第 32 卷 第 7 期 焊 接 学 报 Vol. 32 No. 7
2011 年 7 月 TRANSACTIONS OF THE CHINA WELDING INSTITUTION July 2011

铋和磷元素对 Sn-Zn-RE 电子微连接钎料组织与性能的影响

杜长华[1]， 尹立孟[2]， 苏 鉴[1]， 陈 方[1]， 赵海建[1]
(1. 重庆理工大学 材料科学与工程学院，重庆 400054;
2. 重庆科技学院 冶金与材料工程学院，重庆 401331)

杜长华

摘 要：制备了含不同 Bi，P 元素的(Sn-9Zn0.05Ce)*x*Bi 和(Sn-9Zn0.05Ce)*x*P 钎料合金，观察并分析了钎料的显微组织形貌，测试了钎料的抗拉强度、断后伸长率以及维氏硬度．结果表明，添加 Bi 元素能显著提高 Sn-9Zn0.05Ce 钎料合金的抗拉强度和硬度，但同时会明显降低其断后伸长率，而添加微量 P 元素对钎料的抗拉强度与硬度没有明显的影响．此外，添加 Bi 和 P 元素均能促使钎料析出针状或颗粒状富锌相，富锌相随 Bi 或 P 元素添加量的增加而增多，并因此影响钎料合金的力学性能．

关键词：锡 - 锌钎料； 显微组织； 抗拉强度； 硬度
中图分类号：TG113 文献标识码：A 文章编号：0253 - 360X(2011)07 - 0017 - 04

0 序 言

目前，国内外研究和应用相对成熟的无铅钎料包括 Sn-Cu，Sn-Ag 和 Sn-Ag-Cu 系等合金．然而，与传统共晶与近共晶 Sn-37Pb 钎料合金相比，这几种合金仍然存在着熔点偏高、成本偏高以及工艺性能欠佳等系列缺点．Sn-9Zn 二元共晶合金的熔点为 198 ℃，与 Sn-37Pb 钎料的熔点(183 ℃)最为接近，且锌资源丰富，其成本相对低廉，同时该钎料具有较好的力学性能．因此，Sn-9Zn 被认为是 Sn-Pb 共晶钎料的另一种非常具有潜力的替代合金[1,2]．遗憾的是，Sn-Zn 系钎料合金本身也存在着高温下易氧化，与基板间的润湿性较差等问题．近期研究表明，添加 0.05%(质量分数，下同)稀土元素 Ce 可以有效抑制锌的选择性氧化，并改善钎料的润湿性能[3,4]．

作者在前人工作的基础上，制备了不同 Bi，P 元素含量的(Sn-9Zn0.05Ce)*x*Bi 和(Sn-9Zn0.05Ce)*x*P 钎料合金，研究了微量添加元素 Bi，P 对 Sn-9Zn0.05Ce 钎料微观组织、抗拉强度与硬度等力学性能的影响．以期为 Sn-9Zn 系新型钎料合金的研究和开发提供重要的参考依据和理论指导．

收稿日期：2010 - 05 - 21
基金项目：重庆市重点自然科学基金资助项目(2006BA4034)；重庆科技学院校内科研基金项目(CK2010B23)

1 试验方法

1.1 钎料的准备

钎料的制备原料为 99.95% Sn，99.99% Zn，99.7% Ce，99% Bi，P > 99.5%．按表 1 所示标称成分配料后，在保护性气氛下置于不锈钢坩埚中加热熔炼，熔炼温度约 400 ℃．待物料充分熔化后充分搅拌均匀，将液态钎料合金在不锈钢模中浇铸成锭．

表 1 钎料合金的标称成分(质量分数，%)
Table 1 Nominal composition of solders

序号	标称成分	序号	标称成分
1	Sn-9Zn0.05Ce	5	(Sn-9Zn0.05Ce)0.01P
2	(Sn-9Zn0.05Ce)2Bi	6	(Sn-9Zn0.05Ce)0.02P
3	(Sn-9Zn0.05Ce)3Bi	7	(Sn-9Zn0.05Ce)0.03P
4	(Sn-9Zn0.05Ce)4Bi		

