Influence of Tin addition on the Microstructure, Melt Properties and Mechanical Properties of Ag-Cu-Zn-Sn Braze Filler

Thanut Jintakosol and Walaikorn Nitayaphat

Abstract—**The influence of Sn addition on the microstructure, melt properties and mechanical properties of Ag-Cu-Zn-Sn braze filler were investigated in this study. Microstructural analysis reveal that increase of Sn content with increased the eutectic phase and promote the formation of Cu_3Sn intermetallic compound. The differential thermal analysis show that increase of Sn content dramatically decrease the melting temperature of the Ag-40Cu-1Zn-7Sn braze filler are <700 °C. The tensile strength and elongation of brazing joint was improved by increasing Sn content in braze filler.**

Index Terms—**Ag-Cu-Zn-Sn braze filler, brazing, melt properties, microstructure, mechanical properties.**

I. Introduction

Silver based braze filler are well known as the material of choice for joining alloys, ferrous and non-ferrous metals [1], ceramics [2] and ceramics to metals [3], [4] due to their high strength, excellent ductility, electrical and thermal conductivity, and oxidation resistance. In the silver based braze filler system, the alloys based on Ag–Cu–Zn–Cd system are brazing filler alloys widely used in aerospace, power electronics, and household appliance industries [5]. The addition of cadmium to silver–copper–zinc system reduces the solidus temperature and the melting range, reduces silver content and improves the fluidity of the alloys [6]. However, significant amount of silver are lost in the effluents discharged from such industries and due to the toxicity of Cd to living organisms, utilizations of braze filler containing Cd are in process of being limited. Therefore, a large quantity of work has been made to improve the combination properties of the Cd-free silver based braze filler of which Ca [7], Ce [8], La [9] Ga, Ni, and Sn [10] were reported to positively affect the properties of silver based braze filler. Sn has a relatively low melting point of 231.9 ℃, and a high boiling point of 2603 ℃. Moreover, Tin is not easily oxidized and resists corrosion because it is protected by an oxide film. Tin resists corrosion from distilled sea and soft tap water, and can be attacked by strong acids, alkalis and acid salts [11]. Due to its specific physical and chemical properties, Sn is added to adjust the eutectic point of Cd-free silver based filler metals [12], [13]. However, there are no studies exploring the potentiality of addition of Sn in the Cd-free silver based braze filler and using it for jewelry industry.

In this study, the brazing of sterling silver using braze filler based on Ag–Cu–Zn–Sn system were studied. The effect of Sn on the microstructure, mechanical and melt properties of Ag–Cu–Zn–Sn braze filler was examined.

II. Experiments

The Ag-Cu-Zn-Sn braze filler were prepared by cast ingot using frequency induction furnace (SEIT, elettronica). Pure materials (ingot of 99% Ag, powder of 99% Cu, 99.99% Zn and 99.5% Sn) were mixed in the crucibles, then they were melted at 1,000 °C under argon atmosphere for 15 min and cooling in induction furnace to produce Ag-40Cu-1Zn-*x*Sn (*x*=3, 5, 7). The composition of cast ingots were analyzed by X-ray Fluorescence (XRF) are shown in Table I. The weight loss were measured to be <1 wt% after melting. All the cast ingots were hard drawn into wires with a diameter of 0.5 mm. For brazing test were performed on sterling silver (92.5%Ag, 7.5%Cu) substrates, 0.5 mm wide, 1.25 mm long and 0.5 mm thick. Before brazing, the brazing surface of the base metal were polishing with 600 grit SiC paper, and then ultrasonically cleaned in an acetone bath. The brazing experiment in this study were used flame of the mixing between oxygen and liquid propane gas. After joining process, the cross section of brazed joint were prepared by standard polishing technique and subsequently etch with 5% HNO_3. The morphology and microstructure of brazing joint were characterization by scanning electron microscopy (SEM, model: VEGA3-LM, TESCAN) in back scattered electron (BSE) mode. Qualitative phase identification was conducted by using energy dispersive spectroscopy (EDS). The phase composition of braze fillers were analyzed using X-ray diffraction (XRD, Bruker: D8) analyzer. The solidus temperature (T_S) and liquidus temperature (T_L) of these Ag-Cu-Zn-Sn braze filler were determined using Differential Thermal Analysis (DTA, NETZSCH STA449C) under nitrogen atmosphere with heating at a 20 °C/min. Hardness test were measured used Micro Vickers Hardness (HV) with a load of 980.7 mN for 30 s indenting time. Tensile test were performed at constant loading rate of 10 N/mm by universal testing machine according to the ISO: 6892 are shown in Fig. 1. To ensure the accurate of result, three specimens were brazed with the same filler metal and in same condition.

