Sn-Zn 系钎料专用助焊剂

韩若男[1]，　薛松柏[1]，　胡玉华[2]，　王宗阳[1]，　贾建漪[1]
（1. 南京航空航天大学 材料科学与技术学院，南京　210016；2. 中国电子科技集团第五十五研究所，南京　210016）

摘　要：采用铺展试验法研究了 Sn-9Zn 钎料配合自制 Sn-Zn 系钎料专用助焊剂、NH_4Cl-$ZnCl_2$ 助焊剂、树脂型助焊剂以及水溶性助焊剂在铜板上的铺展能力. 结果表明，使用自制助焊剂 A_4 匹配 Sn-9Zn 钎料铺展性能相比其它助焊剂铺展面积明显增大. 自制助焊剂不含卤素，钎料的铺展面积最大为 65.7 mm^2，相比 NH_4Cl-$ZnCl_2$ 助焊剂、树脂型助焊剂、水溶性助焊剂分别提高了 16.1%，116.1%，85.1%. 此外，复配助焊剂能进一步促进钎料在铜板上的铺展，最大铺展面积分别达到 76.5，72.5 mm^2，控制磺酸亚锡的含量为 20%（质量分数），二乙醇胺，丁二酸的最佳添加量依次为 8%，10%（质量分数）.

关键词：Sn-Zn；助焊剂；铺展面积
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韩若男

0 序　　言

电子封装产业飞速发展，传统的 Sn-Pb 钎料危害人类健康且不满足绿色钎料的要求，尤其欧盟 WEEE/ROHS[1] 指令的实施，无铅电子封装材料的开发与应用受到了广泛关注[2]. Sn-Zn 系钎料被认为是最有可能替代传统 Sn-Pb 钎料的无铅钎料合金之一[3]. 但是，Sn-Zn 系无铅钎料润湿性能较差，限制了该钎料的广泛应用. 国内外学者致力于采用微合金化的方法研究新合金成分的 Sn-Zn 钎料来改善钎料的钎焊性能[4-6]，并且取得了一定的进展，但仍未达到理想的效果. 仅用微合金化方法来改善 Sn-Zn 钎料钎焊性能目前还是有一定的难度，新型助焊剂的研发为 Sn-Zn 钎料润湿性能的改善提供了新思路[7]. 目前，国内外关于 Sn-Zn 无铅电子封装钎料专用助焊剂的研究报道尚少. 已报道的 Sn-Zn 钎料专用助焊剂一方面在钎焊效果上有待改善[8]；另一方面在焊后腐蚀以及焊后残留方面存在一定的欠缺[9]. 因此研究和制备绿色、高活性、低腐蚀性的 Sn-Zn 系钎料专用助焊剂显得尤为紧迫. 文中通过研究不同组分对专用助焊剂铺展性能的影响规律，并与几种典型市售助焊剂进行对比研究，得到了具有优异助焊性能的无卤素 Sn-Zn 系钎料专用助焊剂配方.

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1 试验方法

1.1 助焊剂的配制

采用混合醇为溶剂，聚乙二醇为基体，不同含量磺酸亚锡作为活性剂配制 A 组助焊剂，依磺酸亚锡含量递增顺序标号为 A_1 ~ A_5；将 A_4 成分分别与不同含量的二乙醇胺、丁二酸复配制备 B 组（B_1 ~ B_5），C 组（C_1 ~ C_5）助焊剂.

每组助焊剂样品以 10.0 g 为总量，采用精度为 0.01 g 的电子天平准确称量各组分，分别放置于 100.0 mL 烧杯里，然后将烧杯置于 80 ℃ 水浴磁力搅拌器中，搅拌至所有组分全部溶解，然后使其自然冷却. 对各组助焊剂进行标号，各助焊剂具体组分见表1~表3.

