

## 表面强化及功能化

热喷涂制备 TiO<sub>2</sub> 光催化涂层研究进展任坤<sup>1,2</sup>, 黄晶<sup>2</sup>, 贺小燕<sup>2</sup>, 叶卫平<sup>1</sup>, 程旭东<sup>1</sup>, 方丹丹<sup>3</sup>, 李华<sup>2</sup>

(1. 武汉理工大学 材料科学与工程学院, 武汉 430070; 2. 中科院宁波材料技术与工程研究所  
海洋新材料与应用技术重点实验室 浙江省海洋材料与防护技术重点实验室, 浙江 宁波 315201;  
3. 宁波智慧城市研究院, 浙江 宁波 315048)

**摘要:** TiO<sub>2</sub> 光催化剂因其利用可持续的太阳光进行光催化反应, 在环境保护、医疗卫生等领域具有潜在的应用价值, 近年来引起了研究者的广泛关注。目前, 颗粒状 TiO<sub>2</sub> 催化剂获得了一定的实际应用, 但在液相中使用后需要回收, 不仅增加了工艺的复杂性, 而且提高了设备等成本的投入。负载型催化剂和涂层技术是将 TiO<sub>2</sub> 固定在载体上, 可有效避免颗粒状催化剂难回收的问题。在众多涂层制备技术中, 热喷涂技术可快速高效大面积地制备 TiO<sub>2</sub> 光催化涂层, 且涂层机械性能优异, 喷涂成本低廉, 因而使 TiO<sub>2</sub> 的工业化制备和应用更具前景。综述了近年来国内外制备 TiO<sub>2</sub> 涂层常用的传统热喷涂技术、改进后的液相热喷涂技术和冷喷涂技术, 并论述了影响 TiO<sub>2</sub> 光催化性能的材料相组分、涂层结构和元素掺杂等因素, 总结了相应的性能改进措施, 指出了目前 TiO<sub>2</sub> 光催化涂层的应用研究存在的问题和研究方向。

**关键词:** TiO<sub>2</sub> 涂层; 光催化; 热喷涂; 锐钛矿相; 金红石相

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## Research Progress in Thermal Spray Fabrication of Titania Photocatalytic Coatings

REN Kun<sup>1,2</sup>, HUANG Jing<sup>2</sup>, HE Xiao-yan<sup>2</sup>, YE Wei-ping<sup>1</sup>, CHENG Xu-dong<sup>1</sup>, FANG Dan-dan<sup>3</sup>, LI Hua<sup>2</sup>

(1. School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China;  
2. Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China;  
3. Ningbo Academy of Smart City Development, Ningbo 315048, China)

**ABSTRACT:** Titania is of increasing interest due to its using sustainable sunlight to drive photocatalytic reaction and its potential

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作者简介: 任坤(1991—), 男, 河南人, 硕士研究生, 主要从事热喷涂表面涂层技术及二氧化钛光催化技术研究。

Biography: REN Kun (1991—), Male, from Henan, Master graduated student, Research focus: thermal spray coating technology and titania photocatalysis technology.

通讯作者: 李华(1971—), 男, 山东人, 博士, 研究员, 主要从事热喷涂表面涂层技术和生物材料研究。

Corresponding author: LI Hua (1971—), Male, from Shandong, Ph. D., Researcher, Research focus: thermal spray coating technology and biomaterials.

application in environmental protection, health care and so forth. At present, particle-type titania catalyst has been putting into practice, but those catalyst powders servicing in liquid phase always need recycling process, which increases not only the complexity, but also the cost of equipment. Supported catalysts and coating technology could overcome the difficulty in the recycling of granular catalysts through immobilization of TiO<sub>2</sub> on various supports. Among numerous coating preparative techniques, thermal spray has the ability to prepare large-area coating with high mechanical performance quickly and efficiently at a low cost, which shows a bright prospect in the industrialization of titanium dioxide. This paper summarized the common thermal spraying techniques, the modified liquid thermal spray and cold spray technologies used to elaborate TiO<sub>2</sub> coatings in China and foreign countries in recent years, and discussed the influencing factors on the photocatalytic performance, such as the material phase composition, coating structure, element doping and so on. The corresponding performance improvement measures were summarized, and the existing problems of current researches on TiO<sub>2</sub> photocatalytic coatings and future research direction were pointed out.

