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Microstructural evolution and tensile properties of Sn–5Sb solder alloy containing small amount of Ag and Cu

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ABSTRACT

The near peritectic Sn–5Sb Pb-free solder alloy has received considerable attention for high temperature electronic applications, especially on step soldering technology, flip-chip connection. In the present study, a separate addition of the same amount of Ag and Cu are added with the near-peritectic Sn–5Sb solder alloy to investigate the effect of a third element addition on the microstructural, thermal and mechanical properties of the newly developed ternary solder alloys. The results indicate that the melting point of Sn–5Sb solder is enhanced by Ag and Cu additions. Besides, the Ag and Cu content refine the microstructure and form new intermetallic compounds (IMCs) with the near-peritectic Sn–5Sb solder alloy. The tensile tests revealed that all alloys exhibit higher mechanical strength with increasing strain rate and/or decreasing testing temperature, suggesting that the tensile behavior of the three alloys is strain rate and temperature dependence. The yield and ultimate tensile strength are higher for Sn–5Sb–0.7Cu alloy compared with Sn–5Sb and Sn–5Sb–0.7Ag alloys. Good mechanical performance of Sn–5Sb–0.7Cu solder is often correlated to a fine β-Sn grain size and more dispersed Cu-Sn IMC particles, which makes the solder exhibit high strength and yield stress.

1. Introduction

Owing to the realization of the harmful influence of lead and lead containing alloys on the environment and human health, many Pb-free solder-alloys have been developed to replace Sn–Pb solders in electronic applications [1]. The near peritectic Sn–5Sb Pb-free solder alloy has received considerable attention for high temperature electronic applications, especially on step soldering technology, flip-chip connection [2–4], solder ball connections and bonding a semiconductor device onto a substrate. It also has proposed as cathode materials for use in lithium ion batteries [5,6]. Although demand for higher I/O counts on chips requires finer pitches to improve performance, cost effectiveness and higher yield, such increases in I/O density lower the conventional pitches to very fine sizes (20 μm). Since one role of the solder alloys is to serve as a structural material to connect the components, one of the major concerns in the development of electronic packaging is the reliability of the solder joints [7]. A viable approach to improve the performance of a solder joint in terms of low melting point, higher strength, better microstructure properties, and high creep resistance is to add appropriate second phase particles, of a ceramic, metallic or intermetallic, to a solder matrix [1,8,9].

Recently, lead-free Sn–Sb solders have been identified as potential materials with higher microstructure stability and better mechanical properties as compared to conventional Sn–Pb solders [10–12]. The addition of hard obstacles to dislocation motion can have profound effects on the tensile strength and creep resistance of a metal. Precipitation and dispersion strengthening have received significant attention in the fields of high-temperature structural materials due to markedly better creep resistance. El-Daly et al. [8] studied the influence of Ag and Au additions on the physical properties of Sn–Sb solder alloy. Mechanical and thermal property measurements indicated significant increase in creep resistance, rupture time with the alloying of Ag and Au elements. However, addition of Au can improve the melting temperature and increase fusion heat of Sn–5Sb alloy. Chen et al. [13] studied the interfacial reactions in the Sn–Sb/Ag and Sn–Sb/Cu couples and reported that all the reaction products of IMCs could grow linearly with the square root of reaction time, which suggest that the interfacial reactions are diffusion controlled. For the reliability of Sn–5Sb Pb-free solder alloy, Alam et al. [9] reported also that additions of Ag and Au into the Sn–5Sb alloy can enhance the solder properties, such as the ultimate tensile strength (UTS), ductility, and fusion heat. This is because the formation of intermetallic compounds (IMCs) $AuSn_4$ and Ag_3Sn can enhance the microstructure stability

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and retains the formation of SbSn precipitates in the solidification microstructure, thus significantly improves their strength and ductility. For all alloys, it was found that the UTS and yield stress YS increase with increasing strain rate and decrease with increasing temperature in tensile tests, but changes in ductility are generally small with inconsistent trends. However, the result of a literature search revealed that little studies have been reported on lead-free Sn–5Sb solder joints containing small amount of Ag and Cu. In this work, the incorporation of the same amount of Ag and Cu to Sn–5Sb Pb-free solder alloy was studied. Microstructural and mechanical data of the ternary solder alloys were measured and compared with the Sn–5Sb solder alloy. The effect of strain rate and temperature during mechanical testing has been studied. Correlations between the evolution of the microstructure and mechanical testing properties are proposed. 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 tensile 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 a high purity argon atmosphere to produce rod-like specimen with a diameter of approximately 10 mm. The melt was held at 500 °C for 2 h 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 this investigation. A solution of 2% HCl, 3% HNO_3 and 95% (vol.%) ethyl alcohol was prepared and used to etch the samples. The evolution of microstructure with the Ag and Cu contents in the Sn–5Sb solder alloy was studied using optical and scanning electron microscopy (SEM) with an energy dispersive X-ray spectrometer (EDS) after etching. Phase identification of the alloy samples was carried out by X-ray diffractometry (XRD) at 40 kV and 20 mA using Cu Kα radiation with diffraction angle (2θ) from 25° to 85° and a constant scanning speed of 1°/min. Differential scanning calorimetry (DSC) (shimadzu DSC-50) was carried out to understand the melting process of the three solder alloys. Heating the specimens in DSC was carried out at 5 °C/min of heating rate in Ar flow. The solder ingots were then mechanically machined into a wire samples with a gauge length marked 3×10^{-2} m for each sample and 2.0 mm in diameter. To obtain samples containing a fully precipitated phases, the samples were annealed at 130 °C for 15 min, then left to cool slowly to room temperature. Tensile tests were carried out with a tensile testing machine (Instron 3360 Universal Testing Machine). The tests were conducted at room temperature using strain rates ranging from 10^{-3} to 10^{-2} $s^{-1}$to determine the effect of Ag and Cu contents on the mechanical properties of mixed alloy as well as to determine the effect of strain rate on strength. Also, the tests were conducted at different temperatures ranging from 25 to 120 °C with a constant strain rate of 1.2×10^{-2} s^{-1} to obtain data on the stress–strain curves, which contain information of elongation at fracture and UTS. 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. Microstructure change with addition of Ag and Cu