表1　A组助焊剂配方成分（质量分数，%）

Table 1　Formula compositions of flux-A

编号	基体	磺酸亚锡	溶剂
A_1	35.0	5.0	60.0
A_2	35.0	10.0	55.0
A_3	35.0	15.0	50.0
A_4	35.0	20.0	45.0
A_5	35.0	25.0	40.0

1.2 铺展试验

试验材料采用 Sn-9Zn 钎料，将钎料熔融后浇铸

表 2 B 组助焊剂配方成分(质量分数,%)
Table 2 Formula compositions of flux-B

编号	基体	磺酸亚锡	二乙醇胺	溶剂
B_1	35.0	20.0	1.0	44.0
B_2	35.0	20.0	3.0	42.0
B_3	35.0	20.0	6.0	39.0
B_4	35.0	20.0	8.0	37.0
B_5	35.0	20.0	10.0	35.0

表 3 C 组助焊剂配方成分(质量分数,%)
Table 3 Formula compositions of flux-C

编号	基体	磺酸亚锡	丁二酸	溶剂
C_1	35.0	20.0	1.0	44.0
C_2	35.0	20.0	3.0	42.0
C_3	35.0	20.0	5.0	40.0
C_4	35.0	20.0	10.0	35.0
C_5	35.0	20.0	15.0	30.0

在金属模中制成钎料条,然后通过压片机压成 1 mm 片状钎料,并剪成大小均匀,质量为 0.2 g ± 0.005 g 的块状备用. 铺展试验采用 SX-4-10 箱式电阻炉,按照国家标准《GB/T 11364—2008,钎料润湿性试验方法》进行,以 40 mm × 40 mm × 2 mm 规格的紫铜板作为试验基板.

试验前分别用 5.0% H_2SO_4 + 95.0% C_2H_5OH 溶液去除铜片表面的氧化膜及油脂,再用丙酮进行超声清洗,最后用去离子水清洗、干燥. 将 0.2 g 块状钎料置于铜板中央,覆盖上制备的助焊剂,置于 SX-4-10 电阻炉中进行铺展试验,试验温度设置为 260 ℃,保温时间 50 s. 每组试样进行五次试验,采用 Image-Pro Plus 软件计算铺展面积,取平均值.

2 试验结果与分析

2.1 不同助焊剂对 Sn-9Zn 钎料铺展性能的影响

图 1 和图 2 为 Sn-9Zn 分别配合 $ZnCl_2$-NH_4Cl,水溶性以及树脂型助焊剂在铜基板上的焊点形貌及铺展面积. 从图 2 中发现,采用 $ZnCl_2$-NH_4Cl 助焊剂时,钎料铺展面积为 56.6 mm^2,明显大于采用水溶性 35.5 mm^2 和树脂型 30.4 mm^2 钎焊时的铺展面积. 另外图 1 表明采用 $ZnCl_2$-NH_4Cl 助焊剂时,焊点形貌较为规则,表面平整光亮,而采用水溶性及树脂型助焊剂时,焊点表面暗沉且凹凸不平.

图 3 和图 4 为配合自制 A 组助焊剂时 Sn-9Zn 钎料在铜基板上的焊点形貌及铺展面积. 结果表明,磺酸亚锡含量小于 20.0%(质量分数)时,钎料在铜基板上的铺展面积随磺酸亚锡含量的升高而增大,并且光亮度逐渐增强; 磺酸亚锡含量等于 20.0%(质量分数)时,铺展面积 65.7 mm^2 最大,相对 $ZnCl_2$-NH_4Cl、水溶性和树脂型助焊剂分别提高了 16.1%,116.1%,85.1%; 当磺酸亚锡含量继续上升到 25.0%(质量分数)时,铺展面积反而略有下降. 由试验表明,A_4 组分即含磺酸亚锡 20.0%(质量分数)的助焊剂不含卤素,残留物较少,能够显著提高

