

镁合金表面金属有机框架材料的制备 及防腐应用研究综述

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摘要: 镁合金具有密度小、比强度高、电磁屏蔽性能优异、生物相容性好等优点, 是一种具有广阔应用前景的金属结构材料, 然而耐腐蚀性差是限制其发展的主要因素。近年来, 为了解决镁合金在应用环境中腐蚀严重的问题, 新兴材料金属有机框架化合物 (Metal-Organic Framework, MOFs) 被逐步应用到镁合金表面。MOFs 由金属中心及有机配体组成, 具有比表面积大、活性位点丰富、结构组成可控、易于功能化等特点, 是一种性能优越的新型防腐材料。综述了 2020 年以来镁合金表面 MOFs 材料的制备方法及其防腐应用。首先根据不同的制备方式, 将 MOFs 在镁合金上的合成分为粉体制备和原位合成, 综述了沉积法、溶剂热法、电化学法等常见合成手段; 其次从缓蚀剂、保护涂层、填料和纳米容器 4 个方面介绍了 MOFs 在镁合金上的防腐应用, 探讨了不同功能 MOFs 在镁合金表面的防腐效果, 与传统防腐材料相比, MOFs 新型材料具有 pH 响应、可设计性强等特点, 进一步扩展了其应用场景; 最后总结了 MOFs 作为防腐材料时异相制备困难、涂层较薄等不足之处, 对其在镁合金表面防腐应用做了进一步展望。

关键词: 镁合金; 金属有机框架; 防腐材料; 涂层; 填料; 纳米容器

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Review on the Preparation and Corrosion-resistant Application of Metal-organic Frameworks for Magnesium Alloy Surface

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ABSTRACT: Magnesium alloy has the advantages of low density, high specific strength, excellent electromagnetic shielding performance and good biocompatibility, making it a promising structural material in aerospace, automobile manufacturing, electronic devices, biomedicine and other fields. However, its development has been hindered by inadequate corrosion resistance in application environments. In recent years, in order to address the severe corrosion issues of magnesium alloys in practical applications, the emerging material metal-organic frameworks (MOFs) has been extensively utilized for surface modification. MOFs consist of the metal centers and the organic ligands, offering high specific surface area, abundant active sites, controllable structure composition, and easy functionalization, thus making them a superior new type of corrosion-resistant material. The work aims to present a comprehensive review on the recent preparation methods and the corrosion-resistant applications of

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MOFs on magnesium alloys. The synthesis of MOFs on magnesium alloys can be classified into two primary methods, including powder preparation and in-situ synthesis. The main difference between these two methods lies in whether the MOFs are prepared as powders or grown directly on the surface of the magnesium alloy. This difference is crucial as it impacts the final properties and applications of the resulting MOFs. The advantages and disadvantages of these two methods are discussed in detail, along with the most common synthetic techniques, such as the deposition method, the solvothermal method, and the electrochemical method. Each method has its unique benefits and drawbacks, making it necessary to carefully consider the specific requirements of each application when a synthesis method is adopted. The application of MOFs materials is discussed for the corrosion protection of magnesium alloys, encompassing corrosion inhibitors, protective coatings, fillers, and nano-containers. The utilization of MOFs with corrosion-inhibiting properties requires careful selection of the metal centers and the organic ligands. Several MOFs has been employed as corrosion inhibitors in engine coolants to reduce the corrosion rate of magnesium-based engines. Extensive data presented by researchers demonstrate the enhanced corrosion resistance achieved through the use of MOFs, including the electrochemical impedance and the corrosion current density measurements. Additionally, the MOFs materials can be directly applied as corrosion-resistant coatings. However, the weak adhesion between the MOFs coating and the magnesium alloy is observed due to the rapid corrosion rate of the magnesium alloy. To improve the adhesion strength, the MOFs coatings are typically prepared on a surface film composed of oxides or hydroxides. Furthermore, MOFs materials can serve as fillers or nano-containers in coatings. The addition of MOFs not only increases the tortuosity of the corrosion pathway but also enhances the compatibility and the dispersion of MOFs within most organic coatings. As nano-containers, certain types of MOFs exhibit pH-responsive characteristics that enable them to effectively respond to the external stimuli and prolong the service life of coatings by reducing the waste of corrosion inhibitors. Some specific types of MOFs exhibit hydrophobicity which diminishes the contact between the coating and the aggressive water environments, thus slowing down the corrosion rate of magnesium alloys. Finally, the challenges of using MOFs as corrosion-resistant materials are summarized, including limited types with corrosion inhibition properties, difficulties in heterogeneous nucleation, and thin coating thicknesses. Despite these challenges, the potential application of MOFs materials is promising in protecting magnesium alloys against corrosion. It is necessary to carry out further research on optimizing their properties and broadening their application on the surface of metallic materials.

