A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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K. BUKAT*, Z. MOSER**, W. GĄSIOR**, J. SITEK*, M. KOŚCIELSKI*, J. PSTRUŚ**

TRENDS IN WETTABILITY STUDIES OF Pb-FREE SOLDERS. BASIC AND APPLICATION. PART II. RELATION BETWEEN SURFACE TENSION, INTERFACIAL TENSION AND WETTABILITY OF LEAD-FREE Sn-Zn AND Sn-Zn-Bi-Sb ALLOYS

KIERUNKI BADAŃ ZWILŻALNOŚCI LUTOWI BEZOŁOWIOWYCH. BADANIA PODSTAWOWE I APLIKACYJNE. CZĘŚĆ II. KORELACJE POMIĘDZY NAPIĘCIEM POWIERZCHNIOWYM, NAPIĘCIEM MIĘDZYFAZOWYM I ZWILŻALNOŚCIĄ BEZOŁOWIOWYCH STOPÓW Sn-Zn I Sb-Zn-Bi-Sb

The surface tension of a molten alloy plays an important role in determining the wetting behavior of solders. The systematic measurements of surface tension by the maximum bubble pressure method, in Ar + H_2 atmosphere, were performed at the Institute of Metallurgy and Materials Science, Polish Academy of Sciences in Krakow (IMIM PAS). In parallel, the surface tension and interfacial tension were measured by the Miyazaki method, using wetting balance technique, in air and in N_2 atmospheres, at the Tele and Radio Research Institute (ITR) in Warsaw. Both of these methods were used for a comparative analysis of the Sn-Zn and Sn-Zn-Bi-Sb alloys manufactured by Institute of Non-Ferrous Metal in Gliwice (INMET INM). The authors would like to know how the addition of Bi and Sb elements to the eutectic Sn-Zn alloy influences the changes of the surface tension and wettability on copper substrate. It has been found that addition of Bi and Sb to the Sn-Zn alloy decreases surface tension. A more evident decreasing tendency of surface tension was noted in wetting balance(meniscographic) measurements, especially of an interfacial tension measured in presence of a flux. The results of the surface tension from both methods are comparable. Strong interaction between Bi and Sb elements in the Sn-Zn-Bi-Sb alloys was demonstrated by variance analysis (ANOVA). The wettability results of investigated zinc alloys on Cu substrate were unexpected: the better wettability of eutectic Sn-Zn alloy than this modified by addition of Bi and Sb Sn-Zn was obtained. It appeared therefore that modified Sn-Zn-Bi-Sb solders were useless for soldering from technological point of view. So, the next wettability investigation will concentrate on new Sn-Zn-Bi alloy compositions with small amount of Zn. The surface tension of this alloy is not known.

Napięcie powierzchniowe ciekłych stopów odgrywa ważną rolę w zwilżalności lutowi. Systematyczne badania napięcia powierzchniowego za pomocą metody maksymalnego ciśnienia w pęcherzykach gazowych w atmosferze argonu z wodorem zostały przeprowadzone w Instytucie Metalurgii i Inżynierii Materiałowej Polskiej Akademii Nauk (IMIM PAN) w Krakowie. Równolegle prowadzono pomiary napięcia powierzchniowego i napięcia międzyfazowego za pomocą metody Miyazaki techniką meniskograficzną w powietrzu i w atmosferze azotu w instytucie Tele i Radiotechnicznym w Warszawie. Wyniki z obu instytutów zostały porównane dla stopów Sn-Zn i Sn-Zn-Bi-Sb wykonanych w Instytucie Metali Nieżelaznych w Gliwicach (INMET IMN). Celem tych badań było wykazanie w jakim stopniu dodatki Bi i Sb do eutektyki Sn-Zn wpływaja na zmiany napięcia powierzchniowego i zwilżalności na podkładach z miedzi. Wykazano, że dodatki Bi i Sb do stopów Sn-Zn obniżają napięcie powierzchniowe. Znacznie wyraźniejszą tendencję obniżania napięcia powierzchniowego zanotowano w pomiarach meniskograficznych, a w szczególności w napięciu międzyfazowym z użyciem topnika. Wyniki napięcia powierzchniowego z obu metod są porównywalne.

1. Introduction

The new lead-free solders characterize with higher surface tension than Sn-Pb solder, traditionally used for soldering in electronics. The main trend of the investigations is to find out how to decrease the surface tension by addition to Sn different elements such Ag, Cu, Bi, Sb, In, Zn [1, 2, 3, 4]. The Sn-Ag-Cu alloys are currently used in soldering praxis but properties of new lead-free solders are still under consideration, especially their surface tension, because this property plays an important role in determining the wetting behavior of solders.

