第35卷第11期　　焊 接 学 报　　Vol. 35 No. 11
2014年11月　TRANSACTIONS OF THE CHINA WELDING INSTITUTION　November 2014

湿热环境对 Zn-2Al 钎料显微组织及力学性能的影响

吕登峰[1]， 龙伟民[1]， 张冠星[1]， 王星星[1]， 何 鹏[2]
(1. 郑州机械研究所 新型钎焊材料与技术国家重点实验室，郑州 450001；
2. 哈尔滨工业大学 先进焊接与连接技术国家重点实验室，哈尔滨 150001)

摘 要： 针对 Zn-2Al 钎料在湿热环境下的时效劣化行为，通过高温高湿加速腐蚀试验模拟了湿热大气环境，研究了在恒定湿热环境下腐蚀时间对钎料显微组织、力学性能及润湿性能的影响. 结果表明，钎料表观腐蚀深度与腐蚀时间呈线性关系，水汽腐蚀主要发生在晶界处，当腐蚀达到一定程度后，钎料内形成了大量的腐蚀裂纹和腐蚀孔洞. 晶间腐蚀是晶内富锌 η 相为阴极，晶界处富铝 α 相为阳极而溶解的电化学腐蚀. 钎料的抗拉强度、塑性和韧性均随着腐蚀时间的延长而降低，钎料在 1060 铝板上的润湿面积随着腐蚀时间的增加而急剧减小.

关键词： 锌铝钎料； 湿热环境； 晶间腐蚀； 力学性能； 显微组织
中图分类号： TG 425　**文献标识码：** A　**文章编号：** 0253－360X(2014)11－0063－04

0 序 言

药芯 Zn-Al 钎料是 Cu/Al 连接最常用的钎料，具有成本低、塑性优良、易加工成型、焊接效率高等优点，一方面避免了 Sn-Pb 系、Cd-Zn 系钎料中元素 Pb 和 Cd 对环境的危害，另一方面解决了用 Sn-Zn 系钎料所得到的 Cu/Al 接头强度较低、耐腐蚀性差的问题，同时钎焊温度比 Al-Si 钎料低，铝母材不易过热或过烧[1-3].

然而，工程应用中发现，药芯 Zn-Al 钎料在较湿热的环境中会发生明显的时效劣化行为，脆性明显增大，导致钎料铺展性、润湿性及填缝性严重恶化，此现象给实际生产和工程应用带来了极大的经济损失和不便，从而制约其广泛应用.

目前国内外关于药芯 Zn-Al 钎料时效劣化的理论研究报道相对较少，该钎料在湿热环境中的时效劣化机理尚不清楚，钎料加工工艺优化缺少理论支撑. 因此，文中选用 Zn-2Al 钎料为研究对象，通过高温高湿加速腐蚀试验模拟湿热大气环境，考察 Zn-2Al 钎料的组织和性能随腐蚀时间的变化规律，进一步分析其腐蚀机理，为药芯 Zn-Al 钎料的加工工艺优化提供理论指导.

收稿日期： 2013－06－05
基金项目： 国家高技术研究发展计划资助项目(863 计划，2012AA040208)；哈尔滨工业大学先进焊接与连接国家重点实验室开放课题研究资助；郑州市重大科技专项(131PZDZX032)；华南理工大学国家金属材料近净成形工程技术研究中心开放基金资助项目(2013001)

1 试验方法

试验中所用钎料为 Zn-2Al(质量分数，%)焊丝，其制备过程如下：将高纯锌(99.995 %)、高纯铝(99.9 %)以及稀土按比例配料装入到石墨坩埚中，用高频感应加热炉进行熔炼，浇铸成直径为 50 mm 的铸锭. 将铸锭置于电阻炉中在 320 ℃温度下保温 4 h 进行均匀化退火处理，然后经过挤压、拉拔等工艺，最终得到直径为 2.0 mm 的钎料丝.

采用 1060 铝板作为钎料润湿试验母材，其尺寸为 40 mm × 40 mm × 2 mm，试验前先用 400 号碳化硅砂纸对其表面进行打磨，保证试样表面平整、光洁，再用丙酮去除表面油污，然后依次用清水和无水乙醇进行超声波清洗、热空气干燥后待用.

