A review: microstructure and properties of tin-silver-copper lead-free solder series for the applications of electronics

Muhammad Aamir

School of Engineering, Edith Cowan University, Joondalup, Australia

Riaz Muhammad

Department of Mechanical Engineering, University of Bahrain, Sakheer, Bahrain

Majid Tolouei-Rad

School of Engineering, Edith Cowan University, Joondalup, Australia

Khaled Giasin

School of Mechanical and Design Engineering, University of Portsmouth, Portsmouth, UK, and

Vadim V. Silberschmidt

Wolfson School of Mechanical, Electrical and Manufacturing Engineering, Loughborough University, Loughborough, UK

Abstract

Purpose – The research on lead-free solder alloys has increased in past decades due to awareness of the environmental impact of lead contents in soldering alloys. This has led to the introduction and development of different grades of lead-free solder alloys in the global market. Tin-silver-copper is a lead-free alloy which has been acknowledged by different consortia as a good alternative to conventional tin-lead alloy. The purpose of this paper is to provide comprehensive knowledge about the tin-silver-copper series.

Design/methodology/approach – The approach of this study reviews the microstructure and some other properties of tin-silver-copper series after the addition of indium, titanium, iron, zinc, zirconium, bismuth, nickel, antimony, gallium, aluminium, cerium, lanthanum, yttrium, erbium, praseodymium, neodymium, ytterbium, nanoparticles of nickel, cobalt, silicon carbide, aluminium oxide, zinc oxide, titanium dioxide, cerium oxide, zirconium oxide and titanium diboride, as well as carbon nanotubes, nickel-coated carbon nanotubes, single-walled carbon nanotubes and graphene-nano-sheets.

Findings – The current paper presents a comprehensive review of the tin-silver-copper solder series with possible solutions for improving their microstructure, melting point, mechanical properties and wettability through the addition of different elements/nanoparticles and other materials.

Originality/value – This paper summarises the useful findings of the tin-silver-copper series comprehensively. This information will assist in future work for the design and development of novel lead-free solder alloys.

Keywords Wettability, Alloying element, Mechanical properties, Melting point, Microstructure, Tin-silver-copper series

Paper type Research paper

1. Introduction

Soldering is the joining of two or more metals by means of a third metal, or alloy, with a relatively lower melting point (MP) (Efzan and Marini, 2012). Solder joints are used to physically hold assemblies together, allowing contraction and expansion of different components, dissipating any generated heat and transmitting electrical signals. Therefore, the reliability of a solder joint depends on the performance and quality of the solder alloy (Aamir *et al.*, 2015). In the early era of the microelectronics industry, tin-lead ($Sn_{63}-Pb_{37}$) was most commonly used (Ma and Suhling, 2009). This was due to the

combined merit of low cost and good mechanical, metallurgical and physical properties, mainly facilitated by the lead (Pb) (Lee, 1997). However, lead's use in electronics is now restricted by legislation worldwide due to environmental concerns (Cheng *et al.*, 2017). Therefore, electronics manufacturers require a reliable lead-free solder (LFS) that is environmentally benign (Lee, 1997).

The most popular LFS alloys are in the tin-silver-copper (SAC) series (Aamir *et al.*, 2017a; Aamir *et al.*, 2017b). A survey has shown that almost 70 per cent of accepted lead-free solders (LFS s) are SAC alloys, due to their comparatively good properties (Shnawah *et al.*, 2012). In addition, the SAC series provides better mechanical support in electronic devices because of its good joint strength (Harrison *et al.*, 2001). In

SAC, the near eutectic composition consists of a high volume of a β -tin (*Sn*) matrix and intermetallic compounds, (*IMCs*) namely Ag_3Sn , Cu_6Sn_5 and Cu_3Sn (El-Daly *et al.*, 2013). In comparison to the *Sn*-matrix, the *IMCs* are brittle in nature (Sadiq *et al.*, 2013). It is worth noting that the formation of Ag_3Sn is due to the reaction between *Sn* and Silver (*Ag*), whereas Cu_6Sn_5 is possibly formed by the reaction between *Sn* and copper (*Cu*). No reaction has been found between *Ag* and *Cu* for the formation of any types of *IMCs* (Vianco and Shangguan, 2006). It has also been reported that Cu_3Sn does not form at the eutectic point unless the content of *Cu* is high enough for its formation at high temperature (Ma and Suhling, 2009). *Cu* additions in the SAC series improve their wettability and lower their melting temperature (Nimmo, 2004). Furthermore, higher *Ag* contents in the *Sn*-rich matrix yield a higher amount of Ag_3Sn , which may result in higher strength. However, high *Ag* contents with high elastic moduli (*E*) and yield strengths (*YS*) show reasonably low ductility (Che *et al.*, 2010).