The systematic measurements of surface tension by the maximum bubble pressure method in Ar + H_2 atmo-

* TELE AND RADIO RESEARCH INSTITUTE, 03-450 WARSZAWA, 11 RATUSZOWA STR., POLAND
** INSTITUTE OF METALLURGY AND MATERIALS SCIENCE, POLISH ACADEMY OF SCIENCES 30-059 KRAKÓW, 25 REYMONTA STR., POLAND

sphere, and parallel measurements of the surface tension and interfacial tension by the Miyazaki method using wetting balance technique [5], in air and in N_2 atmospheres, were performed at the IMIM PAS in Krakow and at the ITR in Warsaw. The previous results of the comparative investigations of the Sn-Ag-Cu-Bi and Sn-Ag-Cu-Bi-Sb alloys have shown the tendency of decreasing the surface tension and interfacial tension measured by both methods with increasing amounts of Bi and Sb elements. Additionally it was shown that the results are independent of the atmosphere of measurement [4, 6].

In this study, we investigated the surface tension, interfacial tension and wettability on Cu of quaternary alloys obtained by addition Bi and Sb elements to the Sn-Zn solders with 9.9 or 7.4 mass % of Zn element. These alloys were manufactured by INMET IMN which creates, together with IMIM PAS and ITR, the national network "Advanced soldering materials". Two ranges of Bi and Sb content in Sn-Zn-Bi-Sb were considered:
1 and 2 mass %. In zinc-containing alloys oxidation occurs quickly. It forced us to measure surface tension and interfacial tension by the wetting balance technique in inert atmosphere (N_2). We observed that the Sn-Zn-Bi-Sb alloys show the same tendency of decreasing the surface tension and interfacial tension with increasing amounts of Bi and Sb like Sn-Ag-Cu-Bi and Sn-Ag-Cu-Bi-Sb alloys, which were investigated earlier [7]. It was also shown that this effect is not sufficient to improve their wettability on Cu substrate. The influence of added elements on these properties was evaluated by the analysis of variance (ANOVA). The strong interaction between Bi and Sb elements in Sn-Zn-Bi-Sb alloys was found. This will be the subject of the other publication [8].

The melting temperature of the eutectic Sn9Zn alloy (199°C) is very close to the Sn-Pb alloy (183°C). Compared to Sn-Pb this alloy shows higher fatigue resistance. These advantages suggest the application of Sn-Zn alloy as a solder in consumer electronics especially for soldering components that cannot tolerate high temperatures. But zinc-containing alloys are prone to oxidation and often poor wetting ability occurs during reflow soldering currently used in electronics [9,10]. To improve wettability several elements are added to the eutectic Sn-Zn alloy. The Sn8Zn3Bi alloy which has a melting range 189 to 199°C is the most popular in Japan (Senju Metal, Nihon Genma, Nihon Handa) [9]. The advantages of this alloy are: very low cost and lowering of a soldering temperature which influences the energy saving during soldering processes. Disadvantage is that it is prone to oxidation. Also the Indium Co., global solders producer, manufactures zinc-containing systems: Sn-In8.8-Zn7.6 (mp. 181-187°C) and Sn5.5Zn4.5In3.5Bi (mp. 174-186°C). It should be pointed out that very little information is available on their wettability on copper substrate.

Alloys based on the eutectics Sn-Zn are under the main subject of investigations. Non eutectic alloys with content of the Zn element above 9 mass % causes the increase of the melting temperature [11]. Xiuqin Wei at al. [12] concluded, after investigation the Sn6.5Zn alloy, that its properties are similar to the eutectic Sn-Zn alloy. They noticed also the lower melting temperature and better wetting properties of this alloy.

The Sb element addition to SAC alloys improves the mechanical properties, the best results were found for 1 mass % of Sb [13]. A.Z. Miric [14] described the 65Sn25Ag10Sb alloy (known as Motorola J Alloy), which demonstrates very weak wettabillity. He suggests that the high content of Sb and the presence of the Ag_3Sn intermetallic in alloy is responsible for this property.

