Surface Tension, Density, and Thermal Expansion of (Bi-Ag)_{eut}-Zn Alloys

JANUSZ PSTRUŚ,¹ PRZEMYSŁAW FIMA,^{1,2} and WLADYSŁAW GAŚSIOR¹

1.—Institute of Metallurgy and Materials Science, Polish Academy of Sciences, ul. Reymonta 25, 30-059 Krakow, Poland. 2.—e-mail: nmfima@imim-pan.krakow.pl

The thermophysical properties of Bi-Ag eutectic-based alloys with additions of 3 at.%, 6 at.%, and 9 at.% Zn are presented. The density of liquid alloys was determined using the dilatometric method, while the surface tension was measured using the maximum bubble pressure method. Thermal expansion of solid alloys was measured with an optical dilatometric technique. It was found that addition of zinc to the Bi-Ag eutectic slightly decreases density, while an increase of the surface tension and thermal expansion coefficient is observed. Relatively good agreement is observed between surface tension calculated from the thermodynamic model and the experimental data.

Key words: Bi-Ag-Zn alloys, density, Pb-free solders, surface tension, thermal expansion, thermodynamic modeling

INTRODUCTION

Alloys based on the Bi-Ag eutectic are considered as a possible replacement for high-temperature solders based on Pb.¹ The Bi-Ag eutectic has an acceptable melting point (the eutectic temperature is 535 K), and a reasonable cost,² however it is prone to brittleness due to a high concentration of Bi. Modification of the Bi-Ag eutectic alloy with a third component is supposed to improve its mechanical, electrical, thermal, and wetting properties. It was recently reported³ that addition of Sn to Bi-Ag eutectic improves its wetting of copper (lowering of the wetting angle), but we did not observe such an effect for Zn addition. Wetting is an important characteristic, as it has a direct effect on the quality of the joint; in particular, the lower the contact angle, the larger the area of the substrate covered with the solder. The surface tension of the solder is the main parameter affecting wetting, as it is correlated with the wetting angle according to Young's equation.⁴ For experimental determination of the surface tension, knowledge of the liquid density is required. Density, if known in a certain range of temperatures, gives information on the thermal expansion of the liquid solder.⁵ This, com-

bined with the thermal expansion of the solid solder and of the substrate, is crucial when designing the soldering process as well as for joint quality due to the risk of cracks. To assess the applicability of a solder, reliable data on the discussed properties are required. To the best of the authors' knowledge, no data regarding the density and surface tension of liquid and thermal expansion of solid Bi-Ag-Zn alloys exist in literature. Therefore, the aim of this work is to determine these properties of Bi-Ag eutectic-based alloys with additions of Zn over a broad range of temperatures. The results of the surface tension measurements are compared with surface tensions calculated from the model.⁶

EXPERIMENTAL PROCEDURES

High-temperature solders based on Bi-Ag eutectic containing 0 at.%, 3 at.%, 6 at.%, and 9 at.% Zn were used for the study of thermophysical properties. The alloys were prepared by melting accurately weighted amounts of pure metals (99.995%) in graphite crucibles under Ar (99.9992%) protective atmosphere. The densities (ρ) of the liquid alloys were measured with a dilatometric technique over a broad range of temperatures, 550 K to 1000 K. This method is based on measurement of the height (H) of a known mass (m) of liquid enclosed in a crucible of known diameter (D) (Eq. 1). A detailed description

(Received November 25, 2010; accepted September 21, 2011; published online October 14, 2011)

of the apparatus and experimental method was given previously.⁷

$$\rho = \frac{4m}{\pi D^2 H}. \quad (1)$$

Surface tension was determined using the maximum bubble pressure method (MBP) over the 550 K to 1100 K temperature range, with the use of the experimental setup described in detail in Ref. 7. Sugden's procedure⁸ was applied to the surface tension calculations. Protective atmosphere of Ar + 10% H₂ was used for the measurements of both density and surface tension. The experimental uncertainty did not exceed 1% for density and 2% for surface tension. The thermal expansion of solid alloys was measured with an optical dilatometric technique at 310 K to 490 K. A cubic sample was placed in the center of the dilatometer, and the change of its dimensions was observed using a digital camera. The resulting pictures were analyzed by image analysis software, and the thermal expansion was calculated according to the equation

$$\alpha = (L - L_0)/(L_0(T - T_0)), \quad (2)$$

where α is the coefficient of thermal expansion (CTE), L_0 is the dimension of the sample at tem-

perature T_0 , and L is the dimension of the sample at higher temperature T .

