

不同 Ag 元素含量 Sn-Ag-Cu 无铅钎料性能分析

刘 平^{1,2}, 顾小龙¹, 赵新兵², 刘晓刚¹, 钟海峰¹

(1. 浙江省冶金研究院有限公司 浙江省钎焊材料与技术重点实验室, 杭州 310011;

2. 浙江大学 材料科学与工程学院, 杭州 310027)

摘 要: 分别研究了 Ag 元素含量(质量分数, %) 为 0.3 1.0 2.0 3.0 3.8 的 Sn-Ag-Cu (SAC) 无铅钎料合金的显微结构、熔化行为、力学性能、润湿性和界面金属间化合物(IMC) 形貌。结果表明, 随着 Ag 元素含量的增加, 钎料内部金属间化合物晶粒越小, 晶粒在钎料中的密度越高, 晶粒间距越小, 金属间化合物产生的弥散强化越明显, 钎料的抗拉强度越高, 但韧性越低。随 Ag 元素含量的提高, 钎料越接近共晶成分, 熔化温度范围越小。Ag 元素含量对润湿性影响不明显, SAC0307/Cu 焊点界面 IMC 晶粒比其它钎料细小。

关键词: 无铅钎料; 金属间化合物; 显微组织; 熔点

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刘 平

0 序 言

为适应电子信息产品无毒无害的要求,近年来无铅钎料在电子及微电子工业被广泛使用,其中 Sn-(3.0~3.9) Ag-(0.5~0.7) Cu(质量分数, %,下同) 高 Ag 元素含量的无铅钎料,由于具有较好的综合力学性能和工艺性能而得到行业的推广^[1,2]。然而,随着绿色无铅化的深入实施和推进,电子工业界发现,在消费电子产品运输和服役过程中容易受到意外的颠簸、震动、碰撞和跌落,从而引入电子组装互连中由力学冲击引起的一种新的失效机制^[3],而高 Ag 元素含量的钎料在这方面的问题尤为突出。低 Ag 元素含量的无铅钎料具有较好的韧性,在抗跌落性能方面优于 Sn-3.0Ag-0.5Cu,且材料成本有所下降,在业界受到广泛关注,日本电子信息产业协会 JEITA 已于 2007 年推出的第二代无铅钎料方案即为低银钎料^[4]。

目前 Ag 元素含量对钎料性能影响的研究不多,研究者在选择何种合金基体进行试验的论据也不充分,暂未形成统一的认识,文中旨在评价不同 Ag 元素含量 Sn-Ag-Cu(SAC) 无铅钎料的熔化行为、力学性能、润湿性和界面反应等,为后期开发多元 SAC 无铅钎料提供理论和试验基础。

1 试验方法

称取适量的纯 Sn、Sn-10Cu 中间合金、Sn-5Ag 中间合金,按照合金配方 Sn-0.3Ag-0.7Cu(简称 SAC0307,下同), SAC105, SAC205, SAC305, SAC387 无铅钎料在真空熔炼炉中进行熔炼,熔炼温度为 600 ℃,时间 1 h,然后在钢模中浇注。从各钎料上取出合适大小的合金,重熔制备成约 200 mg 的焊锡球,将其焊接在紫铜板上,进行随后的性能测试分析。

采用标准的金相制备方法制备焊锡球的横截面样品,然后对金相样品进行腐蚀,腐蚀液为盐酸含量 5%(体积分数)的酒精溶液。文中还制备了 IMC 的晶粒形貌,步骤是将焊接的试样先用 240 号砂纸将焊点大部分钎料打磨掉,然后用硝酸含量 30%(体积分数)的水溶液腐蚀多余的钎料,进行超声波清洗^[5]。横截面和晶粒形貌使用扫描电子显微镜(SEM)观察,X 射线能谱仪(EDS)分析界面金属间化合物(IMC)的成分。

将浇注好的棒料加工成标准拉伸试样如图 1,放置 2 天以去除残余应力。拉伸试验在万能试验机上进行,拉伸试验参照国家标准 GB/T 228—2002《金属材料室温拉伸试验方法》,拉伸速度为 10 mm/min。每种钎料合金均做 3 个试样,取其平均值作为该钎料的抗拉强度。

