

光热自修复涂层的研究进展

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摘要: 综述了光热触发自修复涂层的结构设计、修复机制、填料的种类及其特点、涂层的修复效率与防腐应用, 重点阐述了基于碳基填料、等离子体纳米材料、有机填料、四氧化三铁纳米颗粒等光热响应物质自修复涂层的国内外最新研究进展, 详细分析了填料含量、光照波长、光照强度、基体类型等对涂层的自修复性能和耐蚀性能的影响规律。最后, 提出了光热自修复涂层目前存在的问题以及发展前景, 未来应进一步优化涂层的制备工艺, 提升光热转换效率, 降低制备成本, 并将涂层的多重修复机制相结合, 共同提升涂层的长效防护能力, 使之早日实现工业应用。

关键词: 自修复; 涂层; 光热响应; 耐蚀性; 缓蚀剂

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Research Progress of Photothermally Triggered Self-healing Coatings

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ABSTRACT: In recent years, the development of intelligent self-healing coatings has become one of the frontier research hotspots in the field of corrosion and protection. After being damaged by external force, the self-healing coating can repair the damaged areas timely and efficiently, so as to restore the corrosion resistance of the coating. By adding fillers with photothermal performance, the photothermally triggered self-healing coating can be realized. When cracks and scratches occur on the coating surface, the coating can be healed by a series of physical and chemical reactions triggered by light, achieving long-term protection such as removing gap and crack and restoring coating. Photothermal self-healing has many advantages such as high precision, high speed and long operating distance, possessing broad application prospects. This paper reviewed the structure design and repair mechanism of photothermally triggered self-healing coatings, the types and characteristics of fillers, as well as the repairing efficiency and the anti-corrosion applications of coatings. It mainly summarized the latest research progress of self-healing coatings based on photothermal responsive materials such as

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carbon-based fillers, plasmonic nanomaterials, organic fillers and Fe_3O_4 nanoparticles, and analyzed the effects of filler content, illumination wavelength, illumination intensity, matrix type, etc. on self-healing efficiency and corrosion resistance of coatings. Finally, the existing problems and the development prospects of photothermal self-healing coatings were proposed. In the future, the coating preparation process should be further optimized, and the photothermal conversion efficiency should be improved, and the preparation cost should be reduced. In addition, multiple healing mechanisms of coatings should be combined to jointly improve the long-term protection ability of coatings, so that the industrial application can be realized very soon.

KEY WORDS: self-healing; coating; photothermal response; corrosion resistance; corrosion inhibitor

金属的腐蚀破坏现象不仅造成了巨大的资源浪费,还会带来环境污染、安全隐患等一系列问题。涂层防护作为物理屏蔽,可以有效抑制金属基体表面腐蚀电化学反应的发生^[1-3]。该方法具有简单易行、价格低廉、可大面积涂刷的特点,是最有效的金属防腐手段之一。然而,涂层在服役过程中不可避免地会产生破损和开裂,造成防腐性能和使用寿命的显著下降^[4-5]。近年来,开发具有自行修复破损功能的涂层已经成为国内外腐蚀与防护领域的前沿研究热点之一,具有巨大的研究价值和经济效益。

自修复涂层起源于生物体系的自愈现象,在遭到外力破坏后,可自行修复裂口和划痕,从而有效隔离金属基材与腐蚀介质^[6-7]。现有涂层常通过包埋成膜物质^[8-9]或缓蚀剂^[10-11]以及借助外界环境刺激^[12-15],达到自行修复破损并恢复其防腐性能的目的。在利用成膜材料修复涂层时,修复剂的含量、力学性能及与基体的相容性均会影响涂层的防护能力。基于缓蚀剂的自修复涂层可在涂层破损处释放缓蚀剂,通过物理或化学作用使金属表面再次进入钝化状态,抑制基体的腐蚀。然而,直接在涂层中掺杂缓蚀剂不利于缓蚀剂的可控释放,而存储缓蚀剂的微纳米容器的制备步骤相对复杂繁琐,尚不具备大规模工业生产的可行性。基于成膜物质或缓蚀剂的自修复原理还限制了涂层的修复次数。因此,亟需开发新型的智能自修复涂层,以期在满足防腐性能的同时,提高涂层的自修复能力和使用寿命。