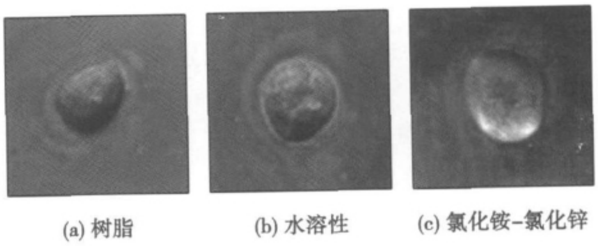

图 1 配合不同助焊剂时的焊点形貌
Fig. 1 Appearance of soldered joints using different fluxes

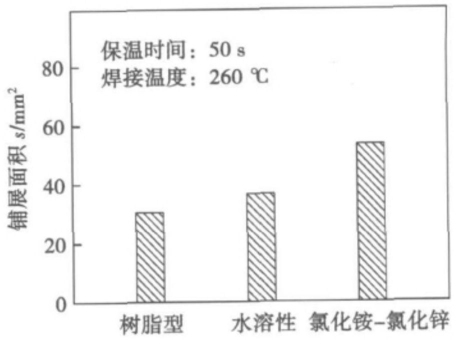

图 2 配合不同助焊剂时钎料的铺展面积
Fig. 2 Spreading areas of solders using different fluxes

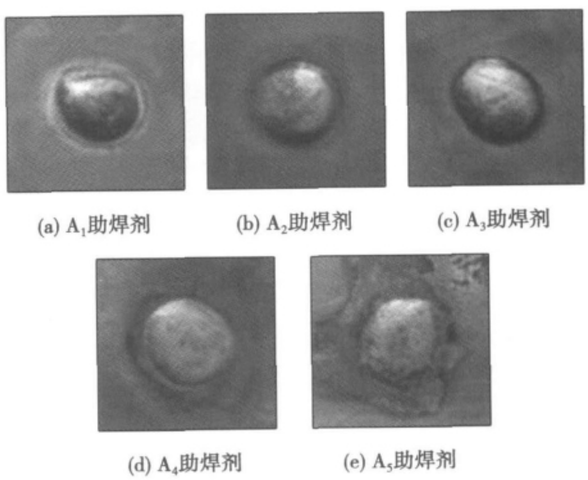

图 3 配合 A 组助焊剂时的焊点形貌
Fig. 3 Appearance of soldered joints using flux-A

Sn-9Zn 钎料在铜基板上的铺展能力，焊点形貌较为规则，但过多磺酸亚锡的添加导致助焊剂粘度过大，阻碍钎料在铜基板上的铺展.

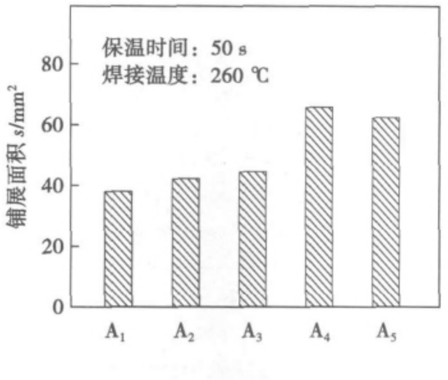

图 4　配合 A 组助焊剂时钎料的铺展面积

Fig. 4　Spreading areas of solders using flux-A

2.2　B 组助焊剂对 Sn-9Zn 钎料铺展性能的影响

图 5 和图 6 为 Sn-9Zn 钎料复配 B 组助焊剂在铜基板上的焊点形貌及铺展面积. 由图 5 可知，焊点较规则平整、表面光亮、残留物较少. 由图 6 可知，配合 B_4 成分助焊剂即含二乙醇胺 8.0%（质量分数）的助焊剂时，钎料铺展面积最大，铺展面积 76.6 mm^2 相对 A_2 成分助焊剂 65.7 mm^2 提高了 16.6%. 有机胺作为活性剂能够与金属氧化物反应，化学反应通式为

$$2RNH_2 \cdot HX + MeO \rightarrow 2RNH_2 + MeX_2 + H_2O \quad (1)$$

式中: $RNH_2 \cdot HX$ 为有机胺; MeO 为金属氧化物; $RNH_2 + MeX_2$ 为反应产物.

