

Thermophysical Properties of Sn–Ag–Cu Based Pb-Free Solders

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Abstract Lead–tin (Pb–Sn) alloys are the dominant solders used for electronic packaging because of their low cost and superior properties required for interconnecting electronic components. However, increasing environmental and health concerns over the toxicity of lead, combined with global legislation to limit the use of Pb in manufactured products, have led to extensive research and development studies of lead-free solders. The Sn–Ag–Cu ternary eutectic alloy is considered to be one of the promising alternatives. Except for thermal properties, much research on several properties of Sn–Ag–Cu alloy has been performed. In this study, five Sn– x Ag–0.5Cu alloys with variations of Ag content x of 1.0 mass%, 2.5 mass%, 3.0 mass%, 3.5 mass%, and 4.0 mass% were prepared, and their thermal diffusivity and specific heat were measured from room temperature to 150 °C, and the thermal conductivity was calculated using the measured thermal diffusivity, specific heat, and density values. Also, the linear thermal expansion was measured from room temperature to 170 °C. The results show that Sn–3.5Ag–0.5Cu is the best candidate because it has a maximum thermal

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conductivity and a low thermal expansion, which are the ideal conditions to be a proper packaging alloy for effective cooling and thermostability.

Keywords Coefficient of thermal expansion · Lead-free solder · Thermal conductivity · Thermophysical property

1 Introduction

Lead–tin (Pb–Sn) base solders have long been the most popular materials for electronic packaging, because of their low cost and superior properties required for interconnecting electronic components. However, the toxic nature of the lead and the increasing awareness of the adverse effect on the environment and health have given rise to the pressing need for development of lead-free solders in recent years [1]. Research efforts have been successful to identify several candidates (such as Sn–Bi, Sn–In, Sn–Zn, Sn–Ag, Sn–Ag–Cu, and Sn–Cu) to replace the conventional Sn–Pb solder. Among them, the most promising one is undoubtedly the Sn–Ag–Cu ternary alloy, which has advantages of good wetting property, superior interfacial properties, high creep resistance, low coarsening rate, and so on [2]. Recently, much research about the effect of the Ag content on several properties except thermal properties for a fixed Cu content in the Sn–Ag–Cu alloy have been performed [3–6].

In this study, five Sn–Ag–Cu alloys with variations of Ag content (Sn–1.0Ag–0.5Cu, Sn–2.5Ag–0.5Cu, Sn–3.0Ag–0.5Cu, Sn–3.5Ag–0.5Cu, and Sn–4.0Ag–0.5Cu) were prepared and their thermal diffusivity and specific heat were measured from room temperature to 150 °C, and the thermal conductivity was calculated using the experimentally obtained thermal diffusivity, specific heat, and density data. Also, the thermal expansion was measured from room temperature to 170 °C.

2 Experiments

2.1 Sample Preparation

Sn– x Ag–0.5Cu ternary alloys with x mass% of Ag content were made by weighing fractions of pure Ag (99.99 mass%), Sn (99.999 mass%), and Cu (99.99 mass%) according to the formation of the alloys in evacuated transparent quartz capsules at 300 °C for 2 h. To make the solder bar, the melted alloy is put in an aluminum mold with a diameter and length of 11.5 mm and 60 mm, respectively, for allowance of shrinkage and machining of 10 mm diameter samples. To prevent blind shrinkage and surface distortion caused by sudden cooling, the mold is preheated at 200 °C before casting. The molded solder bar is cut into disks with a thickness of 2 mm. Table 1 shows the compositions of the prepared samples along with the measured densities and melting temperatures.

Table 1 Compositions of five samples along with measured densities and melting temperatures

No.	Composition (mass%)	Density ($10^3 \text{ kg} \cdot \text{m}^{-3}$)	Melting temperature ($^{\circ}\text{C}$)
1	Sn–1.0Ag–0.5Cu	7.329	220.63
2	Sn–2.5Ag–0.5Cu	7.351	220.23
3	Sn–3.0Ag–0.5Cu	7.357	220.94
4	Sn–3.5Ag–0.5Cu	7.379	221.85
5	Sn–4.0Ag–0.5Cu	7.397	226.11

2.2 Thermal-Diffusivity Measurements

The thermal diffusivity (a) was measured by the laser flash method [7] over a temperature range from room temperature to 150°C using a laboratory-made laser flash apparatus. The thermal diffusivity is determined by measuring the half time, which is the time that the temperature of the rear surface of the sample increases to half of its maximum temperature rise. A HgCdTe infrared detector senses the temperature rise of the sample. The sample is located at the center of a cylindrical heater made of molybdenum foil in a vacuum atmosphere. To stabilize the absorption of the incident energy, graphite is sprayed on the surface of the sample. The experimental data for thermal diffusivity were corrected for the pulse width effect by the method of Azumi and Takahashi [8]. The thermal-diffusivity data were obtained from the average of five measurements, and the standard deviation in the measurements of thermal diffusivity is estimated to be 5%.