Unfortunately, SAC solders still exhibit some problems such as higher *MP*, poor wettability and coarser microstructures (Sadiq *et al.*, 2013). To overcome these problems, and to further improve the reliability of solder joints, different elements and/or micro or nanoparticles have been added to change the microstructure and enhance other properties (Sona and Prabhu, 2013). In this review, the impact of adding different elements/nanoparticles and other materials on the *MP*, microstructure, mechanical properties and wettability of all SAC family members is presented.

2. Melting point

Melting temperature (*MT*) is one of the most important properties for the development of LFSs (El-Daly and Hammad, 2012). *MT* is the liquidus temperature (T_L) making the solder alloy completely molten, which is necessary for soldering operations (Abtey and Selvaduray, 2000). The *MT* is essential to develop better solder joints and occurs if the solidus temperature (T_S) is low (Mei *et al.*, 1996) because rapid solidification can provide a better and more refined microstructure which has a direct impact on a solder joint's strength (Kanlayasiri *et al.*, 2009). Moreover, a good solder alloy should have a narrow melting range ($\Delta T = T_L - T_S$) and low *MT* (El-Daly and Hammad, 2012). Taking into account that a conventional eutectic *Sn-Pb* solder melts at 183°C, this can be considered as the benchmark for new LFSs (Jeon *et al.*, 2008). However, the *MP* of SAC is approximately 217°C, which results in thicker *IMCs* than those of *Sn-Pb*. Therefore, some researchers have added alloying elements, or nanoparticles, to reduce the *MT* of the SAC series. For instance, Kanlayasiri *et al.* (2009) reported that the doping of indium (*In*) into SAC lowers the T_S and T_L . Their results concluded that, upon addition of 3 Wt.% *In* to SAC, T_S (219.4°C) and T_L (241.7°C) decreased by 21.7°C and 11.5°C, respectively. Subsequently, the difference between T_S and T_L of the SAC increased from 22.3 °C to 32.5 °C. However, *In* is expensive and it increases the cost of LFSs. Chuang *et al.* (2012) investigated the influence of titanium (*Ti*) on the *MT* of SAC. Their results showed that the addition of 1.0 Wt.% of *Ti* into SAC decreased the T_S and T_L from 216.92°C and

221.58°C to 216.59°C and 219.47°C, respectively. In addition, the melting range of SAC also decreased from 4.66°C to 2.88°C. A narrow melting range is one of the desirable thermal properties of solders, meaning they exist in the liquid form only for a very short time during solidification for the formation of acceptable joints. In another study by Shnawah *et al.* (2013), differential scale calorimetry (DSC) analysis was used to check the thermal behaviour of SAC after the addition of iron (*Fe*). They found that 0.6 Wt.% of *Fe* gave a lower *MP* by showing one endothermic peak at 221.35°C at a eutectic composition. Huang and Wang (2005) also reported a decrease in the *MP* of SAC upon addition of bismuth (*Bi*). According to their findings, the T_S of SAC-2*Bi* and SAC-4*Bi* were 213.08°C and 206.40°C, respectively. However, peeling of the solder joint appeared when the *Bi* addition was > 4 Wt.%.

Furthermore, the addition of Rare-Earth (*RE*) elements (Wu and Wong, 2007) and nanoparticles (Efan Mhd Noor *et al.*, 2013) have also contributed better properties to SAC, while not drastically affecting the *MP*. For instance, Dudek and Chawla (2010) studied the DSC curves of SAC and SAC-0.5*RE*. Their selected *RE* elements were lanthanum (*La*), cerium (*Ce*), and yttrium (*Y*), where it was found that all solders (*La*, *Ce*, and *Y*) displayed a single endothermic peak between 217°C and 219°C. Liu *et al.* (2008) studied the minor addition of silicon carbide (*SiC*) nanoparticles to the SAC and found that it did not change its *MT* noticeably. However, upon the addition of only 0.2 Wt.% *SiC*, a lower *MP* value was observed as the endothermic peak shifted from 219.9°C to 218.9°C. Tsao *et al.* (2013) analysed DSC curves of SAC doped with aluminium oxide (Al_2O_3) nanoparticles. It was found that the *MP* of SAC, which was 221.2°C, slightly increased as the amount of Al_2O_3 nanoparticles increased. Gain *et al.* (2011) also observed no significant change in the *MP* of SAC with 1 Wt.% of titanium dioxide (TiO_2) nanoparticles. It was concluded that DSC analyses gave only a eutectic peak from 217.00°C to 217.64°C. Similar behaviour was noted in another study by Chang *et al.* (2011). In conclusion, adding alloying elements and nanoparticles to SAC alloys had little effect on the *MT*.

