

低银 SnAgCuBi- x Ni/Cu 焊点塑性及蠕变性能

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摘 要: 借助纳米压痕方法, 基于压痕做功和压痕蠕变的原理, 对 SnAgCuBi- x Ni/Cu ($x=0, 0.05, 0.1, 0.15, 0.2$) 低银焊点的塑性和抗蠕变性能进行了研究。结果表明, 在 SnAgCuBi- x Ni/Cu 焊点中, Ni 元素含量为 0.05% 和 1%, 焊点的硬度和塑性提高, 抗蠕变性能变化不明显; Ni 元素含量为 0.15% 和 0.2%, 焊点的硬度和抗蠕变性能提高, 但焊点塑性下降。Ni 元素的添加有利于提高 SnAgCuBi/Cu 焊点的高温稳定性。在 150 °C 下经 400 h 老化, 焊点的抗蠕变性能随着 Ni 元素含量的增加而增强, 含镍焊点的硬度均高于 SnAgCuBi/Cu 焊点, Ni 元素含量为 0.1% 的焊点塑性最好。

关键词: 纳米压痕; 塑性; 蠕变; 硬度

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0 序 言

受微小焊点“尺寸效应”的影响, 传统的试验方法获得的试验结果已不能准确反映微小焊点的塑性和蠕变性能。纳米压痕法具有直观、便捷等特点, 在微焊点的力学性能研究方面主要集中在硬度、弹性模量、蠕变应力敏感指数等方面^[1-4]。根据国际标准 ISO14577: 2007《金属材料硬度和材料参数的仪器化压痕试验》, 在纳米压痕试验中, 通过压痕功和压痕蠕变可直接得到材料的塑性及蠕变性能。压痕形成时消耗的总能量(总功), 由弹性功和塑性功组成, 其中弹性功占总功的比例越小, 表明材料的塑性越好。纳米压痕仪通过测量保载阶段压痕深度的变化, 即可获得材料的蠕变信息, 具有适应范围广, 自动记录数据, 测试方式多样等特点。

与高银 SnAgCu 钎料相比, 低银 SnAgCu 钎料具有较好的抗冲击性能和成本优势, 逐渐成为研究热点, 但其存在熔点偏高, 强度、硬度较低, 抗蠕变性能较差等问题, 影响其推广使用。在低银 SnAgCu 钎料中加入 Bi 元素, 可以降低钎料熔点, 能够在一定程度上抑制界面金属间化合物(IMC)的生长, 同时钎料的强度和硬度增大, 但熔程增加导致原始组织粗大及组织中的富铋相的影响, 钎料的塑性大幅降低^[5-8]。国际电子生产商联盟(iNEMI)报告中还指出, 通过向低银钎料中添加少量的 Ni 元素, 可增加液态

钎料的流动性, 提高焊点的抗跌落冲击性能, 阻止锡枝晶形成, 可以在高温老化过程中抑制化合物长大等作用^[9]。然而对 Ni 元素在改善焊点塑性和抗蠕变塑性的作用和机理的研究较少, 有待进一步研究。文中采用纳米压痕法, 基于压痕做功和压痕蠕变的原理, 研究了高温老化前后, Ni 元素对低银 SnAgCu-Bi- x Ni/Cu ($x=0, 0.05, 0.1, 0.15, 0.2$) 焊点体钎料的塑性、抗蠕变性能及硬度的影响。

1 试验方法

试验钎料按 Sn0.7Ag0.5Cu3.5Bi- x Ni ($x=0, 0.05, 0.1, 0.15, 0.2$) 质量配比, 选用化学纯 Sn, Ag, Cu, Bi 和 Ni 五种元素, 在氩气保护下的石英器皿中高频感应加热熔炼而成。每种钎料重熔 3 次确保其成分均匀。

将钎料制成直径 760 μm 的小球, 置于直径 690 μm 的铜盘上, 焊盘厚度 30 μm , 使用松香酒精助焊剂, 在 T340C 回流炉中进行焊接。回流焊峰值温度为 260 °C, 保温 60 s, 总焊接时间为 560 s。焊点在 150 °C 下进行 400 h 的高温老化试验。

纳米压痕试验在 DUH-W201S 型纳米压痕仪上进行, 采用玻氏三棱锥压头在焊点体钎料上进行压痕试验。为避免相邻压痕对试验数据的影响, 相邻压痕之间间隔在压痕尺寸 1 倍以上(图 1)。

