塑性变形对热镀锌板耐蚀性的影响

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[摘 要] 为了研究塑性变形对热镀锌板耐蚀性的影响,用称量法测试了不同塑性变形状态下的热镀锌板在 5%NaCl溶液全浸腐蚀试验中的腐蚀速率,发现全浸蚀腐蚀试验 7周后,原始镀锌板质量下降 0.09%,拉伸应变为 10%的镀锌板质量下降 0.22%,腐蚀程度是前者的 2.4倍。结果表明,塑性变形会降低热镀锌板的耐蚀性,而耐蚀性的降低是由塑性变形引起的裂纹密度的增加所致。

[关键词] 热镀锌板; 腐蚀; 裂纹; 塑性变形
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0 前 言

在汽车、家电和装备制造等领域,由于对钢板耐蚀性的要求越来越高,而使用镀锌钢板逐渐替代裸板。当完整的锌镀层受到破坏而使基体表面暴露出个别不太大的部分时 (如镀锌层出现少量微裂纹),锌将作为铁 -锌原电池的阳极,以电化学作用仍然保护着基体[1,2]。但在冲压成型加工中,热镀锌板会发生剧烈而复杂的塑性变形,导致热镀锌板表面粗糙化[3]、大量镀层微裂纹萌生[4]以及局部界面开裂[5,6]等变化。这些变化是否会影响热镀锌板的耐蚀性,目前尚缺乏深入的研究和试验依据。

全浸腐蚀试验能模拟水分或氯化物滞留在钢板结合部内部所出现的腐蚀行为,为此,对处在不同拉伸应变下的热镀锌板进行了全浸腐蚀试验,运用称重法比较了不同拉伸应变下热镀锌板的耐蚀性,并运用 Sinon400NC扫描电镜及 AF-L104三维形貌仪对影响热镀锌板耐蚀性的因素进行了分析讨论。

1 试 验

1.1 材 料

所用试件材料为市售 ST04Z 120 g/m^2 双面热镀锌钢板,厚度 0.8 mm,试件为标准带肩拉伸板状件 (GB 228 - 76),屈服点 155 MPa,延伸率 24%,镀层截面形貌及 Zn、Fe在镀层与基体中的分布见图 1;镀层表面形貌见图 2。

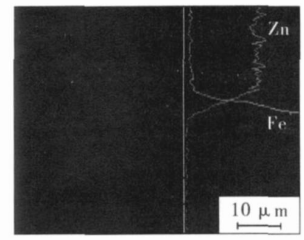

图 1 镀锌层横截面 SEM 形貌

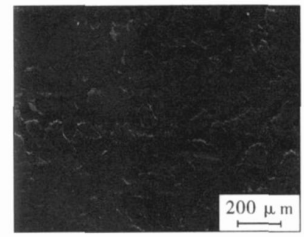

图 2 镀锌层表面 SEM 形貌

1.2 方 法

(1)单向拉伸 每 5件为 1组,共 4组试件,保留 1组作为原始试件用于试验比较,其余 3组分别拉伸至 3%, 5%, 10%应变状态,拉伸速率为 1 mm/min。拉伸后,针对平行段中部区域,用三维形貌仪测量 4组试件的表面粗糙度,并用扫描电镜观察锌层表面裂纹形态,记录典型数据,以便进一步分析影响锌板抗腐蚀性能的因素。最后,通过对试件进行线切割,以获取 30 mm长的平行段用于全浸腐蚀试验。

(2)全浸腐蚀试验 在静态腐蚀介质中进行腐蚀性能试验[7]:采用对比法,室温下用 5%NaCl作为腐蚀

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介质对拉伸应变为 4组试件进行全浸腐蚀试验,时间为 7周;全浸腐蚀试验前和试验后的每周,取试件放入丙酮溶液中用超声波清洗 10 min,清除腐蚀产物和其他污染物,并用 Sartorius BP211D型电子天平称重(精确至 0.1 mg)。每次均记录每组 5件试件的质量,以便作平均值处理,同时肉眼观察腐蚀情况。由于试验容器均为敞口,腐蚀介质中的水分会持续蒸发而改变腐蚀介质浓度,所以每天往容器中补充适量的纯净水,以维持腐蚀介质的浓度。

2 结果与讨论

(1)腐蚀试验观测结果　1周后应变为零的试件(原始板)表面仍保持光亮,腐蚀溶液没有明显变化,有应变为 3组试件表面出现小片棕黑色暗斑,腐蚀溶液均出现淡黄色絮状物;5周后,零应变试件表面也开始出现小片暗斑块,腐蚀溶液出现淡黄色絮状物,有应变试件表面棕黑色暗斑明显增大,腐蚀溶液中絮状物明显增多;7周后,零应变和 3%应变试件均有部分暗斑,且仍有局部表面保持光亮,5%和 10%应变试件整个表面均为暗斑(见图 3)。

