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Sn-Ag-Cu-In无铅钎料润湿性能及显微组织

王俭辛， 尹 明， 赖忠民， 李 雪
(江苏科技大学 先进焊接技术省级重点实验室，镇江 212003)

摘 要: 在Sn-1.2Ag-0.6Cu合金中添加0～1.0%的In元素，研究了Sn-Ag-Cu-In无铅钎料的熔化温度、润湿性能及显微组织. 结果表明，添加In元素对钎料的熔化温度有一定的降低作用，在相同的试验温度下，含铟钎料粘度更低，流动性更强，钎料的润湿性能随之改善. 低银Sn-Ag-Cu钎料在空气中的润湿时间在260 ℃才达到$t_0 \leqslant 1$ s，而Sn-Ag-Cu-1.0In无铅钎料在氮气保护下在250 ℃时就已满足美国电子工业标准IPC/EIA J—STD—003B对于波峰焊润湿时间的推荐值$t_0 \leqslant 1$ s的要求. 添加1.0%左右的In元素时，低银Sn-1.2Ag-0.6Cu钎料合金中Ag_3Sn化合物有长大趋势，将不利于钎料合金的力学性能，因此添加铟含量宜控制在1.0%以内.

关键词: 无铅钎料; 润湿性; 显微组织
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王俭辛

0 序 言

在电子制造行业进入“绿色制造”时代的今天，电子封装中使用环保型钎料的观念已经深入人心，以Sn-3Ag-0.5Cu，Sn-3.8Ag-0.7Cu等产品为代表的Sn-Ag-Cu系列钎料，具有较好的钎焊性能和力学性能等优点，成为当今无铅钎料中的主流合金[1]. 由于金属原材料的快速上涨，钎料成本居高不下，业界不得不考虑在保证质量的前提之下，通过研发低银无铅钎料来控制成本，继续推进电子封装的无铅化进程，这已成为当前国内外的研究热点之一[2].

目前研究以及应用较多的低银无铅钎料以Sn-0.3Ag-0.7Cu合金为主，由于银在Sn-Ag-Cu钎料中对降低熔化温度、提高润湿性效果显著，因此降低银含量首先要考虑的就是熔化温度范围是否合适以及润湿性能能否达标[3]. 在低银钎料中添加合金元素是改善钎焊效果的重要途径，在Sn-0.3Ag-0.7Cu合金中添加Bi元素，可降低钎料合金熔化温度、提高润湿性，但同时会导致合金熔化温度范围扩大，从而容易导致结晶裂纹的形成，不利于形成可靠的焊点[4]; 添加微量Ni元素能改善低银Sn-Ag-Cu钎料的热疲劳性能，有效地降低焊盘镍层在时效过程中的消耗速率[5,6]; In元素能有效降低Sn-0.3Ag-0.7Cu钎料熔点，并降低焊点跌落失效的几率[7,8].

低银Sn-Ag-Cu钎料已被定位为第二代无铅钎料，由于润湿性不够理想等问题，现阶段主要应用在波峰焊场合，因此在竞争激烈的电子封装行业中对低银Sn-Ag-Cu钎料进行深入研究开发具有重要的理论意义和应用价值. 文中将银含量调整到1.2%左右，并添加In元素，研究铟对钎料熔化温度、润湿性能以及显微组织的影响规律，以期为新一代无铅钎料的研发提供借鉴.

1 试验方法

试验选用99.95%(质量分数)纯度的锡和铟，以及Sn-Ag，Sn-Cu合金来制备不同铟含量(0，0.3%，0.5%，0.7%和1.0%)的Sn-1.2Ag-0.6Cu钎料合金，将原材料放入坩埚内熔化并搅拌，待充分熔化后保温，随后在金属型中浇注成钎料条.

钎料合金熔化温度的试验过程按照日本工业标准JIS Z 3198—1—2003《无铅钎料试验方法—第一部分: 熔化温度范围测定方法》的规定进行，使用美国Perkin Elmer的Pyris Diamond TG-DTA/DSC型热分析仪，将待测钎料合金试样放入样品室中，在氩气保护条件下以5 ℃/min的速率进行升温.