2.3 Specific-Heat-Capacity Measurements

The specific heat capacity (C_p) was measured by using differential scanning calorimetry (DSC) using Perkin–Elmer Pyris 1 over a temperature range of room temperature to 150°C . The measurements were carried out at a heating rate of $5 \text{ K} \cdot \text{min}^{-1}$ in a nitrogen atmosphere with a flow rate of $30 \text{ ml} \cdot \text{min}^{-1}$. The specific heat capacity was determined by using NIST synthetic sapphire, SRM 720 as a reference material. The standard deviation in the measurement of specific heat capacity is estimated to be 2% [7].

2.4 Calculation of the Thermal Conductivity

The thermal conductivity of the samples can be directly calculated from the following equation,

$$\lambda = \rho a C_p, \quad (1)$$

where ρ is the bulk density ($\text{kg} \cdot \text{m}^{-3}$), a is the thermal diffusivity ($\text{m}^2 \cdot \text{s}^{-1}$), C_p is the specific heat capacity ($\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$), and λ is the thermal conductivity ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$).

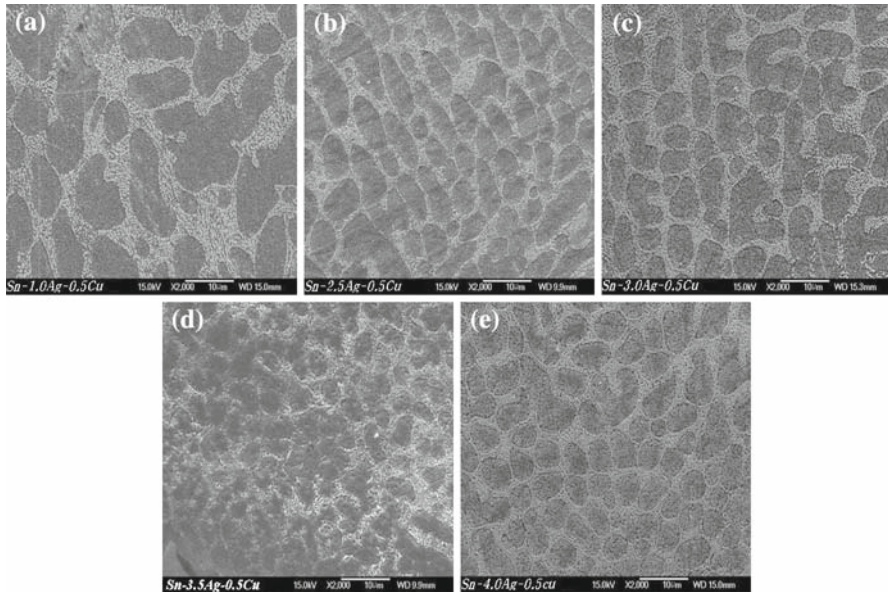


Fig. 1 Micro-photograph of the prepared Sn–Ag–Cu alloy samples. (a) Sn–1.0Ag–0.5Cu; (b) Sn–2.5Ag–0.5Cu; (c) Sn–3.0Ag–0.5Cu; (d) Sn–3.5Ag–0.5Cu; and (e) Sn–4.0Ag–0.5Cu

2.5 Measurement of Thermal Expansion

The thermal expansions of the samples were measured in the axial direction with a linear variable differential transformer (LVDT) transducer over a temperature range of room temperature to 150 °C by a push-rod-type dilatometer (DIL 402C, Netzsch) [9]. The measurements were carried out with a constant heating rate of 5 K · min^{−1} in vacuum. The maximum error of the dilatometer used in our experiment is within 2 % for a standard material of Al₂O₃.

3 Results and Discussion

The density and melting temperature shown in Table 1 were measured using the Archimedes method and DSC, respectively. As the Ag content increases, the density increases monotonically because the density of Ag is larger than Sn; however, the melting temperature does not decrease although Ag has a lower melting temperature than Sn [10].

