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Wetting of Cu by Bi–Ag based alloys with Sn and Zn additions

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Abstract Contact angles on copper substrate of Bi–Ag–Sn and Bi–Ag–Zn ternary alloys containing 3, 6, and 9 at.% of Sn and Zn, respectively, were studied with the sessile drop method. Wetting tests were carried out at 573 and 603 K with or without the use of a flux. Without the flux, the examined alloys do not wet copper, i.e., the observed contact angles are higher than 90°. However, in the presence of the flux wetting of copper is observed. In the case of alloys with Sn, the contact angles decrease with increasing content of Sn, while in the case of alloys with Zn no such tendency is observed. Solidified solder–substrate couples were cross-sectioned and examined with scanning electron microscopy coupled with electron dispersive X-ray analysis.

Introduction

Studies directed on finding lead-free replacement for traditional solders were initiated at IMMS PAS nearly 10 years ago. Several binary [1–6], ternary and multicomponent [7–18] alloys were examined including Sn–Ag–Cu [10, 12, 14–16] alloys with additions of In, Bi and Sb in the framework of COST 531 Program, quinary Sn–Ag–Cu–Bi–Sb alloys [16, 17], and Sn-Zn with alloying additions of Bi and Sb [18]. A wide range of properties was studied including wetting [14, 17], electrical resistivity [11, 13], surface tension, and density [8, 12]. In addition to experimental work, some modeling of thermophysical properties were done [15, 19] and the obtained data together with some results of other groups were collected in a free SURDAT database of physical properties of metals and alloys [20]. The activities of our and other research groups [21] let us assume that the development of lead-free solders (mainly Sn-based) for low-temperature applications seems to be soon completed successfully. Sn–Ag and Sn–Ag–Cu eutectics, and recently Sn–Zn based ternary alloys were selected as the most suitable replacement for Pb–Sn eutectic solder.

Despite apparent success with low-temperature Pb-free solders, there is still a need of further research on solders for high-temperature applications, as up to now a drop in replacement for Pb solders (for example Pb–10Sn, Pb–5Sn) has not been found [22, 23]. COST Action MP0602 “Advanced solder materials for high-temperature application—HISOLD” is common cooperation, which is aimed at the development of new soldering materials. Out of candidate alloys, the Bi–Ag eutectic-based alloys seem to be promising. The Bi–Ag eutectic has acceptable melting point (the eutectic temperature is 535 K), reasonable cost, and similar hardness to that of Pb–5Sn [24]. Owing to this, it was applied as die-attach solder in power devices and light-emitting diodes (LEDs) [23, 25]. Modification of Bi–Ag system with a third component is supposed to improve mechanical, electrical, thermal, and wetting properties of solder alloy. Although there are numerous papers on Pb-free solders wettability on copper [21], data on wetting properties of Bi-rich Bi–Ag alloys are scarce [22].

Determination of the contact angle between liquid solder and solid substrate is a simple tool in assessment of joint quality. The substrate is considered wettable by the solder if the contact angle is low (below 90°). Good wetting

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should result in good bonding between the solder and the substrate, which affects electrical, thermal, and mechanical [26] properties of the joint. Another factor affecting quality of the joint is the structure of connection at the interface, in particular the formation of interlayers. In the case of Sn-based and Zn-based solder alloys, formation of intermetallic compound layers is reported [27, 28] between the Cu substrate and the solder. On the other hand, previous report on Bi–Ag eutectic solder and Cu substrates does not show formation of any interlayer [25]. To authors' best knowledge, there are no available data on the interface between Cu substrate and Bi–Ag eutectic-based alloys with low additions of Sn or Zn.

Therefore the aim of this work is: (1) to investigate the effect of Sn and Zn additions on wettability of Bi–Ag eutectic-based alloys on Cu substrate under different experimental conditions, and (2) to characterize the microstructure of the interface between solders and Cu substrate.

