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
Volume 51 2006 Issue 4

G. WNUK*, J. ROMANOWSKA*

INFLUENCE OF Cu AND Sn ON THE ACTIVITY OF Bi IN Cu-Sn-Bi LIQUID ALLOYS

WPŁYW Cu I Sn NA AKTYWNOŚĆ Bi W CIEKŁYCH STOPACH Cu-Sn-Bi

The activies of Bi in liquid dilute Cu-Sn-Bi alloys were determined by the method of equilibrium saturation with metal vapour, at T= 1373K. As the method of equilibrium saturation is a comparative one, it is necessary to have an appropriate reference solution. The Cu-Bi alloy was accepted as the reference one. The interaction parameters ε_{Bi}^{Cu} and ε_{Bi}^{Sn} were determined by the least squares method. The experimental data of ε_{Bi}^{Cu} and ε_{Bi}^{Sn} were compared with data calculated on the basis of the "central atom" theory.

Keywords: activity, activity coefficient, interaction parameter; Cu-Sn-Bi alloys

Metodą równowagowego nasycania wyznaczono aktywność bizmutu w ciekłych, rozcieńczonych stopach Cu-Sn-Bi w temperaturze 1373 K. Jako że metoda równowagowego nasycania jest metodą porównawczą, konieczne jest stosowanie roztworu wzorcowego. Jako roztwór wzorcowy przyjęto stop Cu-Bi. Metodą najmniejszych kwadratów wyznaczono parametry oddziaływania miedzi i cyny na aktywność bizmutu w stopie Cu-Sn-Bi, ε_{Bi}^{Cu} i ε_{Bi}^{Sn}, a wartości eksperymentalne porównano z wartościami obliczonymi na podstawie modelu atomu centralnego.

1. Introduction

The toxicity of lead containing solders resulted in the EU decision forbiding the use of this metal. Therefore, in the current situation, the most prominent lead-free solders are based on alloys of tin with small amounts of silver and copper, as for example Sn-3.0Ag-0.5Cu (the most prominent in Japan), Sn-3.9Ag-0.6Cu (the most prominent in the USA) and Sn-3.8Ag-0.7Cu (the most prominent in Europe). All these compositions are in the close vicinity of the ternary Ag-Cu-Sn eutectic. Unfortunately, the melting temperatures of these solders are more than 30 degrees higher than that of the traditional Sn-37Pb solders (436 K), which puts additional thermal stress on the various components. In addition, many properties of these new solder materials as well as of the corresponding solder joints are still not fully known, which is the cause of possible reliability concerns. That is why other types of solders on the base of Sn-In, Sn-Bi and Sn-Zn systems are under development. As the microstructures formed during soldering are related to phase equilibria, their knowledge is essential for the correct description of technological processes.

This paper presents results of experimental investigation of the Cu-Sn-Bi alloys at the temperature 1373K carried out by means of the equilibrium saturation method with metal vapour using Cu-Bi alloy as the reference solution. This method can be used for determining the activity of the volatile component in any multicomponent system with one volatile component. In the studied system the volatile component is bismuth. The experimental value of the interaction parameters was compared to the values calculated on the basis of the "central atom" theory.

2. Experimental

The analyzed alloys show considerable differences between vapour pressures of their components at T = 1373 K: p_{Sn}^{*} = 0.16 Pa, p_{Cu}^{*} = $6*10^{-2}$ Pa, p_{Bi}^{*} = 891 Pa [1]. Since the vapour pressure of Bi is much higher than that of the other elements, the activity measurements of Bi were carried out by the comparative method

* RZESZÓW UNIVERSITY OF TECHNOLOGY, 35-959 RZESZÓW, 2 W. POLA STR., POLAND

of equilibrium vapour saturation. This method has been successfully applied for alloys with one volatile component [2-5]. The studied Cu-Sn-Bi solution and the reference solution Cu-Bi were placed inside a closed crucible under a reduced argon pressure and saturated with the vapour of bismuth until equilibrium was reached. At equilibrium state, the activity of Bi is the same in all samples inside a closed system. Unless the activity of Bi in the reference Cu-Bi (l) alloy is known, it is possible to calculate the activity of Bi in the Cu-Sn-Bi (l):

$$a_{Bi(Cu-Sn-Bi)} = a_{Bi(Cu-Sn)} \quad (1)$$

$$\gamma_{Bi(Cu-Sn-Bi)} = x_{Bi(Cu-Bi)} * \gamma_{Bi(Cu-Bi)}/x_{Bi(Cu-Sn-Bi)}, \quad (2)$$

where $x_{Bi(Cu-Bi)}$ and $x_{Bi(Cu-Sn-Bi)}$ denote the equilibrium mole fractions of Bi in Cu-Bi and Cu-Sn-Bi, respectively, and $\gamma_{Bi(Cu-Bi)}$ and $\gamma_{Bi(Cu-Sn-Bi)}$ are the corresponding activity coefficients of Bi.