Manuscript received October 31, 2017; revised January 16, 2018. This work was financially supported by the Srinakharinwirot University.

Thanut Jintakosol is with the Department of General Science, Faculty of Science, Srinakharinwirot University, Bangkok, 10110, Thailand (e-mail: thanut@g.swu.ac.th).

doi: 10.18178/ijmmm.2018.6.4.394

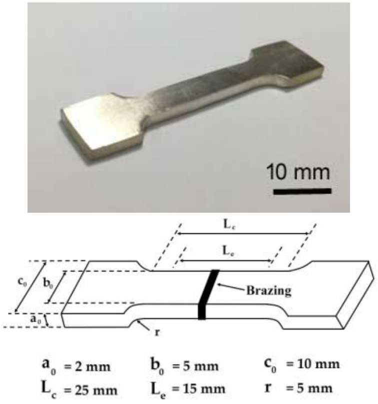

Fig. 1. Image of sterling silver sample for tensile test.

III. Result and Discussions

The experiment result showed that the solidus and liquid temperature of Ag-Cu-Zn-Sn braze filler depend on Sn contents. Fig. 2 shows the differential thermal analysis curves of the various braze filler specimens and the solidus and liquid temperature. The solidus temperature (T_S), liquidus temperature (T_L) and melting range ($\Delta T = T_L - T_S$) of these braze filler were calculated and presented in Table II. It can be seen that the increase Sn content of braze filler from 3 to 7 wt%, the solidus and liquidus temperature decrease from 750 to 700 ^oC and 802 to 752.1 ^oC, respectively. The increasing Sn content, the solidus and liquidus temperature of braze filler decrease 50 ^oC obviously, which could be explained in terms of increased low melting point Sn dissolved in Ag-Cu alloy.

TABLE I: The Composition of Braze Filler (Weight %)

Alloy	Ag	Cu	Zn	Sn
Ag-40Cu-1Zn-3Sn	55.55	39.76	1.5	3.19
Ag-40Cu-1Zn-5Sn	54.92	38.77	1.21	5.1
Ag-40Cu-1Zn-7Sn	55.21	36.67	0.88	7.23

The BSE image of microstructure of Ag-Cu-Zn-Sn braze filler are shown in Fig. 3. The microstructure have shown white α-Ag, black α-Cu solid solution and eutectic structure content Ag, Cu, AgCu and CuSn compound. As the Sn content of Ag-Cu-Zn-Sn braze filler was increased to 7 %wt, the quantity of α-Ag and α-Cu solid solution decrease while that eutectic structure increase, shown in Fig. 3c.

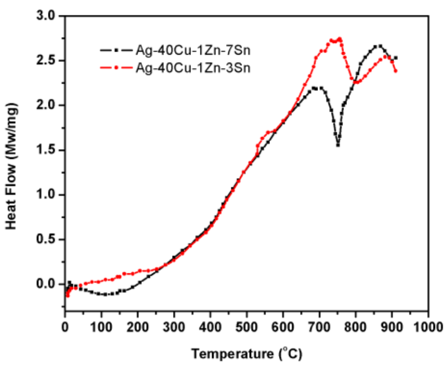

Fig. 2. DTA curve of Ag-Cu-Zn-Sn braze filler.

