

镁合金表面电弧喷铝层的微观结构及界面分析

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摘 要: 为获得性能优良的镁合金表面复合涂层, 用自动送进的双铝丝做两个电极产生电弧, 用压缩空气把熔化的铝熔滴喷到 AZ91D 镁合金表面, 形成镁铝复合涂层。通过选用不同电压和气压进行喷涂试验, 分析其对涂层组织性能的影响规律, 找出最佳工艺参数。利用现代分析手段研究涂层的微观结构及界面特点, 并通过测定涂层电极电位和盐雾试验分析涂层的耐腐蚀性能。结果表明, 一定的电压和气压条件可使涂层致密, 界面有新生组织, 涂层中产生了小于 50 nm 的纳米级晶团束和微米级层片状双重结构, 涂层耐腐蚀性能明显优于镁合金基体。

关键词: 镁合金; 电弧喷铝; 纳米晶; 耐腐蚀性能

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0 序 言

镁合金作为最轻的工程金属结构材料, 具有比强度和比刚度高、良好的阻尼减震和电磁屏蔽性能及易于回收再利用等一系列优点, 被誉为二十一世纪最有前途的绿色结构材料^[1,2], 在航天、航空、汽车、电子、交通及国防军工等领域具有广阔的应用前景。但是, 由于镁合金的耐蚀性和耐磨性差, 大大限制了其作为工程结构材料的应用范围。镁合金表面处理技术主要有电镀、热喷涂、离子注入、激光、气相沉积、阳极氧化、扩散、转化涂层、氢化物涂层、有机涂层等^[3]。采用电弧喷涂在镁合金表面形成 Al 元素涂层的方法简单, 但对涂层界面特性和微观结构研究较少。曲明等人^[4]研究了用电弧在镁合金表面喷涂铝锌层的组织, 谭成文等人^[5]研究了用电弧在镁合金表面形成 Al 元素涂层的界面结合性能, 梁永政等人^[6]研究了用电弧在镁合金表面形成 Al 元素涂层的基本工艺。文中采用双铝丝做电极产生电弧, 在镁合金表面制备 Al 元素涂层, 分析涂层的微观结构和耐腐蚀性, 其目的是为镁合金表面性能的进一步改善提供一些必要依据。

1 试验方法

基体材料为 AZ91D 镁合金板, 喷涂材料为直径

3 mm, 纯度 $\geq 99.5\%$ 的铝丝。

采用 XDP-1 电弧喷涂机; JSM-5600LV 扫描电子显微镜; D/Max 2500Pc 型 X 射线衍射仪; JEM-2000EX 透射电子显微镜; YWX/Q-0160 腐蚀试验箱; GX71 金相显微分显系统。用线切割技术在镁合金铸锭上切取 70 mm \times 40 mm \times 8 mm 试件并分组编号, 对表面喷砂粗化。

试验采用优化后的焊接电流 180 A, 喷涂距离 100 mm, 改变喷涂电压和喷涂气压进行喷涂, 分析其对涂层组织及性能的影响。

在喷好的各编号试件上切下 10 mm \times 10 mm \times 8 mm 做成金相试样; 把涂层从基体上剥下, 做成 SEM, XRD 和 TEM 分析试样。

2 试验结果及分析

2.1 涂层的微观结构及界面分析

2.1.1 电弧电压对涂层微观组织的影响

图 1 为经优化后最佳参数(电弧电压 30 V, 喷涂气压 0.6 MPa)时的涂层金相组织。图 2 为 0.6 MPa 气压下, 电弧电压分别为 26 V 和 33 V 时的涂层金相组织。图 1 的涂层组织致密, 涂层与基体结合较好。其原因是: 电压增高会增加电弧区的温度, 从而增加了熔融颗粒的温度, 高温熔融的粒子在基体上的润湿度增加, 延长了粒子之间的熔融时间, 使粒子与基体之间, 粒子与粒子之间融合得更加充分, 组织更加致密。但当电弧电压增加到图 2b 的 33 V 时,