试验采用加载—保载—卸载方式, 压力为 50 mN。加载速率与卸载速率同为 4.44 mN/s, 保载时间为 10 s。

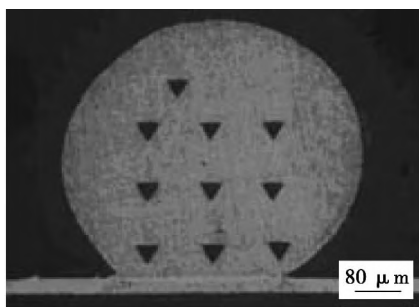


图 1 焊点压痕形貌

Fig. 1 Indentation of solder joint

2 力学参数的确定

2.1 纳米压痕试验中的弹性功

如图 2 所示,通过计算压痕深度—载荷曲线下方面积,可获得形成压痕所做的总功 W_t ,包括弹性功 W_e 和塑性功 W_p .

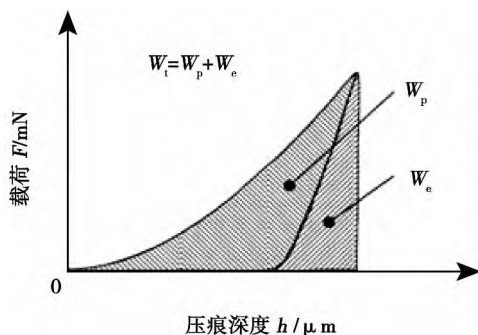


图 2 纳米压痕深度—载荷曲线

Fig. 2 Nano-indentation test load-depth curve

定义 η 为弹性功与总功的比值,其值可由纳米压痕仪直接获得,可反映材料的塑性. 其数值越小,代表材料的塑性越好,即

$$\eta = \frac{W_e}{W_t} \times 100\% \quad (1)$$

2.2 压痕蠕变

在纳米压痕试验中,达到最大压力后保载,压痕深度会继续增加,即材料产生了蠕变. 定义保载时压痕深度变化与达到最大压力时压痕深度的比值为压痕蠕变(C). 其值越小,表明材料的抗蠕变能力越强,即

$$C = \frac{h_2 - h_1}{h_1} \times 100\% \quad (2)$$

式中: h_1 为达到最大加载力时的压痕深度; h_2 为卸载时的压痕深度.

2.3 蠕变速率敏感指数

通过纳米压痕试验结果,可得到材料在压痕蠕变阶段的蠕变深度与蠕变时间对应数据,根据下式计算得到材料的蠕变速率,即

$$\dot{\epsilon} = \frac{dh}{hdt} \quad (3)$$

式中: $\dot{\epsilon}$ 为蠕变速率; h 为蠕变位移; t 为蠕变时间.

根据 Mayo-Nix 方法^[10],蠕变应力 σ 与蠕变过程中材料的硬度成正比,材料的蠕变速率敏感指数 m 可由下式确定,即

$$m = \frac{d \ln \sigma}{d \ln \dot{\epsilon}} = \frac{d \ln H}{d \ln \dot{\epsilon}} \quad (4)$$

式中: H 为马氏硬度.

3 试验结果与分析

3.1 Ni 元素对 SnAgCuBi- x Ni/Cu 焊点塑性的影响

表 1 为不同焊点老化前后的 η 与 C 值. 老化前, SnAgCuBi/Cu 焊点的 η 为 5.131. 加入 Ni 元素后, SnAgCuBi-0.05Ni/Cu 和 SnAgCuBi-0.1Ni/Cu 焊点的 η 分别为 3.878 和 3.66, 表明焊点的塑性得到提高,而 SnAgCuBi-0.2Ni/Cu 焊点的 η 为 6.601, 表明 SnAgCuBi-0.2Ni/Cu 焊点塑性最差. 这是因为镍可以作为焊点凝固时的形核质点,阻止粗大锡枝晶的形成,细化组织^[8]. 因而在 SnAgCuBi 钎料中加入少量 Ni 元素后,焊点的塑性得到提高. 但 Ni 元素含量较多时,形成的粗大化合物对焊点塑性有一定的负面影响.

