Citation: Amares Singh, Teow Sinn Khai, Rajkumar Durairaj, et al. Preliminary investigation of copper joints soldered with Sn58Bi. *Journal of Harbin Institute of Technology (New Series)*, 2022, 29(1): 57-63. DOI: 10.11916/j.issn.1005-9113.2020040.

Preliminary Investigation of Copper Joints Soldered with Sn58Bi

Amares Singh[1,2], Teow Sinn Khai[1], Rajkumar Durairaj[2] and Amer Ahmed Qassem Saleh[1]*

(*1. Center for Advanced Materials Research and Manufacturing Processes, SEGi University, Petaling Jaya 47810, Selangor, Malaysia; 2. Lee Kong Chian Faculty of Engineering and Science, University Tunku Abdul Rahman, Kajang 43000, Selangor, Malaysia*)

Abstract: In recent years, intensive studies have been carried out to find an alternative for Tin (Sn)-Lead (Pb) solder alloys with increasing demand over lower temperature solder alloys in current electronic packaging industry. High temperature operational solder alloys seem to produce drawback to other components on the printed circuit board (PCB). Low melting temperature Sn58Bi substrate as a potential replacement was investigated in this paper based on the melting properties, wettability, and shear strength. The Sn58Bi was soldered at a temperature below 200 ℃ on the Cu substrate, and the shear strength and contact angle were calculated. A peak temperature (melting temperature, T_M) of 144.83 ℃ was identified. Single lap joint method was performed at a strain rate of 0.1 mm/min and an average shear strength of 23.4 MPa was found from three samples. The contact angle (wettability) was calculated to study the solder joint behaviour at reflow temperature of 170 ℃. The contact angle of the Sn58Bi was found to be 32.4 ° and considered to be desired value since the angle is less than 50 °. The low temperature soldering provides a preliminary result to allow further application on the real PCB.

Keywords: SnBi solder; low temperature; shear strength; contact angle

CLC number: TG49 **Document code**: A **Article ID**: 1005-9113(2022)01-0057-07

0 Introduction

In microelectronics industries, the most commonly used solder alloy is Sn37Pb with melting temperature of 183 ℃. Due to its desirable properties, this solder alloy is used as the medium of connection within the printed circuit board (PCB). This usage of lead (Pb) solder as the attaching die accounts for almost 90% in the flip chip connection, while the other 10% usage involves Pb-free solders such as the Au/Sn or In/Sn solders. These solders are used in the flip chip to connect between the silicon (Si) chip and an FR4 substrate[1-2]. However, Pb usage has been restricted due to health and environmental concerns. The European Union (EU) has taken legal action on banning the implementation of Pb in solder alloy[3]. In soldering process, efficiency of a solder alloy is affected by its alloying process, where solder alloys such as SnPb, SnBi, and SnAgCu are a mixture of one or more elements to the base materials, Tin (Sn). In alloying process, alloying elements will undergo a diffusion process and form intermetallic compounds or serve as solid solution in the solder alloy. This alloying process was found to boost the performance of a solder alloy by enhancing some important properties by reducing the melting temperature (e. g., SnPb, SnBi), producing higher shear strength (e. g., SnZnBi), and enabling long term reliability (e. g., SnAgCu) due to excellent joint property[4].

Currently, problem concerning high temperature soldering seems to damage other components during solder pasting. In addition, thermal distortion occurs with differences of temperature between the solder and substrate[5]. Higher process/soldering temperature causes negative impact on components performance such as thermal damage on the chip and PCB which makes them difficult to integrate within conventional processing devices[6]. This leads to unnecessary maintenance cost which is not desired by electronic industries[7]. However, sacrificing high melting soldering could be non-beneficial regarding formation of unreliable microstructure that consequently deteriorates the mechanical strength. Furthermore,

Received 2020-08-04.
* Corresponding author. E-mail: amaressinghgill@segi.edu.my.