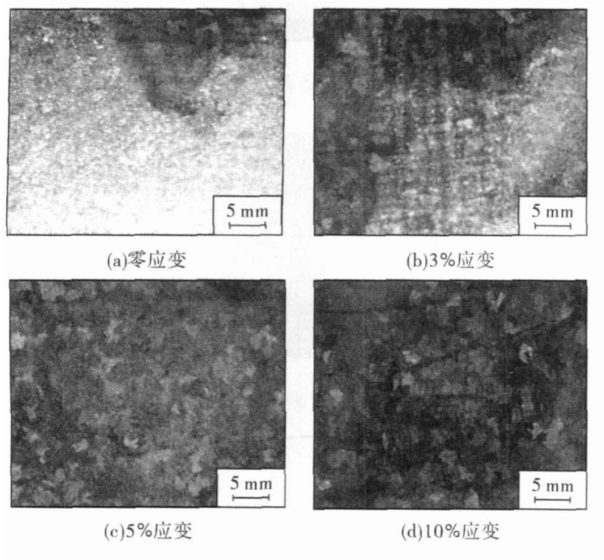

图 3　腐蚀 7周后试样表面的形貌

(2)腐蚀失重结果　为了便于比较,试件腐蚀后的失重情况采用相对质量来表示,即$\frac{m_n}{M}\times 100\%$,其中 m_n 为第 n周的试件质量,M 为腐蚀前的试件质量。腐蚀试验后各组试样的平均失重情况见图 4。

从上述结果可以发现:未经拉伸的热镀锌板耐蚀性最好;经过拉伸的热镀锌板耐蚀性明显下降,这种腐蚀现象是镀层在塑性变形过程中出现裂纹所造成的,其中受 3%和 5%拉伸应变的试件耐蚀性稍差,而且在有些阶段耐蚀性差异并不大。受 10%拉伸应变的试件与其他试件相比耐蚀性明显下降,所受的腐蚀也最为严重,这种现象也说明塑性变形越大的镀锌板耐蚀性越差。

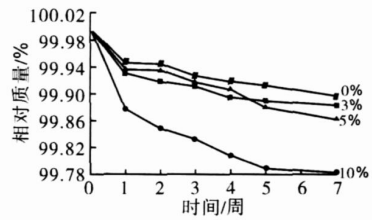

图 4　腐蚀过程中 4组试件相对质量变化

为了揭示塑性变形后影响热镀锌板耐蚀性的因素,全浸腐蚀试验之前对单向拉伸前后的热镀锌板表面粗糙度和裂纹形态进行了分析和测试,这种抗应变的粗糙度数据见表 1。从表 1可以看出,随着应变量的增加,热镀锌板的表面粗糙度也随之增加,这种粗糙化现象与镀锌层的变形断裂有关。

表 1　粗糙度测量结果

锌板拉伸应变	0	3%	5%	10%
R_a/μm	0.443 9	0.652 0	0.926 9	1.230 9
R_z/μm	2.206 4	2.755 4	4.787 6	5.110 8

在全浸腐蚀试验前发现,裂纹密度随着应变量的增加而增加(见图 5),由此可以推断,耐蚀性的变化应该与裂纹密度的变化相对应。这样,全浸腐蚀试验和

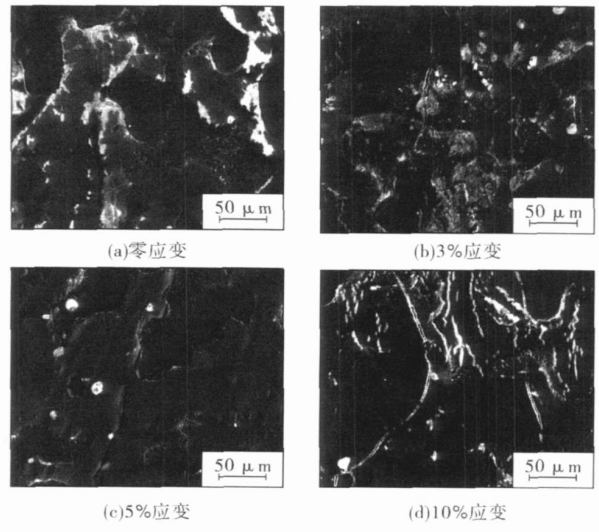

图 5　不同应变状态下镀层的表面形貌

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和工艺稳定,增加稀土添加剂即可续用。

(2)用市售的三价铬钝化液做有无稀土添加剂的钝化工艺对比试验。结果加稀土添加剂的钝化膜的耐蚀性能明显好于无稀土添加剂的钝化膜。这说明稀土添加剂用于钝化工艺有较广泛的适应性。

