. 3 Corrosion self-warning of smart coating^[71]

综上所述, 金属有机框架材料是理想的纳米载体, 其自身结构和成分具有丰富的可调变性, 其孔道结构及表面活性对缓蚀剂、腐蚀预警剂有高的负载率, 部分金属有机框架材料自身组分还具有一定的缓蚀作用, 将金属有机框架填料应用在有机防腐涂层中有效改善了涂层的物理阻隔效应、耐蚀性、力学性能等, 实现了涂层的自修复和腐蚀自预警功能, 对金属基体表现出良好的防护与腐蚀检测性能。

2 金属有机框架防腐转化膜的制备

金属有机框架材料在防腐涂层应用中的另一种思路是, 直接在金属表面制备金属有机框架防腐转化膜。金属有机框架防腐转化膜的生长机理可以分为三个过程^[73]: 一是在初期金属离子与配体自组装, 形成金属有机框架纳米小晶体颗粒; 二是金属有机框架材料通过有序组装形成相貌规则的超结构; 三是超结构逐渐形成完美的金属有机框架材料单晶层。目前, 生长金属有机框架防腐转化膜的方法包括原位生长^[74-81] (原位室温生长、原位水热生长、原位溶剂热生长)、电化学沉积^[82-86]、电泳沉积^[87-89]、静电纺丝技术^[90-93]和蒸汽固相转化^[94], 其中, 采用原位溶剂热生长金属有机框架膜的研究居多, 原因是制备的膜层耐蚀性好、膜层更致密均匀。金属有机框架防腐转化膜的缓蚀机理可分为主动和被动防护, 被动防护指金属有机框架膜的物理阻隔效应, 可有效防止腐蚀因子的侵入; 主动防护指金属有机框架膜受到外界刺激 (pH、压力、光照等) 后, 响应释放缓蚀剂抑制金属腐蚀。近几年金属有机框架防腐转化膜在金属防腐领域受到越来越多的研究与关注 (表 1)。

2.1 原位生长

目前, 金属表面原位生长的金属有机框架转化膜可以分别在室温、水热 (水溶液)、溶剂热 (有机

溶剂或非水溶媒)条件下制备。一是在室温下合成金属有机框架转化膜,该方法操作简单,易于大规模制备^[74-76]。NI 等^[74]首先在锌合金表面氢氟酸处理制备羟基氟化锌(ZnF_2)层,将合金置于硝酸锌和 2-甲基咪唑混合液中成功制备了附着力良好的 ZIF-8/ ZnF_2 复合膜层,在 3.5 wt.% NaCl 腐蚀环境下复合膜层对锌合金表现出较好的耐蚀性能,原因一方面 ZIF-8 释放的咪唑分子被金属表面吸附,具有缓蚀作用,另一方面是基体本身提供部分锌源,膜层与基体产生强的界面结合力,且结构紧密。CHEN

等^[76]首先在镁合金表面制备了微弧氧化(MAO)层,再采用溶剂热法制备氧化石墨烯(GO)和 MgAl-NO_3 双氢氧化物(LDH)复合层,这一复合层能够为 ZIF-8 提供金属源,并促进 ZIF-8 的成核生长,最后在镁合金表面原位合成出纯相、均匀、良好共生的 ZIF-8 转化膜,ZIF-8 膜层具有优异的稳定性和耐腐蚀性:一方面是由于 ZIF-8 减少了 GO/LDH 层晶界缺陷,且 ZIF-8 转化膜与 GO/LDH 层的强相互作用提升了整个膜层的稳定性;另一方面,GO 具有高渗透阻力和高纵横比,增强了膜层的阻隔性能。