mechanical properties of solder alloy could be a decisive factor as the shear strength is dependent on the solder joint which is a factor influenced by the melting temperature. Much research was performed to find a replacement for SnPb solder alloys by providing concise analysis using different solder alloys and the electronic industry still has concern on making the change. Solder alloys like Sn3.5Ag[8], Sn0.1Cu[9], and Sn9Zn[10] have been developed as potential candidates to replace the SnPb solder, but their properties negatively impact the soldering process[11]. For a solder to be applicable in the industry, it should have better or similar physical and mechanical properties corresponding to a eutectic SnPb solder. In other words, SnPb acts as a benchmark. Table 1 shows some detailed data for SnPb solder alloy. This research will provide a preliminary result based on shear strength, wettability, and melting properties of low temperature Sn58Bi soldered with Cu to form a soldered joint with low consumption of mass. The data obtained will reduce the research gap involving the study of low melting temperature solder alloys.

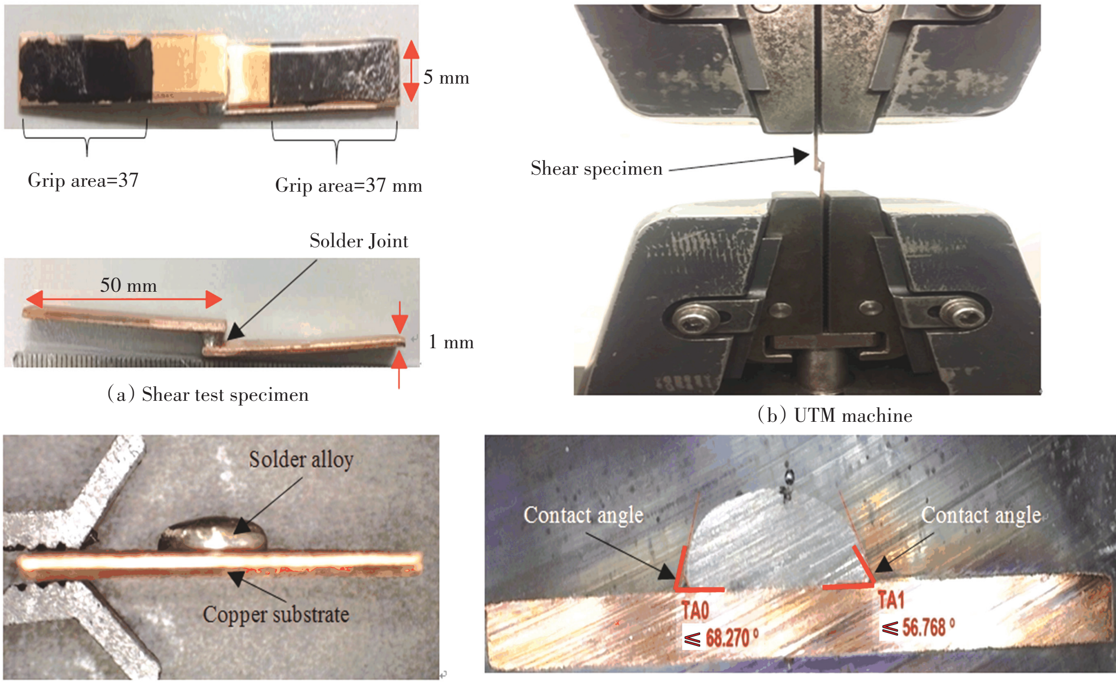
Table 1 Properties of Sn, Pb, and Sn37Pb[12-13]

Material Properties	Melting temperature(℃)	Surface tension (N/m)	Shear strength(MPa)	Tensile strength(MPa)	Elongation(%)
100Sn	232.0	0.545	27.57	21.5	<0.82
100Pb	327.5	0.435	13.79	17.3	55.00
Sn37Pb	183.0	0.490	23.79	27.5	40.00

