

等离子喷涂 FeCrBC-NiAl-TiB₂ 复合 涂层制备及性能研究

陈东, 卢静*, 孙澄川, 吴应东, 李挺

(季华实验室, 广东 佛山 528200)

摘要: **目的** 提高风机等机械设备关键部件的耐磨损性能, 延长设备的使用寿命。**方法** 以 304 不锈钢为基体, 利用等离子喷涂技术, 制备 FeCrBC 涂层和 FeCrBC-NiAl-TiB₂ 复合涂层。采用 X 射线衍射仪、金相显微镜、扫描电子显微镜、显微硬度计, 分别对涂层的微观组织、物相、显微硬度进行表征。利用摩擦磨损试验机, 对 FeCrBC 涂层和 FeCrBC-NiAl-TiB₂ 复合涂层的磨损性能进行研究, 并分析其磨损机理。**结果** FeCrBC 涂层和 FeCrBC-NiAl-TiB₂ 复合涂层表面均由致密光滑区域和较为疏松的半熔融颗粒等组成, 涂层与基体结合得较为紧密, 界面处无明显裂纹, 结合强度较高, 2 种涂层的结合强度分别为 69.5、69.1 MPa。FeCrBC 涂层和 FeCrBC-NiAl-TiB₂ 复合涂层的显微硬度相当, 分别为 823.3HV0.1、810.8HV0.1。FeCrBC-NiAl-TiB₂ 复合涂层的磨损体积为 0.11 mm³, 与 FeCrBC 涂层相比, 复合涂层的磨损率减小了 38.1%, 具有良好的耐磨损性能。FeCrBC-NiAl-TiB₂ 复合涂层的磨损机理主要为磨粒磨损和疲劳磨损。**结论** 复合涂层中 TiB₂ 与 FeCrBC 相和 NiAl 相的润湿性良好, 结合紧密。FeCrBC-NiAl-TiB₂ 复合涂层因其存在均匀分布的 TiB₂、(Fe, Cr)₂(B, C)、(Fe, Cr)₃(B, C) 等硬质相, 显著提高了涂层的耐磨性能。FeCrBC-NiAl-TiB₂ 复合涂层可以有效提高基体的耐磨损性能, 具有良好的应用前景。

关键词: 大气等离子喷涂; 复合涂层; 微观组织; 涂层性能

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Preparation and Properties of Plasma-sprayed FeCrBC-NiAl-TiB₂ Composite Coating

CHEN Dong, LU Jing*, SUN Cheng-chuan, WU Ying-dong, LI Ting

(Jihua Laboratory, Guangdong Foshan 528200, China)

ABSTRACT: Composite coatings can effectively improve the strength, fracture toughness, wear resistance, and other properties of traditional single material coatings, which becomes one of the research hotspots in recent years. Due to high hardness, low density (4.5 g/cm³), and good oxidation resistance, TiB₂-metal composite coating is believed to be one of the more potential candidates for improving the surface wear resistance of key components. In this paper, the microstructure, phase structure, and bonding strength of plasma-sprayed FeCrBC-NiAl-TiB₂ composite coatings were characterized. The abrasion resistance of

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FeCrBC 和 FeCrBC-NiAl-TiB₂ composite coatings was also studied systematically.

Raw materials TiB₂ (10wt.%), NiAl (10wt.%), and FeCrBC (80wt.%) powder were mixed in a three-dimensional mixer for 60 min in proportion to prepare the FeCrBC-NiAl-TiB₂ composite powder. The 304 stainless steel (30 mm×10 mm×3 mm and ϕ 25.4 mm×10 mm) was selected as the substrate. Before sandblasting, the samples were cleaned with acetone to remove the surface oil. An atmospheric plasma spraying system (BSX-80, Xiamen Baisunxing Automation Co., LTD.) was used to deposit the FeCrBC and FeCrBC-NiAl-TiB₂ composite coating. The phase of powder and coating was determined by an X-ray diffractometer (XRD, CuK α , D8 Advanced, Bruker). The microhardness of the coating was measured with a Vickers hardness tester (Laizhou Huayin, HVS-1000). The bonding strength of the coating was determined with an electronic universal testing machine (WJinan Liantai, DW-100Y). The morphology of the coating was observed with a scanning electron microscope (JSM-6390LA) and an energy-dispersive X-ray spectroscopy (EDX, INCA X-MAX). The wear resistance of samples was tested with a pin-disc friction and wear testing machine (Zhongke Kaihua, SFT-2M). Before the test, the surface of the samples was polished with SiC sandpaper to keep a similar roughness (Ra 0.2-0.5 μ m). A displacement sensor probe was applied for the morphology of the grinding of the samples. The wear rate was calculated and the morphology after the friction surface was observed.

The surfaces of FeCrBC and FeCrBC-NiAl-TiB₂ composite coatings were both composed of dense and smooth areas and loose molten particles. Because the melting point of TiB₂ particles was higher than the metal phase, the spreading deformation after particle impact was smaller, hence the surface roughness of the composite coating increased. Both FeCrBC and FeCrBC-NiAl-TiB₂ composite coatings were closely bonded to the substrate, and there was no obvious crack at the interface. The bonding strength of FeCrBC and FeCrBC-NiAl-TiB₂ composite coatings was 69.5 MPa and 69.1 MPa respectively. TiB₂ in the composite coating had good wettability with the FeCrBC phase and NiAl phase. The microhardness of FeCrBC coating and FeCrBC-NiAl-TiB₂ composite coating were equivalent, which were 823.3HV0.1 and 810.8HV0.1 respectively. The wear volume and wear rate of the FeCrBC-NiAl-TiB₂ composite coating were 0.11 mm³ and 0.65×10⁻⁵ mm³/(N·m), respectively. Compared with the FeCrBC coating, the wear rate of the FeCrBC-NiAl-TiB₂ composite coating was reduced by 38.1%, which exhibited good wear resistance. The wear mechanism of FeCrBC-NiAl-TiB₂ composite coating was mainly abrasive wear and fatigue wear. Because of the uniform distribution of hard phases such as TiB₂, (Fe, Cr)₂(B, C), and (Fe, Cr)₃(B, C) on the surface of the coating, the wear resistance of the FeCrBC-NiAl-TiB₂ composite coating is significantly improved. The FeCrBC-NiAl-TiB₂ composite coating can effectively improve the wear resistance of the substrate and has a good application prospect.