The experimental set enabled simultaneous measurements of up to a dozen alloys. All the studied alloys had exactly the same conditions of saturation. The number of samples was limited only by the lenght of the isothermal zone in the furnace. The essential part of the apparatus (see figure 1) consisted of a set of graphite blocks with grooves for alloys and orifices which allowed free evaporation and migration of the vapour of Bi inside the system. The set of blocks was placed inside a tube made of extra-fine, creep-resistant steel, which served as a vacuum chamber, placed inside a resistance furnace. The blocks with alloys were placed exactly in the isothermal zone of the furnace. The temperature was measured with a {Ni-(Ni-Cr)} thermocouple. The accuracy of temperature measurements was ±5K. The pressure in the furnace was measured with a vacuum meter APG-010 manufactured by Balzers. The accuracy of pressure measurements was ±10 Pa. Alloys were prepared from elements of purity at least 99.98 mass fraction purchased from Aldrich. Graphite elements were made of EK-412 type graphite purchased from Ringsdorf. The reference and the studied solutions of appropriate compositions were prepared by melting carefully weighed masses of metals at an argon pressure of 0.1 Pa. The compositions of the alloys were determined by the weighing method. The accuracy of weighing was $\pm 10^{-5}$g.

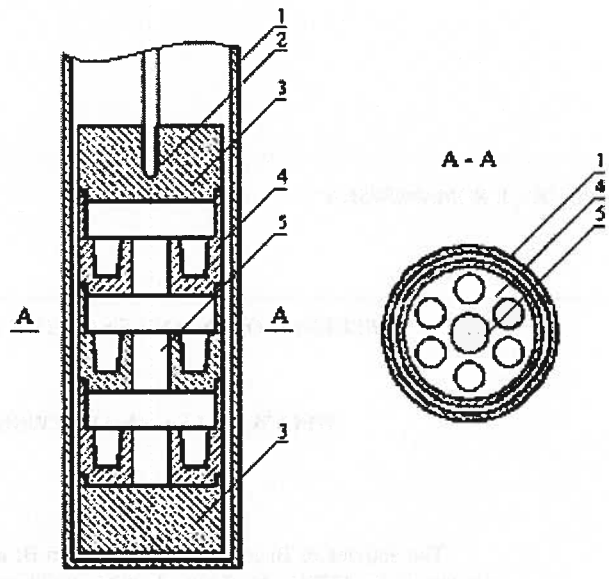

Fig. 1. Apparatus for the equilibrium saturation with metal vapour. 1, vacum chamber; 2, thermocouple and alundum sheath for thermocouple; 3, graphite cover; 4, graphite blocks with grooves for alloys; 5, orifices and a channel which enable free evaporation and migration of vapour; 6, grooves containing mixtures

The quantities determined experimentally, *i.e.* the argon pressure and the equilibration time were meant to ensure the attainment of equilibrium between Bi(g) in the reference and the studied solution. In preliminary tests, in all groves were Cu-Bi alloys of different compositions. The equilibrium state was attained when the mole fraction of Bi was the same in all solutions. The value of argon pressure was specially chosen to be higher than the vapour pressure of bismuth in order to limit the evaporation process to that of bismuth only with a sufficient rate.

It was established, that for the temperature 1373 K, the time necessary to reach equilibrium was 2 hours and the argon pressure was 2.2 kPa.

3. Results

The activities of bismuth in Cu-Sn-Bi at T = 1373 K were determined by the equilibrium saturation method. The activity coefficients of bismuth, γ_{Bi} in this alloy were calculated from equation (2). For describing the activity coefficient of bismuth γ_{Bi} in the reference solution Cu-Bi the equation (3) proposed by Teppo [6], with the following Redlich-Kister parameters was used:

$$^0L_{Bi-Cu} = 23844 - 9.84341*T[J/mol]$$

$$^1L_{Bi-Cu} = -1260.32 - 1.19289*T[J/mol]. \quad (3)$$

TABLE

Experimental values of activity coefficient in the studied and the reference solutions