智能自修复涂层还可以通过光、电、热、磁、酶等外界刺激^[12-15],促使受损区域的涂层熔融而愈合损伤界面^[16-17]。该方法可以高效修复较大尺寸的表面损伤,有利于恢复涂层自身的物理化学性质和屏蔽作用。热引发自修复是目前最常用的触发手段,但是传统的加热方法只能在短距离范围内引发自修复,加热过程还会破坏材料受损区域以外的涂层结构^[18],造成能源浪费和经济损失。近几年来,通过光照产热的新颖自修复涂层受到了学者们的广泛关注。光热触发自修复具有以下显著的优点^[18-22]:对涂层材料的种类没有严苛要求,共价键与非共价键均可修复;可以利用光源远距离触发自修复过程,对于在特殊环境(如水下、真空等)的材料修复有着极其重要的意义;通过

调整光照位置和光斑大小,可以实现涂层的局部高精度自修复,避免对涂层完好区域的热损伤和副作用,这是以往的修复方式难以实现的;通过调节光源波长和强度等条件,可最大化光热效应,还可直接利用太阳光源修复涂层。因此,光照产热方法在涂层研究与开发中拥有巨大的发展潜力。

本文综述了光热自修复涂层的研究现状,重点介绍了光热自修复涂层的修复机理、填料种类和功能特点,并展望了该研究方向的发展前景。

1 光热自修复机理

光热自修复涂层的修复机理在于:涂层划口处的填料经光照产热,触发涂层内的一系列物理和化学反应,从而实现间隙闭合、裂纹消失,以至恢复涂层的物理屏障作用^[8-15]。因此,填料的光热响应和涂层基体的物理、化学反应是实现涂层光致愈合的两个重要研究方面。

涂层的光热自修复机理包括涂层熔融修复^[23-24]、填料熔融修复^[8-9]、热可逆反应修复^[25-26]等类型。涂层熔融修复一般是指涂层通过局部受热转变成粘流态,树脂在涂层受损处自由地扩散移动,链段相互穿插缠结,从而实现划口处界面融合。涂层的熔融修复机制一般适用于热塑性树脂材料,为保证涂层在服役过程中的完整性,避免涂层失效,对涂层粘流温度的调控是实现其工业应用的关键环节。填料熔融修复是在涂层中分散低熔点的填料,使填料受热熔融,并填补涂层间隙,这是另一种常见的自修复手段。热可逆反应修复是指交联线性高分子通过热可逆反应的温度响应机制实现涂层的多次重复自修复过程。狄尔斯-阿尔德反应(Diels-Alder, DA反应)^[25-27]或硫醇-二硫化物^[28-30]可逆反应是目前应用较多的热可逆反应,当受热达到一定程度时,涂层内的共价键分解,使分子链段流动到涂层伤口处重新交联以实现涂层愈合。

2 自修复涂层的光热响应填料

光热自修复涂层的另一个研究重点是光热响应物质的选择、含量控制、分散性优化及其对涂层性能的影响规律。现有的报道已通过聚合物中引入石墨

烯、碳纳米管、贵金属纳米粒子、聚多巴胺、 Fe_3O_4 颗粒等实现了涂层的光热自修复。

2.1 碳基填料

石墨烯和碳纳米管作为新型的碳纳米材料，具有优异的光吸收特性、良好的导热性、大的比表面积以及独特的力学性能^[31-33]。因此，将石墨烯或碳纳米管加入有机涂层中，不仅能够实现损伤裂纹的快速、高精度修复，还能有效改善材料的综合耐蚀性能。Cai 等^[34]制备了基于交联环氧树脂和石墨烯的复合材料。石墨烯在近红外激光的照射下产生热量，触发了环氧树脂的 DA 反应，使环氧-石墨烯复合材料的局部裂纹逐渐愈合，实现了涂层的快速自修复和再循环使用，如图 1 所示。Li 等^[35]利用多壁碳纳米管(MWCNT)作为光热转换器，产热升温触发环氧树脂的 DA 热可逆反应，具体分析了碳纳米管的含量（质量分数为 0.2%~2%）、近红外光源到样品的距离以及激光功率强度等对修复效果的影响规律。通过调节以上参数，