**KEY WORDS:** titania coating; photocatalysis; thermal spray; anatase; rutile

光催化技术是在光的照射作用下,借助光催化剂加速化学反应的技术,可利用持续的太阳能驱动光催化反应,在环境、能源等领域具有潜在的应用价值。同时,它催化效率高,无毒副产物生成,被认为是解决环境问题的可行技术。光催化技术分为均相光催化和非均相光催化两种类型。均相光催化降解中较常见的是以 Fe<sup>2+</sup> 或 Fe<sup>3+</sup> 及 H<sub>2</sub>O<sub>2</sub> 为介质,通过 photo-Fenton 反应来降解污染物,催化剂和反应物同处于气态或液态。非均相光催化降解中,较常见的是向污染体系中加入一定量的半导体催化剂,在光照射条件下实现污染物的降解,此时催化剂与反应物处于不同状态,催化剂为固态,反应物是气态或液态,催化反应后催化剂较容易分离,便于反复利用、节约成本。

在众多半导体催化剂中, TiO<sub>2</sub> 凭借其稳定的化学性质、高耐久性、低价、无毒和强氧化能力等优点,广泛应用于光催化氧化过程<sup>[1-3]</sup>。其中,颗粒状 TiO<sub>2</sub> 催化剂,尤其纳米颗粒状催化剂,颗粒粒径小,比表面积大,催化活性较高,成为研究者最热捧的研究对象之一。然而在实际应用过程中,尤其在液相中,颗粒状催化剂需要后续的离心或过滤装置进行回收利用,这无疑增加了经济投入和技术复杂度。此外,颗粒状催化剂作为外界添加物,还可能引起二次环境污染<sup>[4-5]</sup>。而负载型 TiO<sub>2</sub> 催化剂或 TiO<sub>2</sub> 膜/涂层制备技术能够将 TiO<sub>2</sub> 颗粒固定到载体上,从而有效克服上述难题,具有很好的研究和应用价值。目前,制备 TiO<sub>2</sub> 膜/涂层的常用方法主要有:溶胶凝胶法<sup>[6-8]</sup>、浸涂/烧结法<sup>[9-10]</sup>、物理气相沉积<sup>[11-13]</sup>、化学气相沉积<sup>[14-16]</sup>、热喷涂<sup>[17-23]</sup>等。相比于其他制备方法,虽然热喷涂过程中较高的热输入会使得 TiO<sub>2</sub> 发生一定程度的晶型转变,并且制备的 TiO<sub>2</sub> 涂层厚度大,粗糙度大,但是高孔隙率条件下,厚度和粗糙度的增加会增大涂层的比表面积,从而提高涂层的光催化活性;

一定程度的相转变产生的混晶效应也会提高光催化性能。此外,热喷涂技术在大尺寸、快速高效制备涂层,涂层机械稳定性和工业化大规模、低成本生产等方面有显著优势。因此,有必要在现有热喷涂制备 TiO<sub>2</sub> 涂层技术的基础上继续深入研究,以获得能够广泛应用于实际的热喷涂 TiO<sub>2</sub> 涂层产品。

## 1 热喷涂制备 TiO<sub>2</sub> 光催化涂层

### 1.1 传统热喷涂技术

传统热喷涂技术制备 TiO<sub>2</sub> 光催化涂层,一般是将微米级 TiO<sub>2</sub> 粉末或纳米颗粒团聚后的 TiO<sub>2</sub> 粉末加热到熔化或半熔化状态,并借助火焰焰流自身或者压缩空气沉积到基体而形成涂层。一般热喷涂技术均可实现 TiO<sub>2</sub> 光催化涂层的制备,包括大气等离子喷涂(Atmospheric plasma spraying, APS)、粉末火焰喷涂(Flame spraying, FS)、超音速火焰喷涂(High velocity Oxy-fuel, HVOF)等。

Lee 等<sup>[24]</sup>将纳米 TiO<sub>2</sub> 粉末喷雾干燥团聚后,再借助等离子喷涂制备出具有纳米结构的 TiO<sub>2</sub> 涂层。其中,在低功率条件下获得的 TiO<sub>2</sub> 涂层保留了较多的锐钛矿相并且晶粒比较细小,光催化效果较好。Yang 等<sup>[25]</sup>同样选用喷雾干燥后的 TiO<sub>2</sub> 粉末,利用超音速火焰喷涂制备了 TiO<sub>2</sub> 涂层。结果表明,燃气流量的大小调控热输入的大小,从而影响了喂料在热喷涂过程中的熔化状态,最终可以影响涂层中锐钛矿的含量。降低燃气流量可使涂层中锐钛矿的质量分数从 30% 提升到 70%。利用该工艺制备的 TiO<sub>2</sub> 涂层对苯酚的光催化降解有显著的效果。

