

不同电流类型对电沉积铝镀层微观结构的影响机理

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摘要 电镀铝+热处理扩散工艺是制备阻氚涂层的常用方法,铝镀层表面微观形貌影响后续热处理效果,进而对阻氚性能有着重要影响。在 AlCl_3 -1-乙基-3-甲基咪唑(1-Ethyl-3-methylimidazolium Chloride, EMIC)离子液体中,采用不同工艺参数在316L不锈钢基体表面制备铝镀层。利用X射线衍射(X-ray Diffraction, XRD)、扫描电子显微镜(Scanning Electron Microscopy, SEM)等手段,分析不同工艺参数对铝镀层相结构及内部微观形貌的影响机理。XRD结果表明:所有镀层成分均为单质铝;SEM结果表明:镀层表面部分晶粒随直流电流密度而增大,较优电流密度范围为 $10\sim 20\text{ mA}\cdot\text{cm}^{-2}$;与直流电沉积工艺相比,单向脉冲电流波形电沉积所得铝镀层厚度最大,双向脉冲电流形成铝镀层晶粒和厚度最小,晶粒大小均匀。主要原因在于,单向脉冲模式下瞬时峰值电流较大,促进镀层晶粒生长,厚度变厚;双向脉冲模式中的反向电流可溶解掉部分镀层,明显抑制镀层内较大晶粒长大,导致所形成镀层晶粒均匀细小。

关键词 阻氚涂层, AlCl_3 -EMIC 离子液体, 室温电镀铝, 电流类型, 微观结构

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Effect of different current types on the microstructure of electrodeposited aluminium coatings

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Abstract [Background] Tritium permeation leakage exists in fusion reactor such as International Thermonuclear Experimental Reactor (ITER), which leads to a series of problems such as fuel loss and environmental pollution, etc. Al_2O_3 coating is a hot research topic for preventing tritium permeation. The preparation of Al_2O_3 coatings on the surface of materials is an effective way to solve this problem. Electrodeposition of Al and heat treatment diffusion technology is a common method to prepare tritium-resistant coatings. The relevant parameters during the preparation process have important effects on the microstructure and tritium-resistant performance of Al coatings. [Purpose] This study aims to analyse the mechanism of the effect of different electrodeposition process parameters on the phase

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structure and internal micro-morphology of aluminium coatings, and to obtain good quality aluminum coatings. **[Methods]** Firstly, the aluminum coating was prepared on the surface of 316L stainless steel substrate at room temperature with 316L stainless steel as cathode, aluminum wire (99.99% purity) as anode, and AlCl_3 -1-Ethyl-3-methylimidazolium Chloride (EMIC) ionic liquid as plating solution. Then, the changes of surface and cross section morphology of aluminum coating were observed by changing the current density under direct current mode whilst the plating time (60 min) was fixed, and the difference of the microstructure of the aluminum coating prepared under the three current modes, i. e., direct current ($15 \text{ mA}\cdot\text{cm}^{-2}$), unidirectional pulse and bidirectional pulse current, was compared. Both the X-ray diffraction (XRD) and scanning electron microscopy (SEM) were employed to characterize the phase structure and internal microstructure of aluminum coatings. **[Results]** The experimental results show that the coatings are all composed of Al element and have a face-centered cubic structure, in which the preferred orientation of the crystal faces of the direct current and bidirectional pulsed electrodeposition coatings is different. In the direct current mode, some grains on the coating surface increase with the increase of direct current density, and the optimal current density of direct current electrodeposition ranges from $10\sim 20 \text{ mA}\cdot\text{cm}^{-2}$. Compared with the direct current electrodeposition process with similar parameters, under the condition of the same current density and electroplating time, the grain size of the coating microstructure obtained by pulsed current and bidirectional pulse electrodeposition is more uniform, and the grain size after bidirectional pulse electrodeposition is smaller, and the thickness of the aluminum coating obtained by unidirectional pulse current waveform electrodeposition is the largest. The grain and thickness of aluminum coating formed by bidirectional pulse current are the smallest and the grain size is uniform. **[Conclusions]** The introduction of pulse current has a significant effect on the size and uniformity of particles on the surface of aluminum coating. The coating obtained by pulse current is relatively dense, the grain thinning phenomenon is obvious, and the grain size is relatively uniform. The reason is that the large instantaneous peak current can inhibit the excessive growth of the grain and play a leveling role, so as to further improve the micro-morphology of the coating and improve the quality of the coating.