3. Microstructure

A thin layer of *IMCs* is required to attain a better metallurgical bond for the reliability of electronic solders; however, their higher growth has undesirable impacts on the mechanical properties due to their brittle nature (Liang *et al.*, 2014). Therefore, it is important to expand the knowledge of *IMCs* for the reliability of solder interconnections (Aamir *et al.*, 2017c; Aamir *et al.*, 2019). In this review, the addition of alloying elements etc into SAC alloys is discussed to highlight the impact of precipitates in suppressing the growth of *IMCs* for refined and uniform microstructures.

Chuang *et al.* (2012) concluded that, after the addition of different amounts of *Ti* into SAC, the microstructure became uniform due to the active properties of *Ti*, which gave rise to heterogeneous *IMCs* and reduced the dendritic size. However, it was recommended that the *Ti* concentration should not exceed 1.0 Wt.%, which in turn gave rise to coarse Ti_2Sn_3 in the eutectic colonies and made the microstructure worse. Sabri *et al.* (2013) found that inclusions of aluminium (*Al*) in

SAC led to the arrangement of a large amount of additional Ag_3Sn and Al_2Cu IMCs. These IMCs possessed snowflake, circle, rod, and quadrangle shaped morphologies and were lightly distributed within the microstructures located in and at the vicinity of interdendritic regions. Moreover, these additional IMCs refined the microstructure of SAC by restraining the growth formation of IMCs (Ag_3Sn and Cu_6Sn_5). In another study by [Leong and Haseeb \(2016\)](#), the effect of a minor addition of Al into SAC on the interfacial structure between the solder and copper substrate during reflow was investigated. It was determined that the minor addition of Al into SAC formed small equiaxed $Cu-Al$ particles, Cu_3Al_2 , which suppressed the growth of the interfacial Cu_6Sn_5 IMC after reflow. [Zhang et al. \(2012a\)](#) investigated doping of zinc (Zn) into SAC, which remarkably refined the microstructure with the condition that concentrations of Zn should be limited to 0.8 Wt.%. The refinement in microstructure was due to the formation of dispersed $Cu-Zn$ IMCs which reduced the thickness of the IMCs and ultimately changed the morphology. [Hammad \(2013\)](#) found that adding 0.05 Wt.% Ni into SAC formed $(Cu, Ni)_6Sn_5$ IMCs in the eutectic regions, which decreased the inter-particle spacing and resulted in a more refined morphology. [Wang et al. \(2019\)](#) fabricated SAC with 0.2 Wt.% zirconium (Zr) using a vacuum induction melting method. Their study demonstrated that Zr refined the microstructure of SAC by reducing the size of the IMCs, which further participated in improving the strength of the solder alloy. Moreover, 0.2 Zr Wt.% gave significantly better results, even after isothermal aging. However, no change in the melting range was observed.

RE elements are good surface-active agents and are considered vital materials for improving the microstructure and mechanical properties ([Sadiq et al., 2013](#)). They can accumulate at grain/dendrite boundaries and can lower the energy of the grain/dendrite boundary by restricting the motion of the boundaries. Thus, they restrict the growth of IMCs and give a refined microstructure ([Xia et al., 2002](#)). [Dudek and Chawla \(2010\)](#) reported that RE addition into SAC produced RE -containing particles, i.e. $RESn_3$ IMC, apart from Cu_6Sn_5 and Ag_3Sn , which were responsible for the refinement of the microstructure as shown in [Figure 1](#).

In addition, [Yasmin and Sadiq \(2014\)](#) concluded that the appropriate composition of La in SAC reduced the grain size and provided better microstructure by effectively suppressing the growth rate of IMCs (Ag_3Sn and Cu_6Sn_5) even during thermal ageing. This refinement in the SAC microstructure was due to the aggregation of La at the interface, which provided blockage for the production of large IMCs. The same recommendation was made in another study by [Sadiq et al. \(2013\)](#). Moreover, a careful examination of the microstructure after Ce inclusion in SAC was done by [W Chen et al. \(2011\)](#). Their results showed that adding Ce promoted the formation of $Ce-Sn$ IMCs which acted as a blockage to decrease the growth of Ag_3Sn and Cu_6Sn_5 ; thus, giving a refined microstructure. [Zhang et al. \(2012b\)](#) also studied the contribution of 0.03 Wt.% Ce in SAC. Their study showed that the activation energy for the growth of IMCs was higher for Ce -based SAC, which was responsible for reducing the growth of IMCs and increasing the strength of the solder joint. Furthermore, [Tu et al. \(2017\)](#) reported that 0.15 Wt.% of Ce in SAC improved the

Figure 1 SEM micrographs of (a) SAC with the addition of 0.5 Wt.% of (b) La , (c) Ce and (d) Y

Source: Dudek and Chawla (2010)

microstructure by reducing the thickness of the IMCs. [Zhang et al. \(2014\)](#) reported that additions of 0.05 Wt.% of ytterbium (Yb) in SAC improved the properties for electronic packaging and refined the microstructure by retarding the growth of IMCs during soldering. In another study ([Gao et al., 2010b](#)), the incorporation of a small concentration of praseodymium (Pr) in SAC was shown to produce extra $PrSn_3$ particles which restricted the IMC growth because of the heterogeneous nucleation by lowering the reaction time of the liquid solder with the substrate. However, more than 0.05 Wt.% of Pr resulted in the arrangement of the bulk $PrSn_3$ compound.

