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不同加热方式对 Ni-P-SiC化学复合镀层性能的影响

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[摘　要] 采用炉内加热处理和激光加热处理两种方式对 Ni-P-SiC化学复合镀层进行了晶化处理。运用显微硬度计、M-2000磨损试验机等对采用两种加热方式处理后的 Ni-P-SiC复合镀层进行了性能测定。结果表明，采用激光加热处理后，复合镀层的硬度和耐磨性均高于经炉内加热处理的镀层。

[关键词] 化学复合镀层；Ni-P-SiC；镀后加热处理；硬度；耐磨性
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0 前　言

化学镀 Ni-P合金以其工艺简便、镀层厚度均匀、性能优良等特点而日益受到重视。在化学镀液中加入适量 SiC粒子制取的 Ni-P-SiC复合镀层，不仅具有化学镀 Ni-P层的优良性能，而且当第二相不溶性硬质微粒 SiC复合在化学镀镍层中时，将获得更高的硬度和耐磨性[1]。但 Ni-P-SiC镀态时多为非晶态，这是一种热力学亚稳定态，经过适当的加热处理可发生晶化转变，晶化后 Ni-P-SiC镀层的硬度和耐磨性比镀态时又有进一步提高。因此实际使用的镀件多是经过适当加热处理的。目前对化学镀层的晶化处理都采用炉中加热，但要获得高硬度、高耐磨的镀层，加热温度通常要在 400 ℃左右，这一温度范围对很多要求淬火+低温回火的工具和模具钢来说偏高，会导致基体硬度降低，从而使镀层应用受到一定的限制。激光作为一种高密度能量源，已广泛应用于钢的表面淬火领域，与炉中加热相比，激光加热可以只对镀层进行处理，避免了对基体的影响。但国内对复合镀层激光处理的研究报道较少，为此，研究了 Ni-P-SiC复合镀层经炉内加热和激光加热两种不同的加热方式处理后镀层硬度和耐磨性的变化，以选择出更适合镀层镀后热处理的方式，扩大镀层的应用领域。

1 试　验

1.1 试验材料

试验材料为退火态 45钢，尺寸为 19.5 mm×10.0 mm×8.0 mm。

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1.2 镀液配方

硫酸镍	25～30 g/L
次磷酸钠	20～25 g/L
柠檬酸三钠	10～15 g/L
乙酸钠	10～15 g/L
乳酸	30 g/L
碳化硅	6 g/L
醋酸铅	3 mg/L
pH值	4.4～4.6
温度	88～90 ℃
机械搅拌	420 r/min

本试验在镀液中加入了具有催化活性的 SiC固体颗粒，其在镀液中易成为结晶核心，从而使镀液发生自分解，生成金属镍的颗粒，导致镀液很快失效。为了避免这种现象的发生，在镀液中加入了适量的醋酸铅，Pb^{2+}对镀液中次磷酸钠的氧化反应具有明显的阻化作用，它的加入可以在很大程度上推迟镀液的自分解，从而能够稳定镀液。

1.3 试验方法

镀层：将经过预处理的样品放入上述镀液中镀覆 2 h，用金相显微镜测量镀层厚度，约为 25 μm。

加热处理：将所镀样品分别进行炉内加热处理和激光加热处理。炉内处理样品的加热温度分别为 200，250，300，350，400，450，500，550 ℃，其中除 200 ℃保温 6 h外，其他均为 1 h。样品激光处理采用 CO_2连续轴流激光器进行，试样表面涂黑色吸收涂料，本次试验在光斑直径为 3 mm，扫描速度为

0.5 m/min的条件下,通过改变激光输出功率来研究对复合镀层的影响,其功率分别为 150, 200, 250, 300, 350, 400, 450, 500, 550, 600 W。试验中为防止样品发生氧化,辐射区域采用氩气保护。

表面形貌及成分:采用扫描电镜、能谱仪和 X 射线衍射仪对镀态和处理后的镀层进行表面形貌、成分及物相分析。硬度:在 HXD-1000T型数字显微硬度计上测定镀层的硬度,载荷 1 N,加载时间 15 s。磨损试验在 M-2000型磨损试验机上进行。

2 试验结果与讨论

2.1 不同加热方式对镀层硬度的影响

Ni-P-SiC复合镀层镀态下的平均硬度为 685 HV_{1N}。为了进一步提高镀层的硬度,按试验方法对镀层进行加热处理,表 1和表 2分别是炉内加热处理和激光加热处理后镀层的硬度值。