Key words Tritium-resistant coating, AlCl_3 -EMIC ionic liquid, Room temperature aluminium plating, Current type, Microstructure

国际热核聚变实验堆 (International Thermonuclear Experimental Reactor, ITER) 是目前世界上第一个可控核聚变实验堆,其聚变燃料主要为氢的同位素氘和氚,它们结合生成氦原子并释放出大量能量。然而,聚变反应堆中存在氚的渗透泄漏,将导致反应堆结构材料中的氚大量积累并产生许多污染物^[1-3]。聚变堆中的燃料极易渗透到金属结构材料中,从而造成燃料损失、材料脆性断裂和放射性污染等危害^[4-5]。目前,解决这一问题的有效方案是在金属结构材料表面制备具有阻氚渗透性能的涂层。

氧化物涂层是最早研究的一类阻氚涂层,常见的氧化物涂层主要包括 Cr_2O_3 、 Er_2O_3 、 SiO_2 、 Al_2O_3 、 Y_2O_3 等^[6-11]。其中, Al_2O_3 涂层的氚渗透降低因子远大于其他材料,是目前阻氚涂层材料研究的热点。 Al_2O_3 涂层一般先在结构材料基体表面制备铝浓度呈梯度分布的铝化物表层,然后经过原位氧化形成一层致密氧化膜,使其阻氚性能进一步提升^[12-13]。基体表层铝化物的制备方法,主要有热浸铝 (Hot Dipped Aluminized paint, HDA)、包埋法 (Pack

Cementation, PC)等直接工艺,以及沉积铝(磁控溅射、电化学沉积等)+热处理扩散工艺,各种方法对应制备的铝化物涂层的质量和阻氚性能存在较大差异^[14-17]。

与磁控溅射镀铝工艺相比,电化学沉积铝工艺具有设备简单、易于操作、厚度可控、适用于复杂形状表面制备等优点,在工业上得到广泛应用^[18]。由于Al的沉积电位为 -1.66 ,属于一种负电性金属,不能从普通的水溶液中电沉积,导致镀液只能采用无机盐或离子液体等非水溶液体系^[19]。 AlCl_3 -1-乙基-3-甲基咪唑 (1-Ethyl-3-methylimidazolium chloride, EMIC) 离子液体,具有低蒸气压、宽电化学窗口、高溶解度、低毒性、高热稳定性、环保性等特点^[20-21],被认为是最有前途的电解质^[18,20,22-24]。目前,铝镀层的制备大多采用直流电沉积法以及单向脉冲电沉积法,而双向脉冲电沉积法制备铝镀层的研究较少,更缺少不同电流模式对形成镀层微观结构的影响机理分析。

本文采用 AlCl_3 -EMIC 离子液体为电镀介质,分别在直流、单向脉冲、双向脉冲等不同电流模式下,

开展316L基体表面的电沉积铝实验,并对铝镀层的相结构、表面、截面等进行分析表征,探索不同电流类型对电沉积铝的表面和截面微观形貌的影响机理及形成机制。

1 实验材料与方法

1.1 电镀液配制与基体的前处理

本实验镀液采用 AlCl_3 -EMIC离子液体,在氩气保护的手套箱内称取摩尔比为1:2的EMIC和无水氯化铝,将无水氯化铝缓慢加入EMIC中,不断搅拌,直至全部溶解,配好的离子液体放入高纯铝丝(99.99%)在室温下精制7 d,即可用于后续电沉积实验。

