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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A CONTRIBUTION TO THE THERMODYNAMIC STUDY OF THE (Cu,CO)-Ni-Zn SYSTEMS

WKŁAD DO BADAŃ TERMODYNAMIKI UKŁADÓW (Cu,CO)-Ni-Zn

Estimation of the thermodynamic properties of Cu-Ni-Zn and Co-Ni-Zn systems has been done by means of the general solution model. The calculations have been performed in wide temperature range – from 1000 to 2000K. Based on known thermodynamic data for constitutive binary systems, ternary interaction parameters for the liquid phases in both systems were determined.

Keywords: thermodynamics, general solution model, ternary interaction parameter, Cu-Ni-Zn, Co-Ni-Zn, ternary system

Dokonano oszacowania własności termodynamicznych układów Cu-Ni-Zn i Co-Ni-Zn z zastosowaniem modelu „general solution model". Obliczenia przeprowadzono w szerokim zakresie temperatur, pomiędzy 1000, a 2000 K. W oparciu o znane dane termodynamiczne dla składowych układów podwójnych określono współczynniki oddziaływania dla fazy ciekłej obydwu układów potrójnych.

1. Introduction

The Cu-Ni-Zn and Co-Ni-Zn systems are important for the non-ferrous metallurgy [1], while recently they are interesting as potential lead-free solder materials [2]. Both systems, as well as their binary subsystems, have already been thermodynamically investigated.

Few thermodynamic data have been reported for the Cu-Ni-Zn system [1-5]. The vapour pressure measurement of Zn activity in the α-field of the Cu-rich region has been done at 1000 K by Chadwick and Argent [3]. Using the same technique, Sugino and Hagiwara [4] determined the zinc activities in dilute Cu-Ni-Zn melt at 1373 and 1423K. The isoactivity curves of Zn at 1048K were evaluated and calculated by Sisson and Dayananda [5]. Recently, Vassilev [6,7] has investigated the phase boundaries in the zinc-rich corners of the Cu-Ni-Zn at 868 K. Ternary compounds non-related with the binary systems have not been found. The ternary extension of the Cu-Zn ε- phase contains up to 4 at% Ni. The locations of the phase boundaries of the ternary liquid and γ-phases have been precised.

The thermodynamic parameters of the ternary Cu-Ni-Zn system, at zinc contents up to 70 wt% and at temperatures above 873K, were optimized using the experimental thermodynamic and phase equilibrium data in the work of Miettinen [8]. The most recent reference on thermodynamic calculation of phase equilibria in the Cu-Ni-Zn system is the work of Jiang et al. [1], where this system has been thermodynamically analyzed based on extensive experimental information and thermodynamic modeling by the CALPHAD approach.

The Co-Ni-Zn system has also been thermodynamically investigated, but still has not been completely determined and assessed. In the papers of Vassilev [10-12], thermodynamics of the ternary Co-Ni-Zn fcc solutions and zinc thermodynamic activities in Co-Ni-Zn β_1 and β' phases, as well as thermochemical studies in the frame of phase equilibria investigation, have been presented. This author has investigated the zinc-rich corner as well [5,6] and isothermal sections at 868 K and 1083 K have been constructed.

As a contribution to the completion of the thermodynamic knowledge of the above-mentioned two ternary Ni-Zn-based systems, the results of calculation of thermodynamic properties in wide temperature range are presented in this paper, using general solution model. Based on known thermodynamic data for constitutive binary systems, ternary interaction parameters for the liquid phase were determined and comparison between calculated results and available literature data was done.

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2. Theoretical fundamentals

Thermodynamic properties of the Cu-Ni-Zn and Co-Ni-Zn systems have been calculated using general solution model [12,13], based on three corresponding binary systems.