TABLE II: The Melting Temperature of Braze Filler

Alloy	T_S (^oC)	T_L (^oC)	ΔT (^oC)
Ag-40Cu-1Zn-3Sn	750	802	52
Ag-40Cu-1Zn-7Sn	700	752.1	52.1

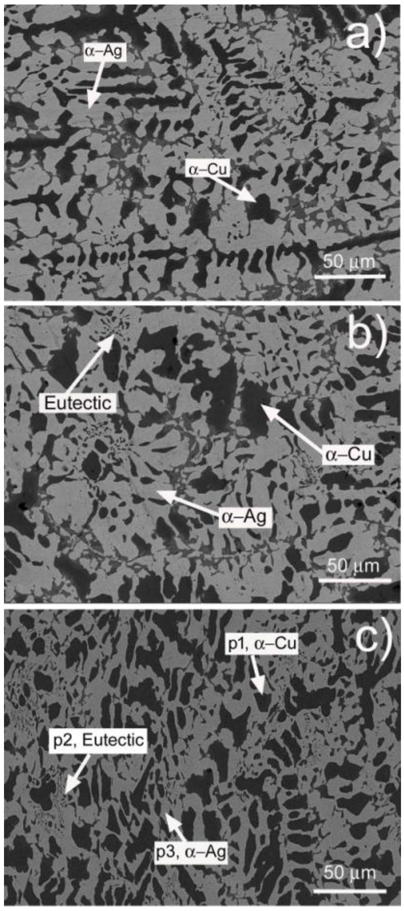

Fig. 3. BSE image of braze filler microstructure: a) Ag-40Cu-1Zn-3Sn, b) Ag-40Cu-1Zn-5Sn and c). Ag-40Cu-1Zn-7Sn.

TABLE III: The Measured Chemical Composition in Braze Filler by EDS (Atomic %)

Element	Point 1 Cu	Point 2 Cu_3Sn	Point 3 Ag
Cu	92.54	69.54	18.02
Zn	3.12	3.37	1.05
Ag	3.20	3.79	76.00
Sn	1.14	23.30	4.04

The composition of Ag-Cu-Zn-Sn braze filler was determined by EDS analysis are shown in Fig. 4. The EDS results of Point 1, Point 2 and Point 3 were analyzed using the point-scanning mode as shown in Fig. 3c and the chemical compositions in braze filler are shown in Table III. According to the above testing results and the Sn-Cu phase diagram, the braze filler in Point 2 were considered to be Cu_3Sn owing to the ratio of Cu and Sn nearly 3:1, while braze filler in Point 1 and Point 3 are considered to Cu and Ag owing respective, which was consistent with the results of the BSE image and DTA (Fig. 2), the melting temperature of braze filler decrease with the increase in Sn content of braze filler. Because the melting temperature of α-Ag and α-Cu solid solution were higher than of Cu_3Sn phase, the quantity of Cu_3Sn phase was increased at the lower melting temperature of Ag-Cu-Zn-Sn braze filler.

Fig. 5 shows the XRD patterns of Ag-Cu-Zn-Sn braze filler. It shows that Ag, Cu and a small amount of Cu_3Sn phase in the Ag-Cu-Zn-Sn braze filler. However, the excessive addition of Sn will increase the brittleness of Ag–Cu–Zn–Sn braze filler owing to the formation of Cu_3Sn brittle compounds, which needs to be on the alert.

