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Recent Progress in the Research on Electrodeposition of Composite Coatings

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复合电沉积的最新研究动态

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摘要: 综述近年来国内外复合电沉积技术最新研究动态. 重点探讨纳米复合镀层, 电催化复合镀层以及光活性复合镀层等方面的研究现状和发展趋势. 纳米复合镀层比一般的复合镀层具有更高的硬度, 更好的耐磨性和耐蚀性; 电催化复合镀层则可在纯金属电极, 合金电极的基础上进一步降低电极反应的过电位. 以金属氧化物, 导电聚合物作为基质材料的电催化复合镀层已为现代复合电沉积技术开辟了一个新领域.

关键词: 复合电沉积; 复合镀层; 纳米粒子; 电催化; 光活性

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复合镀层^[1]是利用金属电沉积方法将一种或数种不溶性的固体微粒均匀地夹杂在金属镀层当中而形成的特殊镀层. 自 1920 年德国科学家得到第一个复合镀层以来, 至今, 复合电镀工艺及其应用已经取得了巨大发展. 电沉积制备复合镀层最初主要用于提高材料的硬度, 耐磨, 耐蚀性能, 而目前则正进一步用于制备电催化和光活性材料, 以及在储能等领域方面的开发利用, 并从早期的主要以镍, 铜, 钴等单金属为基质金属, 以 SiC, SiO₂, Al₂O₃, Cr₃C₂ 等耐高温陶瓷粉末作为夹杂物的复合电镀, 发展到能满足特殊功能需要的各种合金, 多种颗粒的复合镀工艺^[2~4], 近年来又出现了以金属氧化物, 导电聚合物作为基质的复合镀层^[5]. 同时, 除在水溶液中沉积复合镀层外, 还可以从非水溶液中沉积复合镀层^[6]. 另外, 通过采用周期换向电流, 脉冲电流等获得的复合镀层^[7~10], 特别是由纳米技术得到的夹杂有纳米颗粒的复合镀层^[10~15]具有比直流电流下获得的复合镀层更为优异的性能, 从而进一步拓宽了复合镀层的应用范围.

以下, 仅就纳米粒子, 电催化, 光活性等各类型的复合镀层的研究动态作一综述.

1 纳米复合镀层

传统复合镀层所夹杂的固体微粒粒度基本上局限于 μm 甚至 mm 级, 由于纳米微粒 (0.1 ~ 100 nm) 本身具有小尺寸效应, 表面效应, 量子尺寸效应和宏观量子隧道效应等独特性能, 使得纳米复合镀层比普通复合镀层具有更高的硬度, 耐磨性, 减摩性以及耐蚀性. 以下, 略举目

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前研究较多的几种纳米复合镀层,以示一斑.

1.1 耐磨减摩纳米复合镀层

Petrova 等^[16]制备的 Ni-纳米金刚石(20~50 nm)硬度(3150 N/mm²)远远高于纯镍的硬度(1737 N/mm²). Lee 等^[8]在直流电流或脉冲电流条件下,通过向镀液中加入粒度为 25 nm 的金刚石制得的 Ni-纳米金刚石复合镀层,其硬度分别为 HV = 540 和 HV = 611,也都远远高于纯 Ni 镀层的硬度(HV = 210),且该复合镀层的摩擦系数($\mu = 0.16$)也低于纯镍镀层的摩擦系数($\mu = 0.44$),于金库等^[17]通过复合电刷镀技术制得的 Ni-纳米金刚石具有更高的硬度(HV = 860),其耐磨性为纯镍镀层的 6 倍.

由 Muller 等^[18]制得的 Ni-(14 nm) Al₂O₃ 复合镀层硬度较之纯镍镀层大有提高. Ferkel 等^[19]指出,在镍基复合镀层中只要含有 0.5 Vol % 粒度为纳米尺寸的 Al₂O₃ 颗粒就会明显提高该镀层硬度. Jeong 等^[20]研究发现,当镀层中 Ni 晶粒的尺寸从 10~100 μm 减少到 10~20 nm 时,其镀层耐磨性则提高了近 100~170 倍,而摩擦系数降低了 40%~50%;当镀层中加入的 Al 颗粒尺寸由 1 μm 减少到 16 nm 时,其摩擦系数相应下降了 57%.