Nr	The studied Cu-Sn-Bi solution				The reference Cu-Bi solution (after [6])	
	x_{Cu}	x_{Bi}	γ_{Bi}	$\ln\gamma_{Bi}$	x_{Bi}	γ_{Bi}
1.	0.9326	0.0636	2.6774	0.9849	0.0656	2.5962
2.	0.9344	0.0618	2.6562	0.9769	0.0626	2.6189
3.	0.9318	0.0638	2.6707	0.9823	0.0656	2.5962
4.	0.9340	0.0616	2.6611	0.9787	0.0626	2.6189
5.	0.9612	0.0318	2.9596	1.0851	0.0328	2.8669
6.	0.9622	0.0308	2.9631	1.0862	0.0317	2.8769
7.	0.9618	0.0307	1.9290	0.6570	0.0199	2.9874
8.	0.9300	0.0618	2.7581	1.0145	0.0656	2.5962
9.	0.9321	0.0596	2.7535	1.0129	0.0626	2.6189
10.	0.9601	0.0296	3.0566	1.1173	0.0314	2.8803
11.	0.9700	0.0196	3.0300	1.1086	0.0199	2.9874
12.	0.9272	0.0596	2.8587	1.0504	0.0656	2.5962
13.	0.9288	0.0579	2.8316	1.0408	0.0626	2.6189
14.	0.9486	0.0273	3.3045	1.1953	0.0314	2.8803
15.	0.9574	0.0184	3.2285	1.1720	0.0199	2.9874
16.	0.8778	0.0326	4.9545	1.6003	0.0615	2.6275
17.	0.8220	0.0223	7.2338	1.9788	0.0615	2.6275
18.	0.7817	0.0109	8.3224	2.1189	0.0314	2.8803
19.	0.7851	0.0065	9.1639	2.2153	0.0199	2.9874
20.	0.7487	0.0115	8.2150	2.1060	0.0328	2.8669
21.	0.7487	0.0115	7.9716	2.0759	0.0317	2.8769
22.	0.6535	0.0285	5.6739	1.7359	0.0615	2.6275
23.	0.6443	0.0236	8.0411	2.0846	0.0753	2.5239
24.	0.5624	0.0225	4.0130	1.3895	0.0314	2.8803
25.	0.5676	0.0134	4.4144	1.4849	0.0199	2.9874
26.	0.4148	0.0402	2.3406	0.8504	0.0328	2.8669
27.	0.4151	0.0395	2.3135	0.8388	0.0317	2.8769
28.	0.2799	0.1013	1.5961	0.4675	0.0615	2.6275
29.	0.2957	0.0778	2.4438	0.8936	0.0753	2.5239
30.	0.2530	0.0610	1.4972	0.4036	0.0317	2.8769
31.	0.2531	0.0607	1.5518	0.4394	0.0328	2.8669
32.	0.1886	0.1222	1.3225	0.2795	0.0615	2.6275

The results are presented in Table. As the solutions are dilute ones, they can be described by the means of the Wagner equation [7]:

$$\ln\gamma_{Bi} = \ln\gamma^0_{Bi} + \varepsilon^{Bi}_{Bi}x_{Bi} + \varepsilon^{Cu}_{Bi}x_{Cu} \qquad (4)$$

or

$$\ln\gamma_{Bi} = \ln\gamma^0_{Bi} + \varepsilon^{Bi}_{Bi}x_{Bi} + \varepsilon^{Sn}_{Bi}x_{Sn},$$

where γ^0_{Bi} is the activity coefficient of Bi in Cu-Bi at $x_{Bi} \to 0$, $\varepsilon^{Bi}_{Bi} = (\partial\ln\gamma_{Bi}/\partial x_{Bi})$ is the interaction parameter of Bi in Cu-Bi alloy at $x_{Bi} \to 0$, and $\varepsilon^{Cu}_{Bi} = (\partial\ln\gamma_{Bi}/\partial x_{Cu})$ is the interaction parameter of Cu in Cu-Sn-Bi alloy at $x_{Bi} \to 0$ and $x_{Cu} \to 0$ and $\varepsilon^{Sn}_{Bi} = (\partial\ln\gamma_{Bi}/\partial x_{Cu})$ is the interaction parameter of Sn in Cu-Sn-Bi alloy at $x_{Bi} \to 0$ and $x_{Sn} \to 0$.

