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ScienceDirect

Microelectronics Reliability 47 (2007) 1113–1119

MICROELECTRONICS RELIABILITY

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Properties of low temperature Sn–Ag–Bi–In solder systems

Keun-Soo Kim [a,*], Takayuki Imanishi [a], Katsuaki Suganuma [a], Mimoru Ueshima [b], Rikiya Kato [b]

[a] ISIR, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan
[b] Senju Metals Industries, Co. Ltd., Senju Hashido-cho 23, Adachi-ku, Tokyo 120-8555, Japan

Received 26 January 2006; received in revised form 22 June 2006
Available online 8 September 2006

Abstract

The metallurgical and mechanical properties of Sn–3.5 wt%Ag–0.5 wt%Bi–$x$wt%In ($x = 0$–16) alloys and of their joints during 85 °C/85% relative humidity (RH) exposure and heat cycle test (−40–125 °C) were evaluated by microstructure observation, high temperature X-ray diffraction analysis, shear and peeling tests. The exposure of Sn–Ag–Bi–In joints to 85 °C/85%RH for up to 1000 h promotes In–O formation along the free surfaces of the solder fillets. The 85°C/85%RH exposure, however, does not influence the joint strength for 1000 h. Comparing with Sn–Zn–Bi solders, Sn–Ag–Bi–In solders are much stable against moisture, i.e. even at 85 °C/85%RH. Sn–Ag–Bi–In alloys with middle In content show severe deformation under a heat cycles between −40 °C and 125 °C after 2500 cycles, due to the phase transformation from β-Sn to β-Sn + γ-$InSn_4$ or γ-$InSn_4$ at 125 °C. Even though such deformation, high joint strength can be maintained for 1000 heat cycles.

1. Introduction

Lowering the melting temperature of solder has been shown to be one of the key factors required for achieving lead-free electronics packaging. The Sn–Ag–Cu ternary alloy has been widely used as a reliable lead-free solder, but because its melting temperature is about 34 °C higher than that of Sn–Pb eutectic alloy, it requires a higher soldering temperature than Sn–Pb alloy. A low processing temperature is desirable for preventing heat damage to electronic devices during soldering, and this is a reason for the adoption of other low melting temperature alloys, i.e., Sn–Ag–In, Sn–Zn–Bi and Sn–Ag–Bi [1–3]. The addition of In to Sn–Ag eutectic alloy can reduce its melting temperature effectively and can promote wetting on Cu 8 wt%. In addition reduces the liquidus temperature down to 206 °C and this alloy has been adopted in the fabrication of laptop type computers [1–5]. Thus, Sn–Ag–In alloy has recently attracted considerable attention as a possible replacement for Sn–Pb eutectic solder that will not increase the soldering temperature. However, some effects resulting from the addition of In to Sn–Ag eutectic alloy are still unknown, with respect to both metallurgical properties and reliability. Some properties of Sn–Ag–In have already been studied, both experimentally and by thermodynamic modeling [1,4,5]. In the previous work, differential scanning calorimeter (DSC) was used to understand the melting/solidification behavior of the alloys in the Sn-rich corner of the Sn–Ag–In ternary diagram. Strong segregation occurs during cooling of some In-bearing solder as In is rejected from the solid, with excess In remaining in the liquid. At a high enough In concentration (>16 wt%), this segregation results in partial melting of the solder at temperatures above 113 °C. Thus, excess amounts of In may degrade mechanical properties, particularly fatigue resistance, because a low-temperature soft phase is formed.

Though the addition of In to Sn–Ag–Bi alloy is known to be effective, we need further data before this alloy system can be utilized to assemble reliable products. The purpose of the present work is to clarify the effect of thermal

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[*] Corresponding author. Tel.: +81 6 6879 8521; fax: +81 6 6879 8522.
E-mail address: kskimm12@sanken.osaka-u.ac.jp (K.-S. Kim).

0026-2714/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.microrel.2006.06.012

and moisture exposure on the reliability of various Sn–Ag–Bi–In joints.

2. Experimental

The several types of solder alloys, Sn–*x*wt%In ($x = 0$–16) and Sn–3.5 wt%Ag–0.5 wt%Bi–*x*wt%In ($x =$ 0–16) were supplied by Senju Metal Co., Ltd. Hereafter, the composition unit "wt%" is omitted. The alloy ingots were re-melted at 300 °C for 1 h and were cast into a steel mold [6]. The bulk samples were polished with 3 μm Al_2O_3 powders. The three types of solder paste, Sn–3.5Ag–0.5Bi–0In, Sn–3.5Ag–0.5Bi–4In and Sn–3.5Ag–0.5Bi–8In, were supplied by Harima Chemicals, Inc. The chemical compositions of Sn–Ag–Bi–In pastes are listed in Table 1. The Sn–3.5Ag–0.5Bi–*x*In ($x = 0$, 4 and 8) solder pastes were printed on the Cu pads of FR-4 printed wiring boards (PWBs). Resistor chips (1608R) with Sn–10Pb termination and small outline packages (SOPs) with Sn–1.5 Cu plated Cu leads were assembled on the Cu pads of the PWBs [7]. Reflow was carried out in air. The peak temperature of reflow treatment was 240 °C.