KEY WORDS: magnesium alloy; metal-organic framework; corrosion-resistant material; coating; filler; nano-container

镁合金是一种物理和化学性能优异的轻质金属材料^[1], 具有高比强度、高比刚度与优良的抗冲击性能, 可以应用在航空航天领域, 如制造飞机结构件、发动机零部件等^[2]。镁合金的密度较低, 有利于轻量化设计, 在汽车工业中被用于制造发动机零部件、传动系统等^[3]。镁合金还具有良好的导电性和散热性, 可以被用于制造电脑、手机等电子产品的外壳^[4]。此外, 镁合金具有生物相容性, 可以制备医疗器械和植入物, 如骨板、植入支架等^[5]。

镁合金性能优异的同时也具有致命缺陷, 其中最影响镁合金使用寿命的是其耐腐蚀性差。镁的标准电极电位为 -2.37 V , 比大部分金属的电极电位要负, 在自然环境中很容易发生电化学腐蚀^[6]。为了提高镁合金的耐腐蚀性, 必须采取适当的表面防护处理。常见的镁合金表面防腐技术主要有缓蚀剂保护技术和防腐涂层技术。缓蚀剂保护技术是将钼酸盐^[7]、8-羟基喹啉^[8]、苯并三唑^[9]等缓蚀剂以极低的浓度加入腐蚀环境中, 使缓蚀剂分子在基材上通过吸附或络合作用形成保护膜, 减少腐蚀介质与基材表面的接触, 有效抑制基材腐蚀的方法^[10]。防腐涂层技术主要是指通

过物理或化学方法在金属表面形成一层致密的隔离层, 阻挡腐蚀性介质与金属基体的接触, 从而延缓金属腐蚀的方法。应用在镁合金表面的防腐涂层主要有金属氢氧化物^[11-12]、羟基磷灰石 (HA)^[13]、石墨烯^[14]等无机涂层, 以及丙烯酸^[15]、聚氨酯^[16]、硅烷^[17]等有机涂层。

近年来, 为进一步提高镁合金的耐腐蚀性, MXene^[16]、氮化硼^[18]、金属有机框架 (Metal-Organic Frameworks, MOFs)^[19]等新型功能化材料被应用到镁合金表面。其中, MOFs 材料以其优异的性能引起了科研工作者的广泛关注。MOFs 是一类新型的有机-无机杂化材料, 其具有由金属离子和有机配体通过配位键形成高度有序的晶体结构。MOFs 材料的特点是比表面积大、活性位点丰富、结构及孔隙大小灵活可调、有机配体可官能化修饰等^[20], 在气体储存、催化、防腐和药物释放等领域均有广泛应用。在增强镁合金耐腐蚀性方面, MOFs 材料可以通过不同方式达到防腐的效果。相比无机材料, MOFs 材料与有机涂层的相容性良好, 可以作为填料均匀分散到涂层中, 增强涂层的防腐性能^[21]。MOFs 材料的高比表面积使

其适合作为载体负载缓蚀剂, 提供防腐蚀功能^[22]。此外, 一些 MOFs 本身具有缓蚀能力, 例如具有沸石咪唑结构的 MOFs^[23]。

鉴于 MOFs 优异的性能及其应用在镁合金表面防腐方面的巨大潜力, 本文从镁合金表面 MOFs 的制备方法和应用 2 个方面, 对 2020 年以来的文献进行了综述。

1 MOFs 的制备方法

MOFs 的制备方法多种多样^[24], 常见的有溶剂热法、水热法、电化学法、微波法、声化学法等^[25]。应用在镁合金表面上的 MOFs 制备方法, 根据合成步骤可以分为 2 种: 一种是粉体制备, 即先合成 MOFs 粉体, 再通过物理化学方法制备在镁合金表面; 另一种是直接在镁合金表面进行原位生长。

1.1 粉体制备

MOFs 粉体制备的优势显而易见, 即先制备 MOFs 粉体, 可以根据需要方便地对其进行修饰, 接枝不同的官能团, 赋予其不同的性能。这种方法制备出的 MOFs 材料形貌、结构易控, 通用性较好, 同一种材料可以应用在不同基材表面。常用的粉体制备方法主要有沉积法^[26]、溶剂热法^[25]、微波法^[27]、声化学法^[28]等, 其中应用在镁合金表面比较多的是沉积法和溶剂热法, 下面主要介绍这 2 种方法。

