热喷涂与冷喷涂技术

Cu过渡层对冷喷涂CuCrZr涂层性能的影响

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摘要：目的 针对冷喷涂CuCrZr涂层与CuCrZr板材在界面处的开裂问题，采用Cu涂层为过渡层，并探究Cu过渡层对CuCrZr涂层组织及性能的影响。**方法** 采用高压氮气为工作气体，使用冷喷涂技术在CuCrZr基板上先制备一层Cu涂层打底，再继续喷涂多层CuCrZr涂层。通过金相显微镜、扫描电镜、显微硬度仪和激光热导仪，对涂层的组织和性能进行表征。**结果** Cu+CuCrZr涂层与基板界面结合良好，涂层的孔隙率约为0.624%，CuCrZr颗粒的扁平率为(43.62±4.54)%。Cu涂层的平均硬度约为153HV，冷喷涂CuCrZr涂层的平均硬度约为173HV。采用Cu涂层打底获得的CuCrZr涂层的热导率随温度的升高而升高，在500 ℃时与基体相当。**结论** Cu过渡层促进颗粒与基体之间发生良好结合，有效防止CuCrZr涂层与CuCrZr板材开裂。采用Cu+CuCrZr涂层能满足CuCrZr结晶器力学与导热性能的要求。

关键词： CuCrZr结晶器；冷喷涂；Cu过渡层；导热性能

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Effect of Cu Transition Layer on Performance of Cold Sprayed CuCrZr Coating

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ABSTRACT: Cold spraying has become a potential technology for repairing continuous casting crystallizer due to its advantages of small thermal impact, no damage to the substrate and unrestricted shape of the repair workpiece. At present, the crystallizer material commonly used for continuous casting is CuCrZr alloy, but the thermal expansion coefficient difference between the CuCrZr substrate and the cold-hardened coating is large, and the interface between the coating and the substrate is very likely to crack under the service conditions of the crystallizer with rapid cooling and heating. Therefore, the introduction of Cu particles with good plastic deformation ability was considered as an intermediate layer between the cold sprayed CuCrZr coating and the CuCrZr substrate to solve the cracking problem at the interface of the CuCrZr coating, and the influence of the Cu transition layer on the organization and properties of the CuCrZr coating was investigated, so as to provide a new idea for the repair of the copper crystallizer by cold spraying.

With high-pressure nitrogen as the working gas, compressed air as the powder feeding gas, cold spraying technology was

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used in the CuCrZr substrate to prepare a layer of Cu coating primer, and then a multi-layer CuCrZr coating was sprayed. The CuCrZr and Cu powder were spherical, with a particle size range of 10-100 μm. The average size was 30.2 μm and 34.4 μm, respectively. The substrate material was CuCrZr, and sandblasting was performed before coating. The cold spraying distance was 20 mm, the spraying speed was 20 mm/s, the powder feeding rate was 20 g/min, the pressure was 3.4 MPa, and the temperature was 500 ℃. Axio Oberver A1m Zeiss inverted metallurgical microscope and scanning electron microscope were used to observe the coating organization, combined with Image-J software to count the coating porosity and flattening. A DHV-1000ZTRDT microhardness tester was used to characterize the coating hardness. The thermal conductivity was determined with a NETZSCH LFA-427 Laser Thermal Conductivity Meter at test temperature of 50 ℃, 250 ℃, and 500 ℃, and the specimens were ϕ10 mm×2.7 mm discs.

It was found that the Cu+CuCrZr coating was well combined with the interface of the substrate, and the thickness of the Cu coating was about 50 μm, and the CuCrZr coating was deposited on the top of the Cu coating sequentially. The porosity of the coating was about 0.624%, and the flattening rate of CuCrZr particles was (43.62±4.54)%. The hardness of the CuCrZr substrate was about 160HV, and there was a work-hardening layer of the substrate near the interface, with the hardness of about 163HV-168HV, and the thickness of about 160 μm. The average hardness of the Cu coating was about 153HV, and that of the cold-sprayed CuCrZr coating was about 173HV. The thermal conductivity of the coating increased with the increase of test temperature, which arrived at the value of the substrate at 500 ℃. The Cu transition layer promoted a good bonding between the coating and the substrate, and thus effectively prevented the cracking of CuCrZr coating from the CuCrZr plate. The use of Cu+CuCrZr coating can meet the mechanical and thermal conductivity requirements of the CuCrZr crystallizer.