### 1.2 液相热喷涂

传统热喷涂射流速度、冷却速度均较快,但其较

高的焰流温度会造成  $\text{TiO}_2$  颗粒在喷涂过程中发生强烈的晶型转变,从而影响涂层的光催化性能。为了减少或控制  $\text{TiO}_2$  粉末晶粒在热喷涂过程中受热长大和晶型转变,研究者对传统粉末送粉器进行了改造并取得了长足进步。其中,液相热喷涂技术,即以液体(水或有机溶剂)替代气体作为粉末原料的运输介质进行热喷涂的涂层制备技术,与传统热喷涂工艺相比,其喂料不受粉末尺寸的限制,可直接对纳米级粉末进行喂料喷涂。同时,由于喷涂过程中液相溶剂的蒸发带走了大量的热量,从而可以避免  $\text{TiO}_2$  晶粒受热发生过分长大和过多晶型转变,能够将更多的纳米颗粒在喷涂后得以保存,最终提高涂层光催化性能<sup>[26]</sup>。

Filofteia-Laura Toma 等<sup>[27]</sup>对比研究了液相等离子喷涂和传统大气等离子喷涂技术制备的  $\text{TiO}_2$  涂层。结果表明,液相等离子喷涂制备的  $\text{TiO}_2$  涂层中保存了较多的原始锐钛矿相, $\text{TiO}_2$  晶粒生长受到抑制,光催化降解  $\text{NO}_x$  的性能显著优于大气等离子喷涂制备的涂层。Filofteia-Laura Toma 等<sup>[17]</sup>借助悬浮液超音速火焰喷涂制备的  $\text{TiO}_2$  涂层也获得了类似结果,相比于传统超音速火焰喷涂相比,悬浮液超音速火焰喷涂制得的涂层中锐钛矿相含量较高,光催化降解有机物性能更佳。Giovanni Bolelli 等<sup>[28]</sup>采用高速悬浮液火焰喷涂制备了  $\text{TiO}_2$  涂层。通过调整工艺参数,可促进未熔颗粒在涂层中的保存,从而增大了锐钛矿相含量和涂层孔隙率,最终获得了较好的光催化性能。但是,液相热喷涂条件下,喂料颗粒熔融程度差,涂层孔隙率较高,会导致涂层结合强度等机械性能的下降和颗粒沉积效率的降低。因此,如何控制工艺参数或改进工艺来调整涂层孔隙率和机械性能之间的关系以及提高涂层的沉积效率,仍需开展系统的探索性研究。

冷喷涂是近年来新发展的一种喷涂技术,它是利用高压气体将固体粉末粒子以超音速撞击并发生塑性变形,最终沉积于基体表面形成涂层。相比于传统热喷涂和液相热喷涂技术,冷喷涂技术采用较低的喷涂温度,避免了传统热喷涂过程中涂层与基体材料氧化或相变、发生冶金形变和残余应力等问题。Motohiro Yamada 等<sup>[29]</sup>借助冷喷涂制备了锐钛矿相的  $\text{TiO}_2$  涂层。结果表明,当喷涂所用气体温度从  $200\text{ }^\circ\text{C}$  提高到  $400\text{ }^\circ\text{C}$  时,喷涂颗粒的沉积效率增大,所制备涂层的厚度由  $20\text{ }\mu\text{m}$  增加到  $50\text{ }\mu\text{m}$ 。由于沉积机理相同,该工艺制备的所有涂层比表面积都较大,喷涂过程中无相转变发生,涂层中  $\text{TiO}_2$  全部以锐钛矿相形式存

在,涂层对  $\text{NO}$  气体降解具有优异的光催化效率,体现出了冷喷涂技术制备  $\text{TiO}_2$  涂层的优势。但冷喷涂技术的高昂成本限制了其广泛应用。