沉积法是在常温条件下, 将溶剂中的反应物在指定时间内连续搅拌或是常温老化后混合在溶剂中, 随后沉淀或结晶形成 MOFs 结构的方法, 是制备 MOFs 纳米颗粒的常见方法之一。沉积法制备 MOFs 的前提是反应所需要的活化能较低, 反应过程中的成核动力学受反应物浓度、pH 值等影响较大^[24]。因此, 沉积法对溶剂浓度、反应物纯度与实验操作过程的要求较高。

科研工作者采用沉积法制备了沸石咪唑酯骨架结构 (Zeolitic Imidazolate Framework, ZIFs)^[29]、富马酸铝 (AlFu)^[30]等 MOFs 材料, 并将其应用在金属防腐领域。ZIFs 是一类由 Zn^{2+} 或 Co^{2+} 和咪唑盐组成的具有沸石结构的 MOFs 材料^[31], 常见的有 ZIF-8^[32]、ZIF-67^[33]、ZIF-90^[34]等。ZIFs 的孔径可调、结构高度稳定、制备方法简单, 可以用作填料与有机涂层结合, 延缓金属表面腐蚀^[32]。Li 等^[32]在室温下采用共沉积的方法, 洗涤干燥后得到粉末状 ZIF-8 纳米颗粒, 而后与层状双金属氢氧化物 (Layered Double Hydroxide, LDH) 粉末混合, 在镁合金表面水热制备涂层, 在 37 °C 的模拟体液中材料的防腐蚀性能显著提高。Xiao 等^[35]利用沉积法制备粉末状的 ZIF-8 纳米容器, 包裹 Ce^{3+}/Ce^{4+} 后, 加入环氧树脂中并喷涂到基材表面, 在质量分数为 3.5% NaCl 溶液中的阻抗测试表明涂层表面具有良好的防护性能, 同时在 pH=3 时, Ce^{3+}/Ce^{4+} 释放速率远高于中性条件下的释放速

率, 具有良好的 pH 响应能力。富马酸铝是由 Al^{3+} 和富马酸根配位形成的骨架结构^[36], 可以被用作冷冻液中镁合金的缓蚀剂。Mohamadian-Kalhor 等^[30]利用沉积法制备了富马酸铝材料, 其对镁合金表面腐蚀速率的抑制接近 88%。

溶剂热法是 MOFs 材料制备中最普遍的方法之一, 反应过程需要水或高沸点有机溶剂^[37], 能够有效地控制反应速率、提高产物纯度^[38]。MOFs 的生成过程与溶剂密切相关, 用于防腐蚀的 MOFs 常利用溶剂热法制备。Rajabalizadeh 等^[39]利用溶剂热法合成了铝基 MIL-53 MOF, 再掺入 Ni-P 溶液中电镀至镁合金表面, 其在质量分数为 3.5% 的 NaCl 溶液浸泡 6 h 后阻抗值为 $93\text{ k}\Omega\cdot\text{cm}^2$, 不仅提高了镁合金表面的防腐蚀性能, 还提高了涂层的化学稳定性。此外, Amin 等^[40]先水热合成 ZIF-8 颗粒, 掺入壳聚糖溶液后通过静电纺丝沉积在镁合金表面, 加入 MOFs 改性后的镁合金表面在 37 °C 的模拟体液 (Simulated Body Fluid, SBF) 中降解速率和腐蚀电流密度减少 65%, 拓展了镁合金在生物体内的应用。

沉积法和溶剂热法是 MOFs 粉体制备最为常见的 2 种办法, 操作简单。其他制备方法, 如声化学法^[41]可以有效节省时间和能源, 然而只有某些特定的 MOFs 可以由声化学法合成, 局限性大^[25], 因此较少应用在镁合金表面 MOFs 的制备上。

1.2 原位生长法

原位生长法是指 MOFs 直接生长在金属或氧化物/氢氧化物表面, 这种方法需要将基体浸入含有金属盐和配体的前驱溶液中。一般情况下, 由于缺少成核位点, 这种方法在裸露的合金表面上生长的保护层往往不均匀且结合力很弱。故而, 为了增强与基体的结合力, MOFs 原位生长常常应用在镁合金表面已有的保护涂层上, 例如微弧氧化层 (Micro-Arc Oxidation, MAO)^[12]、LDH^[42]等。