将 Zn-2Al 钎料放入老化试验箱中，试验采用的湿热环境腐蚀条件为：$RH = 100\%$，温度 116 ℃，腐蚀时间设定为 3，5，8，10，12，16，20 h. 采用 ZEISS AXIOSCOPE 金相显微镜和 AIS2100 扫描电镜(SEM)对 Zn-2Al 钎料腐蚀前后显微组织进行观察. 采用 C45.105 万能拉伸试验机对 Zn-2Al 钎料的力学性能进行测试. 根据国家标准 GB/T 11364—2008《钎料铺展性及填缝能力试验方法》，使用 Zn-2Al 钎料配合 $CsF-AlF_3$ 钎剂对 1060 铝板进行润湿性试验. 试验时取 0.1 g 钎料，在母材上加热到 490 ℃，钎料熔化后保温时间 60 s，在空气中冷却到室温. 使用 AutoCAD 软件计算钎料润湿铺展面积，取五次试验均值作为最终结果. 采用弯折试验法对 Zn-2Al 钎料的韧性进行评定，通过考察钎料发生断裂时的弯折

次数来评估其韧性的优劣，以 ϕ 2.0 mm × 100 mm 钎料的中点为弯折点对其进行对折，每种试样进行 20 次弯折试验，取其断裂周次平均值.

2 结果与分析

2.1 腐蚀过程中的微观组织演化

对不同腐蚀时间下 Zn-2Al 钎料微观组织形貌进行分析，结果如图 1 所示. 可以看出，与原始态钎料显微组织相比，经过腐蚀钎料表面层截面组织发生了明显变化，在近表层区域，出现大量沿钎料长度方向的狭长腐蚀孔洞.

随着腐蚀时间的增加，腐蚀深度增加，腐蚀孔洞尺寸逐渐增大，孔洞相连形成腐蚀裂纹；当膜内出现贯通的微裂纹时，构成 O_2 和 H_2O 的扩散通道，水蒸汽可直接与基体发生反应，增大钎料的腐蚀深度. 随着腐蚀深度的增大，腐蚀产物将慢慢从钎料的表层剥离，逐渐形成剥离区.

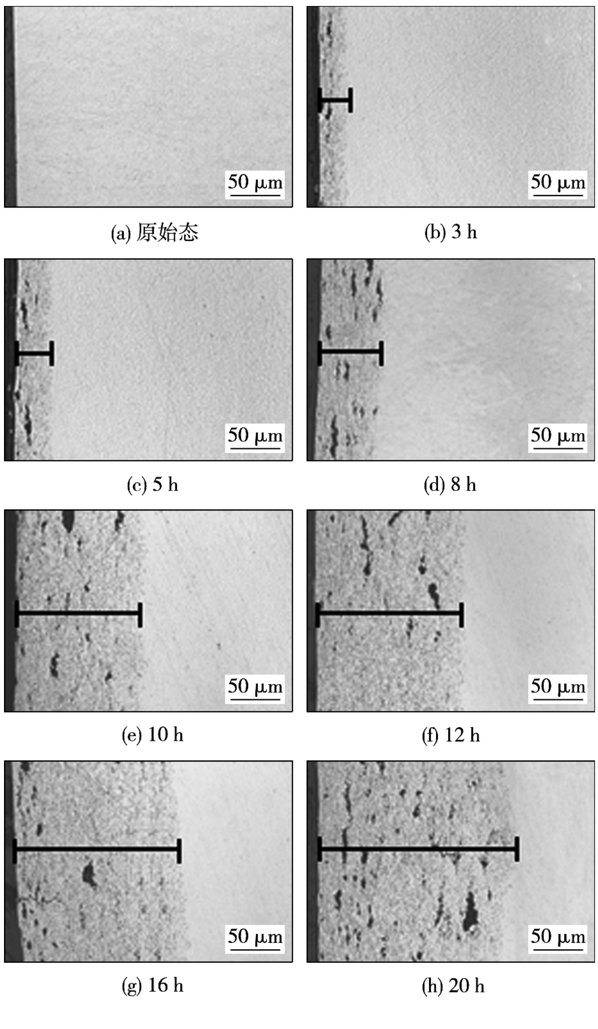

图1 不同腐蚀时间条件下 Zn-2Al 钎料截面显微组织

Fig. 1 Cross-sectional microstructure of Zn-2Al filler metal after corrosion at different time

根据图 1 测量出不同腐蚀时间条件下钎料表层腐蚀深度，如图 2 所示.

