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EXPERIMENTAL STUDY ON THERMODYNAMICS OF THE Bi-Cu-Sn SYSTEM

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Bismuth thermodynamic activities in Bi-Cu-Sn liquid alloys were measured by means of the vapour saturation method at 1373K, 1423K and 1473K. These results were coupled with literature data for binary systems Bi-Cu, Bi-Sn and Cu-Sn in order to obtain a thermodynamic description of the ternary liquid by use of the geometrical Muggianu approach.
Keywords: activity, Liquid alloys, Muggianu approach

Metodą równowagowego nasycania wyznaczono aktywność bizmutu w stopach Bi-Cu-Sn w temperaturze 1373, 1423 I 1473K. Na podstawie uzyskanych wyników i danych literaturowych dotyczących stopów dwuskładnikowych Bi-Cu, Bi-Sn i Cu-Sn i stosując model Muggianu uzyskano opis termodynamiczny ciekłego stopu trójskładnikowego.

1. Introduction

The toxicity of lead containing solders resulted in the EU decision forbidding the use of lead. Therefore, there are intensive studies of prospective multicomponent lead-free systems, mainly based on tin plus bismuth or zinc. Moreover, copper substrates are commonly applied in the electronic devices. In this view, investigations of alloys containing these elements should be carried on.

Interfacial reaction kinetics between molten Sn-Bi solder and Cu substrates was studied by Li et al. [1]. Thermodynamic properties of the liquid Bi-Cu-Sn alloys were determined by calorimetric method by Flandorfer at al. [2], tin activities were measured by e.m.f. method by Kopyto et.al. [3] and Bi activities in liquid Cu-Sn-Bi alloys were determined by Wnuk and Romanowska [4]. This paper presents results of experimental investigations of Bi-Cu-Sn alloys at the temperature 1373K, 1423K and 1473K carried out by means of the equilibrium saturation method using Cu-Bi alloy as the reference solution. These results were coupled with literature data for binary systems Cu-Bi, Cu-Sn and Bi-Sn in order to obtain a thermodynamic description of the ternary liquid by the application of the geometrical Miggianu approach.

2. Experiments

The experiments were carried out using the equilibrium saturation method, a modified isothermal isopiestic method [5-8] in a set of graphite cells placed in an isothermal zone of the resistance furnace (Fig. 1 – in which 1 denotes a thermocouple and an alundum sheath for thermocouple, 2 – a graphite cover, 3 – graphite blocks with groves for alloys, 4 – a vacuum chamber).