实现了小范围内的高精度、高效率裂纹修复，同时对未受损伤的区域没有明显影响，有利于扩展靶向修复的实际应用。

Chen 等^[36]利用碳黑实现了改性环氧树脂的光热自修复。环氧涂层的化学结构和性质可以通过二元胺和单胺的添加比例来调控。在自修复的过程中，链段需要快速扩散到裂纹或断裂面的接口处，因此具有较低的玻璃化转变温度 (T_g) 是光触发自修复聚合物的一个重要特点。随着二元胺逐渐被单胺替代，涂层的交联密度和玻璃化转变温度降低，为热诱导的自愈合提供了足够的分子链段移动性。随后将 0.05%~1.0% 碳黑添加到涂层中，在近红外光的照射下可产生良好的光热转换效果。随激光功率密度线性增长，复合涂层的温度上升（见图 2），在碳黑超过 0.5% 后达到饱和（见图 3）。在 1.2 W/cm^2 的近红外光下暴露 3 min，含有 0.5% 碳黑的复合涂层的表面划痕（约 $65\text{ }\mu\text{m}$ ）即可愈合。线性扫描伏安法的测试结果表明，修复后的涂层具有优异的抗腐蚀性能（见图 4）。

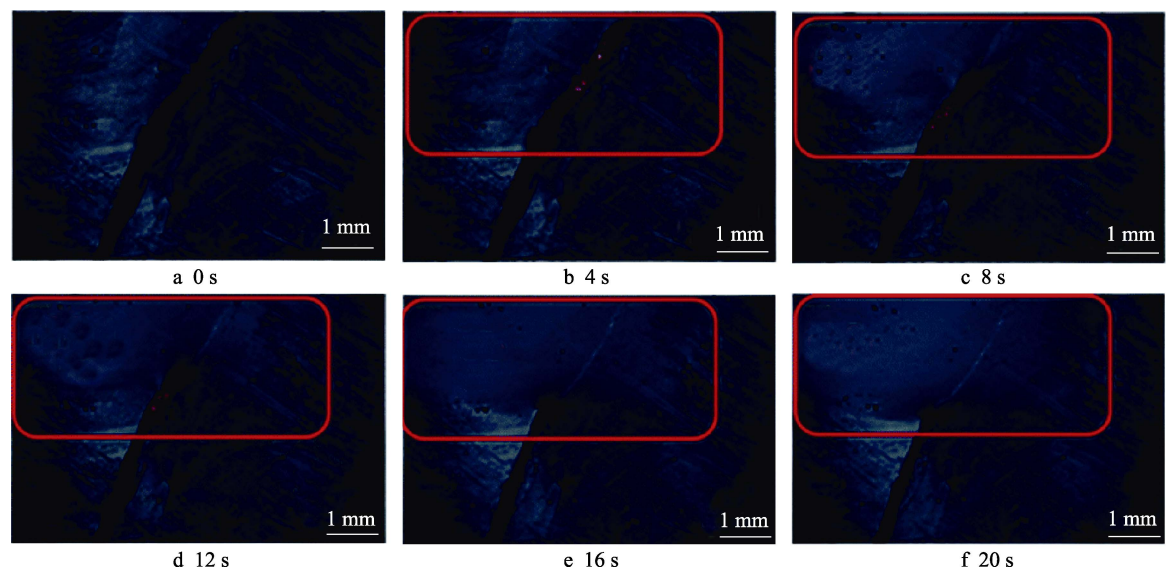


图 1 环氧-石墨烯复合材料的局部裂纹在红外激光照射过程中的修复过程
Fig.1 The healing process of local crack on epoxy-graphene composite under infrared laser irradiation