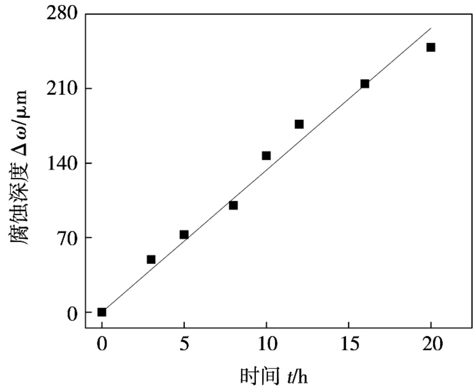

图2 腐蚀深度随腐蚀时间的变化关系

Fig. 2 Variation of corroding depth with increasing corroding time

腐蚀 3 h 后钎料表层腐蚀深度约 50 mm，随腐蚀时间增加，腐蚀深度急剧增大，20 h 后腐蚀深度可达 249 mm. 对腐蚀深度与腐蚀时间的变化关系进行线性回归分析，得到腐蚀深度随腐蚀时间的变化关系为

$$\Delta\omega = at \tag{1}$$

式中：$\Delta\omega$ 为腐蚀深度(mm)；常数 a = 13.34；t 为时间(h)，式(1)的相关性系数为 0.99. 从式(1)可以看出，在文中恒定温度湿热条件下，Zn-2Al 钎料表层腐蚀深度与腐蚀时间呈线性关系，腐蚀时间越长腐蚀深度越深，Zn-2Al 钎料的腐蚀没有自抑制倾向.

图 3 为 Zn-2Al 钎料在湿热环境下腐蚀 12 h 的扫描电镜形貌. 根据 Zn-Al 合金相图[4]，Zn-2Al 钎料在常温下的组织由富铝 α 相和富锌 η 相组成. 为了进一步研究腐蚀后 Zn-2Al 钎料晶界和晶内两个区域的组织变化，对腐蚀 12 h 的 Zn-2Al 钎料进行了能谱分析，结果如表 1 所示.

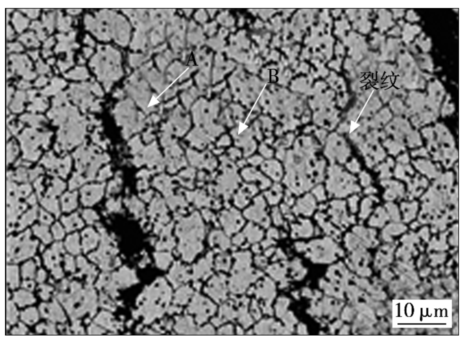

图3 腐蚀时间 12 h 的 Zn-2Al 钎料 SEM

Fig. 3 SEM morphology of Zn-2Al filler metal after water vapor corroded for 12 h

表 1　Zn-2Al 钎料不同区域能谱分析(质量分数，%)

Table 1　EDS analysis of different zones of Zn-2Al filler metal in Fig. 3

区域	Zn	Al	O
A	97.52	0.88	1.60
B	61.86	14.22	23.92

由图 3 和表 2 可以看出：晶界被腐蚀呈网状形态；白色的晶内区域(标记为 A 处)为富 Zn 的 η 相，晶界区域(标记为 B 处)为富铝的 α 相；晶界区域氧含量明显偏高，晶界 α 相发生严重的氧化，说明湿热环境中 Zn-2Al 钎料优先在晶界处发生了氧化腐蚀；晶界腐蚀后造成沿晶开裂形成大量的腐蚀微孔洞，使钎料表面组织疏松，腐蚀微孔洞逐渐长大并串联形成裂纹．这与图 1 所示宏观裂纹分析结果一致．