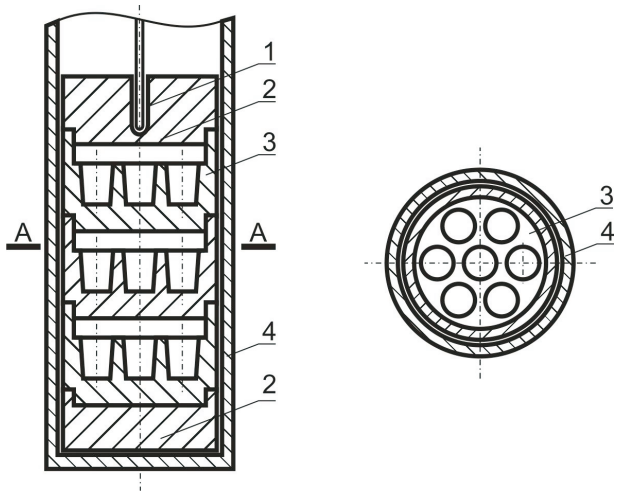

Fig. 1. Apparatus for the equilibrium saturation

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Half of the cells contained the studied Bi-Cu-Sn alloy and half of them the reference alloy Bi-Cu. During the experiment, the system had to attain the state of equilibrium, that is equal bismuth activities in all mixtures. The equilibrium was executed through the gaseous phase. As the vapour pressure of Bi is much higher than that of the other elements (at T=1373K: p^*_{Sn}= 0.16 Pa, p^*_{Cu}= $6*10^{-2}$ Pa, p^*_{Bi}= 891 Pa [9]), pure bismuth vapour was a gaseous phase. Alloys of appropriate compositions were prepared by melting weighed masses of metals. The amounts of copper and tin did not change during the experiments, but bismuth evaporated and therefore its concentrations were lower at the end of each experiment (see Tables 1-3). The compositions of the alloys were determined by the weighing and spectroscopic methods. In the preliminary tests, it had been established that at 1373K, 1423 K and 1473K the time necessary to reach equilibrium was 2 hours and the argon pressure was 2.2 kPa. The quantities determined experimentally, that is argon pressure and equilibration time are meant to guarantee the attainment of equilibrium between all alloys in the closed system. The argon pressure, which was taken *a priori* 2.2 kPa, was higher than the vapour pressure of Bi (891 Pa) in order to limit the evaporation process to that of bismuth only but at a sufficient rate without the possibility of boiling. In the preliminary tests there were Bi-Cu alloys of different composition and pure Bi. Alloys were saturated with Bi vapour for 0.5, 1, 1.5, 2 and 2.5 hours. After the saturation Bi mole fractions were determined in all alloys. The equilibrium was reached when Bi mole fractions in all alloys were equal. Although the time necessary to reach equilibrium is 1.5 hour, in the test alloys were saturated for two hours for better reliability.

At the equilibrium state, the activity of Bi is the same in all samples inside a closed system. Since the activity of Bi in the reference Bi-Cu is known [10], it is possible to calculate the activity of Bi in the Bi-Cu-Sn (l):

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

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

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

3. Results and calculation

The activities of bismuth in Bi-Cu-Sn at T=1373K, 1423K and 1473K were determined by the equilibrium saturation method. The activity coefficients of bismuth,

TABLE 1

Experimental values of Bi activity at 1373K

Lp	Bi-Cu-Sn				Bi-Cu	
	x_{Cu}	x_{Sn}	x_{Bi}	γ_{Bi}	x_{Bi}	γ_{Bi}
1.	0.7851	0.2084	0.0065	9.1639	0.0199	2.9874
2.	0.7817	0.2075	0.0109	8.3224	0.0314	2.8803
3.	0.7487	0.2399	0.0115	7.9716	0.0317	2.8769
4.	0.7487	0.2399	0.0115	8.2150	0.0328	2.8669
5.	0.5676	0.4189	0.0134	4.4144	0.0199	2.9874
6.	0.7862	0.1963	0.0175	8.3599	0.0547	2.6813
7.	0.7412	0.2407	0.0181	8.0957	0.0547	2.6813
8.	0.9574	0.0243	0.0184	3.2285	0.0199	2.9874
9.	0.9700	0.0104	0.0196	3.0300	0.0199	2.9874
10.	0.8320	0.1482	0.0198	7.4124	0.0547	2.6813
11.	0.8220	0.1556	0.0223	7.2338	0.0615	2.6275
12.	0.5624	0.4151	0.0225	4.0130	0.0314	2.8803
13.	0.6965	0.2808	0.0227	6.7785	0.0579	2.6559
14.	0.6443	0.3321	0.0236	8.0411	0.0753	2.5239
15.	0.8792	0.0944	0.0264	5.5586	0.0547	2.6813
16.	0.9486	0.0240	0.0273	3.3045	0.0314	2.8803
17.	0.6535	0.3180	0.0285	5.6739	0.0615	2.6275
18.	0.9601	0.0103	0.0296	3.0566	0.0314	2.8803
19.	0.9622	0.0070	0.0308	2.9631	0.0317	2.8769
20.	0.9612	0.0070	0.0318	2.9596	0.0328	2.8669
21.	0.8778	0.0896	0.0326	4.9545	0.0615	2.6275
22.	0.4151	0.5454	0.0395	2.3135	0.0317	2.8769
23.	0.4148	0.5450	0.0402	2.3406	0.0328	2.8669
24.	0.6153	0.3435	0.0412	3.7292	0.0579	2.6559
25.	0.5234	0.4295	0.0471	3.2632	0.0579	2.6559
26.	0.4184	0.5313	0.0504	2.1123	0.0377	2.8242
27.	0.1920	0.7529	0.0550	1.2430	0.0231	2.9561
28.	0.3736	0.5693	0.0571	1.8620	0.0377	2.8242
29.	0.9288	0.0133	0.0579	2.8316	0.0626	2.6189
30.	0.4667	0.4751	0.0582	2.6412	0.0579	2.6559
31.	0.1441	0.7969	0.0590	1.1601	0.0231	2.9561
32.	0.9321	0.0083	0.0596	2.7535	0.0626	2.6189
33.	0.9272	0.0133	0.0596	2.8587	0.0656	2.5962
34.	0.2531	0.6862	0.0607	1.5518	0.0328	2.8669
35.	0.2530	0.6860	0.0610	1.4972	0.0317	2.8769
36.	0.5640	0.3748	0.0611	2.5157	0.0579	2.6559
37.	0.9340	0.0044	0.0616	2.6611	0.0626	2.6189
38.	0.9300	0.0083	0.0618	2.7581	0.0656	2.5962
39.	0.9344	0.0038	0.0618	2.6562	0.0626	2.6189
40.	0.9326	0.0038	0.0636	2.6774	0.0656	2.5962
41.	0.9318	0.0044	0.0638	2.6707	0.0656	2.5962
42.	0.3280	0.6077	0.0643	1.6540	0.0377	2.8242
43.	0.0899	0.8457	0.0643	1.0634	0.0231	2.9561
44.	0.0471	0.8835	0.0694	0.9857	0.0231	2.9561
45.	0.2790	0.6488	0.0722	1.4735	0.0377	2.8242
46.	0.2957	0.6265	0.0778	2.4438	0.0753	2.5239
47.	0.0295	0.8776	0.0929	0.9827	0.0317	2.8769
48.	0.0295	0.8773	0.0932	1.0103	0.0328	2.8669
49.	0.2799	0.6189	0.1013	1.5961	0.0615	2.6275
50.	0.1886	0.6891	0.1222	1.3225	0.0615	2.6275

