Effects of TiO$_2$ and Al$_2$O$_3$ nanoparticles addition on the thermal properties and wettability of Sn-3.0Ag-0.5Cu-xTiO$_2$-xAl$_2$O$_3$

Nur Haslinda Mohamed Muzni$^1$, Ervina Efzan Mhd Noor$^{2,1}$, Mohd Mustafa Al-Bakri Abdullah$^3$ and Canan Aksoy$^4$

$^1$Faculty of Engineering and Technology, Multimedia University, 75450 Ayer Keroh, Malacca, Malaysia
$^2$Centre of Manufacturing and Environment Sustainability, Multimedia University, 75450 Ayer Keroh, Malacca, Malaysia
$^3$Centre of Excellence Geopolymer and Green Technology (CEGeoGTech), School of Materials Engineering, Universiti Malaysia Perlis, 01000 Kangar, Perlis, Malaysia
$^4$Karadeniz Technical University, 61080, Trabzon, Turkey

Abstract. This study investigated the effects of adding titanium dioxide (TiO$_2$) and aluminium oxide (Al$_2$O$_3$) nanoparticles into Sn3.0Ag0.5Cu (SAC) lead-free solder alloy on the thermal properties and wettability. In comparison with SAC lead-free solder without addition of nanoparticles, the melting temperature is very similar and comparable. The solidus temperature is in the range of 217.1 to 217.2 °C with the addition of TiO$_2$ and Al$_2$O$_3$ nanoparticles. The results shows that the addition of 0.25-1.0 wt% of TiO$_2$ and Al$_2$O$_3$ nanoparticles caused the liquidus temperature to decrease from 222.4 to 220.5 °C. The spreading area of SAC-xTiO$_2$-xAl$_2$O$_3$ lead-free solder increases from 5.7 to 7.1mm at 0-0.5wt% of TiO$_2$ and Al$_2$O$_3$ nanoparticles. The contact angle decreased from 66.09˚ to 46.84˚ when the composition of TiO$_2$ and Al$_2$O$_3$ increases from 0-0.5wt%.

1 Introduction

Conventional Sn-Pb solders are widely used in electronics industries thanks to their comprehensive properties. However, due to the toxicity of lead the restriction of lead in the electronic products was implemented for environmental and health considerations. Thus, the replacement of lead in the electronics industries is one of the main issues in the current effort towards manufacturing of eco-friendly electronic products. Following the restriction of lead in electronics industry, a huge number of lead-free solders were explored and developed in a way of replacing Sn-Pb solders [1-3]. Among all of these alternative lead-free solders, Sn–Ag–Cu (SAC) solders are regardless the most favourable candidate in replacing Sn–Pb solders for their relatively significant performance [4-7].

1Corresponding author: ervina.noor@mmu.edu.my
A continuous trend towards miniaturisation in electronic industry has made it possible to be widely use in more fields of application. The miniaturisation of electronic system had made efforts to develop micron-scaled solders that gives high performance. However, these micron-scaled solder which are said to have poor joint reliability because they are made in a small space. Then, when the solder is subjected to high temperatures, it can cause an excessive buildup of intermetallic compound at the joint interface and could deteriorate the joint reliability [8]. Thus, these have driven the demand to develop a high performance lead-free solders which can strengthen their properties. Numerous research have revealed that producing nanocomposite solders by incorporating a small amount of nanoparticles into SAC solder is one of the feasible solutions [4,9-10]. Nanocomposite solders were discovered to have melting temperatures similar to SAC solders which exhibits the excessive growth of IMC. The aim of incorporating nanoparticles into lead-free solders is to reinforce the solder through particle dispersion, that improves solder deformation resistance by preventing dislocation movement and constraining grain boundaries in the solder matrix [11,12].

2 Experimental procedures

SAC solder was prepared based on weight percentage (wt%) of 96.5% Tin (Sn), 3.0% Argentum (Ag), and 0.5% Copper (Cu). Mechanically dispersing 0.25, 0.50, 0.75, and 1.0 wt% of TiO₂ and Al₂O₃ nanoparticles in the lead-free SAC solder at 250°C in a graphite crucible for 1 hour to prepare Sn-3.0Ag-0.5Cu-xTiO₂-xAl₂O₃ nanocomposite solders. Differential scanning calorimetry (DSC) was used to investigate the melting temperatures of the lead-free SAC nanocomposite solders. Specimens were heated at a rate of 10°C/min in an Argon environment, with a temperature range of 30-300 °C. The spread area and contact angle were used to determine the solder wettability. The solder balls were cut into 5mm diameter billet with 1mm thickness. The lead-free SAC nanocomposite solders were soldered on copper (Cu) substrate at size of 10x10 mm at temperature of 250°C on a laboratory hotplate for 60s.