润湿性试验按照日本工业标准JIS Z 3198—4—2003《无铅钎料试验方法—第四部分: 基于润湿平

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衡及接触角法的润湿性试验方法》的规定进行，采用日本 RHESCA 公司的 SAT-5100 型可焊性测试仪进行，试验用标准铜片的规格为 30 mm × 5 mm × 0.3 mm，并选用绿色环保的免清洗钎剂. 试验中将附有钎剂的铜片以 4 mm/s 的速度垂直浸入熔融钎料中，浸入深度为 2 mm，保持时间为 10 s.

2 试验结果及分析

2.1 钎料熔化温度

图 1 为 3 种钎料合金的熔化温度，在主吸热峰之前，都存在着一个次吸热峰，这是由于 Sn-1.2Ag-0.6Cu 合金中 Ag 元素含量较低，并非共晶合金的缘故. 铟是低熔点金属，Sn-1.2Ag-0.6Cu 钎料中添加 In 元素后，合金的吸热峰往低温方向移动，且随着铟含量的增加，合金熔化温度有降低趋势，添加 0.5% 的铟后钎料熔化温度比原先降低了 2 ℃左右，添加 1.0% 的铟后钎料的熔化温度降低了 4 ℃左右. 钎料熔化温度的降低有利于电子封装的顺利进行，并且从结果中看，含铟合金的熔化温度范围基本没有扩大，否则将导致工艺窗口变窄，不利于形成可靠焊点.

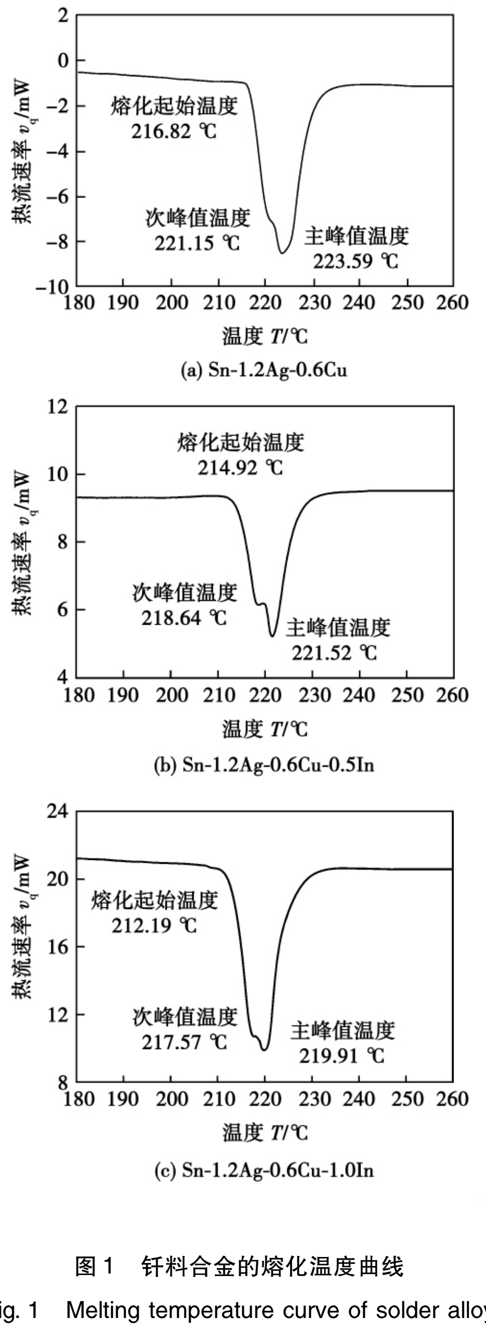


图 1 钎料合金的熔化温度曲线

Fig. 1 Melting temperature curve of solder alloy

2.2 钎料润湿性能

在两种试验气氛(空气与氮气)中测定了 Sn-Ag-Cu-In 无铅钎料在铜基板上的润湿性能，图 2 为 Sn-1.2Ag-0.6Cu 钎料分别在 240，250，260，280 ℃温度条件下的润湿曲线. 润湿时间越短，或者润湿力越大，表明钎料的润湿性能越好. 在 240 ℃时，钎料的润湿性能较差，润湿时间长达 2.4 s 之多; 当温度上升至 250 ℃时，润湿时间缩短至 1.58 s，润湿性能改善显著; 在 260 ℃时，润湿时间已缩短至 1 s 之内，满足了 IPC/EIA J—STD—003B 标准中润湿时间不超过 1 s 的要求; 在 280 ℃时钎料的润湿时间只有 0.7 s 左右.