RESULTS AND DISCUSSION

Density

The results of the density measurements shown in Fig. 1 were analyzed with the least-squares method and the obtained linear equations $\rho = (A - BT)$, together with estimated errors of the parameters A and B , and density calculated at 573 K are collected in Table I. For all of the examined alloys, it was found that the density decreases linearly with increasing temperature. These results indicate that addition of Zn to the Bi-Ag eutectic seems to have a negligible effect on density, as the densities of the alloys containing Zn are very similar to that of the Bi-Ag eutectic. The density of the Bi-Ag eutectic is close to values reported previously.⁹ Based on density data, the molar volume of (Bi-Ag)_{eut}-Zn alloys was calculated with the use of Eq. (3) under the assumption that the Bi-Ag eutectic is treated as one "component" and Zn is the other component. In Eq. (3) $M_{\text{Bi-Ag}}$, M_{Zn} , $x_{\text{Bi-Ag}}$, x_{Zn} , $\rho_{\text{Bi-Ag-Zn}}$, and V_M are the atomic masses of Bi-Ag eutectic and Zn, the mole fractions of Bi-Ag eutectic and Zn, and the density and molar volume of the alloy, respectively.

$$V_M = (x_{\text{Bi-Ag}}M_{\text{Bi-Ag}} + x_{\text{Zn}}M_{\text{Zn}})/\rho_{\text{Bi-Ag-Zn}}. \quad (3)$$

As can be seen from Fig. 2, in the examined concentration range the calculated molar volume of (Bi-Ag)_{eut}-Zn alloys (points) deviates slightly from the molar volume calculated under the assumption

Fig. 1. Temperature dependence of the density of liquid (Bi-Ag)_{eut}-Zn alloys.

Fig. 2. Concentration dependence of the molar volume of (Bi-Ag)_{eut}-Zn alloys at 573 K.

Table I. Temperature dependence of the density of (Bi-Ag)_{eut}-Zn alloys and density calculated at 573 K, together with assessed errors of the linear coefficients A and B

x_{Zn} (at.%)	$\rho = A - BT$ (K) (g cm ⁻³)	ρ (573 K) (g cm ⁻³)	Err(A) (g cm ⁻³)	Err(B) (g cm ⁻³ K ⁻¹)
0	10.6933-0.001250	9.977 ± 0.097	±0.188	±0.000238
3	10.7940-0.001391	9.997 ± 0.161	±0.348	±0.000430
6	10.6128-0.001180	9.937 ± 0.086	±0.153	±0.000205
9	10.6594-0.001287	9.922 ± 0.079	±0.142	±0.000183

of additivity of molar volumes of components (dashed line). Equation (4) shows the molar volume dependence on Zn concentration at 573 K.

$$V_{M(573K)} = 20.4696 - 14.5705x_{Zn} + 22.07304(x_{Zn})^2. \quad (4)$$

Surface Tension

The results of the surface tension measurements shown in Fig. 3 were analyzed with the least-squares method and the obtained linear equations, together with estimated errors and surface tension calculated at 573 K, are collected in Table II. For all of the examined alloys, the surface tension decreases linearly with increasing temperature. The surface tension of the Bi-Ag eutectic is in excellent agreement with the earlier experimental results⁹ over the investigated temperature range. The values in Table II are, depending on the Zn content, 9 to 13.5% lower than the surface tension values reported earlier for Sn-89Pb (450 mN m⁻¹)¹⁰ and Sn-95Pb (440 mN m⁻¹, at 620 K)¹¹ alloys. Generally, the surface tension of Bi-Ag-Zn alloys increases with increasing concentration of Zn. According to the data obtained, the surface tension of the alloy

containing 3 at.% Zn is nearly the same as the surface tension of Bi-Ag eutectic, while for greater concentrations of Zn the surface tension is higher.

Utilizing the model, based on the equation originally developed by Butler,⁶ the surface tension of ternary Bi-Ag-Zn alloys can be calculated with Eq. (5).