1 Experimental Procedure

The raw materials of 99.9% Sn and 99.9% Bi (Alfa Aesar) were weighted by a total composition of 20 g to prepare the Sn58Bi (wt. %). Mass of 8.4 g and 11.6 g for Sn and Bi respectively was weighted according to the eutectic percentage. Both materials were mixed together and melted in a vacuum furnace at 600 ℃ for an hour of soaking time to ensure occurrence of homogeneous mixture. Subsequently, the mixture produced SnBi solder alloy and was let to solidify under room temperature. Melting temperature was analyzed by using differentials scanning calorimetry (DSC) with heat flow maintained at 20 ℃/min from 100 ℃ to 300 ℃. Nitrogen gas was used as the atmospheric medium for the tests in order to avoid contamination and external activity on the solder alloy during the process. The DSC curve is represented by the heat flow (y-axis) and temperature (x-axis) generated that relate to the energy released or absorbed at a certain temperature, which shows the melting properties of a solder alloy.

The SnBi solder alloy was made into a pellet shape of 5 mm × 1 mm. The dimensions of the pellets were kept small in order to comply with the miniaturization of devices. To investigate the contact angle and perform shear strength test, copper (Cu) substrates were used. The substrates were initially cleaned using ethanol and distilled water. The soldering of SnBi solder to Cu plates was done with the aid of ZnCl flux to reduce the oxidation. The soldering temperature was maintained at 170 ℃ and the time was set for 30 s to tally with the standard soldering procedure implemented in industry. The shear test specimens were prepared corresponding to the single shear lap joint method as shown in Fig.1(a) and was inserted inside a vacuum furnace for soldering process. This method allows proper soldering without exposing the specimen to the room atmosphere. After soldering, the samples were cleaned for 10 min using an ultrasonic machine with ethanol to remove dirt and debris. Five samples from each solder alloy were tested using the Universal Testing Machine (Instron 5582Q4970) as shown in Fig.1(b). In the analysis of the shear strength test, the maximum shear strength (MPa) and the maximum load (kN) at break were calculated to discuss the reliability of the solder joint. The crosshead speed of 1.3 mm/min was used to replicate the slow failure that usually occurs in the actual electronic assemblies. This is also the recommended speed by the ASTMD1002 standard. These mounted samples were cross-sectioned as shown in Fig.1(c) and the contact angles as shown in Fig.1(d) were measured using the VIS Pro software incorporated within the optical microscope.



(a) Shear test specimen

(b) UTM machine

(c) Wettability specimen

(d) Cross section of wettability specimen

Fig.1 Specimens for shear test and wettability test

2 Results and Discussion

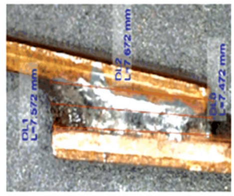
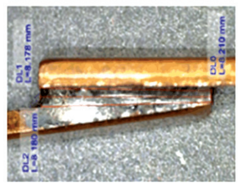
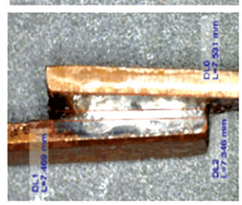
2.1 Shear Strength

The shear strengths of Sn58Bi are shown in Table 2, and the average soldered area is average length times width. The average shear strength was 23.4 MPa calculated from the three tested specimens. This shear strength is considered medium-to-high shear strength in electronic industry. The shear strength was calculated using the shear strength formula:

$$\tau = \frac{F}{A}$$

where F is the load at break point and A is the area of the joint. According to Ref. [14], a higher surface area per unit volume is needed to improve the overall performance of specimens in term of shear strength. The shear strengths of Sn90Pb and Sn37Pb are 20.24 MPa and 23.80 MPa, respectively. In another research, Sn9Zn solder joint shear strength was reported to be ranging from 26.0 MPa to 27.5 MPa[15], which falls in agreement with sample A of the shear specimen in this research. The average shear strength result in this research can be categorized as compatible with the Pb solder alloy and even with some other Pb-free solder alloys. The increment observed in shear strength values are due to the presence of Bismuth (Bi) that prevented the diffusion process between Sn and Cu thus forming thin Intermetallic Compound (IMC) layers[16]. Without presence of Bi, the vast diffusion of Sn toward Cu will produce thick IMC layers between solder and substrate, which subsequently leads to crack. The fracture surface of each samples was also observed as shown in Fig. 2. The fracture in sample A reveals brittle fracture morphology, whereas the fracture surface of the sample B and C showed a mixed brittle and ductile with presences of voids. This finding shows that IMC layer in between SnBi solder and Cu substrate was thin enough that the fracture surface was flat and even. Meanwhile, small voids were observed in both sample B and C, which clarifies that the gap or vacancy was left by the un-diffused Sn towards Cu because Bi was present. Such findings commonly exist in the joint between solder and substrate[17-18]. This research presents a novel idea on the types of fracture in the SnBi solder joint at lower soldering temperature. Furthermore, at low temperature, the reactivity of elements will be reduced to avoid enormous diffusion rate between Sn and Cu, and the clarification can be obtained with the aid of SnBi phase diagram[19].