由于过高的电压会使粒子散射增大,降低了粒子的速度以及撞击力,反而降低了涂层结合的致密度。

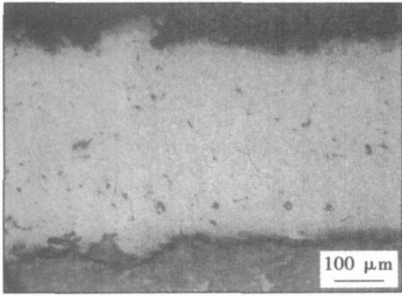
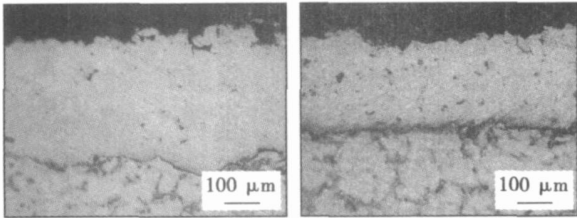


图 1 电弧电压为 30 V 时的涂层微观组织
Fig. 1 Microstructure of coating at voltage 30 V

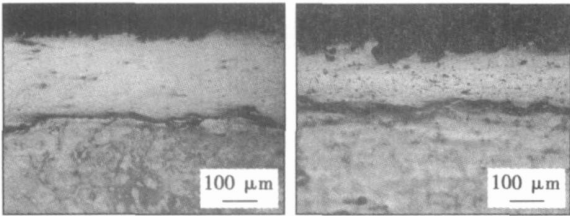


(a) 电压 26 V (b) 电压 33 V

图 2 电弧电压分别为 26 V 和 33 V 时的涂层微观组织
Fig. 2 Microstructure of coatings at voltages of 26 V and 33 V

2.1.2 喷涂气压对涂层微观组织的影响

图 3 为电弧电压 30 V 时 0.5 MPa 和 0.7 MPa 两个喷涂气压下的金相组织。由图可见,两涂层都不如图 1 致密。其原因是:适当提高空气压力,可使熔化材料的雾化效果好,熔滴细小,涂层组织细化,致密度高。同时,熔滴的飞行速度快,撞击力强,变形量大,与基体的结合面积增大,涂层与基体结合紧密。但喷涂气压过高则会干扰热源,使热源温度降低,粒子与基体及粒子与粒子之间的融合差。而喷涂气压过低,粒子在空气中滞留的时间长,容易被氧化。



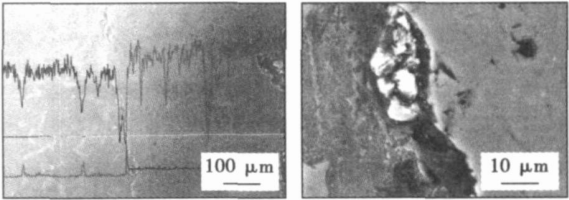
(a) 气压 0.5 MPa (b) 气压 0.7 MPa

图 3 不同喷涂气压下涂层的微观组织
Fig. 3 Microstructure of coatings at different spray air pressure

2.1.3 涂层与基体界面组织分析

图 4 为涂层与基体界面的扫描电子显微图像。

由图 4a 可见,基体与涂层被一条弯曲的亮白界面分隔为左右两部分,贯穿基体和涂层的一条亮白色的横线为线扫描的路线,深色曲线代表 Mg 元素的成分变化,浅色的曲线代表 Al 元素的成分变化,在基体与涂层的交界面,Al 元素的含量虽然陡降,但并未降到最低,而是向镁基体内部继续延伸、降低,同时,Mg 元素的扫描线在交界处也未直接降为零,而是深入涂层一段距离后才下降为零,说明涂层与基体发生了互扩散。



(a) 涂层与基体界面的线扫描像 (b) 涂层与基体界面的微观放大像

图 4 涂层与基体界面扫描电子显微图像形貌
Fig. 4 Line scan and SEM photography in boundary area of coating and matrix

图 4b 为涂层与基体界面的微观放大图,图中亮白色块状组织是新生组织。由 Mg-Al 二元相图判断此组织是 $Mg_{17}Al_{12}$ ^[7]。其原因是:铝的熔点较低,过热度较大,随着喷涂电压和喷涂气压的提高,粒子的温度和飞行速度也有所增加,飞行过程中粒子的热能损耗少,撞击到基体表面的粒子热能增加,而镁合金的熔点也低,遇到高温熔融的铝粒子就会发生冶金反应。晶界中形成的新生相 $Mg_{17}Al_{12}$ 相对于镁基体,电极电位高,耐腐蚀性好。