采用差式量热分析仪(DSC)测试钎料合金的熔

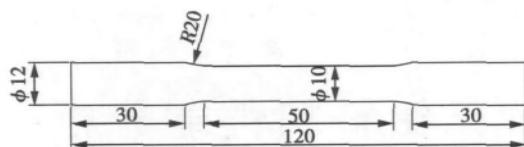


图 1 拉伸试样 (mm)

Fig. 1 Tensile test specimen

化特性. 取试样约为 10 mg, 放入 DSC 铝制坩埚中, 然后以 $10\text{ }^{\circ}\text{C}/\text{min}$ 的升温速率从室温加热到 $300\text{ }^{\circ}\text{C}$.

用扩展率来评价钎料的润湿性, 并按国家标准 GB/T11364—1989《钎料铺展性及填缝性试验方法》进行扩展率测试, 铺展基板为 0.2 mm 厚的紫铜薄板. 各钎料扩展率测试工艺均相同, 测试温度为 $260\text{ }^{\circ}\text{C}$, 时间为 10 s , 所用助焊剂为中等活性 RMA 助焊剂. 扩展率计算公式为

$$L = (1 - h/D) \times 100\% \quad (1)$$

式中: L 为扩展率; h 为扩展钎料的高度; D 为由钎料

量换算成球状的直径.

2 试验结果与分析

2.1 钎料显微组织分析

SAC 无铅钎料典型的组织特征为树枝状初晶与其间的共晶组织, 初晶为 $\beta\text{-Sn}$ 相, 共晶组织包含 $\text{Cu}_6\text{Sn}_5 + \beta\text{-Sn}$ 和 $\text{Ag}_3\text{Sn} + \beta\text{-Sn}$ 两种二元共晶以及 $\beta\text{-Sn} + \text{Ag}_3\text{Sn} + \text{Cu}_6\text{Sn}_5$ 一种三元共晶, 共晶组织中 Cu_6Sn_5 和 Ag_3Sn 亚微米级晶粒混在一起, 如图 2 所示, 很难区别. 随着 Ag 元素含量的增加, 钎料本体金属间化合物晶粒越来越细且逐渐增多, SAC0307 由弥散分布的岛状 Cu_6Sn_5 , 点状 Ag_3Sn IMC 的共晶组织和 $\beta\text{-Sn}$ 相组成, 其 IMC 晶粒明显比其它合金粗大, 当 Ag 元素含量达到 1% 时, IMC 颗粒成网状分布于基体中, 且晶粒有所细化, 随着 Ag 元素含量的进一步增加, IMC 晶粒越细小, 钎料中 IMC 的密度越大, 且 $\beta\text{-Sn}$ 相成胞状分布.