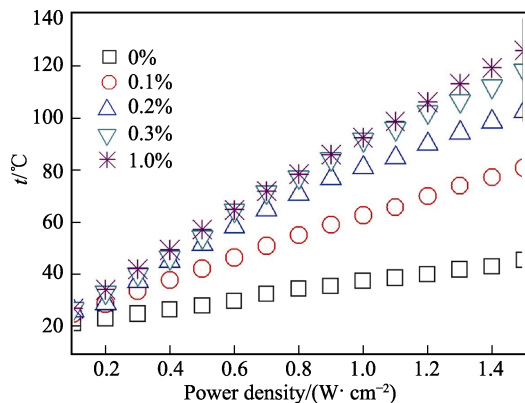


图 2 不同碳黑含量改性环氧涂层的温度与光功率密度之间的关系

Fig. 2 Relationship between temperature and lightpower density for modified epoxy coating of different content of carbon black

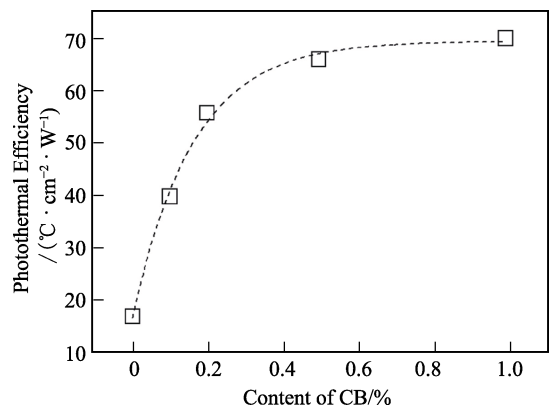


图 3 碳黑含量对环氧涂层光热效率的影响规律

Fig.3 The effect of CB content on photothermal efficiency of epoxy coating

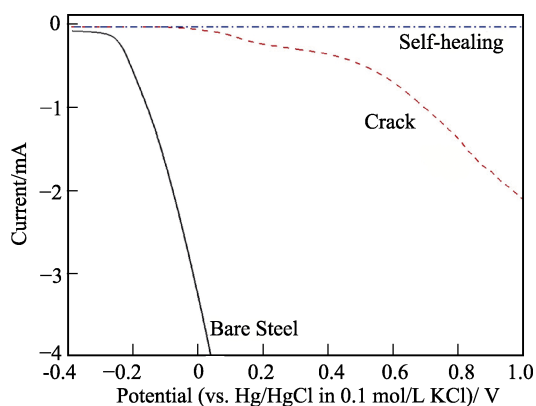


图4 裸钢、划口涂层、自修复涂层的线性扫描伏安测试结果

Fig.4 Linear scanning voltammetry test results for bare steel, scratch coatings, and self-healed coatings

2.2 等离子激元纳米材料

近年来,科学家们发现了等离子激元(Plasmonics)

纳米结构的光热效应^[37-38],即利用表面等离子共振将入射光能转化为热能的产热效应。当纳米结构与入射光相互作用时,电子气团会剧烈振荡而大量产热,使纳米粒子迅速升温,并有效加热周围环境^[39]。常见的等离子激元材料包括金、银等贵金属^[40-42]。Peng等^[43]在热塑性涂层中添加了0.005%~0.04%的金纳米颗粒,激光照射下金颗粒产生大量的热量,最大温升达到200℃以上。光热效应使树脂熔融,并流向断口处,冷却后重新结晶进而修复表面损伤,最终达到恢复其表面状态及力学性能的目的,如图5所示。该方法可实现多种热塑性涂料(聚乙酸乙烯酯PVAc、聚丙烯酸PAA、聚氨酯TPU、聚苯乙烯PS)的多次修复。Li等^[44]在聚己内酯/聚乙烯醇(PCL/PVA)复合膜表面沉积了一定厚度的银纳米线,在812nm的近红外激光照射下,银纳米线通过光照产热将涂层的表面温度提升至65℃以上,使其表面划伤在150s之内完全修复。研究表明,有机涂层的种类和厚度均会影响其高温熔融效果,从而影响自修复性能。