Experimental

High-temperature solders based on Bi–Ag eutectic containing 3, 6, and 9 at.% of Sn or Zn, respectively, were used for the study of wetting of copper (99.9%) substrate with the sessile drop method (SD). Alloys were prepared by melting pure metals (99.995%) in graphite crucibles under Ar (99.9992%) protective atmosphere. Wetting tests were carried out under three different experimental conditions: Ar protective atmosphere, no flux, 573 K; Ar protective atmosphere, no flux, 603 K; Ar protective atmosphere, flux, 573 K.

Wetting tests were carried out in specially designed furnace with Kanthal heating elements, constructed by Tele and Radio Research Institute (ITR) in Warsaw and schematically shown in Fig. 1. The construction of the furnace enables fast transfer of the examined solder/substrate couple from the cold to the hot zone of the furnace (2–3 s). Owing to this and a special copper block located in the center of the furnace, which serves as heat accumulator, the temperature of the specimen increases rapidly. The temperature of the specimen is measured by a type K thermocouple located in the copper block (5 mm below the sample) with an accuracy of ±1 K. Before the experiment, copper substrates of dimensions 25 × 20 × 0.2 mm underwent multistep cleaning. We used nonpolished substrates in order to have copper surface resembling the surface of copper in the actual soldering process. The cleaning procedure consisted of subsequent cleaning in acetone, etching in commercial solution for PCB etching, washing in demineralized water, cleaning in acetone, etching in 5% HNO_3 and 25% H_2SO_4 acid solution, washing in demineralized water and again cleaning in acetone. Specimens of solder were in form of 3 × 3 mm cylinders. Before the experiment, they were mechanically cleaned and ultrasonically cleaned in acetone. The solder specimen was placed on the substrate in a cold zone of already heated furnace. In the case of the tests without flux, after closing the furnace it was evacuated to 1 Pa and flushed with argon three times in a sequence, followed by steady flow of argon lasting 1 h before the sample was moved to the hot zone. In the case of the tests with flux, directly before closing the furnace, the specimen was covered with the flux. The flux was a mixture of esters and isopropanol, with additions of organic acids, rosin and halides. The amount of the flux was enough to cover the solder and surrounding part of the substrate. After closing the furnace a steady flow of Ar (99.9992%) of 1 L/min was switched on and the couple immediately transferred to the hot zone of the furnace. The images of the solder/substrate couple were taken for 30 min with the use of monochrome digital camera, and the contact angles were obtained directly from the digital pictures by an image analysis software. The error of contact angle measurements with the experimental setup was estimated to be ±2°. After wetting tests, solidified drops were cut perpendicular to the plane of the interface, mounted in conductive resin and polished for microstructural characterization. FEI E-SEM XL30 system was used for microstructural analysis. EDX analysis was performed at 20 kV and working distance of 10 mm, with the use of the standardless Analysis EDAX System based on Genesis for 2000 software.

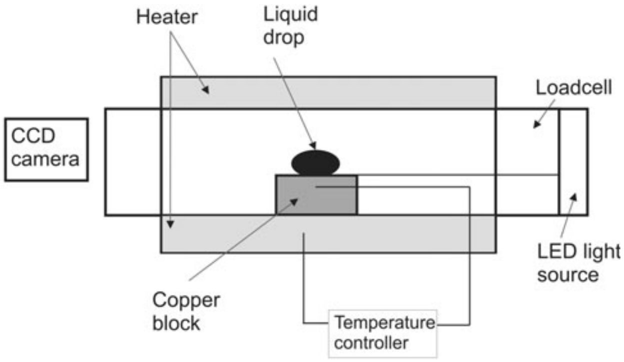

Fig. 1 Experimental setup for wetting tests with the sessile drop method

Results

Wetting properties

The results of wetting of copper substrates with Bi–Ag–Sn alloys are graphically presented in Fig. 2 and the results for Bi–Ag–Zn alloys are in Fig. 3. Both figures show wetting