2.1.4 涂层断面形貌分析

图 5 为涂层断口的 SEM 照片。由图可见,涂层截面呈细微条层状结构,几乎没有杂质颗粒和氧化物,但存在一定量光滑近圆形的孔隙。涂层断面中存在大量塑性韧窝状断裂,属于典型的塑性断口,当

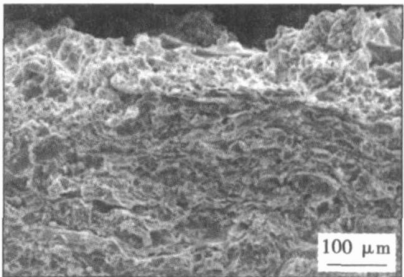


图 5 涂层断面形貌
Fig. 5 Fracture morphology of coating

涂层受到外力冲击时, 不容易产生微裂纹和应力腐蚀, 提高了涂层的防应力腐蚀性能。

2.1.5 涂层的 XRD 分析

图 6 是涂层 X 射线衍射结果。图中 4 个主峰均为 Al 元素, 而且没有其他衍射峰, 表明喷涂后涂层的主要成分是 Al 元素, 涂层中没有氧化物杂质。说明在喷涂过程中, 铝丝材被加热雾化以后并没有被空气氧化, 这与断口形貌分析结果相符。其主要原因是: 纯铝粒子在高温电弧中严重过热, 在喷向基体的过程中, 大量金属蒸气排开周围空气, 导致铝粒子未被氧化。同时, 熔融的铝粒子被雾化后经高压气雾向基体的过程中, 雾化粒子速度太快, 还未被空气氧化就已喷到基体上并与基体结合。

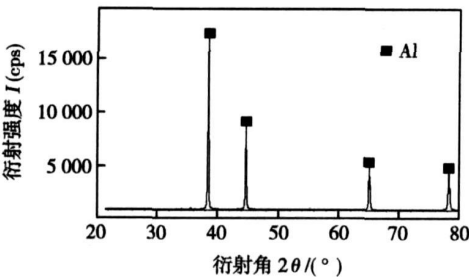


图 6 涂层的 X 射线衍射图
Fig. 6 XRD spectra of coating

2.1.6 涂层相结构分析

图 7 为铝涂层透射电子显微像。由图 7a 可见, 涂层中组织成分均一, 晶粒尺寸一般在 100~200 nm 左右, 同时在涂层的部分区域存在着约为 50 nm 左右的明显细化的小晶粒。图 7b 为涂层局部区域电子衍射花样像。图中除可以看到衍射环以外, 还可以看到一些分散的衍射光斑, 这是典型的纳米晶衍射花样。对图 7b 中的衍射花样计算表明, 对应的图 7a 中的浅色区域为 Al 元素。

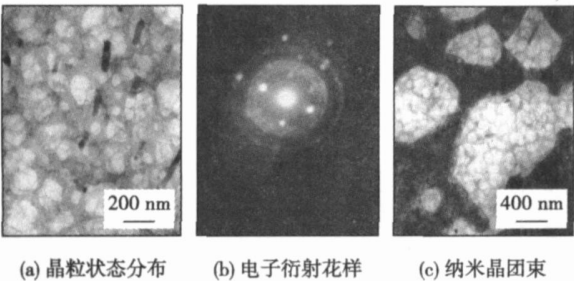


图 7 涂层透射和局部区域电子衍射花样像
Fig. 7 Transmission and local electron diffraction photography of coating

由图 7c 可以看到白色的纳米晶团束和分散的纳米粒子。这也说明涂层中存在双重微观组织, 对涂层性能增强提供了保证。涂层组织细化的主要原因是: 低熔点的铝在高温下熔化充分, 部分熔融颗粒经压缩气体雾化之后直接就形成了纳米级颗粒喷射到基体上。同时, 由于基体散热较快, 加速了铝粒子的冷却速度, 增加了形核率, 细化了颗粒。