表 1 金属有机框架防腐转化膜的总结

Table 1 Summary of metal organic framework anti-corrosion films

Film forming method	Metal-organic framework	Substrate	Advantages	Disadvantages	Range of application	Refs.
In situ room temperature synthesis	ZIF-8	Zn, carbon steel, and Mg	Simple process Low cost No pollution Safe	Poor corrosion resistance and adhesion Serious reunion phenomenon Poor mechanical performance	Prepare the material for reaction at room temperature	[74-76]
In situ hydrothermal synthesis	Mg-MOF-74	Mg	Good corrosion resistance No pollution	Serious reunion phenomenon Poor mechanical performance Insecurity High cost Difficult to control temperature and pressure	Preparation of materials insensitive to water	[77]
In situ solvothermal synthesis	ZIF-8	Al	Good corrosion resistance Uniform and dense film layer	Poor mechanical performance Pollute the environment Insecurity High cost Difficult to control temperature and pressure	Preparation of materials insensitive to organic solvents	[78-81]
	Bio-MOF-1	Mg				
	ZIF-90 ZIF-9 UiO-66	Al, Mg, Cu, and carbon steel				
	ZIF-8	Al				
Electrochemical deposition	MIL-125	Ti	Good corrosion resistance Low cost Simple process Rapid deposition rate	Uncontrollable growth rate of the crystal nucleus Most films are polycrystalline or amorphous	Commercial process	[82-86]
	ZIF-8	Ti	Good mechanical properties Uniform film layer No pollution			
Electrophoretic deposition	HKUST-1	Cu	Good corrosion resistance Uniform and dense film layer	Large materials investment Poor mechanical performance High drying temperature	Electrophoretic paint coating	[87-89]
Electrospinning method	ZIF-8	Mg	Good corrosion resistance Low cost Simple process Adjustable morphology and size Uniform film layer Easily functional surface No pollution	Low production Difficult to apply on a large scale Low strength	Disperse stable colloids or suspensions	[90-93]
Vapour-solid transformation	ZIF-8	Zn	Good corrosion resistance Uniform film layer Simple film forming device Fast film formation speed	Poor mechanical performance High cost High reaction temperature	Coating on workpieces with complex shapes	[94]

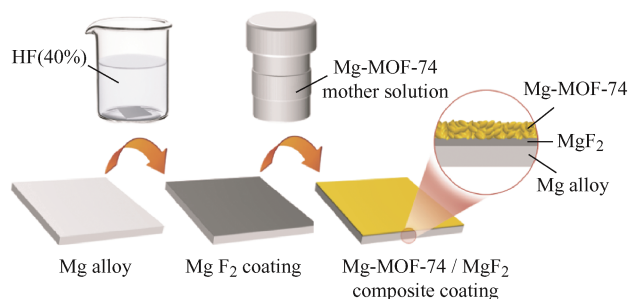
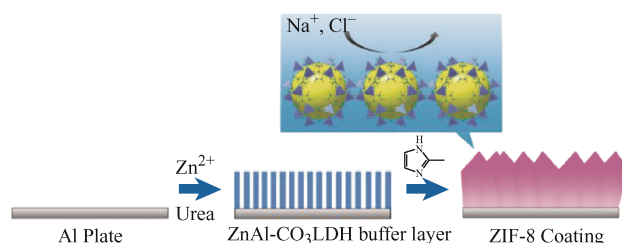
二是采用原位水热法合成金属有机框架转化膜,水热法指在密封的容器里,以水溶液作为反应介质,使粉末溶解和再结晶的过程^[77]。LIU 等^[77]先在镁合金表面氢氟酸处理后制备 MgF_2 膜层,再将样品放入反应釜中原位水热生长 Mg-MOF-74 膜层(图 4a),Mg-MOF-74/ MgF_2 复合膜层在模拟体液(SBF)中对镁合金具有良好的防腐性能,由于采用

“双镁源法”(MgF₂ 和前驱体溶液同时提供 Mg^{2+})制备的 Mg-MOF-74 膜与 MgF_2 层具有强附着力,同时表现出良好的物理阻隔作用。此外,复合膜层还具有良好的抗菌性和超亲水性,使其在生物医用领域具有更高的潜在应用价值。

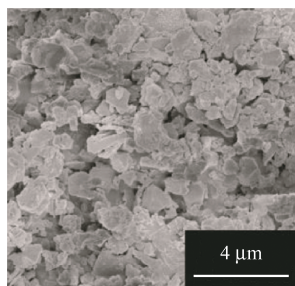
三是原位溶剂热合成金属有机框架转化膜,与原位水热合成法类似,溶剂热法是以有机溶剂或非