Gyttou 等^[21]研究发现,通过脉冲电流可以镀出更高含量和更均匀分布的 Ni-nmSiC 复合镀层,纳米 SiC 的嵌入导致 Ni 晶粒的生长受到抑制,晶体缺陷数增加,硬度随着 SiC 含量的增加而相应增加. 经过 500 °C 热处理后,硬度进一步提高,硬化效应一直持续到 800 °C,达到 650 kgf/mm². 陈小华等^[22]发现碳纳米管镍基复合镀层也具有极高的耐磨性和减摩性能.

1.2 耐蚀纳米复合镀层

Benea 等^[12]研究发现,在镀液中加入粒径约 20 nm 大小的 SiC 微粒后,形成的 Ni-SiC 复合镀层的腐蚀电位 $E_{\text{corr}} = -198 \text{ mV (vs. Ag/AgCl)}$ 比纯镍的腐蚀电位 $E_{\text{corr}} = -260 \text{ mV (vs. Ag/AgCl)}$ 正移了 62 mV. 这是因为此时在 Ni-SiC 复合镀层表面形成了具有保护作用的 SiO₂ 或 Si(OH)₂ 腐蚀产物,从而使其耐蚀性明显提高. 在 0.5 mol/L Na₂SO₄ 介质中,测得 Ni-SiC 和纯镍的极化电阻分别为 80 k $\Omega\cdot\text{cm}^2$ 和 26 k $\Omega\cdot\text{cm}^2$; Ni-SiC 和纯镍的腐蚀电流 i_{corr} 分别为 0.74 $\mu\text{A}/\text{cm}^2$ 和 7.8 $\mu\text{A}/\text{cm}^2$.

王健雄^[23]等研究发现,通过复合电沉积方法制得的碳纳米管镍基复合镀层在 20% NaOH 溶液和 3.5% NaCl 溶液中的耐蚀性明显优于同条件下制备的纯镍层. 作者指出,耐蚀性的提高可能有以下几方面原因: (1) 碳纳米管的存在增加了镀层表面的致密度并缩小镀层孔隙的尺度,以致腐蚀液难以浸润镀层内微孔,同时由于化学活性很低的碳纳米管缠绕覆盖于晶粒表面,可将腐蚀介质和晶粒隔离,防止腐蚀的进一步加深. (2) 当 Ni 和碳纳米管相接触后作为阳极的 Ni 发生了阳极极化并促进 Ni 的钝化,减少其于介质中的腐蚀,从而使镍层对基体金属的保护作用增强.

Burkat 等^[24]研究发现, Zn-金刚石(4~6 nm)在 3% NaCl 溶液中的耐蚀性比纯 Zn 的要好.

另外,纳米复合镀层也逐渐应用于装饰防护性,耐高温氧化性和电接触等方面,同样表现出了良好的性能.

2 电催化复合镀层

根据所采用的基质材料,电催化复合镀层可分为单金属基,合金基,金属氧化物基和导电

高分子聚合物基等不同类型.

2.1 单金属基电催化复合镀层

Kunugi 等^[25~30]首次利用复合电沉积技术制备的 Ni-PTFE 复合电极对于一些水溶性有机物的电化学反应具有很高的电流效率.最初认为这是由于 Ni-PTFE 复合电极提高了电极上副反应的过电位而造成的,然而,进一步研究表明,Ni-PTFE 复合电极较之纯镍电极还能更进一步降低析氢和析氧反应的过电位,也能降低醇类和醛类氧化反应的过电位.随后,有关 Cu-PTFE^[31]复合电极对甲醇的电催化氧化以及其在流动注射分析上的应用又见报道.