Table 2 Shear strength test results

Sample	Average soldered area(mm^2)	Sample picture	UTS(MPa)	Load at break(N)	Shear strength (MPa)
Sample A	37.86		174.98	874.89	23.11
Sample B	40.95		205.91	1028.42	25.14
Sample C	37.24		164.05	820.27	22.03
Average values	38.68		181.60	907.80	23.40

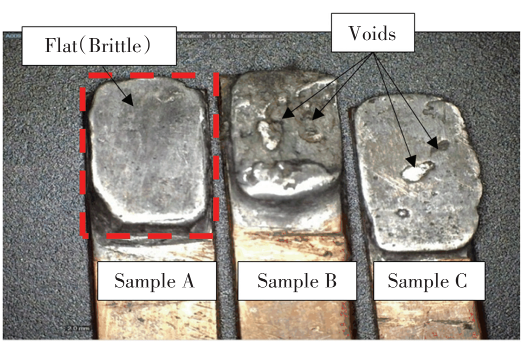


Fig.2 Fracture surface of all three shear specimens

2.2 Wettability

The contact angle was taken as a parameter to study the wettability of Sn58Bi solder on Cu substrate. Contact angle measurement is one of the factors that could be used to evaluate the wettability of a solder alloy apart from surface area, wetting time, wetting force, and surface tension. Based on three readings, an average contact angle of 32.4° was tabulated in Table 3. In Ref. [20], the contact angle of Sn3.0Ag0.7Cu on a bare Cu provided an average contact angle of 39°. In fact, many other studies show the range of contact angle is between 40° and 50°[7]. Low melting point of Sn58Bi in this study promoted easier melting of solder on the substrate, which provides wider spreading area and lower contact angle. Another reason for low contact angle is the presence of Bi that improves interfacial tension by reducing the surface tension. Similar statement was also made by Refs. [21-22]. By referencing various studies and literature, the range of a contact angle below 40° could be categorised as decent wettability properties. In addition, improvement of wetting properties will enhance the mechanical properties of this solder as well. Low contact angles will improve the shear strength capabilities of solder alloy by a huge margin, therefore the importance of obtaining low contact angle is crucial. This is reported in an early study done by Mei et al.[23] in 1996.

Table 3 Contact angle measurement of Sn58Bi solder

Readings	Contact angle (°)
1	32.4
2	32.2
3	32.7
Average	32.4

2.3 Thermal Properties

Another important property that should be thoroughly investigated is thermal properties of the Sn58Bi solder alloy. It is one of the main concern in this research as it focuses on obtaining solder alloys with low melting temperature. The thermal properties focus on three main aspects, i.e., melting (T_M), solidus (T_S), and liquidus temperature (T_L), and each represents its own definition. The peak temperature is the temperature when the solder is in mixture of solid and liquid phase (considered melting temperature), the solidus temperature is the point of temperature when the solder starts to melt, and the liquidus temperature is the point where the solder is in liquid form[24]. According to Ref. [25], low melting solder alloys are solder alloys with temperature less than 250 ℃.