$$\sigma = \sigma_i + \frac{RT}{A_i} \ln \frac{x_i^S}{x_i^B} + \frac{1}{A_i} (\text{ex}G_i^S - \text{ex}G_i^B), \quad (5)$$

where R is the gas constant, T is the absolute temperature in K, σ_i is the surface tension of pure component i , A_i is the molar surface area in a monolayer of pure liquid i ($i = \text{Bi, Ag, Zn}$), x_i^S and x_i^B are the mole fractions in the surface and the bulk phase, respectively, and $\text{ex}G_i^S$ and $\text{ex}G_i^B$ are the partial excess Gibbs energies of component i in the surface and bulk phase. The molar surface area, A_i is calculated from the equation

$$A_i = 1.091N^{1/3}V_i^{2/3}. \quad (6)$$

In Eq. (6), N is Avogadro's number, and V_i is the molar volume of pure liquid i . Finally, the relationship between excess Gibbs energy of component i in bulk and surface phases is assumed to be as follows:

$$\text{ex}G_i^S = \beta \text{ex}G_i^B. \quad (7)$$

β is a parameter corresponding to the ratio of the coordination number Z in the surface phase to that in the bulk phase Z^S/Z^B and is assumed to be equal to 0.83 for liquid.^{12,13} Thermodynamic parameters required for calculations were taken from the COST 531 thermodynamic database,¹⁴ whereas surface tension data and density for pure liquid Ag and Bi were taken from Ref. 9 and for Zn from Ref. 15. Figure 4 illustrates a comparison between the results of calculations (lines) and the experimental data (triangles) for respective compositions. Surface tensions calculated from the model decrease with the increase in temperature and increase with the increase of Zn concentration, which is in accordance with experimental results. Good agreement is observed between the calculated and experimental data for both the Bi-Ag eutectic and the alloys containing 3 at.% and 6 at.% Zn. In the case of alloy containing 9 at.% Zn the results of the calculations

Fig. 3. Temperature dependence of the surface tension of liquid (Bi-Ag)_{eut}-Zn alloys.

Table II. Temperature dependence of the surface tension of (Bi-Ag)_{eut}-Zn alloys and surface tension calculated at 573 K, together with assessed errors of the linear coefficients A and B

x_{Zn} (at.%)	$\rho = A - BT$ (K) (mN m ⁻¹)	σ (573 K) (mN m ⁻¹)	Err(A) (mN m ⁻¹)	Err(B) (mN m ⁻¹ K ⁻¹)
0	416.2–0.0589	382.5 ± 7.7	±9.1	±0.0110
3	420.8–0.0638	384.2 ± 6.1	±11.4	±0.0150
6	425.1–0.0616	389.8 ± 4.9	±9.2	±0.0117
9	430.5–0.0567	398.0 ± 4.0	±7.1	±0.0090

Fig. 4. Temperature dependence of the surface tension of (Bi-Ag)_{eut}-Zn alloys. Experimental data (triangles) compared with Butler model calculations (lines).

are about 2% lower than the experimental data over the whole temperature range.

Thermal Expansion

Similarly to the density and the surface tension, the results of the measurements of CTE shown in Fig. 5 were analyzed with the least-squares method, and the obtained linear equations, together with estimated errors and thermal expansion calculated at 473 K, are collected in Table III. It was found that, for all of the examined alloys, the samples expand linearly with increasing temperature. Also, the higher the concentration of zinc in the alloy, the higher the CTE. This can be easily explained by the fact that the CTE of Zn is roughly two times larger than that of Bi.¹⁶ Generally, coefficients of thermal expansion for pure elements are reported as constant over a certain temperature range.¹⁶ However, coefficients of thermal expansion determined in this

Fig. 5. Temperature dependence of thermal expansion coefficient of (Bi-Ag)_{eut}-Zn alloys.

Table III. Coefficient of linear thermal expansion α of (Bi-Ag)_{eut}-Zn alloys

x_{Zn} (at.%)	$\rho = A - BT$ (K) (10^{-6} K^{-1})	α (473 K) (10^{-6} K^{-1})	Err(A) (10^{-6} K^{-1})	Err(B) (10^{-6} K^{-1})
0	12.6833 + 0.003499	14.34 ± 0.056	±0.037	±0.000315
3	12.8653 + 0.004344	14.92 ± 0.160	±0.123	±0.000918
6	13.0583 + 0.004849	15.35 ± 0.129	±0.099	±0.000738
9	13.1625 + 0.005446	15.74 ± 0.115	±0.088	±0.000657

work are temperature dependent within the examined temperature range and increase slightly with increasing temperature. Small variation of CTE with increasing temperature suggests that the studied alloy is thermally stable.¹⁷ The CTE of Bi-Ag-based alloy containing 9 at.% Zn determined in this work is close to the CTE of copper, which according to Smithells metals reference book is $17.1 \times 10^{-6} \text{ K}^{-1}$ for the 293 K to 573 K range.¹⁶ This is promising information considering the possible application of this alloy in actual soldering process. Generally, thermal expansion data for solders are scarce and only a few sources could be found. According to Fig. 5, the CTE for Bi-Ag-Zn alloys for the 298 K to 373 K range is lower than the $27.5 \times 10^{-6} \text{ K}^{-1}$ reported for Sn-3.5Ag-0.5Cu solder¹⁷ or the $28.7 \times 10^{-6} \text{ K}^{-1}$ reported for Sn-95Pb solder.¹⁸