Chen 等^[43]在室温下用沉积法在 AZ31 表面原位生长 MAO/ZIF-67 复合涂层。MAO 的存在不仅提高了涂层的防腐蚀性能, 还可以为制备的 MOFs 与涂层提供良好的附着力; ZIF-67 则有效地封闭 MAO 涂层的孔隙, 增加腐蚀介质侵入路径的曲折度, 显著提高镁合金的耐腐蚀性。Jiang 等^[44]采用溶剂热方法在镁合金 MAO 上同源金属诱导生成 ZIF-8 涂层, 并用硬脂酸对样品表面进行疏水改性, 该超疏水复合涂层具有较强的疏水性和自清洁性能, 可防止水和腐蚀性离子 (Cl^-) 渗入镁合金表面, 提高了镁合金表面的耐腐蚀性。

此外, 用电沉积的方法也能够金属或涂层表面制备 MOFs, 如可以采用一步电化学法在多孔阳极氧化铝 (AAO) 和聚偏氟乙烯 (PVDF) 基膜上制备 ZIF-8 分离层^[45]。这种利用阴极沉积法制备 ZIF-8 的方法简单易于控制, 形成的膜层较为均匀。但由于镁合金表

面耐腐蚀性较差,利用电化学法在镁合金表面一步制备 MOFs 膜还没有得到广泛应用。相信在不久的将来,随着表面处理的进一步发展,MOFs 原位生成方法会更加多样化、产品性能会更好。

2 MOFs 的主要应用

MOFs 的孔隙结构可以通过选择合适的有机配体和金属离子进行精确调控,较大孔径的 MOFs 可以作为装载缓蚀剂的纳米容器^[46-50],孔径较小的 MOFs 可以作为保护涂层^[19,51-52,54]或填料^[55-57]。此外,还可以通过调整配体和金属离子,以及特殊的表面功能化处理,制备具有不同功能的 MOFs,为 MOFs 赋予多种特性,例如缓蚀^[58-59]、光催化^[60]、抗菌^[61]、超疏水等性能。

MOFs 凭借其优异的性能和独特的结构,可以单独或与其他涂层联用,提高镁合金表面的防腐蚀性。如图 1 所示,按照在镁合金表面的不同用途,MOFs 可以分为 4 类:缓蚀剂、保护涂层、填料与纳米容器。以下将按照这 4 类分别介绍 MOFs 材料。

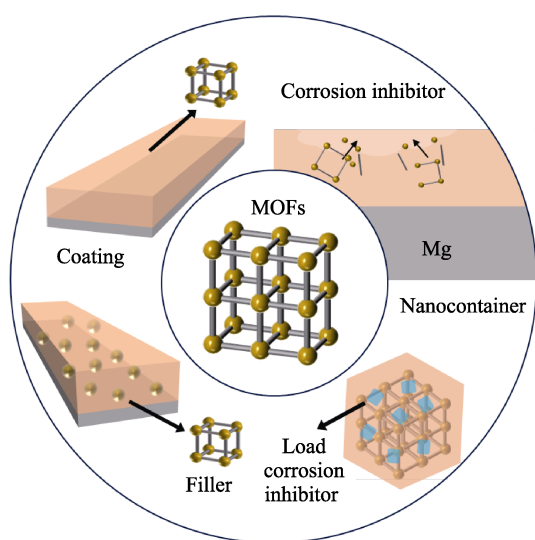


图 1 应用在镁合金表面常见 MOFs 用途及分类
Fig.1 Application and classification of common MOFs on magnesium alloy surface

2.1 缓蚀剂

使用缓蚀剂是减缓金属腐蚀常见的方法之一。缓蚀剂会影响腐蚀电化学反应的动力学过程,从而减缓金属腐蚀^[62]。缓蚀剂可以分为有机、无机 2 种类型,其中无机缓蚀剂主要有磷酸盐类、硅酸盐类^[63]等,有机缓蚀剂包括十二烷基苯磺酸钠 (SDBS)、硬脂酸钠和八羟基喹啉 (8-QH) 等^[64]。缓蚀剂可以与金属表面作用,形成不溶性膜或吸附在金属表面,抑制基材进一步腐蚀^[65-66]。

相较于单一的无机或有机缓蚀剂,MOFs 可以通

过设计调控合适的金属中心和有机配体实现不同的功能,使其兼具二者的优点。当腐蚀介质破坏 MOFs 结构时,金属离子和有机配体分离,在镁合金表面产生具有保护性质的膜层或抑制剂。较为常见的镧系金属 (Cd、Ce 等) 与咪唑类衍生物^[59,67-68],均具有优越的缓蚀性能。其中 ZIFs 可以看作典型的缓蚀剂,它由过渡金属离子 (Zn^{2+} 或 Co^{2+}) 和咪唑组成^[69],具有丰富的氮杂环化合物,通过氮原子/ π 电子和金属原子的配位作用,物理/化学吸附在金属表面,达到缓蚀的效果^[23]。