## 2 影响 $\text{TiO}_2$ 涂层光催化性能的因素及改进措施

当光子能量高于  $\text{TiO}_2$  禁带宽度的光照射到热喷涂  $\text{TiO}_2$  表面时, $\text{TiO}_2$  的价带电子受到激发,跃过禁带迁移至导带,从而产生导带处的光生电子( $e^-$ )和价带处的空穴( $h^+$ )。但同时光生电子-空穴也以极快的速率复合,使得  $\text{TiO}_2$  量子化产率较低。当存在合适的俘获剂、表面缺陷或者其他因素时,电子和空穴的复合得到抑制,就会在催化剂表面发生氧化-还原反应。光生电子-空穴与吸附在  $\text{TiO}_2$  颗粒表面的  $\text{H}_2\text{O}$ 、 $\text{OH}^-$ 、 $\text{O}_2$  等发生反应,生成羟基自由基( $\cdot\text{OH}$ )、超氧负离子( $\cdot\text{O}_2^-$ )等活性氧自由基。这些活性氧自由基具有很强的氧化性,能将吸附在催化剂表面的有机物氧化至最终产物  $\text{CO}_2$  和  $\text{H}_2\text{O}$ ,从而达到降解有机物的目的。 $\text{TiO}_2$  涂层在光催化过程中,会受到很多因素的影响,如光照强度、反应物浓度、pH 值、温度等。目前,影响  $\text{TiO}_2$  涂层光催化性能的主要因素有:涂层相组分、涂层结构特征以及涂层元素掺杂。

### 2.1 涂层相组分

涂层相组分对其性能有重大影响,光催化剂  $\text{TiO}_2$  主要有两种晶型:锐钛矿相和金红石相。研究发现,锐钛矿相的禁带宽度比金红石相约大  $0.2\text{ eV}$ ,热稳定性略差,但其具有高密度的局域态和表面吸附的羟基自由基以及较慢的载流子复合速度,因此光催化性能更强<sup>[30]</sup>。进一步研究发现,由锐钛矿和金红石复合组成的混合晶型  $\text{TiO}_2$  比单一相的  $\text{TiO}_2$  有更好的光催化效果,这是由于混合晶型中的金红石相可对光生电子进行捕获,从而改善载流子的分离,最终减少光生电子-空穴的复合<sup>[31-32]</sup>。因此,可通过抑制相转变提高锐钛矿相含量或促进相转变达到一定的混晶效应,提高  $\text{TiO}_2$  光催化性能。目前,改进  $\text{TiO}_2$  涂层相组分可采取的常用措施有:选用合适的喷涂手段,调节喷涂参数,加快基体和涂层的冷却速率等。Filofteia-Laura Toma 等<sup>[22]</sup>采用液相等离子喷涂技术制备  $\text{TiO}_2$  光催化涂层过程中发现,涂层锐钛矿相含量还与配制  $\text{TiO}_2$  悬浮液的溶剂有关。当悬浮液溶剂由水换为酒精时,锐钛矿体积分数由  $78\% \sim 80\%$  下降至  $23\%$  以

下。

Maryamossadat Bozorgtabar 等<sup>[18]</sup>利用超音速火焰喷涂技术制备 TiO<sub>2</sub> 涂层时采用液相燃料,通过控制燃料流量可提高涂层中锐钛矿相的含量,当燃料流量为 120 mL/min 时,涂层中锐钛矿相高达 80%,可高效地降解乙醇。

Filofteia-Laura Toma 等<sup>[33]</sup>采用不同热喷涂技术制备 TiO<sub>2</sub> 涂层。结果表明,液相等离子喷涂制备了的涂层保存了原有的锐钛矿相成分,TiO<sub>2</sub> 涂层比表面积大,光催化效率最高。而利用传统等离子喷涂和超音速火焰喷涂技术制备的涂层中锐钛矿相含量较少,光催化降解 NO<sub>x</sub> 污染物的效率不足 5%。

## 2.2 涂层结构特征

### 2.2.1 表面形貌

TiO<sub>2</sub> 光催化时生成的光生电子-空穴复合速率极快,导致光催化反应只能在 TiO<sub>2</sub> 表面或近表面区域进行,因此涂层比表面积对涂层光催化性能影响较大<sup>[29]</sup>。比表面积越大,TiO<sub>2</sub> 与被降解物质的接触面积越大,越有利于有机物的预吸附,发生光催化反应位点越多,光催化反应速率和降解效率越大。目前,涂层制备过程中,调整工艺参数可有效控制 TiO<sub>2</sub> 晶粒长大或熔化程度及纳米颗粒在涂层中的残留量,从而调控涂层表面粗糙度和比表面积。细小晶粒构成的涂层比表面积大,可参与光催化反应的活性位点多,且发生光生电子和空穴简单复合的几率小,光催化活性较高。此外,涂层表面的相组分分布对光催化性能也有一定的影响。Yang 等<sup>[34]</sup>通过液相火焰喷涂制备了纳米结构 TiO<sub>2</sub> 涂层,喷涂后涂层中锐钛矿相含量较高,涂层经热处理后由于纳米颗粒表面发生相转变,表面形成了的金红石相层包裹着内层的锐钛矿相,使得光催化反应主要由金红石相参与,导致涂层整体光催化效果不佳。