As $\ln\gamma^0_{Bi(Cu-Sn-Bi)}$ is the limiting value of $\ln\gamma_{Bi(Cu-Sn-Bi)}$ function depending on the direction of achieving the limiting value, it is esential to estimate the copper, bismuth and tin concentrations influence on the limiting value of the bismuth activity coefficient. It has been achieved by choosing points situated in one direction (ϕ = const) and calculating line equations $\ln\gamma_{Bi(Cu-Sn-Bi)} = a + br$, where $r = \sqrt{x^2_{Sn} + x^2_{Bi}}$ for low Sn and Bi concentrations or $r = \sqrt{x^2_{Cu} + x^2_{Bi}}$ for low Cu and Bi concentrations.

Nevertheless, in the case if this study, the small number of experimental points on one direction made it impossible to determine the limiting value of the activity coefficient. Therefore their values were accepted from the binary alloys Cu-Bi [6] and Bi-Sn [8]. Subsequently, using the dependences $x_{Sn} = r\cos\phi$ and $x_{Bi} = r\sin\phi$ the Wagner equation was transformed and the following form was obtained: for low Sn and Bi concentrations:

$$\frac{\ln\gamma_{Bi(Cu-Sn-Bi)} - \ln\gamma^{0}_{Bi(Cu-Bi)}}{r} = \varepsilon^{Bi}_{Bi}\cos\phi + \varepsilon^{Sn}_{Bi}\sin\phi \quad (5)$$

for low Cu and Bi concentrations:

$$\frac{\ln\gamma_{Bi(Cu-Sn-Bi)} - \ln\gamma^{0}_{Bi(Sn-Bi)}}{r} = \varepsilon^{Bi}_{Bi}\cos\phi + \varepsilon^{Cu}_{Bi}\sin\phi \quad (6)$$

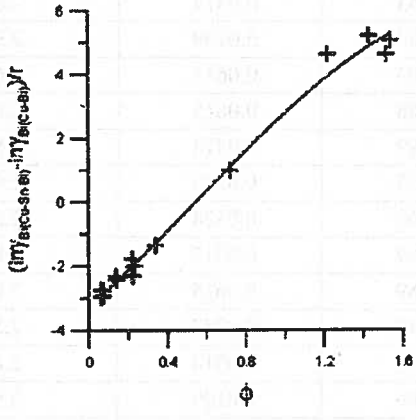

Fig. 2. The $(\ln\gamma_{Bi(Cu-Sn-Bi)} - \ln\gamma^{0}_{Bi(Cu-Bi)})/r = \varepsilon^{Bi}_{Bi}\cos\phi + \varepsilon^{Sn}_{Bi}\sin\phi$ dependence for low Bi and Sn concentrations

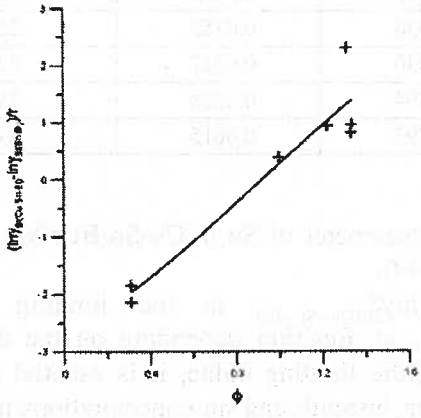

Fig. 3. The $(\ln\gamma_{Bi(Cu-Sn-Bi)} - \ln\gamma^{0}_{Bi(Sn-Bi)})/r = \varepsilon^{Bi}_{Bi}\cos\phi + \varepsilon^{Cu}_{Bi}\sin\phi$ dependence for low Cu and Bi concentrations

The left sides of the equations (5) and (6) were calculated for each experimental point and the interaction parameters ε^{Bi}_{Bi} and ε^{Sn}_{Bi} or ε^{Cu}_{Bi} were calculated by means of the least-squares method. The results are presented in figures 2 and 3. On the basis of the experimental results of the studied alloy the following equations have been obtained: for the low Bi and Sn concentrations:

$$ln\gamma_{Bi(Cu-Sn-Bi)} = 1.159 - 3.240x_{Bi(Cu-Sn-Bi)} + 5.383x_{Sn(Cu-Sn-} \quad (7)$$

for the low Bi and Cu concentrations:

$$ln\gamma_{Bi(Cu-Sn-Bi)} = 0.191 - 2.715x_{Bi(Cu-Sn-Bi)} + 2.070x_{Cu(Cu-Sn-} \quad (8)$$