CAO 等^[70]利用 ZIF-8 作为金属表面缓蚀剂,使得 ZIF-8 衍生物吸附在铜基底上,在金属表面形成疏水膜,从而有效地抑制了侵蚀性离子引起的腐蚀,抑制效率高达 87.2%。ZIF-8 在中性和碱性环境中有一定的热稳定性、化学稳定性^[71],因此 ZIF-8 常作为高碱度环境下钢筋混凝土的缓蚀剂。Wang 等^[23]在含氯水泥提炼物溶液中加入 ZIF-8 颗粒,由于 ZIF-8 具有高比面积特性,其在浸泡初期就能被吸附在钢材的表面,从而提高了钢筋在该溶液的耐腐蚀性,实现了钢筋混凝土在氯化物污染环境下的有效防腐。

ZIFs 应用在镁合金表面作为缓蚀剂可以增强基体耐腐蚀性,但这类研究较少,仍然处于起步阶段。Cao 等^[72]将 ZIF-67 作为缓蚀剂, ZIF-8 作为纳米容器制备到镁合金表面上,发现在酸性条件下浸泡 120 h,镁合金表面仍然具有良好的耐腐蚀性,在镁合金表面防腐方面有潜在的应用价值。此外,研究者还发现 MOFs 的缓蚀性能与其晶体形态密切相关。Zhang 等^[59]通过熔化 ZIF-62 晶体 (c-ZIF-62) 得到非晶态 ZIF-62 (g-ZIF-62),并通过电化学测量研究了其在 AZ91 镁合金的缓蚀性能。结果表明,相比于 ZIF-62 能有效抑制镁合金的腐蚀, g-ZIF-62 表现出更好的缓蚀效果,缓蚀效率高达 83.6%,有效阻碍了腐蚀性介质如水分子、 Na^+ 和 Cl^- 的侵入,从而提高了镁合金在海水中的稳定性。

除 ZIFs 类缓蚀剂以外, Mohamadian-Kalhor 等^[58]合成了富马酸铝 MOFs 缓蚀剂,加入乙二醇溶液中有效提高了镁合金的耐腐蚀性。防腐蚀性能测试与电化学阻抗谱 (EIS) 测试表明,抑制效率随着缓蚀剂浓度的增加而提高,在缓蚀剂质量浓度为 0.4 g/L 时高达到 88.35%,表明富马酸铝具有良好的缓蚀性能。Mirzayi 等^[73]发现对苯二甲酸铝 (AlTp) 在乙二醇+水溶液中作为镁发动机缸体的冷却剂具有很高的潜力,加入 AlTp 后,镁合金的抑制效率可高达 86.52%;并且在 AlTp 中加入 Fe 或氧化石墨烯 (GO),还可以进一步提高缓蚀剂的缓蚀性能。

2.2 保护涂层

具有良好化学稳定性和热稳定性的 MOFs 可以在镁合金表面形成稳定的保护膜,阻止氧气、水分子

和其他腐蚀介质对镁合金的侵蚀, 减缓腐蚀的发生。

2.2.1 防腐涂层

MOFs 具有孔隙与结构高度可控性, 可以作为保护涂层制备在镁合金表面, 延缓腐蚀性介质的进一步渗透, 从而达到减缓镁合金腐蚀的效果。正如前文所述, 由于镁合金的高腐蚀活性以及 MOFs 材料异相成核困难, MOFs 涂层通常不是直接制备在镁合金表面, 而是制备在氧化物或氢氧化物膜层上, 如 LDH、MAO 等。这些“中间”涂层不仅增强了基材与 MOFs 的结合力, 还可以为 MOFs 的生长提供或引入金属源^[19]。

Khan 等^[74]在 LDH 上制备了新型 MOFs (Co 为金属中心, 色氨酸为有机配体), 所制备的 MOFs 涂层具有致密的结构与极佳的稳定性, 当镁合金表面的 MOF-LDH 在暴露于质量分数为 3.5% 的 NaCl 溶液时表现出卓越的稳定性, 远超纯 PEO 和纯 LDH 涂层。Chen 等^[57]在 LDHs 层掺入 GO, 原位生长 ZIF-8 防腐涂层, GO/LDHs 缓冲层不仅作为镁合金 MAO 的连接, 还促进生长出连续、均匀的 ZIF-8 膜。不同生长时间的 ZIF-8 颗粒在不同程度上修饰了 GO/LDHs 涂层的表面缺陷, 进一步防止腐蚀性介质的渗透。ZIF-8 与 GO/LDHs 的协同作用, 使得修饰后的涂层表现出优异的稳定性和耐腐蚀性。后期, 他们还在镁合金表面 LDH 上原位生长了 ZIF-67^[75], ZIF-67/LDHs 复合涂层之间键的结合力非常强, 浸泡在质量分数为 3.5% 的 NaCl 溶液中 30 d 后, 仍保持良好的耐蚀效果。

