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微量银对Sn-0.7Cu钎料物理性能及钎焊工艺性能的影响

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摘 要：Sn-Cu共晶钎料是公认的Sn-Pb钎料最具潜力的替代品，尤其在波峰焊上，但与其它无铅钎料相比，该钎料物理性能及铺展性能差，影响其广泛应用。通过在Sn-0.7Cu合金基础上添加微量银来改善合金性能。结果表明，银含量对Sn-0.7Cu-xAg钎料熔点影响不大，最大变化仅为0.3℃；随银含量增加，电阻率逐渐升高；同时，在Sn-0.7Cu基体上添加微量银可以改善钎料合金铺展性能，Sn-0.7Cu-0.2Ag钎料铺展面积最大为28.61 mm²，较基体提高了25.5%，这主要与形成的富银相及钎料与基板间金属间化合物状态有关。

关键词：共晶钎料；熔点；电阻率；铺展面积
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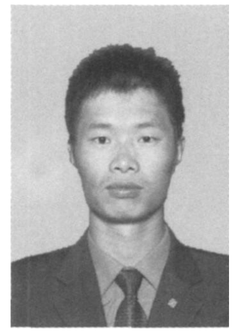

赵快乐

0 序 言

铅有毒，世界各国纷纷立法限制含铅钎料使用，无铅化已成为电子产品发展的必然趋势[1,2]。Sn-Cu共晶钎料价格便宜，来源丰富，是国际上公认的Sn-Pb钎料最佳替代品之一，尤其在波峰焊上[3]，但是其润湿性能较差。Hunt等人[4]测试了SnCu等钎料合金的铺展性能，对铺展性能的优劣排序如下：SnPb共晶＞SnAgCu＞SnAg＞SnCu。镍可以改善Sn-Cu钎料的铺展性能，改变熔融钎料中金属化合物的形状，避免焊接时出现焊点桥连等缺陷。铋的加入可使钎料的熔点下降，润湿铺展能力提高，但同时也使钎料的电阻率增大并使钎料变脆，冷却时易产生微裂纹，因而不适合气密性封装。微量RE可以改善钎料断后伸长率，明显改善钎料的力学性能[5,6]。在Sn-Cu基体中添加银颗粒形成颗粒增强复合钎料，可以大大提高Sn-Cu钎料钎焊接头蠕变寿命且增加了钎料的润湿性能，但制备复合钎料工艺复杂[7,8]。

作者在Sn-0.7Cu共晶钎料基体上添加微量银，研究了银含量对基体钎料物理性能(熔点和电阻率)以及钎焊工艺性能的影响，并深入分析了银的作用机理。

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1 试验方法

1.1 合金制备

试验所用原材料为Sn-30Cu合金和银粒，银纯度为99.95%。将Sn-30Cu合金和银粒按照表1比例用电子天平进行称取，然后在真空度为5×10^{-2} Pa非自耗真空电弧熔炼炉中熔炼。为保证合金均匀度，将合金翻转反复熔炼3次，取出待用。

表1 钎料合金成分(质量分数，%)
Table 1 Composition of solder alloys

	Sn-30Cu	Sn	Ag
第一组	2.3	97.7	0
第二组	2.3	97.5	0.2
第三组	2.3	97.4	0.3

1.2 熔点

用电子天平称称量钎料0.3 g采用差示扫描量热仪(DSC)测定钎料合金熔点。测试条件为：最高温度500℃，加热速度30℃/min，冷却方式为空冷。

1.3 电阻率

将钎料熔化，浇铸成如图1所示电阻率试样。采用精密欧姆仪测量标定长度的电阻，并且按式(1)计算出电阻率。每个试棒分别测量3组数据，求其平均值。

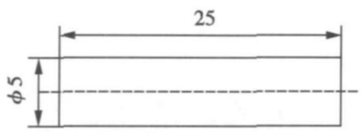

图 1 电阻率试样(mm)
Fig. 1 Schematic diagram of resistance rate specimen

$$\rho=\frac{RS}{L} \tag{1}$$

式中: ρ为电阻率; R为电阻; S为试棒横截面积; L为对应长度值.

1.4 铺展面积

按照国家标准 GB11364—89《钎料铺展性及填缝性试验方法》,铺展面积试验采用 40 mm×40 mm×0.2 mm的紫铜片作为基板,将 0.2 g钎料和 0.03 g松香钎剂放置于打磨并用酒精清洗干净的基板中央,置于 260 ℃箱式电阻炉中,保温 5 min,取出空冷. 铺展试验完成后,用丙酮清洗铺展试样表面,然后用扫描仪扫描试样,如图 2所示,将其拷贝到 AutoCAD中,利用面积查询功能求铺展面积. 每种钎料合金均做 3个铺展面积,求其平均值.