The thermal and moisture exposure test was carried out by putting the bulk solders and the joining samples into an oven. The heat/humidity exposure conditions were 85 °C/85% relative humidity (RH). A heat cycle test was also carried out in the temperature range between −40 °C and 125 °C. The holding time at the peak temperatures was 0.5 h. Joint strength was evaluated by a shear and peeling test. The shear and peeling tests were carried out at room temperature using a Dage Bondtester 4000. The shear speed was 500 μm/s. The lead frames of SOPs were peeled along the 45° inclined direction to the surface of PWBs. The cross head speed was 333 μm/s.

The microstructure was analyzed by optical microscope (OM), scanning electron microscope (SEM), and electron probe microanalysis (EPMA). High temperature X-ray diffraction (XRD) analysis was performed on the Sn–Ag–Bi–In bulk samples to study the phase change on heating. The analysis was performed every 25° from 100 to 150 °C at a heating rate of 2 °C/min for a dwell time of 1 h per scan.

3. Results and discussion

3.1. Stability of Sn–Ag–Bi–In soldered joints to thermal and moisture exposure

To understand the effect of thermal and moisture exposure on the microstructures of Sn–Ag–Bi–In alloys, Sn–3.5Ag–0.5Bi–0In, Sn–3.5Ag–0.5Bi–4In and Sn–3.5Ag–0.5Bi–8In bulk samples were exposed to heat/humidity at 85 °C/85%RH for up to 1000 h. Fig. 1 shows the surface morphology of Sn–3.5Ag–0.5Bi–8In alloy after 85 °C/85%RH exposure for 1000 h. Many nodules and needle type phases, as short as a few μm in length and composed of Ag and In not but Sn (as determined by EPMA), are observed for the Sn–3.5Ag–0.5Bi–4In and Sn–3.5Ag–0.5Bi–8In alloys after 500 h of exposure. These phases are likely to be an intermetallic compound of Ag and In because In and Ag do not form a stable solid solution. In our previous study, we reported on the formation of Ag–In and In–Sn intermetallic phases in Sn–Ag–Bi–In alloys [1]. Thus, these phases are likely to be an Ag–In intermetallic phase that has grown out of the free surface by some driving force such as internal stress due to oxidation or residual stress due to casting. In contrast, the surface of Sn–3.5Ag–0.5Bi–0In does not show any nodules or needle type phases, even after long-term 85 °C/85%RH exposure.

To investigate the effect of thermal and moisture exposure on the mechanical properties of the soldered joints, 1608R chip components were mounted on FR-4 boards and they were exposed to 85 °C/85%RH for up to 1000 h. While the solder fillets of the Sn–3.5Ag–0.5Bi–4In and Sn–3.5Ag–0.5Bi–8In solders just after reflow treatment exhibited shiny surfaces, those of the Sn–Ag–Bi–In solders lost surface gloss after 85 °C/85%RH exposure for 1000 h, as shown in Fig. 2. Nevertheless, the surface of the Sn–Ag–Bi–In solder fillets showed no nodules or needle type phases after long-term exposure. Thus, identification of the needle type phase growth mechanism for bulk alloys still requires further study. Fig. 3 shows the interfacial microstructures of Sn–3.5Ag–0.5Bi–8In joints before and after 85 °C/85%RH exposure. In the case of the Sn–3.5Ag–0.5Bi–0In joint, typical eutectic ζ-Ag_3Sn phases are finely dispersed in the solder fillet. For the Sn–Ag–Bi–In joints, fine precipitates are also observed inside β-Sn grains in the solder fillets, and particulate

Table 1
Chemical composition of solder pastes (wt%)

	Ag	In	Bi	Pb	Sb	Cu	Sn
Sn–3.5Ag–0.5Bi–0In	3.51	0	0.49	0.03	0.01	0.003	Bal.
Sn–3.5Ag–0.5Bi–4In	3.50	4.0	0.50	0.02	0.02	0.001	Bal.
Sn–3.5Ag–0.5Bi–8In	3.50	8.0	0.52	0.02	0.02	0.001	Bal.

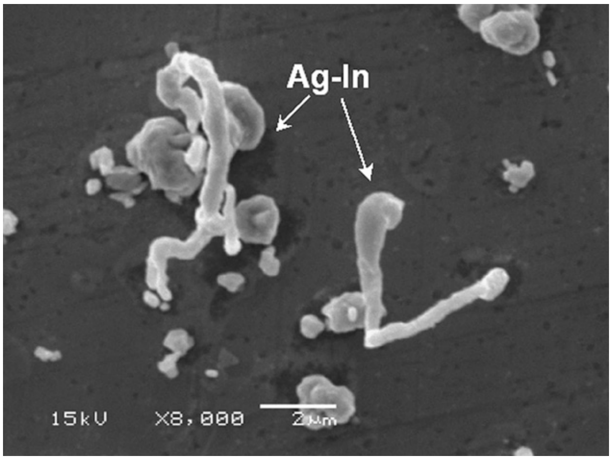

Fig. 1. Surface morphology of Sn–3.5Ag–0.5Bi–8In alloy after 85 °C/85%RH exposure for 1000 h.