X-ray diffraction analysis was performed to determine the phase composition of the IMCs particles in the three as-cast Sn–5Sb, Sn–5Sb–0.7Ag and Sn–5Sb–0.7Cu alloys. As can be seen in Fig. 1, all the three as-cast alloys are mainly composed of peaks indexed to a tetragonal cell of Sn with $a = 0.584$ and $c = 0.319$ nm and precipitated SbSn phase. The Ag_3Sn phase was found in the XRD pattern of Sn–5Sb–0.7Ag alloy, indicating the successful alloying of Sn and Ag after the melting process. At the same time, the Cu_6Sn_5 and Cu_3Sn phases were formed, which were due to the alloying of Sn and Cu in the Sn–5Sb–0.7Cu alloy. Moreover, the relative intensity of β-Sn was found to be slightly decreased with the addition of Cu, due to the formation of Cu_6Sn_5 and Cu_3Sn phases.

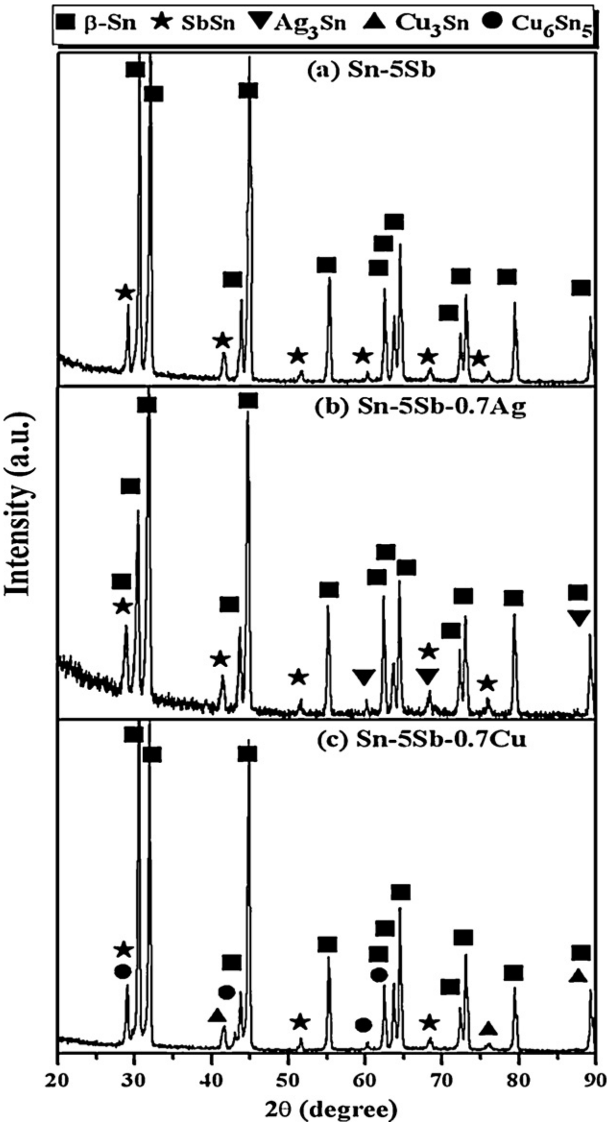

Fig. 1. XRD patterns of (a) Sn–5Sb, (b) Sn–5Sb–0.7Ag and (c) Sn–5Sb–0.7Cu solder alloys.

The microstructural evolution of the Sn–5Sb-based alloys plays a vital role in determining the mechanical properties of these alloys. Fig. 2 illustrates the ability of alloying elements to refine the grain size of Sn–5Sb, indicating that Cu was significantly stronger than Ag. In Fig. 2(a), it is generally observed that the Sn–5Sb Pb-free alloy exhibits typical near-peritetic Sn–5Sb microstructure [14,21] composed of light gray areas of equiaxed β-Sn grains and dark network-like eutectic regions of SbSn and Sn phases precipitated at the grain and grain boundaries. As the sample was a hypoeutectic composition, the volume ratio of the β-Sn phase was very high and its grain size was relatively large (40 μm). With the addition of Ag into the Sn–5Sb Pb-free solder alloy, the morphology of the β-Sn phase in the Sn–5Sb alloy gradually changes from equiaxed β-Sn grains to a relatively fine dendritic β-Sn shape with the average size less than 30 μm (Fig. 2(b)). The resultant solder alloy contains a segregated phase that appears dark or black in the interdendritic regions. It has been reported that primary Ag_3Sn IMCs might act as heterogeneous nucleation sites for Sn dendrites upon solidification [20]. According to the XRD results shown in Fig. 1(b), the ternary eutectic regions were β-Sn phase, SbSn and Ag_3Sn intermetallic compounds (IMCs). Compared with the equiaxed and fine dendritic shapes of β-Sn phase observed in Sn–5Sb and Sn–5Sb–0.7Ag alloys, respectively, the same content of Cu in the Sn–5Sb solder was found to alter the microstructure of the newly developed alloy