The basic equations of the general solution model [12,13] are given as follows:

$$G^E = x_1x_2G^E_{12} + x_2x_3G^E_{23} + x_3x_1G^E_{31} + x_1x_2x_3f_{123}, \quad (1)$$

where:

$$G^E_{ij} = X_iX_j(A^o_{ij}+A^1_{ij}(X_i-X_j)+A^2_{ij}(X_i-X_j)^2+...+A^n_{ij}(X_i-X_j)^n) \quad (2)$$

and A^o_{ij}, A^1_{ij}, A^2_{ij} are parameters (independent of composition, only relying on temperature, being analogue to the Redlich-Kister parameters) belonging to the binary system "ij"; X_i and X_j indicate the mole fractions of component "i" and "j" in "ij" binary system; f_{123} is the ternary interaction coefficient, expressed as:

$$\begin{aligned} f_{123} = {} & (2\xi_{12}-1)\{A^2_{12}((2\xi_{12}-1)x_3 + 2(x_1-x_2)) + A^1_{12}\}+ \\ & +(2\xi_{23}-1)\{A^2_{23}((2\xi_{23}-1)x_1 + 2(x_2-x_3)) + A^1_{23}\}+ \\ & +(2\xi_{31}-1)\{A^2_{31}((2\xi_{31}-1)x_2 + 2(x_3-x_1)) + A^1_{31}\}, \end{aligned} \quad (3)$$

Here ξ_{ij} are similarity coefficients, defined by η_i – called the deviation sum of squares:

$$\xi_{ij} = \eta_i/(\eta_i + \eta_j), \quad (4)$$

where:

$$\begin{aligned} \eta_I &= \int_{X_i=0}^{X_i=1} (G^E_{12} - G^E_{13})^2\, dX_1 \\ \eta_{II} &= \int_{X_i=0}^{X_i=1} (G^E_{21} - G^E_{23})^2\, dX_2 \\ \eta_{III} &= \int_{X_i=0}^{X_i=1} (G^E_{31} - G^E_{32})^2\, dX_3 \end{aligned} \quad (5)$$

and

$$X_{1(12)} = x_1+x_3\xi_{12}\ ;\ X_{2(23)} = x_2+x_1\xi_{23}\ ;\ X_{3(31)} = x_3+x_2\xi_{31}. \quad (6)$$

The ternary interaction coefficient, f_{123}, is related to the Redlich-Kister ternary interaction parameter [14], so it can be written in the form:

$$f_{123} = x_1 \cdot L^0_{123} + x_2 \cdot L^1_{123} + x_3 \cdot L^2_{123} \quad (7)$$

with a temperature dependence taken as

$$L^v_{123} = a^v + b^v \cdot T(v = 0, 1, 2), \quad (8)$$

where L^v_{ijk} are the Redlich-Kister parameters for the ternary system ijk; and x_i – mole fraction of the component i.

In all above-given equations, G^E and G^E_{ij} correspond to the integral molar excess Gibbs energies for ternary and binary systems, respectively, while x_1, x_2, x_3 correspond to the mole fraction of the respective components in the investigated ternary system.

3. Results and discussion

For the purpose of further calculation, basic thermodynamic information on the constitutive subsystems in the Cu-Ni-Zn and Co-Ni-Zn systems were taken from Refs. [8,14-18], and presented in the form of Redlich-Kister [14] parameters in Table 1.

TABLE 1

Redlich-Kister parameters for the investigated systems

System *ij*	L^o_{ij} (T)	L^1_{ij} (T)	L^2_{ij} (T)
Cu-Ni [6]	11760+1.084T	-1672	0
Ni-Zn [14]	-50721.64+7.34178T	8436.3+1.97211T	-25136.08+11.79211T
Cu-Zn [6]	-40696+12.653T	4403-6.554T	7818-3.254T
Co-Zn [15]	-15017+12.735T	51758-29.752T	0
Co-Ni [16]	1331	0	0

The alloys in the Cu-Ni-Zn and Co-Ni-Zn systems, with molar content of copper and cobalt equal to 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1, were investigated in the sections with Ni/Zn molar ratio equal to 1/3, 1/1 and 3/1, respectively. The calculation was done in the temperature interval from 1000 to 2000 K. The values for the integral Gibbs excess energies, G^E, and the ternary interaction coefficients, f_{123}, have been calculated according to the general solution model, based on the parameters given in Tab.1 and Eqs.(1,3), respectively.

The calculated integral molar Gibbs excess energies (G^E) of the investigated systems Cu-Ni-Zn and Co-Ni-Zn, along selected sections and at given temperatures, are presented in Figs.1 and 2.