水溶媒作为反应介质^[78-81], 制备的金属有机框架膜均匀致密、耐蚀性好、结合力较强。ZHANG 等^[78]采用溶剂热法在铝基体表面制备 ZnAl-CO_3 LDH 层, 接着采用配体辅助转换策略将双氢氧化物层转换为 ZIF-8 膜层 (图 4b), LDH 层不仅作为 ZIF-8 膜的异质成核中心, 而且可为 ZIF-8 提供单一金属源。LDH / ZIF-8 膜层的铝合金在 3.5 wt % NaCl 溶液中表现出良好的耐蚀性能, 其自腐蚀电位相比裸铝降低了 4 个数量级, 其防腐机理在于: 一是优异的物理屏蔽作用, 采用“双 Zn 源”(双氢氧化物层和前驱体溶液都提供了形成 ZIF-8 所需的 Zn^{2+}) 制备的 ZIF-8 膜具有良好共生、均匀的微观结构 (图 4c、4d); 二是良好的缓蚀作用, ZIF-8 释放的咪唑在金属表面形成不溶性保护膜。随后 YANG 等^[79]又进一步

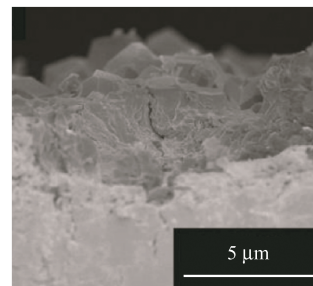
改进了 LDH / ZIF-8 膜层体系, 他们使用 5, 6-二甲基苯并咪唑 (DMBIM) 改性膜层, 在镁合金表面成功制备改性 ZIF-8-DMBIM / LDH 复合膜, 表面呈光滑致密的六边形形态, 具有致密的双层结构, 复合膜层在 3.5 wt.% NaCl 溶液中表现出优异的耐蚀性能, 测得 E_{corr} 为 -165 mV (相比裸基体提升 1 391 mV), I_{corr} 为 $2.4 \mu\text{A} \cdot \text{cm}^{-2}$ (相比基体降低约 1 个数量级), 缓蚀效率达到 99.87%, R_{ct} 为 $1.1 \text{M}\Omega / \text{cm}^2$, ZIF-8-DMBIM / LDH 复合膜的耐蚀性明显好于 LDH / ZIF-8 膜层 ($E_{\text{corr}} = -596 \text{mV}$, $I_{\text{corr}} = 7.05 \mu\text{A} \cdot \text{cm}^{-2}$, $\eta = 82.34\%$, $R_{\text{ct}} = 260 \text{k}\Omega / \text{cm}^2$), 性能改善的主要原因是 DMBIM 与 ZIF-8 的有机配体发生交换, 使 ZIF-8-DMBIM / LDH 复合膜具有光滑的表面和良好的疏水性, 更有效地防止腐蚀因子侵入。

(a) Mg-MOF-74 / MgF_2 

(b) LDH / ZIF-8



(c) Cross-sectional views of LDH / ZIF-8



(d) SEM images of LDH / ZIF-8

图4 不同涂层的制备及表面形貌^[77-78]Fig. 4 Preparation process and surface morphology of different coatings^[77-78]

2.2 电化学沉积

电化学沉积是指在外电场作用下, 电解质溶液中有正负离子迁移并在电极发生氧化还原反应, 使离子沉积到表面形成镀层的技术, 通过控制工艺条件 (pH、电流、溶液浓度、温度、沉积时间等) 可精准控制沉积层的厚度, 采用电化学沉积法制备金属有机框架膜具有更高的沉积速度和环保性^[82-86]。ZHANG 等^[84]先后采用阳极氧化技术、电化学沉积法在钛基体表面制备二氧化钛层、 Nd^{3+} 离子掺杂 ZIF-8 和羟基磷灰石的复合膜层, 在磷酸盐缓冲液

(PBS) 溶液表现出较好的耐蚀性并兼具良好的抗菌性和生物相容性, 归因于 ZIF-8 自身的缓蚀作用, 且复合膜层释放的 Zn^{2+} 、 Nd^{3+} 具有抗菌活性, 并有利于骨生长和伤口愈合, 紧接着他们^[85]又合成出掺杂 Ce^{3+} 的 MIL-125 衍生物, 同样采用电化学沉积法在钛基体表面将其与羟基磷灰石混合制备出抗菌、耐腐蚀的复合膜层, 同源 (钛表面与前驱体溶液共同提供钛金属源) 制备的 MIL-125 与基体间结合紧密, 膜层中的 MIL-125 具有良好的成骨活性和细胞相容性, 其释放的 Ce^{3+} 具有一定的缓蚀作用和抗菌性能,