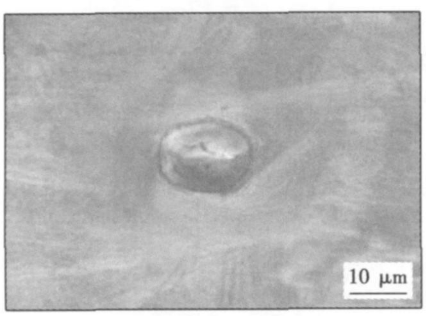

图 2 钎料铺展面积
Fig. 2 Schematic diagram of spreading area of solder

1.5 组织观察与界面金属间化合物测定

将铺展试样沿钎焊金属中心剖开,打磨并抛光剖开界面,采用 JSM—5610LV扫描电镜进行组织观察. 扫描电镜图经扫描仪扫描,将其拷贝到 AutoCAD中,利用面积查询功能求钎料/基板界面处金属间化合物面积,并标定这段金属间化合物的长度,求出金属间化合物厚度.

2 试样结果与分析

2.1 银对 Sn0.7Cu钎料熔点影响

Ag元素含量对 Sn0.7CuAg钎料的熔点影响不大(图 3);当 Ag元素含量为 0.2%时, Sn0.7Cu0.2Ag熔点为 227.3 ℃,较基体钎料最大变化为 0.3 ℃.

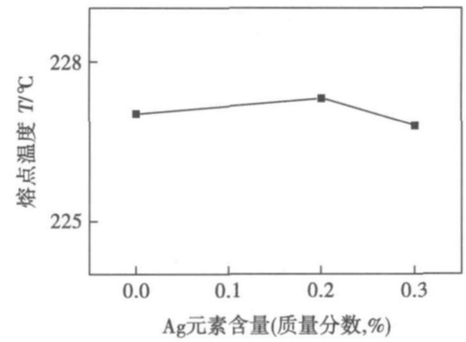

图 3 Ag元素含量对 Sn0.7CuxAg钎料熔点的影响
Fig. 3 Effect of content of Ag on melting point of Sn0.7CuxAg

图 4为 Sn0.7CuxAg钎料合金微观组织形貌,

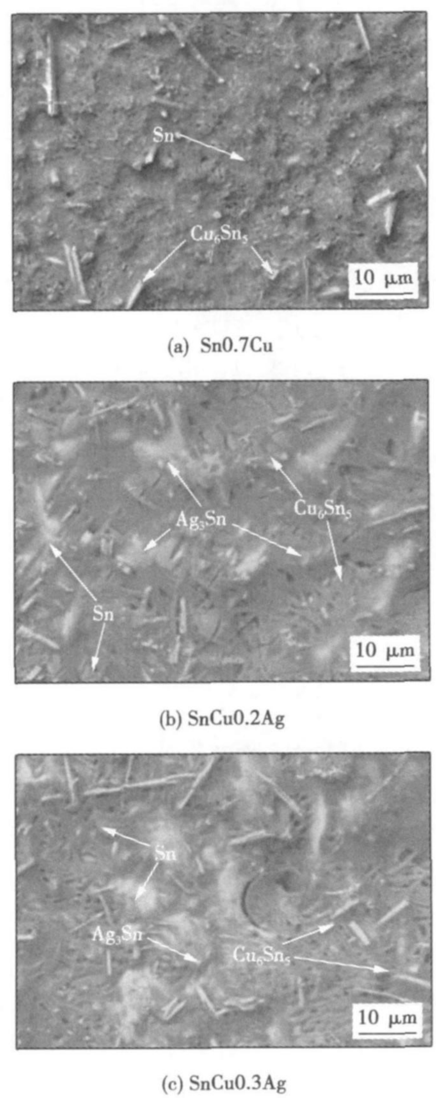

图 4 不同 Ag元素含量的 Sn0.7Cu微观组织形貌
Fig. 4 Microstructure of Sn0.7Cu with different contents of Ag

可以看出, Sn0.7Cu钎料(图 4a)主要由灰色块状基体锡以及呈条状、岛状分布的 Cu_6Sn_5 中间合金组成. 添加 0.2% Ag元素后,银与基体锡反应形成新相弥散分布于基体和 Cu_6Sn_5 中间合金中, XRD分析该相为 Ag_3Sn,其熔点为 724 ℃,使 Sn0.7Cu0.2Ag熔点升高;随着 Ag元素含量增加, Ag_3Sn逐渐减少, SnAg共晶相逐渐增加(图 4c), SnAg共晶相熔点为 221 ℃,锡熔点为 232 ℃,这使得钎料合金熔点降低.