Wetting properties of solders during soldering processes can be improved by fluxes. Choice of an appropriate flux is a key and critical factor of soldering, production efficiency and solder joints reliability of printed board assemblies. Fluxes are used for removing oxides and other contaminations from the surface before soldering and they can decrease the surface tension of solders. Higher chemical activity of the flux creates better wetting properties but can cause corrosion of the soldered joints. For zinc-containing solders several types of fluxes were used for investigation: pure rosin (R), rosin middle activated fluxes (RMA), rosin-free organic fluxes (OA) activated by dimethylammonium chloride (DMA HCl) [12, 15-22].

The aim of this article is the investigation of the wetting properties of selected Sn-Zn and Sn-Zn-Bi-Sb alloys. Based on our own experiences with advantage of Bi and Sb elements added to the SAC solders, we decided to add Bi and Sb elements to the Sn-Zn alloy with two levels of Zn content: 9.9 and 7.4 mass %. For such lead-free solders we did not find information on surface tension, interfacial tension and wettability on copper substrate. An investigation was carried out using our own elaborated fluxes RA and OA types.

2. Wetting balance studies

Surface tension measurement

The Miyazaki method using the wetting balance technique was applied for testing of surface tension of liquid zinc-base solders [5]. The principle of the method consists in immersion of unwettable sample into molten solder bath under the fixed speed, temperature and atmosphere. The vertical force acting on the sample was measured and the surface tension was calculated using Laplace equation:

$$F_r = \gamma_{LV} \cdot l \cdot \cos\theta - \rho \cdot V \cdot g, \tag{1}$$

where:
F_r – measured wetting force, γ_{LV} – surface tension between liquid solder and air phases, l – circumference of immersed part of the sample, ρ – density of the molten alloy in the bath, V – volume of the forced solder equal the volume of the immersed sample (V = P · h, where: P – cross-sectional area of the sample, h – immersion depth of the sample, g – acceleration of gravity (9.81 m/s^2).

The investigations were carried out using unwettable politetrafluoroethylene (PTFE) coupons in air and inert N_2 atmospheres in two temperatures 230°C and 250°C.

TABLE 1

Surface tension of the Sn-Zn-Bi-Sb alloys with ~ 9Zn mass %

Surface tension [mN/m]				Alloy composition Mass %	
Air		N_2			
230°C	250°C	230°	C 250°C	Bi	Sb
617 ± 19	540 ± 21	487 ± 16	469 ± 4	0	0
611 ± 12	617 ± 13	484 ± 11	488 ± 12	1.17	1.13
617 ± 17	411 ± 5	477 ± 6	407 ± 10	2.20	1.18
631 ± 18	553 ± 23	499 ± 10	456 ± 25	1.08	2.45
576 ± 19	589 ± 5	460 ± 28	447 ± 25	2.27	2.17

TABLE 2

Surface tension of the Sn-Zn-Bi-Sb alloys with ~ 7Zn mass %

Surface tension [mN/m]				Alloy composition Mass %	
Air		N_2			
230°C	250°C	230°C	250°C	Bi	Sb
655 ± 6	597 ± 10	510 ± 7	470 ± 7	0	0
581 ± 45	599 ± 16	442 ± 12	458 ± 32	1.07	1.24
601 ± 8	575 ± 30	490 ± 10	445 ± 10	2.25	1.25
558 ± 27	597 ± 30	429 ± 15	428 ± 12	1.06	2.18
559 ± 15	564 ± 23	418 ± 8	446 ± 21	2.30	2.20

The results depend on test temperature and atmosphere (Table 1 and 2). Higher temperature and inert atmosphere decrease the measured surface tension of the zinc-containing alloys. The results of the surface tension of the Sn9.9Zn in air atmosphere are higher than in N_2 for both temperatures of the tests. Very similar results were obtained by J.H. Vincent at al. [23]. The surface tension results measured on PTTF coupons at 250°C using wetting balance technique were the following: in air 518 mN, in N_2 487 mN.

Interfacial tension measurement

The Miyazaki method using the meniscographic technique was also applied to interfacial tension measurements of zinc-base alloys. In this case, an unwettable sample before measurement was immersed into liquid flux, next into the molten solder bath under the fixed speed, temperature and atmosphere. The organic flux (OA) activated by mixture of aliphatic ammonium chlorides was used for tests.