表 1 不同焊点的 η 与 C 值Table 1 η and C of different solder joint

焊点成分	参数	老化时间	
		0 h	400 h
SnAgCuBi/Cu	η	5.131	6.956
SnAgCuBi/Cu	C	8.381	7.025
SnAgCuBi-0.05Ni/Cu	η	3.878	7.316
SnAgCuBi-0.05Ni/Cu	C	8.149	6.490
SnAgCuBi-0.1Ni/Cu	η	3.660	6.051
SnAgCuBi-0.1Ni/Cu	C	8.690	6.397
SnAgCuBi-0.15Ni/Cu	η	5.621	6.654
SnAgCuBi-0.15Ni/Cu	C	6.800	6.066
SnAgCuBi-0.2Ni/Cu	η	6.601	6.749
SnAgCuBi-0.2Ni/Cu	C	5.820	5.101

图 3 为 SnAgCuBi- x Ni/Cu 焊点高温老化前后的 η 分布. 经 400 h 老化后,五种焊点的 η 值分别为 6.956、7.316、6.051、6.654 和 6.749. 这表明老化后

SnAgCuBi-xNi/Cu ($x=0, 0.05, 0.1, 0.15, 0.2$) 焊点塑性都有所降低, SnAgCuBi-0.1Ni/Cu 焊点的塑性最好. 老化后五种焊点的 η 分别增加了 1.825, 3.438, 2.391, 1.033 和 0.148. 随着焊点中 Ni 元素含量的增加, 焊点的塑性稳定性增强. 老化过程中晶粒的长大是塑性降低的主要原因. 回流焊后, 焊点中的晶粒度及金属间化合物数量与分布的差异造成老化后塑性下降程度不同.

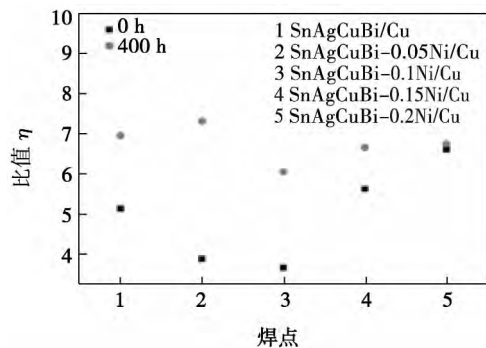


图3 高温老化对焊点的 η 值的影响

Fig. 3 Effect of aging time on η of different solder joint

3.2 Ni 元素含量对焊点蠕变性能的影响

对比表 1 中的 C 值, SnAgCuBi/Cu, SnAgCuBi-0.05Ni/Cu 和 SnAgCuBi-0.1Ni/Cu 焊点室温下 C 值分别为 8.381, 8.149 和 8.69, 抗蠕变性能相近. 文献 [11] 中的试验结果发现, 与 Bi, Sb 等元素相比, Ni 元素对提高 Sn 元素抗蠕变性能的效果不显著. 文中 Ni 元素少于 0.1%, 焊点的抗蠕变性能未随 Ni 元素含量的增高出现规律性变化. 这与 Bi, Ni 元素在焊点中的主要作用及蠕变机制有关. 压痕蠕变的主要机制是以晶内滑移为主, 晶界的粘性流动为辅 [11, 12]. 根据相关研究结果, 铋以固溶体的形式存在于晶粒中 [6-8, 12], 阻碍晶内滑移的进行, 为焊点抗蠕变性能的主要影响因素. Ni 元素主要起细化晶粒和改变化合物分布的作用, 其主要分布于化合物中. Ni 元素含量少于 0.1% 时, 因含量较少, 相对 Bi 元素, Ni 元素对焊点的抗蠕变性能贡献较小. 因此 SnAgCuBi-xNi/Cu ($x=0, 0.05, 0.1$) 焊点的抗蠕变性能相近. SnAgCuBi-0.2Ni/Cu 焊点的 C 值为 5.82, 抗蠕变性能明显提高. 当 Ni 元素较多时, 形成的金属间化合物弥散分布于基体中, 阻碍由晶界粘性流动引起的蠕变, 因此 SnAgCuBi-0.2Ni/Cu 焊点的抗蠕变性能最好.

图 4 为 SnAgCuBi-xNi/Cu 焊点高温老化前后 C 值分布. 经 400 h, 150 °C 高温老化, 五种焊点的 C 值分别为 7.025, 6.490, 6.397, 6.066 和 5.101, 较老化

前均有所降低, 焊点老化后的抗蠕变性能提高. 根据 Hanson 等研究结果, 晶粒尺寸较小时, 蠕变速率较高 [11, 12]. 根据金属学原理, 高温老化可使晶粒长大, 材料的蠕变速率降低. 因而与高温老化前相比, 材料的抗蠕变能力增强.