2.2 银对 Sn0.7Cu钎料电阻率的影响

Ag元素含量对 Sn0.7Cu钎料电阻率的影响如图 5所示,可以看出, Sn0.7Cu钎料合金电阻率为 $4.68\times10^{-7}\ \Omega\cdot m$. 随着 Ag元素含量增加(Ag元素含量不大于 0.3%),钎料合金的电阻率逐渐升高,当 Ag元素含量增加到 0.3%时,合金电阻率为 $6.67\times10^{-7}\ \Omega\cdot m$.

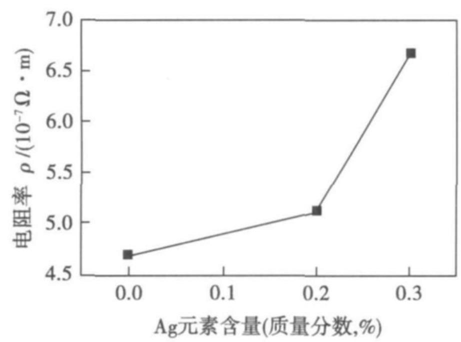

图 5　Ag元素含量对 SnCuxAg钎料电阻率的影响
Fig. 5　Effect of content of Ag on resistance rate of SnCuxAg

从图 4可以看出,在 Sn0.7Cu中添加 0.2% Ag会形成 Ag_3Sn相和 SnAg共晶相, Ag_3Sn迅速增多,弥散分布在基体锡上,电阻率增加; Ag元素含量达到 0.3%时, Cu_6Sn_5 增多呈网状均匀分布,网格更加细小,并且银颗粒逐渐细化,弥散分布在基体锡上,使得电阻率显著上升.

电阻率过高,钎焊过程容易过热,使钎料的可靠性降低,对钎焊不利,所以 Sn0.7CuAg钎料合金 Ag元素含量应控制在 0.2%以内.

2.3 银对 Sn0.7Cu钎料铺展面积的影响

Ag元素含量对 Sn0.7Cu钎料铺展面积的影响如图 6所示,可以看出,添加微量银可以明显改善 Sn0.7Cu钎料的钎焊工艺性能. 当 Ag元素含量为 0.2%时, Sn0.7Cu0.2Ag钎料铺展面积最大,达到 28.61 mm^2,比基体铺展面积增大 25.5%. 当 Ag元素含量大于 0.2%时,随着 Ag元素含量的增加,钎料合金铺展面积有下降趋势.

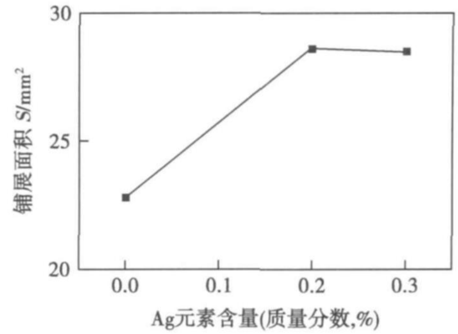

图 6　Ag元素含量对 SnCuxAg钎料铺展面积的影响
Fig. 6　Effect of contents of Ag on spreading area of SnCuxAg

钎料铺展面积与金属间化合物厚度及形状密切相关. 一般的,钎料与基体轻微发生冶金反应,对铺展性能有利[9]. 钎料/基体界面金属间化合物光滑平整,铺展性能好. 图 7为 Sn0.7Cu和 Sn0.7CuxAg