The result in Fig. 3 shows an exothermic peak with temperature of T_M = 144.83 ℃, T_S = 142.30 ℃, and T_L = 146.35 ℃ respectively for Sn58Bi solder alloy. The result could be concluded that the melting temperature of Sn58Bi in this research is below the eutectic temperature 139 ℃[26]. Nevertheless, the material composition of 42 wt.% Sn and 58 wt.% Bi used in this research will correspond to phases of β-Sn and Bi at this melting point. This finding is important to show that Sn and Bi do not react with each other and are presented as discrete phases at this temperature. A similar finding was pointed out in the research of Ref. [27] with these two phases present. Meanwhile, the solidus and liquidus temperature are related to microstructure formation[28]. The difference between these two temperatures are called pasty range, T_R, where $T_R = T_L - T_S$ and was calculated to be 4.05 ℃. A narrow pasty range points out that the solidification occurs quickly which contributes to finer grain size formation[29-30]. In this research, it is predicted to provide similar beneficial impact to the grain refinement.

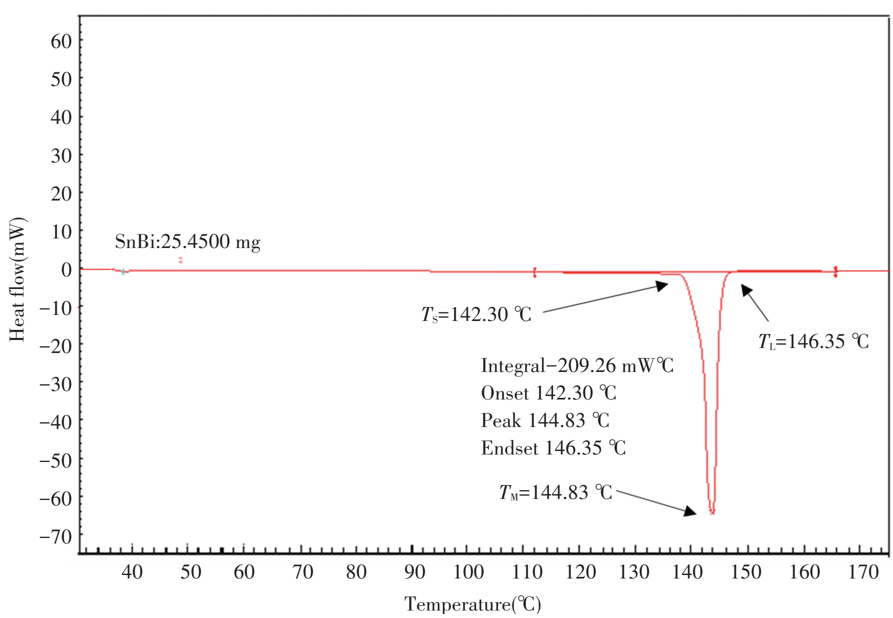


Fig.3 Thermal profile of Sn52Bi

3 Conclusions

This research provides a preliminary result comprising shear strength, wettability (contact angle), and thermal properties that were obtained by using low temperature Sn58Bi solder alloy. Important conclusions drawn from this research are as follows:

1) The Sn58Bi solder alloy possessed high shear strength averaging at 23.4 MPa, which well-matched that of the traditional Sn37Pb (23.8 MPa). The presence of Bi contributed to the high shear strength achieved.

2) Mixture of fracture morphology on the surface of sample B and C with voids suggests the fracture occurred at the IMC layer rather than at the solder side, contributing to the higher shear strength obtained.

3) Contact angle of 32.4° calculated by the solder joint falls in the category of low contact angle solders. This result is supported by high shear strength values. Presence of Bi are predicted to block a vast diffusion process between Sn and Cu that would have thicken the IMC layer and increased the contact angle.

4) Melting temperature of 144.83 ℃ confirms that the Sn58Bi is a low melting temperature solder. Accompanied with lower pasty range of 4.05 ℃, the prediction of finer microstructure could be made since the pasty range relates to the solidification of the grains within a soldered joint. Additionally, low temperature soldering can be done by using Sn58Bi solder alloy as the reflow temperature will be less than 200 ℃, which at the same time protects other components in the flip chip from damage.