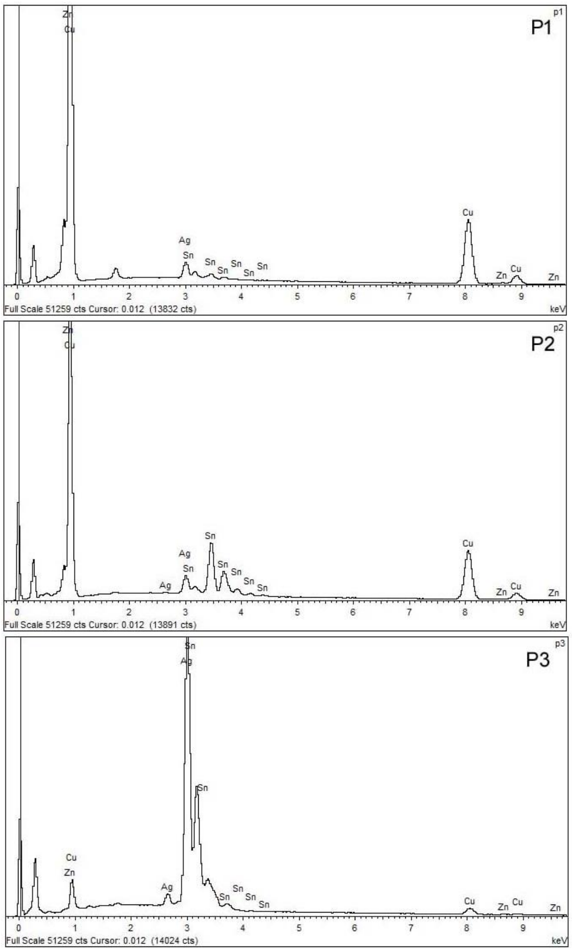

Fig. 4. EDS analysis of Ag-40Cu-1Zn-7Sn braze filler to differentiate the distribution of phase and correspond with Fig. 3 c).

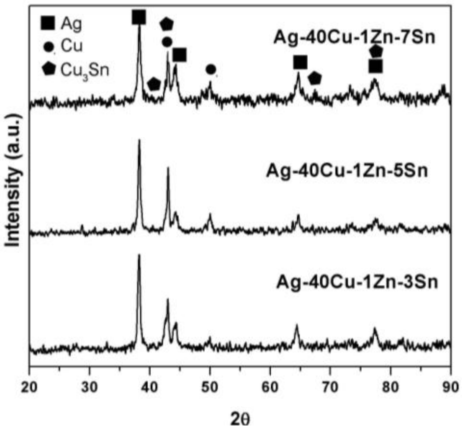

Fig. 5. XRD of Ag-Cu-Zn-Sn braze filler.

Fig. 6 demonstrates the BSE image of silver joint using Ag-40Cu1-Zn-7Sn braze filler. It can be seen that the braze filler exhibits good wettability on sterling silver substrate. The bonding interface were smooth and compact, and no voids appear at the interface and brazing seam. The microstructure of braze filler have shown Ag, Cu phase and Cu_3Sn brittle compound form at grain boundary and sub boundary.

The mechanical properties of sterling silver brazing joint using Ag-Cu-Zn-Sn braze filler is shown in Fig. 7. The tensile test was performed at room temperature with a constant loading rate 10 N/mm. From the result, it was found that with the Sn content increasing from 3 to 7 wt%, the tensile strength increases dramatically from 186.45 MPa to 214.02 MPa. The tensile strength can be explained by dispersion strengthening mechanism. It is known that the brittle Cu_3Sn phase within microstructure of braze filler have a significant strengthening effect when the tensile deformation was controlled by dispersion strengthening mechanism. Therefore, it was expected that the Cu_3Sn phase has the main contributor to the strength of braze filler. Hence, the dislocations cannot find their suitable direction to move freely and thus, piles up at the interfaces to increase the tensile strength of braze filler. As shown in Table IV, the Sn content is up to 7 wt%, the elongation was increased, probably caused by coarsening of Cu_3Sn eutectic, and enhancement effect of grain boundary and sub boundary of braze filler result in Fig. 6.