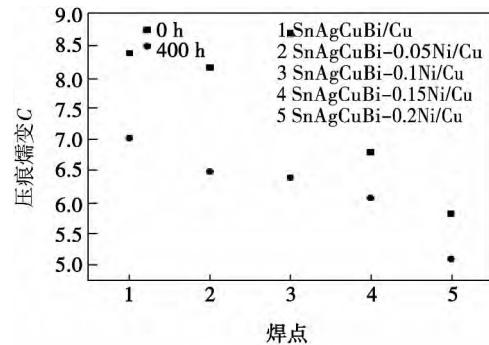
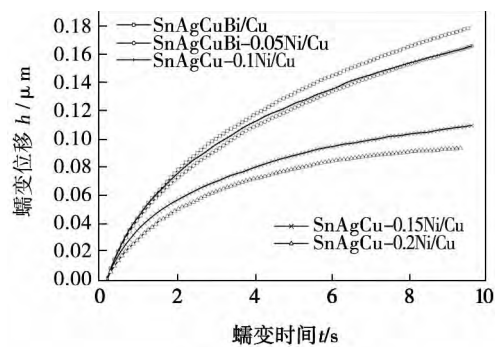


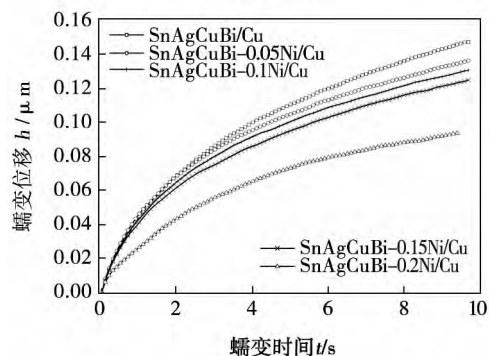
图4 高温老化对焊点 C 值的影响

Fig. 4 Effect of aging time on C of different solder joint

图 5 分别为老化前、后五种成分焊点的蠕变位移—蠕变时间曲线. 蠕变时间相同, 蠕变位移越小, 材料的抗蠕变性能越好. 由图 5 可以看出, 含镍焊点的位移均小于 SnAgCuBi/Cu 焊点. 老化前, SnAgCuBi-0.05Ni/Cu 和 SnAgCuBi-0.1Ni/Cu 焊点的蠕变位移相近, 略小于与 SnAgCuBi/Cu 焊点的蠕变



(a) 老化前



(b) 老化后

图5 蠕变位移—蠕变时间曲线

Fig. 5 Creep displacement-creep time profile

位移, SnAgCuBi-0.2Ni/Cu 焊点的蠕变位移最小. 老化后, 蠕变位移随着 Ni 元素含量的增加而减小, 这与 C 值的变化规律相同, 表明 Ni 元素可以提高焊点的抗蠕变性能.

根据 Mayo-Nix 方法, 可由硬度与蠕变应变速率的双对数坐标曲线最小二乘法拟合, 斜率即为蠕变应变速率敏感指数. 经计算得到老化前 SnAgCuBi- x Ni/Cu ($x=0, 0.05, 0.1, 0.15, 0.2$) 焊点的蠕变速率敏感指数分别为 0.044 5, 0.036 9, 0.031 6, 0.016 8 和 0.015 1; 老化后 SnAgCuBi- x Ni/Cu ($x=0, 0.05, 0.1, 0.15, 0.2$) 焊点的蠕变速率敏感指数分别为 0.016 9, 0.015 3, 0.014 1, 0.013 4 和 0.012 7. 蠕变速率敏感指数越低, 材料的抗蠕变性能越好. 这与前面的结果一致, 表明 Ni 元素有利于提高焊点高温老化后的抗蠕变能力.

4 结 论

(1) Ni 元素含量 0.1% 时, 焊点塑性得到明显改善, 抗蠕变性能无明显提高. Ni 元素含量达到 0.2% 时, 焊点的抗蠕变性能最好, 但焊点塑性最差. SnAgCuBi-0.1Ni/Cu 焊点塑性最好, 并保持了较高抗蠕变性能.

(2) Ni 元素有利于提高 SnAgCuBi- x Ni/Cu 焊点的高温稳定性. 老化后, SnAgCuBi- x Ni/Cu 焊点的塑性和抗蠕变性能均优于 SnAgCuBi/Cu 焊点.