Nanoparticles also play a vital role in changing the microstructure of SAC alloys. For instance, [Liu et al. \(2008\)](#) concluded that the inclusion of 0.05 Wt.% SiC nanoparticles remarkably decreased the average grain size, due to the strong adsorption effect and high surface free energy, which led to refined IMCs. [Sharma et al. \(2019\)](#) used a simple mechanical blending and casting method to add zirconia (ZrO_2) nanoparticles to SAC. It was concluded that, after the addition of ZrO_2 nanoparticles, the thickness of the grain size, and IMCs such as Ag_3Sn and Cu_6Sn_5 were refined by 46 per cent, 14 per cent, and 26 per cent, respectively compared to the original SAC alloy. [Bashir et al. \(2016\)](#) used a nanoparticle-doped flux technique to add 2 Wt.% Co nanoparticles into SAC. The influence of the Co nanoparticle-doped flux was then investigated with an electro-migration (EM) test performed in an oil bath at 80°C for a duration of 1128 h with a current density of 1×10^4 A/cm². Their study concluded that the presence of 2 Wt.% Co nanoparticles in SAC restricted the size of the IMCs, both at the cathode and anode sides. In addition, the tensile strength of the solder joint increased after the addition of Co nanoparticles when the EM test was performed at 150°C for 0 h and 192 h. This study showed that a 2 Wt.% Co nanoparticle-doped flux improved the reliability of SAC solder joints. [Sujan et al. \(2017\)](#) also worked on the addition of Co nanoparticles using the flux doping technique. This method is useful with surface mount technology and does not require any further steps in the manufacturing line. Their results showed that the addition of Co -nanoparticles with an average

size of 58 nm into SAC stabilised the formation of Cu_6Sn_5 IMC and improved the growth of Co containing IMCs. Haseeb *et al.* (2017) provided an overview to discuss the effects of metallic nanoparticles on the characteristics of interfacial IMCs in Sn-based solder joints on Cu substrates during reflow and thermal aging. The Ni, Co, Zn, Mo, Mn, and Ti nanoparticles were mechanically blended with the SAC solder paste. It was shown that, through the paste mixing route, the Ni, Co, Zn and Mn nanoparticles greatly contributed to changing the morphology and reducing the thickness of the IMCs, which helped the solder joint to perform in a favourable way. Basak *et al.* (2018) investigated the addition of minor amounts of Fe or Al_2O_3 nanoparticles into SAC. Their results indicated that supplements of Fe nanoparticles formed $FeSn_2$, together with the IMCs of SAC alloy, i.e. Ag_3Sn and Cu_6Sn_5 , which stopped the growth of grains/IMCs during aging/reflowing. However, Al_2O_3 nanoparticles did not participate in phase formation but acted as a grain refiner. Yakymovych *et al.* (2017) added Ni nanoparticles into SAC using a cold-pressing method in which powders of SAC and Ni nanopowders were mixed mechanically, and processed into 8 mm diameter rods. It was observed that the presence of Ni nanoparticles in SAC formed a $(Cu, Ni)_6Sn_5$ phase which participated in the refinement of the microstructure due to the fine distribution of IMCs in the Sn matrix. Gain and Zhang (2019) found that 0.5 Wt.% Ni-nanoparticles in SAC produced new (Cu, Ni) -Sn IMC phases as shown in Figure 2. The new IMC phase refined the microstructure of SAC and improved the mechanical reliability of electronic interconnections which, subsequently, enhanced the lifespan of miniaturised electronic products.

Carbon nanotubes (CNTs) have been acknowledged as offering better physical, electrical and mechanical properties, which make them suitable for the fabrication of novel composites (Nai *et al.*, 2008). Zhu *et al.* (2018) worked on doping CNTs with three different ranges of diameters, 10-20, 40-60, and 60-100 nm, into SAC (Figure 3). Their studies concluded that the addition of CNTs into SAC provided better performance. Among all, the addition of CNTs in SAC in the range of diameter (40-60 nm) produced a refined microstructure by lowering the growth rate of the IMCs up to

30.9 per cent. The refinement in microstructure was attributed to the agglomeration and adsorption of CNTs in the solder matrix and IMCs interface.