(3)对加稀土添加剂的蓝白和五彩钝化膜中性盐雾试验的结果表明,其耐腐蚀性能比未加稀土添加剂的提高 1～2个周期,且外观色泽更纯正艳丽。如果在氯化钾镀锌液中也加稀土添加剂,钝化后镀锌层的耐蚀效果更为明显。

(4)在低铬和无铬钝化液中添加稀土添加剂 0.4～0.8 g/L,对提高镀锌层钝化膜的耐蚀性也有明显的效果,特别是无铬钝化更加明显,但处理时间要达到 2 min。

(5)稀土钝化膜耐腐蚀机理:稀土钝化膜主要是在锌表面形成了稀土氧化物和稀土氢氧化物膜,由于稀土氧化物和稀土氢氧化物性质十分稳定,这层膜不仅降低了阴极反应速率,同时也阻碍了电子的传递与传输,从而使腐蚀延缓,稀土膜层的耐腐蚀性能优于钼、钛、镍、钴等其他金属盐的转化膜层[1]。

3 结 语

(1)氯化钾镀锌液中加入稀土添加剂 0.4～0.6 g/L,能明显提高钾盐镀锌层的防腐蚀能力,且略优于氯化镀锌层的耐蚀性。

(2)同等厚度的氯化钾镀锌层在各种三价铬蓝白钝化和五彩钝化液中,加稀土添加剂 0.3～0.5 g/L 和不加稀土的钝化膜相比,其中性盐雾试验能提高 1～2个周期,而且稀土添加剂具有广泛的使用适应性。

(3)在氯化钾镀锌工艺和镀锌层三价铬钝化工艺中都添加稀土添加剂,其耐蚀性能有较大的提高,基本能满足高档产品和高耐蚀产品对耐蚀性能的要求,但使用成本略有提高。所以使用稀土添加剂进行镀锌和钝化,必须根据产品的质量要求和对耐蚀性能要求来确定,不必盲目使用。

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裂纹形貌观测的结果就能很好地吻合。至于裂纹密度是如何成为影响热镀锌板耐蚀性的关键因素,还存在哪些影响因素,该结论是否适用于非镀锌层涂层板料等问题,还需进一步结合试验进行深入研究。

3 结 论

(1)塑性变形所导致的镀层裂纹会降低热镀锌板的耐蚀性,虽然存在阴极保护作用,但耐蚀性的变化还是可观的。

(2)塑性变形后,热镀锌的耐蚀性由变形量或镀层裂纹密度的大小所决定。

(3)对采用镀锌板经过剧烈塑性变形所获得的产品,不能完全用原始镀锌板的耐蚀性来衡量最终产品的耐蚀性。

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ted plates were bright within low region of 1.5 cm but inadequate to cover the polished scratches, and mirror bright coating was formed within remnant region.
Key words: brightener for electroplating of acidic copper; preparation; application

Corrosion Resistance of Arc-Sprayed Aluminum Coating on Aluminum Alloy
WANG Zhen, SONG Gang, LIU Li-ming (State Key Laboratory of Materials Modification & School of Material Science and Engineering, Dalian University of Technology, Dalian 116024, China). *Cailiao Baohu* 2008, 41(07), 61～65(Ch). Aluminum alloys used in marine environments are liable to pitting by Cl^-. Thus aluminum protective coating was prepared on aluminum alloys using arc-spraying technique. The corrosion behavior of the resulting Al coating was examined making use of neutral salt spray test (NSS), salt solution immersion test (SIT) in 5% NaCl, and electrochemical test. Results indicated that after being immersed at ambient temperature for 144～480 h or continuously salt-sprayed for 500～720 h, the porosities on the surface of the coating were blocked by the corrosion products, which contributed to keep off Cl^- ions, promote the formation of oxidation layer, decreasing the corrosion current and corrosion rate as well, and hence well protected the Al alloy. Moreover, after being sealed with epoxy resin, the arc-sprayed Al coating showed better corrosion resistance and protection to Al alloys.
Key words: aluminum alloys; arc spraying; aluminum coating; Cl^-; corrosion resistance