对镁合金表面的防腐涂层进行疏水改性, 可以进一步提高其耐腐蚀性能。疏水改性可以使涂层表面形成一层疏水膜, 防止水分和其他液体在表面停留, 从而减少腐蚀的可能性^[76]。同时, 许多 MOFs 本身也具有疏水性和水稳定性, 例如 ZIF、UIO、TMU 等^[77], 可以应用到疏水涂层制备中。Jiang 等^[51]以 MAO 为过渡层, 利用 ZnO 为模板在镁合金上合成了 ZIF-8 结构, ZnO 不仅可以为后期 ZIF 的生长提供模板, 还可以提供金属配体。所制备的 ZnO@ZIF-8 纳米棒可以捕获一层空气, 使涂层表面在没有硅烷等物质疏水改性的情况下具有超疏水的特点, 并且在质量分数为 3.5% 的 NaCl 腐蚀性环境中, 腐蚀电流密度降低了 4 个数量级, 表现出优异的化学稳定性、耐久性与自清洁性。这种 MOFs 型核壳结构在金属防腐蚀方面具有很大的发展潜力。

2.2.2 医用防腐抗菌涂层

医用镁合金常作为支撑材料植入人体内部, 但由于镁合金耐腐蚀性差, 其在人体内的降解速度较快, 需要对其进行表面处理以提高耐腐蚀性和抗菌性^[78]。选择合适的 MOFs 涂层可以同时满足这 2 种要求。MOFs 涂层具有良好的耐腐蚀效果的同时, 还可以插入抗菌性金属离子。例如 Ag^+ 、 Cu^{2+} 、 Zn^{2+} 等金属离子本身就具有抗菌作用, 这可以增强涂层的抗菌性与

生物相容性。

肖天铸等^[52]用水热法在镁合金表面原位生成了 Mg-Cu-MOF-74 双金属涂层。改性后镁合金上 Mg-Cu-MOF-74 涂层的结构致密、水接触角大、腐蚀电流密度小, 有效提高了镁合金表面耐腐蚀性。同时, Cu 元素的掺杂能够在保持涂层良好亲水性, 进一步提高耐腐蚀性与抗菌性。

具有抗菌性的 MOFs 涂层常制备在一些生物相容性良好的涂层上方, 以减少医用镁合金在人体内的排斥反应^[79-80]。Liu 等^[19]在三氟钛酸铵 (NH_4TiOF_3 , NTiF) 上制备了 MOF-74 涂层。先利用 NTiF 层改性镁合金基体, 而后制备双层涂层 (MOF-74/NTiF), 提高了镁合金表面的防腐性能、抗菌性能和细胞相容性。内部 NTiF 层作为镁合金基体的主要保护和 MOF-74 膜生长的稳定表面, 外层 MOF-74 膜进一步增强了腐蚀防护性能。同时 MOF-74 膜显著促进细胞黏附和增殖, 表现出优异的细胞相容性^[81]。Ling 等^[54]则在羟基磷灰石涂层上制备了掺杂 Cu 的 ZIF-8 涂层, 相较于单一的羟基磷灰石涂层, 复合涂层形貌更加致密、均匀。电化学测试表明, 腐蚀电流密度显著降低, 并且 Cu 含量更高的复合涂层显示出更好的耐蚀效果。随着腐蚀的进行, Cu^{2+} 逐渐从复合涂层中释放出来, 使得涂层具有良好的抗菌性。Li 等^[32]在 MAO 表面制备了 Ag/ZIF-8/LDH 复合涂层, 含 ZIF-8 的复合涂层在体外表现出更好的耐腐蚀性。

MOFs 可通过增加通道的曲折度、抑制腐蚀介质的渗入, 达到延缓镁合金表面腐蚀的效果, 有效改善镁合金表面的耐腐蚀性。可以选用同时具有防腐性、抗菌性的 MOFs, 提高镁合金的耐腐蚀性与生物相容性, 扩大镁合金在医疗领域的应用。

2.3 填料

在镁合金上的一些防腐涂层, 如 MAO^[82]、PEO^[83]、LDH^[32,84] 等可以显著提高镁合金表面的防腐蚀能力, 但不可避免地会出现小孔和缺陷^[85]。这些孔隙和缺陷不仅会成为腐蚀介质渗入基体的通道, 导致腐蚀的产生, 也会使得腐蚀介质在其缺陷处积聚, 形成腐蚀点^[85]。因此, 为了进一步提高涂层的防腐性能, 需要添加填料来增加腐蚀性介质传输路径的曲折度, 提高涂层性能。