KEY WORDS: CuCrZr crystallizer; cold spraying; Cu transition layer; heat conduction

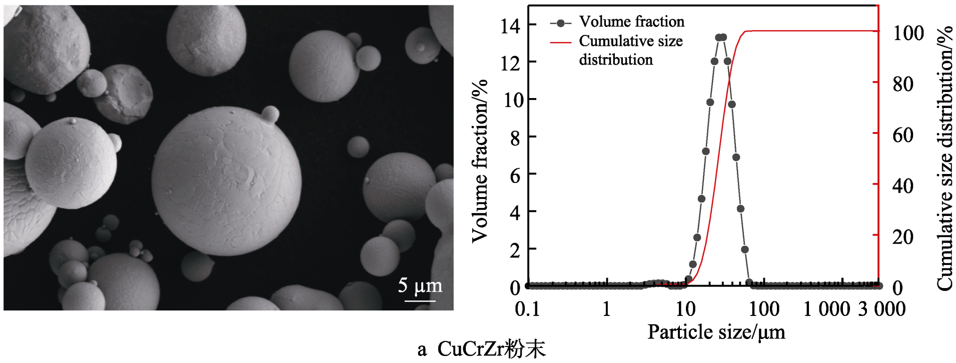
冷喷涂作为一种新型的喷涂技术，其原理是通过高压气体将颗粒加速到一定的速度撞击基板，产生塑性变形沉积在基板的表面形成涂层[1-2]，具有沉积温度低、灵活性高、修复层制备效率高等特点，因此在零部件修复领域具有很好的应用前景[3-5]。以连铸结晶器为例，目前常用材料为 CuCrZr 合金[6-7]，在高温钢水的热负荷及钢坯的磨损作用下，表面镀层常以热裂纹、热疲劳、磨损等方式失效[8-9]。目前常用的修复方法有电刷镀技术[10-11]、超音速火焰喷涂技术[12-13]以及等离子喷涂技术[14-15]等，但均存在工艺复杂、界面结合弱等问题。冷喷涂因其热影响小、对基体无损伤以及修复工件形状不受限制等优点，成为了修复连铸结晶器的潜在技术[16-17]。

张俊宝等[18]首次在 CuCrZr 合金板上制备了 CuCrZr 涂层，涂层致密度达 98.7%，显微硬度为 310HV，结合强度大于 37 MPa，证实了冷喷涂修复结晶器的可行性。张田宇等[19]在加热过程中原位观察冷喷涂 CuCrZr 涂层组织演变发现，涂层发生回复、再结晶形核与晶粒长大。Coddet 等[20]制备的冷喷涂 CuCrZr 涂层孔隙率低于 0.1%，涂层的拉伸强度为 515 MPa，电导率为 25% IACS。Yang 等[21]研究发现，冷喷涂 CuCrZr 涂层在高温下（400~600 ℃）显示出优异的抗氧化性和耐磨性。但 CuCrZr 基体与冷作硬化态涂层热膨胀系数相差较大，在结晶器急冷急热服役条件下，涂层与基体界面极易发生开裂，由此考虑引入塑性变形能力更好的 Cu 颗粒作为冷喷涂 CuCrZr 涂层与 CuCrZr 基体的中间层。对于冷喷涂纯铜涂层，国内外学者已进行了大量研究，发现界面再结晶行为和氧化膜破碎挤出行为的共同作用是影响冷喷涂铜涂层界面微观结合的关键[22]。张龙龙等[23]使用氦气在不锈钢表面成功制备了冷喷涂铜涂层，结合强度大于 81.7 MPa，热处理后电导率达到了 93.94% IACS。胡凯玮等[24]在铝合金试件表面上制备了纯铜涂层，铜涂层与铝合金基体形成了良好的结合，并且涂层导热系数能达到纯铜块材 50%的水平。Zhou 等[25]在 CuCrZr 基体上沉积了纯铜涂层，当粒子入射角为 90°时，Cu 涂层的维氏硬度达到 CuCrZr 基体的 82.7%，热导率达到基板的 95.3%，纯铜块的 90.7%。因此，本文引入冷喷涂纯 Cu 涂层为过渡层，解决 CuCrZr 涂层界面处的开裂问题，并探究 Cu 过渡层对 CuCrZr 涂层组织及性能的影响，为冷喷涂修复铜结晶器提供新思路。