表 1 炉内加热处理后镀层的硬度值

加热温度/℃	200	250	300	350	400	450	500	550
硬度值/HV_{1N}	714	798	1 032	1 343	1 247	1 148	984	753

表 2 激光加热处理后镀层的硬度值

功率/W	150	200	250	300	350	400	450	500	550	600
硬度/HV	676	743	827	1 012	1 128	1 359	1 436	1 185	967	818

从表 1和表 2可以看出,镀层经过两种方式加热后,镀层硬度都呈先上升后下降的趋势,其原因是在加热晶化转变过程中,Ni_3P的析出和 SiC粒子弥散硬化的共同作用导致镀层硬度逐渐升高,当Ni_3P析出量达到最大后,继续升温或提高激光输出功率,均会使 Ni_3P聚集粗化,从而镀层使硬度又逐渐下降。而激光处理后镀层的最高硬度高于炉内处理的最高硬度,其原因是采用激光热处理后,析出 Ni_3P的数量比炉内加热处理的多[2],并且还析出了稳定的 Ni_2Si化合物,这一点可以从图 1的 X 射线衍射图谱上得到证实。析出的 Ni_2Si会对晶界起到钉扎作用,抑制晶粒的长大,并且这种化合物在镀层晶化的过程中容易发生沉淀,从而硬化了镀层[3]。

2.2 不同加热方式对镀层耐磨性的影响

镀层耐磨性采用 M-2000型磨损试验机测量。

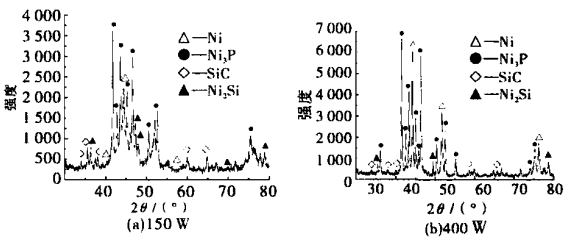

图 1 镀层经不同功率激光处理后的 XRD图谱

采用平板与圆环滑动摩擦,平板即为被磨件(镀件),将其固定,圆环为对磨件,材料为 GCr15钢,淬火+低温回火,硬度为 62 HRC,对磨件转速为 400 r/min,载荷为 196 N,间歇滴油,试验时先将对磨件与被磨件在不加载荷的情况下跑合 20 min,然后在加载的情况下磨损 7 h,试验中每隔 1 h称重一次。试样磨损前后用 BP211D型万分之一的电子天平称量磨损量,摩擦系数 μ按下列公式计算得出:$\mu = T/(R \times P)$, T为摩擦力矩,可在试验机上直接读得, P为试样所承受的垂直载荷,即为 196 N, R为下试样的半径,本试验中 R为 20 mm。表 3是炉内加热处理及激光加热处理后镀层的磨损性能。

表 3 镀层的磨损性能

镀层处理方式	磨损量/(mg·h^{-1})	摩擦系数
350 ℃炉内热处理	0.120 0	0.089
400 ℃炉内热处理	0.147 1	0.102
400 W激光热处理	0.144 3	0.098
450 W激光热处理	0.104 3	0.077

由表 1和表 2已知,复合镀层在炉内 350 ℃热处理时硬度值达到最大,而激光热处理时在 450 W时硬度值达到最大,且 450 W激光处理后硬度值高于炉内 350 ℃处理的硬度值。结合表 3可知,镀层 450 W激光热处理后,其磨损失重小于炉内 350 ℃加热处理,并且 450 W时硬度值最高时,其摩擦系数最小,磨损失重也最小,这一现象符合摩擦学原理,即材料的高硬度能有效地提高材料抗黏着磨损和磨粒磨损的能力。镀层经激光处理后,复合镀层中 SiC体积分数增大, SiC微粒间间距减小,有利于润滑油膜的形成,在具有良好强化效果和耐磨性能的 Ni-P合金基质的支撑下,硬质相 SiC的弥散分布起着抗磨作用,并且析出的较炉内处理更多的 Ni_3P以及新形成的 Ni_2Si也对复合镀层的高耐磨性起着积极的作用,从而使镀层的磨损量减小。

图 2a和 2b分别为经过两种方式加热的镀层

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磨损试验后的表面形貌。从图中可以看出,SiC粒子都均匀地分布在 Ni-P合金基质上,但炉内加热处理的复合镀层表面有很多大的犁沟,而激光处理的复合镀层表面仅有少数小的轻微的犁沟,而且磨损试验后磨痕基本上还未到基体,这表明复合镀层激光处理后具有更高的耐磨性。

