Enhanced thermal and microstructure properties of Sn-1.0Ag-0.7Cu based lead-free solder with Titanium Oxide addition

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Abstract. This paper presented the effects on thermal and microstructure properties of Sn–1.0Ag–0.7Cu (SAC107) lead-free solder alloy with the addition of titanium oxide (TiO2) particles. The SAC107 solders were reinforced with 0.25, 0.5, 0.75 and 1.0 weight percentage (wt.%) of titanium oxide (TiO2) particles to produce SAC107+TiO2 solder alloy composite. The solder alloy was prepared by microwave-assisted powder metallurgy route. Based on the results, it showed that the addition of TiO2 particles influenced the properties of the solder alloy composite by refining the intermetallic compound (IMC) at the bulk microstructure area and slightly decreasing the melting temperature.

1 Introduction

In recent years, many lead-free solder alloys have been developed due to the toxicity and environmental concern of lead-containing solder that widely used in the electronic assemblies [1-5]. This situation has driven many researchers to find suitable lead-free solder alloys such as Sn-Ag, Sn-Ag-Cu (SAC) [6], Sn-Cu and Sn-Zn. The lead-free solder candidates have shown potential to replace the traditional Sn-Pb solder. The use of lead-free solder SAC system is advancing throughout the world with better mechanical properties and wettabiity [7]. Considerable research efforts into the characteristics of lead-free solder are started to improve lead-free solder technologies as joining materials in the electronics industry as well as their unique physical and mechanical properties have facilitated printed circuit board (PCB) assembly [7-10].

In order to meet the demand for increasingly finer pitch and functional devices, there are some problems need to be resolved for these lead-free solder, such as the formation of large brittle intermetallic compounds (IMC) [11]. When the size of IMC is large, the brittle property of Ag3Sn and Cu6Sn5 in SAC can weaken the properties of lead-free solder joint and crack can easily propagate along their interface [12].

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The brittle Ag$_2$Sn intermetallic compounds (IMC) in SAC solder will weaken the mechanical properties of the solder joints, yet leading to the failure under stress conditions during the actual service [13]. The low-silver content such as Sn–1.0Ag–0.7Cu (SAC107) formed more β-Sn phase (large β-Sn grains) and decreases the number of Ag$_2$Sn IMC particles in the bulk solder [14]. It has been proposed that incorporating ceramics reinforcement into these alloys would affect the properties of lead-free solders by refining the microstructure and retarding the IMC growth of the eutectic phase [15-16]. It is well known that ceramic element have excellent properties which are can be improved the properties of SAC107 lead-free solder. The ceramic reinforcement such as titanium oxide (TiO$_2$) particle was selected to enhance the solder performance due to its various advantages over ferrous and other non-ferrous metallic materials. The high strength-to-weight ratio and excellent corrosion resistance of TiO$_2$ particles make it selected for reinforcement doped into lead-free solder alloys [17]. Mavoori and Jin have studied TiO$_2$ and Al$_2$O$_3$ particles as reinforcements for a conventional Sn–Pb solder and found significant enhancements of creep and mechanical properties [18].

In this work, SAC107+TiO$_2$ solder alloy composite properties such as the melting temperature and microstructure properties with varying weight percentages of TiO$_2$ particles were investigated.

### 2 Experimental procedure

The SAC107 lead-free solder alloy was mixed with different weight percentages (wt. %) of TiO$_2$ particles by using planetary mill. The composite solder were compacted into pallet size 12mm x 2mm and the compacted sample was sintered using rapid microwave-assisted sintering technique to grasp the temperature of 185 °C under an ambient condition in 2.45GHz (800W) generated by a 1.27kW SANYO microwave oven. The samples were then reflowed on the copper (Cu) substrate to produce a solder joint.

#### 2.1 Microstructure characterization

Microstructural analysis of the metallographically polished samples of the composite materials were carried out using optical microscope (Eclipse L300N).