相比于以往单一的有机填料 (如偶氮、导电聚合物等) 或无机填料 (如铬酸盐、金属氧化物等填料^[86-87]), MOFs 具有独特的灵活可控性, 可以根据需求被设计成目标大小的填料。作为一种混合型纳米填料, MOFs 对无机或有机涂层的相容性都较好, 大多情况下制备 MOFs-有机/无机复合涂层来提高基材的耐腐蚀性。例如, Majidi 等^[88]在环氧树脂涂层中掺入 Cu-MOF 和 Ni-MOF 纳米颗粒, 添加了 MOFs 填料后, 涂层表面平均粗糙度明显下降, EIS 响应也说明防腐涂层掺入纳米填料后, 耐腐蚀性显著提高。此外, 含

有 MOFs 的高分子涂层可以兼具高聚合物的韧性和 MOFs 材料的热稳定性等优点,可以有效弥补单一聚合物涂层脆性大、热机械性能差等缺点^[89]。在环氧树脂涂层中掺杂的铈基 MOFs^[90],可以增强纳米复合材料的热机械性能。在拉伸实验中,铈基 MOFs 的加入明显提高了涂层的拉伸强度和韧性,表现出良好的力学性能、热稳定性和抗剪应力。

MOFs 填料在镁合金表面防腐方面有极大的应用潜力。李耀辉^[55]用水热法制备了 Mg-MOF-74 微米级粉体,利用浸渍提拉法在 AZ31B 镁合金表面的硅烷涂层上掺杂 Mg-MOF-74 粉体。由于 MOFs 中的羟基与水解后的硅烷可以脱水缩合形成交联密度高的网状结构,增加了腐蚀介质渗透镁合金基底的难度。Mg-MOF-74 结构中的羟基还能够与硅烷水解生成的 Si—OH 基团发生共价反应,生成 Si—O—C 键,使硅烷涂层更加致密,进一步提高镁基底的耐腐蚀性。相比于单一的硅烷涂层,掺杂后的复合涂层表面更加平整、致密,腐蚀电流密度下降了 1 个数量级,有效提高了镁合金表面涂层的耐腐蚀性。

MOFs 作为纳米填料保护镁合金表面具有高度可修饰性、良好的保护性,但也存在不可忽视的缺点。例如,单一的 MOFs 材料与镁合金基底的相容性较差,需要对镁合金进行前处理(MAO、PEO 等)。同时,一些 MOFs 的不稳定性不可忽视^[91],例如 MOF-74 在潮湿条件下金属中心会发生离解反应,反应产生的 OH⁻与 H⁺会显著削弱 MOFs 的骨架结构,缩短材料的使用寿命^[92],因此有时需要在涂层表面进行疏水改性,提高涂层的水稳定性。

正如前文所述,一些特定结构的 MOFs 具有缓蚀作用,这种特殊 MOFs 作为填料掺入镁合金表面的保护涂层时,其本身还可以作为缓蚀剂,不仅可以提高镁合金表面的耐腐蚀性,还可以提高涂层的机械性、稳定性以及长期保护性^[21,93]。

2.4 纳米容器

以往应用在镁合金表面上的纳米容器中,有机类有环糊精^[94]、纳米纤维^[95]、壳聚糖^[96]等,无机类则有二氧化硅^[97]、埃洛石纳米管^[98]、LDH 类^[99]等。纳米容器可以有效负载缓蚀剂或目的药品,提高涂层的防腐能力或实现可控释放的目的。

相较于上述纳米容器,MOFs 具有大量的孔隙结构,并且可以通过调控自身的结构和组成形成不同尺寸和形状的孔隙,储存和包裹小分子、离子或纳米粒子。同时 MOFs 具有非常高的比表面积,这也意味着 MOFs 可以提供大量的活性表面用于吸附和储存分子或纳米粒子。通过这些活性表面,MOFs 可以作为纳米容器来容纳和分离不同的物质^[100]。此外,一些 MOFs 材料还具有可控制的开关功能,可以通过改变外界条件(如温度^[101]、pH 响应^[102]等)来调控孔隙