2.2 涂层的耐腐蚀性能分析

2.2.1 电极电位测定

采用传统三电极体系, 试样为工作电极, 铂电极为辅助电极, 饱和甘汞电极为参比电极, 腐蚀介质为 5%NaCl 溶液, 试验温度 25℃, 扫描速度 0.01 V/min, 扫描区间 -2.0~0.0 V。图 8 为基体与涂层的 Tafel 极化曲线 (E -lg I 曲线, lg I 为腐蚀电流的对数值)。由图可见, 基体的曲线(实线)无钝化区, 而涂层的曲线(虚线)有明显的钝化区, 随着电位的变化, 在钝化区 AB 内, 电位从 -1.0~-0.76 V 时电流基本保持不变, 涂层的溶解速度很小, 说明铝涂层具有良好的耐蚀性。由自腐蚀电位可知, 铝涂层的电极电位低于镁合金的电极电位, 它会作为阴极与镁合金形成原电池, 从而对镁合金起到牺牲阳极阴极保护作用。

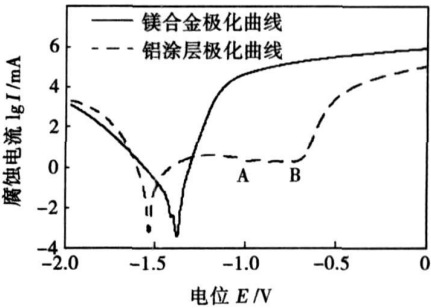


图 8 塔菲尔极化曲线
Fig. 8 Tafel polarization curve

2.2.2 涂层孔隙率测定

采用图像分析技术, 用阈值法在图像中将孔隙与背景进行分离, 用像素标记法测定涂层孔隙率。涂层孔隙率越小, 耐腐蚀性能越好, 有孔隙则腐蚀速率将增加^[8]。表 1 是在电流为 180 A, 喷涂距离为 100 mm 下测得的几个不同电弧电压和喷涂气压时的涂层孔隙率。由表 1 可见, 30 V 电压, 0.6 MPa 气压的孔隙率最低, 只有 5.09%, 这与上述分析是相符的。

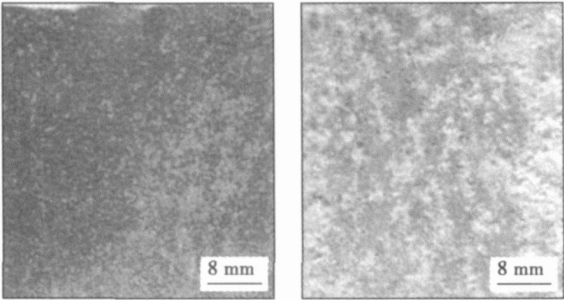
2.2.3 中性盐雾试验

参照 GB6458—86, 取基材镁合金和涂层镁合金试件放入腐蚀试验箱进行对比试验。试验用 pH 值为 6.8 的 5%NaCl 溶液, 每隔一段时间开箱观察,

表 1 涂层的孔隙率
Table 1 Porosity of coating

试件组号	电压 U/V	气压 p/MPa	孔隙率 $\eta/\%$
1	33	0.6	7.18
2	30	0.6	5.09
3	26	0.6	12.15
4	23	0.6	22.88
5	30	0.7	9.34
6	30	0.5	15.01

总计连续喷雾 48 h。通过观察发现, 试验 1 h 后, 基材镁合金试件表面 35% 的面积出现白色锈斑和银灰色蚀痕, 而铝涂层试件只有小面积出现棕色锈斑。试验 4 h 后, 基材表面已出现白色腐蚀锈斑及深色蚀痕, 腐蚀严重, 而涂层表面刚出现棕色锈斑。图 9 给出了试验 48 h 的照片。此时基材表面(图 9a)已完全腐蚀并变为黑色, 而涂层表面(图 9b)大部分变为深棕色, 并出现白色斑点。虽然, 盐雾试验 48 h 后涂层大部分变为棕色, 对于铝涂层来说, 表面氧化膜的存在可使铝涂层在水中的溶解速度比按其电化学位所预计的要慢得多, 与镁合金相比, 腐蚀时间越长越能体现出铝涂层的高耐蚀性。同时进行的试验还有涂层封孔试件, 一直腐蚀到 48 h 涂层仍完好无损。



