



Creep behavior of near-peritectic Sn–5Sb solders containing small amount of Ag and Cu

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ABSTRACT

Sn–5Sb is one of the materials considered for replacing Pb-bearing alloys in electronic packaging. In the present study, the effects of minor additives of Ag and Cu on the as-cast microstructure and creep properties of the Sn–5Sb solder alloy are investigated by means of optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and tensile tests. Results show that addition of Ag and Cu resulted not only in the formation of new Ag₃Sn and Cu₆Sn₅ intermetallic compounds (IMCs), but also in the refinement of the grain size of Sn–5Sb solder. Accordingly, the creep properties of the Ag or Cu-containing solder alloys are notably improved. Attention has been paid to the role of IMCs on creep behavior. The lead-free Sn–5Sb–0.7Cu solder shows superior creep performance over the other two solders in terms of much higher creep resistance and vastly elongated creep fracture lifetime. An analysis of the creep behavior at elevated temperatures suggested that the presence of hard Cu₆Sn₅ and fine SbSn IMCs in the Sn–5Sb–0.7Cu alloy increases the resistance to dislocation movement, which improves the creep properties.

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1. Introduction

Global concerns over the environmental impact and health effects of Pb-based solders in consumer electronics have led to the development of Pb-free solder alternatives. Among these lead-free solders, near-peritectic Sn–5Sb solder alloy is one of the candidates for the replacement of the Pb-rich solders, which has been extensively used in electronic packaging. The Sn–5Sb solder has a solder–substrate contact angle of about 43° with higher mechanical properties than the conventional Sn–Pb solders. The melting temperature of Sn–5Sb solder (245 °C) is about 62 °C higher than eutectic Sn–Pb solder (183 °C), which causes manufacturing difficulties for low temperature applications. Although the disadvantage of this higher melting point, it has proven to be more suitable for higher temperature applications such as step soldering technology, flip-chip connection [1–3] and solder ball connections [4], where either Si chips or modules are mounted onto ceramic substrates. It has also been proposed as cathode materials for use in lithium ion batteries [5,6]. Several other electronic applications of Sn–5 wt.%Sb alloy have also been reported, including hermetic

seal band of multichip modules [7] and bonding semiconductor device onto a substrate [7]. Lee et al. [8] also reported that ternary Sn–Sb–Cu alloys may be considered as promising lead-free solders.

For applications requiring dimensionally stable solders, a very low creep rate is required. Understanding the creep behavior of Sn–5Sb based solders is one of the pre-requisites for employing these solders in the manufacturing of electronic products. Since the alloy is targeted for applications at high temperatures. In this case, the time-dependent deformations, i.e. creep mechanisms, play an important role because of high homologous temperatures involved. Moreover, creep properties of the alloy are influenced by a number of factors such as phase morphology, phase dimensions, presence of Sb as solid solution in the matrix or its precipitation as SbSn and degree of ageing [9–11]. Optimizations of these factors require standardization of the thermo-mechanical processing. Geranmayeh and Mahmudi [10] found that the creep behavior of near-peritectic Sn–5Sb solder alloy depends on the chemical composition as well as the crystal size and the distribution of SbSn phase. In addition, the authors also considered that the creep resistance of alloy depends on the volume fraction of the hard intermetallic compound (IMC) phases and the deformation resistance of such precipitates during steady state creep [11]. Recent studies have concentrated their attention on investigating the creep response of Sn–Sb alloys by means of creep tests,

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room-temperature indentation creep tests and in one case by the automated ball indentation (ABI) method [10–16]. Their results suggested that the Sn–Sb alloys with higher concentrations of antimony provide a significant composite strengthening effect resulted in creep rate reduction of the material, especially at temperatures below 100 °C [17].

Although the above studies have been carried out to understand the formation effects of SnSb precipitates in the Sn–Sb alloys, another important factor influencing the creep resistance of the alloy is the presence of other alloying elements such as Ag and Cu. There are a little works focusing on the effects of alloying element additions. At present, some studies have been carried out to understand the effect of Cu addition on the wetting force and wetting time of the Sn–10Sb alloys [19]. It was found that Cu addition can successfully modify the wetting time on a Cu substrate and effectively improves the wetting angles of Sn–10Sb–5Cu lead-free solder more than those of 95Pb–Sn solder, in the whole test temperature range of 340–400 °C. In our previous work, the Ag and Au additions have been reported to improve the microstructure of Sn–5Sb alloys as well as their strength and ductility [2,20]. The study revealed also that the Sn–5Sb–1.5Au solder alloy has potential to give a good combination of higher creep resistance, longer rupture time, lower melting temperature and higher fusion heat compared with the Sn–5Sb–3.5Ag and Sn–5Sb alloys. From the viewpoint of lowering material's cost as the cost of silver and gold has increased significantly in recent times, the purpose of the present study is to identify the effects of separate addition of small amounts of Ag and Cu on the microstructure and creep properties of Sn–5Sb lead-free solder alloys. The key factors that affect the creep behavior of the solder alloy are discussed. Hopefully, these small element additions can play a positive role in the improvement of the overall mechanical properties of the Sn–5Sb-based alloys. The results are wished useful in the further development of new solder alloys for different electronic packaging applications.