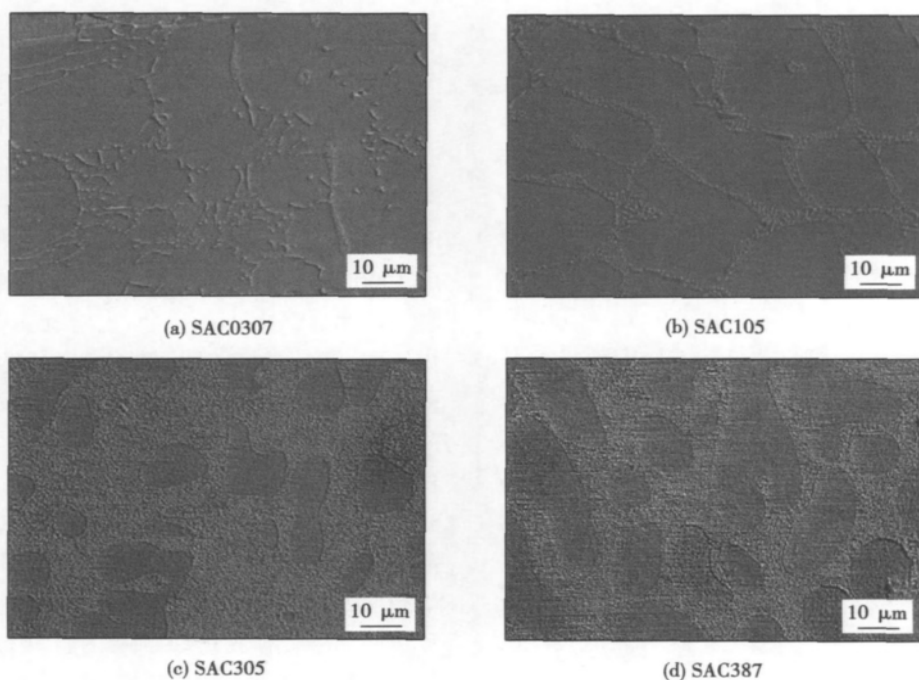


图 2 SAC 无铅钎料 SEM 显微形貌

Fig. 2 SEM micrographs of SAC solder alloys

2.2 室温力学性能分析

不同 Ag 元素含量的钎料抗拉强度和断后伸长率见图 3. 随 Ag 元素含量增加, SAC 无铅钎料抗拉强度逐渐增加, 断后伸长率逐渐减小, SAC387 钎料的抗拉强度较 SAC0307 提高了 80% , 但断后伸长率减少了 41% .

SAC 无铅钎料的力学性能与组织形态和 Ag 元素含量有关, 合金中各相形态、数量、分布以及晶粒大小对合金力学性能有很大影响, 如图 2 所示, Ag 元素含量增加使 Cu_6Sn_5 共晶组织数量增多, 尺寸变小, 同时 Ag 元素和 Sn 元素反应形成 Ag_3Sn 新相. Cu_6Sn_5 和 Ag_3Sn 颗粒的弥散分布对钎料产生弥散强

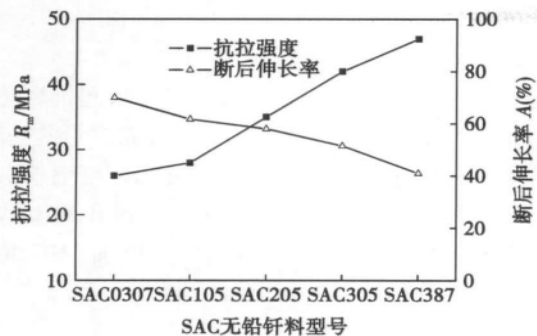


图3 不同Ag元素含量SAC无铅钎料的拉伸力学性能

Fig. 3 Tensile property of SAC solder alloys

化作用;而且材料内部晶粒越小,晶粒间距越小,材料的强度越高,SAC387无铅钎料具有最小的IMC晶粒和细小的显微结构,因此其抵抗变形的能力最强,但韧性最低。据报道低银合金由于具有较好的韧性,能吸收由于形变和热疲劳产生的能量,从而传递到界面的能量减少,达到阻止界面断裂的目的,因此抗跌落性能方面表现优异^[6]。

2.3 钎料熔化特性和润湿试验

图4为SAC无铅钎料在加热阶段吸热峰处的DSC曲线,可以看出所有钎料合金的起始熔化温度均约为217℃左右^[7],说明含Ag元素钎料合金的起始熔化温度均为三元共晶反应温度。图5为不同Ag含量SAC无铅钎料的熔化行为,随Ag元素含量的增加,峰值温度逐渐下降,SAC305与SAC387无铅钎料峰值温度非常接近,说明合金已接近共晶成分,Ag元素含量增加,钎料合金熔程减小,熔程从SAC0307的10℃降低为SAC387的2.1℃。SAC305和SAC387无铅钎料均为近共晶合金成分,共晶合金相比非共晶合金而言,具有更低的缩孔风险,同时有更低的熔点和较小的糊状区范围,在焊接过程中显微组织均匀,热量分散均匀,在熔融和冷却过程中