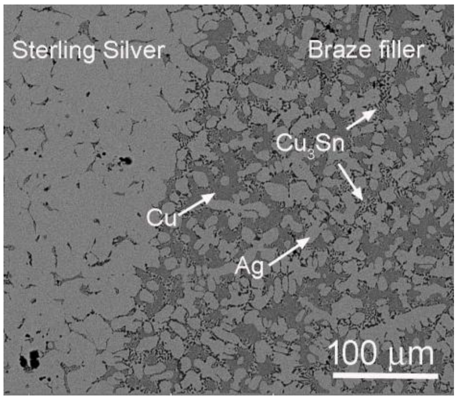

Fig. 6. BSE image of brazing joint layer between the Ag-40Cu1-Zn-7Sn braze filler and sterling silver substrate.

The Vickers microhardness testing is shown in Table IV. It can be seen from the results that the microhardness of brazed joint increased from 102 to 122 HV with Sn content increasing from 3% to 7 %. Zhang [14] found that the hardness of Cu-based solid solution is higher than that of Ag-based solid solution and most of Sn preferred to form solid solution with Cu. Thus, the microhardness of the joint increased with increase of Sn content in the braze filler. The effect of heat affect zone (HAZ) on the microhardness of samples are shown in Fig. 8. The hardness of brazing seam was higher than sterling silver substrate.

TABLE IV: THE MECHANICAL PROPERTIES OF STERLING SILVER BRAZING JOINT

Sample	Ultimate Tensile Strength (MPa.)	Elongation (%)	Micro Vickers Hardness (HV)
Ag-40Cu-1Zn-3Sn	186.45	62	102
Ag-40Cu-1Zn-5Sn	189..33	80	108
Ag-40Cu-1Zn-7Sn	214.02	81	122

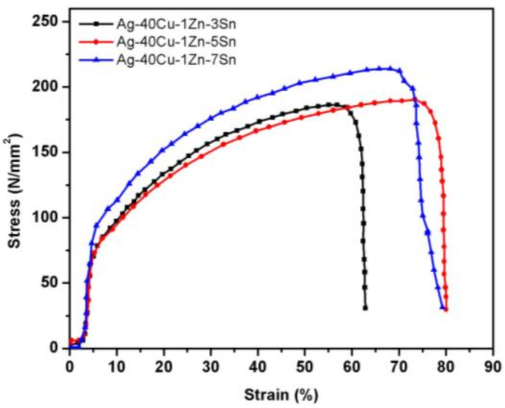

Fig. 7. Tensile curves of sterling silver brazing joint using Ag-Cu-Zn-Sn braze filler.

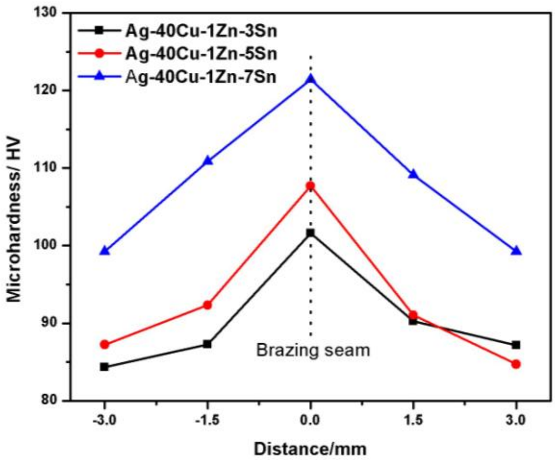

Fig. 8. Distribution of the microhardness in the sterling silver/Ag-Cu-Zn-Sn braze filler joint.

IV. Conclusion

The effect of Sn addition on the microstructure, thermal and mechanical properties of Ag-Cu-Zn-Sn braze filler were investigated. Sn addition is established to control the melt temperature of braze filler. The melt temperature is decreased below 700 ^{o}C, when increased Sn content of 7 wt%. The microstructure of braze filler mainly consist eutectic structure, α-Ag, α-Cu solid solution and Cu_3Sn intermetallic compound. The tensile strength, microhardness and elongation are increased with increase Sn content. The brazing of sterling silver was successfully achieved using Ag-Cu-Zn-Sn braze filler.

References

[1] T. Luo, Z. Chen, A. Hu, M. Li, and P. Li, "Study on low-Ag content Sn-AgZn/Cu solder joints," *Microeletronics Reliability*, vol. 53, pp. 2018-2029, 2013.