### 2.2.2 孔隙率

提高涂层孔隙率可有效增大涂层的比表面积,反应物可沿孔隙或裂纹进入涂层内部,使得反应物与 TiO<sub>2</sub> 的接触面积增加,从而提高涂层光催化性能。目前,喷涂过程中,可调节喷涂功率、喷涂距离、喂料速率等参数调节涂层孔隙率。对于液相热喷涂工艺,可向液相中添加一定的有机物等措施提高涂层孔隙率<sup>[22,35-36]</sup>,因为喷涂过程中,有机物受热分解或烧蚀会留有一定的孔隙,产生气体来不及逸出在涂层中形成空洞结构。同时,工艺对颗粒相转变和涂层机械性

能也有明显影响。

Zhang 等<sup>[37]</sup>调整等离子喷涂的功率和喂料速率在不锈钢基体上制备了不同孔隙率的 TiO<sub>2</sub> 涂层。在低喷涂功率(16 kW)和高喂料速率(10.9 g/min)条件下,制备的涂层孔隙率较高、比表面积大、光催化效率较好。Yang 等<sup>[38]</sup>利用旋转蒸发工艺将 PEG 和纳米 TiO<sub>2</sub> 制成复合喂料粉末,采用真空冷喷涂技术制备了不同孔隙结构的 TiO<sub>2</sub> 涂层。SEM 结果表明,制备的涂层中存在由微孔和大孔构成的复合孔隙结构。这种结构更有利于污染物进入到涂层内部,增加污染物与 TiO<sub>2</sub> 的接触反应位点,从而提高涂层光催化性能。

## 2.3 元素掺杂

TiO<sub>2</sub> 的禁带宽度较宽(3.0~3.2 eV),能够激发 TiO<sub>2</sub> 光催化反应的紫外光仅占太阳光总量的 4%,太阳能利用率非常低,因此开发可见光波段激发的 TiO<sub>2</sub> 产品极具应用前景。此外,光生电子-空穴极易复合,易导致 TiO<sub>2</sub> 量子化效率降低,这些问题亟需解决。近年来,通过掺杂金属、非金属元素等提高 TiO<sub>2</sub> 光催化性能的研究报道日益增多。掺杂的作用和目的主要有:1)降低 TiO<sub>2</sub> 的禁带宽度<sup>[39-41]</sup>,增强其对可见光区的响应;2)引进中间能带状态(mid-gap states)<sup>[42-44]</sup>,促进光生电子-空穴的生成;3)增强光生载流子的分离<sup>[45-47]</sup>,降低其复合速率;4)增加表面吸附物的数量级别<sup>[48-49]</sup>,加快光催化反应速率。目前常用的掺杂金属元素主要有 Fe<sup>[46,50-51]</sup>,Cu<sup>[48,52]</sup>,Cr<sup>[47,53]</sup>,Mn<sup>[51]</sup>,Ni<sup>[54-55]</sup>,V<sup>[56-57]</sup>,Zr<sup>[51]</sup>,Ag<sup>[45,58-59]</sup>,Sn<sup>[60-62]</sup>,镧系稀土(Th<sup>[63]</sup>,Ce<sup>[51,64-65]</sup>,Nd<sup>[66]</sup>,Pr<sup>[42]</sup>,Er<sup>[67]</sup>)等;非金属元素主要有 B<sup>[44]</sup>,C<sup>[68-69]</sup>,N<sup>[44,70-72]</sup>,F<sup>[73-75]</sup>,S<sup>[76-77]</sup>等。