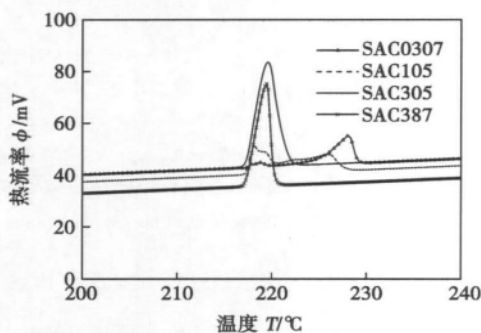


图4 SAC无铅钎料的DSC曲线图

Fig. 4 DSC curve of SAC solder alloys

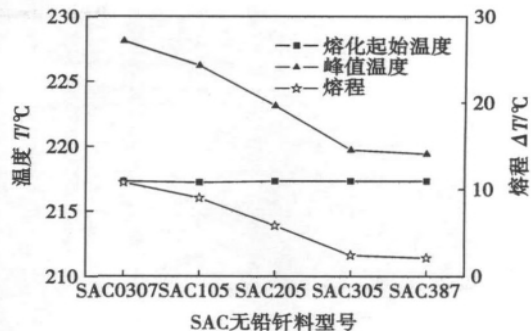


图5 SAC无铅钎料的熔化行为

Fig. 5 Melting behaviour of SAC solders

时间较短,减少了焊点内部应力,可避免焊接缺陷的产生。

SAC无铅钎料合金在铜上的扩展率随Ag元素含量变化曲线如图6所示,结果表明当使用中等活性的助焊剂时,Ag元素含量对润湿性的影响不大。

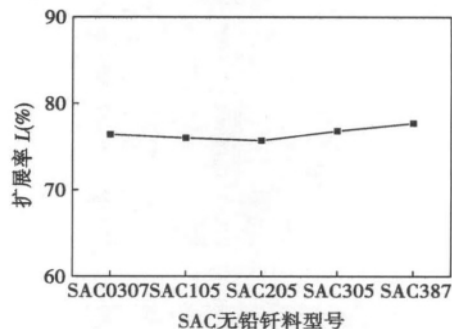


图6 不同Ag元素含量SAC无铅钎料在铜上的扩展率

Fig. 6 Spreading rate of SAC solder alloys on Cu pad

2.4 界面显微形貌

图7为不同Ag元素含量SAC无铅钎料与铜焊接界面的金属间化合物形貌,所有合金焊点界面IMC晶粒均为 Cu_6Sn_5 化合物,形貌为粒状。SAC0307焊点界面IMC晶粒比其他钎料的小,说明Ag元素含量的提高,可促进IMC晶粒的长大。从图7c,d可看出,在 Cu_6Sn_5 晶粒表面和沟槽中,存在一些微小的颗粒吸附在界面,这些颗粒为 Ag_3Sn 。由于IMC脆性的本质以及IMC层存在内部缺陷,还有外部应力传导到界面等原因,焊点在冲击载荷作用下的断裂一般发生在界面IMC层,因此防止此类失效的方法有两种:(1)提高钎料的塑性以吸收外部应力,(2)控制IMC的形成与生长。而低银SAC0307无铅钎料同时满足上述条件,因此适合应用于普通消费电子领域^[8]。