Kumar *et al.* (2008) concluded that adding single-walled carbon nanotubes (SWCNT) into SAC played a significant role in reducing the average size of the IMCs due to the dispersion of nanotubes at the grain boundaries of the Ag_3Sn , which resulted in a uniform morphology. Xu *et al.* (2015) studied the impact of graphene-nano-sheets (GNSs) on SAC. Their study found that GNSs participated in restricting grain growth and gave fine IMCs. The average sizes of the IMCs, after addition of 0.03, 0.07, and 0.10 Wt.% GNSs reduced to 1.35, 1.24 and 1.21 μm , respectively, compared to 1.96 μm for SAC. All these reduced size IMCs played a vital role in enhancing the solder joint reliability.

Overall, the addition of an appropriate composition of alloying elements, nanoparticles and composites can significantly change the microstructure of SAC alloys. However, the addition of more than a critical composition can negatively impact the properties of the solder joints. Therefore, selecting the optimum doping concentrations is highly recommended.

4. Mechanical properties

Alloying elements and nanoparticles also play a significant role in improving the mechanical properties of SAC alloys (Sun and Zhang, 2015). Table I shows the impact of adding alloying elements, nanoparticles or other materials on the mechanical properties of SAC.

Chuang *et al.* (2012) found that up to 1.0 Wt.% of Ti in SAC improved the mechanical properties. Their study also concluded that excess concentrations of Ti produced coarse Ti_2Sn_3 in the eutectic colonies which, subsequently, degraded the mechanical properties of SAC. Fallahi *et al.* (2012) determined that adding 0.2 Wt.% and 0.6 Wt.% of Fe increased the shear strength of SAC up to 40 MPa and 53 MPa, respectively. Zhang *et al.* (2012a) concluded that the addition of 0.8 Wt.% of Zn increased the strength of the SAC. However, more than 0.8 Wt.% of Zn gave disperse Cu-Zn IMCs, which resulted in coarsening of the microstructure because of the

Figure 2 SEM images of (a) SAC and (b) SAC-0.5 Wt.% nanosized Ni particles

Source: Gain and Zhang (2019)

Figure 3 (a) Schematic diagram of *MWCNTs* structure and TEM images of *CNTs*: (b) 10–20 nm, (c) 40–60 nm and (d) 60–100 nm

Source: Zhu *et al.* (2018)

great affinity of *Zn* towards oxygen. Therefore, an excessive *Zn* content resulted in the formation of ZnO_2 which untimely reduced the tensile strength. El-Daly and El-Taher (2013) reported that *YS*, *UTS*, and the ductility of *SAC* were improved after the addition of 0.05 Wt.% of *Ni* because of the refined microstructure. However, addition of 0.1 Wt.% of *Ni* into *SAC* resulted in an abrasive microstructure which in turn degraded the mechanical properties. Li *et al.* (2006) and Chen and Li (2004) found, in their studies, that doping of *Sb* also improved the tensile strength of *SAC*. This improvement in strength was due to the reduced size of *IMCs* which ultimately refined the microstructure. The same investigation was detailed by Hammad (2018), who recommended adding 0.5 Wt.% of *Sb* into *SAC* to improve the mechanical strength and ductility of the solder joint. In another study by Luo *et al.* (2014), the addition of up to 0.5 Wt.% of *Ga* was recommended to improve the shear strength of *SAC* by 17.9 per cent.

Regarding *RE* elements, Ali (2015) concluded that the optimum *La* concentration in *SAC* for desired mechanical properties including *YS*, *UTS* and ductility was 0.3 Wt.%. Aamir *et al.* (2017b) reported that better mechanical properties could be obtained when the *La* composition was less than 0.4 Wt.%, even after thermal ageing. Hao *et al.* (2007) found improvement in the strength of *SAC* after the addition of *Y*; however, the joint strength decreased dramatically for *Y* concentrations beyond 0.15 Wt.%. Shi *et al.* (2008) reported that adding ≤ 0.1 Wt.% *Er* to *SAC* increased the shear strength significantly, due to the reduced size of Ag_3Sn and Cu_6Sn_5 . Gao *et al.* (2010a) concluded that, when the *Nd* supplement was 0.05 Wt.%, the pull force and shear force of the solder joint was improved by 19.4 per cent and 23.6 per cent, respectively. The improvement in pull force and shear force was due to the refinement in the *IMCs* by *Nd*. Their study also suggested that the amount of *Nd* in *SAC* should not exceed 0.25 Wt.%. In another study by Gao *et al.* (2010b), the addition of up to

0.05 Wt.% of *Pr* also increased both the pull force and shear force by 18.5 per cent and 19.4 per cent, respectively. Similarly, Zhang *et al.* (2014) reported that inclusions of 0.05 Wt.% *Yb* to the *SAC* increased the tensile force of *SAC* solder joints by 25.4 per cent. Tu *et al.* (2017) concluded that addition of 0.15 Wt.% of *Ce* into *SAC* improved *E*, *YS* and *UTS* of *SAC*. Furthermore, *SAC-0.15Ce* also gave better shear strength, even after thermal ageing, as shown in Figure 4.

