含纳米铝颗粒SnAgCu钎料组织与性能

张　亮[1,2]，　韩继光[1]，　郭永环[1]，　何成文[1]，　张　剑[1]
(1. 江苏师范大学 机电工程学院，徐州　221116；2. 江苏科技大学 先进焊接技术省级重点实验室，镇江　212003)


张　亮

摘　要： 选择在SnAgCu钎料中添加纳米铝颗粒，改善无铅钎料的性能. 结果表明，微量纳米铝颗粒可以增加SnAgCu钎料的润湿铺展面积，显著提高SnAgCu焊点的拉伸力和剪切力，添加过量时钎料的润湿性能会有一定程度的下降，经过优化分析发现纳米铝颗粒的最佳添加量应该控制在0.1%附近. 对SnAgCu-*x*Al钎料的组织分析，发现纳米颗粒的添加，钎料组织得到明显的细化，树枝晶间距明显减小. 对SnAgCu-*x*Al焊点进行蠕变拉伸测试，发现纳米铝颗粒可以显著提高SnAgCu焊点的蠕变断裂寿命，主要归因于纳米颗粒对位错的钉扎作用.

关键词： 纳米颗粒； 无铅钎料； 力学性能； 蠕变断裂寿命
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0　序　　言

近年来，新型无铅钎料的研究成为电子工业中一个重要的研究方向. 在诸多的无铅钎料中，SnAgCu以其优越的性能被推荐为替代传统SnPb钎料的最佳选择[1]，但是该系列钎料也有其自身的缺点，例如，服役期间内部组织容易出现大块的脆性金属间化合物[2]，导致焊点的提早失效，同时由于电子器件向着高密度、细间距方向发展，对焊点的性能要求也越来越高[3]. 因此新型SnAgCu基无铅钎料的开发成为国内外学者争相研究的热点.

在研发新型无铅钎料中，添加纳米颗粒是提高焊点性能以及细化组织的一种较为有效的方法. 刘彬等人[4]选择在SnAg基无铅钎料中添加纳米POSS颗粒，钎料的润湿性以及焊点的抗剪强度都得到明显的提高. Gain等人[5]在Sn9Zn和SnZn3Bi钎料中添加镍颗粒，发现纳米颗粒的添加可以明显提高焊点的剪切力，同时在服役期间保持相同的趋势. 而纳米钴颗粒的添加容易降低钎料的润湿性，但是对焊点的硬度有明显的改善作用[6]. 纳米钼颗粒的添加可以提高SnAgCu钎料的力学性能[7]. 目前含纳米无铅钎料的研究成果均针对单一性能进行研究，而系统的研究鲜见报道.

针对SnAgCu钎料，探讨含纳米铝颗粒SnAgCu润湿性、力学性能和蠕变断裂寿命的变化规律，同时研究纳米铝颗粒对SnAgCu钎料微观组织的影响，进而解释性能的变化，研究结果为新型无铅钎料的研究提供一定的数据支撑.

1　钎料制备和试验方法

选用的基体粉末材料为Sn3.8Ag0.7Cu，添加的纳米铝颗粒直径为50 nm，将金属粉末(SnAgCu粉末+纳米铝颗粒)混合RAM钎剂制成焊膏，然后进行试验研究. 试验根据国家标准GB/T113634—1989《钎料铺展性及填缝试验方法》测试钎料的润湿性能. 润湿铺展面积测试选择40 mm×40 mm×0.5 mm铜板作为基板，选择0.2 g钎料进行回流焊(小型回流焊炉)，回流焊的峰值温度为245 ℃. 测试后的样品通过数码相机拍照，将图片输入电脑，采用Image-J软件进行面积计算，分析纳米颗粒对钎料铺展面积的影响.

选择QFP256和片式电阻(RC)两种电子器件，采用回流焊接方法焊接电子器件，选择焊点形态成形良好的器件进行力学性能测试，力学性能采用的设备为微焊点测试仪(STR-1000). 为了分析纳米颗粒对钎料组织的影响，选择SnAgCu-*x*Al钎料进行金相试验，经过剖面、打磨、抛光等程序制成需要的样

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品,采用 5% HNO_3 +95% CH_3CH_2OH 溶液进行腐蚀,然后采用金相显微镜观察组织. 采用 CTM104-Al 机械式高温持久蠕变试验机进行蠕变试验,研究在室温 12.5 MPa 载荷作用下不同纳米含量无铅焊点的蠕变断裂寿命.

