现代镀镍光亮剂与中间体浅谈

陈正法
(温岭市华星电镀有限公司, 浙江 温岭 317500)

[摘 要] 回顾了镀镍工艺的发展历程,指出主要是添加剂在各个时期的应用改变,使镀镍工艺逐步向光亮一步法镀镍推进。叙述了各种镀镍中间体的性能、特点和作用,并按不同使用要求给予分类。探讨了现代镀镍光亮剂的配制要点和各组分中间体的协同作用,介绍了一种由多种中间体配制的光亮剂配方。

[关键词] 镀镍; 中间体; 光亮剂
[中图分类号] TQ153.1 [文献标识码] A [文章编号] 1001-1560(2007)03-0078-02

0 前 言

镀镍工艺已有一百多年的历史,其主要变化在于添加剂的不同。早期采用无机添加剂如镉盐等,可得到洁白半光亮的镀层。20世纪 50年代末,美国发现了光亮和稳定性较好的 1,4-丁炔二醇和糖精,从而结束了镀镍后经机械抛光后再镀铬的历史,为一步法光亮电镀奠定了基础。到了 20世纪 70年代末,国外将丁炔二醇与环氧乙烷、环氧丙烷、环氧氯丙烷等催化缩合,得到一系列单或双取代醚化物。缩合物的整平光亮效果大为提高,用量少且化学性能稳定,推进了光亮镀镍的大规模工业化生产[1]。另外,还有半亮镍、高硫镍、镍封等工艺也开始应用。20世纪 90年代初期,德国巴斯夫公司镀镍中间体进入中国,各种进口的高档镀镍光亮剂也涌入国内沿海经济发达地区,一些电镀厂家开始应用。现在,光亮剂制造商用这些中间体再进行复配,可制得一系列品种齐全、品质高效、性能卓越的现代镀镍光亮剂。人们通常称之为第四代光亮剂。

1 镀镍中间体的分类与特性

(1)初级镀镍中间体:包括 BSI、BBI、ALS、PS、VS、BSS、ATPN、PESS、SSO_3、PN等。其主要作用是提高镀层柔软性,使结晶细化,增强低区的光亮性和填平性,促进走位,掩蔽杂质,有的还兼有去极化作用[2]。

(2)次级镀镍中间体:包括 PPS、PPS-OH、DEP、TC-DEP、PABS、PME、PAP、PMA、MAP、PA、BEO等。这些中间体都具有一定的整平光亮作用,能加快填平产品抛光丝纹,如 DEP可使镀层快速达到镜面光亮,具有丰满平滑的光泽。

(3)不含硫的镀镍中间体:包括 HD-M、HD-N、TCA、BEO、POPDH、PABS、PAP、DEP、PA、PME。这类中间体可用在半亮镍光剂中,使镍底层不含硫。用这种工艺镀得的半光亮镍层具有柱状的显微结构,镀层中含硫低于 0.005%。

(4)含硫的镀镍中间体:包括 PS、ATPN、PN、PPS、PPS-OH、SSO_3、BSS、BBI、SAS、VS、EHS等。含硫的中间体一般都用在镍光亮剂中,使光亮镍层与半亮镍层之间达到一定的电位差,其 STEP值在 130 mV以上。由文献[3]可知,BSS和 ATPN可用在高硫镍添加剂中,采用三层镍组合电镀,其 STEP值可达 160 mV,其防腐蚀性能更好。

(5)白亮镍中间体:包括 MOSS、TPP、BBI、EHS、PPS-OH等。这些中间体配制的光亮剂,镀出的产品具有银白珍珠色泽。

(6)乌光镍中间体:包括 MAP、PAP、BMP等。以这些中间体为主要组分配制的光亮剂,镀出的产品具有乌亮、高雅的效果。

(7)辅助中间体:包括起润湿作用的 TC-EHS、MA-80,起除杂走位作用的 ATP、ATPN、PN等。

2 复配镀镍光亮剂的要点及其作用

在我国东南沿海经济发达地区,特别是珠三角、长三角一带电镀厂用中间体自配光亮剂非常普遍。1995年,笔者根据有关文献介绍的各种中间体的作用和消耗量进行了镀镍光亮剂的复配。通过赫尔槽试验和生产实际相结合,摸索出一个基础光亮剂配