的开合,从而实现对纳米容器内部物质的释放和储存。

由于上述特点,MOFs 可以作为具有多功能性的纳米容器,用于储存、传输和释放各种分子和纳米级物质,因此在纳米技术和纳米医学领域应用前景广泛。

2.4.1 负载缓蚀剂

MOFs 材料作为一种多孔的纳米容器,可以搭载尺寸合适的缓蚀剂。释放缓蚀剂的主要过程是腐蚀介质渗透到 MOFs 结构中时,缓蚀剂开始释放,吸附或者络合在金属表面^[103]。常见的能够负载缓蚀剂的 MOFs 材料有 ZIF-8^[46-47]、Uio-66^[48-49]与 MIL-53^[50]。例如,Wu 等^[104]将有机缓蚀剂苯并三唑(BTA)负载到 ZIF-8/GO 杂化物(GZB)中,涂层受到破坏后释放的缓蚀剂有效延缓了镁合金表面的腐蚀。

环境变化(如 pH、Cl⁻浓度或光照等)会导致某些 MOFs 分解速率的改变,缓蚀剂的释放量也随之变化^[105]。随着金属表面腐蚀的进行,局部 pH 值也会不断变化。在阴极活性区,会发生析氧反应或析氢反应,消耗 H⁺产生 OH⁻,导致 pH 的增大;在阳极活性区,金属阳离子发生水合作用,使得局部 pH 减小^[106]。因此,具有 pH 响应特性的 MOFs 结构可以减少缓蚀剂的浪费,延长涂层的使用寿命。一些有机配体为咪唑/苯并咪唑配体的 MOFs 材料(如 ZIF-8^[46-47])在酸性或碱性条件下更容易分解,是具有 pH 响应特性的智能纳米载体。如 NH₂-MIL-125(Ti)纳米容器包裹缓蚀剂 2-巯基苯并噻唑(MBT)^[50],能够对 pH 敏感响应,在碱性条件下缓蚀剂释放速率更大。

Cao 等^[22]利用 MOF-5 材料包裹缓蚀剂 BTA,同时赋予涂层主动、被动的抗腐蚀性能,在 MOF-5 涂层外用原硅酸四乙酯(TEOS)包裹,使得涂层只会在酸性和碱性条件下破裂,达到 pH 特性响应的效果,避免了缓蚀剂的浪费。为了再次增加被动防腐性能,将复合材料与 GO 进一步结合。GO 具有优异的阻隔性能和不渗透性,其上的含氧官能团也可以改善复合材料在环氧涂层内的分散性,在增强金属表面的缓蚀性能上具有巨大潜力。

MOFs 材料在镁合金表面作为纳米容器负载缓蚀剂或药物等物质时,必须选择合适的 MOFs 类型,不但要有高比表面积,而且配体或中性粒子不能加速镁合金的腐蚀,进一步提高负载的同时实现精准释放。

2.4.2 载药

医用镁合金需要具有较好的耐腐蚀性以实现长期给药,具有较好亲水性以实现良好的生物相容性。MOFs 不仅可以作为药物载体,还可以通过涂层的破裂释放出具有杀菌性、促进组织生长的金属离子^[107](如 Ag⁺、Cu²⁺)。例如,Mg-MOF-74 是一种既可以负载药物又可以释放 Mg²⁺的 MOFs 材料^[108],其释放的 Mg 不仅能够参与成骨细胞的黏附、生长、增殖和进一步的骨矿化^[109],从而缓解骨质疏松引起的骨痛

问题^[110], 还能够 MOF-74 进行双重给药^[111], 在提高镁合金表面耐腐蚀性的同时扩展镁合金的应用范围。

3 总结与展望

本文主要论述了 MOFs 新型材料的特点、常见的制备方法及其在镁合金上的防腐应用。MOFs 材料类型多样、容易调控的特征, 赋予了其更多的功能和更广阔的应用可能性。MOFs 是一种性能优异的多孔纳米材料, 为进一步开发其在镁合金表面的应用, 可以从下面几个方面来开展。

1) 缓蚀剂类型的 MOFs 可以协同有机/无机物的优点, 提供更高效更安全的缓蚀效果。但由于镁合金的高腐蚀性, 能够在镁合金表面应用的 MOFs 缓蚀剂种类较少, 需要开发适用不同环境条件的镁合金 MOFs 缓蚀剂。

2) 在大多数文献中, MOFs 常与各类有机/无机物质制备成复合材料, 在镁合金表面防腐上发挥协同作用。然而, 这类复合涂层仍存在涂层较薄、异相成核困难等问题, 制备更加均匀致密、不同厚度的 MOFs 复合涂层也是未来的发展方向之一。

3) 利用 MOFs 独特的多孔结构负载大小合适的缓蚀剂或药物, 需要进一步研究 MOFs 材料在不同条件下的响应行为 (pH 响应、温度响应等) 以及在镁合金表面的附着性、相互作用方式及对镁合金本身性能的影响, 确保其在实际应用中的稳定性和可靠性, 拓展其在生物医学、航空航天、汽车制造等领域的实际应用研究。

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