在湿热环境中，Zn-Al 合金晶间腐蚀的主导原因是电化学腐蚀[4-6]．根据 Zn-Al 合金相图，382 ℃时铝在锌中的固溶度最大，约 1.0%，而室温下仅为 0.03%左右(质量分数)，表明 Al 原子倾向存在于原子排列混乱且结构疏松的晶界上，即它在 η 相中是不稳定的，锌中加入一定量的铝后，就会在晶界上聚集析出富铝 α 相．Zn-2Al 钎料中 Al 的标准电位(－1.660 V)比 Zn(－0.763 V)低，在湿热环境中，钎料内形成了微电池，致使 η 相作为阴极，α 相作为阳极而优先溶解，从而引起晶间电化学腐蚀[4-6]．一般来说，铝在中性溶液中容易钝化，但 Zn-2Al 钎料发生电化学腐蚀时，阴极发生吸氧反应，即

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \quad (1)$$

使 OH^- 过剩，导致晶界区的 pH 值升高，氧化铝在碱性介质中是不稳定的，从而破坏了 α 富铝相氧化膜的保护作用，又加速了作为阳极的 α 相溶解，促使晶间腐蚀进一步反应[5-7]．

研究表明，应力的存在也能加剧 Zn-Al 钎料在湿热环境中的晶间腐蚀[5,8,9]．应力的来源主要有三方面：(1) 钎料经过挤压、拉拔等工艺后的残余应力；(2) 钎料的腐蚀产物由 ZnO 和 α-Al_2O_3 组成[6]，而这两种氧化物又比消耗掉的纯金属体积大，随着腐蚀的进行，钎料晶界区腐蚀产物的累积导致其体积膨胀，产生局部内应力，增强晶界区活性，使得在晶界区产生应力，促进晶界腐蚀进一步发生；(3) 钎料在腐蚀初期氧化膜生长时表现出明显的择优取向，当氧化膜在基体金属上取向生长时，造成晶格畸变，导致膜内产生应力．在应力和水汽的共同作用下，易在晶界处形成腐蚀裂纹，裂纹沿晶界扩展，引起 Zn-2Al 钎料晶间腐蚀，导致其脆化．

2.2　腐蚀过程中的钎料力学性能变化

图 4 为 Zn-2Al 钎料的抗拉强度和断后伸长率在恒定湿热温度条件下随腐蚀时间的变化曲线．不同腐蚀时间的 Zn-2Al 钎料发生断裂时弯折次数如图 5 所示．

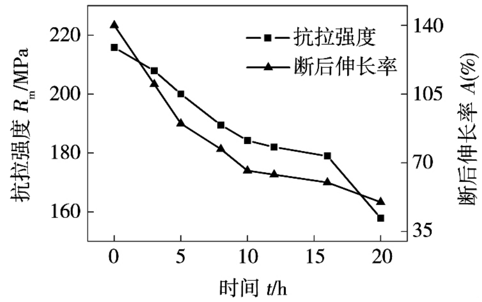

图 4　不同腐蚀时间的 Zn-2Al 钎料抗拉强度及断后伸长率

Fig. 4　Tensile strength and elongation of Zn-2Al filler metal corroded for different times

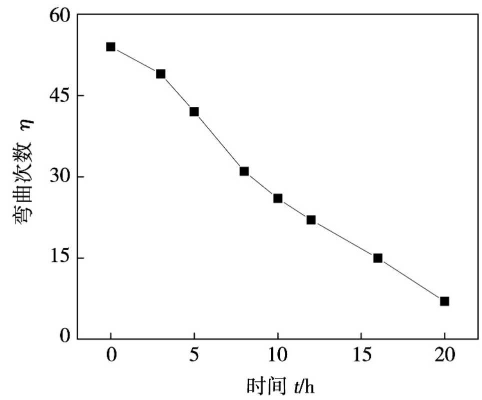

图 5　不同腐蚀时间的 Zn-2Al 钎料发生断裂时弯折次数

Fig. 5　Bending fracture cycles of Zn-2Al filler metal corroded for different times