TABLE 3

Interfacial tension of the Sn-Zn-Bi-Sb alloys with ~ 9 Zn mass %

Surface tension [mN/m]				Alloy composition Mass %	
Air		N_2			
230°C	250°C	230°C	250°C	Bi	Sb
460 ± 7	462 ± 7	455 ± 7	460 ± 5	0	0
435 ± 10	440 ± 11	429 ± 9	443 ± 2	1.17	1.13
424 ± 3	420 ± 14	427 ± 14	422 ± 9	2.20	1.18
421 ± 7	425 ± 6	415 ± 11	411 ± 8	1.08	2.45
420 ± 8	429 ± 13	414 ± 7	423 ± 10	2.27	2.17

TABLE 4

Interfacial tension of the Sn-Zn-Bi-Sb alloys with ~ 7% Zn mass %

Surface tension [mN/m]				Alloy composition Mass %	
Air		N_2			
230°C	250°C	230°C	250°C	Bi	Sb
452 ± 4	455 ± 5	451 ± 3	462 ± 4	0	0
436 ± 15	445 ± 5	434 ± 7	437 ± 4	1.07	1.24
429 ± 5	432 ± 10	431 ± 8	437 ± 7	2.25	1.25
439 ± 2	436 ± 3	431 ± 8	434 ± 6	1.06	2.18
422 ± 6	430 ± 6	420 ± 6	422 ± 9	2.30	2.20

The presence of flux causes the expected decrease of interfacial tension of alloys compared to their surface tension. The lowest values of interfacial tension were obtained for the alloys with maximum content of added Bi and Sb measured at 250°C (Table 3 and 4). Furthermore, we observed the strong approach of the obtained results (411 - 445 mN/m) to the results for Sn-Pb alloy: 406 mN/m (Table 10). It suggests a qualitative improvement in wettability of zinc containing alloys with Bi and Sb at the maximum concentration.

3. Comparison of surface tension and interfacial tension from different methods for Sn-Zn and Sn-Zn-Bi-Sb alloys

The results of surface tension of Sn-Zn and Sn-Zn-Bi-Sb obtained by the maximum bubble pressure method (Ar + H_2 atm.) as well as by modeling Butler's method described in details in Part 1 [7], were compared with surface tension and interfacial tension from Miyazaki's method. We compare only the results obtained in inert atmosphere at 250°C, the temperature mostly used for soldering in electronics (Table 5 and Fig. 1 and 2).

TABLE 5

Comparison of surface tension and interfacial tension from different methods. Temperature 250°C (523 K), inert atmosphere

Surface tension σ_{LV} (523 K) [mN/m]			Interfacial tension (Miyazaki method) σ_{LF} (523 K) [mN/m] flux+N_2	Alloy composition Mass %		
Bubble pressure method Ar + H_2	Calculated from Butler's method	Miyazaki method N_2		Zn	Bi	Sb
552 ± 8	550.5	469 ± 4	460 ± 5	9.92	0	0
545 ± 4	537.5	488 ± 12	443 ± 2	9.43	1.17	1.13
544 ± 8	530.6	407 ± 10	422 ± 9	9.55	2.20	1.18
545 ± 4	533.3	456 ± 25	411 ± 8	9.54	1.08	2.45
534 ± 4	425.0	447 ± 25	423 ± 10	9.03	2.27	2.17
550 ± 4	547.8	470 ±7	462±4	7.41	0	0
542 ± 6	527.2	458 ± 32	437 ± 4	6.99	1.07	1.24
538 ± 3	535.0	445 ± 10	437 ± 7	7.00	2.25	1.25
569 ± 3	531.2	428 ± 12	434 ± 6	6.76	1.06	2.18
533 ± 3	522.4	446 ± 21	422 ± 9	6.90	2.30	2.20