[收稿日期] 2006-12-17

方,通过生产中的应用和观察,了解各组分的协同效应,调整不足部分,确定实际消耗量后获得了成功应用。现在用中间体配制滚镀、挂镀、三层镍光亮剂的技术已比较成熟。

初级光亮剂也称柔软剂,主要成分是糖精(BSI),如果用于滚镀镍,宜选用 BBI,综合性能较好,使镀层面洁白。其他配方选用 PS、ALS、VS,它们的组合作用主要是使镀层形成细致的结晶,脆性降低,晶粒细化,平衡次级光亮剂的张应力,使低区光亮;加入少量 ATPN 可加强走位,提高低区深镀能力,消除异金属杂质的不良影响。滚镀、空气搅拌等镀镍工艺宜加入低泡润湿剂 TC-EHS或 MA-80,降低界面表面张力,防止针孔产生。使用润湿剂的另一个好处是能够减少镀液的带出量。润湿剂以前也称为辅助光亮剂,也可一起复配到柔软剂中,使工艺管理简单化。由以上几种中间体组成的柔软剂,其效果已相当不错。

次级光亮剂也称主光剂,袁诗璞认为[4]:主光剂至少应包括一种吡啶类化合物如 PPS或 PPS-OH;至少有一种丙炔类化合物,如 TC-DEP、PABS、PME、PAP等;至少有一种低电区光亮整平中间体如 PS、PN;至少有一种低区走位剂如 ATP、ATPN、VS、ALS等。MOSS、PESS等也具有很好的走位、除杂作用。

主光剂主要由三类中间体组成,即吡啶衍生物、炔胺类化合物和丙炔醇衍生物。这三类首选组分,每类都有几种功效相近的中间体,选用其中一种就可以了。为了降低成本,也可选用一些长效光亮剂如 BEO、BMP等,所谓长效就是它们的消耗量较低,对高中电流密度区有一定的光亮整平性,但远不及上述三类中间体,可它们能支持上述三类中间体的持久发光、快速整平。

PPS在高电流密度区具有优异的整平性能,特别是与丙炔醇衍生物和炔胺类化合物配合使用时,有较明显的协同效应,PPS的用量范围在 0.05～0.15 g/L。PPS-OH作用与 PPS相似,对镀层还可以产生一定的白亮效果,PPS-OH的用量为 0.1～0.4 g/L,但其消耗量比前者大 4倍,配比时要注意这一点。吡啶类衍生物是主光剂的必备组分,但其成品中不得有游离的吡啶,否则会出现不良后果。DEP是强整平剂,也是主光剂中必不可少的组分,它对结晶生长的阻化作用很强,在镀液中含量 ≥0.001 g/L就有光亮作用,性价比高;足量加入后,镀层细腻丰满。一些市售的高级镍光剂都含有该组分。TC-DEP和 PABS的作用与 DEP相似,是 DEP的衍生物,它们的整平性都很优越,但其消耗量比前者多一倍,选用时要换算。PME和 PAP整平好,出光快,但发光力不持久。如果需要乌亮,应选用 MAP、PAP等组分复配。PA(丙炔醇)的加入能增强阴极极化效应,从而获得快速出光的效果及整平良好的镀层,但过量加入会使镀层发脆且结合力差。曾经有一种市售光亮剂,3 min达到全光亮,但稍过量,镀层表面有疏水现象、挂水珠,严重时起"鳞",低区易漏镀,滚镍产品隔几天后,低区镀层有"泛红"现象。这些问题可能都是 PA引起的,因此,不主张使用或慎用 PA。PS是低区光亮剂,能提高低区的光亮性和填平性,效果明显,作为滚镀镍光亮剂,其使用配比应高一点。加入少量 ATPN就有明显的走位效果,可提高镀液的遮盖能力,促进低区镀层均匀光亮。除杂剂也就是杂质掩蔽剂,常采用配位剂。加入适当的配位剂对重金属离子进行配位,使其和镍离子一起沉积,可避免异金属离子长期积累产生不良影响,从而延长处理周期。一些配位剂作为除杂剂使用,实际上又具有去极化作用,生产中发现加入除杂剂后,因次级光亮剂过量、阴极表面发生过分极化而造成的漏镀现象就会消失。而一些进口的光亮剂里面也含有除杂剂,生产中不会出现低区漏镀现象。

下面介绍一种由多种中间体复配的镀镍光亮剂配方,供电镀生产厂家自配光亮剂参考[5]。

主光剂:

PME	30 g/L
DEP	10 g/L
PPS	30 g/L
PA	20 g/L
PS	10 g/L
配槽添加量	0.5～1.5 mL/L
消耗量	80～150 mL/(kA h)

柔软剂:

BSI	250 g/L
HPSS	5～10 g/L
MSEE	50 g/L
配槽用量	6～8 mL/L
消耗量	100～150 mL/(kA h)

3 小 结

技术力量强的电镀厂家可购买中间体自配光亮剂。用中间体自配是一项细致、耐心的工作,要经过几十次甚至上百次的试验,组分配比合理的光亮剂应该经得起工业化连续生产运行的考验。在电镀过程中,

(下转第 82页)

前两道清洗水采用流动水,后两道清洗水采用纯水;对于盲孔件、形状复杂件等不易清洗的,要求浸锌后人工加大工件清洗摆动幅度,确保清洗质量。

2.5 加强生产全过程管理

化学镀镍生产线为自动线,但必须注重人工环节的管理。如化学镀镍搅拌采用压缩空气搅拌,虽经过滤,但过滤器无清洗更换措施,难免会带入灰尘等杂物。另外化学镀操作经验性问题也很重要,化学镀镍日常维护不规范,如清洗配制用水质没有要求等,槽液中将带入其他杂质离子。针对此问题,编制了化学镀日常维护与操作工艺规程、规范操作细节,如定期清洗或更换空气过滤器、制定专门的纯水制作工艺、使用水水质国标化等。

生产规范管理后的 4个月 9次开缸中,工作生产 600多批次 25万多件零件,槽液正常生产 6至 8个周期均没有出现自分解现象。

3 结 语

通过对铝合金化学镀镍生产过程的规范控制,最终使铝合金化学镀镍溶液寿命稳定在 6个周期甚至更高,与同行只能用 3～4个周期相比,槽液使用寿命提高了 30%以上,槽液瞬间报废不再出现,产品质量得到了提高(一次交检合格率稳定在 98%以上),基本杜绝了因零件粗糙而重新返工或报废的现象,提高了生产效率,取得了较好的经济效益。

[参 考 文 献]

[1] 罗守福,胡文彬. 铝合金化学镀镍镀层的性质和工业应用[J]. 材料保护,1996,29(9):9～11.

[2] 曾华梁,吴仲达,秦月文,等. 电镀工艺手册[K]. 北京:机械工业出版社,1989.

[编辑:王 宇]

(上接第 77页)

组织老化程度比其他样品严重,且各样品的外壁组织比内壁老化严重,这与外壁温度较高有关。试样 5内壁有明显的疲劳微裂纹存在,与机组的频繁启停及冷热频繁交换有关。对叶片基体腐蚀产物和外壁垢层的能谱分析结果表明,垢层和基体成分主要是高温氧化产物,且其中硫和钒含量较高。断口的扫描电镜分析结果表明,断口具有沿晶脆性断裂特征,这与合金长期在高温和应力作用下的晶界弱化有关。燃气轮机喷嘴叶片的工作温度为 1 100 ℃,燃烧介质为重油,喷嘴叶片在高温下工作时,基体金属与沉积在工作表面的沉积盐及周围气体发生综合作用而产生热腐蚀以及硫和钒的腐蚀导致叶片强度不足是断裂失效的主要原因,疲劳微裂纹与断裂无直接关联。喷嘴叶片断裂不是正常寿命周期内的自然磨损或腐蚀损坏。

4 结 论

综上所述,燃气轮机叶片断裂的主要原因是:叶片在高温下的热腐蚀及硫和钒腐蚀引起叶片壁厚严重减薄且材料老化,导致强度不足而断裂。

[参 考 文 献]

[1] 上海交通大学编写组. 金相分析[M]. 北京:国防工业出版社,1982.

[2] 蔡玉林. 高温合金的金相研究[M]. 北京:国防工业出版社,1986.