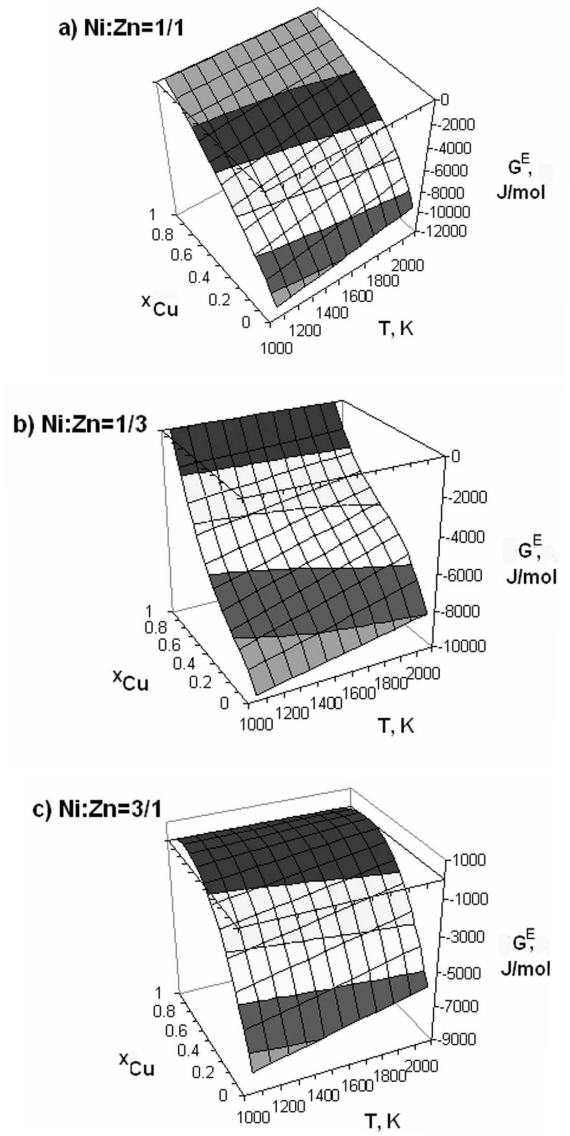

Fig. 1. Results of G^E calculation according to the general solution model for the Cu-Ni-Zn system in temperature interval 1000-2000 K (the sections with Ni/Zn molar ratio equal to: (a) - 1/1, (b) - 1/3 and (c) - 3/1)