Tsao *et al.* (2013) concluded that the addition of 1.0 Wt.% of Al_2O_3 nanoparticles increased the shear strength of *SAC* after 1 and 8 reflow cycles by 14.4 per cent and 16.5 per cent, respectively. Tang *et al.* (2014) added different compositions of TiO_2 nanoparticles into *SAC* which improved the mechanical properties at the 0.1 Wt.% level. The improvement was due to refinement of the microstructure after the reduced space between the Ag_3Sn *IMCs*. Bashir *et al.* (2016) concluded that a 2.0 Wt.% *Co* nanoparticle-doped flux improved the reliability of *SAC* solder joints because their tensile strengths increased after 0 h as well as 192 h of *EM* testing at 150°C. Gain and Zhang (2018) reported that adding 1.0 Wt.% of TiO_2 nanoparticles into *SAC*, prepared by a mechanical mixing process, enhanced the creep and shear strength. It was also noted that the Cu_6Sn_5 and Cu_3Sn phases were observed on the *Cu* substrate through interfacial structure characterisation, and a ternary (*Cu*, *Ni*)-*Sn* phase had grown on an *Au/Ni*-plated *Cu* pad of a Ball Grid Array. These *IMCs* started growing during thermal ageing, however, TiO_2 nanoparticles suppressed the growth of the *IMCs* and thus, the creep, shear strength and thermal shock resistance were improved. Gain and Zhang (2019) found that, in addition to the improvement in electrical properties, the elastic modulus, shear modulus, and microhardness were also improved by 8 per cent, 11.2 per cent, and 16.7 per cent, respectively, when the addition of *Ni*-nanoparticles into *SAC* was 0.5 Wt.%. The reason for the overall good properties of the solder joints was the appearance of relatively fine *IMCs* dispersed in a β -*Sn* matrix and the fine microstructure. Roshanghias *et al.* (2012) recommended that the best combination of mechanical properties was achieved with 0.75 Wt.% of CeO_2 nanoparticles into *SAC*. Nai *et al.* (2006) suggested that the addition of 3.0 Vol.% of titanium diboride (TiB_2) nanoparticles resulted in improved levels of *YS* and *UTS* by 26 per cent and 23 per cent, respectively. Yang *et al.* (2014) concluded that adding 0.05 Wt.% *Ni*-coated carbon nanotubes (*Ni-CNTs*) into *SAC* significantly improved the tensile strength. The prime reason for its better tensile strength was that the *CNTs* obstructed the start of dislocation motion in the *SAC*. Kumar *et al.* (2008) concluded that 1.0 Wt.% of *SWCNT* enhanced the *UTS* of *SAC* up to 50 per cent. Zhu *et al.* (2018) also found that the reinforcement of *CNTs* in *SAC* improved *E*, *YS*, and *UTS*. The recommended range of the diameter of the *CNTs* was 40–60 nm, which contributed to reducing the growth of *IMCs* and thus, provided superior mechanical properties. Furthermore, upon addition of 0.03 Wt.% of *GNSs*, the *UTS* of *SAC* was improved by ~ 10 per cent, because of the refined microstructure due to the reduced average size of the *IMCs* (XD Liu *et al.*, 2013). Overall, the use of alloying elements and nanoparticles significantly contributed to the refinement of microstructure and improved mechanical properties of *SAC* series solders. However, it should be noted that