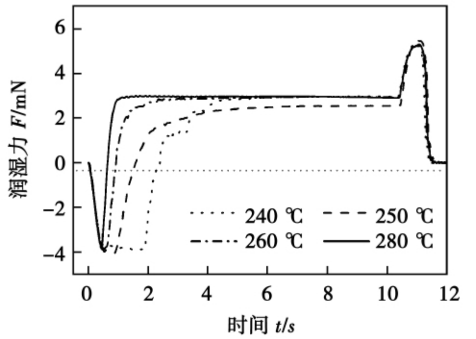


图 2 空气中 Sn-1.2Ag-0.6Cu 钎料润湿曲线

Fig. 2 Wetting curve of Sn-1.2Ag-0.6Cu solder in air

空气中以及氮气保护条件下，Sn-Ag-Cu-xIn 钎料的润湿时间随温度的变化趋势如图 3 所示. 在 240 ~ 280 ℃范围内，随着温度升高，钎料润湿时间逐渐缩短，在氮气保护条件下，钎料的润湿时间均有不同程度的缩短，润湿性能表现更好.

在 Sn-Ag-Cu 钎料中添加 In 元素后，发现其润湿性能随温度变化的规律与无铟钎料类似，只是在相同条件下钎料的润湿时间更短了，而且钎料的润湿力也有了一定程度的提高. 由于 In 元素的添加，降低了钎料合金的熔化温度，因此在相同的钎焊温度时，含铟液态钎料合金的过热度较大，粘度降低，流动性增强，从而改善了钎料的润湿性.