1.2 显微组织观察

将钎料切取成尺寸为 5 mm × 5 mm × 10 mm 的试样，用环氧树脂镶嵌后，依次采用 200 号 ~ 2500 号系列砂纸进行粗磨与精磨后抛光，腐蚀液选用 5% 硝酸酒精溶液，腐蚀时间为 5 s．采用 Leica DM 2500P 观察钎料合金的显微组织．

1.3 拉伸性能测试

将钎料先在不锈钢模具中浇铸成直径 15 mm 的圆棒，再加工成直径 10 mm 的标准拉伸试样．采

用 ZDM-30T 液压万能试验机进行拉伸试验，加载速率为 2 mm/min. 试样断裂后逐一精细测量并计算其断后伸长率，同时采用 Philips ESEM × L30-FEG 扫描电镜观察断口形貌.

1.4 硬度测试

将钎料切取成尺寸为 10 mm × 10 mm × 5 mm 的试样，精细磨平抛光后，采用 MHV2000 型数字显微硬度仪测量硬度. 每个试样至少测量五个点，结果取其平均值.

2 试验结果及讨论

2.1 铋对 Sn-9Zn0.05Ce 合金显微组织的影响

图 1 给出了(Sn-9Zn0.05Ce) xBi 钎料合金的光学显微组织形貌，图 1 中灰色部分为 β-Sn 相，黑色针状或球状部分为富锌相. 从图 1 中可以发现，当在 Sn-9Zn0.05Ce 中添加铋以后，富锌相析出明显，且钎料中富锌相随铋含量的增加而增多，而富锌相的分布也随铋含量的增加变得更加杂乱无序. 文献[5,6]在 Sn-9Zn 中加入 2% ~ 10% 的铋时，发现合金中也会形成富锌的初生相，并呈粗大的针状相或细小的条状颗粒相，这与文中在 Sn-9Zn0.05Ce 中添加铋的研究结果一致.

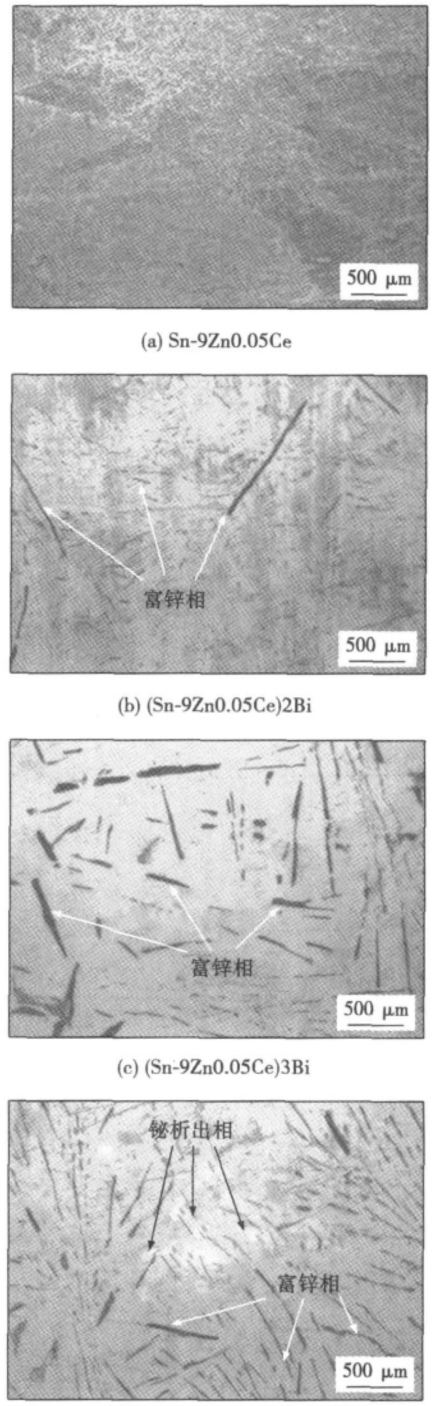
铋含量较低时一般以固溶状态存在于锡基体中，随着铋含量的增加，钎料基体 β-Sn 组织有细化的趋势，而当铋含量增加到固溶极限时，便开始析出并聚集在富锌相周围. 从图 1d 可以看出，当铋含量达到 4% 时，钎料中白色的铋析出分离相已经非常明显.