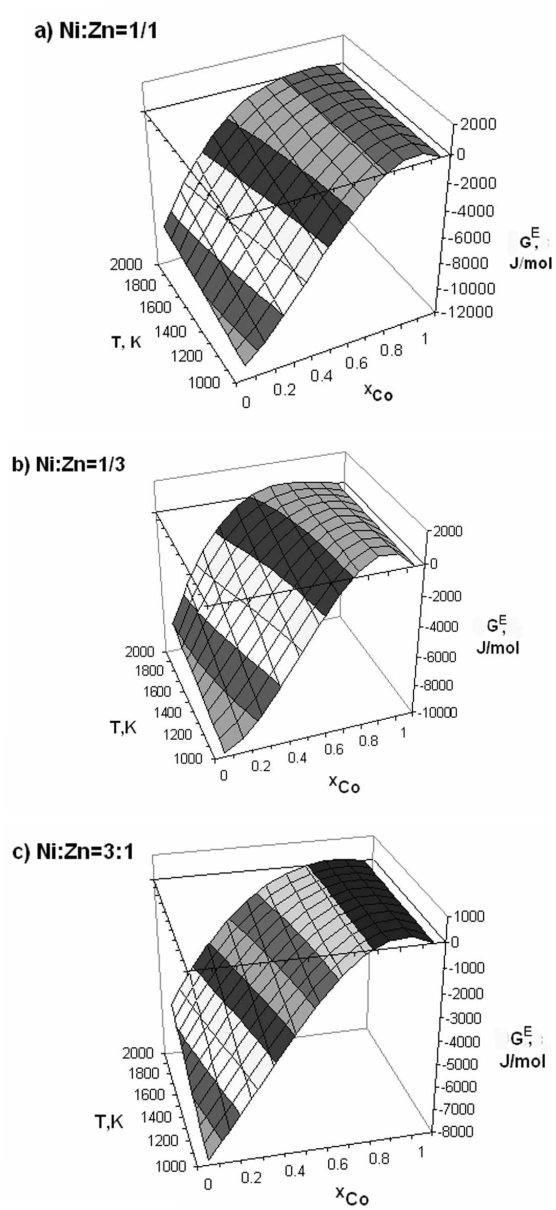

Fig. 2. Results of G^E calculation according to the general solution model for the Co-Ni-Zn system in temperature interval 1000-2000 K (the sections with Ni/Zn molar ratio equal to: (a) - 1/1, (b) - 1/3 and (c) - 3/1)

The calculated ternary interaction coefficients are presented in Tabs. 2 and 3.

TABLE 2

Results of f_{123} calculation according to the general solution model for the Cu-Ni-Zn system in temperature interval 1000-2000 K

Cu-Ni-Zn											
T, K	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
Ni:Zn=1:1											
x_{Cu}	f_{123}										
0	5700.701	5605.068	5538.029	5502.534	5501.614	5538.326	5615.689	5736.594	5903.701	6119.312	6385.224
0.1	5603.774	5524.229	5472.296	5451.028	5463.601	5513.263	5603.279	5736.843	5916.982	6146.429	6427.486
0.2	5506.847	5443.39	5406.563	5399.523	5425.587	5488.199	5590.868	5737.091	5930.262	6173.547	6469.748
0.3	5409.92	5362.551	5340.831	5348.017	5387.574	5463.136	5578.458	5737.34	5943.542	6200.665	6512.01
0.4	5312.993	5281.712	5275.098	5296.511	5349.56	5438.073	5566.047	5737.589	5956.822	6227.782	6554.272
0.5	5216.066	5200.874	5209.365	5245.005	5311.547	5413.01	5553.637	5737.837	5970.103	6254.9	6596.534
0.6	5119.139	5120.035	5143.632	5193.499	5273.533	5387.946	5541.226	5738.086	5983.383	6282.018	6638.796
0.7	5022.212	5039.196	5077.9	5141.993	5235.52	5362.883	5528.816	5738.334	5996.663	6309.136	6681.058
0.8	4925.285	4958.357	5012.167	5090.487	5197.507	5337.82	5516.405	5738.583	6009.944	6336.253	6723.32
0.9	4828.357	4877.519	4946.434	5038.981	5159.493	5312.756	5503.995	5738.831	6023.224	6363.371	6765.582
Ni:Zn=1:3											
x_{Cu}	f_{123}										
0	14648.8	13702.65	12792.35	11921.39	11093.37	10312.02	9581.068	8904.239	8285.161	7727.279	7233.749
0.1	13657.06	12812.05	12001.18	11227.99	10496.19	9809.588	9172.12	8587.723	8060.295	7593.6	7191.159