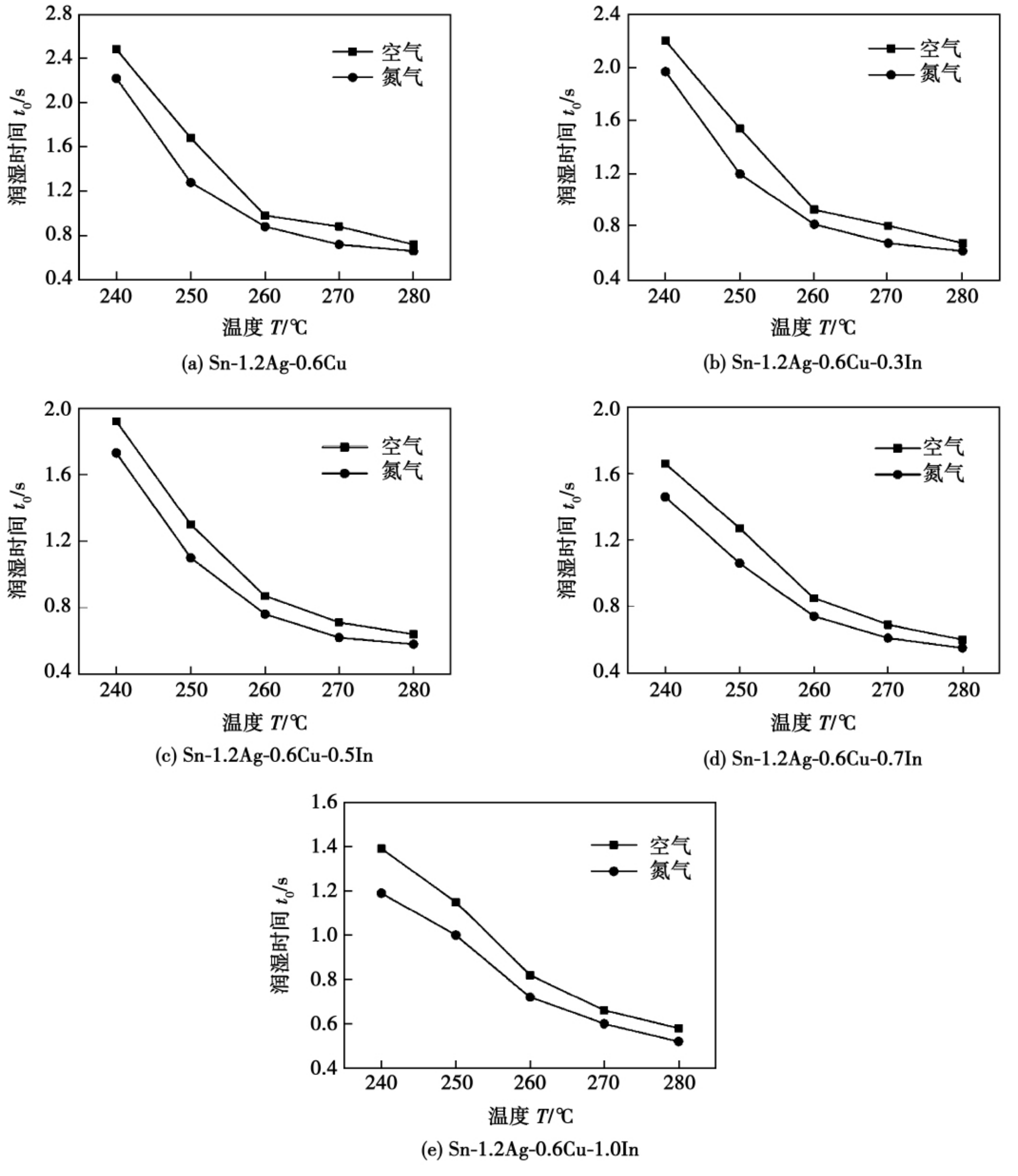


图 3　Sn-1.2Ag-0.6Cu-xIn 钎料润湿时间

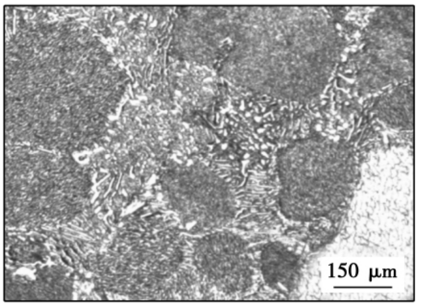
Fig. 3　Wetting time of Sn-1.2Ag-0.6Cu-xIn solder

2.3　钎料显微组织

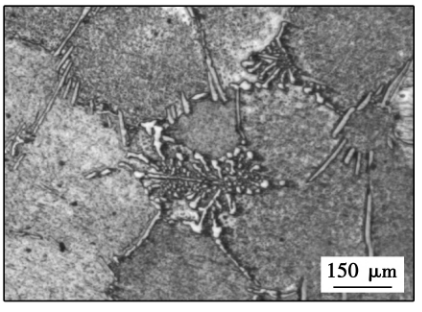
将 Sn-1.2Ag-0.6Cu 以及添加了 0.5% 和 1.0% In 的钎料取样、镶嵌、研磨、抛光后分析其显微组织. 图 4a 为 Sn-1.2Ag-0.6Cu 钎料的显微组织，主要由富锡相及晶粒边界处的 $Ag_3Sn + Cu_6Sn_5 + \beta$-Sn 等组成，银与锌所形成的细小金属间化合物 Ag_3Sn，均匀分布在 β-Sn 周围，这对于改善钎料合金的力学性能有较大贡献[9].

图 4b 为铟含量为 0.5% 的钎料合金显微组织形貌，基本保持了原来 Sn-1.2Ag-0.6Cu 的显微组织特征，拥有细颗粒状或者短棒状的 Ag_3Sn. 添加 1.0% In 元素后(图 5c)，形成的金属间化合物 Ag_3Sn 较为明显，即由颗粒状变为了长条状，这一转变值得引起注意.

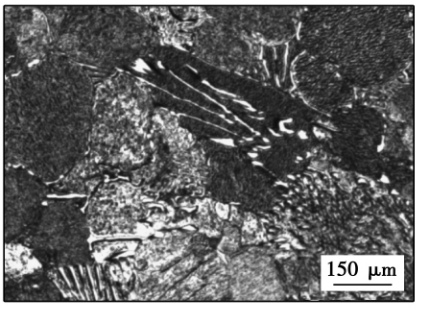
在 β-Sn 周围弥散分布的细小 Ag_3Sn 颗粒，对提高钎料合金的力学性能起到了积极作用，但银含量若超过 3.2% 左右时，除细小 Ag_3Sn 外，还会形成粗大的板状 Ag_3Sn，这不仅降低断后伸长率，还对疲劳和热冲击性能产生了不良影响[9]. 因此目前市场上最成熟的钎料产品 Sn-3.0Ag-0.5Cu，在成分设计时，没有进一步提高银含量使其更接近共晶点，这除了成本考虑外，避免产生粗大的板状 Ag_3Sn 也是一个重要因素[9]. 在银含量较低的 Sn-1.2Ag-0.6Cu 钎料中，便可避免粗大板状 Ag_3Sn 产生. 但添加 1.0% 左右的 In 元素后出现了较大尺寸条状金属间



