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EXPERIMENTAL STUDY ON THERMODYNAMICS OF THE Cu-Ni-Sn-Zn SYSTEM

BADANIA TERMODYNAMICZNE UKŁADU Cu-Ni-Sn-Zn

The urgent need of finding new, non toxic, high temperature solders caused the abundance of research of multicomponent systems, as to find new materials that could substitute lead-containing solders. This work presents the results of thermodynamic research of Cu-Ni-Sn-Zn system, that is the Zn activity measurements by the means of the vapour saturation method and interaction parameters calculations. These experimental results enable phase diagram calculation in the frame of the COST action MP0602.

Keywords: activity, activity coefficient, interaction parameter, Cu-Ni-Sn-Zn alloys

Konieczność znalezienia nowych bezołowiowych materiałów na wysokotemperaturowe stopy lutownicze spowodowała znaczny rozwój badań nad stopami wieloskładnikowymi w celu znalezienia materiału, który mógłby zastąpić dotychczas stosowane stopy zawierające ołów.

W pracy przedstawiono wyniki badań termodynamicznych stopów Cu-Ni-Sn-Zn.

Metodą równowagowego próżniowego nasycania zmierzono aktywność cynku i obliczono parametry oddziaływania. Uzyskane dane eksperymentalne umożliwią obliczenie diagramu równowagi fazowej w ramach programu COST MP0602.

1. Introduction

New lead-free soldering materials have to fulfill a lot of requirements such as good wettability, conductivity, suitable mechanical properties and form strong boundings with substrates, be environmentally friendly, not expensive and easy to access. In other words, new soldering materials should have properties similar to the actual ones in order to minimize problems related with their introduction in industry. It is known, that phase diagrams are the source of fundamental information (phase stabilities, temperatures of melting and crystallization, compositions of phases). Therefore, multicomponent alloys, that may become new solders should be investigated in order to get a correct description of crystallization processes related to their practical usage.

The general agreement concerning the composition of new lead-free solders is that, alloys based on low-melting metals such as tin and zinc, seem to be the most promising ones. On the other hand, cooper and nickel are the most common substrates. Therefore, it is obvious that the Cu-Ni-Sn-Zn system is worth thorough investigation in order to construct a thermodynamic data base needed for the computer modeling of the system and pointing compositions prospective for practical applications.

2. Experimental

The analyzed alloys show considerable differences between the vapour pressures of their elements at T=1373K: p^*_{Sn}= 0.16 Pa, p^*_{Ni} = 3.87*10^{-4}Pa, p^*_{Cu}= 6*10^{-2} Pa, p^*_{Zn}= 4.9 *10^5 Pa [1]. As the vapour pressure of Zn is much higher than that of the other elements, the activity measurements of Zn were carried on by the comparative method of equilibrium vapour saturation. This method has been successfully applied for multicomponent alloys with one volatile component [2-5]. The studied Cu-Ni-Sn-Zn alloy and the reference alloy Sn-Zn were placed inside a closed crucible under a reduced argon pressure and saturated with the zinc vapour until equilibrium was reached. At the equilibrium state, the

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activity of Zn is the same in all alloys inside a closed system. If the activity of Zn in the reference Sn-Zn (l) is known, it is possible to calculate the activity of Zn in the Cu-Ni-Sn-Zn :

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

$$\gamma_{Zn(Cu-NiSn-Zn)} = x_{Zn(Sn-Zn)} * \gamma_{Zn(Sn-Zn)}/x_{Zn(Cu-Ni-Sn-Zn)} \quad (2)$$

where $x_{Zn(Sn-Zn)}$ and $x_{Zn(Cu-Ni-Sn-Zn)}$ denote the equilibrium mole fraction of Zn in the Sn-Zn and the Cu-Ni-Sn-Zn, alloys respectively, and $\gamma Zn(Sn-Zn)$ and $\gamma Zn(Cu-Ni-Sn-Bi)$ are the corresponding activity coefficients of Zn.

The reference and the studied alloys of appropriate compositions were prepared by melting carefully weighed masses of metals at an argon pressure of 0.1 Pa. The equilibrium compositions of the alloys were determined by the weighing method. The accuracy of weighing was $\pm 10^{-5}$g.