从图 4 和图 5 可以看出，随着腐蚀时间的延长，Zn-2Al 钎料的抗拉强度、断后伸长率和弯折断裂次数都降低．腐蚀 20 h 后，Zn-2Al 钎料抗拉强度由原始态的 215 MPa 下降到 157 MPa，降低了 27%左右；腐蚀时间超过 16 h 时，钎料的强度下降得更严重；断后伸长率也由原始态的 140%下降到 50%，说明钎料的塑性严重恶化．钎料断裂时弯折次数随着腐蚀时间的延长而减少，说明钎料脆性增大，抗疲劳性能恶化．

Zn-2Al 钎料腐蚀后力学性能下降的主要原因是钎料在湿热环境中发生的晶间腐蚀使其外层组织变疏松，晶界处产生局部微裂纹，拉伸时局部微裂纹向钎料内部迅速扩展，钎料塑性和韧性下降，导致脆性断裂发生．另一可能原因是晶间腐蚀导致的晶粒之间的结合力减弱，随着腐蚀时间的延长，微裂纹和孔

洞相互连接,形成长裂纹,在内外应力作用下晶粒沿晶界开裂,导致力学性能下降.

2.3 钎料润湿性变化

图 6 为经过腐蚀后 Zn-2Al 钎料在 1060 铝板上润湿面积的变化曲线. 可以看出随着腐蚀时间的增加,钎料润湿铺展面积急剧减小. 在腐蚀时间超过 10 h 后,Zn-2Al 钎料对 1060 铝板的润湿性很差,铺展面积从原始态的 210 mm^2 降低到 32 mm^2. 说明腐蚀后钎料的钎焊工艺性已严重恶化. 钎焊工艺性恶化的主要原因是 Zn-2Al 钎料在湿热环境中腐蚀后生成了 ZnO 和 α-Al_2O_3 组成的氧化物,这些氧化物熔点较高,附着在界面形成阻流点,导致钎料对 1060 铝板的润湿性变差.

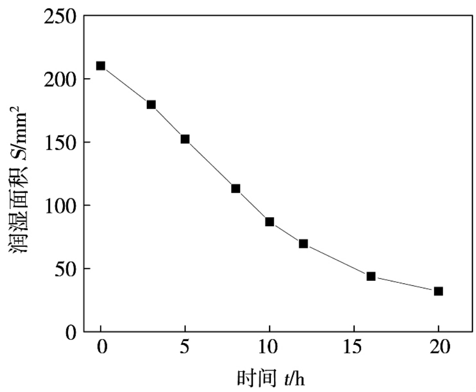

图 6 不同腐蚀时间的 Zn-2Al 钎料润湿面积变化曲线

Fig. 6 Spreading areas of Zn-2Al filler metal corroded for different times

3 结 论

(1) 湿热环境下 Zn-2Al 钎料腐蚀主要发生在晶界处,当腐蚀达到一定程度后,形成了大量的腐蚀裂纹和腐蚀孔洞.

(2) Zn-2Al 钎料表层腐蚀深度与腐蚀时间呈线性关系.

(3) Zn-2Al 钎料的晶间腐蚀过程是晶内的富锌 η 相作为阴极,晶界的富铝 α 相作为阳极而溶解的电化学腐蚀过程,应力的存在加剧了腐蚀的进行.

(4) Zn-2Al 钎料抗拉强度、塑性及韧性均随着腐蚀时间的延长而降低,且钎料在 1060 铝板上的润湿面积随着腐蚀时间的增加而急剧减小.

参考文献:

[1] 张 满,薛松柏,戴 玮,等. Ag 元素对 Zn-Al 钎料性能的影响 [J]. 焊接学报, 2010, 31(10): 73 - 76.
Zhang Man, Xue Songbai, Dai Wei, *et al*. Effect of Ag on properties of Zn-Al brazing filler metal [J]. Transactions of the China Welding Institution, 2010, 31(10): 73 - 76.