The microstructures of the samples have apparently coarse β -Sn grains as shown in Fig. 1. The dark regions are β -Sn grains, and as the content of Ag increases from 1.0 mass% to 3.5 mass%, the average grain size decreases from 15 μ m to 4 μ m; however, when the content of Ag is 4.0 mass%, it becomes 6 μ m. The energy dispersive X-ray (EDX) analysis shows that the light area between β -Sn and the edge are Ag₃Sn precipitates, and these particles are uniform and much finer.

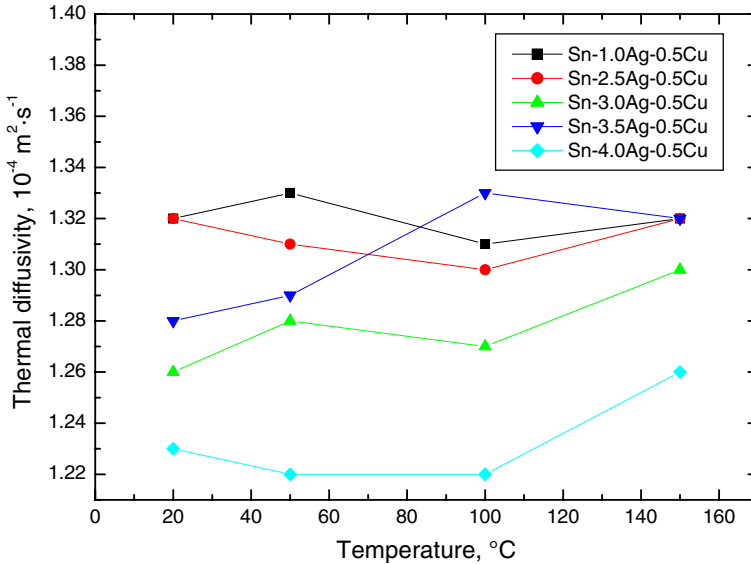


Fig. 2 Experimental thermal diffusivity of Sn–Ag–Cu alloy samples obtained by laser flash apparatus

The measured thermal diffusivities for five samples are shown in Fig. 2, and all the data points are averages of five measurements. It shows that the thermal diffusivities of all samples slightly change depend on the increment of sample temperature. Also, it shows that as the content of Ag increases, the thermal diffusivity decreases except for the case of 3.5 mass% Ag. This can be qualitatively explained by the abnormal disorder of the β -Sn grains and Ag_3Sn precipitates as shown in Fig. 1d; however, to explain quantitatively, additional experiments to compare the thermal diffusivities of different grains and the changes of microstructure with the increment of temperature need to be performed.

The obtained average specific-heat-capacities are shown in Fig. 3. As the temperature rises, the values of the specific-heat capacities increase and become constant above 140 °C. With an increase in the Ag content, the specific-heat capacity increases and becomes a maximum at 3.5 mass% Ag, and after that, slightly decreases. This can be also expected to be explained by the microstructure of the sample at 3.5 mass% Ag.

The thermal conductivities of the samples were calculated by using Eq. 1 and are shown in Fig. 4. As the temperature rises, all the samples show increasing thermal conductivities because the thermal carriers are electrons in the alloy and the electrons are more activated as the temperature increases. The thermal conductivities of the Sn–3.5Ag–0.5Cu sample show maximum values at all temperatures, and this means that this sample is the most appropriate packaging alloy for effective cooling of the electronic components or devices.

As shown in Figs. 2 and 4, for the small variation of Ag content from $x = 3.5$ to 4.0, there were rapid decreases of the thermal diffusivity and thermal conductivity.