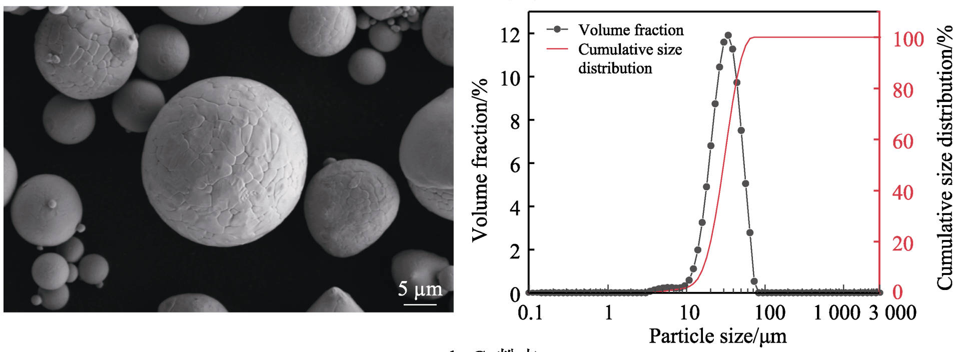
1 试验

1.1 粉末及涂层制备方法

喷涂材料为 CuCrZr 和 Cu 商用粉末（长沙天久金属材料有限公司），其微观形貌及粒径分布如图 1 所示。CuCrZr 和 Cu 粉末均为球形，粒径范围为 10～100 μm，平均粒径分别为 30.2、34.4 μm。基板材料为 CuCrZr，喷涂前进行喷砂处理。采用 SST^{TM} EPX 冷喷涂系统（Centerline，加拿大）制备涂层，采用 UntiFlow 喷嘴，喉部直径为 7 mm，长度为 120 mm。采用高压氮气为工作气体，压缩空气为送粉气体，工艺参数如表 1 所示。



a　CuCrZr粉末



b　Cu粉末

图 1　粉末微观形貌及粒径分布

Fig.1 Powder micro-morphology and particle size distribution: a) CuCrZr powder; b) Cu powder

表 1　冷喷涂工艺参数

Tab.1 Cold spray process parameters

Powder	Distance/mm	Spraying speed/($mm\cdot s^{-1}$)	Feeding speed/($g\cdot min^{-1}$)	Pressure/MPa	t/℃	Overlap width/mm
Cu, CuCrZr	20	20	20	3.4	500	1.2

1.2　涂层表征及性能测试方法

采用 Axio Oberver A1m 蔡司倒置金相显微镜对涂层组织进行观察，结合 Image-J 软件统计涂层的孔隙率和扁平率。颗粒扁平率的计算如图 2 所示。