(a) 基材表面48 h腐蚀状况 (b) 涂层表面48 h腐蚀状况

图 9 盐雾腐蚀对比

Fig. 9 Salt spray corrosion contrast between base metal and coating

3 结 论

- (1) 电弧电压为 30 V, 喷涂气压为 0.6 MPa 的工艺下可得到均匀致密的铝涂层。
- (2) 涂层与基体发生了互扩散, 并有冶金结合生成物 $\text{Mg}_{17}\text{Al}_{12}$, 涂层中存在纳米晶团束和微米层片状双重结构。
- (3) 涂层的耐腐蚀性能明显优于镁合金基体。

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Finite element analysis of residual stress of welding repair for gas pipeline

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Abstract By the finite element analysis software ABAQUS and the function of coupling process between heat and stress, the methods of entirety welding repair and local welding repair were simulated for 20-steel gas pipeline, and the distributions of the two kinds of welding residual stress were obtained. At the same time, the stress of welding-repair joint was analyzed by ABAQUS under inner pressure and welding residual stress. The results indicate that the residual stress of the entirety welding repair is lower than that of the local welding repair. And under inner pressure and welding residual stress, the tensile stress of the entirety welding repair is lower than that of the local welding repair too. It shows that the entirety welding repair joint is stronger than the local welding repair joint. The method of the entirety welding repair can reduce the probability of stress corrosion cracking and fit for the engineering application. The research results provide theory base for optimizing welding repair technology.

Key words: gas pipeline; entirety welding repair; local welding repair; welding residual stress; finite element analysis

Temperature control system of electron beam brazing joint

WANG Xuedong, LIU Peng, WANG Wei (Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China). p81—84

Abstract: High precision digital PID control system used in temperature control of electron beam brazing joint was realized. In order to keep the predefined joint temperature during brazing process, digital control model and controller were constructed based on computer control and discrete control theories. The type of the controlled object was determined by open-loop and closed-loop step responses, and the effect of the expanded ultimate-sensitivity method and the expanded step-response method were compared when the PID parameters were tuning. The PID parameters obtained by the ultimate-sensitivity method were optimized by the through normalization on line, and each group of parameters and the corresponding experimental results were provided. Integration separation algorithm was also used to enhance the dynamic performances. The experimental results show that overshoot is so small that can be ignored and time is not needed to adjust; the temperature control precision can reach $\pm 2.5\text{ }^{\circ}\text{C}$.

Key words: electron beam brazing; closed-loop control; discrete control system

Effects of trace indium on properties and microstructure of Ag-Cu-Zn filler metal

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Abstract Melting temperature, spreadability, microstructures of silver filler metal bearing different content of indium, and the mechanical properties of brazed joints were studied respectively. By using copper and brass plates as base metal, brazing with flame method, the mechanical properties of the joints brazed with lap-joint and butt joint were tested and analyzed at the same time. Results show that adding indium can decrease the melting temperature and improve the spreadability of the silver filler metal, and the microstructures of the silver filler metal bearing different content of indium are refined significantly. For the lap-joint of brass, the tensile strength of the joints gradually strengthens, presenting parabolic shape, with the increasing of the element indium; the fractures position of two kinds of brazed joints happens on the base metal, except for the lap-joint of brass, which shows better mechanical properties of the joints brazed with the silver filler metals bearing indium.

Key words: silver filler metal; melting temperature; spreadability; mechanical properties; microstructure

Microstructure and interface analysis of aluminum coating sprayed by electro-arc spraying on AZ91D magnesium alloy

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Abstract In order to obtain the excellent composite coating on magnesium alloy, double aluminum wires as two electrodes were automatically fed to create electric arc, the melting aluminum drops were sprayed on the AZ91D magnesium alloy surface by compressed air, and then the Mg-Al composite coating was formed. The optimum processing parameters were found by selecting different voltages and air pressure to carry on the spray experiments and analyzing the influence of the parameters on the coating structure performance. The characteristics of the coating microstructure and interface were researched by using the modern analysis methods, and the coating corrosion resistance was analyzed by test the coating electrode potential and the salt-spray experiment. The results indicate that certain voltage and air pressure can cause the coating to be compact. There is the newborn microstructure in the interface. The dual-structures of nano-scale crystal beam and micron-scale lamellar under 50 nm appear in the coating. The corrosion resistance of the coating surpasses that of the magnesium alloy matrix obviously.

Key words: magnesium alloy; arc spray aluminium; nano-crystalline; corrosion resistance

Effects of heat treatment technology on mechanical properties of friction welding drill rod

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