Iwakura 等^[32]研究发现,与纯镍电极相比,Ni-RuO₂在析氢反应上表现出更高的催化活性.在 90 ℃,10 mol/L NaOH 溶液中,当 $I = 100 \text{ mA/cm}^2$ 时,Ni-RuO₂ 电极上的析氢过电位比 Ni 电极的约降低 360 mV,并指出这是由于:1) RuO₂ 本身具有催化活性;2) RuO₂ 的嵌入大大提高了镀层的真实表面积(经测定,Ni-RuO₂ 电极的真实面积是几何面积的 50 倍).

燃料电池中阳极催化剂一般为 Pt,但单一的 Pt 催化剂对甲醇氧化的电催化活性较低,而易被甲醇氧化的中间产物 CO 毒化.近年来相继报道 Pt-Sn,Pt-Ru,Pt-WO_x 和 Pt-Ru-WO_x 等复合催化剂可同时提高对甲醇氧化的电催化活性和抗中毒能力.但 Pt-Sn,Pt-WO_x 等催化剂在酸性介质中的长期稳定性还存在一定问题.最近,刘长鹏等^[33]报道了用电化学阴极还原-阳极氧化法制得的 Pt-TiO_x/Ti 和 Pt-Ru-Ti_x/Ti 电极对甲醇氧化呈现出较高的电催化活性和稳定性,并发现后者性能比前者更好.循环伏安法,计时电位法和 FTIR 反射光谱测量结果表明,在上述两种电极上 Pt,Ru 都得到了较好的分散,同时由于 Pt,Ru 与 TiO_x 协同作用导致弱的 CO 吸附而使电极不易中毒.

2.2 合金基电催化电复合镀层

除了以 Ni,Zn 等单金属作为基质金属外,以 Ni-P,Co-P,Ni-Co,Ni-Co-P,Ni-Mo 等合金作为基质金属制备的复合电极同样具有良好的电催化性.

成旦红等^[34]用复合电沉积方法制备了 Ni-P-ZrO₂ 复合电极,实验表明,在 80 ℃,25% NaOH 碱性溶液中,Ni-P-ZrO₂ 复合电极比 Ni 电极和 Ni-P 电极具有更高的析氢催化活性和良好的电化学稳定性.例如,在 $I = 135 \text{ mA/cm}^2$ 时,Ni-P-ZrO₂ 的析氢电位分别比纯 Ni 和 Ni-P 正移了 458 mV,186 mV.且其表观交换电流密度 i^0 是纯 Ni 电极的 46 倍,Ni-P 电极的 21 倍.进一步分析发现,表面粗糙度的增大和析氢反应标准活化焓的降低是提高 Ni-P-ZrO₂ 电极催化性能的两个主要因素.此外,本文作者还利用复合电沉积技术制备了 Ni-S-ZrO₂,Ni-P-WC 等复合电极,这些电极对析氢反应同样具有很好的催化性能.

Gierlokta 等^[35]研究指出,在碱性和酸性环境中,Ni-P-TiO₂ 复合电极对析氢反应具有明显的电催化活性,大幅度降低其析氢反应的过电位,并由此提出了相应的反应机理.

蔡乃才等^[36]报道了高比表面 NiMo-RuO₂ 复合镀层对析氢反应也具有较高的催化性.Oleksy 等^[37]则发现 Co-P-Sc₂O₃ 对于析氧反应具有优良的电催化性,只要复合镀层中含有少量的 Sc₂O₃ (4%) 就会明显地增大交换电流的值.文献[38]则报道了 Ni-Mo-PTFE 复合电极对甲醇的氧化具有较高的催化性.

2.3 金属氧化物基电催化复合镀层

Musiani^[5,39~41]研究小组从 1996 年开始研究通过复合电沉积技术,以 PbO_2 , Ti_2O_3 作基质材料,用具有催化性能的 RuO_2 , Co_3O_4 固体微粒作分散相制备复合电极,在析氧反应电催化应用上取得了显著的效果.进一步拓宽了复合电沉积技术在电催化材料方面的应用.