这项研究大大促进了钛金属作为骨植入体的应用。

2.3 其他方法

还可以采用电泳沉积、静电纺丝和蒸汽固相转化法在金属表面制备金属有机框架转化膜。电泳沉积是指在稳定的悬浮液中通过直流电场的作用沉积胶体粒子的过程,电泳沉积膜具有均匀、平整、光滑等优点,且力学性能良好^[87-89]。LI 等^[87]采用一锅合成法将缓蚀剂十六烷基三甲基溴化铵(CTAB)封装在 HKUST-1 孔隙中,接着采用电泳沉积技术在铜板表面制备 HKUST-1@CTAB 膜层,其中 CTAB 的疏水尾部(CH₃基团)暴露在金属有机框架膜层外, HKUST-1 膜与暴露在膜层表面的 CTAB 缓蚀剂疏水端可有效隔离腐蚀介质,表现出良好的金属防腐性能。

静电纺丝是利用电场力将聚合物熔体、溶液牵引成纳米纤维的技术,具有安全性、环保性、高效性等优点^[90-93]。KHALILI 等^[90]采用溶剂热法制备出 ZIF-8 纳米粉末,将粉末与壳聚糖聚合物溶液混合后在镁合金表面静电纺丝出 ZIF-8 / 壳聚糖复合膜层,经上述膜层修饰的镁合金兼具两方面的特点:一是较理想的耐蚀性,经 ZIF-8 / 壳聚糖改性的膜层在 SBF 溶液中测得的 I_{corr} 相比裸基体降低了 80%, 主要由于 ZIF-8 自身的缓蚀作用;二是良好的生物相容性,亲水性的膜层为细胞粘附和骨整合提供了更好的平台, ZIF-8 / 壳聚糖复合膜层对镁合金植入材料表面改性展现出广阔的应用前景。

蒸汽固相转化(Vapour-solid transformation, VST)不同于溶剂热法,是通过配体蒸汽氛围下在基体表面发生反应沉积成膜的一种方法^[94]。KASNERYK 等^[94]首先在锌合金表面制备了等离子电解氧化(PEO)层,再采用蒸汽固相转化法将 PEO 层可控地转化为 ZIF-8 膜,其中含氧化锌的 PEO 层能为 ZIF-8 提供金属源,与溶液中的配体结合形成 ZIF-8@PEO 新型膜层。PEO 层力学性能良好,与基体间结合紧密, ZIF-8 膜具有较好的化学稳定性、水稳定性和疏水性,因此 ZIF-8@PEO 复合膜层表现出良好的物理化学性能,拓展了金属有机框架防腐转化膜的潜在应用。

2.4 金属有机框架转化膜结构与性能的联系

不同类型金属有机框架材料的结构稳定性存在差异,导致金属有机框架转化膜对基体的防护效果不一。LI 等^[95]在石英晶体微天平(QCM)表面分别制备出 4 种常见金属有机框架膜(UiO-66、UiO-67、HKUST-1 和 ZIF-8),将不同膜层长期暴露在潮湿空气条件下以研究它们的稳定性,瞬态吸收(甲苯、

环己烷等作探针分子)、红外光谱等结果表明, ZIF-8 和 UiO-66 的吸附性能稳定,不受环境的影响。而 HKUST-1 和 UiO-67 的结构明显被破坏,表面形成屏障导致吸附性能变差。归因于 UiO-66 是由 [Zr₆O₄(OH)₄]金属簇与 12 个 H₂BDC 配位连接而成的,结构单元十分密集,使整个结构稳定连接,较强的 Zr-O 键也增强了其稳定性; ZIF-8 为三维十二面体结构,由五元咪唑环通过将锌中心与环上 1, 3 位的 N 原子桥接而成,相比 UiO-67 和 HKUST-1 有较好的水稳定性。