3 Results and discussion

Fig. 1 shows the differential scanning calorimetry (DSC) curves for all specimens reinforced with various TiO₂ and Al₂O₃ nanoparticle compositions, which are described in Table 1. 0.25, 0.50, 0.75 and 1.0 wt% of TiO₂ and Al₂O₃ nanoparticles reinforced respectively into the nanocomposite SAC solders. During the heating process of the DSC analysis, the lead-free SAC solder forms a eutectic alloy with a melting temperature of 222.4°C. All of the lead-free SAC composite solders had similar solidus temperatures (Tₕ) to lead-free SAC solder, ranging from 217.0 to 217.2 °C.

Also, as can be seen in Fig. 1, the lead-free SAC nanocomposite solders reinforced with different composition of nanoparticles show different curves and melting points. When 1.0 wt% TiO₂ and Al₂O₃ nanoparticles were reinforced to the lead-free SAC solder, the solidus (Tₕ) temperature increased from 217.0 to 217.1 °C and the liquidus (Tₜ) temperature decreased from 222.4 to 220.5 °C, respectively. When TiO₂ and Al₂O₃ nanoparticles composition were increased from 0.25 to 1.0 wt%, the liquidus (Tₜ) temperature were decreased from 221.9 to 220.5 °C. However, this result differs from other studies in which the liquidus (Tₜ) temperature of lead-free SAC nanocomposite solder are elevated [14-17]. The high melting point of TiO₂ and Al₂O₃ nanoparticles, which dissolved at a high solubility in lead-free SAC composite solder, can result to an increase in liquidus (Tₜ) temperature. [13-15].
Table 1. Solidus, liquidus, and melting range of lead-free SAC solder with TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} nanoparticles addition

| Specimen            | Wt% TiO\textsubscript{2} | Wt% Al\textsubscript{2}O\textsubscript{3} | T\textsubscript{s} (°C) | T\textsubscript{L} (°C) | ∆T   |
|---------------------|---------------------------|-------------------------------------------|-------------------------|-------------------------|-------|
| SAC                 | -                         | -                                         | 217.0                   | 222.4                   | 5.4   |
| SAC-0.25TiO\textsubscript{2}-0.25Al\textsubscript{2}O\textsubscript{3} | 0.25                       | 0.25                                      | 217.1                   | 221.9                   | 4.8   |
| SAC-0.50TiO\textsubscript{2}-0.50Al\textsubscript{2}O\textsubscript{3} | 0.50                       | 0.50                                      | 217.2                   | 221.1                   | 3.9   |
| SAC-0.75TiO\textsubscript{2}-0.75Al\textsubscript{2}O\textsubscript{3} | 0.75                       | 0.75                                      | 217.1                   | 221.9                   | 4.8   |
| SAC-1.0TiO\textsubscript{2}-1.0Al\textsubscript{2}O\textsubscript{3} | 1.0                        | 1.0                                       | 217.2                   | 220.5                   | 3.3   |

Ts : Solidus, T\textsubscript{L} : Liquidus, ∆T : Melting range

Fig. 1. DSC curves of lead-free SAC solder and lead-free SAC solder reinforced with TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} nanoparticles.

Referring to Table 1, the melting range (ΔT) were seen to be decreased lies in the range of 4.8 to 3.3 when 0.25-1.0 wt% of TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} nanoparticles were reinforced into lead-free SAC solder. The solder’s narrow melting range indicates that the solder exists as part liquid momentarily during solidification [16]. The melting temperature of solders is part of its most important characteristics which displaying the reflow soldering profile and is affecting the wetting and solidification process [17]. As the melting temperature of solder was low, the alloy surface tension can be reduced and allows rapid wetting at lower operating temperature. Moreover, a wide melting range indicates that solder alloy will remain as liquid form for a long period during solidification and also a reliable soldering joints cannot be
formed during soldering process [18]. The melting temperature of a promising solder alloy should be low, and the melting range should be narrow [16,19].