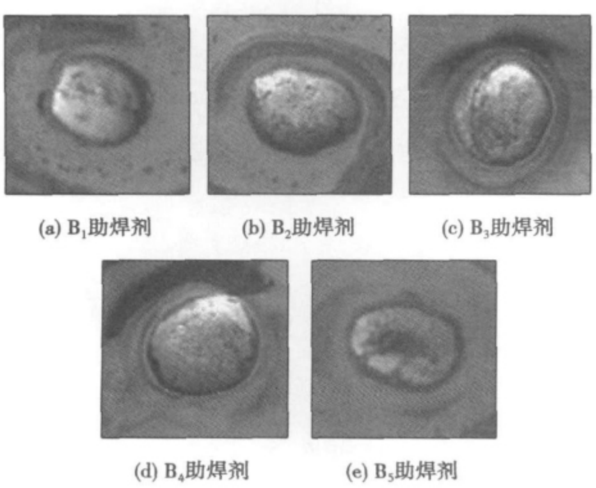

图 5　配合 B 组助焊剂时的焊点形貌

Fig. 5　Appearance of soldered joints using flux-B

研究可知，使用含二乙醇胺 8.0%（质量分数）的助焊剂钎焊时，能够有效减少锡和锌的氧化倾向，并能一定程度上去除铜基板上的氧化物，促进钎料在铜基板上的铺展.

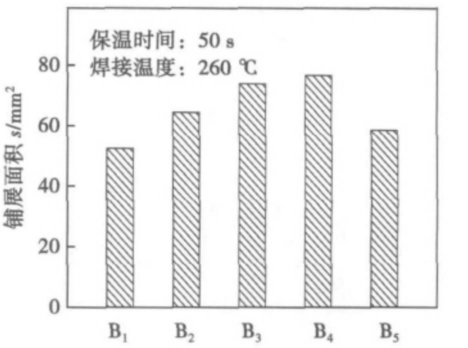

图 6　配合 B 组助焊剂时钎料的铺展面积

Fig. 6　Spreading areas of solders using flux-B

2.3　C 组助焊剂对 Sn-9Zn 钎料铺展性能的影响

图 7 和图 8 为 Sn-9Zn 钎料复配 C 组助焊剂在铜基板上的焊点形貌及铺展面积. 由图 7 可知，焊点铺展形貌较规则、表面光亮、残留物较少. 采用 C_4 成分助焊剂即含丁二酸 10.0%（质量分数）时，钎料在铜基板上的铺展面积最大，铺展面积 72.5 mm^2 相对 A_2（65.7 mm^2）组提高了 10.4%. 有机酸与金属氧化物的反应通式为

$$2R(COOH)_n + nMeO \rightarrow n(RCOO)_2Me + nH_2O \quad (2)$$

式中: $R(COOH)_n$ 为有机酸; MeO 为金属氧化物; $(RCOO)_2Me$ 为反应产物.

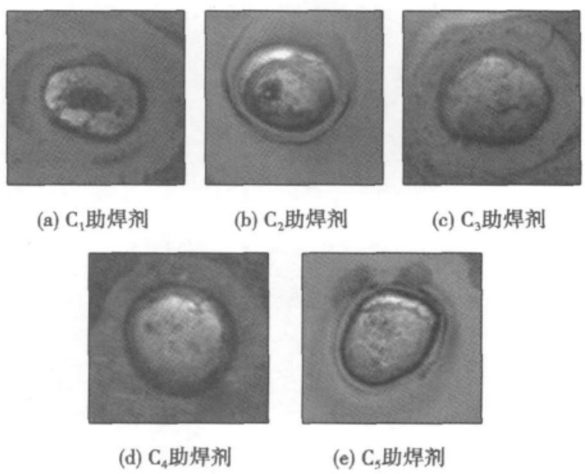

图 7　配合 C 组助焊剂时的焊点形貌

Fig. 7　Appearance of soldered joints using flux-C

由试验可知，丁二酸含有两个羧基活性功能团，活性较好，添加丁二酸 10.0%（质量分数）可以一定程度上提高助焊剂的助焊性能.