2 试验结果与讨论

2.1 润湿性

润湿性是衡量无铅钎料性能的一个重要指标,测量钎料的铺展面积是分析钎料润湿性能的一种常用方法. 图1为不同纳米铝含量的 SnAgCu 系钎料的润湿铺展面积数据,可以看出纳米铝颗粒的添加可以在一定程度上提高钎料的润湿性,但是提高幅度相对较小,最高幅度为9.6%. 纳米颗粒含量超过0.1%以后,钎料的润湿性能明显下降. 同时纳米颗粒添加量增加到0.4%时,钎料的铺展面积仍然高于 SnAgCu 钎料.

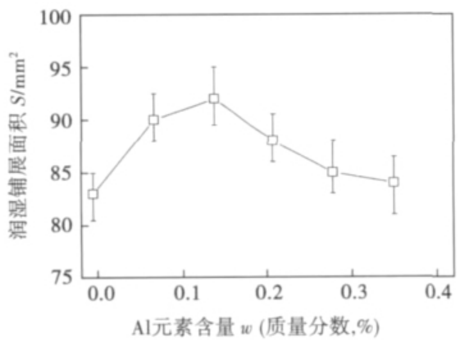

图1 含纳米铝颗粒 SnAgCu 钎料铺展面积

Fig. 1 Spreading area of SnAgCu solders with nano-Al particles

纳米铝颗粒活性较强[8],趋于表面富集,容易降低钎料的表面张力,增加钎料的流动性,进而提高钎料的润湿性. 当钎料中纳米颗粒的含量进一步增加时,钎料的润湿性有一定的下降,这主要归结于纳米颗粒的团聚,导致钎料的流动性变差.

2.2 力学性能

图2为不同纳米铝含量 SnAgCu 焊点拉伸力数据,可以看出随着纳米铝颗粒含量的增加,焊点的拉伸力明显增加,纳米铝颗粒含量为0.05%时,焊点的拉伸力提高近18%,当纳米颗粒进一步增加时,焊点的拉伸力有一定的增加,增加的幅度相对较小.

图3为不同纳米铝含量时 SnAgCu 焊点的剪切力曲线,可以看出纳米铝颗粒的添加,焊点的剪切力明显增加,且随着纳米颗粒的增加剪切力呈现抛物

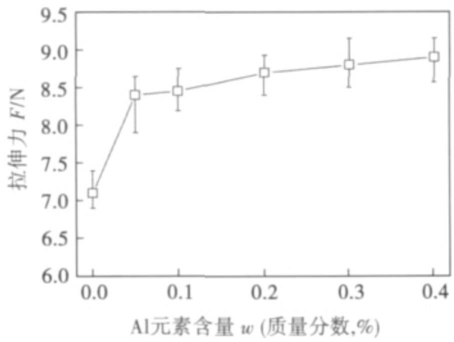

图2 含纳米铝颗粒 SnAgCu 焊点拉伸力

Fig. 2 Tensile force of SnAgCu-Al solder joints

线的方式增加. 这也在一定程度上说明,纳米颗粒的强化作用并不是无限制的,而是存在明显的极限值. Gain 等人[9]在研究含纳米铝颗粒 SnAgCu (Au/Ni/Cu 基板) 焊点剪切力时,也发现了纳米铝颗粒类似的强化作用.

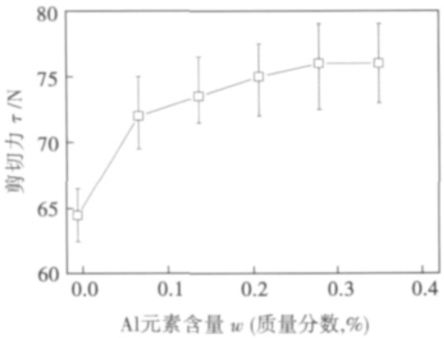

图3 含纳米铝颗粒 SnAgCu 焊点剪切力

Fig. 3 Shear force of SnAgCu-Al solder joints

纳米颗粒的添加,可以在熔融钎料中充当形核质点,使金属间化合物依附在纳米颗粒表面形核,同时部分纳米铝颗粒参与反应,生成 Sn-Al-Ag 金属间化合物[9],最终在钎料凝固过程中,使金属间化合物析出并均匀分布在钎料基体中,达到第二相颗粒强化. 纳米铝颗粒和其它纳米颗粒的强化机制不同,例如纳米 SiC 颗粒的添加[10],SiC 颗粒在钎料基体内部不发生反应,仅仅提供形核质点的作用.