以 Bertoncello 等^[39]制得的 PbO_2 - Co_3O_4 和 Ti_2O_3 - Co_3O_4 复合电极作阳极分别应用于析氧反应,结果表明:1) 复合电极中的 Co_3O_4 含量和电极表面粗糙度是影响析氧反应的两个重要因素.2) Ti_2O_3 - Co_3O_4 的粗糙度与镀层中 Co_3O_4 的含量(用 (Co_3O_4) 表示)无关,而 PbO_2 - Co_3O_4 的粗糙度则随 (Co_3O_4) 的增大而增大.这主要是因为 Co_3O_4 对 Ti_2O_3 晶粒的成核和生长具有显著的催化活性,而对 PbO_2 晶粒的成核和生长则没有影响.而且只有当 (Co_3O_4) 值比较大时, PbO_2 - Co_3O_4 才能获得较高的粗糙度.3) PbO_2 - Co_3O_4 复合电极的催化活性明显高于 Ni - Co_3O_4 复合电极,由此可见, Co_3O_4 的催化活性与基质有关.

Bertoncello 等^[40]应用两种不同方法在 Ti 基体上分别制得了 $(\text{PbO}_2\text{-RuO}_2)/\text{Ti}$ 和 $(\text{PbO}_2\text{-RuO}_x)/\text{Ti}$ 复合电极.对析氧反应 $(\text{PbO}_2\text{-RuO}_2)/\text{Ti}$ 复合电极比 $(\text{PbO}_2\text{-RuO}_x)/\text{Ti}$ 具有更高的催化活性;扫描电镜(SEM)示出,前者的表面粗糙度明显高于后者.在 0~0.5wt% 范围内, $(\text{PbO}_2\text{-RuO}_2)/\text{Ti}$ 的催化活性随 RuO_2 含量的增加而增加,之后电极的催化活性不再继续提高.再者,还与制备过程所使用的电解质溶液品种有关.Cattarin 等^[41]进一步研究表明,用共沉积生成的 PbO_2 和 RuO_x 作为基质材料制备的 $(\text{PbO}_2 + \text{RuO}_x)\text{-Co}_3\text{O}_4$ 复合电极对析氧反应具有更高的催化活性.其表面粗糙度也比 $\text{PbO}_2\text{-RuO}_2$ 和 $\text{PbO}_2\text{-RuO}_x$ 的明显增大.

除了以 RuO_2 , Co_3O_4 作分散相微粒外,Belkaid 等^[42]还制备出 $\text{PbO}_2\text{-Fe}_2\text{O}_3$, $\text{PbO}_2\text{-Bi}_2\text{O}_3$, $\text{PbO}_2\text{-SnO}_2$ 等复合电极,应用在析氧反应上,也表现出了较高的催化活性.

2.4 导电高分子聚合物基电催化复合镀层

除单金属,合金,金属氧化物作基质外,还可应用电聚合方法生成具有导电性能的聚合物作基质材料,即将高度分散的过渡金属微粒通过电沉积技术嵌入到导电聚合物中形成具有电催化性能的复合电极,这方面近年来已逐渐成为一个新的研究热点,已有不少研究者利用导电聚合物(如聚吡咯(PPy),聚苯胺(PAN),聚噻吩(PTp)等)作基质制备出具有电催化活性的电极,大量应用于析氢,析氧及有机物(如醇类,醛类和氯酚等)氧化反应方面的研究.

钟起玲等^[43]报道了甲酸,甲醛,甲醇在铂微粒修饰聚苯胺(PAN)电极上的氧化行为,发现 PAN(Pt) 电极对甲酸,甲醛,甲醇均有较高的电催化氧化活性,其循环伏安(CV)正向扫描峰电位分别为 0.28 V,0.70 V,0.75 V,峰电流密度分别为 330.4,735.7 和 878.6 mA/cm^2 ,但随着 pH 值的升高,PAN(Pt) 电极对甲酸电催化氧化的活性逐渐降低,活化能增大,这可能是由于 pH 值的增加造成 PAN 导电能力减少所致.一般来说,pH 值控制在 0.7 左右为宜.在 0.01~1.0 mol/L 的甲酸浓度范围内,可用 PAN(Pt) 电极作传感器定量检测甲酸.