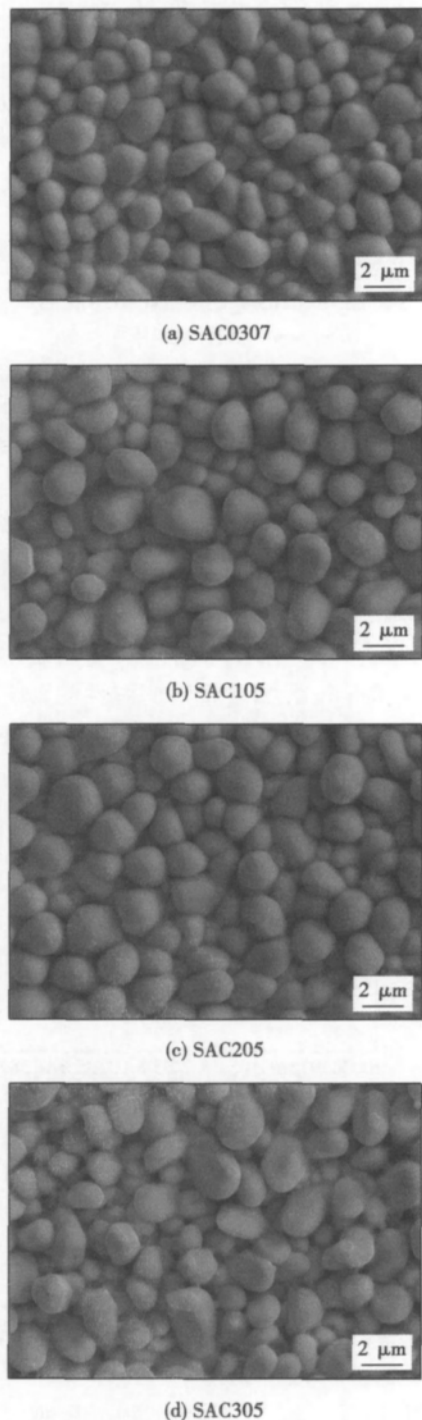


图 7 SAC/Cu 焊点界面金属间化合物形貌

Fig. 7 Interfacial IMC top view morphology of SAC/Cu solder joint

3 结 论

(1) 随着 Ag 元素在 SAC 无铅钎料中的含量增加, 钎料内部金属间化合物晶粒越小, 晶粒在钎料中的密度越高, 金属间化合物产生的弥散强化越明显, 因此高银无铅钎料的抗拉强度越高, 断后伸长率越

小; 而低银无铅钎料的抗拉强度稍低、韧性好, 合金在应用中的跌落可靠性更好。

(2) 不同 Ag 元素含量的无铅钎料, 起始熔化温度均在 217 ℃ 左右, 随着钎料中 Ag 元素含量的提高, SAC 无铅钎料越接近共晶成分, 熔化温度范围越小。

(3) Ag 元素含量对 SAC 无铅钎料在铜上的润湿性影响不明显, SAC0307/Cu 焊点界面 IMC 晶粒比其它钎料细小。

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作者简介: 刘 平, 男, 1976 年出生, 博士, 高级工程师。主要从事微电子焊接技术与新型无铅钎料的研究。发表论文 20 余篇。
Email: liuping_davy@yahoo.com.cn

Properties of Sn-Ag-Cu lead free solders with different silver content

LIU Ping^{1,2}, GU Xiaolong¹, ZHAO Xinning², LIU Xiaogang¹, ZHONG Haifeng¹ (1. Zhejiang Province Key Laboratory of Soldering & Brazing Materials and Technology, Zhejiang Metallurgical Research Institute, Hangzhou 310011, China; 2. Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China). pp 55 – 58

Abstract: The microstructure, melting behavior, mechanical properties, wettability and interfacial intermetallic compound (IMC) were studied on Sn-Ag-Cu (SAC) lead free solders with different Ag content (0.3, 1.0, 2.0, 3.0, 3.8wt%). The result indicates that SAC solders with higher Ag content present finer and denser IMC particles in the bulk solder, as a result of which the tensile strength of SAC solders increases with the increasing of Ag content, while the ductility decreases. The melting temperature of SAC305 and SAC387 solders was close to eutectic point as they have small melting temperature range. It was found that the wettability and interfacial IMC grain size of SAC0307/Cu joint are better than other tested solders.

Key words: Sn-Ag-Cu; lead-free solder; IMC; microstructure; melting temperature

Numerical simulation and experiments test of residual stress of longitudinal weld of thick SA508-3 steel pipe for nuclear power

CHI Luxin^{1,2}, MA Yonglin², XING Shuqing², CHEN Furong², CHEN Zhongyi² (1. College of Materials Science and Engineering, Chongqing University of Technology, Chongqing 400050, China; 2. College of Material and Metallurgy, Inner Mongolia University of Science and Technology, Baotou 014010, China). pp 59 – 62, 67