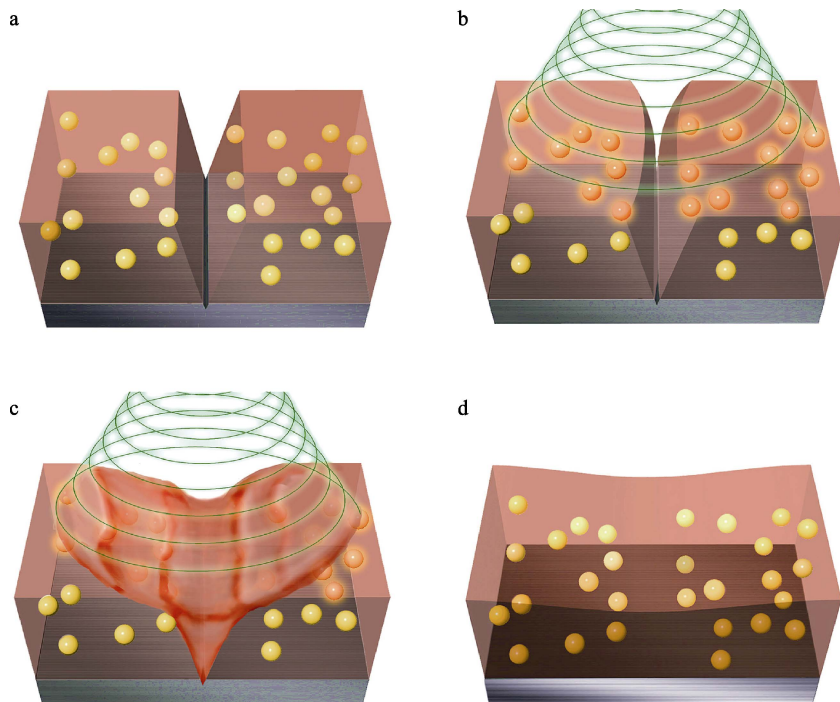


图5 金纳米颗粒-热塑性树脂的光热自修复机理

Fig.5 Scheme of photothermal self-healing mechanism on Au nanoparticle-thermoplastic resin

光热效应不仅可以促进有机涂层的高温熔融,还有利于缓蚀剂的可控释放。Skorb等^[45]介绍了一种利用激光控制的“智能”防腐涂层。该技术首先在介孔二氧化钛或介孔二氧化硅内添加缓蚀剂,然后采用层层自组装(Layer-by-layer self-assembly, LBL)的方法在表面包覆修饰有银纳米颗粒的聚电解质壳,再将其分散于有机基质中。在光照的条件下,银颗粒由于等离子激元共振而升温,从而破坏聚电解质壳,并使负载

的缓蚀剂从容器中释放(如图6和图7所示)。研究表明,纳米颗粒的尺寸、浓度、入射光强、光照波长与材料等离子激元共振峰的匹配程度均会影响涂层的升温情况。值得注意的是,激光照射下的缓蚀剂释放速率是pH刺激下缓蚀剂释放速率的3倍,这对于迅速修复涂层缺陷起到了至关重要的作用。图6的微区电化学结果证明,激光照射后铝合金表面的腐蚀电流迅速下降,该方法可作为涂层自修复的常用手段。