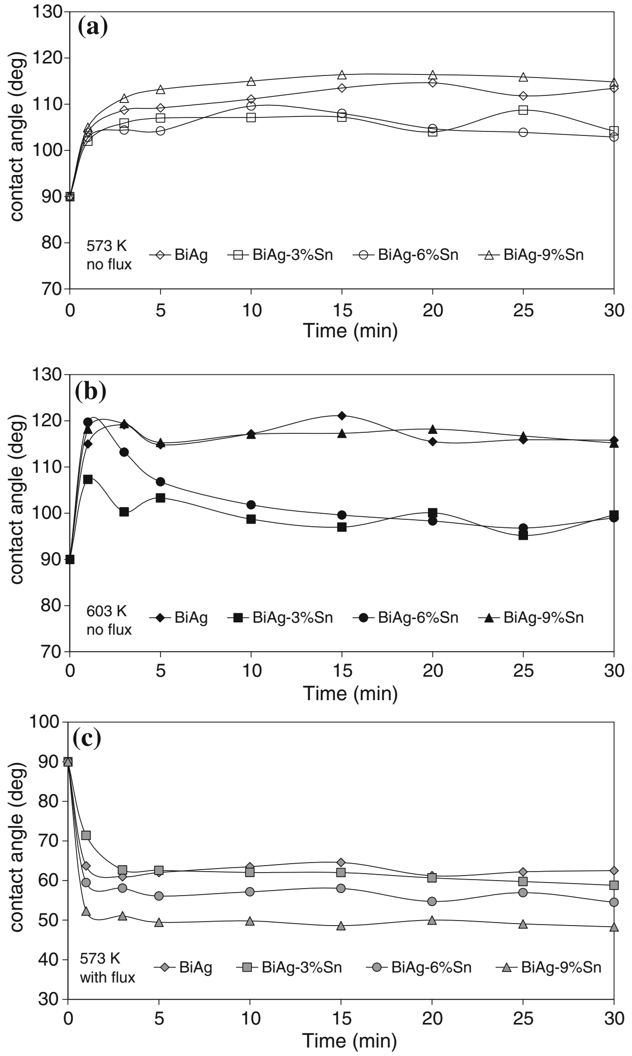

Fig. 2 Contact angles of Bi–Ag–Sn alloys versus time: **a** without the flux at 573 K, **b** without the flux at 603 K, and **c** with the flux at 573 K, respectively