KEY WORDS: atmosphere plasma spray; composite coating; microstructure; coating properties

风机是一种能够将机械能转化为气体或流体势能的机器,广泛应用于电力能源、化工、矿产等工业领域,是企业加工生产中最重要支持性辅助设备。由于其工作环境(杂质灰尘、泥沙、漂浮物和烟气等有害物质等)较为恶劣,容易受到磨损和腐蚀,导致设备的可靠性和稳定性大大降低^[1-2]。磨损的叶片还将造成设备停机维修次数增加,而且叶片的制造成本较高,消耗大量的人力物力,带来高额的经济损失。提高风机叶片等关键易损零部件的耐磨损性能,对延长生产设备服役寿命,保障长时间安全稳定运行具有重要意义^[3]。

表面工程技术,如等离子喷涂^[4-5]、超音速火焰喷涂^[6]、PVD^[7]、表面热处理等,可以有效提高零部件表面的硬度和耐磨性能,是提高风机等零件使用寿命的有效手段之一。其中,等离子喷涂具有工艺便捷、可靠性高、材料体系适用性广、基体热影响小等特点,在提升关键零部件表面综合服役性能和延长工程机械装备的使用寿命方面有广泛应用^[8]。

常见的耐磨涂层材料有碳化钨-钴(Co)涂层^[9]和电镀硬铬涂层^[10],由于其优异的耐磨性和良好的耐腐蚀性,在工程中应用广泛。然而,材料中的Co和六价铬被归类为致癌物质,将对人员健康和环境安全产生危害^[11-12]。因此,研究人员积极开发和研究无毒和可持续的耐磨材料,如Cr₃C₂-NiCr^[13]、铁基涂层^[14]、陶瓷氧化物^[15-16]等。其中,Fe基合金材料组成成分(如Fe、B、C)丰富,符合无毒、经济和绿色可持续发展要求,成本也较低,被认为是很有应用前景的耐磨涂层候选材料之一^[17-19]。王永谦^[20]采用等离子喷涂制备了FeCrBSi合金涂层,并对其结合强度和摩擦性能进行了考核。研究发现,FeCrBSi涂层中硬质相主要为铬的硼化物和碳化物,涂层的结合强度为43.1 MPa,涂层表面易发生塑性变形,从而形成沟槽,属于典型的磨粒磨损。刘黎明^[21]对大气等离子喷涂FeCrBSi涂层和316L不锈钢涂层的微观组织和摩擦性能进行了研究,结果显示,喷涂态FeCrBSi涂层的耐磨性明显优于316L不锈钢涂层,且经700℃热处理

理后, 涂层的耐磨性能达到最佳, 为 $(0.481 \pm 0.023) \times 10^{-5} \text{ mm}^3/(\text{N} \cdot \text{m})$ 。

复合涂层可以有效地提高传统单一材料涂层的强度、断裂韧性和耐磨性等性能, 成为近年来的研究热点之一^[21-23]。硼化物陶瓷材料中 TiB₂ 具有高硬度 ($30\,000 \text{ N/mm}^2$)、低密度 (4.5 g/cm^3) 和耐 $1\,000^\circ\text{C}$ 氧化性能, 但纯 TiB₂ 脆性较大, 且在高温下容易发生氧化, 与金属结合形成 TiB₂-金属复合涂层能综合金属和陶瓷材料的性能优势, 是较具潜力的材料体系之一^[24]。对于 TiB₂ 来说, 其与金属中的 Ni 和 Fe 具有较好的润湿性^[25]。铝包镍复合粉末可在喷涂过程中发生放热反应, 促进粉末粒子充分熔化, 有助于形成高结合强度的涂层^[26]。同时, Ni 的增加也有利于提高涂层的耐磨和耐腐蚀性能。本文采用等离子喷涂制备 FeCrBC-NiAl-TiB₂ 复合涂层, 对复合涂层的微观组织、物相结构和结合强度进行研究, 采用摩擦磨损试验机对 FeCrBC-NiAl-TiB₂ 复合涂层和 FeCrBC 涂层磨损行为进行对比分析, 研究等离子喷涂 FeCrBC-NiAl-TiB₂ 复合涂层和 FeCrBC 涂层的磨损失效机理。

1 试验

1.1 材料及涂层制备

本试验的粉末材料为 FeCrBC 粉末和 FeCrBC-NiAl-TiB₂ 复合粉末。以 TiB₂ (99.5%, 秦皇岛一诺新材料有限公司)、铝包镍粉末 (Ni-Al, 99.5%, 湖南兆益热喷涂材料有限公司) 和 FeCrBC 为原料, 按比

例将粉末在三维混料机中混合 60 min 制备 FeCrBC-10wt%NiAl-10wt%TiB₂ 复合粉体。粉末微观形貌如图 1 所示, FeCrBC 呈球状, 粒度为 $15 \sim 53 \mu\text{m}$; NiAl 为球状和近球状, 粒度为 $15 \sim 75 \mu\text{m}$; TiB₂ 为不规则状, 粒度为 $10 \sim 35 \mu\text{m}$ 。复合粉末中, 3 种粉末较均匀存在。采用试样基材为 304 不锈钢, 试样尺寸为 $30 \text{ mm} \times 10 \text{ mm} \times 3 \text{ mm}$ 和 $\phi 25.4 \text{ mm} \times 10 \text{ mm}$ 。首先, 采用丙酮进行超声波清洗处理, 去除基体表面的油污, 再经过 24~60 目的白刚玉进行喷砂处理。喷砂机为压入式喷砂机, 型号为 PS1010AP, 盘星新型合金材料 (常州) 有限公司, 压缩空气压力为 $0.6 \sim 0.8 \text{ MPa}$ 。大气等离子喷涂设备使用的是厦门佰顺兴自动化有限公司的 BSX-80 喷涂系统, 喷枪型号为 F4 型, 主气和载气为氩气, 辅气为氮气, 具体参数见表 1, 其中送粉量为 40 g/min , 喷枪移动速度为 500 mm/s , 步距为 2 mm 。喷涂时, 使用冷却气 (压缩空气, 6 L/min) 对试样进行降温, 以防止基体过热。

1.2 性能测试及组织观察

用 X 射线衍射仪 (XRD, CuK α , D8 Advanced, Bruker) 测定粉末和涂层的物相, 试验电压为 40 kV , 电流为 40 mA , 扫描范围为 $20^\circ \sim 80^\circ$, 扫描速度为 $6 (^\circ)/\text{min}$ 。用维氏硬度仪 (莱州华银 HVS-1000) 测量涂层的显微硬度, 试验载荷为 100 g , 加载 15 s , 每组样品在不同的位置测试 5 次, 取平均值进行分析。采用胶黏法制备结合强度测试样品, 利用电子式万能试验机 (济南联泰, WDW-100Y) 测量涂层的结

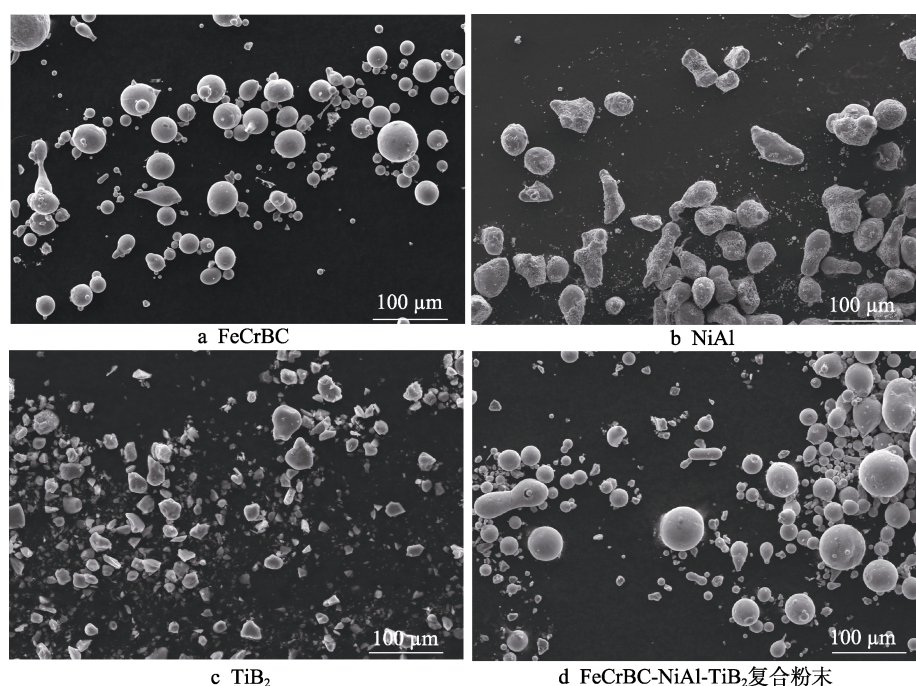


图 1 粉末微观组织形貌

Fig.1 Morphology of powder: a) FeCrBC; b) NiAl; c) TiB₂; d) FeCrBC-NiAl-TiB₂ composite powder