TABLE 2
Experimental values of Bi activity at 1423K

Lp	Bi-Cu-Sn				Bi-Cu	
	x_{Cu}	x_{Sn}	x_{Bi}	γ_{Bi}	x_{Bi}	γ_{Bi}
1.	0.7821	0.1953	0.0226	7.0093	0.0651	2.4325
2.	0.7373	0.2394	0.0233	6.7910	0.0651	2.4325
3.	0.8273	0.1474	0.0252	6.2680	0.0651	2.4325
4.	0.6916	0.2788	0.0296	5.9194	0.0739	2.3743
5.	0.8722	0.0936	0.0342	4.6339	0.0651	2.4325
6.	0.6161	0.3439	0.0399	4.3929	0.0739	2.3743
7.	0.5721	0.3802	0.0477	3.6746	0.0739	2.3743
8.	0.9056	0.0465	0.0479	3.3071	0.0651	2.4325
9.	0.5169	0.4242	0.0589	2.9763	0.0739	2.3743
10.	0.4134	0.5250	0.0616	2.1088	0.0514	2.5279
11.	0.3688	0.5619	0.0693	1.8755	0.0514	2.5279
12.	0.4601	0.4684	0.0715	2.4540	0.0739	2.3743
13.	0.1887	0.7398	0.0715	1.2412	0.0333	2.6645
14.	0.1414	0.7818	0.0768	1.1556	0.0333	2.6645
15.	0.3232	0.5988	0.0780	1.6664	0.0514	2.5279
16.	0.0881	0.8282	0.0837	1.0599	0.0333	2.6645
17.	0.2744	0.6380	0.0876	1.4827	0.0514	2.5279
18.	0.0461	0.8640	0.0900	0.9865	0.0333	2.6645
19.	0.0194	0.8860	0.0946	0.9383	0.0333	2.6645
20.	0.2224	0.6794	0.0982	1.3234	0.0514	2.5279