2.2 磷对 Sn-9Zn0.05Ce 合金显微组织的影响

图 2 为 (Sn-9Zn0.05Ce) xP 钎料合金的显微组织形貌. 由图 2 可见，加入微量 P 元素也会促使钎料中生成颗粒状或针状的富锌相.

付小琴等人[7]发现，在 Sn-8Zn-3Bi 中添加 P 元素后其显微组织发生了明显的变化. 当磷含量达到 0.04% 时，钎料组织中出现粗大的针状相，随着磷含量的升高，针状相尺寸进一步增加. 另外在显微组织中还发现大量细小颗粒状相，通过 SEM 和能谱分析表明，针状和颗粒状相均为富锌相.

图 2 还表明，当磷含量为 0.02% 或以下时，在 (Sn-9Zn0.05Ce) xP 钎料中富锌相主要呈颗粒状; 当磷含量为 0.03% 时，钎料中富锌相以颗粒状和粗大的针棒状形态存在. 由此可见，随着磷含量的增加，钎料中将首先出现富锌相颗粒，随着颗粒状富锌相的集聚，逐渐演变成针状富锌相，且富锌相尺寸也随之逐渐变大.



(a) Sn-9Zn0.05Ce

(b) (Sn-9Zn0.05Ce)2Bi

(c) (Sn-9Zn0.05Ce)3Bi

(d) (Sn-9Zn0.05Ce)4Bi

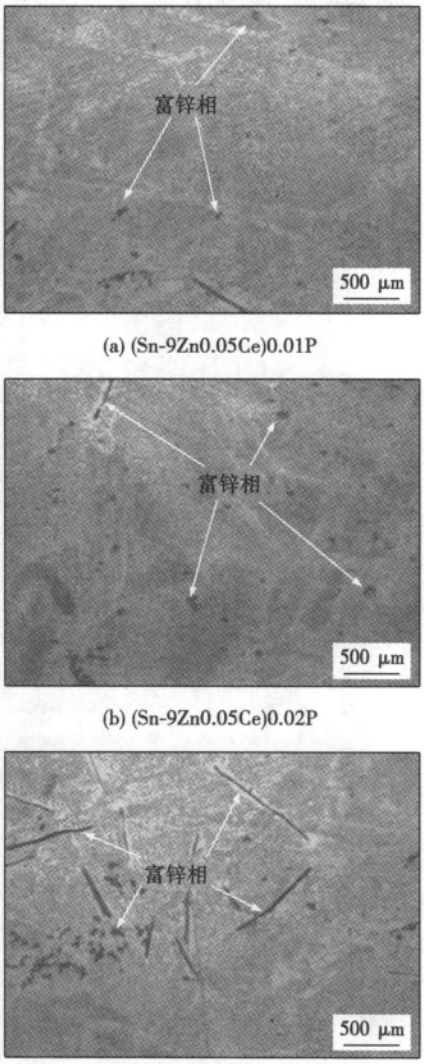
图 1 (Sn-9Zn0.05Ce) xBi 合金的显微组织

Fig. 1 Microstructure of (Sn-9Zn-0.05Ce) xBi alloys

2.3 铋对 Sn-9Zn0.05Ce 合金拉伸性能的影响

铋对 Sn-9Zn0.05Ce 钎料抗拉强度和断后伸长率的影响如图 3 所示.