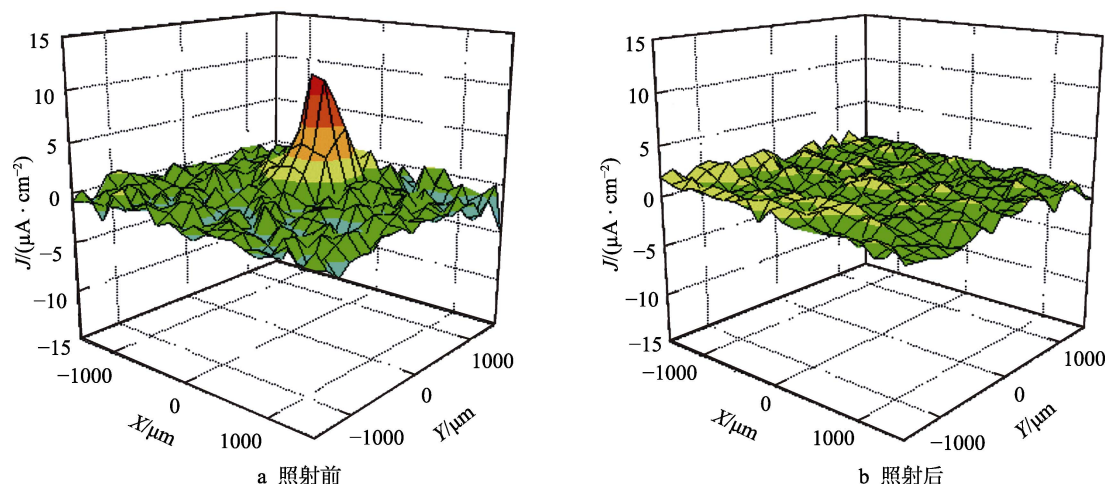


图 6 腐蚀区域在激光照射前后的 SVET 离子电流

Fig. 6 Scanning vibrating electrode measurements (SVET) ionic currents (a) before and (b) after laser irradiation of the corrosion area

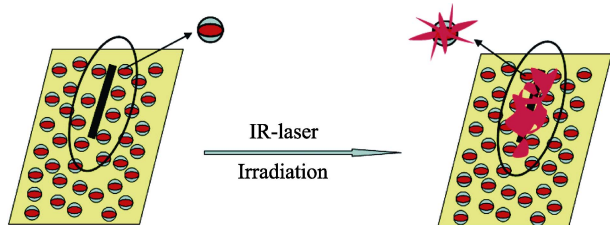


图 7 局部激光照射后缓蚀剂释放而修复涂层缺陷
Fig. 7 Healing of coating defect by inhibitor release after local laser irradiation

2.3 有机填料

聚多巴胺 (PDAP) 在整个可见光范围内具有很强的光吸收率。红外相机测温的结果表明, 含有 1% PDAP 的聚合物可迅速升温至 150 °C 以上^[46]。PDAP

强烈的光热转换效率使之成为极具潜力的新型光热响应物质^[46-48]。另一种常见的有机光热填料是苯胺黑 (Aniline black, AB), 它在可见光及近红外光的范围内均具有良好的光吸收能力。Fang 等^[49]通过调整单胺和二元胺固化剂的比例, 使单胺 4-(十七氟辛基) 苯胺 (HFOA) 逐步取代二元胺间苯二甲胺 (MXDA), 达到降低环氧涂层的玻璃化转变温度和交联密度的目的, 从而使其具备基于链扩散和再缠结的热诱导愈合性能。随后向该环氧涂层中加入苯胺黑颗粒, 利用放大聚焦的太阳光 (光密度达到 0.7~0.9 W/cm²) 愈合涂层的表面缺陷, 涂层划口的最大修复宽度为其厚度的 3 倍 (如图 8 所示), 并且修复后涂层的耐蚀性与完整涂层相当。

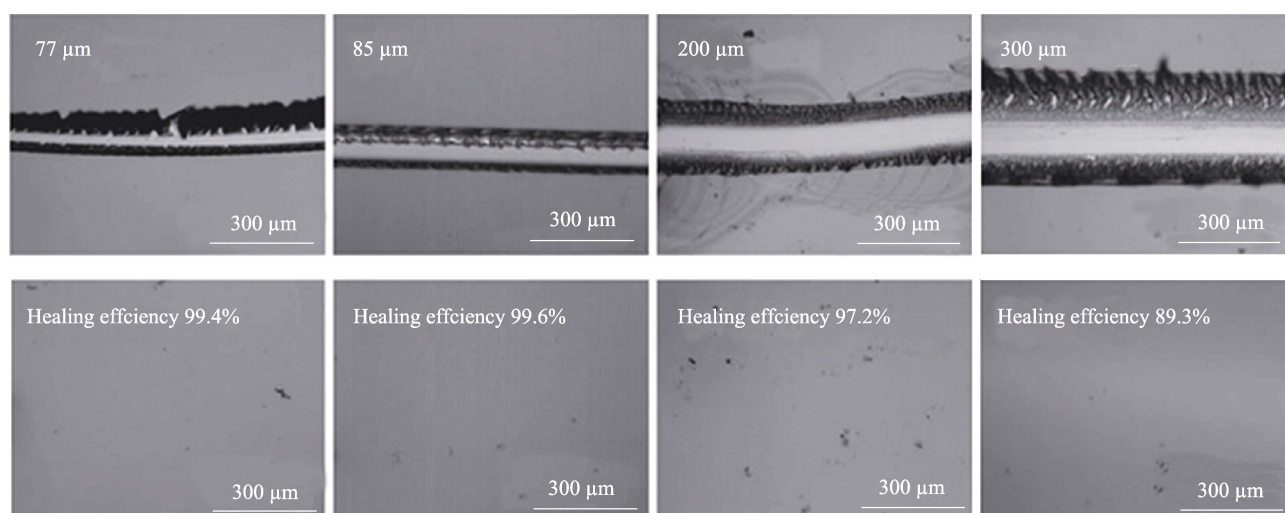
图 8 不同划口宽度的苯胺黑涂层在太阳光 (0.9 W/cm²) 照射 10 min 后的形貌照片