The quantities determined experimentally, *i.e.* the argon pressure and the equilibration time were meant to ensure the attainment of equilibrium between Zn(g) in the reference and the studied alloy.

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 activity of zinc in Cu-Ni-Sn-Zn at T=1373K was determined by the equilibrium saturation method. The activity coefficients of zinc, in this alloys were calculated from equation (2). For describing the activity coefficient of zinc γ_{Zn} in the reference alloy Sn-Zn the equation proposed by Ptak [6] was used:

$$\ln\gamma_{Zn} = (2489/T) + 1.824(\ln T - 1) - 12.929)(1 - x)^{1.1} \quad (3)$$

The results are presented in Table 1.

TABLE

The experimental values of activity coefficient in the studied and the reference alloys

Lp.	The studied Cu-N-Sn-Zn alloys					The reference Sn-Zn alloy	
	x_{Cu}	x_{Ni}	x_{Sn}	x_{Zn}	$\ln\gamma_{Zn}$	x_{Zn}	γ_{Zn}
1.	0.8298	0.0089	0.0328	0.1286	-0.9640	0.0391	1.2556
2.	0.7802	0.0381	0.0259	0.1558	-1.1561	0.0391	1.2556
3.	0.7625	0.0607	0.0348	0.1420	-1.0637	0.0391	1.2556
4.	0.7175	0.0582	0.0335	0.1907	-0.8534	0.0652	1.2471
5.	0.7055	0.0682	0.1102	0.1160	-0.8611	0.0391	1.2556
6.	0.7048	0.0318	0.0338	0.2295	-1.0088	0.0672	1.2464
7.	0.6776	0.0216	0.1118	0.1890	-0,8144	0.0672	1.2464
8.	0.6627	0.0760	0.0252	0.2361	-1.0299	0.0677	1.2462
9.	0.6358	0.1247	0.0413	0.1982	-1.3248	0.0420	1.2546
10.	0.6200	0.1382	0.1016	0.1403	-1.0511	0.0391	1.2556
11.	0.6082	0.0409	0.2004	0.1505	-0.5869	0.0672	1.2464
12.	0.5965	0.1520	0.0872	0.1642	-0.9843	0.0490	1.2523
13.	0.5892	0.1664	0.0277	0.2167	-1.2616	0.0490	1.2523
14.	0.5888	0.0861	0.2092	0.1159	-0.3109	0.0682	1.2461
15.	0.5842	0.1650	0.0985	0.1524	-0.,5845	0.0682	1.2461
16.	0.5834	0.1719	0.0569	0.1878	-1.1810	0.0460	1.2533
17.	0.5815	0.1467	0.1084	0.1634	-1.0418	0.0460	1.2533
18.	0.5639	0.1812	0.0600	0.1949	-1.1537	0.0491	1.2523
19.	0.5625	0.1523	0.0504	0.2348	-1.0243	0.0677	1.2462
20.	0.5460	0.1542	0.0573	0.2425	-1.3742	0.0490	1.2523
21.	0.5388	0.1522	0.1553	0.1538	-0.6381	0.0652	1.2471
22.	0.5251	0.2049	0.0679	0.2021	-1.2543	0.0460	1.2533
23.	0.5164	0.1358	0.1379	0.2099	-0.6067	0.0924	1.2383
24.	0.5126	0.1348	0.0911	0.2615	-0.8267	0.0924	1.2383
25.	0.5100	0.2195	0.0727	0.1978	-1.3226	0.0420	1.2546
26.	0.5026	0.1321	0.0984	0.2669	-0.7783	0.0992	1.2361

As it has not been found any experimental data for Cu-Ni-Sn-Zn system, and the authors wanted to compare theirs results with any literature data, it was decided to elaborate a formula describing Zn activity in the studied quaternary alloy and compare it with experimental values for ternary alloys.