由图 3 可见，添加铋能明显提高 Sn-9Zn0.05Ce 合金的抗拉强度，但同时导致其断后伸长率显著下降. 当铋含量 w(Bi) < 2% 时，抗拉强度随铋含量的增加而迅速增大，而当 w(Bi) > 2% 时，其增加的趋



(a) (Sn-9Zn0.05Ce)0.01P

(b) (Sn-9Zn0.05Ce)0.02P

(c) (Sn-9Zn0.05Ce)0.03P

图 2　(Sn-9Zn0.05Ce)xP 合金的显微组织

Fig. 2　Microstructure of (Sn-9Zn-0.05Ce) *x*P alloys

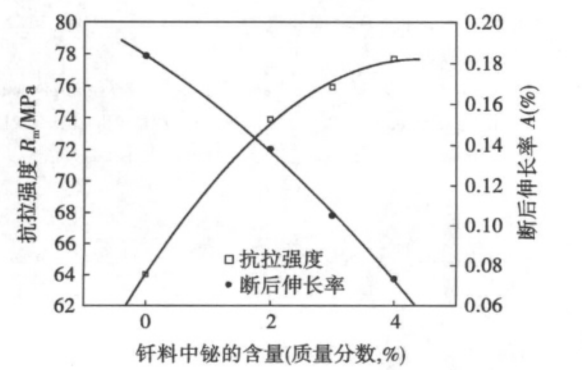
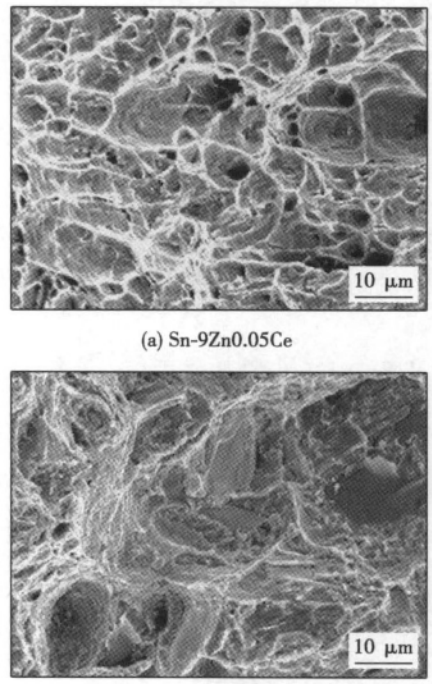


图 3　Bi 含量对 Sn-9Zn0.05Ce 抗拉强度和断后伸长率的影响

Fig. 3　Effect of Bi content on tensile strength and elongationof Sn-9Zn0.05Ce

势变缓. 这一结果与 Song 等人[8] 对 Sn-Zn-Bi 合金的研究结论基本一致. 其原因是当铋含量较低时,铋固溶在基体中,由于晶格的畸变而获得强化; 当铋含量过高时,析出的富铋相将成为疲劳裂纹的萌生点而导致强度增加趋势变缓. 同时,由于铋凝固时体积会膨胀,导致裂纹产生而使断后伸长率下降.

图 4 为 Sn-9Zn0.05Ce 与 (Sn-9Zn0.05Ce) 4Bi 钎料合金拉伸断口的 SEM 形貌. 由图 4 可见未添加铋时,钎料断口形貌为典型的等轴韧窝,而添加铋的钎料断口形貌为等轴韧窝与解理面混合断口,这可能是由于 Bi 元素达到临界固溶量后将从基体析出形成单独的分离相所致.



(a) Sn-9Zn0.05Ce

(b) Sn-9Zn0.05Ce)4Bi

图 4　(Sn-9Zn0.05Ce) *x*Bi 断口 SEM 形貌

Fig. 4　SEM photographs of (Sn-9Zn0.05Ce) *x*Bi solders

2.4　磷对 Sn-9Zn0.05Ce 合金拉伸性能的影响

微量磷对 Sn-9Zn0.05Ce 钎料合金抗拉强度和断后伸长率的影响如图 5 所示.

由图 5 可见,在 Sn-9Zn0.05Ce 中添加 0.01% ~ 0.03% 的磷,对钎料合金的抗拉强度和断后伸长率没有太大的影响.

2.5　铋和磷对 Sn-9Zn0.05Ce 合金硬度的影响

铋、磷含量与钎料合金硬度的关系如图 6 所示.