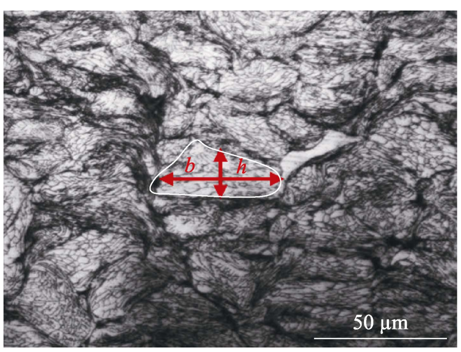


图 2　颗粒扁平率计算示意图

Fig.2 Schematic diagram of particle flattening rate calculation

扁平率的计算公式为：

$$\varepsilon = \frac{d-H}{d} \tag{1}$$

$$d = \sqrt[3]{b^2 h} \tag{2}$$

式中：ε 为扁平度，%；b 为变形颗粒长边长度，μm；h 为短边长度，μm。

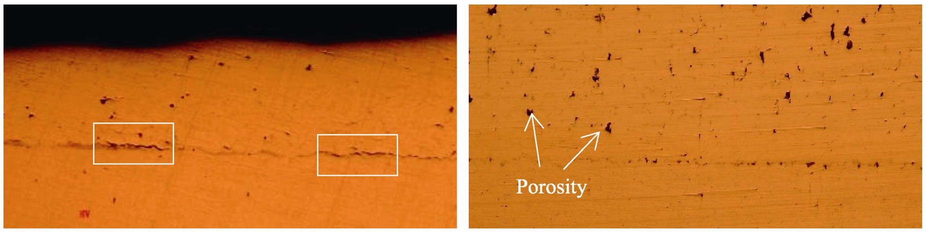
采用 DHV-1000ZTRDT 显微硬度仪对涂层硬度进行表征，加载力为 0.98 N，保载时间为 15 s，每隔 40 μm 测量试样的横截面，取 3 次测试的平均值作为结果。采用耐驰 LFA-427 型激光热导仪进行导热系数测定，测试温度为 50、250、500 ℃，试样为 ϕ10 mm×2.7 mm 的圆片。

2　结果与讨论

2.1　涂层组织

采用表 1 的工艺参数在 CuCrZr 板材上制备的 CuCrZr 涂层，在冷却水作用下切割，涂层与基体界面发生开裂，如图 3a 所示，这印证了 CuCrZr 涂层-基体较大的开裂倾向。图 3b 为采用 Cu 涂层打底制备的 Cu+CuCrZr 涂层，在相同的切割条件下，涂层与基体界面良好，无开裂现象，表明 Cu 过渡层可以防止界面开裂。这是因为纯 Cu 颗粒的强度低于 CuCrZr 颗粒，更易发生塑性变形，在相同的喷涂工艺参数下，Cu 颗粒撞击 CuCrZr 板材时将以更高的应变成射流，有助于氧化膜的破碎和挤出，使颗粒与基体之间发生良好结合；另一方面，硬的 CuCrZr 颗粒会嵌入软的 Cu 涂层中，CuCrZr/Cu 包嵌式结合会增加接触面积，提高机械结合强度。

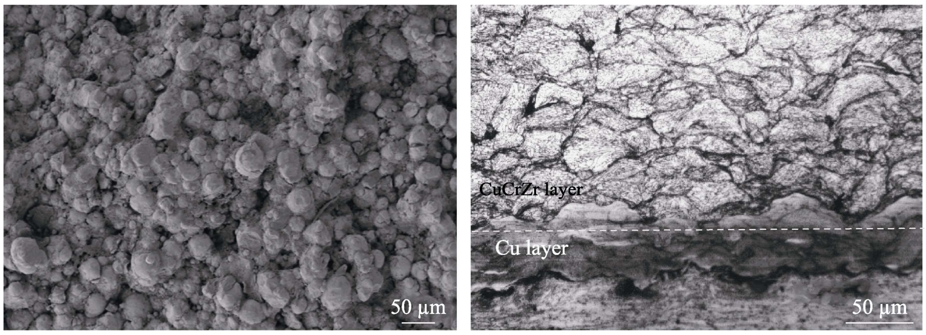
图 4a 为 CuCrZr 涂层上表面形貌。CuCrZr 粉末以高速碰撞基体时发生塑性变形，其形貌由球状变形为扁平状。对腐蚀后的涂层截面金相图选择多个不同



a 无Cu涂层打底 b Cu涂层打底

图 3 冷喷涂涂层与基体界面

Fig.3 Interface between cold sprayed coating and substrate: a) without Cu coating; b) with Cu coating



a 上表面 b 截面

图 4 冷喷涂 Cu 打底层+CuCrZr 涂层形貌

Fig.4 Morphology of cold sprayed Cu coating+CuCrZr coating: a) upper surface; b) cross-sectional

颗粒进行测试，得出其扁平率平均值为(43.62±4.54)%。但涂层因颗粒变形不充分，仍存在孔洞，采用图像分析法获得了涂层截面的孔隙率约为0.624%。图 4b 是 Cu 涂层为过渡层的 CuCrZr 涂层截面 SEM 组织，Cu 涂层厚度约为 50 μm，CuCrZr 涂层依次沉积于 Cu 涂层之上。