Fig.8 Morphology images of AB coatings with different crack widths after irradiation of sunlight (0.9 W/cm²) for 10 min

2.4 Fe₃O₄ 纳米颗粒

Yin 等^[50]设计了一种简便且实用的光热自修复

方法, 通过将 Fe₃O₄ 纳米颗粒分散于热塑性聚合物中, 利用红外或近红外光照 Fe₃O₄ 颗粒产生的光热效应, 可在空气、水下等各种工作环境中对涂层缺陷进行原

位修复。 Fe_3O_4 纳米颗粒具有价格低廉、易于制备、光热转换性能好等优点^[51-53], 同时它在丙酮、正己烷、三氯甲烷等溶剂中的分散性良好。添加 0.5% Fe_3O_4 纳米颗粒的涂层在红外光照射 30 s 后可升温至 60 °C 以上。该温度高于热塑性聚氨酯的玻璃化转变温度, 满足了涂层自修复的必要条件。作者还详细分析了在水下自修复的过程中, 样品随着浸泡深度的变化而引起的光照升温效果差异, 通过近红外激光照射实现了涂层在静态水、动态水中的愈合, 恢复了对 Q235 碳钢的保护作用 (见图 9)。由图 10a 可知, 表面具有缺陷的 TPU/ Fe_3O_4 涂层的开路电位与裸露 Q235 钢的开路电位一致。在自修复过程中, 复合涂层的自修复电位随着愈合时间的增长而逐渐升高, 在 57 s 后与完好涂层的开路电位一致。表明预先损坏的涂层可以完全修复, 且修复后的涂层具有优异的耐蚀性。

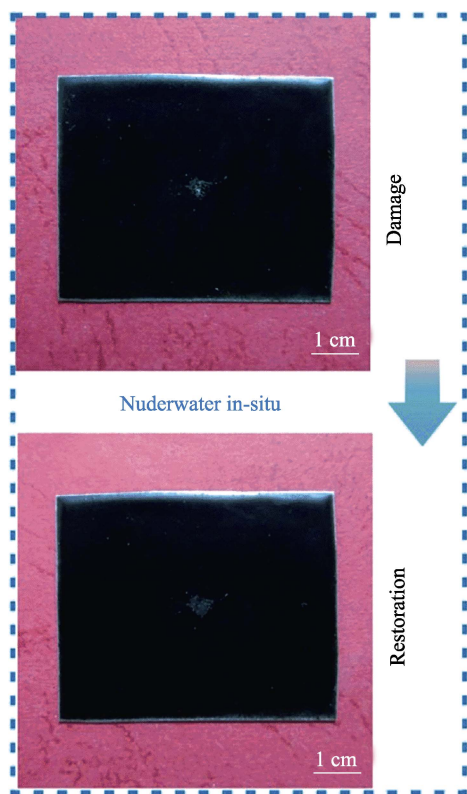


图 9 表面具有涂层缺陷和涂层修复的 Q235 碳钢在 3.5% NaCl 溶液中浸泡 120 h 后的形貌照片

Fig. 9 Morphology images of Q235 carbon steel of defective coating and healed coating after immersion in 3.5% NaCl for 120 h