2. Experimental procedures

In the present work, characterizations of the microstructure and creep behavior were conducted on three lead-free solder alloys with the compositions (wt.%) of Sn–5Sb, Sn–5Sb–0.7Ag and Sn–5Sb–0.7Cu. The lead-free solders were prepared from Sn, Sb, Ag and Cu (purity 99.97%) as raw materials. The process of melting was carried out in a vacuum arc furnace under high purity argon atmosphere to produce rod-like specimen with a diameter of approximately 10 mm. The melt was held at 500 °C for 60 min to complete the dissolution of Sn, Sb, Ag and Cu and then poured in a steel mold to prepare the chill cast ingot. A cooling rate of 6–8 °C/s was achieved, so as to create the fine microstructure typically found in small solder joints in microelectronic packages. Table 1 lists the actual chemical compositions of the experimental alloys used in the present investigation. The microstructure was examined by optical microscopy (OM) and scanning electron microscopy (SEM) with an energy dispersive X-ray spectrometer (EDS) after etching. A solution of 2% HCl, 3% HNO₃ and 95% (vol.%) ethyl alcohol was prepared and used to etch the samples. Phase identification of the alloy samples was carried out by X-ray diffractometry (XRD) at 40 kV and 20 mA using Cu K α radiation with diffraction angles (2 θ) from 25° to 85° and a constant scanning speed of 1°/min. The solder ingots were then mechanically machined into a wire samples with a gauge length marked 5×10^{-2} m for each samples and 1.5×10^{-3} m in diameter. To obtain samples containing the fully precipitated phases and free from any plastic strain accumulation during machining, the samples were annealed at 130 °C for 10 min, then left to cool slowly to room temperature. Tensile tests were carried out with a tensile testing machine (Instron 3360 Universal

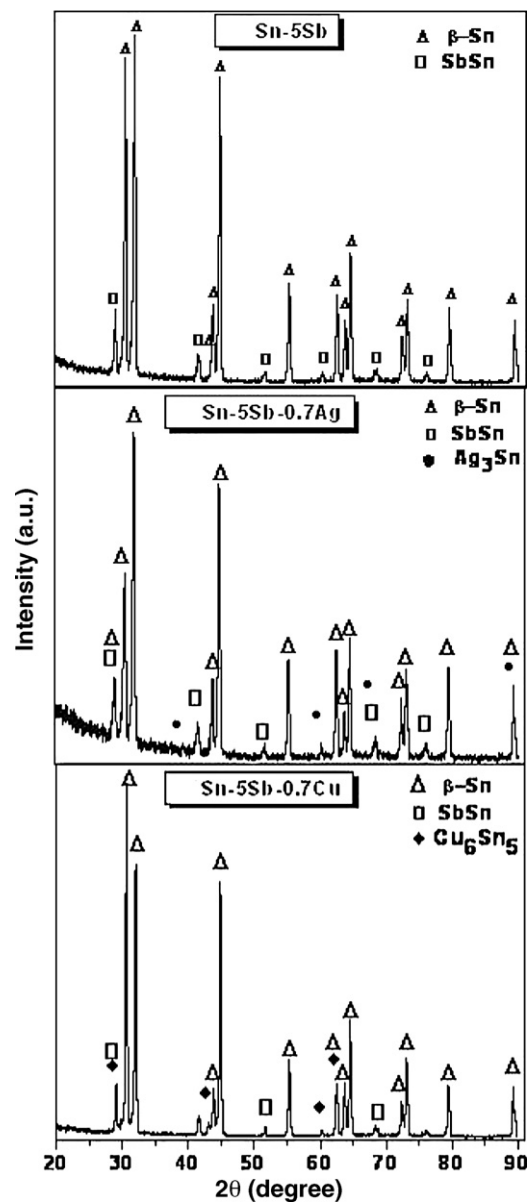


Fig. 1. XRD patterns of (a) Sn–5Sb, (b) Sn–5Sb–0.7Ag and (c) Sn–5Sb–0.7Cu solder alloys.

Testing Machine). Creep testing was performed at 25, 70, and 120 °C after waiting time of 5 min for the test temperatures to be reached. Each datum represents an average of three measurements. The environment chamber temperature could be monitored by using a thermocouple contacting with specimen.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the XRD results of the as-cast Sn–5Sb, Sn–5Sb–0.7Ag and Sn–5Sb–0.7Cu experimental alloys. In general, all the as-cast experimental alloys are mainly composed of β -Sn phase and precipitated SbSn phase. However, the alloys containing Ag and Cu exhibited additional IMCs such as Ag₃Sn for Ag-containing solder and Cu₆Sn₅ for Cu-containing solder, along with the peaks of β -Sn phase and SbSn phase in all alloys.

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