[编辑:王 宇]

(上接第 79页)

由于协同效应等因素,各组分中间体并非等同消耗,也不按单独试验的消耗量消耗,经过一段时间后,镀液中的某些中间体组分往往出现严重过剩或不足,造成比例失调。其主要原因是销售商列出的中间体消耗量大都是单组分实验室数据,当几种组分混合在一起时,因协同效应,各消耗数据都会发生变化。所以在配制时,不但要求中间体质量优质,而且更重要的是配方要科学合理,各组分大致按设计的比例消耗。补充添加剂后,能回到原来开始状态,这样才是一个好的配方,笔者采用武汉吉和昌公司的中间体和部分进口中间体配制成的高整平、快光亮镀镍光亮剂系列产品,用于出口产品电镀,采用双层镍(直上镍工艺),在达到 7级盐雾试验合格前提下,缩短了镀双层镍时间,降低了镍耗,已取得了很好的经济效益。

[参 考 文 献]

[1] 邓 靖. 镀镍光亮剂工艺研究报告[A]. 99宁波市电镀年会论文集[C]. [出版地不详]:[出版社不详],1999.

[2] 许强龄,吴以南. 现代表面处理新技术[M]. 上海:上海科学技术文献出版社,1994.

[3] 张允诚. 电镀手册(第 2版)[K]. 北京:国防工业出版社,1997.

[4] 袁诗璞. 谈谈第四代镀镍光亮剂[J]. 电镀与涂饰,2001,20(4):47.

[5] 周长虹,王宗雄. 实用镀镍及镍合金工艺[M]. 北京:机械工业出版社,1998.

[编辑:王 宇]

relevant field, owing to their unique advantages. Meanwhile, it was believed that the development of material science, surface technology and computer analysis technology has facilitated a very good ground for the development of novel generation epoxy resin-based lubricative and wear resistant composite coatings. And it was suggested to put more attention to the development of new coating materials, optimizing of coating thickness and structure, establishment of new technology for coating preparation, and realization of synergism between solid and liquid lubrication, so as to further improve the performances of new generation epoxy resin-based lubricative and wear-resistant composite coatings.
Key words: epoxy resin; lubricative; wear resistant; composite coating

Countermeasures for Clean Production in Electroplating with Focus on Wastewater Reduction

ZHONG Zhan-tie[1], ZHAI Bao-qing[2] (1. Bureau for Environment Protection of Yuyao City, Yuyao 315400, China; 2. Center for Clean Production of Zhejiang Province, Hangzhou 310027, China). *Cailiao Baohu* 2007, 40(03), 61 ~ 64 (Ch). Wastewater reduction is one of the key goals for implementing clean production in electroplating industry. Thus the potential for wastewater reduction in electroplating was analyzed in relation to the current situation of technology and management in electroplating industry. And the corresponding countermeasures for clean production were suggested with respect to the technique improvement, drag-out reduction, clean efficiency enhancement, water management, and reuse of the electroplating wastewater.
Key words: electroplating; clean production; wastewater reduction

Adsorption of Cu^{2+} and Ni^{2+} by Manganese Mine Tailings

YANG Ming-ping, FU Yong-jian (School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201, China). *Cailiao Baohu* 2007, 40(03), 65 ~ 67 (Ch). The adsorption of heavy metal ions such as Cu^{2+} and Ni^{2+} by manganese mine tailings was studied. The adsorption dynamics of the manganese mine tailings to the Cu^{2+} and Ni^{2+} ions was analyzed. The effects of adsorbing time, concentration of Cu^{2+} or Ni^{2+}, and pH value on the adsorption capacity of the manganese mine tailings were systematically investigated, and the adsorption mechanism of and regeneration method for the manganese mine tailings were primarily discussed as well. The results showed that the manganese mine tailings, under the conditions of temperature of 25 ℃ and pH value of 7.5, had an adsorption capacity above 1.6 mg/g for both Cu^{2+} and Ni^{2+} ions, and the adsorption rates for the Cu^{2+} and Ni^{2+} ions were all over 97.5%. This indicates that the manganese mine tailings could be well used for the treatment of wastewater containing a low concentration of Cu^{2+} or Ni^{2+}. Moreover, ions ion-exchange adsorption and surface complexing adsorption were responsible for the adsorption of the Cu^{2+} and Ni^{2+} ions by the manganese mine tailings.
Key words: manganese mine tailings; adsorption capacity; heavy metal ion; adsorption mechanism