TABLE 3
Experimental values of Bi activity at 1473K

Lp	Bi-Cu-Sn				Bi-Cu	
	x_{Cu}	x_{Sn}	x_{Bi}	γ_{Bi}	x_{Bi}	γ_{Bi}
1.	0.7683	0.1918	0.0398	5.5199	0.1069	2.0578
2.	0.7242	0.2351	0.0407	5.4001	0.1069	2.0578
3.	0.8111	0.1445	0.0444	4.9522	0.1069	2.0578
4.	0.6770	0.2730	0.0500	4.6818	0.1164	2.0117
5.	0.8508	0.0913	0.0578	3.8019	0.1069	2.0578
6.	0.5996	0.3347	0.0657	3.5622	0.1164	2.0117
7.	0.5544	0.3684	0.0771	3.0348	0.1164	2.0117
8.	0.8762	0.0450	0.0788	2.7893	0.1069	2.0578
9.	0.4987	0.4092	0.0921	2.5419	0.1164	2.0117
10.	0.3966	0.5036	0.0997	1.9070	0.0883	2.1535
11.	0.4423	0.4503	0.1075	2.1784	0.1164	2.0117
12.	0.3522	0.5367	0.1112	1.7108	0.0883	2.1535
13.	0.1802	0.7065	0.1134	1.2603	0.0620	2.3044
14.	0.1345	0.7440	0.1215	1.1760	0.0620	2.3044
15.	0.3076	0.5700	0.1223	1.5548	0.0883	2.1535
16.	0.0835	0.7858	0.1306	1.0939	0.0620	2.3044
17.	0.2601	0.6048	0.1352	1.4069	0.0883	2.1535
18.	0.0436	0.8182	0.1381	1.0344	0.0620	2.3044
19.	0.0184	0.8383	0.1434	0.9966	0.0620	2.3044
20.	0.2098	0.6411	0.1491	1.2756	0.0883	2.1535

γ_{Bi} in these alloys were calculated from equation (2). Experimental values of Bi activity coefficient in Bi-Cu-Sn alloys are presented in Tables 1-3. To calculate γ_{Bi} in the reference Bi-Cu liquids, the thermodynamic description by means of the Redlich-Kister polynominals for binary alloys [11] was used.

$$L_{ij}^{\phi} = \sum_{m=0}^{n} {}^{m}L_{ij}^{\phi}\left(x_i - x_j\right)^m \ , \tag{3}$$

where L_{ij}^{ϕ} is the interaction parameter in the $i-j$ binary system. Parameters proposed by Teppo et al. [10] were adopted in this work:

$$\begin{aligned} {}^{0}\mathrm{L}^{\mathrm{L}}_{\mathrm{Bi,Cu}} &= 23844 - 9.84341 * \mathrm{T} \qquad \text{[J/mol]} \\ {}^{1}\mathrm{L}^{\mathrm{L}}_{\mathrm{Bi,Cu}} &= -1260.32 - 1.19289 * \mathrm{T} \qquad \text{[J/mol]} \end{aligned} \tag{4}$$

The ternary liquid phase was described by the subregular solution model, in which the excess free energy is expressed by the Redlich –Kister polynomials for ternary alloys [11].

$$\begin{aligned} {}^{ex}G^{\phi} &= x_{Bi}x_{Cu}L^{\phi}_{Bi,Cu} + x_{Bi}x_{Sn}L^{\phi}_{Bi,Sn} + x_{Cu}x_{Sn}L^{\phi}_{Cu,Sn} + \\ &+ x_{Bi}x_{Cu}x_{Sn}L^{\phi}_{Bi,Cu,Sn}, \\ L^{\phi}_{Bi,Cu,Sn} &= x_{Bi}\,{}^{0}L^{\phi}_{Bi,Cu,Sn} + x_{Cu}\,{}^{1}L^{\phi}_{Bi,Cu,Sn} + x_{Sn}\,{}^{2}L^{\phi}_{Bi,Cu,Sn}, \end{aligned} \tag{5}$$

Where $L^{\phi}_{Bi,Cu,Sn}$ corresponds to the interaction in the Bi-Cu-Sn ternary system. The coefficients of $L^{\phi}_{Bi,Cu,Sn}$ for the temperature 1373K, 1423K and 1473K were evaluated in the present work with the use of the least – squares method. L^{ϕ}_{ij} values for binary alloys were accepted from the literature: for Bi-Cu there were accepted data proposed by Teppo et al. [10] (equation 4), data proposed by Vizdal et al. for Bi-Sn [12] (equation 6) and by Li et al. for Cu-Sn system [13] (equation 7).