[2] 杨金龙,薛松柏,姬 峰,等. Ti 元素对 Zn-22Al 钎料组织和性能的影响 [J]. 焊接学报, 2010, 31(11): 93 - 96.
Yang Jinglong, Xue Songbai, Ji Feng, *et al*. Effect of Ti on properties and microstructure of Zn-22Al brazing filler metal [J]. Transactions of the China Welding Institution, 2010, 31(11): 93 - 96.

[3] 张 满,薛松柏,姬 峰,等. $CuAl_2$ 相对铜铝钎焊接头组织与性能的影响 [J]. 焊接学报, 2011, 32(2): 93 - 96.
Zhang Man, Xue Songbai, Ji Feng, *et al*. Effect of $CuAl_2$ on properties and microstructure of Cu/Al brazed joint [J]. Transactions of the China Welding Institution, 2011, 32(2): 93 - 96.

[4] 孙连超,田荣璋. Zn-Al 二元合金晶间腐蚀问题的研究 [J]. 中南矿冶学院学报, 1988, 19(2): 171 - 177.
Sun Lianchao, Tian Rongzhang. An investigation on intergranular corrosion in cast Zn-Al binary alloys [J]. Journal of Central South Institution of Mining and Metallurgy, 1988, 19(2): 171 - 177.

[5] 孙连超,田荣璋. 锌及锌合金物理冶金学 [M]. 长沙: 中南工业大学出版社, 1994.

[6] Devillers L P, Niessen P. The mechanism of intergranular corrosion of dilute zinc-aluminium alloys in hot water [J]. Corrosion Science, 1976, 16(4): 243 - 247.

[7] Yan X Q, Liu S X, Long W M, *et al*. The effect of homogenization treatment on microstructure and properties of ZnAl15 solder [J]. Materials and Design, 2013, 44: 440 - 445.

[8] 龙伟民,张 雷,黄俊兰,等. 药芯锌铝焊丝脆性断裂浅析 [J]. 材料科学与工艺, 2009, 17(s1): 200 - 204.
Long Weimin, Zhang Lei, Huang Junlan, *et al*. Elementary analysis on the brittle fracture of flux-cored Zn-Al wire [J]. Materials Science and Technology, 2009, 17(s1): 200 - 204.

[9] Yan X Q, Liu S X, Long W M, *et al*. Stress corrosion crack of ZnAl15 alloys in hot and humid environment [J]. Materials Letters, 2013, 93: 183 - 186.

作者简介: 吕登峰,男,1987 年出生,硕士研究生. 主要研究方向为铝钎焊材料的加工工艺及钎焊工艺. Email: lvdengfeng88@126.com

通讯作者: 龙伟民,男,研究员,博士研究生导师. Email: brazelong@163.com.

tion results showed that horizontal clamping gap had greater influence on welding spot than vertical clamping gap, and the maximum stress at each single welding spot reduced with the increasing of welding spots quantity and effective connection area.

Key words: spot welding; welding deviation; stress and strain

Process and performance of cold metal transfer spot plug welding between aluminum alloy and bare steel HUANG Qian[1], CAO Rui[1], ZHU Haixia[1], CHEN Jianhong[1], WANG Peichung[2] (1. State Key Laboratory of Advanced Processing and Recycling of Non-ferrous Metals, Lanzhou University of Technology, Lanzhou 730050, China; 2. GM R&D Center, Warren MI 48090, USA). pp 59 – 62

Abstract: Cold metal transfer (CMT) spot plug welding of Al6061 and bare steel was carried out by using $AlSi_5$ filler metal. Using orthogonal test method to optimize process parameters, the microstructure and mechanical properties of welded joint were investigated with optical microscope, scanning electron microscopy and universal tensile testing machine. The results show that the welded joint between Al6061 and bare steel could obtain satisfied weld appearance and performance using CMT method. The sequence of significance of process parameters was hole size in bare steel sheet, spot welding time and wire feed speed. The results also indicated that the typical spot welding-brazing joint, which consisted of brazing zone and the welding zone, could be performed; the pore was the main defect in the welded joint; the maximum shear strength of the joint was more than 4 kN with tear fracture.