2.3 钎料基体组织

图4为含不同纳米铝颗粒 SnAgCu 无铅钎料基体组织. SnAgCu 钎料的基体组织主要由 β-Sn, Cu_6Sn_5 和 Ag_3Sn 三种相组成,图4a为典型的 SnAgCu 组织,其中黑色的颗粒组织为共晶颗粒 (Cu_6Sn_5 和 Ag_3Sn),树枝晶为 β-Sn. 添加0.05%纳米铝颗粒后,内部组织发生明显的变化,β-Sn 的尺寸得到明显的细化,同时共晶颗粒较为均匀的分布

在 β-Sn 基体中，当纳米铝颗粒添加达到 0.1% 时，钎料组织得到最大程度的细化，进一步增加纳米颗粒的含量(0.2% ,0.3% ,0.4%) ，钎料组织发生一定程度的粗化，但是组织相对 SnAgCu 钎料仍然较为细小. 这主要是因为纳米颗粒添加过量时，由于纳米颗粒易于团聚，导致部分纳米颗粒的形核质点的作用体现的不明显，从而弱化了纳米颗粒的细化作用.

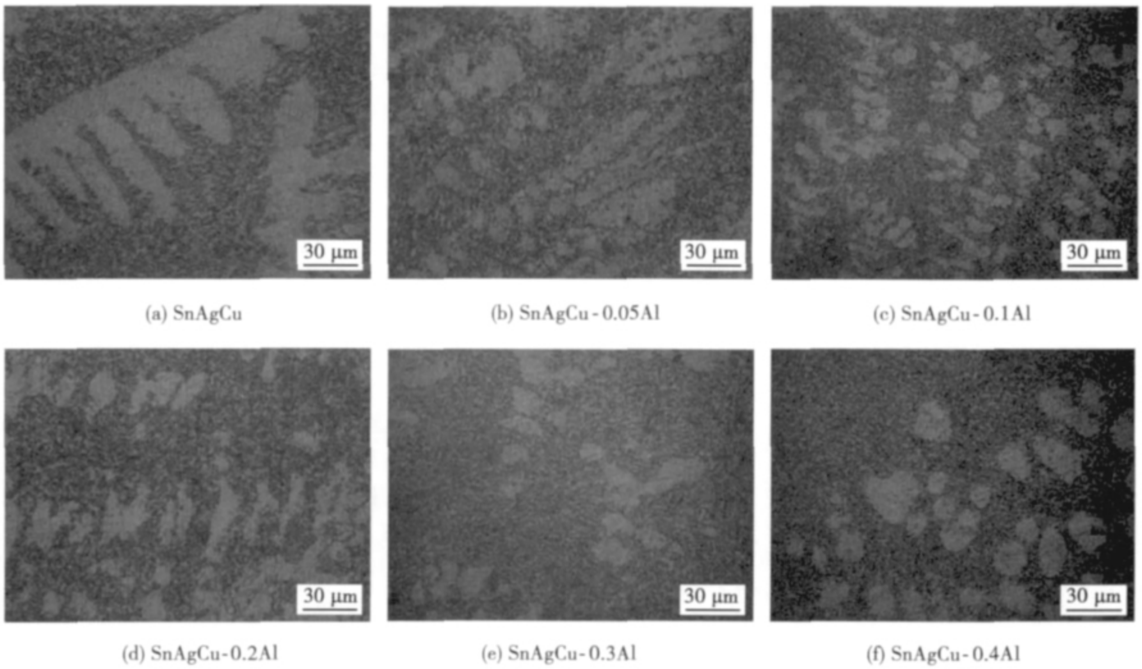

图 4　SnAgCu-xAl 钎料基体组织形貌

Fig. 4　Microstructure of SnAgCu-xAl solders

为了进一步分析钎料基体组织，测量钎料基体 β-Sn 的尺寸. 对 SnAgCu 钎料基体而言，β-Sn 树枝晶的枝晶间距约为 12 μm，当纳米铝颗粒含量为 0.05% 时，枝晶平均间距约为 7 μm，进一步增加为 0.1% 时，枝晶平均间距约为 4.0 μm ，树枝间距减小了 66.6%. 当进一步增加纳米颗粒的含量，枝晶间距有一定的增加. 从而说明钎料组织 β-Sn 枝晶间距和纳米铝颗粒之间具有一定的函数关系. Keller 等人[11] 研究 Sn-xAg-0.4Cu 树枝晶时，发现银含量和 β-Sn 枝晶间距之间也存在类似的规律.

2.4　蠕变寿命分析

室温下测量 SnAgCu-xAl 的蠕变断裂寿命，测量数据如图 5 所示. 可以明显看出纳米颗粒的添加可以显著提高 SnAgCu 的蠕变寿命. 纳米颗粒添加为 0.05% 时，寿命增加幅度较大，随后进一步增加纳米颗粒的含量，蠕变断裂寿命的增加幅度较少. 因此，在一定程度也说明纳米颗粒的添加对钎料性能的影响有一定的极限值. 结合焊点的力学性能以及钎料的润湿性数据，综合分析，发现纳米铝颗粒的最佳添加量应该在 0.1% 左右.