[2] O. Smorygo, J. S. Kim, M. D. Kim, and T. G. Eom, "Evolution of the interlayer microstructure and the fracture modes of the zirconia/Cu–Ag–Ti filler/Ti active brazing joints," *Materials Letters*, vol. 61, pp. 613-616, 2017.

[3] W. B. Hanson, K. I. Ironside, and J. A. Fernie, "Active metal brazing of zirconia," *Acta Materialia*, vol. 48, pp. 4673-4676, 2000.

[4] A. Abdulrahman, J. Issam, and A. Hendry, "Wetting and reaction between β'- sialon, stainless steel and Cu–Ag brazing alloys containing Ti," *Journal of the European Ceramic Society*, vol. 21, pp. 283-290, 2001.

[5] S.C. Dev and C.S. Sivaramakrishnan, "An indigenous technology for a silver brazing alloy," *Materials & Design*, vol. 17, pp. 75-78, 1996.

[6] M.M. Schwartz. "Brazing", *ASM International*, 2nd ed., Materials Park, 2003.

[7] F. Sui, W. Long, S. Liu, G. Zhang, L. Bao, H. Li, and Y. Chen, "Effect of calcium on the microstructure and mechanical properties of brazed joint using Ag–Cu–Zn brazing filler metal," *Materials and Design*, vol. 46, pp. 605–608, 2013.

[8] X. Tu, D. Yi, J. Wu, and B. Wang, "Influence of Ce addition on Sn-3.0Ag-0.5Cu solder joints: Thermal behavior, microstructure and mechanical properties," *Journal of Alloys and Compounds*, vol. 698, pp. 317–328, 2017.

[9] Z. Li, N. Jiao, J. Feng, and Y. Chen, "Effect of P and rare-earth La on microstructure and property of Ag-Cu-Zn-Sn brazing alloy," *Transactions of the China Welding Institution*, vol. 28, pp. 1-4, 2007.

[10] L. Zhongmin, X. Songbai, H. Xianpeng, G. Liyong, G. Wenhua, "STUDY ON MICROSTRUCTURE AND PROPERTY OF BRAZED JOINT OF AGCUZN-X(GA, SN, IN, NI) BRAZING ALLOY," *Rare Metal Materials and Engineering*, vol. 39, pp. 397-400, 2010.

[11] F. Habashi, "Tin, Physical and Chemical Properties. Encyclopedia of Metalloproteins", *Springer New York*, pp. 2233-2234, 2013.

[12] H. Ohtani, M. Miyashita, and K. Ishida, "Thermodynamic study of phase equilibria in the Sn-Ag-Zn system," *Journal of the Japan Institute of Metals*, vol. 63, pp. 685-694, 1999.

[13] M. G. Li, D. Q. Sun, X. M. Qiu, and S. Q. Yin, "Effect of tin on melting temperature and microstructure of Ag–Cu–Zn–Sn filler metals," *Materials Science and Technology*, vol. 21, pp. 1318-1322, 2005.

[14] L. X. Zhang, J. C. Feng, and H. B. Liu, "High frequency induction brazing of TiC cermets to steel with Ag–Cu–Zn foil," *Materials Science and Technology*, vol. 24, pp. 623-626, 2008.

Thanut Jintakosol received his Ph.D. degree in materials science from Chiangmai University, Thailand in 2011. He is currently an assistant professor in the Department of General Science (Gems and Jewelry), Fuculty of Science, Srinakharinwirot University, Thailand. His research areas are Jewelry production, Nanomaterials, Composite materials, Innovation materials and Precious metal.

Walaikorn Nitayapha received her Ph.D. degree in materials science from Chulalongkorn University, Thailand in 2011. She is currently an assistant professor at Fuculty of Science, Srinakharinwirot University, Thailand. Her research area are Composite materials, Adsorbent materials, Textile materials and Precious metal.