CONCLUSIONS

Surface tension and density of liquid Bi-Ag eutectic alloy and alloys containing 3 at.%, 6 at.%, and 9 at.% Zn were determined by maximum bubble pressure and dilatometric methods, respectively. The results of the measurements indicate that the density decreases linearly with increasing temperature for all of the examined compositions, while the concentration of Zn has little effect on its value. The results of density measurements suggest that in the examined concentration range the molar volume of (Bi-Ag)_{eut}-Zn alloys shows slightly negative deviation from additive behavior. The surface tension is a linear function of temperature and decreases with its increase for all of the compositions. The increase of Zn concentration in (Bi-Ag)_{eut}-Zn alloys results in higher surface tension. Using the thermodynamic model based on Butler's equation, surface tension was calculated for respective compositions. The results of the calculations are in good agreement with experimental data for both Bi-Ag eutectic and alloys containing 3 at.% and 6 at.% Zn. For higher Zn concentration (i.e., 9 at.%), poorer agreement between the model calculations and experimental data is observed. Thermal expansion of solid alloys depends on the concentration of zinc; i.e., it is higher for alloys containing more zinc. Also, coefficients of thermal expansion

show dependence on temperature, increasing slightly with increasing temperature.

ACKNOWLEDGEMENTS

This work was financed by the Ministry of Science and Higher Education of Poland under the framework of COST Action MP0602—HISOLD “Advanced Solder Materials for High Temperature Application,” in the years 2007–2010.

OPEN ACCESS

This article is distributed under the terms of the Creative Commons Attribution Noncommercial License which permits any noncommercial use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.

REFERENCES

1. J.M. Song, H.Y. Chuang, and H.Y. Wen, *Metall. Mater. Trans. A* 38, 1371 (2007).
2. J.M. Song, H.Y. Chuang, and Z.M. Wu, *J. Electron. Mater.* 35, 1041 (2006).
3. P. Fima, W. Gasior, A. Sypien, and Z. Moser, *J. Mater. Sci.* 45, 4339 (2010). doi:10.007/s10853-010-4291-0.
4. P.T. Vianco and J.A. Rejent, *J. Electron. Mater.* 28, 1138 (1999).
5. J. Brillo, I. Egry, and I. Ho, *Int. J. Thermophys.* 27, 494 (2006).
6. J.A.V. Butler, *Proc. R. Soc. A* 135, 348 (1935).
7. Z. Moser, W. Gasior, and J. Pstrus, *J. Phase Equilib.* 22, 254 (2001).
8. S. Sugden, *J. Chem. Soc.* 124, 858 (1924).
9. W. Gasior, J. Pstrus, Z. Moser, A. Krzyzak, and K. Fitzner, *J. Phase Equilib.* 24, 40 (2003).
10. D.W.G. White, *Metall. Trans.* 2, 3067 (1971).
11. B.B. Alchagirov, K.I. Ibragimov, T.M. Taova, K.B. Khokonov, *Proceedings of the International Conference High Temperature Capillarity*, ed. N. Eustathopoulos and N. Sobczak (1997).
12. T. Tanaka and T. Iida, *Steel Res.* 65, 21 (1994).
13. T. Tanaka, K. Hack, T. Iida, and S. Hara, *Z. Metallkd.* 87, 380 (1996).
14. A.T. Dinsdale, A. Watson, A. Kroupa, A. Zemanowa, J. Vrestal, and J. Vizdal, *Version 3.0 of the SOLDERS Database for Lead Free Solders*, <http://www.npl.co.uk/science-technology/advanced-materials/materials-areas/thermodynamics/thermodynamic-databases-for-mtdata>.
15. J. Pstrus, Z. Moser, W. Gasior, and A. Debski, *Arch. Metall. Mater.* 51, 335 (2006).
16. W.F. Gale and T.C. Totemair, eds., *Smithells Metals Reference Book*, 8th ed. (Oxford: Elsevier, 2004), p. 14-3.
17. S.W. Kim, J. Lee, and B.-M. Jeon, *Int. J. Thermophys.* 30, 1234 (2009).
18. www.matweb.com.