(a) Sn-1.2Ag-0.6Cu



(b) Sn-1.2Ag-0.6Cu-0.5In



(c) Sn-1.2Ag-0.6Cu-1.0In

图 4 Sn-1.2Ag-0.6Cu-xIn 钎料显微组织形貌

Fig. 4 Microstructure of Sn-1.2Ag-0.6Cu-xIn solder

化合物可解释为金属间化合物晶粒的某些晶面吸附了一定量的 In 原子,使得吸附晶面与未吸附晶面之间的吉布斯自由能差增大,其生长速率的差异也随之加剧. 晶粒在那些未吸附的晶面上生长较快[10],再加上相邻晶粒因长大而发生聚集,就形成了含铟钎料合金中大尺寸的条状金属间化合物,且吸附的铟越多,化合物的形状偏离颗粒状越远. 由此可见,铟含量最好不要超过 1.0% 左右.

3 结 论

(1) 添加 1.0% 以内的 In 元素可逐渐降低 Sn-1.2Ag-0.6Cu 钎料合金的熔化温度,并且钎料合金的熔化温度范围基本没有扩大.

(2) 采用氮气保护有利于 Sn-1.2Ag-0.6Cu-xIn 钎料在铜基板上的润湿、铺展,Sn-1.2Ag-0.6Cu 钎料在空气中的润湿时间在 260 ℃才达到 $t_0 \leqslant 1$ s,Sn-1.2Ag-0.6Cu-1.0In 钎料在 250 ℃氮气保护下就已满足 $t_0 \leqslant 1$ s 的要求.

(3) 当添加 1.0% 左右 In 元素时,Sn-1.2Ag-0.6Cu 钎料合金中 Ag_3Sn 有长大趋势,故添加铟含量宜控制在 1.0% 以内.

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作者简介: 王俭辛,男,1981 年出生,博士,讲师. 主要研究方向为无铅钎料及微电子焊接技术. 发表论文 10 篇. Email: wangjx-just@126.com

The coated electrode had higher ability to prevent the electrode from plastic deformation during welding compared with the un-coated electrode. In addition, there were much more pitting, cracking, intermetallic alloy layer and self-healing layer on the end surface of un-coated electrode. As a barrier, the coatings on the surface of electrode could effectively prevent the adhesions, stripping, and then significantly reduce the diffusion of Zn from the surface of the electrode into the Cr-Zr-Cu electrode to form brittle intermetallic compounds.

Key words: Zn-coated sheet steel; resistant spot welding; coated electrode; metallic ceramic coating; electrode life

Control system for electron beam synchronous scanning based on CPLD PENG Yong[1], WANG Kehong[1], ZHOU Qi[1], WANG Yajun[2], FU Pengfei[3] (1. School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China; 2. School of Mechanical Engineering and Automation, Beijing University of Aeronautics and Astronautics, Beijing 100083, China; 3. National Key Laboratory of High Power Beam Processing Technology, Beijing Aeronautical Manufacturing Technology Research Institute, Beijing 100024, China). p 57 – 60

Abstract: For the quality diagnosis of electron beam in range from 5 mA to 60 mA of a high-voltage electron beam welding machine, a CPLD (Complex Programmable Logic Device)-based control system of electron beam high-speed scanning was established by means of analyzing the principle of electron beam scanning in the electromagnetic deflection coils. The control system consists of industrial PC, CPLD chip, DAC (Digital to Analog Convertor), low pass filter circuits, optical isolation circuits, power amplifiers, electromagnetic deflection coil and external circuits of CPLD. The system controls the special phase relationship between the two waveform and the trigger and sampling frequency of the acquisition card. The scanning frequency can be adjusted within the range 0 ~ 15.6 kHz. The amplified power is the constant current mode and its maximum output current is 5 A. The signal parameters can be adjusted to change the scanning path of electron beam without changing any hardware circuit, so it is highly flexible.