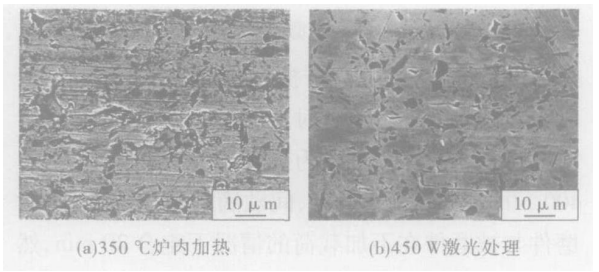

图 2 不同热处理后镀层的磨损形貌

两种处理方式加热后镀层磨损后的表面成分能谱图见图 3。由图 3可以看出,复合镀层经炉内 350 ℃和激光 450 W处理后磨损表面均出现了微量的铁元素,表明在磨损过程中发生了黏着磨损现象,铁为对磨件 GCr15钢的转移产物。复合镀层激光 450 W处理后的硬度值高于炉内 350 ℃处理的,由于高硬度可以有效地提高材料的抗黏着磨损能力,所以前者的抗黏着磨损能力较后者强,因而转移产物的数量也有所不同。

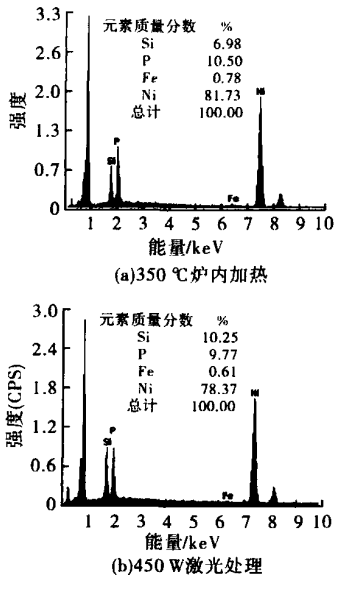

图 3 镀层磨损后的表面成分能谱图

3 结 论

(1) Ni-P-SiC化学复合镀层激光加热处理后,会形成金属间化合物 Ni_2Si。

(2) Ni-P-SiC复合镀层激光加热处理后在析出 Ni_3P的同时,还会析出部分 Ni_2Si化合物,Ni_3P、Ni_2Si弥散析出以及 SiC的共同作用,有利于提高镀层的硬度和耐磨性。

(3) Ni-P-SiC复合镀层激光加热处理后,硬度和耐磨性都优于炉内加热处理。

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detailed, while the optimized parameters for the micro-arc oxidation of Mg alloy pieces with large area were established. It was anticipated that the relevant experimental results could be used to guide the design of the craft and power source for the micro-arc oxidation of large-area Mg alloy pieces.
Key words: magnesium alloy; micro-arc oxidation; process craft

Application of Ti-Doped Nanometer Polymer Paint in Corrosion Protection of Inside-Wall of Electric Fan for Catalyzing and Reforming Facility

WANG Wei (Oil Refining Factory, Daqing Petroleum Company, Daqing 163711, China). *Cailiao Baohu* 2006, 39(10), 71～73 (Ch). The causes leading to the corrosion of the inside-wall of the electric fan in the heating stove for catalyzing and reforming facility were detailed. Then Ti-doped nanometer polymer anticorrosion paint was used to prevent such a type of corrosion. The primary field test results indicated that it was feasible to prevent the inside-wall of the electric fan from corrosion by coating with the Ti-doped nanometer polymer paint, and the titled paint was advantageous in terms of the cost-effectiveness.
Key words: electric fan shell; Ti-doped nanometer polymer paint; corrosion protection

Environmentally Acceptable Chemical Conversion Film for Aluminum and Its Alloys

LUO Kun-ying, YU Guo-qiang, LI Da-xu (Guangzhou Electric Apparatus Research Institute, Guangzhou 510302, China). *Cailiao Baohu* 2006, 39(10), 74～75 (Ch). An environmentally acceptable chemical conversion agent CF-5 was formulated from non-toxic titanium salt, zirconium slat, and organic polymer so as to replace the conventional toxic chromium (Ⅵ) passivation agent used for aluminum and its alloys. The corrosion resistance of the conversion film was primarily investigated. As the results, the final chemical conversion fluid was suggested to be composed of 0.10～2.00 g/L PO_4^{3-}, 0.05～1.00 g/L Ti^{4+}, 0.05～1.50 g/L Zr^{4+}, 0.30～1.50 g/L F^-, 0.50～2.00 g/L oxidizing agent, 0.05～3.00 g/L organic polymer (water-soluble epoxy resin or acrylic acid polymer). It was feasible to prepare desired chemical conversion film of good adhesion to organic coatings and good corrosion resistance using the established conversion fluid.
Key words: chemical conversion film; aluminum and its alloys; titanium; zirconium; organic polymer; non-toxic; corrosion resistance; adhesion