Friction and Wear Behavior of Copper-Base Powder Metallurgical Material Sliding against Cu-Cr Alloys under in the Presence of Electric Current
XU Xiao-feng, SONG Ke-xing, DU San-ming (School of Material Science & Technology, Henan University of Science & Technology, Luoyang 471003, China). *Cailiao Baohu* 2008, 41(07), 66～68 (Ch). A specially designed friction and wear tester was performed to evaluate the friction and wear behavior copper-base powder metallurgical material dry sliding against Cu-Cr alloys in the presence of electric current. The effects of current density, sliding velocity, and contacting pressure on the friction and wear behavior of the frictional pair were systematically investigated. Results indicated that strong interactions existed among the electric current, sliding velocity, and contacting pressure in terms of their effects on the friction and wear behavior of the Cu-base metallurgical material. Namely, due to arc-induced damage, the frictional pair experienced more severe friction and wear in the presence of current, while the introduction of a certain contacting pressure helped to realize a stable surface contact of the frictional pair therein. Moreover, for the locomotives with high-speed and large power, the introduction of a certain contacting pressure was beneficial to keeping good current-loading quality and retarding the formation of electric arc.
Key words: copper-base powder metallurgical material; friction and wear behavior; current-loading

Effect of Plastic Deformation on Corrosion Resistance of Galvanized Steel Sheets
ZHANG Kai[1,2], CHEN Guang-nan[2], ZHANG Kun[2] (1. Graduate School, Chinese Academy of Sciences, Beijing 100080, China; 2. Laboratory for Surface Modification, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100080, China). *Cailiao Baohu* 2008, 41(07), 69～70 (Ch). The corrosion rates of galvanized steel sheets with different plastic deformation states subjected to fully immersing corrosive test in 5% NaCl solution were measured using weight-loss method, aiming at revealing the effect of plastic deformation on the corrosion resistance of the galvanized steel sheets. It was found that after 7-week corrosion test, the galvanized steel sheets without strain recorded a weight-loss of 0.09%, and that with 10% strain had a weight-loss of 0.22%, which was about 2.4 times as much as that of the former. This indicated that plastic deformation leads to worsening in the corrosion resistance of the galvanized steel sheets, which could be attributed to the increased cracking of the coating induced by plastic deformation.
Key words: galvanized steel sheet; corrosion; plastic deformation; cracling

Technology for the Preparation of Tin-Bronze Passivation Coating with Good Corrosion Resistance
BIAN Yun-xia, YANG Yan-qin (Honglin Machinery Factory of Ninth Academy, China Aerospace Science & Industry Corporation, Xiaogan 432000, China). *Cailiao Baohu* 2008, 41(07), 71～72 (Ch). In order to improve the corrosion resistance of the passivation coating on tin bronze, the bath composition of the passivation liquid was optimized by orthogonal test based on traditional technology for passivation of copper. The effects of process parameters on the appearance and corrosion resistance of the passivation coating were investigated. As the results, the optimal bath composition was determined as 150 g/L $K_2Cr_2O_7$, 15 ml/L H_2SO_4, and 1 g/L NaCl, while the optimized process conditions were suggested as room temperature and time of 10～15 s. It was feasible to prepare bright and flamboyant passivation coatings with uniform color and good adhesion strength by adopting the optimized passivation technology, and no air bubbles were observed on the passivation coating after dropping test for 30 s.
Key words: tin bronze; passivation; passivation; corrosion resistance

Line-Like Defect on Continuously Galvanized Steel Sheets
LIU Xi-lin[1], XIAO Bin[2], SU Xu-ping[2], LIU Xue-liang[1], WANG Jian-hua[2], HE Meng[2] (1. Cold-Rolling Mill of Lianyuan Steel Co. Ltd., Loudi 417009, China; 2. Key Laboratory of Materials Design and Preparation Technology of Hunan Province, Xiangtan University, Xiangtan 411105, China). The causes leading to special line-like defects on continuously galvanized steel sheets were analyzed. It was pointed out that dross was taken out from zinc-pot by running strip and scratch the surface of the steel sheets under the force of air knife. This leaded to the generation of smaller granules of zinc in the defect area as compared to the normal area and differences in the reflectivity of the defect area and normal area as well, subsequently generating line-like defects. It was suggested to decrease the amount of dross in the zinc-pot and adjust the parameter of air knife so as to control and avoid special line-like defect, which had been found to be effective in production.
Key words: continuously galvanized sheet; special line-like defect; zinc-pot

Applied Technology for Rare Earths in Surface Treatment of Metals Ⅴ——Effect of Rare Earths on Corrosion Resistance of Zinc Coating from Potassium Chloride Bath and Passivation Coating of Chromium
YANG Sheng-qi (Xinxin Institute of Yixing City for Applied Technology of Rare Earths, Yixing 214246, China). Rare earths were used as additives for zinc plating from KCl bath and tri-valence chromium passivation of the zinc coating. It was found that the introduction of the rare earths as additives contributed to significantly improve the corrosion resistance of the Zn coating.
Key words: zinc plating from KCl bath; tri-valence Cr passivation; rare earth additive; corrosion resistance

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