基体为316L不锈钢,切割后的尺寸为 $20\text{ mm} \times 30\text{ mm} \times 1\text{ mm}$,利用180~600#碳化硅砂纸依次打磨去除表面氧化层,再用氧化铝抛光液进行抛光,得到

样品表面呈镜面。试样片抛光后,采用丙酮和酒精超声清洗5 min后用蒸馏水清洗,接着用吹风机将表面的残余水分吹干后迅速转入手套箱中备用。

为改善铝镀层附着性能,拟在电沉积前对316L不锈钢进行阳极活化,提高基体表面活性。试样阳极活化处理在充满氩气的手套箱中进行,试样和铝丝(99.99%)分别连接到电源正负两极,其中电流密度为 $15\text{ mA} \cdot \text{cm}^{-2}$,处理时间30 min。在阳极活化过程中,采用磁力搅拌器适度搅拌电镀液。

1.2 铝镀层的制备与表征

阴极材料为316L不锈钢试样,阳极材料为纯度高达99.99%的铝丝,分别与电源的负极和正极连接,在室温下分别采用直流、单向脉冲及双向脉冲电流进行电沉积,沉积时间均为60 min。沉积结束后,依次用酒精和蒸馏水冲洗阴极表面并吹干,沉积过程的电沉积参数设计如表1所示。

表1 电沉积参数
Table 1 Electrodeposition parameters

	直流 Direct current	直流 Direct current	直流 Direct current	直流 Direct current	单向脉冲 Unidirectional pulse	双向脉冲 Bidirectional pulse
正向平均电流密度 Forward average current density $+I_{av} / \text{mA} \cdot \text{cm}^{-2}$	10	15	20	35	15	15
反向平均电流密度 Reverse average current density $-I_{av} / \text{mA} \cdot \text{cm}^{-2}$	—	—	—	—	—	5
频率 Frequency	—	—	—	—	300	300
正反向脉冲个数比 Ratio of forward and reverse pulses ($n+$) / ($n-$)	—	—	—	—	—	10:1
正向占空比 Forward duty cycle $+D$	—	—	—	—	40%	40%
反向占空比 Reverse duty cycle $-D$	—	—	—	—	—	40%

使用扫描电子显微镜(Scanning Electron Microscopy, SEM, Merlin Compact, 德国蔡司; LEO 1530vp, 德国LEO)观察涂层表面、截面的微观形貌。使用X射线衍射仪(BRUKER, D8 ADVANCE型)以粉末衍射模式对铝镀层的物相组成进行表征,扫描 2θ 角范围为 $10^\circ \sim 90^\circ$,以连续方式扫描,扫描步长和滞留时间分别为 0.02° 和0.5 s。

2 结果与讨论

2.1 涂层的物相结构

在离子液体中,分别在直流、单向脉冲及双向脉冲模式下进行电沉积铝,得到试样的XRD能谱如下图1所示。由不同衍射峰位置结果可知,不同类型电流下电沉积所得镀层均由Al元素组成,结构为面

心立方结构,主要包括有(111)、(200)、(220)和(311)晶面。当采用直流电流与单向脉冲电流电沉积时,(111)晶面的反射强度相对较强,与铝元素标准卡片(PDF#04-0787)上衍射峰相对高度一致,表明在直流电沉积的作用下,晶粒沿着(111)晶面的生长较为明显,与张桂凯等^[25]短时间电沉积的实验结果一致。当采用双向脉冲电流电沉积时,铝镀层中(220)和(200)晶面的反射强度相对较强,说明铝镀层中呈现(220)和(111)晶面择优生长,结果与Liao等^[26]研究结果一致,即 AlCl_3 -EMIC离子液体中所得电沉积产物晶粒表现出(220)和(200)晶体取向。根据电沉积层形成择优取向理论,在没有其他原子在Al晶面吸附时,面心立方晶格Al可能的生长方向(111)为平行于基体平面和垂直于基体平面,即镀层分别呈现(111)择优取向和呈现(220)晶面择优取