As the Cu concentration is higher than other components, it was decided to use the Wagner equation [7]:

$$\ln\gamma_{Zn} = \ln\gamma^0_{Zn} + \varepsilon^{Zn}_{Zn}x_{Zn} + \varepsilon^{Ni}_{Zn}x_{Ni} + \varepsilon^{Sn}_{Zn}x_{Sn}, \qquad (4)$$

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

In equation (4) values of mole fractions of components and zinc activity coefficient were determined experimentally, whereas values of $\ln\gamma^0_{Zn}$, ε^{Zn}_{Zn}, ε^{Ni}_{Zn} ε^{Sn}_{Zn} were calculated by means of the least -squares method. Finally, the following equation has been obtained:

$$\ln\gamma_{Zn} = -1.2 + 0.53x_{Zn} - 1.64x_{Ni} + 4.06x_{Sn} \qquad (5)$$

Values of $\ln\gamma_{Zn}$ calculated by the use of equation (5) were compared with values calculated by Jansen [8] and Miettinen [9] (ThermoCalc) and experimental data of Sugino [10] for Cu-Sn-Zn system (in equation (5) xNi was accepted 0) (figure 1), and with values calculated by Miettinen [11], (ThermoCalc) and experimental points of Sugino [12] for Cu-Ni-Zn system (in equation (5) x_{Ni} was accepted 0) (figure 2).

Figures 1 and 2 show unambiguously, that the agreement with the experimental and calculated data for both ternary systems is quite reasonable.

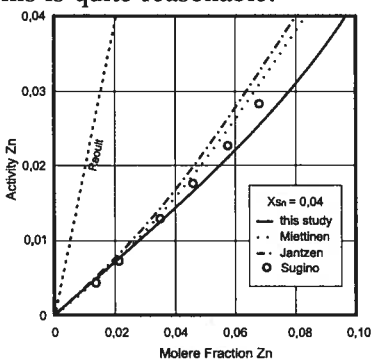

Fig. 1. Calculated zinc activity for x_{Ni} =0 at 1373K together with experimental points of Sugino [9] and calculations of Jantzen [8] and Miettinen [10]

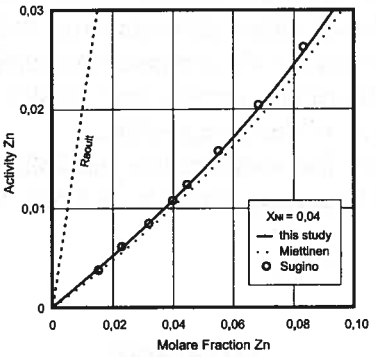

Fig. 2. Calculated zinc activity for x_{Sn}=0 at 1373K together with experimental points of Sugino [12] and calculations of Miettinen [11]

Moreover, as to show that equation (5) well describes experimental points obtained by the authors of this paper figures 3 and 4 present how experimental points fit the surface calculated on the basis of equation (5). Figure 3 presents points situated above the surface, whereas figure 4 presents points situated below the surface.

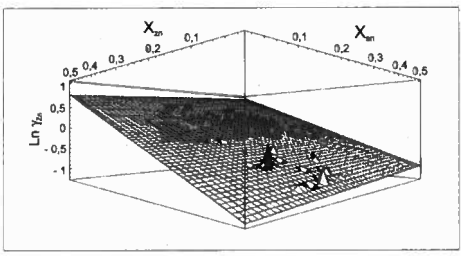

Fig. 3. The surface calculated on the basis of equation (5) and experimental points above the surface

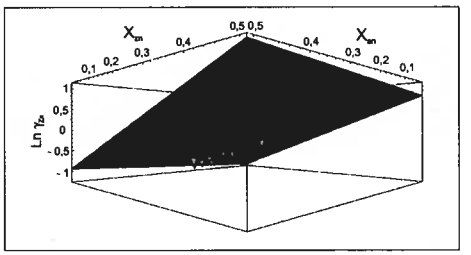

Fig. 4. The surface calculated on the basis of equation (5) and experimental points below the surface

4. Conclusions

Using the vapour saturation method, the Zn activities in Cu-Ni-Sn-Zn alloys at the temperature 1373K were measured and interaction parameters were calculated. This results combined with other measurements

carried on in the frame of the COST action MP0602 "Advanced Solder Materials for High Temperature Application –HISOLD", group project Design, Process and Control in a multiscale domain of Cu-Ni-X-Y (X, Y = Sn, Bi, Zn) based alloys allow construct thermodynamic data base needed for the computer modeling of the system and to determine compositions suitable for practical applications as soldering materials.

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