Key words: electron beam welding; CPLD; synchronous scanning; beam quality

Friction-stir welds (FSW) of spray formed 7475 aluminum alloy plate YAN Keng, SHI Chao (Provincial Key Lab of Advanced Welding Technology, Jiangsu University of Science and Technology, Zhenjiang 212003, China). p 61 – 64

Abstract: Friction-stir welds (FSW) of spray formed 7475 aluminum alloy plate with 4 mm thickness were studied. The shapes and dimensions of FSW tools as well as welding parameters were optimized based on mechanical tests and micro-analysis. Experimental results show that good-appearance welds can be achieved by optimal welding parameters. However, fin and groove defects appear if the welding parameters are not appropriate. It also shows that the mechanical properties of the joints are affected by the welding parameters. Some relations between the mechanical properties and the welding parameters were established. As the rotating speed is 1 200 r/min and the welding speed is 80 mm/min, the good weld is achieved and the tensile strength of the weld reaches 442 MPa.

Key words: spray formed 7475 aluminum alloy; FSW; technique; mechanical property

Influence of Ni on microstructure and processing performance of Ag-Cu-Sn-In brazing alloy XU Jinfeng[1], ZHANG Xiaocun[1], ZHAI Qiuya[1], DAI Weigang[2] (1. School of Materials Science and Engineering, Xi'an University of Technology, Xi'an 710048, China; 2. Changshu Shuanghua Electronic Co., Ltd., Changshu 215500, China). p 65 – 68

Abstract: Influence of Ni on the microstructure and processing performance of Ag-Cu-Sn-In brazing alloy was investigated. The microstructures of Ag-Cu-Sn-In of solder were composed of β-Cu coarse dendrite, (α-Ag) distributing in the interdendritic space and little Ag_5Sn. By adding Ni element, the grains refined, the melting point rised a little, and processability was influenced evidently. With Ni content increasing, rate of deformation is bigger, processability of brazing alloy is better. As Ni content was 0.2%, the rate of deformation reached maxinum. Ni content sequentially increasing, microstructures of brazing alloy are becoming bulkily, and processability is worse. With 0.2% Ni Content, the temperature of solidus and liquidus of alloy foils increased respectively by 18 ℃ and 8 ℃, the temperature interval decreased by 20 ℃. After annealing treatment, brazing alloy with 0.2% Ni can be rolled into foils of 50 ~ 80 μm thickness.

Key words: lower silver electrical vacuum brazing filler; melting point; microstructure; processability

Wettability and microstructure of Sn-Ag-Cu-In solder WANG Jianxin, YIN Ming, LAI Zhongmin, LI Xue (Province Key Lab of Advanced Welding Technology, Jiangsu University of Science and Technology, Zhenjiang 212003, China). p 69 – 72

Abstract: In order to improve the properties of Sn-1.2Ag-0.6Cu solder, small amount of In (0 ~ 1.0%) was added to the base alloys, the melting temperatures of alloys were tested, and the effect of In on the wettability and microstructure of solder alloy was studied. The melting temperature decreases with the addition of In. At the same soldering temperature, the lower melting temperature is, the higher superheat is, thus the viscosity of liquid solder is decreased and fluidity is improved. The zero time of Sn-1.2Ag-0.6Cu in air is below 1s at 260℃, while the zero time of Sn-1.2Ag-0.6Cu-1.0In in N_2 atomsphere is below 1s at 250℃, meeting the demand of IPC/EIA J-STD-003B. The Ag_3Sn in Sn-1.2Ag-0.6Cu alloy becomes coarser with 1.0% In added, which is harmful to the mechanical properties. Thenefore, the content of In addition into the Sn-1.2Ag-0.6Cu is not higher than 1.0%.

Key words: lead-free solder; wettability; microstructure

SMT soldering image denoising based on wavelet packet transform and adaptive threshold ZHAO Huihuang[1,2], ZHOU Dejian[3], WU Zhaohua[3], LI Chunquan[3], LI Kangman[1] (1. Department of Computer, Hengyang Normal University, HengYang 421008, China; 2. School of Mechano-Electronic Engineering, Xidian University, Xi'an 710071, China; 3. School of Mechanical and Electronical Engineering, Guilin University of