2.5 MXene 二维材料

MXene 是一种新兴的二维材料, 它由过渡金属碳化物、氮化物和碳氮化物组成, 对光和微波均有较强的吸收能力^[23]。MXene 在 808 nm 近红外光和聚焦太阳光的照射下可以发生明显的光热效应, 以触发环氧涂层的 DA 效应, 但 MXene 二维片层的存在一定程度上限制了有机分子的移动, 阻碍了涂层的愈合。为此, 将匀染剂加入到涂层体系当中, 促进反向塑性

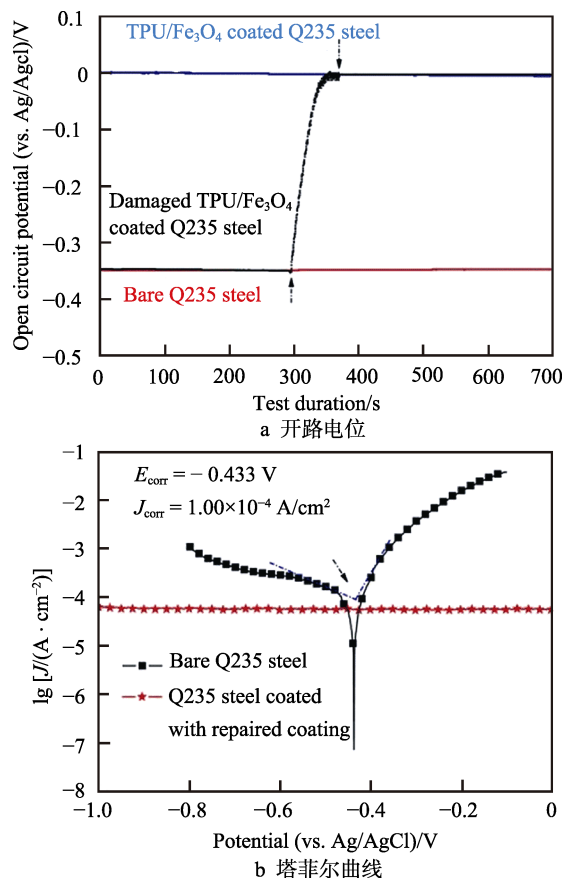


图 10 有无涂层的 Q235 碳钢的开路电位和塔菲尔曲线
Fig.10 The open circuit potential (a) and Tafel curves (b) of Q235 carbon steel and coated Q235 carbon steel in 3.5% NaCl

驱动, 以弥补大分子迁移率的限制, 使涂层划口在功率密度为 6.28 W/cm^2 的 808 nm 近红外光照射 10 s 或功率密度 4.0 W/cm^2 的聚焦太阳光照射 10 min 后即可完成愈合, 防腐性能得到恢复。MXene 的添加不仅实现了环氧涂层的自修复, 还大大提高了环氧涂层本身的硬度和极化电阻。

3 结语

目前, 光热自修复涂层处于实验室的理论研究和初步研发阶段, 相关的产业化报道较少, 还需要在以下几个方面进行更为深入的研究, 以期早日实现工业化应用。

1) 金、银、石墨烯、碳纳米管等物质虽然具有良好的光热转换性能, 但它们的添加会大大提高涂层的制备成本, 因此亟需开发新型的低成本、环境友好型光热材料, 并将其用于涂层的光热自修复领域。

2) 微纳米填料在涂层中的分散性和均匀性会严重影响涂层的防护性能, 应通过合适的物理或化学修饰方法提高填料在涂层中的均匀性和涂层的使用可靠性。

3) 已有的报道多关注于修复较小尺寸的涂层缺陷, 仍缺乏对较大尺寸、复杂几何形状涂层破损的修

复工作, 这对于涂层的实际应用具有重要意义。

4) 新一代光热自修复涂层需要在修复防腐和屏蔽性能的同时, 实现对涂层力学性能和表面性质的多重修复。

综上所述, 光热自修复涂层因其高精度、可远距离修复等特点, 具有广阔的应用前景。今后应进一步优化涂层的制备工艺, 提升光热转换效率, 降低制备成本, 并将涂层的多重修复机制相结合, 共同提升涂层的长效防护能力, 使之早日实现工业应用。

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