由图 6 可见,随着铋含量从 0 增加到 4%,合金的硬度从 17.46 HV 上升到 22.96 HV,这是因为在钎料固态冷却过程中,原来溶解在锡和锌中的铋会大量析出而导致其硬度迅速增加[9]. 由于在 Sn-9Zn0.05Ce 中添加的 P 元素含量很低,且磷一般富集在钎料表面,故使钎料的硬度仅略有上升.

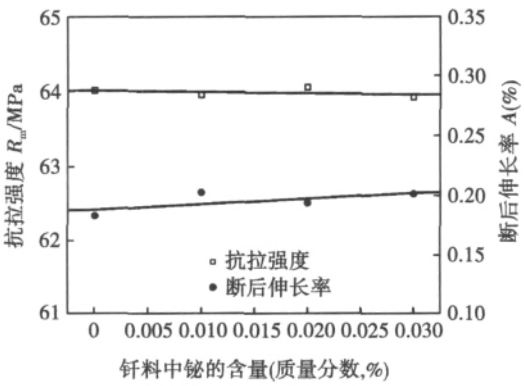


图5 微量磷对 Sn-9Zn0.05Ce 抗拉强度和断后伸长率的影响

Fig. 5 Effect of minute P on tensile strength and elongation of Sn-9Zn0.05Ce

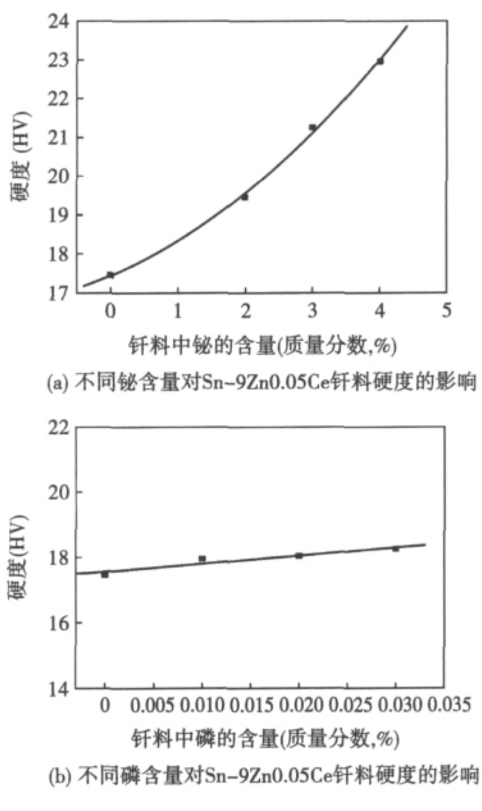


图6 Sn-9Zn0.05Ce 的硬度随铋、磷含量的变化

Fig. 6 Effect of Bi and P content on hardness of Sn-9Zn0.05Ce solder

3 结 论

（1）添加 0～4% 铋能显著提高 Sn-9Zn0.05Ce 钎料合金的抗拉强度和硬度，但会降低钎料的塑性；而添加微量磷（0.01%～0.03%）对 Sn-9Zn0.05Ce 钎料的拉伸性能及硬度均无明显影响.

（2）添加铋能促使 Sn-9Zn0.05Ce 钎料中富锌相析出，并且随着铋含量的增加，针状锌相增多且分布变得杂乱无序，当铋含量达到 4% 时，明显有颗粒状的铋相析出. 添加微量 P 元素也能促使针状锌相的析出.

（3）Sn-9Zn0.05Ce 钎料的断裂为韧性断裂，随着铋、磷含量的增大，其断裂机制会发生显著变化.

参考文献:

[1] 杜长华，陈 方. 电子微连接技术与材料[M]. 北京：机械工业出版社，2008.

[2] Song J M，Lan G F，Lui T S，*et al*. Microstructure and tensile properties of Sn-9Zn-xAg lead-free solder alloys[J]. Scripta Materialia，2003，48(4)：1047－1051.

[3] Wu C M，Yu D Q，Wang L. The properties of Sn-9Zn lead-free solder alloys doped with trace rare earth elements[J]. Journal of Electronic Materials，2002，31(9)：921－927.