万本强^[44]应用电沉积技术制备了铂微粒修饰聚 2,5-二甲氧基胺(PDMA)电极(Pt-PDMA/Pt)并研究其对甲酸的电催化氧化.结果表明,此种复合电极对在酸性介质中甲酸的电催化氧化具有很高的催化活性,较之裸铂电极,其催化电流提高了 100 多倍,通过循环伏安法沉积的铂微粒均匀地分布在聚合物上,其粒径大约为 300 nm.这种催化活性的增强主要是由

于具有特殊组成和结构的 PDMA 与 Pt 微粒相互作用的结果,同时与铂微粒在聚合物中高度分散,几何结构发生变化也有关.这些因素都可以影响毒性中间体和活性中间体电氧化过程中的 Gibbs 自由能,但对活性中间体氧化反应自由能降低更为显著,使反应更易按直接氧化生成 CO_2 的途径进行.另外发现铂微粒载量,搀杂的阴离子种类,反应温度和浓度等因素都会影响电极催化活性.

由 Becerik 等^[45~46]制成的 PPy + Pt 和 PPy + (Pt + Pd) 复合电极对 D-glucose 的氧化均具有比纯 Pt 电极更高的催化活性,而且后者的性能最佳.

3 其他特殊功能的复合镀层

利用半导体微粒(如 TiO_2 , CdS, ZnO_2 , WO_3 等)与导电聚合物或金属共沉积可以制得具有光电活性的复合镀层.例如,由 Kawai 等^[47]制成的 PPy + TiO_2 复合电极具有光敏性, Ni-TiO_2 ^[48,49] 具有光电化学活性, PAN + WO_3 ^[50], PAN + CdS^[53] 则具有光电致变色功能. Deguchi 等^[13,52] 研究发现, Zn-TiO_2 对乙醇,乙醛的氧化具有光催化作用.经过 673 K 热处理 6 h 后,在镀层的表面生成的 ZnO-TiO_2 纳米层比 Zn-TiO_2 具有更高的光催化性能,这是由于 ZnO 和 TiO_2 在光催化方面的协同作用所带来的.

开发高可逆性和低溶解度的阴极活性材料一直是高能非水体系电池领域的研究热点. Kuwabata 等^[53] 研究发现以 PPy + MnO_2 复合镀层作为二次锂电池的正极材料时,由于 PPy 作为导电基质可以大大提高 MnO_2 在 Li^+ 嵌入过程中利用率.另据报道^[54], MoO_3 在有机溶剂中溶解性小和极化程度低,作为高能非水体系电池的阴极材料优于 AgO .这是由于 MoO_3 具有特殊的层状结构,有利于 Li^+ 和电子的自由嵌入和脱嵌.所以采用复合电沉积技术制备含 MoO_3 的复合电极具有很广阔的应用前景.

众所周知,复合镀层还广泛地应用在减摩材料,自润滑材料和电接触材料等,显示出了优良的性能,这方面报道的文献已很多,不再赘述.

Recent Progress in the Research on Electrodeposition of Composite Coatings

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Abstract: Recent progress in the research on composite coatings prepared by electroplating

technology is reviewed. The nanoscaled particles, electrocatalytic, photoactive composite coatings are emphatically discussed. The composite coatings prepared by dispersing nanoscaled particles could attain better hardness, wear resistance and corrosion resistance than those of composite coatings which prepared by adding microscaled particles. As compared with pure metal electrode and alloy electrode, some electrocatalytic composite coatings electrode could markedly reduce the over-voltages of cathodic and anodic electrode reaction. In recent years, the electrocatalytic composite coatings which based on metal oxides and conductive polymer as matrix materials become a newest field of composite electroplating technology.

Key words: Composite electroplating, Composite coatings, Nanoscaled particles, Electrocatalyst, Photoactivity

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