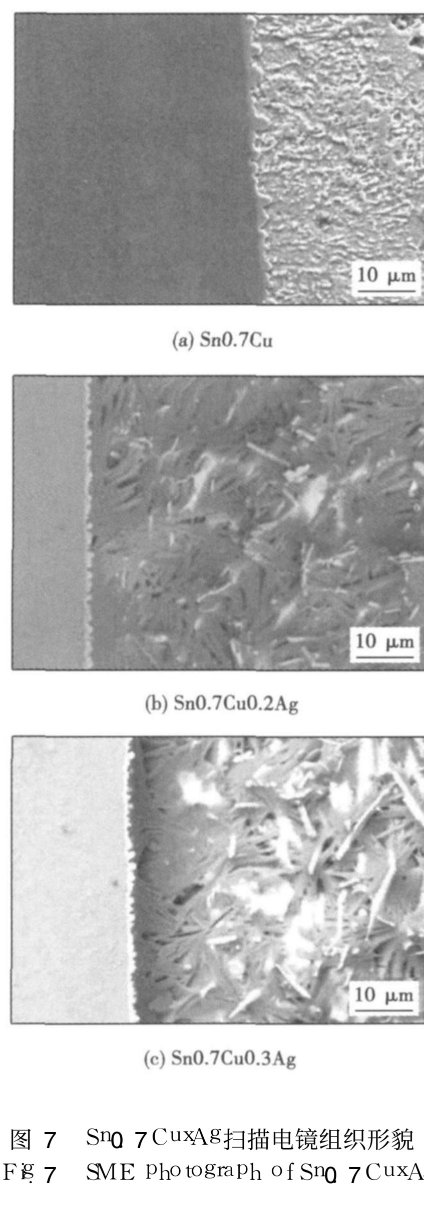

图 7　Sn0.7CuxAg扫描电镜组织形貌
Fig. 7　SME Photograph of Sn0.7CuxAg

微观扫描电镜组织形貌，表2为Sn0.7CuxAg钎料金属间化合物的统计结果. 可以看出添加微量银，Sn0.7CuxAg钎料金属间化合物厚度变薄，即钎料与基板发生了轻微的冶金结合，使得液态钎料向四周扩展阻力减小，钎料易于流动，铺展性能提高. 并且界面较基体更加光滑平整，铺展面积增大.

表2 Sn0.7CuxAg钎料合金厚度(μm)

Table 2 IMC thickness of Sn0.7CuxAg solder alloys

	Sn0.7Cu	Sn0.7Cu0.2Ag	Sn0.7Cu0.3Ag
IMC厚度	3.1	1.6	1.7

高熔点的二次相越多，钎料合金的粘度越大，铺展性能越差. 在Sn0.7Cu中添加微量银，会形成SnAg共晶相，且随着Ag元素含量的增多，SnAg共晶相增多且变大，从而使钎料合金粘度增加，这对钎料合金铺展性能造成不利影响，使得Sn0.7Cu0.3Ag铺展面积较Sn0.7Cu0.2Ag小. 金属间化合物形貌和粘度共同作用使铺展面积呈现图6所示趋势，Sn0.7Cu0.2Ag钎料合金铺展面积较好.

3 结 论

(1) Ag元素含量对Sn0.7CuAg钎料熔点影响不大.

(2) 在Sn0.7Cu基体合金上添加微量银会导致钎料合金电阻率升高. 当Ag元素含量为0.3%时，钎料合金电阻率为$6.67\times10^{-7}\ \Omega\cdot m$，较基体钎料升高了42.5%.

(3) 当Ag元素含量为0.2%时，Sn0.7Cu0.2Ag钎料合金铺展面积最大，较基体钎料提高25.5%. 在Ag元素含量达到0.3%时，铺展面积略有降低.

(4) Ag元素含量对钎料/基板金属间化合物有一定的影响，添加微量银使金属间化合物厚度变薄，界面光滑平整；当Ag元素含量大于0.2%时，金属间化合物厚度略有增加，铺展性能有所降低.

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tic; stress concentration

Microstructures and solderability of SnCuNi-xPr lead-free solder LUO Jiadong, XUE Songbai, ZENG Guang, HU Yuhua (School of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China). p 57—60

Abstract: Effects of rare earth element Pr on the wetting performance, mechanical properties and microstructures of Sn0.7Cu0.05Ni lead-free solder were studied. The inherent relationship between the microstructures and properties of the solder was preliminarily discussed. The experimental results show that the suitable amount of Pr addition is 0.025%-0.075%, and the most appropriate amount is 0.05%, at which composition the solder exhibits the best wetting performance and mechanical properties. The surface tension of the liquid solder was significantly reduced due to the addition of rare earth Pr and the wetting performance was improved. The microstructures of the soldered joints were evidently refined, which resulted from the pinning effect on the grain boundaries migration due to the addition Pr, and the shear strength was improved obviously. It was also found that the activity of the rare earth element of Pr may be reduced because of excessive oxidation and the enlargement of the comprehensive effect of stress field caused by excessive addition of Pr.