Taking these results into consideration, the Sn58Bi solder alloy could be recommended as a potential replacement candidate or as an alternative in the electronics industries. However, further testing in real time application should be carried out to validate and justify the beneficial effect of the Sn58Bi solder alloy. Yet, this research points out that the initial results could be a guideline to be followed. This is important as the current electronic industry is advancing towards low melting point temperature application.

References

[1] Datta M. Manufacturing processes for fabrication of flip-chip micro-bumps used in microelectronic packaging: an overview. Journal of Micromanufacturing, 2020, 3(1): 69-83. DOI:10.1177/2516598419880124.

[2] Singh A, Durairaj R. Effect on the wettability, hardness and shear strength properties of 3%-nano Titanium Oxide (TiO_2) added Sn-3.8Ag- 0.7Cu (SAC)/Copper (Cu) solder joint. MATEC Web of Conferences, 2018, 237: 02013. DOI: 10.1051/matercconf/201823702013.

[3] Kotadia H R, Howes P D, Mannan S H. A review: on the development of low melting temperature Pb-free solders. Microelectronics Reliability, 2014, 54(6-7): 1253-1273. DOI: 10.1016/j.microrel.2014.02.025.

[4] Shen J, Chan Y C. Research advances in nano-composite solders. Microelectronics Reliability, 2009, 49(3): 223-234. DOI: 10.1016/j.microrel.2008.10.004.

[5] Cheng S F, Huang C M, Pecht M. A review of lead-free solders for electronics applications. Microelectronics Reliability, 2017, 75: 77-95. DOI: 10.1016/j.microrel.2017.06.016.

[6] Singh A, Mhd Noor E E. A study of temperature, microstructure and hardness properties of Sn-3.8Ag-0.7Cu (SAC) solder alloy. MATEC Web of Conferences, 2015, 27: 02003. DOI: 10.1051/matecconf/20152702003.

[7] Ren G, Wilding I J, Collins M N. Alloying influences on low melt temperature SnZn and SnBi solder alloys for electronic interconnections. Journal of Alloys and Compounds, 2016, 665: 251-260. DOI: 10.1016/j.jallcom.2016.01.006.

[8] Haseeb A S M A, Leong Y M, Arafat M M. In-situ alloying of Sne3.5Ag solder during reflow through Zn nanoparticle addition and its effects on interfacial intermetallic layers. Intermetallics, 2014, 54: 86-94. DOI: 10.1016/j.intermet.2014.05.011.

[9] Shang S Y, Wang Y F, Wang Y P, et al. Enhancement of hardness of bulk solder by doping Cu nanoparticles at the interface of Sn/Cu solder joint. Microelectronic Engineering, 2019, 208: 47-53. DOI: 10.1016/j.mee.2019.01.009.

[10] Zhang L, Cui J H, Han J G, et al. Microstructures and properties of SnZn-xEr lead-free solders. Journal of Rare Earths, 2012, 30(8): 790-793. DOI: 10.1016/S1002-0721(12)60131-8.

[11] Shalaby R M. Wettability and electrical properties of Bi-Sn based lead free solders alloys. International Journal of Physics and Research, 2013, 3(3): 1-6.

[12] Kar A, Ghosh M, Ghosh R N, et al. Evolution of mechanical and electrical properties of tin-lead and lead free solder to copper joint interface. Materials Letters, 2008, 62(1): 151-154. DOI: 10.1016/j.matlet.2007.04.116.

[13] Winstanley A. The Basic Soldering Guide. http://www.epemag.wimborne.co.uk/solderfaq.htm, 2020-10-20.

[14] Wei X F, Zhang Y K, Wang R C, et al. Microstructural evolution and shear strength of AuSn20/Ni single lap solder joints. Microelectronics Reliability, 2013, 53(5): 748-754. DOI: 10.1016/j.microrel.2013.01.005.

[15] Affendy M G, Yahaya M Z, Mohamad A A. Corrosion of Sn-9Zn solder joints: a review. International Journal Electroactive Material, 2014, 2: 8-16.