Effect of Heat Treatment on Hardness and Wear Resistance of Electroless Ni-P-SiC Composite Coating

WANG Lan, SHAO Hong-hong, JIANG Xiao-yan (School of Material Science and Technology, Jiangsu University, Zhenjiang 212013, China). *Cailiao Baohu* 2006, 39(10), 76～78 (Ch). Electroless Ni-P-SiC composite coatings were crystallized via heating in furnace and heating with laser, respectively. The effect of the heat-treatment on the hardness and wear resistance of the Ni-P-SiC composite coating was investigated based on measurement of the hardness and evaluation of the wear resistance on an M-2000 type test rig. It was found that the electroless Ni-P-SiC composite coating subject to laser heat-treatment had high hardness and better wear resistance than that heated in furnace. This could be attributed to the differences in the microstructures of the composite coatings after being heat-treated in different modes.
Key words: electroless composite coating; Ni-P-SiC; heat treatment; hardness; wear resistance

Characteristics and Application of Water-Retrieving Painting Booth with Movable Gantry

FANG Jin, LIU Yong, WANG Wen-peng (No. 6 Institute of Project Planning & Research, Ministry of Machinery Industry, Zhengzhou 450007, China). *Cailiao Baohu* 2006, 39(10), 79～81 (Ch). The buildup, action, and structural design of water-retrieving painting booth with movable gantry were elucidated, while the design characteristics, cost, and application of the painting booth were introduced as well. The field test results indicated that the developed water-retrieving painting booth with movable gantry was characterized by structure refinement, convenient operation, and low cost. The painting booth could be well used to improve the spray coating quality of workpiece and the operation conditions as well, and in particular, it was applicable to the spray coating of hard-to-move large scale workpiece.
Key words: coating; movable gantry; water-retrieving painting booth; design; characteristics; application

Application of Arc Spraying Technology in Protection of Membrane Water Wall of Gas Hood for Converter

WANG Yin-jun[1], LUO Jia-zhi[2], ZHANG Cai-gui[2], WANG Xiao-jian[1] (1. Technology Center, Meishan Steel Co. Ltd, Nanjing 210039; 2. Meishan Steelmaking Mill, Nanjing 210039, China). *Cailiao Baohu* 2006, 39(10), 82～83 (Ch). The working conditions and the causes leading to leakage of membrane water wall of gas hood for converter were analyzed. In connection with the common faults such as wear, corrosion, and crack of the membrane water wall, it was determined to apply suitable spraying materials and technology to get rid of the faults. Thus the membrane water wall was pretreated by sand blasting. Then an intermediate Al5Ni95 coating and working coating KBF3 were sprayed. Finally, the sprayed coatings were subject to airproof treatment. The membrane water walls after the above-mentioned surface modifications were used to the converter gas hood in Meishan Steelmaking Mill. Encouragingly, the crack and leakage phenomena of the membrane water wall in field test were significantly restrained, which could be critical to extending the service lifespan of the converter gas hood.
Keywords: arc spraying; converter gas hood; membrane water wall

Determination of Trace Chromium (Ⅵ) in Electroplating Wastewater by Spectrophotometry with Piperonal Fluorescence Ketone

PENG Rong-hua, LI Xiao-xiang (School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201, China). *Cailiao Baohu* 2006, 39(10), 84～85 (Ch). In the buffer solution of NH_4Cl-ammonia with a pH value of 9.5, Cr(Ⅵ) reacts with piperonal fluorescence ketone to form a blue complex in the presence of surface active agent CTMAB. Thus a method to determine trace Cr(Ⅵ) in electroplating wastewater was established accordingly. It was found that the blue complex had a maximum absorption at 600 nm and an apparent molar absorptivity of 1.31×10^5 L/(mol·cm). The molar ratio of Cr(Ⅵ) to piperonal fluorescence ketone in the complex was 1∶2. Moreover, Beer's law was obeyed for Cr(Ⅵ) in the range of 0～42 μg/L, and the recovery of the standard addition of Cr(Ⅵ) was as much as 95.5%～106.1%. In general, the trace Cr(Ⅵ) in electroplating wastewater could be readily and accurately determined using the established method.
Key words: Cr(Ⅵ); electroplating wastewater; piperonal fluorescence ketone; spectrophotometry; determination

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