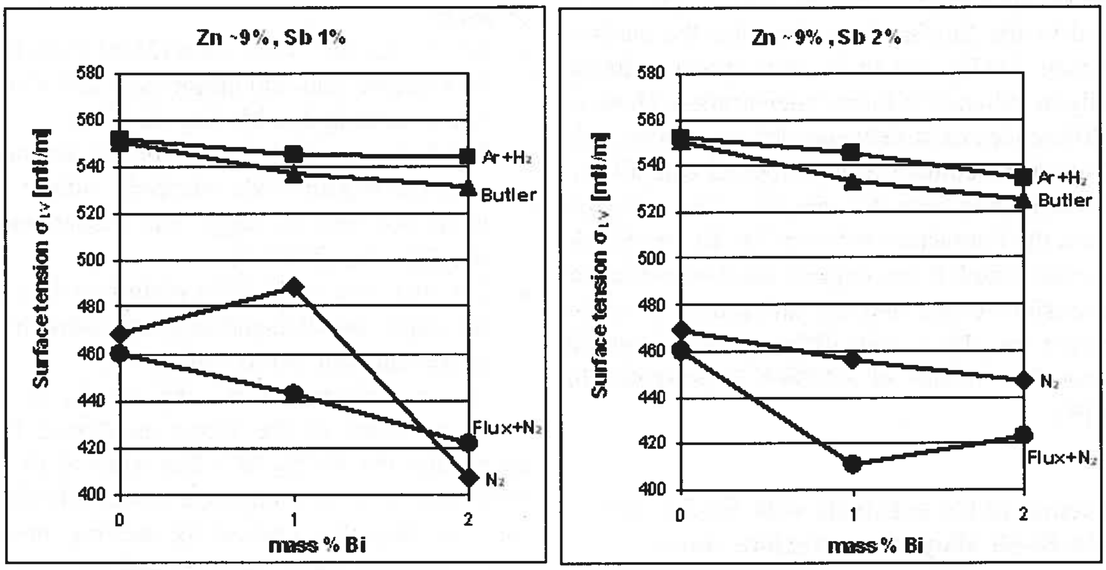

Fig. 1. Comparison of surface tension σ_{LV} and interfacial tension σ_{LF} from different methods of Sn-Zn-Bi-Sb with ~ 9 mass % of Zn

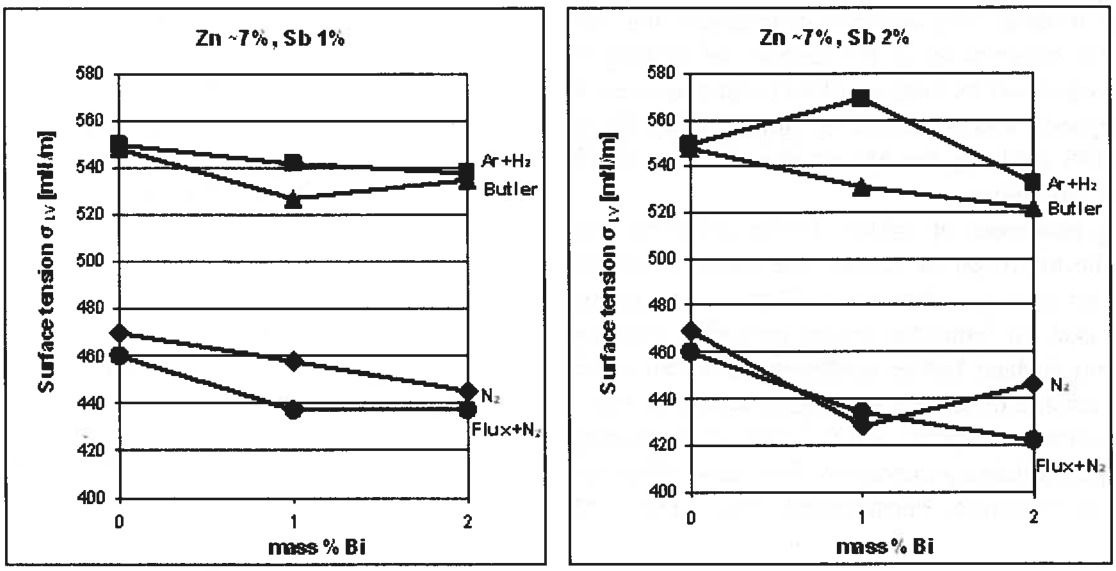

Fig. 2. Comparison of surface tension σ_{LV} and interfacial tension σ_{LF} from different methods of Sn-Zn-Bi-Sb with ~ 7 mass % of Zn

After analyzing the comparison between surface tensions and interfacial tensions, it should be noticed that obtained results were arranged in logical order: from highest results of surface tensions from maximum bubble pressure method, slightly lower from wetting balance to the lowest values of the interfacial tension. The differences of surface tensions measured by different methods result from different atmospheres: maximum bubble pressure method in Ar + H_2 reducing atmosphere and meniscographic technique in inert N_2 atmosphere. The differences of surface tension and interfacial tension measured by the same Miyazaki method and under the same atmosphere, result from the presence of active flux during interfacial tension tests.

The values of surface tension calculated from Butler's model are the closest to the experimental data from maximum bubble pressure method. The same character of changes was observed earlier for the SAC alloys with various additions of Bi [24].