$$\begin{aligned} {}^{0}\mathrm{L}^{\mathrm{L}}_{\mathrm{Bi,Sn}} &= 500 + 1.5 * \mathrm{T[J/mol]} \\ {}^{1}\mathrm{L}^{\mathrm{L}}_{\mathrm{Bi,Sn}} &= -100 + 0.135 * \mathrm{T[J/mol]} \end{aligned} \tag{6}$$

$$\begin{aligned} {}^{0}\mathrm{L}^{\mathrm{L}}_{\mathrm{Cu,Sn}} &= -8266.6 - 6.9973 * \mathrm{T[J/mol]} \\ {}^{1}\mathrm{L}^{\mathrm{L}}_{\mathrm{Cu,Sn}} &= -21662 + 8.4655 * \mathrm{T[J/mol]} \\ {}^{2}\mathrm{L}^{\mathrm{L}}_{\mathrm{Cu,Sn}} &= -26957.2 + 12.888 * \mathrm{T[J/mol]} \\ {}^{3}\mathrm{L}^{\mathrm{L}}_{\mathrm{Cu,Sn}} &= -13222.7 + 10.0420 * \mathrm{T[J/mol]} \end{aligned} \tag{7}$$

Excess free energy was calculated on the basis of experimental values of $\gamma_{Bi(Bi-Cu-Sn)}$.

Values of Redlich-Kister ternary L parameters calculated on the basis of presented experimental results are listed in Table 4. Finally, the following expressions for L parameters were proposed:

TABLE 4

Values of L parameters

T[K]	^{0}L	^{1}L	^{2}L
1373	–13728	74679	–45956
1423	–15991	66549	–54556
1473	–29461	81469	–55059

$$^0L^L_{Bi,Cu,Sn} = 204153.92 - 149.27 * T$$
$$^1L^L_{Bi,Cu,Sn} = -22392.15 + 67.90 * T \quad (8)$$
$$^2L^L_{Bi,Cu,Sn} = 77678.69 - 91.03 * T$$

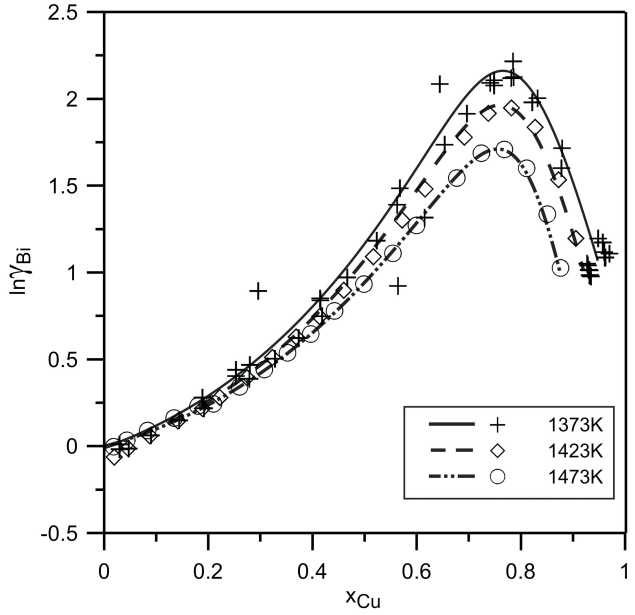

Fig. 2. Experimental and calculated values of Bi activities

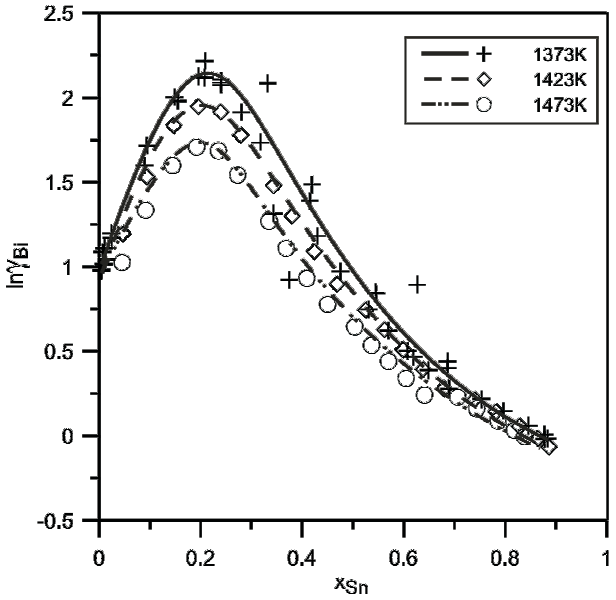

Fig. 3. Experimental and calculated values of Bi activities

Figures 2 and 3 present the comparison between the calculated and experimental values of $\gamma_{Bi(Bi-Cu-Sn)}$ and Figure 4 shows experimental and calculated values of $^0L^L_{Bi,Cu,Sn}$, $^1L^L_{Bi,Cu,Sn}$ and $^2L^L_{Bi,Cu,Sn}$.