表 1 等离子喷涂 FeCrBC 和 FeCrBC-NiAl-TiB₂ 复合涂层工艺参数

Tab.1 Process parameters of FeCrBC coating and FeCrBC-NiAl-TiB₂ coating for plasma spraying

Parameter	Current/ A	Primary gas (Ar)/ (L·min ⁻¹)	Secondary gas (He)/ (L·min ⁻¹)	Distance/ mm
FeCrBC coating	480	35	15	90
FeCrBC-NiAl-TiB ₂ coating	500	40	15	90

合强度, 拉伸速度为 0.5 mm/min, 记录拉伸试样断裂时的最大结合强度, 每组 3 个试样, 取平均值进行分析。采用扫描电子显微镜 (日本电子株式会社 JSM-6390LA) 观察粉末和涂层的微观形貌。采用能谱分析仪对涂层成分进行分析。采用销盘式摩擦磨损试验机 (中科凯华, SFT-2M) 对样品进行摩擦磨损试验。试验开始前, 采用 SiC 砂纸对涂层表面进行打磨, 使表面粗糙度保持一致 (R_a 为 0.2~0.5 μm)。采用直径为 6 mm 的 Si₃N₄ 球作为磨球, 磨损载荷为 30 N, 磨损半径为 3 mm, 磨损时间为 60 mins。使用位移传感器探头对样品磨痕进行测量。采用式 (1) 计算样品的磨损率^[27]。

$$W = \frac{V}{PL} \quad (1)$$

式中: W 为磨损率; V 为磨损体积; L 为总磨损距离; P 为施加的载荷。

2 结果及分析

2.1 涂层微观组织、相组成及力学性能

FeCrBC 涂层表面和截面的微观组织形貌如图 2 所示。由图 2a 可知, FeCrBC 涂层表面由致密光滑区域、未融颗粒和较为疏松熔融颗粒等组成。粉末颗粒经等离子射流加热后, 其熔融状态不同, 其中熔化状态较好的颗粒撞击基体表面变形充分, 冷却凝固后形成致密的光滑区域; 部分熔融颗粒在撞击基体后, 附着在涂层表面, 形成球状颗粒; 而熔化充分的颗粒撞击表面后, 形成细小的飞溅, 因此涂层表面存在部分

球状且疏松的熔融颗粒区域。从图 2b 可以发现, FeCrBC 涂层内部有孔隙、微裂纹和少量未熔颗粒。在喷涂过程中, 一方面, 熔融颗粒的冷凝时间很短, 颗粒内部气体无法及时完全溢出, 而在涂层内部形成细小的气孔; 另一方面, 一部分未完全熔融的颗粒撞击到基体表面时, 变形不充分, 铺展形成的片层不能完全搭接, 导致片层与片层之间出现孔隙。因此, 涂层中存在不同形态的孔隙, 涂层的孔隙率约为 7.6%。微裂纹的产生是由于熔融颗粒凝固过程中收缩量与基体不同, 产生了残余应力, 从而出现微裂纹^[28]。

FeCrBC-NiAl-TiB₂ 复合涂层表面和截面的微观组织如图 3 所示。从图 3a 可以发现, 与 FeCrBC 涂层类似, FeCrBC-NiAl-TiB₂ 复合涂层表面也由致密光滑区域和较为疏松的熔融颗粒区域组成。与 FeCrBC 涂层不同, 复合涂层表面更为粗糙, 这是因为复合涂层中 TiB₂ 颗粒熔点较金属相高, 颗粒撞击后铺展变形能力较小, 增加了涂层的表面粗糙度。从图 3b 可以观察到, FeCrBC-NiAl-TiB₂ 复合涂层与基体结合较为紧密, 界面处无明显裂纹, 涂层内部均匀分布着 TiB₂ 颗粒和 Ni-Al 相。对局部区域进行放大观察可以发现, TiB₂ 颗粒与基体和 Ni-Al 之间结合较好, 说明 TiB₂ 与 FeCrBC 相和 Ni-Al 相具有良好的润湿性。复合涂层的孔隙率约为 5.6%, 与 FeCrBC 涂层相当, 表明添加 TiB₂ 未增加涂层的孔隙率。这是因为 Ni-Al 粉末在热喷涂过程中发生了放热反应, 这种放热反应可在粉末颗粒到达基体表面之后仍然持续, 从而使涂层与基体之间产生微冶金结合, 形成涂层的扁平化程度高^[26], 对 FeCrBC 涂层中的孔隙和裂纹起到填充作用, 使得涂层致密度提高。因此, 尽管 TiB₂ 颗粒的变形能力较差, 但复合涂层较为致密, 孔隙率与 FeCrBC 相当。涂层的拉伸测试结果表明, FeCrBC 涂层和 FeCrBC-NiAl-TiB₂ 复合涂层的结合强度分别为 69.5、69.1 MPa。如图 4 所示, 涂层拉伸断裂位置均位于涂层与基体界面处, 添加 Ni-Al 和 TiB₂ 并未降低涂层的结合强度, 复合涂层具有较高的结合强度。

FeCrBC 粉末、FeCrBC 涂层和 FeCrBC-NiAl-TiB₂ 复合涂层的 X 射线衍射图谱如图 5 所示。XRD 测试结果显示, Fe-Cr-B-C 喷涂粉末主要以 α -(Fe, Cr) 为主,