The experimental results indicate that Bi and Sb elements added to the Sn-Zn alloys decrease the surface tensions in both Ar+H_2 and in N_2 atmospheres almost proportionally to increase of their concentration. However, several differences exist between surface tension values for maximum Bi content in investigated zinc alloys. This conclusion results from the analysis of the variance (ANOVA), and the interaction between Zn, Bi and Sb elements was established. It can explain the disturbance of the surface tension results and the differences between results obtained for alloys with different concentration of Zn element. The details of ANOVA is presented in publication [8].

4. Interaction of Cu substrate with Sn-Zn and Sn-Zn-Bi-Sb alloys using various fluxes

The investigations of wetting of zinc-containing solders on copper substrate were carried out using the wetting balance method. This method is a dynamic one, and allows for the observation of the kinetics of wetting of the surface under test by molten solder in the presence of flux. Investigation was conducted by Solderability Tester Menisco ST88 made by the Metronelec, France, which has an inert gas option.

Wetting properties of solders during soldering processes can be improved by fluxes. The choice of an efficient flux for wetting substrate by alloy is a key factor. Fluxes are used for removing oxides and other contaminations from surface before soldering, they can affect the surface tension of solders causing its decrease. Fluxes should warrant adequate activity without increasing the risk of post soldering corrosion. Zinc-base alloys are vulnerable to oxidation. Furthermore, zinc reacts with alkaline and acidic solutions, reducing its antioxidation activity [9]. The wetting results of Sn9.9Zn alloy on Cu in presence of fluxes of several compositions were the base for the flux selection. Criteria and requirements for wetting after this test are following:

- **wetting time** τ_z [s], the time measured from the moment when the test coupon contacts the surface of the solder bath until the contact angle reaches 90° (only buoyancy force acts on the board). Requirement: $\tau_z \leqslant 2$ s,
- **wetting force** $F_2 \geqslant 2/3$ of the reference wetting force (F_{ref}) calculated from formula (2)

$$F_{ref} = \gamma_{LF} \cdot l \cdot \cos\ \theta - \rho \cdot V \cdot g. \qquad (2)$$

Requirement: $F_2 \geqslant 6.25$ mN

- wetting angle requirement: $\leqslant 55°$
- wetting stability (co to jest – wytłumaczyć) requirement: $\geqslant 0.8$

For wetting tests several compositions of fluxes were prepared:

- RMA type flux: high solid (25%) rosin flux activated by benzoic acid and adipic acid and also by diethylammonium hydrochloride (K 83/1),
- RA flux: low solid (2%) rosin flux activated by blend of dicarboxylic acids -succinic, adipic and glutaric acids and also by ethyl- and diethylammonium hydrochloride, (TG4+3).
- OA flux: low solid (3%) rosin-free flux activated by the ethyl- and diethyammonium hydrochloride in izopropyl alcohol (RNH_2·HCl).

After examination wetting results of Sn9.9Zn on Cu in presence of the above mentioned fluxes it was found that the RNH_2·HCl flux yielded the results that were nearest to the required values (Table 6 and Fig. 3). This flux was chosen for wetting investigation of zinc-containing alloys with Bi and Sb additions.

TABLE 6

Sn9.9Zn alloy wetting results on Cu in the presence of selected fluxes

Type of flux	Flux name	Temp. [°C]	Atmosphere	τ_z [s]	F_{w2} [mN]	F_{wmax} [mN]	Contact angle θ_3 [°]	Wetting stability F_5/F_{10}
RMA	K-83/1	230	N_2	1,01	2,02 ± 0,25	2,08 ± 0,25	77 ± 1	0,99
RA	TG-4+3			0,81	3,95 ± 0,53	5,44 ± 0,21	62 ± 3	0,89
OA	RNH2·HCl			0.51	3.56 ± 1.27	5.61 ± 0.45	62 ±6	0.95

F_2^* – wetting force measured in 2 second,

F_{max}^{**} – maximum measured wetting force,

θ_3^{***} – wetting angle measured in 3 second of test.

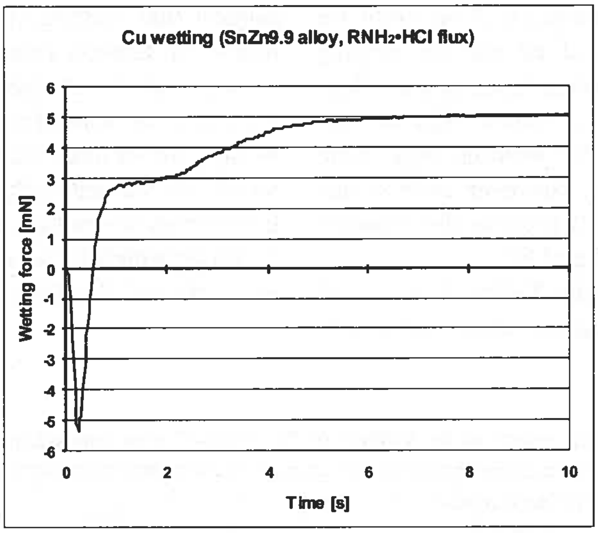

Fig. 3. Wetting balance curve obtained for Cu coupon wetted by SnZn9.9 alloy in the presence of the RNH_2·HCl flux