Key words: Pb-free solder; rare earth element Pr; wetting performance; mechanical properties; microstructure

Analysis on continuous cooling transformation curves of simulated heat affected zone for SA508-3 steel in nuclear power CHI Luxin[1,2], MA Yonglin[2], XING Shuqing[2], ZHAO Yongtao[2], CHEN Furong[2], CHEN Zhongyi[2] (1. School of Materials Science and Engineering, Inner Mongolia University of Technology, Huhhot 010051, China; 2. School of Material and Metallurgy, Inner Mongolia University of Science and Technology, Baotou 014010, China). p 61—64

Abstract: The SA508-3 steel used in nuclear power was used to determine continuous cooling transformation (SH-CCT) diagram of simulated heat affected zone (HAZ) by thermal expansion method on Gleeble 1500D thermal simulation testing machine, and the microstructure characteristics of HAZ at $t_{8/5}$ from 3.75 s to 20 000 s were investigated. It was found that the microstructures were changed much from the base metal because of the influence of the cooling time ($t_{8/5}$). When the $t_{8/5}$ is less than 15 s, the phase transformation to obtain all martensite happens, the cooling time range to get all the bainite is from 60 s to 3 000 s, and if all the ferrite and pearlite can be obtained if the $t_{8/5}$ is more than 6 000 s. The hardness of HAZ is higher than 350 HV and there are harden quenching tendency and the crack sensitivity when the $t_{8/5}$ is less than 100 s, softening phenomena easily happens and the hardness of HAZ is lower than that of the base metal when the $t_{8/5}$ is more than 20 000 s. The cold cracking can be avoided only at the proper preheating temperature.

Key words: SA508-3 steel; cooling rate; continuous cooling transformation curves; crack sensitivity

Effect of content of Ag on physical properties and solderability of Sn0.7Cu solder ZHAO Kuaile, YAN Yanfu, TANG Kun, SHENG Yangyang (School of Materials Science & Engineering, Henan University of Science & Technology, Luoyang 471003, China). p 65—68

Abstract: SnCu eutectic solder is considered as the most potential substitutes of SnPb solder, particularly in wave soldering. But compared to other lead-free solders, its poor physical properties and spreading peformance limits its wide application. A new solder is made by adding trace Ag into Sn0.7Cu alloy to improve its performance. The results show that content of Ag has little influence on the melting point of Sn0.7CuxAg solder. The melting point of Sn0.7Cu0.2Ag is higher only 0.3 ℃ than that of matrix solder. The resistivity increases with the increase of the content of Ag. At the same time, the spreading performance of the new solder is improved by adding trace Ag into Sn0.7Cu. The spreading area of Sn0.7Cu0.2Ag reaches the maximum value of 28.61 mm² and is increased 25.5% than that of the matrix solder, which is mainly related to the formation of the rich Ag phase and the thickness and shape of the metal intermetallic compound between the solder and the substrate.

Key words: eutectic solder; melting point; resistivity; spreading area

Analysis of fatigue life of electron beam welding seam with bell shape YANG Bo[1], YANG Xinhua[1], FU Wei[1], HU Shubing[2], XIAO Jianzhong[2] (1. School of Civil Engineering and Mechanics, Huazhong University of Science and Technology, Wuhan 430074, China; 2. School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China). p 69—72

Abstract: The bell-shaped TC4 titanium alloy joint of electron beam welding were divided into three zones, namely weld seam, heat affected zone and base metal. Considering the gradient distribution of the material strength in the heat-affected zone, the finite element model was founded. The series of software of MSC company were used to analyze the distribution of stress and fatigue life under the simulated experimental loading conditions, and the stress distribution along different paths were investigated, and the simulating results of fatigue life were compared with that of experiments. It is shown that the weld seam has noticeable effect on stress distribution of the weldment, which causes the stress concentration with the stress concentration factor of about 1.3 at the weld toe. The uneven distribution of weldment life is caused by stress concentration, so that the fatigue life of weldment is reduced. The fatigue failure usually starts at the weld toe.

Key words: TC4 titanium alloy; electron beam welding; bell-shaped weld seam; fatigue life

Microstructure and properties of TiC$_p$/Al composite coating by argon arc cladding MENG Junsheng, SHI Xiaoping, WANG Zhenting, WANG Yongdong (School of Materials Science and Engineering, Heilongjiang Institute of Science and Technology, Harbin 150027, China). p 73—76

Abstract: By using argon arc cladding, TiC$_p$/Al composites coating was in-situ synthesized on the ZL104 alloy surface. The microstructures and properties of the composites coatings were investigated by X-ray diffractometer, scanning electron microscope and microhardness tester. The results show that if the content of (Ti+C) is less than 30% during argon arc cladding, both TiC particle and Al_3Ti compounds can be found. If the con-