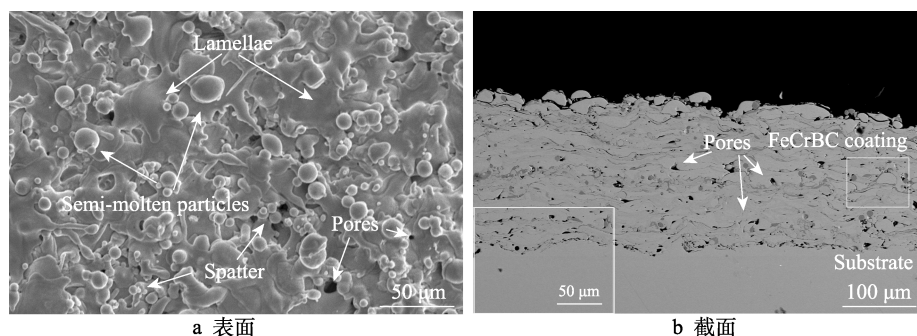


图 2 FeCrBC 涂层微观组织形貌

Fig.2 Morphology of FeCrBC coating: a) surface; b) cross section

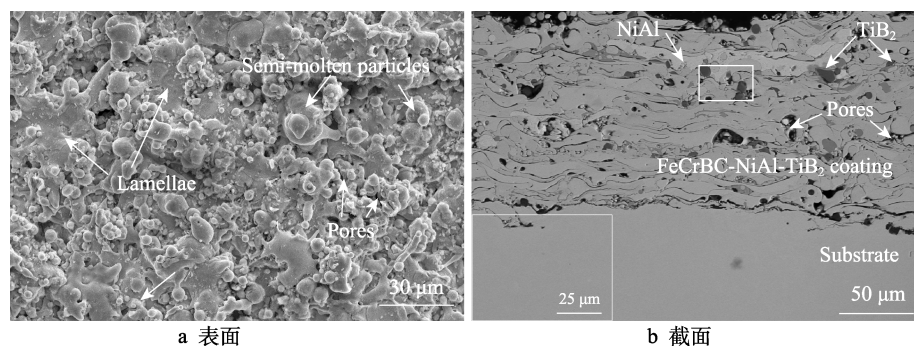
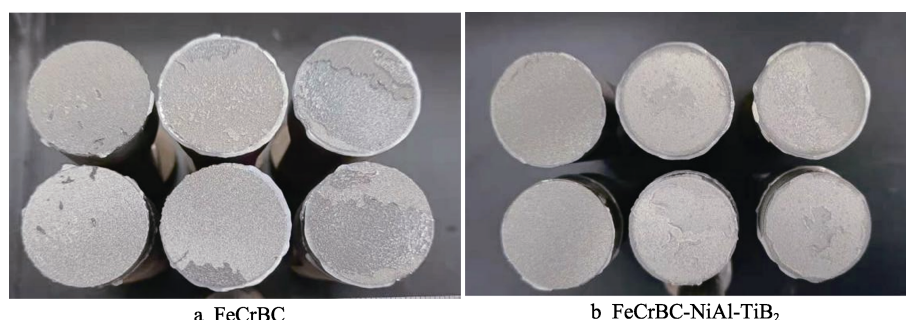
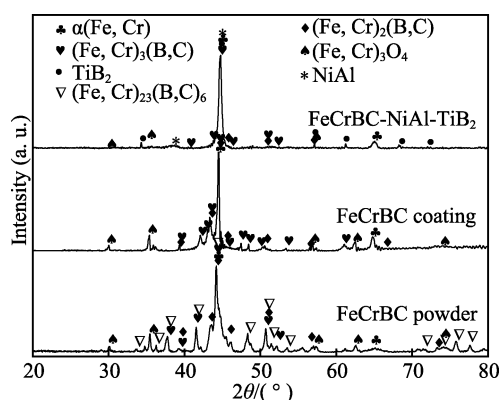
图 3 FeCrBC-NiAl-TiB₂ 复合涂层微观组织形貌Fig.3 Morphology of FeCrBC-NiAl-TiB₂ composite coating: a) surface; b) cross section

图 4 涂层拉伸断口宏观形貌

Fig.4 Tensile fracture morphology images of coating

图 5 FeCrBC 涂层和 FeCrBC-NiAl-TiB₂ 复合涂层 XRD 图谱Fig.5 XRD spectrum of FeCrBC coating and FeCrBC-NiAl-TiB₂ composite coating

并存在(Fe, Cr)₂(B, C)相和(Fe, Cr)₂₃(B, C)₆相, 这之前报道的 Fe-B-C 体系结果基本一致^[29]。同时还可以发现, 粉末中还存在少量的(Fe, Cr)₃O₄, 这与制备和保存过程中粉末表面存在轻微氧化有关。大气等离子喷涂制备的 Fe-Cr-B-C 涂层物相主要以 α-(Fe, Cr)相为主, 同时含有(Fe, Cr)₂(B, C)相、(Fe, Cr)₃(B, C)和少量(Fe, Cr)₃O₄。与粉末相比, 涂层中的(Fe, Cr)₂₃(B, C)₆相基本消失。同时发现, α(Fe, Cr)相、(Fe, Cr)₂(B, C)相、(Fe, Cr)₃(B, C)相的衍射峰位略向右发生移动, 表明这些相的晶格参数略有减小。粉末在等离子焰流中发生了高温熔化, 由室温平衡态的(Fe, Cr)+(Fe,

Cr)₂(B, C)+(Fe, Cr)₂₃(B, C)₆转变为高温下的(Fe, Cr)+(Fe, Cr)₂(B, C)+(Fe, Cr)₃(B, C)相。喷涂时, 高温颗粒高速撞击到基体表面, 迅速铺展, 并急速冷却。在此过程中, (Fe, Cr)₂₃(B, C)₆来不及析出, 而高温稳定相(Fe, Cr)₃(B, C)保留至室温。由于间隙原子 B 和 C 在(Fe, Cr)₃(B, C)相中的浓度要高于(Fe, Cr)₂₃(B, C)₆相, 从而致使体系剩余 B、C 含量减少, 使得 α-(Fe, Cr)基体和(Fe, Cr)₂(B, C)相的固溶度改变, 晶格常数减小, 峰位向右发生偏移。同时发现, 与粉末相比, 涂层中(Fe, Cr)₃O₄的峰强基本保持不变, 意味着高温射流中粉末的氧化不明显。与 FeCrBC 涂层相比, FeCrBC-NiAl-TiB₂复合涂层中还出现了 Ni-Al 相和 TiB₂相, 但由于加入的颗粒含量少, 所以其衍射强度比较低。同时, 由于增加了 Ni-Al 相和 TiB₂相, 较 FeCrBC 涂层, 复合涂层中的(Fe, Cr)₂(B, C)相、(Fe, Cr)₃(B, C)相和少量(Fe, Cr)₃O₄相所占比例降低, 因此衍射峰强度降低。

304 不锈钢、FeCrBC 涂层和 FeCrBC-NiAl-TiB₂复合涂层的平均显微硬度如图 6 所示。可以看出, FeCrBC 涂层和 FeCrBC-NiAl-TiB₂复合涂层的平均显微硬度分别为 823.3HV0.1 和 810.8HV0.1, 明显高于 304 不锈钢 (299.5HV0.1)。FeCrBC 涂层的显微硬度较高, 主要原因是: 涂层中存在(Fe, Cr)₂(B, C)相、(Fe, Cr)₃(B, C)等硬质相, 显著提高了涂层的硬度; 涂层中 C、B 等元素的存在使铁基晶格畸变增大, 阻碍了位错移动, 从而提高了涂层的硬度。FeCrBC-NiAl-TiB₂

复合涂层的硬度较 FeCrBC 涂层略微降低, 但降低幅度较小。一方面, Ni-Al 相的硬度较低, 铺展填充在涂层中, 使得复合涂层的硬度略微降低; 另一方面, 添加的 TiB_2 颗粒的硬度较高, 有利于提高涂层显微硬度。因此, 在两者的综合作用下, 复合涂层的显微硬度与 FeCrBC 涂层相当。

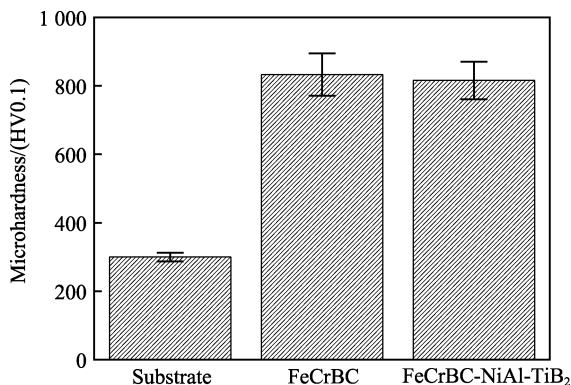


图6 不锈钢、FeCrBC 涂层和 FeCrBC-NiAl-TiB₂ 复合涂层显微硬度

Fig.6 Microhardness of stainless steel, FeCrBC coating, and FeCrBC-NiAl-TiB₂ composite coating