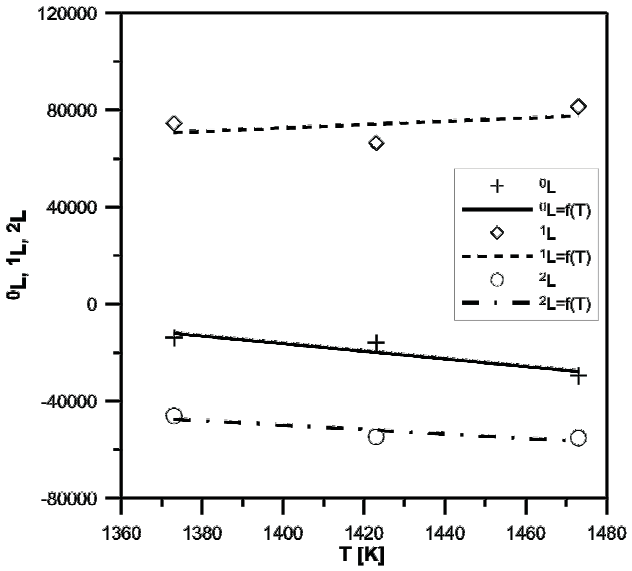

Fig. 4. Experimental and calculated values of L parameters

4. Conclusions

Using the vapour saturation method, the Bi activities in Bi-Cu-Sn alloys at the temperature 1373K, 1423K and 1473K were experimentally determined and the parameters of the Gibbs energy expression for liquid alloys were calculated. The obtained expressions (Eq. (8)) describe well the experimental points (see Figs. 2-4). Values of bismuth activity coefficient (Tables 1-3) indicate slightly negative deviation from the Raoult's law ($\gamma_{Bi(Bi-Cu-Sn)}$ <1) only for low Cu contents (x_{Cu} <0.05 and x_{Sn} >0.8) and positive deviation for the other ones. Values of Bi activity coefficient are bigger for bigger Cu contents, so the positive deviation from the Raoults rule increases with the Cu content. These results, combined with other measurements and optimizations carried out in the frame of the COST action MP0602 "Advanced Solder Materials for High Temperature Application HISOLD", allow the construction of a 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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REFERENCES

[1] J.F. Li, S.H. Mannan, M.P. Clode, D.C. Whalley, D.A. Hutt, Acta Materialia **55**, (11), 2907-2922 (2006).
[2] H. Flandorfer, A. Sabbar, C. Luef, M. Rechchach, H. Ipser, Thermochemica Acta **472**, 1-10 (2008).
[3] M. Kopyto, G. Garzeł, L.A. Zabdyr, J. of Minimg and Metallurgy **45** B, 1, 95-100 (2009).
[4] G. Wnuk, J. Romanowska, Arch. Metall. Mater. **51**, (4), 503-597 (2006).
[5] J. Romanowska, CALPHAD **33**, 723-725 (2009).
[6] J. Romanowska, B. Onderka, G. Wnuk, J. Wypartowicz, Arch. Metal. Mater. 51 (4).
[7] G.P. Vassiliev, J. Romanowska, G. Wnuk, Int. J. Mat. Res. **98**, (6), 1-8 (2007).
[8] J. Romanowska, G. Wnuk, P. Romanowski, Arch. of Metall. and Mater. **53**, (4), 1107-1110 (2008).
[9] O. Kubaschewski, C. Alcock, Metallurgical Thermochemistry, Pergamon Press, Oxford, 1979.
[10] O. Teppo, J. Niemwela, P. Taskinen, Thermochimica Acta, 1973, 137-150 (1990).
[11] O. Redlich, T. Kister, Ind. Enging. Chem. **40**, 345-348 (1948).
[12] J. Vizdal, M.H. Bragga, A. Kroupa, K.W. Richter, D. Soares, L.F. Malheiros, J. Ferriera, CALPHAD **31**, 438-448 (2007).
[13] M. Li, Z. Du, C. Guo, C. Li J, Alloys Compounds **477**, 104-117 (2009).

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