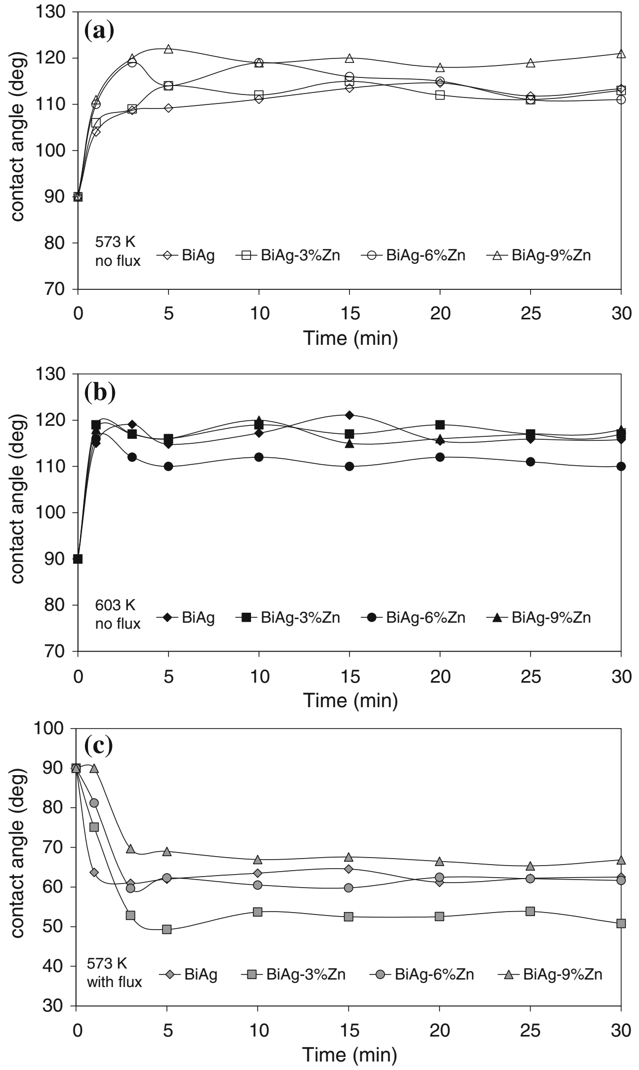

Fig. 3 Contact angles of Bi–Ag–Zn alloys versus time: **a** without the flux at 573 K, **b** without the flux at 603 K, and **c** with the flux at 573 K, respectively

characteristic versus time of respective alloys. Figure 4 presents composition dependence of the contact angles of (a) Bi–Ag–Sn and (b) Bi–Ag–Zn alloys, respectively. In the case of the tests carried out without the flux, examined alloys do not wet copper, i.e., determined contact angles are higher than 90°. The results indicate that Bi–Ag–Zn alloys show no dependence of the contact angles on composition and on temperature. For Bi–Ag–Sn alloys contact angles for alloys containing 3 and 6 at.% of Sn are lower than those for 9 at.% Sn alloy and Bi–Ag eutectic alloy. For these two compositions, the increase of temperature from 573 to 603 K results in lower contact angles. In the case of the tests with the flux, the wetting is improved. After 30 min of wetting at 573 K with the flux, for Bi–Ag–Sn alloys the contact angles are in the range 48–62°, while for Bi–Ag–Zn alloys in the range 50–67°. Both for Bi–Ag–Sn and Bi–Ag–Zn alloys containing 3 at.% of the third component the contact angle is lower compared to Bi–Ag eutectic. However, while further addition of Zn results in higher contact angles, in the case of Sn addition contact angles are lowered step by step.

Microstructural characterization

Figures 5, 6 and 7 show the microstructure of the interface between the solders Bi–Ag, Bi–Ag–9Sn, Bi–Ag–9Zn (in at.%), respectively, and copper substrate after wetting with the flux at 573 K for 30 min, obtained by SEM. The results of EDX measurements of the composition in points shown in Figs. 5, 6 and 7 are listed in Tables 1, 2 and 3, respectively. In the Bi–Ag solder/copper cross section (Fig. 5), the surface of Cu contains 2.4 at.% of Bi, the amount of

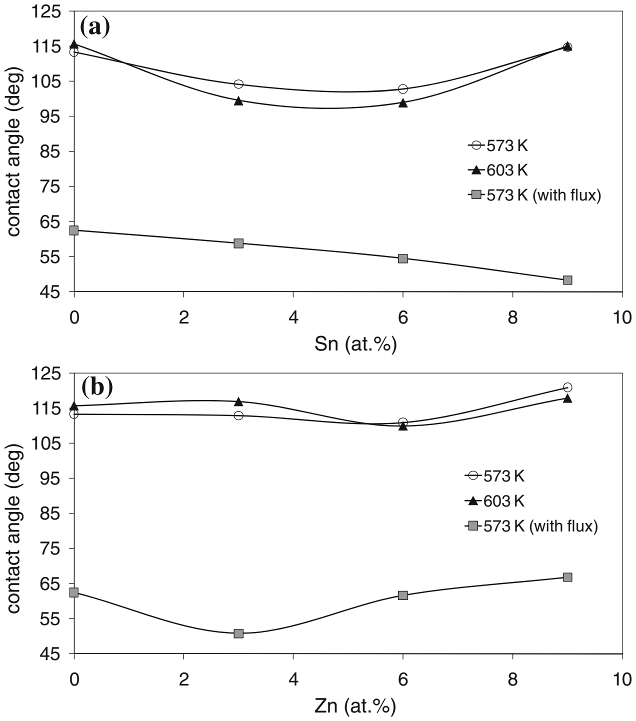

Fig. 4 Contact angle dependence on composition, after 30 min of wetting, for alloys: **a** Bi–Ag–Sn, and **b** Bi–Ag–Zn, respectively