Abstract: Welding process of 60 mm thick SA508-3 steel pipe which is firstly used in nuclear power was simulated by ANSYS to obtain the temperature field and the residual stress. Simulated thermal and mechanical results were compared with the experimental results in the same welding parameters. It was found that the residual stress distribution is close to the measured values. During welding, the peak temperature exists in the centre of the heat source and its vicinity where the temperature gradient is much larger. However, the temperature descends sharply away from heat source. The residual stress on the outer surface of pipe are greater than that in the inner surface, of which the tensile residual stress in the welding zone and adjacent zone are largest, and gradually decreases away from the welding zone. The residual stress in the middle of cylinder is opposite to that in the two longitudinal ends. These results provide theoretical knowledge for the control of welding residual stress of pipe.

Key words: SA508-3 steel; residual stress; numerical simulation

Modeling and simulation for DE-GMAW

HUANG Jiankang¹, ZHU Ming¹, SHI Yu¹, ZHANG Yuming², Fan Ding¹ (1. Key Laboratory of Non-ferrous Metal Alloys and Processing, The Ministry of Education, Lanzhou University of Technology, Lanzhou 730050, China; 2. Center for Manufacturing, University of Kentucky, Lexington, KY 40506, USA). pp 63 – 67

Abstract: A dynamic mathematical model for welding arc was developed by adopting the method of equivalent current path

according to the arc dynamic characteristics of DE-GMAW process and the rule of wire-melting. Based on that, simulations about non-consumable DE-GMAW and consumable DE-GMAW were carried out by MATLAB/Simulink. Then the influence of welding torches angle on stability of DE-GMAW process was simulated and analyzed. The results show that the developed mathematical model can reflect the DE-GMAW process well. When the angel between main and bypass torch is 45°, the response time for welding process to achieve stability is the shortest and is consistent with the actual welding process and the non-consumable DE-GMAW is much more stable than consumable DE-GMAW.

Key words: DE-GMAW; modelling; simulation

Analysis on low temperature toughness of self-shielded flux cored wire used for pipeline

SONG Shaopeng, LI Zhuoxin, LI Guodong, SHI Chuanwei (College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, China). pp 68 – 72

Abstract: Low temperature toughness of deposited metal made by three types self-shielded flux-cored wires used for X70 pipeline has been investigated, by analyzing macroscopic and SEM morphology of impact fracture, microstructure and statistics of inclusion. The results showed that low temperature toughness of deposited metal of three wires was significantly different. No. 3 wire has highest toughness with an impact absorbing energy average value of 330 J at -40 °C, while the toughness of No. 1 wire is the lowest, whose impact absorbing energy average value is only 113 J at -30 °C. Differences of inclusions and microstructure of deposited metal were the main reason for significantly different toughness. Uniform and fine equiaxed grains and small inclusions uniformly and dispersedly distributed in deposited metal are beneficial to improve the low temperature toughness.

Key words: self-shielded flux cored wire; inclusion; microstructure; low temperature toughness

Analysis of residual stress and hardness of T-joint on China low activation martensitic steel laser weld

LEI Yucheng¹, LI Zhennan¹, ZHU Yanshan², JU Xin³ (1. School of Material Science and Engineering of Jiangsu University, Zhenjiang 212013, China; 2. Technical Center of Jinan Iron and Steel Co., Ltd., Jinan 250101, China; 3. Physics Department, University of Science and Technology of Beijing, Beijing 100083, China). pp 73 – 76

Abstract: T-joint of 4mm-thick CLAM steel was welded by 4 kW Nd: YAG laser welding equipment with different incident angles. Forming distribution of residual stress and hardness are observed and analyzed. The result show that there is significant lack of fusion in the joint when the incidence angle is 14° and the joint fully fuses when the angle is 12° or 10° with the decreasing of incidence angle. The residual stress of the joint surface is compressive stress, the stress of flange is larger than that of web when the angle is 12°. But the stress of web is larger when the angle is 10°. Inner stress largely changes in the section of the weld joint, compared with base metal, the hardness of weld zone has significantly increased and HAZ is not softened.

Key words: low activation martensitic steel; YAG laser welding; incidence angle; residual stress; hardness