2.2 涂层性能

涂层截面硬度随界面距离的演变如图 5 所示。CuCrZr 板材硬度约为 160HV，基体靠近界面附近存在加工硬化层，硬度为 163HV~168HV，厚度约为 160 μm。冷喷涂 Cu 涂层平均硬度约为 153HV，冷喷涂 CuCrZr 涂层平均硬度为 173HV，低于 Coddet 等[22]制备的喷涂态 CuCrZr 涂层硬度，但高于 Yang 等[23]报道的喷涂态 CuCrZr 涂层硬度（158HV）。CuCrZr 涂层硬度显著高于基体，这是由于在喷涂过程中 CuCrZr 颗粒发生了较大塑性变形（如图 4 所示）引起的加工硬化作用所致。同时，后续粒子对已沉积颗粒的进一步撞击作用夯实了下部涂层，从而使涂层界面硬度从表面到结合界面呈上升趋势。因此，Cu 过渡层的存在使修复涂层具有硬 CuCrZr 基体-软 Cu 涂层-硬 CuCrZr 涂层的梯度结构。

涂层和基板热导率与温度的关系如图 6 所示。基板与涂层热导率随着测试温度的升高而增加，这是因为温度的升高会增强自由电子热运动和晶格震动，提

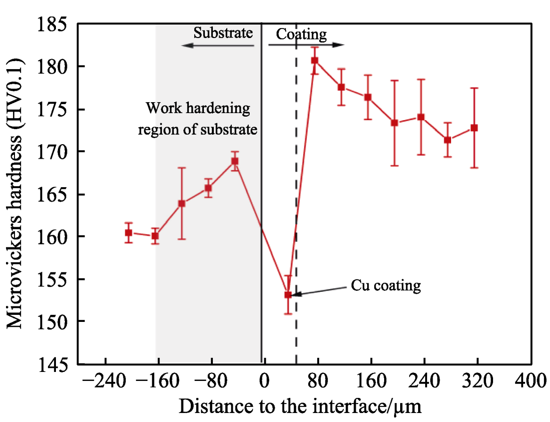


图 5 涂层硬度值随梯度的变化

Fig.5 Variation of coating hardness with gradient

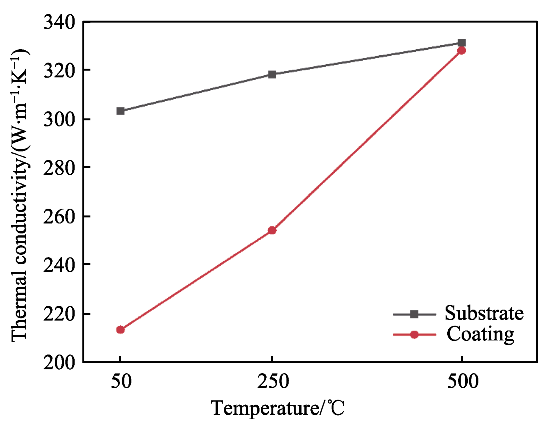


图 6 涂层与基板的热导率与温度关系

Fig.6 Thermal conductivity of coating and substrate with temperature

高导热系数。当测试温度为 50 ℃时，涂层的热导率低于板材，这是因为涂层本身具有一定的孔隙（0.624%），空气的热导率（0.024 W/(m·K)）远低于板材的热导率，同时涂层中的变形应力会阻碍电子运动，降低了涂层的热导率。增加温度可以增强电子的热运动和晶格震动，减弱孔隙和变形应力的影响。因此，在 500 ℃时，涂层能达到与基板相当的热导率。CuCrZr 结晶器的服役温度在 400~500 ℃，因此采用 Cu 打底得到的冷喷涂 CuCrZr 涂层能满足其导热性能要求。

3 结论

1）采用 Cu 为过渡层获得了防裂良好的 CuCrZr 涂层，涂层孔隙率约为 0.624%，CuCrZr 颗粒扁平率约为 43.62%。

2）喷砂处理引起 CuCrZr 板材近表面处加工硬化，加工硬化区硬度为 163HV~168HV，厚度约为 160 μm。冷喷涂 Cu 涂层的平均硬度约为 153HV，冷喷涂 CuCrZr 涂层的平均硬度为 173HV。

3）采用 Cu 涂层打底获得的 CuCrZr 涂层的热导率随温度的升高而升高，并且在 500 ℃时与基体相当。

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