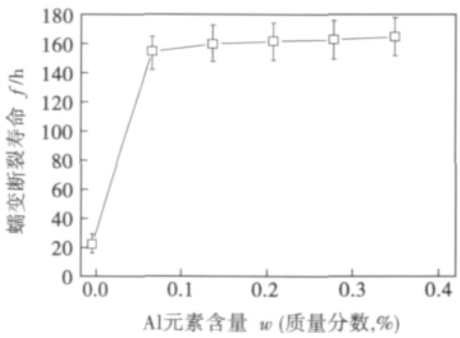

图 5　含纳米铝颗粒 SnAgCu 焊点的蠕变寿命

Fig. 5　Creep rupture life of SnAgCu solder joints

对于给定的材料，在一定的温度/应力下某一种变形机制占优势，当温度/应力条件改变时变形机制也可能发生变化. 在较高的应力状态下，蠕变变形包含位错滑移和攀移，然而晶粒边界扩散(coble creep) 和晶格扩散(nabarro-herring creep) 为较低应力状态下的主要蠕变变形机制[12] . SnAgCu 基无铅钎料在应用于电子工业中服役期间归一化温度远远高于 0.5，因此在较高应力下，位错蠕变是无铅钎料的主要蠕变机制，包括位错攀移和克服能量势垒，在较低应力下，晶格扩散是无铅钎料的主要蠕变机制，

包括间隙原子的扩散和迁移，以及晶格空位在晶粒边界的扩散和迁移，同时在各种应力水平下，以上蠕变机制均伴随着晶粒边界滑移.

Dutta等人[13]研究发现，对于无铅钎料，低应力下主要发生位错滑移—攀移机制，高应力发生颗粒限制位错攀移. 在钎料内部金属间化合物颗粒具有钉扎位错的作用，可以阻止位错在低应力下的滑移—攀移. 由于金属间化合物颗粒具有很高的硬度，所以第二相颗粒被位错切割的机理不可能成立. 根据位错理论，位错只能绕过不可变形的第二相颗粒，故而位错只能攀移越过析出的第二相颗粒. 当应力值高到超过门槛应力值时，先前钉扎位错迅速越过金属间化合物颗粒，引起蠕变变形，因此施加应力超过门槛应力值后位错移动，位错蠕变速率也会迅速增加.

3 结 论

(1) 纳米铝颗粒可以改善SnAgCu钎料的润湿性，显著提高焊点力学性能和蠕变断裂寿命.

(2) 纳米铝颗粒细化钎料基体组织，减小树枝晶的尺寸. 综合材料性能参数和组织演化规律，发现纳米铝颗粒的最优添加量为0.1%左右.

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作者简介: 张 亮，男，1984年出生，博士，讲师，硕士研究生导师. 主要从事钎焊材料、微电子封装材料与工艺、焊点可靠性的研究. 发表论文40余篇. Email: zhangliang@jsnu.edu.cn

established by Michio Inagaki was more suitable to calculate the cooling time $t_{8/5}$ during thick plate welding than D · Vwer's theoretical empirical formula. The coarse grain zone in the heat-affected zone (HAZ) of Q890 steel joint had strong harden quenching tendency, controlling the preheating temperature and welding heat input had little effect on improving the harden quenching tendency. However, preheating could significantly increase the welding cooling time t_{100} and reduce the cold cracking tendency of the steel. Through data fitting, the relationship between the cooling time $t_{8/5}$ and the hardness of coarse grain zone in HAZ was established and had been verified to predict the maximum hardness of Q890 steel.

Key words: Q890 steel; high strength steel; harden quenching tendency; cold cracking susceptibility

Effects of Nd on microstructure and properties of Sn-Zn-Ga Lead-free solder LUO Dongxue[1], XUE Peng[1], XUE Songbai[1], HU Yuhua[2] (1. School of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China; 2. The 55th Research Institute, China Electronic Technology Group Co., Nanjing 210016, China). pp 57 – 60

Abstract: The effects of alloying element Ga and rare earth element Nd on the wettability, microstructure and mechanical properties of the Sn-Zn solder were investigated. The results indicated that the wetting properties of the solder were improved with appropriate addition of Nd. When the Nd content was 0.1wt%, the wetting properties reached the best. It was also found that the wettability was improved when the temperature rose properly. With the Nd content increasing, the amount of black needle-like Zn-rich phases gradually decreased and the matrix microstructure of the solder was refined. When the Nd content reached 0.1wt%, the grains in the solder was the most uniform and smallest. Meanwhile, the mechanical properties of the joints made with solders containing Nd were also improved, and the shear strength of the resultant joints with solder containing 0.1wt% Nd reached the maximum. Therefore, the optimal amount of Nd in the Sn9Zn0.5Ga solder was around 0.1wt%.