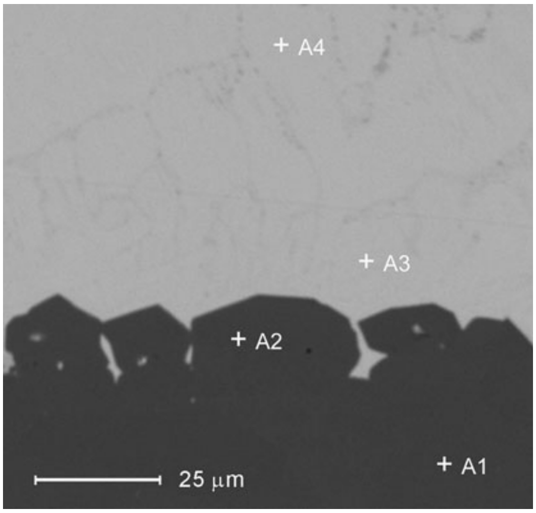

Fig. 5 SEM image of the interface between copper and Bi–Ag alloy after wetting with flux at 573 K, 30 min

copper dissolved varies from 11.0 at.% close to the interface to 1.7 at.% further in the bulk of the solder. Silver segregates from the bulk of the solder toward the interface. The interface between the ternary solder alloys and copper substrate is more complicated than in the case of Bi–Ag eutectic. In the case of Bi–Ag–9Sn solder, its interface with copper shows presence of two interlayers (Fig. 6). The interlayer adjacent to the substrate has high concentration of Bi, while the second has a composition close to Cu_3Sn intermetallic. The bulk of the substrate shows large precipitates of the phase close in composition to Ag_3Sn in pure Bi matrix. Also, in the case of Bi–Ag–9Zn/copper interface

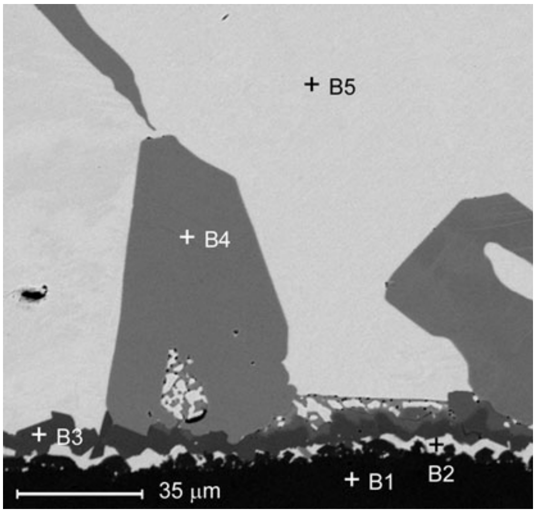

Fig. 6 SEM image of the interface between copper and Bi–Ag–9Sn alloy after wetting with flux at 573 K, 30 min

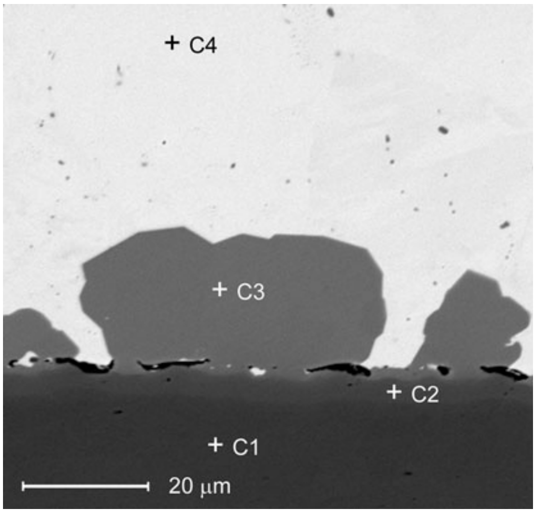

Fig. 7 SEM image of the interface between copper and Bi–Ag–9Zn alloy after wetting with flux at 573 K, 30 min