The experimental conditions of the wetting investigations of the Sn-Zn-Bi-Sb alloys by meniscographic method were as follow:

1 Atmosphere: Nitrogen,

2 Cu coupons: 6 mm × 25 mm × 0,2 mm cleaned in H_2SO_4 and HNO_3 acids mixture than rinsing in distilled water and drying,

3 Flux: RNH_2∘HCl,

4 Immersion depth: 4 mm,

5 Immersion time 10 s,

6 Immersion speed: 21 mm/s,

7 Test temperature: 230°C,

TABLE 7

Wetting results of the Sn-Zn-Bi-Sb alloys with ~ 9 Zn mass % on Cu at 230°C, inert atmosphere

Flux	τ_z [s]	Fw 2 [mN]	Fw max [mN]	Contact angle θ_3 [°]	Wetting stability F_5/F_{10}	Alloy element Mass %	
						Bi	Sb
RNH_2∘HCl	0.51	3.56 ± 1.27	5.63 ±0.45	62 ± 6	0.95	–	–
	0.94	1.53 ± 0.31	2.31 ± 0.21	80 ± 2	0.55	1.17	1.13
	0.73	1.30 ± 0.21	3.03 ± 0.07	81 ± 1	0.61	2.20	1.18
	1.18	1.39 ± 0.79	2.49 ± 0.39	81 ± 4	0.58	1.08	2.45
	5.58	-0.40 ± 0.34	1.13 ± 0.34	93 ± 2	0.24	2.27	2.17

TABLE 8

Wetting results of the Sn-Zn-Bi-Sb alloys with ~7 Zn mass % on Cu at 230°C, inert atmosphere

Flux	τ_z [s]	F_{w2} [mN]	F_{wmax} [mN]	Contact angle θ_3 [°]	Wetting stability F_5/F_{10}	Alloy composition Mass %	
						Bi	Sb
$RNH_2{\circ}HCl$	0.79	1.81 ± 0.58	4.15 ± 0.38	74 ± 3	0.86	–	–
	1.24	0.22 ± 0.39	0.55 ±0.29	89 ±2	0.47	1.07	1.24
	0.92	0.82 ± 0.20	1.76 ± 0.18	84 ±1	0.52	2.25	1.25
	>10	-0.35 ± 0.12	-0.32 ± 0.18	93 ±1	1.00	1.06	2.18
	>10	-0.52 ± 0.31	-0.50 ± 0.32	94 ± 2	0.96	2.30	2.20

The wetting time on Cu substrate for most quaternary zinc alloys passed requirement (⩽ 2 s). Only for alloys with the highest amount of Bi and Sb wetting time exceeds the upper limit allowed. None of the alloys fulfill wetting force requirement (> 6 mN). The best results for wetting force and also for wetting angle were obtained for initial Sn9.9Zn alloy. However, even in this case the wetting angle value (62°) exceeds the required level for soldering 55° (Tables 7 and 8).

As it was shown earlier in the Tables 3 and 4 interfacial tensions of the investigated alloys were considerably close to each other (411-445 mN/m) which suggest that wetting properties should be similar. The interfacial tension value of Sn-Pb alloy measured in the same conditions is equal to 406 mN/m (Table 9), i.e. is nearest to the lower level of the Sn-Zn-Bi-Sb values. But wetting forces and calculated contact angles obtained for Sn-Pb are diametrically differ from these for zinc alloys. It confirms the earlier established measure of wettability of alloys which is the not based only on surface tension but it should also take into account contact angle.

TABLE 9

Wetting results of the Sn37Pb on Cu at 230°C, inert atmosphere N_2

Flux	Interfacial tension [mN/m]	τ_z [s]	F_2 [mN]	F_{max}	θ_3	Wetting stability F_5/F_{10}
$RNH_2{\circ}HCl$	406	0.25	7.14±0.15	7.31±0.14	19±5	0.99

5. Discussion

The reason of worse wetting of the Sn-Zn-Bi-Sb alloys on copper substrate was under consideration. Probably the microstructure of investigated alloys and the reactions on zinc alloy/copper interface is responsible for the weak wetting.