[16] Gu Y, Zhao X C, Li Y, et al. Effect of nano-Fe_2O_3 additions on wettability and interfacial intermetallic growth of low-Ag content Sn-Ag-Cu solders on Cu substrates. Journal of Alloys and Compounds, 2015, 627: 39-47. DOI: 10.1016/j.jallcom.2014.12.024.

[17] Sujan G K, Haseeb A S M A, Nishikawa H, et al. Interfacial reaction, ball shear strength and fracture surface analysis of lead-free solder joints prepared using cobalt nanoparticle doped flux. Journal of Alloys and Compounds, 2017, 695: 981-990. DOI: 10.1016/j.jallcom.2016.10.219.

[18] Ma Y, Li X Z, Yang L Z, et al. Effects of graphene nanosheets addition on microstructure and mechanical properties of SnBi solder alloys during solid state aging. Materials Science & Engineering A, 2017, 696: 437-444. DOI: 10.1016/j.msea.2017.04.105.

[19] Hu F Q, Zhang Q K, Jiang J J, et al. Influences of Ag addition to Sn-58Bi solder on SnBi/Cu interfacial reaction. Materials Letters, 2018, 214: 142-145. DOI: 10.1016/j.matlet.2017.11.127.

[20] Takyi G, Bernasko P K. Investigation of wettability of lead free-solder on bare copper and organic solder preservatives surface finishes. International Journal of

Materials Science and Applications, 2015, 4(3): 165-172. DOI: 10.11648/j.ijmsa.20150403.14.

[21] Mhd Noor E E, Mhd Nasir N F. A review: lead free solder and its wettability properties. Soldering and Surface Mount Technology, 2016, 28(3): 125-132. DOI: 10.1108/SSMT-08-2015-0022.

[22] Singh A, Durairaj R, Mhd Noor E E, et al. Reliability study of lead free Sn-3.8Ag-0.7Cu and copper (Cu) substrate based on the microstructure, physical and mechanical properties. Journal of Mechanical Engineering, 2018, 5(2): 169-180.

[23] Mei Z, Holder H A, Vander Plas H A. Low-temperature solders. Hewlett-Packard Journal, 1996, 47(4): 91-98.

[24] Mhd Noor E E, Singh A. Review on the effect of alloying element and nanoparticle additions on the properties of Sn-Ag-Cu solder alloys. Soldering & Surface Mount Technology, 2014, 26(3): 147-161. DOI: 10.1108/SSMT-02-2014-0001.

[25] Yang T L, Wu J Y, Li CC, et al. Low temperature bonding for high temperature applications by using SnBi solders. Journal of Alloys and Compounds, 2015, 647: 681-685. DOI: 10.1016/j.jallcom.2015.05.249.

[26] Ma D L, Wu P. Effects of Zn addition on mechanical properties of eutectic Sn-58Bi solder during liquid-state aging. Transaction of Nonferrous Metal Society of China, 2015, 25(4): 1225-1233. DOI: 10.1016/S1003-6326(15)63719-0.

[27] Ma Y, Li X Z, Zhou W, et al. Reinforcement of graphene nanosheets on the microstructure and properties of Sn58Bi lead-free solder. Materials & Design, 2017, 113(5): 264-272. DOI: 10.1016/j.matdes.2016.10.034.

[28] Mhd Noor E E, Singh A, Chuan Y T. A review: influence of nano particles reinforced on solder alloy. Soldering & Surface Mount Technology, 2013, 25(4): 229-241. DOI: 10.1108/SSMT-11-2012-0026.

[29] Park B G, Myung W R, Lee C J, et al. Mechanical, electrical, and thermal reliability of Sn-58 wt.%Bi solder joints with Ag-decorated MWCNT for LED package component during aging treatment. Composites Part B, 2020, 182: 107617. DOI: 10.1016/j.compositesb.2019.107617.

[30] Shen L, Foo A Q, Wang S, et al. Enhancing creep resistance of SnBi solder alloy with non-reactive nano fillers: a study using nanoindentation. Journal of Alloys and Compounds, 2017, 729: 498-506. DOI: 10.1016/j.jallcom.2017.09.177.