2.2 磨损行为及失效机理

涂层和不锈钢的摩擦系数随时间的变化曲线如图7所示。可以看出, 不锈钢的摩擦系数变化较大, 为 0.4~0.7。FeCrBC 涂层的初始摩擦系数约为 0.75, 在经过 5 min 的磨合阶段后, 摩擦系数快速下降, 到 10 min 时, FeCrBC 涂层的摩擦系数趋于稳定, 最终稳定在 0.6。FeCrBC-NiAl-TiB₂ 复合涂层的摩擦系数变化较小, 在 0.65~0.75。不锈钢、FeCrBC 涂层和 FeCrBC-NiAl-TiB₂ 复合涂层的摩擦磨损试验结果见表2。FeCrBC-NiAl-TiB₂ 复合涂层的磨损质量较不锈钢和 FeCrBC 明显降低, 磨损率仅为不锈钢的 25.5%, FeCrBC 涂层的 64.1%, 磨痕深度和磨损体积明显降

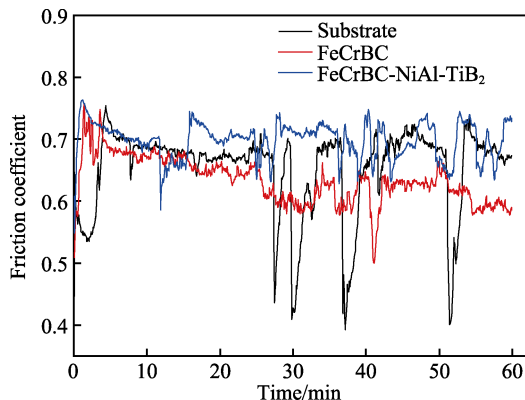


图7 不锈钢、FeCrBC 涂层和 FeCrBC-NiAl-TiB₂ 复合涂层样品摩擦系数随时间的变化曲线

Fig.7 Friction coefficient of stainless steel, FeCrBC coating, and FeCrBC-NiAl-TiB₂ composite coating varies with time

低。2种涂层和基体的磨损率如图8所示。从图8中可以发现, 304 不锈钢的磨损率为 FeCrBC 涂层的 2.4 倍, 约为 FeCrBC-NiAl-TiB₂ 复合涂层的 3.9 倍, 复合涂层的磨损率仅为 $0.65 \times 10^{-5} \text{ mm}^3/(\text{N} \cdot \text{m})$, 说明复合涂层具有良好的耐磨损性能。

表2 锈钢、FeCrBC 涂层和 FeCrBC-NiAl-TiB₂ 复合涂层样品摩擦磨损试验结果

Tab.2 Result of friction and wear test of stainless steel, FeCrBC coating, and FeCrBC-NiAl-TiB₂ composite coating

Sample	Mass loss/mg	Depth/ μm	Width/mm	Volume/ mm^3
Substrate	6.8	27.16	1.325	0.427 1
FeCrBC	3.1	18.59	1.246 9	0.178 4
FeCrBC-NiAl-TiB ₂	1.6	10.8	1.326	0.11

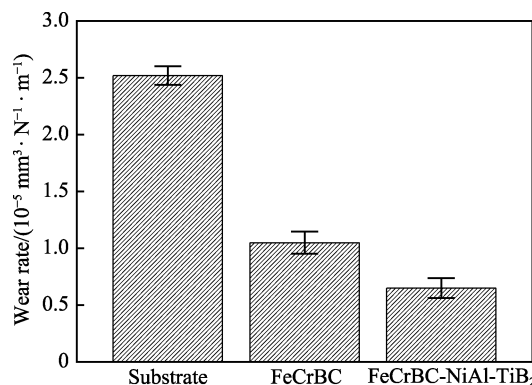


图8 不锈钢、FeCrBC 涂层和 FeCrBC-NiAl-TiB₂ 复合涂层磨损率

Fig.8 Wear rate of stainless steel, FeCrBC coating, and FeCrBC-NiAl-TiB₂ composite coating

不锈钢、FeCrBC 涂层和 FeCrBC-NiAl-TiB₂ 复合涂层经摩擦磨损试验后磨痕的 SEM 形貌如图9所示, 结合能谱分析结果 (见表3) 对磨损机理进行分析。可以发现, 在磨损过程中, 不锈钢表面出现很多弧形磨痕 (如图9a所示), 其磨损机制主要为磨粒磨损, 并且局部区域出现撕裂和剥离现象, 为黏着磨损。这是因为不锈钢的硬度较低 (显微硬度测试显示, 不锈钢的硬度为 299.5HV0.1), 容易产生磨屑, 并与磨球发生黏合, 形成黏着磨损^[30]。磨痕中还存在深色区域 (图9a中A区域), 宽度为 30~40 μm , 内部较为疏松, 存在孔隙。对其进行能谱分析可知, 深色区域主要为 Fe 和 Cr 的氧化物, 还包含少量磨球磨屑。FeCrBC 涂层摩擦磨损后磨痕的微观组织形貌如图9b所示。可以看出, FeCrBC 涂层磨痕中间区域均匀而轻微, 表现出良好的耐磨性。磨痕中存在裂纹和细小坑洞, 主要是因为涂层中较高硬度的未熔颗粒在周期性载荷下发生疲劳开裂和剥落, 形成了浅的剥落坑。此外, 还可以发现, 与中间区域相比, 磨痕上下边缘区域存在较多的黑色磨削屑。这是由于磨损过程中磨

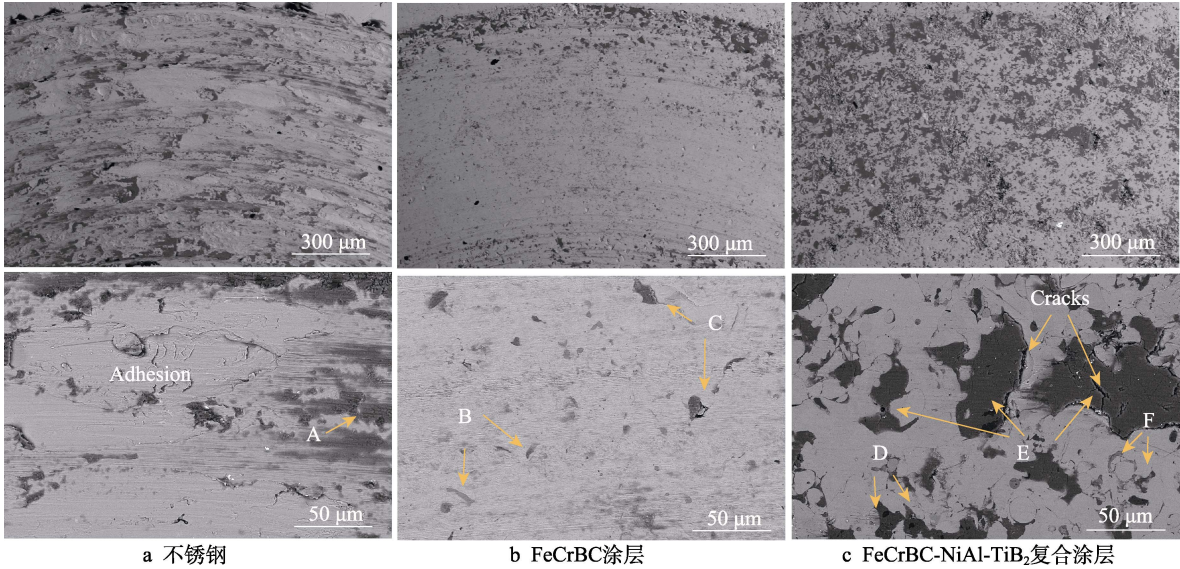


图 9 不锈钢、FeCrBC 涂层和 FeCrBC-NiAl-TiB₂ 复合涂层磨痕的微观形貌
Fig.9 Morphology of grinding crack of stainless steel (a), FeCrBC coating (b), and FeCrBC-NiAl-TiB₂ composite coating (c)