0.2	12665.33	11921.46	11210.02	10534.6	9898.996	9307.155	8763.171	8271.207	7835.429	7459.921	7148.568
0.3	11673.59	11030.86	10418.86	9841.212	9301.806	8804.723	8354.223	7954.691	7610.564	7326.242	7105.978
0.4	10681.85	10140.26	9627.69	9147.821	8704.617	8302.29	7945.274	7638.175	7385.698	7192.563	7063.387
0.5	9690.115	9249.666	8836.525	8454.43	8107.427	7799.857	7536.326	7321.659	7160.832	7058.884	7020.796
0.6	8698.378	8359.068	8045.361	7761.039	7510.238	7297.424	7127.378	7005.143	6935.967	6925.205	6978.206
0.7	7706.641	7468.471	7254.196	7067.648	6913.048	6794.991	6718.429	6688.627	6711.101	6791.526	6935.615
0.8	6714.904	6577.874	6463.031	6374.257	6315.859	6292.559	6309.481	6372.112	6486.235	6657.847	6893.025
0.9	5723.167	5687.277	5671.866	5680.866	5718.669	5790.126	5900.533	6055.596	6261.37	6524.168	6850.434
Ni:Zn=3:1											
x_{Cu}	f_{123}										
0	-3247.4	-2492.52	-1716.29	-916.317	-90.1468	764.6312	1650.31	2568.95	3522.242	4511.344	5536.698
0.1	-2449.51	-1763.6	-1056.59	-325.937	431.0159	1216.937	2034.437	2885.963	3773.668	4699.259	5663.813
0.2	-1651.63	-1034.68	-396.893	264.4418	952.1785	1669.244	2418.565	3202.976	4025.094	4887.173	5790.927
0.3	-853.749	-305.757	262.8063	854.821	1473.341	2121.55	2802.692	3519.989	4276.52	5075.088	5918.042
0.4	-55.8664	423.1622	922.5056	1445.2	1994.504	2573.856	3186.82	3837.002	4527.947	5263.002	6045.156
0.5	742.0164	1152.082	1582.205	2035.579	2515.666	3026.162	3570.947	4154.015	4779.373	5450.917	6172.271
0.6	1539.899	1881.001	2241.904	2625.959	3036.829	3478.468	3955.075	4471.028	5030.799	5638.831	6299.386
0.7	2337.782	2609.921	2901.603	3216.338	3557.992	3930.774	4339.202	4788.041	5282.225	5826.745	6426.5
0.8	3135.665	3338.841	3561.303	3806.717	4079.154	4383.081	4723.33	5105.054	5533.652	6014.66	6553.615
0.9	3933.548	4067.76	4221.002	4397.096	4600.317	4835.387	5107.457	5422.067	5785.078	6202.574	6680.729