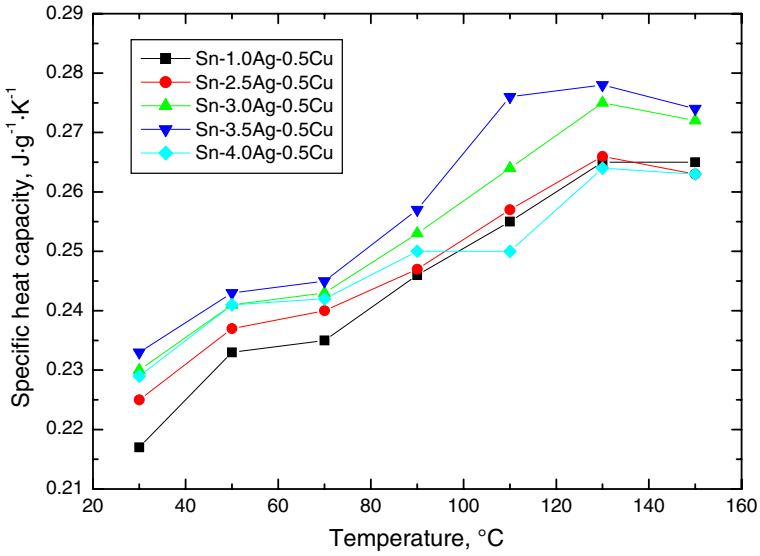


Fig. 3 Experimental specific-heat-capacity of Sn–Ag–Cu alloy samples obtained by DSC

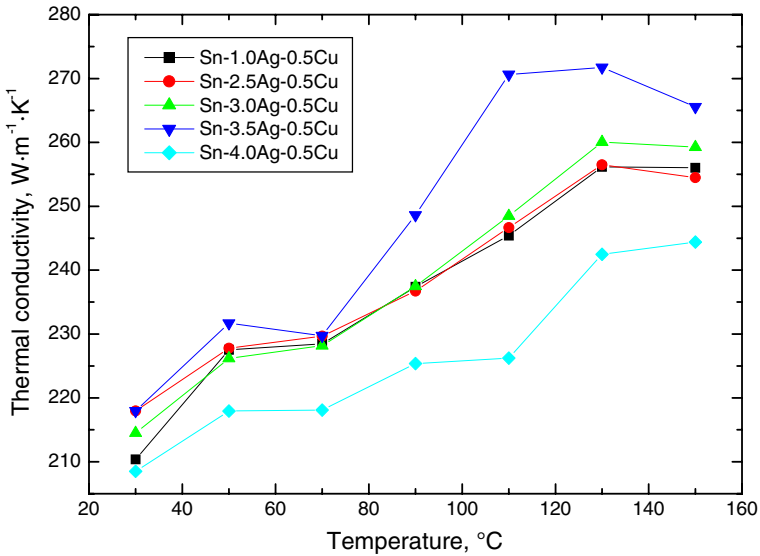


Fig. 4 Thermal diffusivity of Sn–Ag–Cu alloy samples obtained by Eq. 1

To investigate whether this instability is the inherent property of the alloy or caused by the errors introduced by the triple measurements of thermal diffusivity, specific heat, and density, the thermal conductivity must be measured directly.

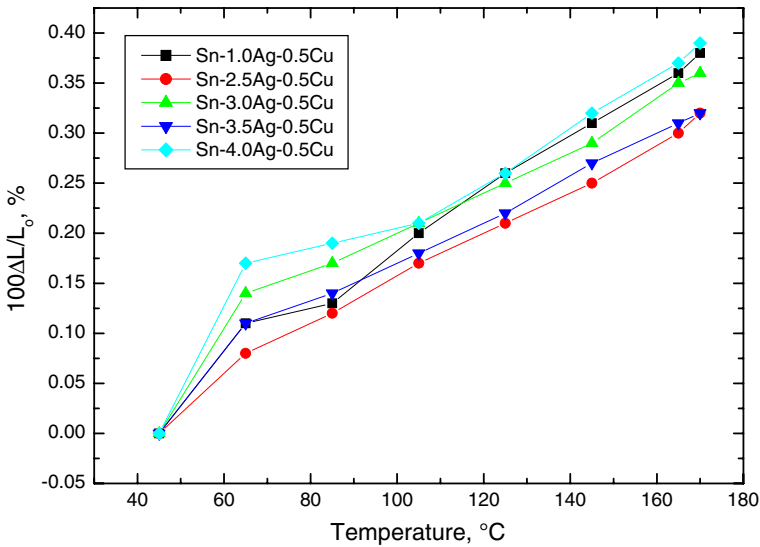


Fig. 5 Linear thermal expansion of Sn–Ag–Cu alloy samples obtained by LVDT

The linear thermal expansion which represents the ratio of the length change to the initial length can be calculated using the following expression [9]:

$$\text{Expansion, } 100 \frac{\Delta L}{L_0} = \frac{L_T - L_{298}}{L_{298}} \times 100(\%), \quad (2)$$

where L_T and L_{298} represent the lengths of the samples at temperature T and at 298 K, respectively. The linear thermal expansions of the samples are plotted against temperature in Fig. 5. From the figure, it is observed that the linear thermal expansions of all the samples increase progressively with temperature and also increase qualitatively with the added increment of Ag content. The thermal expansions of Sn–3.5Ag–0.5Cu are lower than the others except for the case of Sn–2.5Ag–0.5Cu.