屑在磨球挤压下向边缘移动,因此边缘区域黑色磨屑明显较中间区域多。对磨痕中间区域进行放大观察可以看出,磨痕主要有细小的灰色点状(2~5 μm,如图 9b 中 B 所示)、较大疏松深灰色(20~30 μm,如图 9b 中 C 所示)和较为致密的 α-(Fe,Cr)基体 3 个区域。EDS 结果显示,B 区域中 B 和 C 的含量明显较其他区域高得多,结合涂层 XRD 检测结果[涂层中存在(Fe,Cr)₃(B,C)和(Fe,Cr)₂(B,C)]可以判断,灰色小点为(Fe,Cr)₃(B,C)和(Fe,Cr)₂(B,C)等硬质相。这些呈颗粒状的细小碳化物(Fe,Cr)₃(B,C)和(Fe,Cr)₂(B,C)硬质相弥散均匀地分布在 α-(Fe,Cr)上,可以起到弥散强化作用,从而可以提高涂层的硬度和耐磨性^[31]。C 区域以 Fe、O 为主,包含少量的 Cr 和 Si,内部较为疏松。由于摩擦磨损过程中会释放热量,开裂处新暴露的 Fe 和 Cr 与空气中氧发生反应,生成氧化物,磨球也因磨损产生少量碎屑,形成磨屑,这些细小的磨屑堆积在未熔颗粒剥落后所形成的剥落坑中并压实,因此 C 区域主要以 Fe、O 为主,包含少量的 Cr 和 Si,组织也较为疏松。由此可以得出,FeCrBC 涂层的磨损机理包含磨粒磨损和疲劳磨损。图 9c 为 FeCrBC-NiAl-TiB₂ 复合涂层摩擦磨损后磨痕的微观组织形貌。与不锈钢和 FeCrBC 涂层相比,FeCrBC-NiAl-TiB₂ 复合涂层磨痕中的犁沟和黏着磨损痕迹明显减轻,磨痕较浅。TiB₂ 是一种钛硼化合物,密度为 4.52 g/cm³,室温下其维氏硬度为 25~35 GPa,具有良好的抗机械侵蚀能力^[32-33]。当摩擦副发生相对滑移时,复合涂层与对偶界面发生“硬碰硬”的接触,因此摩擦过程中涂层的磨损减轻,相应 FeCrBC-NiAl-TiB₂ 复合涂层的磨痕也变浅。对磨痕进行放大

观察,并结合 EDS 面扫分析结果(见表 3 和图 10)发现,TiB₂ 呈弥散均匀分布在磨痕上,TiB₂ 颗粒与周围 Ni-Al 相与 FeCrBC 结合较为紧密,无明显裂纹,内部产生轻微塑性变形。与 FeCrBC 涂层的磨痕相比,复合涂层磨痕中几乎观察不到划痕,且积累了大量磨屑。这是因为,在磨损过程中,磨损产生的磨粒首先侵蚀较软的基体,然后与硬质相接触,阻碍了磨屑对表面进行微切割^[34]。复合涂层中弥散分布的高硬度 TiB₂ 阻碍了磨屑对表面的切割,因此在复合涂层磨痕中几乎观察不到划痕。与 FeCrBC 涂层类似,未熔颗粒在周期应力作用下发生剥落,形成剥落坑。同时,部分硬度较低的 Ni-Al 相和 α-(Fe,Cr)受到磨粒侵蚀,也将形成坑。TiB₂ 与周围结合较好,且硬度较高,起到了硬质支撑作用^[35],磨屑填充在了这些孔隙。因此,FeCrBC-NiAl-TiB₂ 复合涂层磨痕中积累了大量的磨屑。FeCrBC-NiAl-TiB₂ 复合涂层磨损机理主要为磨粒磨损和疲劳磨损。

表 3 图 8 中不同区域能谱分析结果
Tab.3 Energy spectrum results of different regions in Fig.8 at.%

Zone	Fe	Cr	Ni	Al	Ti	O	B/C	Si
A	40.57	11.21	4.28	—	—	35.63	—	7.51
B	63.3	12.5	—	—	—	0.5	23.7	—
C	43.83	5.78	—	—	—	36.51	—	9.24
D	—	—	—	—	97.6	—	2.09	—
E	52.50	6.81	2.59	—	1.27	30.58	—	7.53
F	67.77	6.80	—	—	—	—	25.43	—

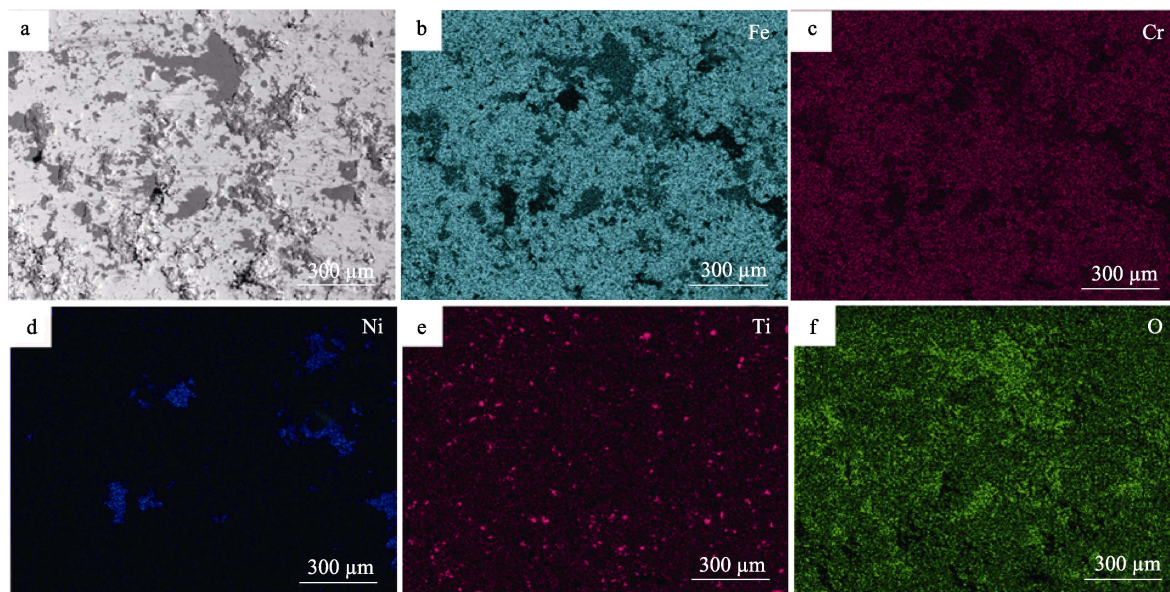


图 10 FeCrBC-NiAl-TiB₂ 涂层磨痕能谱面扫元素面分布
Fig.10 Mapping of elements of energy spectrum of grinding crack of FeCrBC-NiAl-TiB₂ coating