向。此外,双向脉冲电沉积时镀层的(200)晶面的衍射峰也较强,可能原因为反向电流的存在,导致离子液体中 Al_2Cl_7^- 或 AlCl_4^- 对(200)晶面有较强的吸附,形成铝镀层表现为(200)晶面择优取向。

2.2 电流密度对镀层形貌的影响

在相同温度及相同电沉积时间、不同电流密度

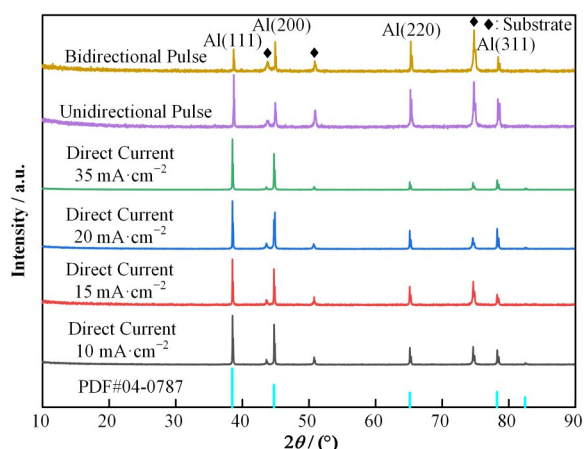


图1 不同电流类型沉积制备铝镀层XRD图谱
Fig.1 XRD patterns of Al coatings prepared by direct current and bidirectional pulsed electrodeposition

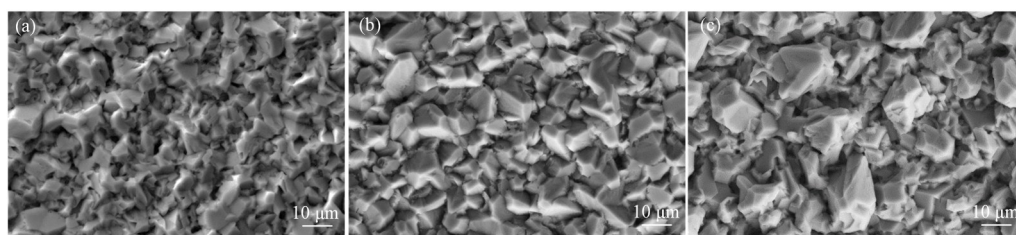


图2 不同电流密度下镀层表面微观形貌 (a) $10 \text{ mA} \cdot \text{cm}^{-2}$, (b) $20 \text{ mA} \cdot \text{cm}^{-2}$, (c) $35 \text{ mA} \cdot \text{cm}^{-2}$
Fig.2 SEM images of aluminium electrodeposits under different current densities (a) $10 \text{ mA} \cdot \text{cm}^{-2}$, (b) $20 \text{ mA} \cdot \text{cm}^{-2}$, (c) $35 \text{ mA} \cdot \text{cm}^{-2}$

2.3 不同电流类型对镀层表面微观结构的影响

在平均电流密度为 $15 \text{ mA} \cdot \text{cm}^{-2}$ 和沉积时间 60 min 的条件下,分别采用直流、单向脉冲及双向脉冲工作模式进行电沉积,所得镀层试样的表面形貌如图 3(a~c)所示。图 3(a)所示为直流电沉积铝镀层表面形貌,主要由较多的小尺寸晶粒及个别尺寸较大的棱柱状晶粒构成,与图 2(a)非常相似。图 3(b)和(c)显示脉冲电沉积后得到镀层的表面形貌,晶粒大小比较均匀,排列致密,气孔较少,与文献中描述的结果一致^[23]。由不同电流模式下镀层表面形貌可知,脉冲电流得到镀层比较致密,晶粒大小相对均匀。可能原因在于,在平均电流密度一定的情况下,降低占空比会增加峰值电流大小,高的峰值电流密度导致阴极极化的增强,进而影响到晶粒的细化程度和电沉积时析氢等副反应所占的比例。同时,