J. Hwang [10] noticed that microstructure of the eutectic Sn9Zn alloy first of all consists of Sn phase and eutectic mixture Zn/Sn. The Zn-reach phase is dispersed in β-Sn matrix nearest interfacial phase (close to the interface), and it causes the very easy oxidation of zinc alloy. Only 0.6% Zn can dissolve in Sn matrix in eutectic temperature. Similar Sn-Zn structures were obtained by R. Mayappan [25], however the published value of Zn which can dissolve in β-Sn matrix is somewhat lower (0.09 mass %). The solidification of the alloy in air results in the segregation of Zn element in tin matrix. D.Q. Yu at al. [26] also concluded presence of the Zn-reach phase in the alloy matrix as a significant factor of weak wetting and corrosion properties of zinc-containing alloys. During the wetting process the zinc atoms can easily oxidize on the liquid solder surface causing significantly increased surface tension and decreased wetting properties of the zinc alloy. Not find any JMCs of Cu-SAn like Cu_6Sn_5 and Cu_3Sn.

Y. Nakamura at al. [27] investigated the microstructure of Sn9Zn and $SnZn_9Bi_3$ alloys and found also the intermetallic compounds (IMC) created in reaction with copper. They confirm that the Sn9Zn microstructure consists of Zn large needle-shaped precipitates in the eutectic structure and they also informed that the addition of Bi decreases the Zn precipitation. Two types of IMCs are created during the $SnZn_9Bi_3$ alloy reaction with Cu: thick, Zn-reach IMC layer which grows into solder direction and second, thin IMC layer on Cu substrate. However, IMC creation in Cu-Zn system is not explicitly explained up to now.

Sb addition to Sn-Zn system probably provokes further changes in microstructure and IMCs formation in

Sn-Zn-Bi-Sb alloys. It can be expected that the alloys of low surface tension, close to this of Sn-Pb, can cause wetting disturbances on Cu substrate. Bailey and Watkins [28] noticed better wetting of solid metal by liquid metal when they mutually dissolve or create IMCs.

The zinc atoms from zinc-base alloys diffuse into copper substrate and create the γ-Cu_3Zn_8 intermetallic compound. This compound was found in intermetallic phases of Sn-Zn-In/Cu, Sn-Zn-Al/Cu, Sn-Zn/Cu systems. Not find any IMC_S of Cu-Sn like Cu_6Sn_5 and Cu_3 Sn. Solubility of Zn in Cu is higher than Zn solubility in Sn and Sn solubility in Cu. It provokes creation thick layer of Cu-Zn IMCs on intermetallic phase.

Solubility of Bi in Sn is only 2% at the room temperature. Sb element creates with Sn solid solutions, its solubility in Sn is only 4% at 190°C and 10.5% at 246°C [12]. If Bi and Sb elements occur together, then at first Sb creates solid solution and next the solubility of Bi can take place in a limited range. Growth of the IMC layer depends of the Zn element diffusion into Cu substrate. Bi element controls grains growth of the Zn-reach phase in alloy matrix. This is probably the reason of unexpected disturbance of wetting results of Sn-Zn-Bi-Sb alloys on Cu substrate.

6. Conclusion

Evident decreasing tendency of surface tension of Sn-Zn-Bi-Sb alloys was noted in the wetting balance measurements, especially of an interfacial tension measured in presence of a flux. The surface tension trend of the changing of Sn-Zn-Bi-Sb alloys with the increase of Bi and Sb additions is comparable for the results from maximum bubble pressure method, Miyazaki wetting balance method as well as the Butler modeling. The same conclusion was drawn in earlier investigations of the Sn-Ag-Cu-Bi and Sn-Ag-Cu-Bi-Sb alloys. The mutual interactions between Zn, Bi and Sb elements in the Sn-Zn-Bi-Sb alloys were demonstrated by analysis of the variance. The wettability results of investigated zinc alloys on Cu substrate were unexpected because of the better wettability of eutectic Sn-Zn alloy than Sn-Zn alloys modified by addition of Bi and Sb elements. It appeared that modified lead-free solders were unusable for soldering from technological point of view. Several authors suggest better zinc alloys wettability when the smaller amounts of zinc than eutectic are used. So, the next wettability investigation will focus on new Sn-Zn-Bi alloy compositions with small amounts of Zn element for which the surface tension results are unknown.

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