参考文献:

- [1] 王俭辛, 赖忠民, 孙丹丹. Sn-Cu-Ni 焊点纳米压痕试验分析[J]. 焊接学报, 2011, 32(12): 59-62.
Wang Jianxin, Lai Zhongmin, Sun Dandan. Nano-indentation measurement of Sn-Cu-Ni joint[J]. Transactions of the China Welding Institution, 2011, 32(12): 59-62.
- [2] 张国尚, 荆洪阳, 徐连勇, 等. 纳米压痕法研究 80Au/20Sn 焊料蠕变应力指数[J]. 焊接学报, 2009, 30(8): 73-76.
Zhang Guoshang, Jing Hongyang, Xu Lianyong, et al. Investigation of creep stress exponent of 80Au/20Sn solder by nanoindentation[J]. Transactions of the China Welding Institution, 2009,

30(9): 73-76.

- [3] 张国尚, 荆洪阳, 徐连勇, 等. 纳米压痕法测量 80Au/20Sn 焊料热力学性能[J]. 焊接学报, 2009, 30(9): 53-56.
Zhang Guoshang, Jing Hongyang, Xu Lianyong, et al. Thermo-mechanical characterization of 80Au/20Sn solders using nanoindentation[J]. Transactions of the China Welding Institution, 2009, 30(9): 53-56.
- [4] Dudek M A, Chawla N. Nanoindentation of rare earth-Sn intermetallics in Pb-free solders[J]. Intermetallics, 2010, 18(5): 1016-1020.
- [5] 权延慧, 孙凤莲, 王丽凤, 等. 回流焊对 SnAgCuBi/Cu 焊点 IMC 及剪切强度的影响[J]. 电子元件与材料, 2009, 28(7): 73-76.
Quan Yanhui, Sun Fenglian, Wang Lifeng, et al. Effect of reflow soldering on the IMC and shear strength of Sn-0.3Ag-0.7Cu- x Bi/Cu solder joints[J]. Electronic Components and Materials, 2009, 28(7): 73-76.
- [6] Li Guoyuan, Shi Xunqing. Effects of bismuth on growth of intermetallic compounds in SnAgCu Pb-free solder joints[J]. Transactions of Nonferrous Metals Society of China, 2006, 16: 739-743.
- [7] Ohnuma I, Miyashita M, Anzai K, et al. Phase equilibria and the related properties of SnAgCu based Pb-free solder alloys[J]. Journal of Electronic Materials, 2000, 29(10): 1137-1144.
- [8] Ye Lilei, Lai Zonghe, Liu Jianchun, et al. Microstructure investigation of Sn0.5Cu3.5Ag and Sn3.5Ag0.5Cu0.5Bi lead free solders[J]. Soldering and Surface Mount Technology, 2001, 13(3): 16-20.
- [9] Gregory Henshall, Robert Healey, Ranjit S Pandher, et al. iNE-MI Pb-free alloy alternatives project report: state of the industry[R]. Orlando: iNEMI, 2009.
- [10] Mayo M J, Nix W D. A micro-indentation study of super plasticity in Pb, Sn and Sn-38% Pb[J]. Acta Metallurgica, 1998, 36(8): 2183-2192.
- [11] Hanson D. A study of the mechanical properties 810 of tin-rich antimony-tin alloys[J]. Journal of the Institute of Metals, 1938, 62: 215-216.
- [12] Alden T H. The origin of super plasticity in the Sn-5% Bi alloy[J]. Acta Metallurgica, 1967, 15(3): 469-480.

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this basis , a welding test was carried out by using the 80% Ar + 20% CO₂ mixture gas as protective gas. The results showed that the bypass arc burned stably on the oxide film of bypass droplet formed by CO₂ in protective gas , so the electromagnetic force and the gravity promoted the bypass metal transfer together and the size of the bypass droplet was significantly reduced.