Table 1 The results of EDX analysis performed on Bi–Ag/Cu couple at the positions indicated in Fig. 5

Point	Composition (at.%)		
	Cu	Bi	Ag
A1	100.0		
A2	97.6	2.4	
A3	11.0	85.3	3.7
A4	1.7	98.3	

Table 2 The results of EDX analysis performed on Bi–Ag–9Sn/Cu couple at the positions indicated in Fig. 6

Point	Composition (at.%)			
	Cu	Bi	Ag	Sn
B1	100.0			
B2	13.7	84.5	1.8	
B3	74.7			25.3
B4	2.6		73.3	24.1
B5		100.0		

Table 3 The results of EDX analysis performed on Bi–Ag–9Zn/Cu couple at the positions indicated in Fig. 7

Point	Composition (at.%)			
	Cu	Bi	Ag	Zn
C1	100.0			
C2	39.0			61.0
C3	2.3	21.2	35.0	41.5
C4		95.1		4.9

(Fig. 7) two interlayers can be distinguished. The first one, adjacent to the substrate, is characterized by high Zn concentration while in the second interlayer both Bi and Ag are present. The bulk of the solder is basically Bi–Zn alloy as all the silver is accumulated in the second interlayer.

Discussion

In the search for Pb-free replacement of traditional solders, a number of requirements need to be fulfilled by newly developed solders. According to [29], the most important of them are solidus and liquidus temperature as well as wettability. Specifically, a replacement for Pb solders needs to have sufficiently high solidus (preferably above 523 K) to survive high-temperature working conditions, and a liquidus lower than 673 K to avoid the damage to polymeric substrate during the soldering. Bi–Ag eutectic-based solders fit in these criteria as eutectic temperature of Bi–Ag is 535 K. As far as wettability is concerned, contact angles should be as close as possible to Pb solders. Due to different methods (sessile drop, wetting balance) and a range of conditions (flux, protective atmosphere, and wetting temperature) it is very difficult to compare results of wetting studies, even for the same solders [21]. For example, for Sn–96Pb solder the contact angles on copper with rosin mildly activated flux determined with the sessile drop method are lower [30] than the ones obtained with wetting balance [31] at higher temperature.

In the case of Bi–Ag solders, the wettability data are very limited [22]. In [22], the contact angle of 40° was determined for Bi–Ag eutectic on copper, after wetting at 613 K for 1 min. It is lower than the value obtained in this work, but no information on the flux used (if any) is given. The wetting characteristics shown in Figs. 2 and 3, indicate that during the first minutes of wetting, the contact angle changes rapidly, evolving from the original 90° of the solid cylinder to that pertaining to the fully molten alloy: in particular, it decreases for solders treated with the flux and it increases for solders without flux. For the remaining wetting time, it changes slowly and to a low extent. In most cases, contact angle determined after 5 min of wetting is close to the value determined after 30 min. In particular, in the case of alloys treated with the flux, after 5 min of wetting contact angle remains relatively stable. The apparent fluctuations of the contact angle observed in Figs. 2 and 3 between 5 and 30 min of wetting (see Figs. 2c and 3c) are, to some extent, a result of error of the experimental uncertainty (±2°).