TABLE 3

The results of f_{123} calculation according to the general solution model for the Co-Ni-Zn system in temperature interval 1000-2000 K

Cu-Ni-Zn											
T, K	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
Ni:Zn=1:1											
x_{Co}	f_{123}										
0	-19802.3	-17723	-15441.9	-13000.6	-10445.5	-7826.04	-5192.35	-2593.53	-75.7058	2319.488	4556.079
0.1	-19805.1	-17723.7	-15441.9	-13001	-10447.3	-7829.69	-5198.12	-2601.18	-84.5209	2310.794	4549.403
0.2	-19807.8	-17724.4	-15441.9	-13001.4	-10449	-7833.35	-5203.88	-2608.83	-93.3361	2302.1	4542.728
0.3	-19810.5	-17725.1	-15441.9	-13001.9	-10450.8	-7837	-5209.65	-2616.49	-102.151	2293.407	4536.052
0.4	-19813.2	-17725.8	-15441.9	-13002.3	-10452.5	-7840.66	-5215.41	-2624.14	-110.966	2284.713	4529.376
0.5	-19815.9	-17726.5	-15441.9	-13002.7	-10454.3	-7844.31	-5221.18	-2631.79	-119.782	2276.019	4522.701
0.6	-19818.6	-17727.2	-15441.9	-13003.2	-10456	-7847.96	-5226.95	-2639.45	-128.597	2267.326	4516.025
0.7	-19821.3	-17727.9	-15441.9	-13003.6	-10457.8	-7851.62	-5232.71	-2647.1	-137.412	2258.632	4509.35
0.8	-19824	-17728.6	-15441.9	-13004	-10459.5	-7855.27	-5238.48	-2654.75	-146.227	2249.939	4502.674
0.9	-19826.7	-17729.4	-15441.9	-13004.5	-10461.3	-7858.92	-5244.24	-2662.4	-155.042	2241.245	4495.999
Ni:Zn=1:3											
x_{Co}	f_{123}										
0	-19200.9	-17430.7	-15420.1	-13207.1	-10834.5	-8347.77	-5793.65	-3217.76	-663.003	1831.985	4233.928
0.1	-19263.8	-17460.6	-15422.3	-13186.9	-10797.3	-8299.25	-5739.28	-3162.99	-613.088	1872.042	4259.468
0.2	-19326.6	-17490.6	-15424.5	-13166.7	-10760.2	-8250.73	-5684.92	-3108.22	-563.174	1912.098	4285.007
0.3	-19389.5	-17520.5	-15426.6	-13146.5	-10723	-8202.21	-5630.55	-3053.45	-513.259	1952.155	4310.547
0.4	-19452.3	-17550.4	-15428.8	-13126.2	-10685.9	-8153.69	-5576.19	-2998.68	-463.345	1992.212	4336.086
0.5	-19515.2	-17580.4	-15431	-13106	-10648.8	-8105.17	-5521.83	-2943.91	-413.43	2032.268	4361.626
0.6	-19578	-17610.3	-15433.2	-13085.8	-10611.6	-8056.65	-5467.46	-2889.14	-363.515	2072.325	4387.165
0.7	-19640.9	-17640.2	-15435.4	-13065.6	-10574.5	-8008.13	-5413.1	-2834.37	-313.601	2112.381	4412.705
0.8	-19703.7	-17670.2	-15437.6	-13045.4	-10537.3	-7959.62	-5358.73	-2779.6	-263.686	2152.438	4438.244
0.9	-19766.6	-17700.1	-15439.7	-13025.1	-10500.2	-7911.1	-5304.37	-2724.83	-213.772	2192.495	4463.784
Ni:Zn=3:1											
x_{Co}	f_{123}										
0	-20403.8	-18015.4	-15463.6	-12794	-10056.5	-7304.31	-4591.06	-1969.3	511.5912	2806.99	4878.229
0.1	-20346.3	-17986.8	-15461.5	-12815.1	-10097.2	-7360.14	-4656.95	-2039.38	444.0464	2749.546	4839.338
0.2	-20288.9	-17958.3	-15459.3	-12836.2	-10137.8	-7415.97	-4722.85	-2109.45	376.5015	2692.102	4800.448
0.3	-20231.5	-17929.8	-15457.1	-12857.3	-10178.5	-7471.79	-4788.74	-2179.53	308.9567	2634.658	4761.557
0.4	-20174	-17901.2	-15454.9	-12878.4	-10219.1	-7527.62	-4854.64	-2249.6	241.4118	2577.215	4722.667
0.5	-20116.6	-17872.7	-15452.8	-12899.4	-10259.8	-7583.45	-4920.53	-2319.68	173.867	2519.771	4683.776
0.6	-20059.2	-17844.2	-15450.6	-12920.5	-10300.4	-7639.27	-4986.43	-2389.75	106.3221	2462.327	4644.885
0.7	-20001.7	-17815.7	-15448.4	-12941.6	-10341.1	-7695.1	-5052.32	-2459.83	38.77728	2404.883	4605.995
0.8	-19944.3	-17787.1	-15446.3	-12962.7	-10381.7	-7750.92	-5118.22	-2529.9	-28.7676	2347.439	4567.104
0.9	-19886.9	-17758.6	-15444.1	-12983.8	-10422.4	-7806.75	-5184.11	-2599.98	-96.3124	2289.995	4528.214

The values of the ternary interaction coefficients for the liquid phases of the investigated systems, calculated using general solution model, were further used in determination of the ternary interaction parameters, L^{v}_{ijk}, according to Eqs. (7,8). Therefore, MLAB software [19] was applied to the process of fitting (Table 4).

TABLE 4

Ternary interaction parameters, L^{v}_{ijk}, obtained using MLAB software for the Cu-Ni-Zn and Co-Ni-Zn systems

System *ij*	L^{o}_{ijk} (T)	L^{1}_{ijk} (T)	L^{2}_{ijk} (T)
Cu-Ni-Zn	5454.98	-30306.8199+17.588T	33365.618-14.635T
Co-Ni-Zn	-7574.07075	-7312.92261	-8339.90114

Comparison between the application of the ternary interaction parameters values for the Cu-Ni-Zn system, obtained in this work and these taken from literature [1,8] was done. The comparative review at the temperature of 1800 K is presented in Fig.3.