Table I Role of the fourth element in the mechanical properties of SAC

Alloying element	Composition weight percentage	Mechanical properties	References
<i>Ti</i>	Up to 1.0 Wt. %	Increase the <i>YS</i> , <i>UTS</i> , and microhardness of SAC	Chuang et al. (2012)
<i>Fe</i>	0.6 Wt. %	Shear strength of SAC increases up to 53 MPa from 29 MPa	Fallahi et al. (2012)
<i>Zn</i>	0.8 Wt. %	Improves the tensile force of SAC joints by 10%	Zhang et al. (2012a)
<i>Ni</i>	0.5 Wt. %	Improves <i>YS</i> , <i>UTS</i> and ductility of SAC	El-Daly and El-Taher (2013)
<i>Sb</i>	0.5 Wt. %	Gives higher strength and ductility	Hammad (2018)
<i>Ga</i>	Up to 0.5 Wt. %	Improves the shear strength of SAC solder joints up to 17.9%	Luo et al. (2014)
<i>La</i>	0.3 Wt. %	Increases in <i>YS</i> , <i>UTS</i> and ductility are found which then improve toughness, creep and fatigue resistance of the SAC	Ali (2015)
<i>Y</i>	<0.15 Wt. %	The strength of the SAC joint is improved	Hao et al. (2007)
<i>Er</i>	≤0.1 Wt. %	Shear strength of SAC solder is improved by 18 %	Shi et al. (2008)
<i>Nd</i>	0.05 Wt. %	Pull force and shear force of SAC joint are increased by 19.4 % and 23.6 %, respectively	Gao et al. (2010a)
<i>Pr</i>	0.05 Wt. %	Improves pull force and shear force of SAC solder	Gao et al. (2010b)
<i>Yb</i>	Up to 0.05 Wt. %	The tensile force of the SAC solder joint increase by 25.4%	Zhang et al. (2014)
<i>Ce</i>	0.15 Wt. %	Increase the shear strength, ductility, <i>E</i> , <i>YS</i> , and <i>UTS</i>	Tu et al. (2017)
<i>Al Nanoparticles</i>	3.0 Wt. %	Improves the shear strength of SAC	Gain et al. (2010)
<i>Al₂O₃ Nanoparticles</i>	1.0 Wt. %	The shear strength after 1 cycle and 8 cycles of reflow is increased by 14.4 % and 16.5 %, respectively	Tsao et al. (2013)
<i>TiO₂ Nanoparticles</i>	0.1 Wt. %	Gives better microhardness and tensile properties	Tang et al. (2014)
<i>CeO₂ Nanoparticles</i>	0.75 Wt. %	Improves <i>YS</i> and <i>UTS</i> of SAC	Roshanghias et al. (2012)
<i>TiB₂ Nanoparticles</i>	3 Vol. %	Increase <i>YS</i> and <i>UTS</i> by 26 % and 23 %, respectively	Nai et al. (2006)
<i>Co- nanoparticles</i>	2 Wt. %	Increases the tensile strength of SAC	Bashir et al. (2016)
<i>Ni-nanoparticles</i>	0.5 Wt. %	The elastic modulus, shear modulus and microhardness increase by 8.0 %, 11.2 % and 16.7 % in SAC, respectively.	Gain and Zhang (2019)
<i>Ni-CNTs</i>	0.05 Wt. %	Improves the tensile strength of SAC solder slabs and joints	Yang et al. (2014)
<i>SWCNT</i>	1.0 Wt. %	Increases the <i>UTS</i> of SAC up to 50 %	Kumar et al. (2008)
<i>MWCNT</i>	10-60 nm	Improvements in <i>E</i> , <i>YS</i> and <i>UTS</i> of SAC were found	Zhu et al. (2018)
<i>GNSs</i>	0.03 Wt. %	Increased the <i>UTS</i> of SAC solder by approximately 10 %	Liu et al. (2013)

there was also an appropriate maximum concentration beyond which those properties degraded.

5. Wettability

Wettability testing is used to examine the wetting properties that include surface tension and wetting force ([Sadiq, 2012](#)). Traditional *Sn-Pb* solder has better wettability due to the presence of *Pb* ([Dharma et al., 2009](#); [Wu et al., 2004](#)). Thus, when changing from *Sn-Pb* to *LFS*, wettability becomes an important concern. Furthermore, most of the *LFS* alloys have good mechanical properties when tested in bulk but their wetting, when soldered on boards, is not good for the reliability of solder joints. This means that wettability, or solderability, is necessary for characterising the solder alloys and becomes important when high solder joint reliability is required ([Sadiq, 2012](#)).

There are two well-known tests used to characterise the wettability of solder: the spread area test and the wetting balance test ([Wu et al., 2004](#)). In the spread area test, a solder disc is coated with flux, melted, and allowed to solidify on a substrate. When a bond is formed, the free energy is reduced and hence the solder changes its shape ([Wu et al., 2004](#)). This change in shape causes an increase in the contact area which shows the wetting behaviour of the solder. In some cases, the ratio of the as-bonded area to this new area (after soldering) is

taken as the wettability of the solder ([Wu et al., 2004](#)). Wetting balance testing is another important technique for evaluating solder wettability. In this method, a coupon (for example *Cu*) is dipped into the molten solder. The molten solder moves up the coupon because of the wetting force exerted on it. Different forces, due to buoyancy, come into action after partial dipping of the coupon into the solder bath, including the surface tension, which are quite high at the solder/flux interface. The resultant force is then the measurement of the meniscus and the wetting angle ([Sadiq, 2012](#)).