Wettability is an important characteristic for soldering system in electronics because it ensures that the joint developed will not fall apart at the interface. Fig. 2, shows the images of spreading area (a)-(e) and cross sectional view images of contact angle (f)-(j) of SAC nanocomposite solder after reflow at different composition of TiO$_2$ and Al$_2$O$_3$ nanoparticles. The diameter of the spreading area after reflow at 250 °C for 60s was 5.7, 6.3, 7.1, 5.8, and 5.7 mm at different composition of 0, 0.25, 0.50, 0.75, and 1.0 wt% of TiO$_2$ and Al$_2$O$_3$ nanoparticles. The spreading area of the SAC nanocomposite solder was increasing with increasing of composition of TiO$_2$ and Al$_2$O$_3$ nanoparticles from 0-0.50 wt% but then decrease with addition of TiO$_2$ and Al$_2$O$_3$ nanoparticles up to 1.0 wt%. The contact angle (f)-(j) was 66.09, 60.68, 46.84, 56.11, and 66.57˚ respectively at different composition of 0.25, 0.50, 0.75, and 1.0 wt% of TiO$_2$ and Al$_2$O$_3$ nanoparticles. The contact angle was decreasing with increasing of composition of TiO$_2$ and Al$_2$O$_3$ nanoparticles from 0-0.50 wt% but then decrease with TiO$_2$ and Al$_2$O$_3$ nanoparticles addition up to 1.0 wt%. From this results, it shows that the surface tension are low when 0.25-0.50 wt% of TiO$_2$ and Al$_2$O$_3$ nanoparticles were added into the SAC solder. As the surface tension are low, it allows the solder to spread easily, reducing the contact angle of the solder indirectly. In other word, the wetting process will be improved by the ability of the solder to spread on the substrate when the surface tension of the liquid is lower or the surface energy of the solid is higher [20].

| Specimens          | Spreading area (mm) | Contact angle (˚) |
|--------------------|---------------------|-------------------|
| SAC                |                     | (f)               |
| SAC-0.25TiO$_2$-0.25Al$_2$O$_3$ | (a)               | (g)               |
| SAC-0.50TiO$_2$-0.50Al$_2$O$_3$ | (b)               | (h)               |
| SAC-0.75TiO$_2$-0.75Al$_2$O$_3$ | (c)               | (i)               |
| SAC-1.0TiO$_2$-1.0Al$_2$O$_3$ | (d)               | (j)               |

Fig. 2. Images of spreading area (a)-(e) and cross sectional view images of contact angle (f)-(j) of SAC nanocomposite solder after reflow at different composition of TiO$_2$ and Al$_2$O$_3$ nanoparticles
Fig. 3. shows the correlation of spreading area and contact angle of SAC nanocomposite solder in corresponding with addition of different composition of TiO2 and Al2O3 nanoparticles. The spreading area and contact angle of solder on Cu substrate will be used to determine its wettability. During soldering process, the solder was heated at a temperature which then melted and solidified. The solder ball melted and spread easily when the surface tension of the solder liquid on the Cu substrate is low, and then solidified at a lower contact angle [20]. The increase in spreading area and reduction in contact angle could be associated with the increase of flux reaction rate [21]. The nanoparticles in the solder probably act as agents in reducing the surface tension during soldering. It can be concluded that wettability property of SAC nanocomposite solders were improved by 0.25-0.5 wt% addition of TiO2 and Al2O3 nanoparticles, while further addition of the TiO2 and Al2O3 nanoparticles up to 1.0 wt% decreased the performance of solders.

![Graph showing spreading area and contact angle of SAC nanocomposite solder at different composition of TiO2 and Al2O3 nanoparticles](image)

4 Conclusions

Lead-free SAC nanocomposite solders reinforced with 0.25, 0.50, 0.75, and 1.0 wt% of TiO2 and Al2O3 nanoparticles were successfully mixed in this study. SAC nanocomposite solders had relatively similar solidus temperature as lead-free SAC solders. The liquidus temperature of SAC nanocomposite solders decreases as the TiO2 and Al2O3 nanoparticles composition increases. The wettability properties were improved by 0.25-0.50 wt% addition of TiO2 and Al2O3 nanoparticles and decreased by up to 1.0 wt% addition of TiO2 and Al2O3 nanoparticles. The lead-free SAC nanocomposite solders shows better properties at 0.50 wt% of TiO2 and Al2O3 nanoparticles.

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