3 结论

本文采用等离子喷涂技术制备了 FeCrBC 涂层和 FeCrBC-NiAl-TiB₂ 复合涂层,并对涂层的微观组织和耐磨损性能进行了研究,可以得出以下结论:

1) 等离子喷涂 FeCrBC 涂层和 FeCrBC-NiAl-TiB₂ 复合涂层均为典型层片状结构,涂层与基体结合紧密,结合强度高,FeCrBC 涂层和 FeCrBC-NiAl-TiB₂ 复合涂的结合强度分别为 69.5、69.1 MPa。

2) FeCrBC 涂层相结构以 α -(Fe, Cr)相为主,同时含有少量的(Fe, Cr)₂(B, C)相、(Fe, Cr)₇(B, C)₂ 和 (Fe, Cr)₃O₄, FeCrBC-NiAl-TiB₂ 复合涂层还存在 TiB₂ 和 NiAl 相。

3) FeCrBC-NiAl-TiB₂ 复合涂层的显微硬度与 FeCrBC 涂层相当,为 810.8HV0.1,显著高于不锈钢的 299.5HV0.1。

4) 与 FeCrBC 涂层相比,FeCrBC-NiAl-TiB₂ 复合涂层的磨痕明显较浅,磨损率为 $0.65 \times 10^{-5} \text{ mm}^3/(\text{N} \cdot \text{m})$,约为 FeCrBC 涂层的 62%,仅为不锈钢的 25.8%,复合涂层具有良好的耐磨损性能。复合涂层的磨损机理主要为疲劳磨损和磨粒磨损。

参考文献:

[1] 丁彰雄, 梁洪弋, 柯杜, 等. 电站锅炉一次风机叶片再制造技术及耐磨涂层性能研究[J]. 热喷涂技术, 2018, 10(4): 33-39.
DING Zhang-xiong, LIANG Hong-yi, KE Du, et al. Research on Remanufacturing Technology and Wear-Resistant Coating Performance of Primary Fan Blades in

Power Plant Boilers[J]. Thermal Spray Technology, 2018, 10(4): 33-39.

[2] 范毅, 丁彰雄, 张云乾. 纳米 WC/¹²Co 涂层在轴流式引风机叶片防磨上的研究[J]. 武汉大学学报(工学版), 2006, 39(3): 135-139.

FAN Yi, DING Zhang-xiong, ZHANG Yun-qian. Study on WC/¹²Co Nanostructured Coatings in Erosion Resistance of Axial-Flow Induced Draft Fan's Blade[J]. Engineering Journal of Wuhan University, 2006, 39(3): 135-139.

[3] 冯驰, 丁彰雄, 刘正强, 等. 表面技术在锅炉一次风机叶片再制造中的应用研究[J]. 表面技术, 2016, 45(9): 82-87.

FENG Chi, DING Zhang-xiong, LIU Zheng-qiang, et al. Application Research of Surface Technology in Primary Fan Blades Remanufacture of Boiler[J]. Surface Technology, 2016, 45(9): 82-87.

[4] PAWLOWSKI L. The Science and Engineering of Thermal Spray Coatings[M]. Second Edition. New York: John Wiley & Sons Ltd, Lech Pawlowski, 2008.

[5] 李长久. 热喷涂技术应用及研究进展与挑战[J]. 热喷涂技术, 2018, 10(4): 1-22.

LI Chang-jiu. Applications, Research Progresses and Future Challenges of Thermal Spray Technology[J]. Thermal Spray Technology, 2018, 10(4): 1-22.

[6] GUO R Q, ZHANG C, CHEN Q, et al. Study of Structure and Corrosion Resistance of Fe-Based Amorphous Coatings Prepared by HVOF and HVOF[J]. Corrosion Science, 2011, 53(7): 2351-2356.

[7] 徐滨士, 谭俊, 陈建敏. 表面工程领域科学技术发展[J]. 中国表面工程, 2011, 24(2): 1-12.

XU Bin-shi, TAN Jun, CHEN Jian-min. Science and

- Technology Development of Surface Engineering[J]. China Surface Engineering, 2011, 24(2): 1-12.
- [8] MEHTA A, VASUDEV H, SINGH S, et al. Processing and Advancements in the Development of Thermal Barrier Coatings: A Review[J]. Coatings, 2022, 12(9): 1318.
- [9] AHMED R, ALI O, BERNDT C C, et al. Sliding Wear of Conventional and Suspension Sprayed Nanocomposite WC-Co Coatings: An Invited Review[J]. Journal of Thermal Spray Technology, 2021, 30(4): 800-861.
- [10] BOLELLI G, CANNILLO V, LUSVARGHI L, et al. Mechanical and Tribological Properties of Electrolytic Hard Chrome and HVOF-Sprayed Coatings[J]. Surface and Coatings Technology, 2006, 200(9): 2995-3009.
- [11] PAUSTENBACH D J, TVERMOES B E, UNICE K M, et al. A Review of the Health Hazards Posed by Cobalt[J]. Critical Reviews in Toxicology, 2013, 43(4): 316-362.
- [12] DHAL B, THATOI H N, DAS N N, et al. Chemical and Microbial Remediation of Hexavalent Chromium from Contaminated Soil and Mining/Metallurgical Solid Waste: A Review[J]. Journal of Hazardous Materials, 2013, 250-251: 272-291.
- [13] AKHTARI ZAVAREH M, SARHAN A A D M, RAZAK B B, et al. The Tribological and Electrochemical Behavior of HVOF-Sprayed Cr₃C₂-NiCr Ceramic Coating on Carbon Steel[J]. Ceramics International, 2015, 41(4): 5387-5396.
- [14] PIAO Zhong-yu, XU Bin-shi, WANG Hai-dou, et al. Influence of Undercoating on Rolling Contact Fatigue Performance of Fe-Based Coating[J]. Tribology International, 2010, 43(1/2): 252-258.
- [15] VERMA R, SHARMA S, MUKHERJEE B, et al. Microstructural, Mechanical and Marine Water Tribological Properties of Plasma-Sprayed Graphene Nanoplatelets Reinforced Al₂O₃-40wt% TiO₂ Coating[J]. Journal of the European Ceramic Society, 2022, 42(6): 2892-2904.
- [16] BOLELLI G, CANNILLO V, LUSVARGHI L, et al. Wear Behaviour of Thermally Sprayed Ceramic Oxide Coatings[J]. Wear, 2006, 261(11/12): 1298-1315.
- [17] 师晓莉. Fe-Cr-B-C 系高硼铁基金属硬质相形态控制及其对性能影响研究[D]. 昆明: 昆明理工大学, 2016.
- SHI Xiao-li. Study on Morphology Control of Hard Phase and Its Influence on Properties of Fe-Cr-B-C High Boron Iron-Based Alloy[D]. Kunming: Kunming University of Science and Technology, 2016.
- [18] LV Zheng, FU Han-guang, XING Jian-dong, et al. Microstructure and Crystallography of Borides and Mechanical Properties of Fe-B-C-Cr-Al Alloys[J]. Journal of Alloys and Compounds, 2016, 662: 54-62.
- [19] 刘奇聪, 马振, 吕鹏, 等. Cr 含量对 Fe-B-C 系耐磨合金堆焊层组织和硬度的影响[J]. 焊接, 2022(2): 26-31.
- LIU Qi-cong, MA Zhen, LYU Peng, et al. Influence of Cr Content on Microstructure and Hardness of Fe-B-C Wear-Resistant Alloy Surfacing Layer[J]. Welding & Joining, 2022(2): 26-31.
- [20] 王永谦. 发动机气缸内壁等离子喷涂材料的研究[D]. 沈阳: 沈阳工业大学, 2013.
- WANG Yong-qian. Study on Plasma Spraying Materials for Engine Cylinder Inner Wall[D]. Shenyang: Shenyang University of Technology, 2013.
- [21] 刘黎明. 气缸内壁耐磨涂层的制备及其摩擦学性能研究[D]. 扬州: 扬州大学, 2018.
- LIU Li-ming. Preparation and Tribological Properties of Wear-Resistant Coating on Cylinder Inner Wall[D]. Yangzhou: Yangzhou University, 2018.
- [22] BAGHERY P, FARZAM M, MOUSAVI A B, et al. Ni-TiO₂ Nanocomposite Coating with High Resistance to Corrosion and Wear[J]. Surface and Coatings Technology, 2010, 204(23): 3804-3810.
- [23] WU C L, XU Tong, WANG Z Y, et al. Laser Surface Alloying of FeCoCrAlNiTi High Entropy Alloy Composite Coatings Reinforced with TiC on 304 Stainless Steel to Enhance Wear Behavior[J]. Ceramics International, 2022, 48(14): 20690-20698.
- [24] LOTFI B. Elevated Temperature Oxidation Behavior of HVOF Sprayed TiB₂ Cermets Coating[J]. Transactions of Nonferrous Metals Society of China, 2010, 20(2): 243-247.
- [25] 熊焰, 傅正义. 二硼化钛基金属陶瓷研究进展[J]. 硅酸盐通报, 2005, 24(1): 60-64.
- XIONG Yan, FU Zheng-yi. Research Development of TiB₂-Based Metal Ceramics[J]. Bulletin of the Chinese Ceramic Society, 2005, 24(1): 60-64.
- [26] 陈辉, 明继青, 陶敏. 新型铝包镍涂层在航空维修上的应用研究[J]. 航空维修与工程, 2016(10): 88-90.
- CHEN Hui, MING Ji-qing, TAO Min. Application Research on Ni-5%Al Coating in Aviation Maintenance [J]. Aviation Maintenance & Engineering, 2016(10): 88-90.
- [27] OUYANG J H, YANG Z L, LIU Z G, et al. Friction and Wear Properties of Reactive Hot-Pressed TiB₂-TiN Composites in Sliding Against Al₂O₃ Ball at Elevated Temperatures[J]. Wear, 2011, 271(9/10): 1966-1973.
- [28] KURODA S, CLYNE T W. The Quenching Stress in Thermally Sprayed Coatings[J]. Thin Solid Films, 1991, 200(1): 49-66.
- [29] LENTZ J, RÖTTGER A, THEISEN W. Mechanism of the Fe₃(B, C) and Fe₂₃(C, B)₆ Solid-State Transformation in the Hypoeutectic Region of the Fe-C-B System[J]. Acta Materialia, 2016, 119: 80-91.
- [30] 冯爱新, 陈凤国, 裴绍虎, 等. 激光熔覆对 304 不锈钢表面摩擦磨损性能的影响[J]. 材料热处理学报, 2015, 36(8): 223-228.
- FENG Ai-xin, CHEN Feng-guo, PEI Shao-hu, et al. Effects of Laser Cladding on Friction and Wear Properties of 304 Stainless Steel[J]. Transactions of Materials and Heat Treatment, 2015, 36(8): 223-228.
- [31] 张志强, 李国禄, 王海斗, 等. 等离子喷涂 Fe 基金属涂