In investigations into improving the wettability of SAC, the addition of *RE* elements was the most noticeable ([Xiong and Zhang, 2019](#)). The wetting properties of SAC and SAC-*La* at 250°C were investigated by [Sadiq \(2012\)](#). It was noticed that the surface tension of SAC decreased due to *La* doping. The wetting force of SAC was 5.7 mN, which increased up to 6.7 mN for SAC-0.25*La* as shown in [Figure 5\(a\)](#). However, when the *La* content increased to 0.5 Wt. %, the wetting force showed a lower value than SAC-0.25*La*. Thus, the addition of *La* in SAC beyond 0.25 Wt. % decreased the wetting force, ultimately affecting the wettability. Therefore, the optimum level of *La* in SAC should be considered as 0.25 Wt. %. In the same study, wetting or contact angle were found on the basis of the surface tensions. An appreciable decrease in contact angle was noted with SAC-0.25*La* having a better (smaller) contact

Figure 4 Mechanical properties of SAC with different levels of Ce

Source: Tu *et al.* (2017)

Figure 5 SAC and SAC-La at 250°C

Notes: (a) Wetting forces; (b) contact angles Sadiq (2012)

angle than *SAC* and *SAC-0.5La* alloys. Figure 5(b) shows that *SAC-0.25La* decreased the wetting angle of *SAC* from 47° to 42° and again *SAC-0.5La* showed a larger wetting angle than *SAC-0.25La*. Therefore, the optimum doping of *La* in *SAC* was 0.25 Wt.%, as beyond this the wetting angle increased, ultimately affecting the wettability.

Gao *et al.* (2010a) concluded that trace amounts of *Nd* remarkably improved the wetting behaviour of *SAC*. Figures 6(a) and (b) show the wetting time and wetting force of *SAC-Nd* at different temperatures, which clearly show that the wettability of *SAC* improved with 0.05 Wt.% of *Nd* because of its lower surface tension. Gao *et al.* (2010b) in another study also reported that 0.05 Wt.% of *Pr* improved the wetting properties of *SAC*. Figure 7 shows that the highest spreading area was 63.27 mm², which was observed for *SAC-0.05Pr*.

Furthermore, the wettability of *SAC-Ce* was studied by Wang *et al.* (2009). They concluded that, after the addition of *Ce*, the wetting behaviour of *SAC* improved significantly. The observed wetting time was ~0.7 s at 250°C, which was very close to that of *Sn-Pb* solder.

Nanoparticles can also improve the performance of *SAC*. Tay *et al.* (2013) concluded that adding *Ni* nanoparticles into *SAC* increased the wetting angle from 19.3° to 29.9°. Yoon *et al.* (2005) reported that *Co* nanoparticles in *SAC* increased the wetting angle, but decreased the spreading rate. Similar effects with *Co* nanoparticles were reported by Haseeb and Leng (2011). Tsao *et al.* (2010) found that 0.5 Wt.% of *Al₂O₃* nanoparticles had the same effect on the wetting behaviour of *SAC*, giving a minimum contact angle of 28.9°. Li *et al.* (2014) produced mechanically mixed *TiO₂* nanoparticles in *SAC*. Their study showed that adding 0.25 Wt.% of *TiO₂* nanoparticles decreased the wetting time by 53.7 per cent, while the wetting force increased to 37.6 per cent. Kanlayasiri and Meesathien (2018) reported that the maximum wettability of *SAC* was achieved with 0.25 Wt.% of zinc oxide (*ZnO*) nanoparticles. Jung *et al.* (2018) worked on different compositions of *TiO₂* and Graphene. All compositions were mixed simultaneously at equal weight fractions into *SAC* molten solder by a mechanical mixing method and melting, to produce a bulk nanocomposite solder. Their results showed that a 0.21 Wt.% nanomaterial addition gave with had

Figure 7 Effect of *Pr* on the solderability of *SAC*

Source: Gao *et al.* (2010b)

wettability and spreadability improvements of 33.67 per cent and 8.66 per cent, respectively.

6. Conclusions

Lead-free solder alloys are considered to be one of the most important segments of the global green electronics environment. The most commonly used lead-free solder alloys are *SAC* as they offer good mechanical properties comparison to conventional tin-lead. Addition of alloying elements or a composite approach can overcome limitations of these *SAC* solders, especially the microstructure, mechanical properties, and wettability. However, no significant effect on the MP was observed and thus, no adjustment should be required in the reflow process to meet the requirement of the present soldering process. Further research is required to ensure that the addition of alloying elements or a composite approach can decrease the MP of tin-silver-copper. Moreover, it is worth noting that the addition of a fourth element or nanoparticles is actively involved in refining the microstructure, giving good mechanical properties and wettability, (with the condition that the added compositions should not be in an excess amount for the solder joint's reliability). In this regard, when developing new lead-free solder alloys, the optimum concentration of the material added to the tin-silver-copper should be carefully examined. Future studies should aim to determine the optimal additive

Figure 6 Effect of *Nd* on the solderability of *SAC* solders

Notes: (a) Wetting force; (b) wetting time

Source: Gao *et al.* (2010a)

compositions that can improve the thermal behaviour, interfacial reactions, tin whiskering, wettability, microstructure and mechanical properties of SAC alloys. Moreover, the work should also be extended to find the desired inclusions into tin-silver-copper that can effectively exhibit better performance under different strain rates and, thermal ageing at different times and temperatures.

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Corresponding author

Muhammad Aamir can be contacted at: m.aamir@ecu.edu.au