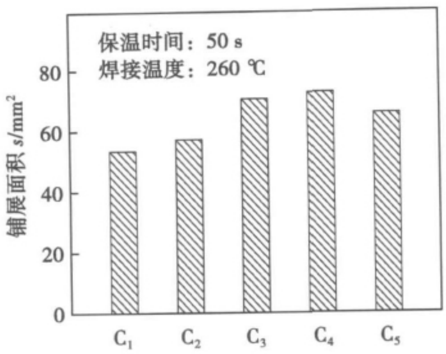

图8 配合C组助焊剂时钎料的铺展面积

Fig. 8 Spreading areas of solders using flux-C

3 结 论

(1) 适量磺酸亚锡20%(质量分数)作为活性剂制备的助焊剂,能够显著提高Sn-9Zn钎料在铜基板上的铺展性能. 铺展面积最大为65.7 mm^2,铺展面积相对NH_4Cl-$ZnCl_2$、树脂型以及水溶性助焊剂分别提高了16.1%,116.1%,85.1%.

(2) 助焊剂中添加二乙醇胺作为活性剂能够增加焊点亮度,降低锡、锌的氧化倾向,促进Sn-9Zn钎料在铜基板上的铺展,当二乙醇胺含量在8.0%(质量分数)时,Sn-9Zn钎料的铺展性能最好.

(3) 向助焊剂中添加丁二酸作为活性剂时,丁二酸能够与金属氧化物反应,降低金属氧化倾向,改善钎料的铺展能力,当丁二酸含量为10.0%(质量分数)时,Sn-9Zn钎料的铺展性能最好.

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作者简介: 韩若男,女,1987年出生,硕士研究生. 主要从事无铅钎料及微电子钎焊的研究工作. Email: nanruohan@126.com

通讯作者: 薛松柏,男,教授. Email: Xuesb@nuaa.edu.cn

creases. On the basis of differences in equivalent cathode/anode drops and the welding arc characters in EN/EP polarity, the welding wire gets more energy as the EN ratio increases, so the wire melting rate is larger than DC MIG welding. At a constant wire feed speed and welding speed, the penetration depth and bead width decrease while the reinforcement becomes high as the EN ratio increases. Accordingly, AC Pulse MIG welding technology can solve the burn through problem in welding thin sheet joints and can greatly improve the gap bridging ability in lap joints. What is more, this technology can also improve the welding speed and welding bead quality for thin sheet joints.

Key words: aluminum alloy welding; AC pulse MIG welding; EN ratio; wire welding rate

Analytical model of wire temperature distribution during hot-wire TIG welding process ZHAO Fuhai[1,2], HUA Xueming[1,2], YE Xin[1,2], WU Yixiong[1,2,3] (1. Welding Engineering Institute of Material Science and Engineering Shanghai Jiaotong University, Shanghai 200240, China; 2. Shanghai Key Laboratory of Materials Laser Processing and Modification, Shanghai Jiaotong University, Shanghai 200240, China; 3. State Key Laboratory of Metal Matrix Composite, Shanghai Jiaotong University, Shanghai 200240, China). pp 97 – 100

Abstract: Based on the law of energy conservation, the mathematical model considering the effect of heat loss on the hot-wire temperature distribution was developed. The accuracy of the mathematical model was validated by comparing the calculating result with the experimental results. The effect of wire diameter, hot-wire current, wire feeding speed, and wire extension on temperature distribution of hot-wire elaborately was discussed. The results show that the mathematical model has so high accuracy that it can be used to analyze the heating process of wire and satisfies the need of controlling the welding quality. The smaller the wire diameter and wire feeding speed are, the higher the temperature of the position on the wire extension having the same distance away from the power-feeding point is. The higher hot-wire current is, the higher the temperature is. However, the larger the wire extension is, the higher the temperature of the position on the wire having the same distance away from the wire-feeding point is.