Key words: cold metal transfer spot plug welding; Al/bare steel sheet; orthogonal test; mechanical property

Effect of hygrothermal environment on microstructure and mechanical properties of Zn-2Al filler metal LÜ Dengfeng[1], LONG Weimin[1], ZHANG Guanxing[1], WANG Xingxing[1], HE Peng[2] (1. State Key Laboratory of Advanced Brazing Filler Metals & Technology, Zhengzhou Research Institute of Mechanical Engineering, Zhengzhou 450001, China; 2. State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin 150001, China). pp 63 – 66

Abstract: The aging degradation behavior of Zn-2Al filler metal in hot and humid environment was studied. High temperature and high humidity accelerating test was conducted to simulate the hygrothermal atmospheric corrosion condition. The influence of corroding time on the microstructure, mechanical properties and wettability of Zn-2Al filler metal was investigated. The experimental results displayed linear relationship between corroding depth and corroding time. Water vapor corroding primarily occurred at grain boundaries, and when corrosion reached a certain extent, corrosion cracks and corrosion holes formed. This intergranular corrosion was electrochemical corrosion with the intragranular zinc-rich η phase as the cathode but the aluminum-rich α phase as the anode that dissolute at grain boundary. The tensile strength, plasticity and toughness of Zn-2Al filler metal decreased, and the wetting area of Zn-2Al filler metal on 1060 aluminum sheet also decreased sharply with the increase of corroding time.

Key words: Zn-Al filler metal; hygrothermal environment; intergranular corrosion; mechanical properies; microstructure

Effect of salt spray environment on mechanical properties of aluminum welded joints treated with ultrasonic impact
LI Da[1], WANG Xiaomin[2], SUN Bing[1], CHEN Hui[1], LIU Liyun[1], LI Peng[3] (1. College of Material Science and Engineering, Southwest Jiaotong University, Chengdu 610031, China; 2. College of Life Science and Engineering, Southwest Jiaotong University, Chengdu 610031, China; 3. CSR SIFANG CO., LTD., Qingdao 266111, China). pp 67 – 70

Abstract: The Al6005 welded joint was treated with ultrasonic impact and the residual stress of the treated and untreated specimens was measured. The results showed that uniform compressive stress distributed in the weld and heat-affected zone (HAZ) after the joint was treated with ultrasonic impact. The properties of welded joint were discussed after salt spray corrosion test. The results indicated that the treated joint produced less corrosion product after corrosion for different times. The hardness of the weld metal and HAZ increased after the joint was treated with ultrasonic impact. The thickness of hardened layer in the weld metal and HAZ was 1.5 mm and 2.1 mm, respectively. The thickness of hardened layer maintained at 0.9 mm after corrosion for 14 days. Besides, the welded joint after treatment could have better mechanical properties than untreated joints.

Key words: aluminum welded joints; ultrasonic impact; salt spray corrosion; residual stress; mechanical property

Section contour analysis of probe during friction stir welding
ZHAO Huaxia, MENG Qiang, DONG Jihong, DONG Chunlin, LUAN Guohong (Beijing Aeronautical Manufacturing Technology Research Institute, Aviation Industry Corporation of China, Beijing 100024, China). pp 71 – 74, 78

Abstract: Based on the section analysis of three-dimensional model of friction stir welding, the moving expressions about feature points on section contour of probe were established. According to the basis of mathematical analysis, the forming mechanisms of hook, cold overlap-defect and onion structure were revealed. In the light of the above research results, the optimization idea of probe shape was proposed. Considering improving plastic metal migration behavior, the s-line of large thickness aluminum alloy friction stir welded butt joint and cold overlap-defect in lap joint of stringer and plate was effectively eliminated by three aspects design. The results provide technical support for the development of friction stir welded products.

Key words: friction stir welding; section analysis; hook; cold overlap-defect

Microstructure evolution during refill friction spot welding of aluminium-lithium alloy ZHANG Chengcong[1], FENG Xiaosong[1], GUO Lijie[1], ZUO Yuting[2] (1. Technical Center, Shanghai Aerospace Equipments Manufacturer, Shanghai 200245, China; 2. National Center of Analysis for Nonferrous