尽管金属有机框架材料的结构稳定性研究取得了一定进展,然而由于腐蚀环境、基体不统一等原因,难以比较不同金属有机框架转化膜的耐蚀性。因此, WEI 等^[96]在相同的金属有机框架材料浓度、铜基体、温度、1 M HCl 腐蚀环境条件下对比了 {[Cu(2,3-Hpyza)]·2(H₂O)} 和 Nd-MOF 膜层对铜板的缓蚀作用。结果表明 Nd-MOF 材料的缓蚀性能更好:一方面是由于 Nd-MOF 材料具有更大的比表面积,更易吸附在金属表面形成保护膜;另一方面在于 Nd-MOF 膜对金属的吸附作用更强,吸附常数测得为 19.048 L / mg, 而 [Cu(2,3-Hpyza)] · 2(H₂O)} 材料仅为 5.95 L / mg。为了将应用在更多不同基体金属有机框架膜的缓蚀性进行研究与对比, LIU 等^[97]在铝、镁、铜和碳钢上对比了经聚多巴胺(PDA)改性后的 3 种金属有机框架膜(ZIF-90, ZIF-9 和 UiO-66)的耐蚀性能。试验结果表明,在不同基体上改性后的金属有机框架膜兼具良好的致密性、疏水性和耐蚀性。在铝基体上, 3 种金属有机框架膜的 R_{ct} 值相比裸基体均提高约 3 个数量级, E_{corr} 分别提升了 35、187、123 mV, I_{corr} 均降低了约 2 个数量级, 但 PDA / UiO-66 对金属的附着力最好, 浸泡 7 天后阻抗值仍略有增加, 具有长期持久的耐蚀性, 原因是由于 UiO-66 晶体的尺寸最小(200 μm), 且 UiO-66 膜层与基体良好共生, 结合更加紧密; 并依次研究了 PDA / UiO-66 在镁、铜和碳钢上的耐蚀性, PDA / UiO-66 的 R_{ct} 值对比裸基体分别提高约 1、2、2 个数量级, E_{corr} 分别提升 72、1 437、913 mV, I_{corr} 分别降低约 1、2、2 个数量级, 对金属基体表现出比较理想的缓蚀作用。

综上所述,采用不同技术制备的金属有机框架膜对金属具有一定的缓蚀作用。经过技术对比分析,在倡导研发高效、节能、经济、环保涂层的大背景下,静电纺丝法和电化学沉积法制备的金属有机框架膜性能较理想(如耐蚀性好、工艺流程简单、无污染等),在未来具有广阔的应用前景。但金属有机

框架膜层在实际的工业化生产与应用中还存在一定局限性(表1),且耐蚀行为受金属有机框架材料的不同结构、浓度等条件的影响较为敏感,可控程度尚待提升。

3 结论与展望

从两方面分类综述基于金属有机框架材料用于金属表面涂层防腐的研究进展:一是金属有机框架基防腐涂层,金属有机框架材料作为功能性填料在防腐涂层的应用;二是金属有机框架防腐转化膜,金属有机框架作为膜层主体在金属防腐的研究。金属有机框架材料应用在防腐涂层中增强了对金属的防护性能,延长了金属基体的使用寿命。近年来,金属有机框架膜层和金属有机框架基防腐涂层不断研究与完善,但仍存在一些技术性、可控性等问题:

(1) 目前制备的金属有机框架转化膜以及金属有机框架基防腐涂层即便表现出较理想的耐蚀性,但由于受成本和工艺的限制,无法大规模制备金属有机框架材料。

(2) 添加不同金属有机框架材料、不同金属有机框架浓度、不同金属基体、不同工艺参数等条件都会影响金属有机框架基防腐涂层的耐蚀性能,且保持金属有机框架基材料的长久耐蚀性能仍存在挑战。

基于此,对金属有机框架材料在金属表面防腐涂层中的应用进行了展望,并提出未来发展趋势:

(1) 充分挖掘金属有机框架材料的组成与结构优势,设计具有多重响应与可控释放性能的金属有机框架纳米容器,进一步提高金属有机框架纳米容器对缓蚀剂的负载效率。

(2) 通过机器学习等方法合理筛选金属离子与配体,制备缓释性能优异的金属有机框架材料,厘清金属有机框架材料结构与缓蚀性能之间的关系,进一步通过涂层设计与金属有机框架纳米容器设计相结合,实现多效、长效、智能防腐。

(3) 未来在合理利用现有制备技术(原位生长、静电纺丝、电化学沉积)的基础上,不断探究可形成致密、结合力良好的金属有机框架防腐转化膜及其制备方法。

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