Key words: hot-wire TIG welding process; heat-loss; temperature distribution of hot-wire; mathematical analytical model

Development of flux for Sn-Zn lead-free solder HAN Ruonan[1], XUE Songbai[1], HU Yuhua[2], WANG Zongyang[1], JA Jianyi[1] (1. College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China; 2. The 55th Research Institute, China Electronic Technology Group Corporation, Nanjing 210016, China). pp 101 – 104

Abstract: The speadabitity of Sn-9Zn solder on Cu substrate with four different types of flux was studied by spreading experiment method. The experimental results indicated that Sn-9Zn solder, matching the flux-A4 with stannous sulfonate (20%) as the main activator without halogen which exhibited excellent wettability. The largest spreading area was 65.7 mm^2, increased respeetively by 16.1%, 116.1%, 85.1% compared with the NH_4Cl-$ZnCl_2$, resin and water-solubility fluxes. Besides, the newly developed flux with combination of 20% stannous sulfonate and diethanolamine, succinic acid could remarkably improve the wettabiltiy of Sn-9Zn solder that the largest spreading areas were 76.5 mm^2, 72.5 mm^2 when the contents of diethanolamine, succinic acid were at 8%, 10%.

Key words: Sn-Zn; soldering flux; spreading areas

Effect of aging temperature on microstructure and properties of deposited metal for type 15-5PH precipitation hardened stainless steel QI Yanchang, ZHANG Xiaomu, PENG Yun, TIAN Zhiling (State Key Laboratory of Advanced Steel Processes and Products, Central Iron & Steel Research Institute, Beijing 100081, China). pp 105 – 108

Abstract: Aging temperature is an important aging treatment parameter of deposited metal for type 15-5PH precipitation hardened stainless steel. The welding deposited metal was conducted by gas tungsten arc welding and aging treatment was carry out at different temperature after solution treatment. After aging treatment the microstructure and properties of deposited metal were investigated. The results indicate that microstructure of deposited metal by aging treatment consists predominately of martensite, residual austenite and ε-Cu. The increasing of aging temperature results in the increasing of amount of austenite and the size of ε-Cu, the variation of ε-Cu from increasing to decreasing. The strength of deposited metal drops and toughness improves with the increasing of aging temperature due to the increasing of amount of austenite.

Key words: aging temperature; microstructure; properties; deposited metal

Structure and mechanical properties of TC4/TC17 linear friction welding joint JI Yajuan[1], LIU Yanbing[2], ZHANG Tiancang[1], ZHANG Chuanchen[1] (1. AVIC Beijing Aeronautical Manufacturing Technology Research Institute, Beijing 100024, China; 2. No. 94170 Unit of People's Liberation Army, Xi'an 710061, China). pp 109 – 112

Abstract: TC4 and TC17 titanium usually used on aero-engine blisk were studied. The microstructures were analyzed by metallograph and transmission electron microscope. The temperature during the welding process was also measured. The investigation showed that the joints included three zones, base metal (BM), thermal mechanical affected zone (TMAZ) and welding zone (W). The TMAZ microstructure was similar to base metal, alpha and beta phase were elongated along the stress direction, recrystallization occurred in the weld zone. The induced microstructures were different from the BM. The maximum temperature can reach 1 270 ℃ which exceeds the titanium beta transformation temperature. the tensile test result showed that joint tensile strength was equal to that of the TC4 at room temperature and 200 ℃, while the testing temperature is 400 ℃, the joint tensile strength can reach 95% of the TC4 base mental.

Key words: linear friction welding; titanium; microstructure; temperature