Key words: gas metal arc welding; protective gas; metal transfer

Investigation on coupling arc electrode GPCA-TIG welding process

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Abstract: A new method named coupling arc electrode GPCA-TIG welding is proposed , which combines coupling arc electrode and GPCA welding method , and with which deep penetration and high-speed welding can be achieved. In this paper , the weld surface appearances and weld cross-section shapes with traditional TIG , coupling arc electrode TIG and coupling arc electrode GPCA-TIG welding are studied. It is found that in the coupling arc electrode GPCA-TIG welding , the weld undercut and humping bead can be avoided , and meanwhile the weld depth increase. The results of the coupling arc electrode GPCA-TIG process shows that the weld depth and width increase with the decreasing of weld speed and the rising of outer nozzle position; with the increasing of arc length and flow rate of the outer gas O₂ , the weld depth and width firstly increase and then decrease. The weld undercut is weaken with the increasing of welding speed , arc length and flow rate of the outer gas O₂. A good weld surface appearance can always be obtained with any outer nozzle position.

Key words: coupling arc electrode; GPCA welding; weld shape; weld undercut; humping bead

Digital control of capacitance charge-discharge pulse in electro-spark deposition power supply

HAN hongbiao , LI Xiangyang (School of Mechatronics Engineering , Henan University of Science and Technology , Luoyang 471003 , China) . pp 23 – 26 , 70

Abstract: The discharge voltage of traditional depositing power supply cannot be continuously adjusted , which limits the application range of electro-spark deposition and the efficiency of electro-spark deposition. In order to overcome this shortage , a digital control of capacitance charge-discharge pulse in electro-spark deposition power supply was developed. This power supply consists of CPU , rectifier and filter circuit , charge and its drive circuit , charge voltage comparison circuit , discharge and its drive circuit , motorial electrode , etc. With alternate charge and discharge process of this power supply , discharge voltage and discharge energy as well as discharge frequency can be adjusted steplessly. Experimental results show that the SCR of this power supply can be shut off safely when a short circuit occurs between the electrode and the workpiece , which greatly improves the effi-

ciency of pulse output. The adjustment of discharge parameters is convenient , thus the power supply meets the requirements of various process condition.

Key words: electro-spark deposition; digital control; voltage regulation

Synthesis and characterization of carbon nanotubes reinforced TiNi composite solder

QI Junlei , WAN Yuhan , ZHANG Lixia , FENG Jicai (State Key Laboratory of Advanced Welding and Joining , Harbin Institute of Technology , Harbin 150001 , China) . pp 27 – 30

Abstract: Low temperature PECVD method was employed for in-situ preparation of CNTs reinforced TiNi composite brazing powder on Ni-TiH₂ base material , in order to solve the problems such as poor dispersity of CNTs , poor structural integrity and reaction of C and Ti. The composite brazing powder was characterized by XRD , SEM , Raman and TEM. Analysis shows that the low temperature PECVD method has not only guaranteed the structural integrity and uniform dispersity of CNTs , but also inhibited the decomposition of TiH₂ at high temperatures and further inhibited the reaction between C and Ti , which realized the reinforcement of CNTs to TiNi brazing powder. The reinforcement of CNTs could release the residual stress in brazed joints , improve the properties of the joints and further achieve the reliable joining and high-temperature application of ceramic , composites and metal.

Key words: carbon nano tube; composite material; low temperature preparation; soldered seam

Plasticity and creep performance of low-Ag SnAgCuBi-xNi/Cu solder joint

YANG Miaosen , SUN Fenglian , ZOU Pengfei (School of Materials Science Engineering , Harbin University of Science and Technology , Harbin 150040 , China) . pp 31 – 34

Abstract: In order to study the effect of Ni on plasticity and creep performance of low-Ag SnAgCuBi-xNi/Cu ($x = 0 , 0.05 , 0.1 , 0.15 , 0.2$) solder joint , the indentation work and indentation creep were measured and analyzed by nanoindentation method. The results show that adding Ni could improve the hardness of solder joint. Adding amounts of 0.05% and 0.1% Ni is helpful to improve the plasticity performance but produce almost no impacts on creep. A further Ni adding amount (0.15% and 0.2%) can improve the creep resistance at the expense of plasticity. It is found that Ni can improve high temperature stability of SnAgCuBi/Cu solder joints. The creep resisting performance of the solder joints is improved with Ni element increasing after 400 h aging at 150 °C. The hardness of solder joints is improved with the Ni addition. The plasticity performance of solder joints with 0.1% Ni content is better than others.

Key words: nanoindentation; plasticity; creep; hardness

Finite element analysis of shot peening treatment to improve welding residual stress of 7A52 aluminum alloy

HUANG Zhiye , CHEN Furong (College of Materials Science and Engineering , Inner Mongolia University of Technology , Hohhot 010051 , China) . pp 35 – 40