[4] 于大全，赵 杰，王 来. 稀土元素对 Sn-9Zn 合金润湿性的影响[J]. 中国有色金属学报，2003，13(4)：1001－1004.
Yu Daquan，Zhao Jie，Wang Lai. Wetting properties of Sn-9Zn solder alloy with trace rare earth elements[J]. The Chinese Journal of Nonferrous Metals，2003，13(4)：1001－1004.

[5] 吴文云，邱小明，殷世强，等. Bi、Ag 对 Sn-Zn 无铅钎料性能与组织的影响[J]. 中国有色金属学报，2006，16(1)：159－163.
Wu Wenyun，Qiu Xiaoming，Yin Shiqiang，*et al*. Influence of Bi，Ag on microstructure and properties of Sn-Zn lead-free solder[J]. The Chinese Journal of Nonferrous Metals，2006，16(1)：159－163.

[6] 周 健，孙扬善，薛 烽. 低熔点 Sn-Zn-Bi 无铅钎料的组织和性能[J]. 金属学报，2005，41(7)：743－749.
Zhou Jian，Sun Yangshan，Xue Feng. Microstructures and properties of Sn-Zn-Bi solder alloys[J]. Acta Metallurgica Sinica，2005，41(7)：743－749.

[7] 付小琴，周 健，孙扬善，等. Sn-8Zn-3Bi-P 无铅钎料微观组织及性能[J]. 东南大学学报(自然科学版)，2006，36(5)：832－835.
Fu Xiaoqin，Zhou Jian，Sun Yangshan，*et al*. Effect of phosphorus on microstructure and properties of Sn-8Zn-3Bi lead-free solder[J]. Journal of Southeast University (Natural Science Edition)，2006，36(5)：832－835.

[8] Song J M，Lui T S，Chang Y L. Compositional effects on the microstructure and vibration fracture properties of Sn-Zn-Bi alloys[J]. Journal of Alloys and Compounds，2005，403(1－2)：191－196.

[9] Islama R A，Wu B Y，Alam M O. Investigations on microhardness of Sn-Zn based lead-free solder alloys as replacement of Sn-Pb solder[J]. Journal of Alloys and Compounds，2005，392 (1－2)：149－158.

作者简介： 杜长华，男，1956 年出生，教授. 主要从事电子微连接技术与材料研究. 获得省部级以上奖励 12 项. 发表论文 60 余篇. Email：duchanghua@cqut.edu.cn

通讯作者： 尹立孟，博士，讲师. Email：yeenlm@163.com

Influence of Bi and P additions on microstructure and mechanical properties of Sn-Zn-RE solder DU Changhua[1], YIN Limeng[2], SU Jian[1], CHEN Fang[1], ZHAO Haijian (1. School of Materials Science and Engineering, Chongqing University of Technology, Chongqing 400054, China; 2. School of Metallurgy and Materials, Chongqing Institute of Science and Technology, Chongqing 401331, China). p 17 – 20

Abstract: The Sn-9Zn0.05Ce lead-free solder with Bi and P additions were prepared, and microstructure, tensile strength, elongation and Vickers hardness of the lead-free solders were studied. Experimental results show that the tensile strength and hardness increase with more Bi addition in Sn-9Zn0.05Ce lead-free solder, while the elongation decreases with Bi addition. P addition in Sn-9Zn0.05Ce lead-free solder does not obviously affect the tensile strength and hardness. In addition, either Bi or P addition in Sn-9Zn0.05Ce lead-free solder would make Zn separate out from Sn-9Zn0.05Ce lead-free solder more easily, and needle-like or grain-like Zn-rich phase can be found in the solder. Moreover, Zn-rich phase increases with more Bi or P additions in the solder, and accordingly has a great effect on the mechanical properties of Sn-9Zn0.05Ce solder.