The corresponding instantaneous coefficient of thermal expansion (CTE), α , is defined by the following expression [9]:

$$\alpha = \frac{1}{L_{298}} \frac{\Delta L}{\Delta T}. \quad (3)$$

The instantaneous CTE of the samples are plotted against temperature in Fig. 6. From the figure it is observed that when the temperature is higher than 70 °C, the variations of CTE for the cases of (2.5 mass%, 3 mass%, and 3.5 mass%) Ag are relatively small compared to those for (1.0 mass% and 4.0 mass%) Ag. This means that the former samples are more thermally stable than the latter samples at high temperatures.

There were rapid changes of all the data for the small variations of Ag content as shown above.

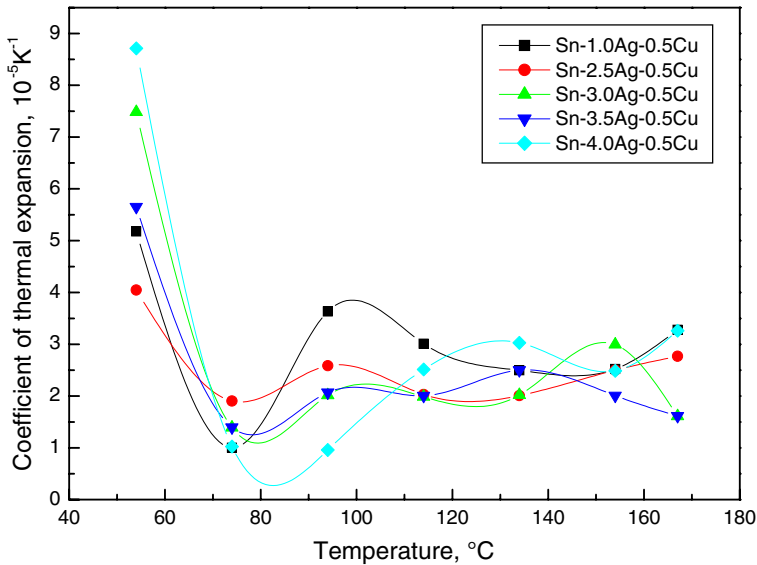


Fig. 6 Instantaneous CTE of Sn–Ag–Cu alloy samples

4 Conclusion

The thermophysical properties of Sn–Ag–Cu-based lead-free ternary eutectic alloys, with variations of Ag content of 1.0 mass%, 2.5 mass%, 3 mass%, 3.5 mass%, and 4 mass%, were measured from room temperature to about 150 °C, and Sn–3.5Ag–Cu is the most appropriate composition for the packaging material, because it has the largest thermal conductivity for effective cooling of electronic devices and has the smaller CTE for greater thermostability at high temperatures.

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References

1. I. Ohnuma, M. Miyashita, K. Anzai, X.J. Liu, H. Ohtani, R. Kainuma, K. Ishida, *J. Electron. Mater.* **29**, 1137 (2000)
2. J.W. Yoon, S.B. Jung, *J. Alloys Compd.* **458**, 200 (2008)
3. K. Sukanuma, *Curr. Opin. Solid State Mater. Sci.* **5**, 55 (2001)
4. I.E. Anderson, B.A. Cook, J. Haringa, R.L. Terpstra, *J. Electron. Mater.* **31**, 1166 (2002)
5. L. Snugovsky, P. Snugovsky, D.D. Perovic, T. Sack, J.W. Rutter, *Mater. Sci. Technol.* **21**, 53 (2005)
6. H.W. Chiang, K. Chang, J.Y. Chen, *J. Electron. Mater.* **35**, 2074 (2006)
7. S.H. Lee, J.C. Kim, J.M. Park, C.K. Kim, S.W. Kim, *Int. J. Thermophys.* **24**, 1355 (2003)
8. T. Azumi, Y. Takahashi, *Rev. Sci. Instrum.* **52**, 1411 (1981)
9. K.H. Kang, K.C. Song, M.S. Yang, *Int. J. Thermophys.* **24**, 1373 (2003)
10. D.R. Lide, *CRC Handbook of Chemistry and Physics*, 73rd edn. (CRC Press, Boca Raton, FL, 1994)