- 层组织及接触疲劳损伤性能的研究[J]. 材料工程, 2012, 40(6): 59-62.
- ZHANG Zhi-qiang, LI Guo-lu, WANG Hai-dou, et al. Study on the Microstructure and Property of Contact Fatigue Damage of Plasma-Sprayed Fe-Based Alloy Coating[J]. Journal of Materials Engineering, 2012, 40(6): 59-62.
- [32] JAROSLAV K, EMMER S, JOSE R, et al. Solar Furnace: Thermal Shock Behaviour of TiB₂ Coating on Steel[C]// METAL 2014: International Conference on Metallurgy and Materials. Ostrava: Tanger Ltd, 2014.
- [33] ZHANG Cheng, SONG Jin-peng, JIANG Long-kai, et al. Fabrication and Tribological Properties of WC-TiB₂ Composite Cutting Tool Materials under Dry Sliding Condition[J]. Tribology International, 2017, 109: 97-103.
- [34] CHENG J B, XU B S, LIANG X B, et al. Microstructure and Mechanical Characteristics of Iron-Based Coating Prepared by Plasma Transferred Arc Cladding Process[J]. Materials Science and Engineering: A, 2008, 492(1/2): 407-412.
- [35] ZHANG Ning, ZHANG Nan-nan, GUAN Sheng, et al. Composition Versus Wear Behaviour of Air Plasma Sprayed NiCr-TiB₂-ZrB₂ Composite Coating[J]. Coatings, 2018, 8(8): 273.

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- [23] 谭金花, 孙荣禄, 牛伟, 等. 激光熔覆钛基金属陶瓷复合涂层的组织与性能[J]. 金属热处理, 2020, 45(7): 189-193.
- TAN Jin-hua, SUN Rong-lu, NIU Wei, et al. Microstructure and Properties of Laser Clad Titanium-Based Cermet Composite Coating[J]. Heat Treatment of Metals, 2020, 45(7): 189-193.
- [24] LU Xiao-long, LIU Xiu-bo, YU Peng-cheng, et al. Effects of Heat Treatment on Microstructure and Mechanical Properties of Ni60/h-BN Self-Lubricating Anti-Wear Composite Coatings on 304 Stainless Steel by Laser Cladding[J]. Applied Surface Science, 2015, 355: 350-358.
- [25] CHEN Zheng-fei, YAN Hua, ZHANG Pei-lei, et al. Microstructural Evolution and Wear Behaviors of Laser-Clad Stellite 6/NbC/h-BN Self-Lubricating Coatings[J]. Surface and Coatings Technology, 2019, 372: 218-228.
- [26] LI Qing-tang, LEI Yong-ping, FU Han-guang. Growth Characteristics and Reinforcing Behavior of In-Situ NBSP in Laser Cladded Fe-Based Composite Coating[J]. Journal of Materials Science & Technology, 2015, 31(7): 766-772.
- [27] CAO Yan, FAROUK N, TAHERI M, et al. Evolution of Solidification and Microstructure in Laser-Clad IN625 Superalloy Powder on GTD-111 Superalloy[J]. Surface and Coatings Technology, 2021, 412: 127010.
- [28] WANG Qian, CHEN Fa qiang, ZHANG Liang, et al. Microstructure Evolution and High Temperature Corrosion Behavior of FeCrBSi Coatings Prepared by Laser Cladding[J]. Ceramics International, 2020, 46(11): 17233-17242.
- [29] ZHU Yang, LIU Xiu-bo, LIU Yi-fan, et al. Development and Characterization of Co-Cu/Ti₃SiC₂ Self-Lubricating Wear Resistant Composite Coatings on Ti₆Al₄V Alloy by Laser Cladding[J]. Surface and Coatings Technology, 2021, 424: 127664.
- [30] ZHAO Yong-li, WANG Yan, YU Ze-xin, et al. Microstructural, Mechanical and Tribological Properties of Suspension Plasma Sprayed YSZ/h-BN Composite Coating[J]. Journal of the European Ceramic Society, 2018, 38(13): 4512-4522.

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