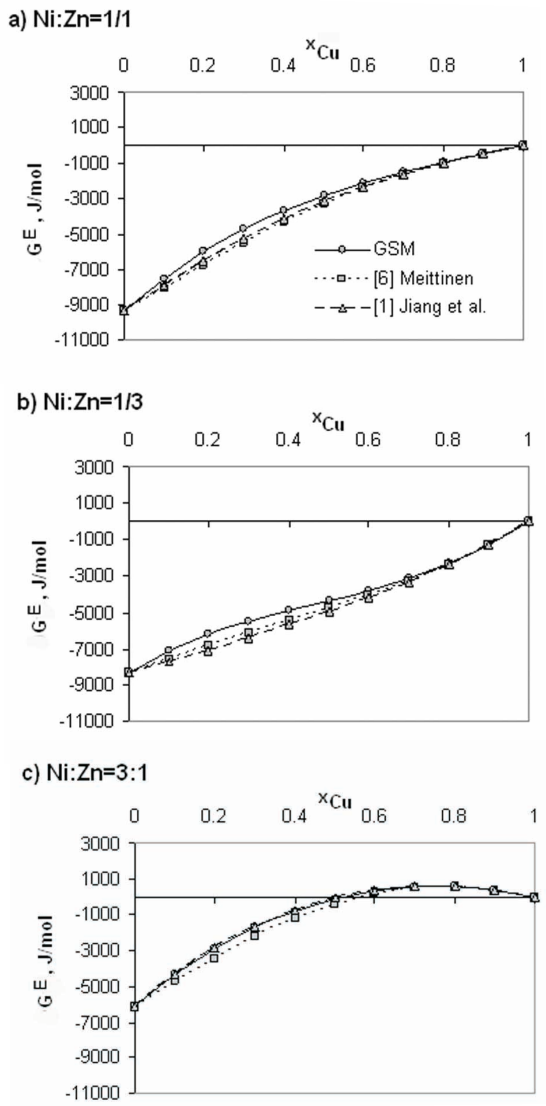

Fig. 3. Comparative review of the ternary interaction parameters application for the Cu-Ni-Zn system at 1800 K: sections with Ni/Zn molar ratio equal to a) 1/1, b) 1/3 and c) 3/1

Although the common way to obtain the ternary interaction parameters is the optimization based on the experimental data from literature, the calculation procedure, given here, showed that it could be also done using the estimation method, without applying any experimental data. Similar procedure was presented recently in literature [20,21], too.

As can be seen (Fig. 3), there is an agreement between the application of ternary interaction parameters for the Cu-Ni-Zn system, calculated in this work, and ones optimized based on existing experimental measurements [1,6], that ahould be tested on the wide group of systems with different deviation from Raoult's low.

Therefore, the results for the Co-Ni-Zn system, presented here, could be taken as a contribution to the better knowledge of that ternary system, which has not been yet fully investigated from the thermodynamic point of view. In order to present additional thermodynamic data for the liquid Co-Ni-Zn alloys, the results of thermodynamic calculation using general solution model for the sections with molar ratio equal to 1/1, 1/4 and 4/1 from all three corners at the temperature of 2000 K, are given in Figs. 4 and 5.