Pavel Citbor 等<sup>[78]</sup>通过等离子喷涂 TiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> 复合粉末实现了 Fe<sup>3+</sup>对 TiO<sub>2</sub> 涂层的掺杂。结果表明,在紫外光和可见光下,Fe<sup>3+</sup>掺杂 TiO<sub>2</sub> 的杂化涂层可在 12 h 内充分降解丁烷。Yang 等<sup>[45,48]</sup>在钛酸丁酯前驱体溶液中分别添加了 Cu<sup>2+</sup>和 Ag<sup>+</sup>,通过液相火焰喷涂技术制备 Cu<sup>2+</sup>,Ag<sup>+</sup>掺杂 TiO<sub>2</sub> 涂层。研究发现,适量掺杂 Cu<sup>2+</sup>可增强涂层对氧和其他反应物的吸收能力。Ag<sup>+</sup>进入 TiO<sub>2</sub> 的晶型可使锐钛矿相晶格扭曲(101)衍射峰左移。此外,Ag<sup>+</sup>易被 TiO<sub>2</sub> 还原为金属 Ag,而金属 Ag 可充当电子清除剂,增强电荷分离和氧还原效率。光催化降解乙醛试验表明,掺杂 Cu<sup>2+</sup>或 Ag<sup>+</sup>可提高涂层的光催化性能,但过量掺杂亦

会导致涂层光催化性能下降。

Georg 等<sup>[43]</sup>在 TiO<sub>2</sub> 悬浮液中添加 TiN, 通过液相等离子喷涂技术制备了 N 掺杂 TiO<sub>2</sub> 涂层。N 掺杂可建立中间能带状态, 以降低光激发电子的能量势垒, 提高可见光的利用率, 从而提高光催化效率。N 元素溶于 TiO<sub>2</sub> 晶格需较高热输入, 会增加相转变程度, 导致涂层中锐钛矿相减少。

此外, 掺杂可能会影响锐钛矿相向金红石相的转变动力<sup>[30]</sup>。对于置换固溶体, 掺杂离子可进入锐钛矿晶格, 影响氧空位水平, 从而影响相转变; 对于间隙固溶体, 由于掺杂元素尺寸、化合价和含量的作用, 晶格约束会影响晶格的稳定状态, 进而影响相转变。涂层中未熔掺杂颗粒可能会导致晶界增加, 限制 TiO<sub>2</sub> 晶粒长大并减少颗粒间接触, 进而抑制相转变。总之, 为了整体上提高 TiO<sub>2</sub> 的光催化性能, 元素掺杂这一措施还需进行大量探索性研究, 以寻求最佳掺杂种类、掺杂量以及合适的喷涂工艺参数。

### 3 结语

随着热喷涂技术的进一步发展以及热喷涂制备 TiO<sub>2</sub> 涂层技术的成熟, TiO<sub>2</sub> 光催化涂层的应用领域会得到进一步拓展。目前, 国内外对其应用主要是基于 TiO<sub>2</sub> 光催化降解有机污染物和光催化杀菌等性能, 应用领域主要集中在环境保护和医疗卫生领域, 如室内外空气净化<sup>[5, 19, 22, 27, 53, 78—80]</sup>, 水处理(污水处理、地表地下水处理、饮用水灭菌等)<sup>[17, 18, 20, 24, 37, 81—86]</sup>, 生物医药<sup>[85]</sup>, 实验室和医院杀菌消毒<sup>[85]</sup>等。此外, TiO<sub>2</sub> 超亲水涂层在防雾自清洁领域已有应用, 将超疏水性能和杀菌性能相结合用于海洋设施生物防污有着潜在的应用前景, 但国内外还未有相关报道。

目前热喷涂 TiO<sub>2</sub> 的研究仍然存在很多不能忽视的问题。1) 热喷涂过程中 TiO<sub>2</sub> 颗粒受热是不可避免的, 研究者试图通过调整工艺来调控 TiO<sub>2</sub> 晶型转变程度、增加孔隙率, 但同时会削弱涂层的结合强度, 如何调配好涂层相组分、比表面积、孔隙率和结合强度之间的关系仍是一个难题。2) 热喷涂制备的涂层易引入外界杂质的干扰, TiO<sub>2</sub> 颗粒在焰流中的飞行状态、受热情况很少对应有具体的实时监测数据, 可能影响涂层结构均匀性, 使得涂层光催化性能存在差异。3) 研究者采用的喷涂类型、喷涂工艺参数各异, 研究过程存在光催化效果评价单一, 催化剂循环使用效果评价缺乏等问题, 应建立统一、标准的性能评估

体系。4) 热喷涂技术虽能实现 TiO<sub>2</sub> 涂层制备的产业化, 但较差的 TiO<sub>2</sub> 应用水平很难与之匹配, TiO<sub>2</sub> 对于高浓度污染物的处理能力不强, 不加外界辅助( UV 灯等) 完全依靠太阳光进行光催化的效率仍较低, 应针对 TiO<sub>2</sub> 可见光利用率及光催化效率等方面提升研究与应用水平。

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