下沉积后镀层表面均为白色,光滑致密,均无漏镀现象。图 2 为不同电流密度下镀层微观形貌图,镀层表面由分布均匀、大小不一的棱柱状晶粒堆积而成,晶粒间存在着一定的空隙。对比图 2(a~b)的镀层表面可知,随着电流密度的增加,铝镀层表面部分晶粒尺寸显著增大,这与张桂凯等^[27]研究结果相似。同时,增大电沉积过程的电流密度,可以提高沉积效率,但晶粒尺寸差别更大,沿着特定方向生长成棱柱状的现象更加明显,与王文轩等的结果一致^[28]。在 $\text{AlCl}_3\text{-EMIC}$ 离子液体中电沉积铝时,晶体的形核与生长受很多因素制约,如阴极极化作用随电流密度增加而增加,但若离子的传质不足仍会影响晶粒生长^[27]。

根据试样沉积前后的重量变化,以上 3 种电流密度下的阴极效率均达到 85% 以上,并结合镀层形貌的变化情况可得,在 316L 不锈钢表面镀铝,较优的电流密度范围为 $10 \sim 20 \text{ mA} \cdot \text{cm}^{-2}$,所得铝镀层晶粒大小均匀,与文献常用的电镀电流范围相符^[29]。电流密度超过 $30 \text{ mA} \cdot \text{cm}^{-2}$ 时,镀层颗粒粗大且均匀性较差,电流密度过高会增强镀层向外生长趋势,产生枝晶状析出物,从而降低电流效率^[30]。

溶液中消耗掉的阳离子可随关断时间的增加充分得到补充,减少浓差极化现象,提高阳极过电位,从而增加形核速率,缩短晶粒生长时间,所以脉冲电流制备的铝镀层晶粒更加均匀致密,可提高镀层的性能。而双向脉冲电流中的反向电流可以抑制晶粒的生长,使晶核的形成速率大于晶核的生长速率,抑制部分晶粒的异常长大。同时,反向脉冲电流可以提供较高的反向电流密度,溶解镀层表面晶粒的凸起部分,对镀层起到明显整平作用,最终导致晶粒尺寸比单向脉冲沉积的晶粒尺寸小。反向脉冲电流的阳极溶解使阴极表面铝离子浓度迅速回升,这有利于随后的阴极周期使用高的脉冲电流密度,而高的脉冲电流密度又使得晶核的形成速度大于晶体的生长速度,因而可以得到更加致密、光亮、均匀的镀层。

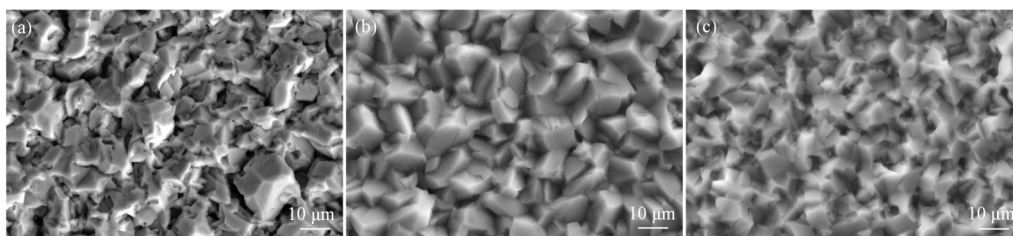


图3 不同电流类型下镀层表面微观形貌 (a) 直流($15 \text{ mA} \cdot \text{cm}^{-2}$), (b) 单向脉冲, (c) 双向脉冲

Fig.3 SEM images of aluminium electrodeposits under different current types

(a) Direct current ($15 \text{ mA} \cdot \text{cm}^{-2}$), (b) Unidirectional pulse, (c) Bidirectional pulse

2.4 不同电流类型对镀层截面微观结构的影响

在相同沉积时间内,分别采用直流、单向脉冲、双向脉冲进行电沉积,所得铝镀层截面的微观形貌如图4所示。由图4可知,铝镀层厚度分别为 $10.29 \mu\text{m}$ 、 $12.04 \mu\text{m}$ 、 $8.49 \mu\text{m}$,其中单向脉冲电沉积的镀层厚度最厚。单向脉冲电流因占空比存在使得峰值电流密度升高,加快镀层沉积速度,所以单向脉冲电流电沉积所得镀层大于直流电流电沉积所得镀层。双向脉冲电流由于反向电流的存在具有消除镀层表面凸起的作用,所以在镀层厚度在一定程度上会降低。