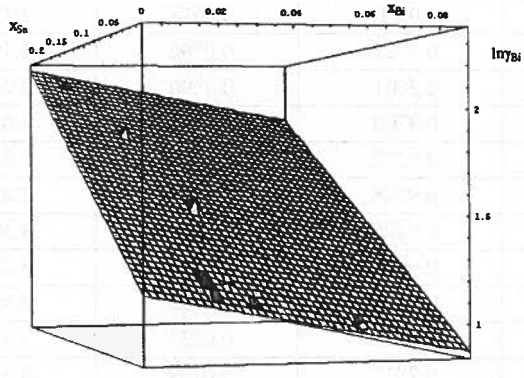

Fig. 4. The surface calculated on the basis of equation 7 and experimental points for low Sn and Bi concentrations

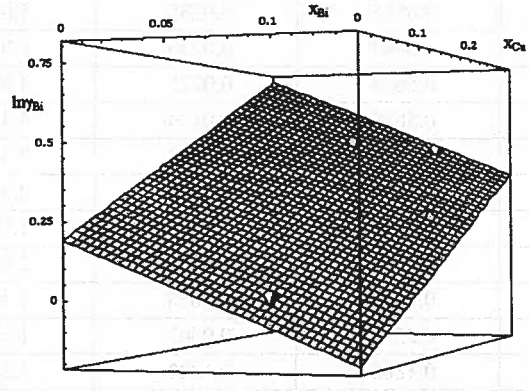

Fig. 5. The surface calculated on the basis of equation 8 and experimental points for low Cu and Bi concentrations

Figures 4 and 5 show unequivocally that equations 7 and 8 describe experimental points in a sufficient way, as most of the experimental points lie on the surfaces and deviations of few of them are not significant ones.

4. Discussion

As it has not been found any experimental data for the Cu-Sn-Bi alloys, interaction parameters values $\varepsilon^{Sn}_{Bi} = 5.383$ and $\varepsilon^{Cu}_{Bi} = 2.07$ obtained experimentally were compared with values calculated on the basis of the "central

atom theory" [9], which presents the ternary interaction coefficient in terms of binary coefficients:

$$\varepsilon_{Bi}^{Sn} = \ln \gamma^{0}_{Sn(Sn-Bi)} - \ln \gamma^{0}_{Sn(Cu-Sn)} - \ln \gamma^{0}_{Bi(Cu-Bi)} \quad (9)$$

$$\varepsilon_{Bi}^{Cu} = \ln \gamma^{0}_{Cu(Cu-Bi)} - \ln \gamma^{0}_{Cu(Cu-Sn)} - \ln \gamma^{0}_{Bi(Sn-Bi)} \quad (10)$$

Values of binary coefficients were calculated on the basis of the literature data [6, 8, 10].

Although calculated values of interaction parameters ε_{Bi}^{Sn} = 2.7 and ε_{Bi}^{Cu} = 1.7, differ from the experimental ones (5.383 and 2.07), the difference is not a significant one and both of them are positive. Therefore the experimental results presented above may be a good basis for the further description of thermodynamic and technological properties of the Cu-Sn-Bi alloy and their usage for soldering.

5. Conclusions

Using the vapour saturation method the Bi activities in Cu-Sn-Bi dilute solutions at the temperature 1373K were measured. The interaction parameters were calculated on the basis of the experimental results and by the use of the "central atom" theory. This method allows the calculation of the ternary interaction parameter basing on binary alloy properties.

Received: 20 September 2006.

REFERENCES

[1] O. Kubaschewski, C. Alcock, Metallurgical Thermochemistry, Pergamon Press, Oxford, 1979.
[2] J. Romanowska, T. Pomianek, G. Wnuk, Arch. of Metallurgy **46**, 3, 255-259 (2001).
[3] G. Wnuk, J. Romanowska, T. Pomianek, J. Chem. Thermodynamics **35**, 711-717, (2003).
[4] B. Onderka, T. Pomianek, J. Romanowska, G. Wnuk, J. Wypartowicz, Archives of Metallurgy and Materials **49**, 1, 143-153 (2004).
[5] G. Wnuk, J. Romanowska, Archives of Metallurgy and Materials **49**, 4, 917-925 (2004).
[6] O. Teppo, J. Niemwela, P. Taskinen, Thermochimica Acta **173**, 137-150 (1990).
[7] K. Wagner, Thermodynamics of alloys Addison-Wesley Reading, Mass. 1952.
[8] D. V. Malakhov, X. L. Liu, I. Ohnuma, K. Ishida, Journal of Phase Equilibria **21**, 6, 514-520, (2000).
[9] C. H. Lupis, J. F. Elliott, Acta Metallurgica **15**, 265-276 (1967).
[10] T. Jantzen, P. J. Spencer, Calphad **22**, 3, 417-434 (1998).