Key words: Sn-Zn0.05Ce solder; microstructure; tensile strength; hardness

Double-layers laser-MIG hybrid welding method in welding thick aluminum alloy YAO Wei[1], WANG Zhimin[1], LI Hongwei[1], WANG Chunming[2] (1. Beijing Hangxing Machinery Manufacturing Corporation, Beijing 100013, China; 2. Material Science and Technology College, Huazhong University of Science and Technology, Wuhan 430074, China). p 21 – 24

Abstract: In this paper, double-layers laser-MIG welding of thick aluminum alloy method was put forward. It welds two layers: the first layer padding welding, to solve the problem of inadequate weld penetration; second welding surface for the cap to address the problem of the poor weld shape. The results showed that: rated at 4 kW lasers when the composite layer by laser-MIG welding materials, welding ZL114A deeps up to 10mm, average joint tensile strength is 238 MPa, tensile strength is greater than 80% of the base metal. Double-layers laser-MIG welding method of welding, a simulation of a cylindrical pieces of aerospace products, forming a good weld, penetration up to 9 mm. With no crack, no incomplete penetration and lack of fusion, no visible inclusions, defects is mainly chain-like porosity, pore diameter less than 1mm, almost no distortion after welding.

Key words: laser-MIG hybrid welding; double-layers welding; thick aluminum alloy

Effect on hardness and microstructures of rail joint with narrow gap arc welding by normalizing QU Yuebo[1,2], CAI Zhipeng[1], CHE Hongyan[1], PAN Jiluan[1] (1. Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China; 2. School of Mechanical Engineering, Xiangtan University, Xiangtan 411105, China). p 25 – 29

Abstract: Narrow gap arc welding on rail is a new way of rail welding to adapt to local condition, and its post weld heat treatments are researching by some researchers. This paper uses the therma simulator of Gleeble-1500D to simulate a series of normalizing treatments on welded joint with narrow gap arc welding, and then measures the Rockwell hardness, watches the microstructure and combines the Vickers microhardness to analyse the welded joint. The result shows that the maximum temperature of normalizing between 925 ℃ to 935 ℃ maybe the best choice, which can make the hardness of welded joint be uniformity distributing, and the effect of grain refining be obvious, and softened zone be eliminated. So it can offer some advice for normalizing treatments in the production practice.

Key words: rail with normalizing; thermal simulation; hardness; microstructure

Solder joint inspection method regarding misalignment
XIE Hongwei, KUANG Yongcong, OUYANG Gaofei, ZHANG Xianmin (School of Mechanical and Automotive Engineering, South China University of Technology, Guangzhou 510640, China). p 30 – 34

Abstract: Misalignment degrades the performance of inspection algorithms. Misalignment problem of solder joint inspection is investigated quantitatively through evaluating the current algorithm's sensitivity to misalignment. A new learning method is proposed in which a set of virtual samples generated by perturbing the original samples on position, angle and scale are used for training. Synthetical false rate is defined to evaluate the performance of the inspection algorithm regarding misalignment. The experiment results showed that the proposed method is robust to the misalignment while the time cost remains unchanged.

Key words: automatic optical inspection; misalignment; virtual samples; solder joint inspection

Research on brazing joints of C_f/SiC and TC4 using AgCu-Ti-Al filler materials GAO Lingling, CAI Chuang, XIONG Jinhui, HUANG Jihua, ZHANG Hua, ZHAO Xingke (School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China). p 35 – 38

Abstract: C_f/SiC composite and TC4 were successfully joined with the AgCuTi-Al mixed powders by appropriate brazing parameters under the vacuum condition. Microstructures of the joints were investigated by SEM, EDS and XRD. The mechanical properties were measured by mechanical testing machine as well. The results showed that Ti element in the brazing filler can react with the carbon fiber and the matrix SiC in the C_f/SiC composite, a mixture of TiC, Ti_3SiC_2 and Ti_5Si_3 finally formed in the reaction layer between the composite and the interlayer. The Ti element in the brazing filler and the Cu in the TC4 generated the mutual diffusion, which form the diffusion-reaction layers between interlayer and TC4. The addition of proper Al power of the Ag-Cu-Ti in-situ synthesized Ti_3Al, finally the performed joints have dense bonding layers reinforced by the Ti_3Al intermetallic compound, which relax the thermal stress of the joints effectively. The shear strength of the joint brazed with the AgCuTi-Al filler was remarkably higher than that of pure Ag-Cu-Ti filler.

Key words: C_f/SiC; TC4; brazing