对比不同电流类型下所得铝镀层截面,可以发

现直流电沉积的铝镀层表面边缘起伏较大,内部有气孔;而脉冲电沉积所得镀层截面相对平整,锯齿状起伏程度明显减小,内部气孔较少,镀层更加均匀。形成这种差别的原因在于,脉冲电流由于占空比的存在具有较大的峰值电流,峰值电流越大,过电位越大,使得结晶过程中形核率增加,减少晶体生长时间,有效抑制部分晶粒过大生长,所以脉冲电流所得镀层截面起伏程度明显减小^[28]。而双向脉冲波形中反向电流的反向阳极溶解作用对镀层具有整平作用,溶解沉积层表面突出处,所以双向脉冲电沉积所得镀层比较致密,且厚度相比较单向脉冲电流所得镀层更为均匀^[31]。

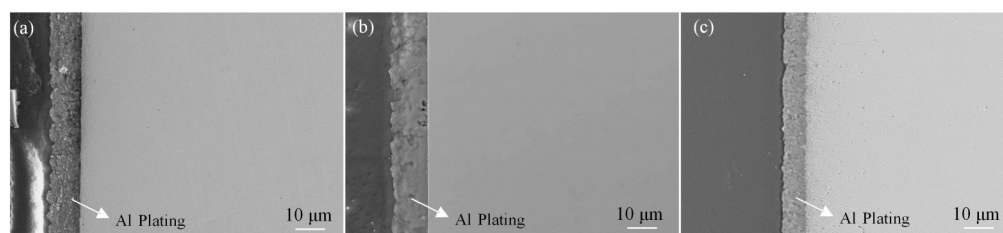


图4 不同电流类型下镀层截面微观形貌 (a) 直流($15 \text{ mA} \cdot \text{cm}^{-2}$), (b) 单向脉冲, (c) 双向脉冲

Fig.4 SEM micro morphology of the cross section of aluminium electrodeposits under different current types

(a) Direct current ($15 \text{ mA} \cdot \text{cm}^{-2}$), (b) Unidirectional pulse, (c) Bidirectional pulse

3 结语

在摩尔比为2:1的 AlCl_3 -EMIC离子液体中,在316L不锈钢基体表面采用三种不同电流模式制备完整的铝镀层,分析不同直流电流密度和不同电流类型对铝镀层相结构以及内部微观形貌的影响机理,主要结论如下:

1) 镀层元素均由Al元素组成,结构为面心立方结构,其中直流和双向脉冲电沉积镀层晶粒晶面择优取向不同。

2) 采用不同直流电流密度进行电镀时,镀层表面形貌存在微小空隙,部分棱柱状晶粒随电流密度而增大,其较优电流密度范围为 $10 \sim 20 \text{ mA} \cdot \text{cm}^{-2}$ 。

3) 在电流密度和电镀时间一致的条件下,单向脉冲及双向脉冲电沉积获得镀层微观结构中晶粒尺寸更均匀,且双向脉冲电沉积后的晶粒尺寸更细小,

其可能原因在于脉冲电流波形可细化晶粒,进一步提高镀层微观形貌平整度,能够改善镀层质量。

4) 由不同电流模式电沉积镀层截面微观结构发现,直流脉冲沉积的镀层厚度最厚,双向脉冲获得镀层厚度最小,但比较致密无明显气孔,可能原因在于反向脉冲波形的引入提升了镀层致密性,导致镀层中大尺寸晶粒的溶解和镀层厚度减小。

5) 通过对比三种不同电流模式下所得镀层,得出结论如下:双向脉冲电流模式下所得镀层表面及截面最为均匀致密,更适合用于后续热处理扩散,以获得性能良好的阻氙涂层。

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