Methods for Testing and Evaluation of Local Corrosion Caused by Carbon Dioxide

WANG Ping, LI Jian-ping, MA Qun (Department of Materials and Chemical Engineering, Xi'an Polytechnical Institute, Xi'an 710032, China). *Cailiao Baohu* 2007, 40(03), 68 ~ 70 (Ch). The testing and evaluation of the local corrosion caused by CO_2 has been remaining a bottleneck in the field of corrosion science and engineering. Thus a test apparatus was developed to measure the local corrosion by CO_2, based on taking into account the features of CO_2-induced corrosion. And a method was established for the measurement of the local corrosion caused by CO_2. It was found that the apparatus could be used to accurately determine the geometric parameters concerning the local corrosion by CO_2 and to quantitatively assess the destruction degree of the local corrosion by CO_2 as well.
Key words: CO_2; local corrosion; testing; evaluation

Effect of WC Addition on Erosion-Wear Behavior of Fused Ni60 Alloy Self-Fluxing Coating

PANG You-xia, LU You-nan (School of Mechanical-Electronic Engineering, Hunan University of Science and Technology, Xiangtan 411201, China). *Cailiao Baohu* 2007, 40(03), 71 ~ 72 (Ch). A rotary-disc type erosion-wear test rig was performed to evaluate the erosion-wear behavior of two kinds of fused nickel alloy based self-fluxing coatings, Ni60 + 25% WC and Ni60 + 35% WC. The effect of the addition dosage of WC on the erosion-wear behavior of the Ni alloy-based composite coatings was investigated, while the erosion-wear mechanisms of the coatings were primarily discussed as well. It was found that the variation in the addition dosage of WC, within a range of 25% ~ 35% (mass fraction), led to little change in the erosion-wear behavior of the Ni alloy-based composite coatings, and both the two kinds of Ni alloy-based composite coatings were dominated by micro-cutting under the selected testing conditions.
Key words: erosion; fused coating; erosion-wear behavior; fused nickel based self-fluxing alloy; WC; micro-cutting

Influence of Soft Nitriding Plus Electroless Nickel Plating on Wear Resistance of Mild Steel

KONG Ling-yun, HUANG Gen-liang (School of Material Science and Engineering, Jiangsu University, Zhenjiang 212013). *Cailiao Baohu* 2007, 40(03), 73 ~ 75 (Ch). The surface of AISI-1045 steel was separately treated by electroless nickel plating, soft nitriding, and soft nitriding plus electroless nickel plating. The thickness and hardness of the resulting modified layers on the steel were measured, while their wear resistance was evaluated at a load of 100 N and 150 N as well. It was found that, as compared with the electroless nickel plating or soft nitriding alone, the modified layer on the steel subjected to dual surface strengthening, i.e., soft nitriding plus electroless plating, had a larger thickness and hardness and better wear resistance, indicating that the dual surface modification technology could be well used for the surface modfication of the mild carbon steel in engineering.
Key words: AISI-1045 steel; electroless nickel plating; soft nitriding; wear resistance

Causes Leading to Fracture Failure of Blade in the First-Phase Nozzle of Gas Turbine

CUI Xiong-hua, LIU Shu-tao, ZHU Bao-tian, WANG Cai-xia, TANG Li-ying (Technology and Material Division of Power Station, Xi'an Academy of Heat Engineering, Xi'an 710032, China). *Cailiao Baohu* 2007, 40(03), 76 ~ 77 (Ch).
Key words: Co-based alloy; fracture; failure analysis; corrosion; aging

Introduction to Brighteners and Intermediates for Contemporary Nickel Electroplating

CHEN Zheng-fa (Huaxing Electroplating Co. Ltd. of Wenling City, Wenling 317500, China). *Cailiao Baohu* 2007, 40(03), 78 ~ 79 (Ch).
Key words: nickel electroplating; intermediate; brightener

Control of the Stability of Plating Bath for Electroless Nickel Plating on Aluminum Alloy

JIA Hai-bo, NIAN De-li, YI Li-hua (No. 693 Plant, Times Electronics Company of China Astronautics, Zhumadian 463000, China). *Cailiao Baohu* 2007, 40(03), 80 ~ 82 (Ch).
Key words: aluminum alloy; electroless nickel plating; plating bath; stability

Journal of Materials Protection Vol.40 No.3, Mar. 2007
Published by Materials Protection Publishing House
Edited by Materials Protection Editorial Department
Add: 126 Baofeng Erlu, Wuhan 430030, P.R.China
Tel: +0086-27-83641679 Fax: +0086-27-83638752
http://www.mat-pro.com
E-mail: bjb@mat-pro.com
Distributor: China International Book Trading Corporatiion (P.O.Box 399)
The Foreign Subscription Rate: USD 60.00 peryear