#### 2.2 Melting point

The melting point of the solders was investigated using differential scanning calorimeter (DSC) from TA Instruments (model number: 2910). The samples were weighed 5 mg then placed into an aluminum pan, which was then heated with a scanned rate of 10 °C/min under a nitrogen atmosphere.
3 Results and discussion

3.1 Microstructure analysis

Fig. 1 shows the morphology of pure SAC107 with a varying weight percentage of TiO$_2$ particles. The addition of a small amount of TiO$_2$ particles into SAC107 solder has refined the microstructure of SAC107 + TiO$_2$ composite solder. It showed that with increasing amount of TiO$_2$ particles in the SAC107 matrix, the $\beta$-Sn area become smaller and eutectic phase (Cu$_6$Sn$_5$ and Ag$_3$Sn IMC phase) of the bulk microstructure become finer. The decreasing of the IMCs growth with respect to the addition of reinforcement particle was also reported in the previous study [14, 19-20]. The results suggested that the theory of adsorption phenomenon plays an important role during a solidification process of solder alloy and would greatly affect the microstructure formation [21]. An adsorption prevents the IMC to further growth on the bulk solder area also at the solder/Cu substrate interface. Zhu et al. found that the microstructure of SnBi-0.2Cr solder composite distinctly refined compared to the pure SnBi solder [22].

![Fig. 1. Optical micrograph of Sn–1.0Ag–0.7Cu with a) 0 wt.%, b) 0.25 wt.%, c) 0.5 w.%, d) 0.75 wt.% and 1.0 wt.% of titanium oxide.](image)
3.2 Melting point behaviour

The effect of TiO$_2$ addition on SAC107 solder alloy composite melting temperature was showed in Figure 2. The melting temperature of SAC107 + 0.25 wt. % TiO$_2$, SAC107 + 0.5 wt. % TiO$_2$, SAC107 + 0.75 wt. % TiO$_2$, and SAC107 + 1.0 wt. % TiO$_2$ were 216.9 °C, 216.8 °C, 216.7 °C, and 216.7 °C, respectively. It is seemed that the melting temperature of SAC107 eutectic was 217.1 °C. Based on the result, reduction in the melting temperature of SAC107 + 0.25 wt. % TiO$_2$, SAC107 + 0.5 wt. % TiO$_2$, SAC107 + 0.75 wt. % TiO$_2$, and SAC107 + 1.0 wt. % TiO$_2$ were 0.2 °C, 0.3 °C, 0.4 °C, and 0.4 °C, respectively. These results indicated that the melting temperature of SAC107 composite solder was lower than that of the pure SAC107 solder alloy. These suggested that the reduction of the melting point is possibly attributed to an increase in the surface instability of the composite solder caused by the addition of the TiO$_2$ particles with a higher surface free energy. It is believed that TiO$_2$ particles act as additional nucleation sites where it may increase the rate of β−Sn solidification and reduce growth time for Ag$_3$Sn formation in SAC107 solder alloy composite. The fine microstructure in the bulk solder was also found during the faster solidification rate [14]. Yang et al. stated that the fast cooling rates produced joints with the best mechanical properties. The reduction in melting temperature of solder composite also reported from the other researcher. Liu et al. [14] have found the melting temperature of Sn−3.8Ag−0.7Cu solder composite with SiC particle were lower than the eutectic solder alloy by about 1 K.

![Fig. 2. Melting temperature of the SAC107 solder alloy with TiO$_2$ addition.](image-url)
4 Conclusion

The influence of TiO₂ addition on the thermal and microstructure properties of Sn-1.0Ag-0.7Cu (SAC107) lead-free solder alloy was studied in this research. The following conclusions can be drawn:

i. The β-Sn and eutectic area which contain Cu₆Sn₅ and Ag₃Sn intermetallic phase in SAC107+ 1wt.% TiO₂ lead-free solder composite were refined after the addition of TiO₂ particles.

ii. A slight reduction in melting temperature of the SAC107+ 1wt.% TiO₂ lead-free solder composite.

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