The results of the EDX analysis of Bi–Ag/Cu couple indicate that there are no reaction products at the interface. The surface of the copper substrate became rough (Fig. 5) and shows some dissolved bismuth, while concentration of silver near the substrate is increased at the expense of the bulk of the solder. This observation is partially confirmed by Song et al. [22], where roughening of copper substrate and small precipitates of silver-rich phase at the interface are observed. Roughening of the surface of copper is explained by the ability of Bi–Ag eutectic to groove and penetrate the grain boundaries of copper [22], and this mechanism is responsible for creating a bond between the solder and the substrate. Also dissolution of copper in the bulk of the solder is observed (Table 1). Song et al. [25] investigated dissolution of copper in Bi–2.5Ag, Bi–11Ag (in wt%) alloys and pure Bi, and found that it is correlated with initial concentration of silver in the alloy. Bi–11Ag dissolves the highest and pure Bi the lowest amount of copper. Ternary alloys have a low relative concentration of silver compared to Bi–Ag eutectic, which added to thermodynamics of interlayers formation, explains why none copper dissolves into the bulk of ternary solder. Contrary to Bi–Ag/Cu, Bi–Ag–9Sn/Cu couple (Fig. 6) shows presence of reaction products at the interface in the form of Cu3Sn layer, which is separated from the substrate by Bi-rich interlayer. In the case of Bi–Ag–9Zn/Cu (Fig. 7) also two interlayers are present that have relatively smooth edges, compared to interlayers in Bi–Ag–9Sn/Cu interface. Dissolution of copper in liquid Bi–Ag alloys is most likely responsible for the observed change in concentration of silver in the solder drop. According to phase diagrams [32], solubility of components in the Ag–Cu system is greater than in the Bi–Cu system. This entails that the thermodynamic properties of Bi–Cu system show strong positive deviation from perfect solution compared to Cu–Ag system. As a result, the attraction between Cu and Ag in the liquid state is stronger than between Cu and Bi. Also the formation of interlayers between copper and alloys containing tin or zinc can be explained by strong interaction in the liquid state between copper and these two metals, which is actually stronger than in the case of Ag–Sn and Ag–Zn systems. In addition, Bi–Cu [32] and to a lesser extent Ag–Bi system show a demixing tendency of the components, resulting from positive deviation of their thermodynamic properties from perfect solution.

Conclusions

The Influence of Sn and Zn additions on wettability of copper by Bi–Ag based alloys was investigated by contact angle measurements with the sessile drop method. It was found that, under the experimental conditions of this study (without flux), the examined alloys do not wet copper, i.e., apparent contact angle is greater than 90° for all seven compositions both at 573 and 603 K. Bi–Ag–Sn alloys with 3 and 6 at.% of tin have slightly lower contact angle, while alloy containing 9 at.% of tin has similar contact angle to Ag-Bi eutectic. For Bi–Ag–Zn alloys, no such tendency is observed. Contrary to the results obtained without the flux, the results obtained with the flux show relatively good wetting of copper (contact angles after 30 min ~60°) with both Bi–Ag–Sn and Bi–Ag–Zn alloys. For Bi–Ag–Sn alloys, contact angle decreases with increasing content of tin. For Bi–Ag–Zn alloys, addition of 3 at.% of Zn results in lower contact angle compared to Bi–Ag eutectic; however, further additions of Zn show the opposite effect.

Microstructural characterization of cross sections of solidified samples shows much complex interface between the droplet and the substrate for alloys Bi–Ag with Sn and Zn additions compared to Bi–Ag eutectic. Bi–Ag/Cu couple shows dissolution of copper in the bulk of the solder and increasing concentration of silver toward the interface, but no interlayers can be distinguished. In the case of both ternary alloys, two interlayers between the substrate and the droplet can be distinguished. For all of the samples, segregation of silver from the bulk of the solder toward the substrate was observed.