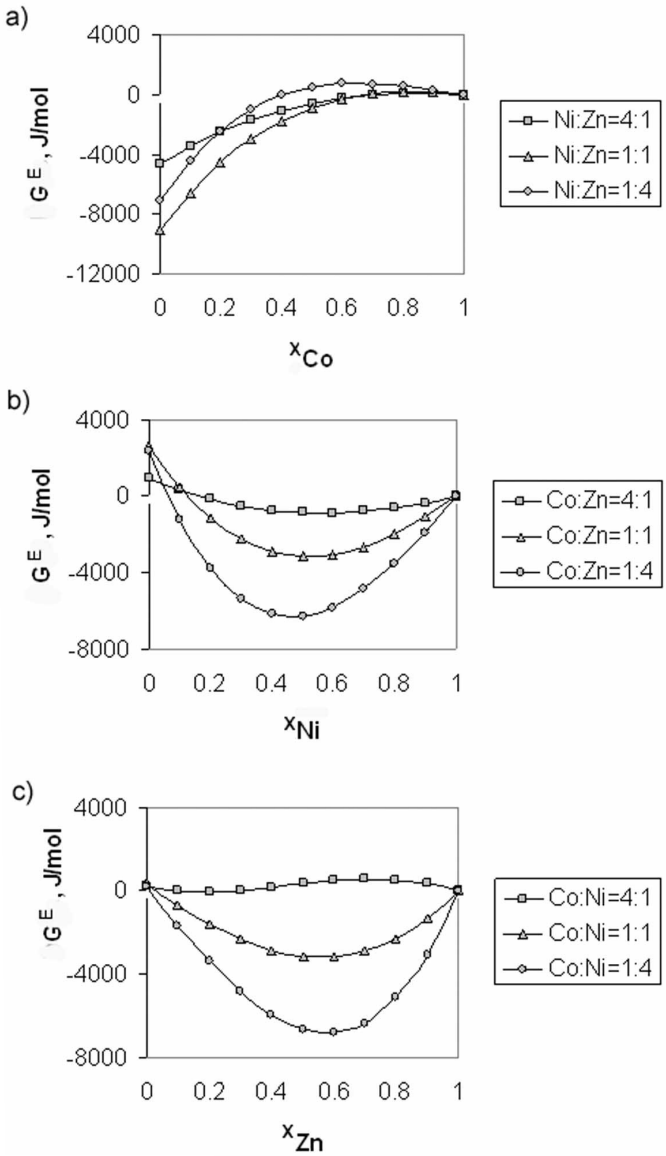

Fig. 4. Dependence of GE on composition for the Co-Ni-Zn system at 2000 K, along the sections from: a) – cobalt corner, b) – nickel corner and c) – zinc corner

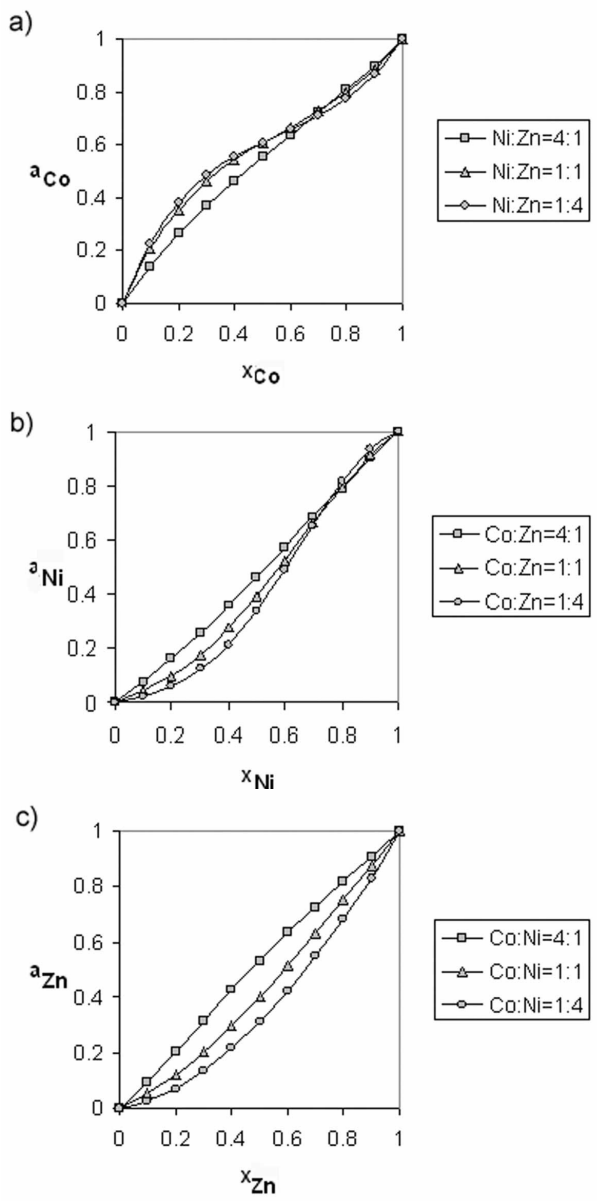

Fig. 5. Dependence of cobalt (a), nickel (b) and zinc (c) activities on composition for the Co-Ni-Zn system at 2000 K

4. Conclusions

Calculation of thermodynamic properties of the Cu-Ni-Zn and Co-Ni-Zn systems was done using the general solution model. The latter was used in order to obtain values of ternary interaction coefficient. Thereafter, Redlich-Kister ternary interaction parameters were obtained for both investigated systems in the temperature interval from 1000 to 2000 K. These values for the Cu-Ni-Zn system have been compared with literature data and have shown good mutual accordance, indicating that such an approach would be possible in the case of systems where no experimental data exist.

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