Key words: Sn-Zn solder; wettability; microstructure; mechanical property

Microstructure and performance of Fe-Cr-Ti-C plasma coatings LIU Junbo[1,2], WANG Peng[2], LI Huiqi[2], LI Min[2], TAN Gaoxu[2], LIU Yanyan[2] (1. School of Mechanical-electronic and Vehicle Engineering, Weifang University, Weifang 261061, China; 2. School of Material, Shandong University of Science and Technology, Qingdao 266510, China). pp 61 – 64

Abstract: Fe-based alloy coatings, with and without adding titanium (keeping other powder ingredients constant), were produced on Q235 steel substrate by plasma cladding process with high-energy plasma jet as the heat source. The microstructure, phase composition and microhardness of the coatings were investigated by optical microscope (OM), scanning electron microscopy (SEM), X-ray diffraction (XRD), electron probe microanalysis (EPMA) and microhardness tester, respectively. The results showed that the grain of the Fe-based coating containing Ti was obviously finer than that without Ti, and more band-like crystals formed in the coatings containing Ti. However, with the increase of Ti content in the coating, the hard phase $(Cr,Fe)_7C_3$ in the eutectic increased gradually and restrained the precipitation of carbides in the coating, consequently, the average and maximum microhardness of the cladding coating decreased.

Key words: plasma cladding; titanium carbide; crystal distribution

Microstructure and properties of SnAgCu solders bearing Al nano-particles ZHANG Liang[1,2], HAN Jiguang[1], GUO Yonghuan[1], HE Chengwen[1], ZHANG Jian[1] (1. School of Mechanical and Electrical Engineering, Jiangsu Normal University, Xuzhou 221116, China; 2. Provincial Key Laboratory of Advanced Welding Technology, Jiangsu University of Science and Technology, Zhenjiang 212003, China). pp 65 – 68

Abstract: Al nano-particles were added into the SnAgCu solder to improve the properties. The results indicate that adding small amount of nano-particles can enhance the wettability of the SnAgCu solder, and the mechanical properties of the soldered joints can be improved significantly. However, excessive nano-particles would reduce the wettability of the solder, and the optimum nano-particles content was about 0.1wt% for the SnAgCu solder. Based on the microstructure examination, it was found that adding nano-particles could obviously refine the microstructure and reduce the dendrite-arm spacing of SnAgCu-xAl solders. In addition, the creep tensile test for the joint made with SnAgCu-xAl solder revealed that the nano-particles could significantly improve the creep rupture life by pinning the dislocations.

Key words: nano-particles; lead free solder; mechanical property; creep rupture life

Investigation on joint establishment and weld microstructure during linear friction welding of dissimilar titanium alloys
ZHANG Chuanchen[1], ZHANG Tiancang[1], JI Yajuan[1], HUANG Jihua[2] (1. Research Department of Aeroengine, AVIC Beijing Aeronautical Manufacturing Technology Research Institute, Beijing 100024, China; 2. School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China). pp 69 – 72

Abstract: Linear friction welding of TC4 to TC17 titanium alloys was conducted, and the joint establishment and weld microstructure was analyzed. The interface temperature in the dynamic equilibrium phase was measured. The results show that large wear particles were easily generated in the interface in the initial phase. During the transition phase, the large wear particles were expelled from the rubbing interface and high temperature plasticized layer formed. Then the viscoplastic metal homogeneously moved out of the rubbing interface and formed a flash, and the grains on both sides of the interface were refined. It was observed that the temperature during the dynamic equilibrium phase exceeded 1 200 ℃, higher than the phase transition temperatures of both base materials, which led to the generation of recrystallized β grain, and then widmanstatten structure by α-β transformation. The microstructure in the thermal-mechanically affected zone (TMAZ) was apparently deformed and elongated.

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

Analysis of microstructure and mechanical properties of refill friction stir spot welded aluminum alloy SHEN Zhikang[1], YANG Xinqi[1], ZHANG Zhaohua[1], YIN Yuhuan[2] (1. Tianjin Key Laboratory of Advanced Joining Technology, Tianjin University, Tianjin 300072, China; 2. Shanghai Spaceflight Manufacture (Group) Co., Ltd., Shanghai 200245, China).