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References

1. Moser Z, Gąsior W, Pstruś J (2001) J Phase Equilib 22:254
2. Moser Z, Gąsior W, Pstruś J, Zakulski W, Ohnuma I, Liu XJ, Inohana Y, Ishida K (2001) J Electron Mater 30:1120
3. Moser Z, Gąsior W, Pstruś J (2001) J Electron Mater 30:1104
4. Gąsior W, Moser Z, Pstruś J, Krzyżak B, Fitzner K (2003) J Phase Equilib 24:21
5. Gąsior W, Moser Z, Pstruś J (2003) J Phase Equilib 24:504
6. Pstruś J, Moser Z, Gąsior W, Dębski A (2006) Arch Metall Mater 51:335
7. Liu XJ, Inohana Y, Ohnuma I, Kainuma R, Ishida K, Moser Z, Gąsior W, Pstruś J (2002) J Electron Mater 31:1139
8. Moser Z, Gąsior W, Pstruś J, Ishida K, Ohnuma I, Kainuma R, Ishihara S, Liu XJ (2004) Mater Trans 45:652
9. Gąsior W, Moser Z, Pstruś J, Bukat K, Kisiel R, Sitek J (2004) J Phase Equilib 25:115
10. Moser Z, Gąsior W, Pstruś J, Ohnuma I, Ishida K (2006) Int J Mater Res (formerly Z Metallkde) 97:365
11. Kisiel R, Gąsior W, Moser Z, Pstruś J, Bukat K, Sitek J (2004) J Phase Equilib 25:122
12. Gasior W, Moser Z, Pstruś (2004) J Arch Metall Mater 49:155
13. Kisiel R, Gąsior W, Moser Z, Pstruś J, Bukat K, Sitek J (2005) Arch Metall Mater 50:1079
14. Moser Z, Gąsior W, Bukat K, Pstruś J, Kisiel R, Sitek J, Ohnuma I (2006) J Phase Equilib Diff 27:133
15. Ohnuma I, Ishida K, Moser Z, Gasior W, Bukat K, Pstruś J, Kisiel R, Sitek J (2006) J Phase Equilib Diff 27:245
16. Kisiel R, Bukat K, Sitek J, Gąsior W, Moser Z, Pstruś J (2007) Global SMT Packag 7:34
17. Moser Z, Gąsior W, Bukat K, Pstruś J, Kisiel R, Sitek J, Ishida K, Ohnuma I (2007) J Phase Equilib Diff 28:433
18. Bukat K, Sitek J, Kisiel R, Moser Z, Gąsior W, Kościelski M, Pstruś J (2008) Solder Surf Mt Tech 20:9
19. Gąsior W (2006) Arch Metall Mater 51:317
20. Moser Z, Gąsior W, Dębski A, Pstruś J (2007) SURDAT—database of lead-free soldering materials. IMMS PAS, ISBN 83 60768 01 03. http://imim.pl/surdat-database
21. Matsumoto T, Nogi K (2008) Annu Rev Mater Res 38:251
22. Song JM, Chuang HY, Wu ZM (2006) J Electron Mater 35:1041
23. Rettenmayr M, Lambracht P, Kempf B, Graff M (2005) Advance Eng Mater 7:965
24. Song JM, Chuang HY, Wen TX (2007) Metal Mater Trans A 38:1371
25. Song JM, Chuang HY, Wu ZM (2007) J Electron Mater 36:1516
26. Sobczak N, Sobczak J, Nowak R, Kudyba A, Darlak P, Mikulowski B, Wojciechowski A (2005) J Mater Sci 40:2547. doi:10.1007/s10853-005-1990-z
27. Kim DG, Jang HS, Jung SB (2005) J Mater Sci Mater Electron 16:523
28. Lee YG, Duh JG (1998) J Mater Sci 33:5569. doi:10.1023/A:1004499728840
29. Hwang JS (2001) Environmental friendly electronics: lead-free technology. Electrochemical Publications Ltd, ISBN 0 901150 40 1
30. Liu CY, Tu KN (1998) J Mater Res 13:37. doi:10.1557/JMR.1998.0006
31. Wang HQ, Ma X, Gao F, Qian YY (2006) Mater Chem Phys 99:202
32. Baker H et al (ed) (1990) Alloy phase diagrams, ASM handbook, vol 3. ASM International, ISBN 0 87170 381 5