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Thermodynamic description of the binary Cu–Zr system

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ABSTRACT

The binary Cu–Zr system is an important material for various implementations. The copper–zirconium alloy is one of the best known transition metal–metal binary system which may be obtained in a glassy state by conventional melt-spinning technique over a wide range of composition. On other hand, substitution of Zr for Al in the CuZnAl oxide system was found to improve the catalytic performance during oxidative steam reforming of methanol. In these cases the knowledge of phase equilibria and thermodynamic properties of the binary Cu–Zr system seems to be important for an industry. A new thermodynamic description of this system was proposed based on Calphad method. A good agreement between experimental information and calculation was found.

1. Introduction

A combined steam reforming and partial oxidation of methanol, which has been termed "oxidative steam reforming of methanol" (OSRM), reported recently is considered to be more efficient and convenient for the selective production of H_2 at a relatively low temperature. The catalysts used in the OSRM reaction were CuZnAl mixed oxides derived from hydroxycarbonate precursors containing hydrotalcite (HT)-like layered double hydroxides (LDHs)/aurichalcite phases. Substitution of Zr for Al in the CuZnAl oxide system was found to improve the catalytic performance [1]. The knowledge of the phase diagram of the quinary Al–Cu–O–Zn–Zr system can help to explain that phenomenon. For a good description of the quinary system, the proper thermodynamic modeling of all of the binary system is needed. The thermodynamic assessment of the Cu–Zr system is the first step of the description of mentioned above quinary system. Moreover, the copper–zirconium alloy is one of the best known transition metal–metal binary system which may be obtained in a glassy state by conventional melt-spinning technique over a wide range of composition (0.3–0.74c mole fraction of Zn) [2] what was an additional driving force for this investigation. Previous optimizations available in literature, in our very humble opinion, did not pay enough attention for thermodynamic behavior of the phases and application of suitable models. The enthalpy of mixing of the liquid Cu–Zr exhibits temperature dependency what should be taken into account during assessment. Two of the previous optimizations, however, used models which allow for modeling enthalpy of mixing as a function of temperature. Unfortunately, one of these propositions describes liquid as an associated solution and the second one used modified quasi-chemical model which is more suitable for slags than for metal–metal liquid phase. Moreover, only one previous optimization agrees with the thermodynamic properties of the solid phases. The further information and discussion about previous optimization is given in Sections 2.3 and 5. The Calphad method [3] was used for deriving a new assessment of the phase diagram and thermodynamic properties of the binary Cu–Zr system. The substitutional solution model was chosen for describing liquid and terminal phases. The intermetallic compounds were treated as line compounds because of lack of homogeneity range.

2. Literature information

2.1. Thermodynamic properties

The investigations of the thermodynamic properties of the binary Cu–Zn system were performed for liquid and solid states. The enthalpy of mixing of the liquid phase was measured by Witusiewicz et al. [4] at temperature range 1468–1485 K, by Sudavatsova et al. [5] at 1480 K, by Sommer and Choi [6] at 1473, by Fitzner and Kleppa [7] at 1473, by Kleppa and Watanabe [8] at 1373 and by Turchanin and Nikolaenko [9] at 1873 K and by Yamaguchi et al. [10] at the temperature range 880–1470 K. Moreover, Yamaguchi et al. [10] measured heat of solubility of solid Zr in BCC_A2 structure in the liquid at 1443 K. The activity of copper was measured by Kleppa and Watanabe [8] at 1499 K, by Berezutski [11] at 1623 K and by Zaitsev et al. [12] using Knudsen cell at 1673 K and by Sommer and Choi [6] who also used the Knudsen cell method at 1499 K. The activity of zirconium was measured by Berezutski [11] at 1623 K and by Bormann et al. [13] at 613 K. Thermodynamic properties of the solid phases were determined by several investigators.

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Zaitsev et al. [12] measured chemical potential of components in heterogeneous Cu–Zr alloys. Based on the result they calculated partial thermodynamic functions for heterogeneous alloys and the functions of the formations of the Cu–Zr intermetallic compounds. Ansara et al. [14] measured enthalpy of formation of the CuZr, $CuZr_2$ intermetallic compounds and for alloy Cu0.45Zr0.55 what does not correspond with one phase region. Yamaguchi et al. [10] measured heat content of seven Cu–Zr alloys at the temperature range between 878 K and 1468 K using calorimetric method. In that range of temperatures all alloys exist in both: solid and liquid states. The enthalpy of formation of $Cu_{51}Zr_{14}$ was measured using calorimetric method by Weihs et al. [15] and by Meschel and Kleppa [16]. Kleppa and Watanabe [8] determined also the enthalpies of formation of four congruent melting compounds: $Cu_{10}Zr_7$, CuZr, $CuZr_2$ and $Cu_{51}Zr_{14}$.

2.2. Phase equilibria information

The whole liquidus line was described first time by Lundin et al. [17]. After that a number of papers about the solid–liquid equilibrium were published. The liquidus line was described by Glimois et al. [18], Kuznetsov et al. [19], Pogodin et al. [20], Braga et al. [21], Raub and Engel [22] and Douglas and Morgan [23]. The phase relationship in the Cu–Zr system was described by Lundin et al. [17] who proposed four intermetallic compounds: Cu_3Zr, Cu_3Zr_2, CuZr and $CuZr_2$ which melt congruently and one phase Cu_5Zr_2 which forms by peritectic reaction. Besides Lundin et al. [17] the system was investigated by Allibone and Syknes [18], by Pogodin et al. [19], by Raub and Engel [22], by Donachie [24], by Vitek [25], by Kuznetsov et al. [19], by Glimois et al. [18] by Forey et al. [26], by Bsenko [27], by Gabathuler et al. [28], by Perry and Hugi [29], by Philips [30] by Kneller et al. [31] and by Braga et al. [21]. Generally speaking, the information agrees one another; however, there are two propositions for a stoichiometry of Cu–rich intermetallic phase. The stoichiometry Cu_3Zr was proposed by Lundin et al. [17], investigated by Allibone and Syknes [18], by Pogodin et al. [20], and by Raub and Engel [22] when Donachie[24], Vitek [25] and Kuznetsov et al. [19] proposed Cu_4Zr or Cu_9Zr_2. The composition Cu_9Zr_2 was finally confirmed by Glimois et al. [18] and by Forey et al. [26].

2.3. Thermodynamic modeling

The binary Cu–Zr system was modeled by several researchers. Zeng and Hamalainen [32] modeled the system using substitonal solution [33] for describing the liquid phase. In their work, the enthalpy of mixing was treated as a function independent on temperature. He et al. [34] kept the description proposed by Zeng and Hamalainen [32] except Gibbs energy of the intermetallic compound CuZr. Abe et al. [35] focused on thermodynamic description of the liquid using associate solution model [36]. Wang et al. [37] proposed another thermodynamic description of the binary Cu–Zr system. Also in this work, the enthalpy of mixing was treated as a function independent on temperature. Finally, Kang and Jung [38] used modified quasi-chemical model [39] for the description of the liquid phase.

3. Thermodynamic description of the phases

The binary Cu–Zr system contains 12 phases: HCP_A3 (low temperature Zr), BCC_A2 (high temperature Zr), FCC_A1 (Cu), intermetallic compounds Cu_9Zr_2, $Cu_{51}Zr_{14}$, Cu_8Zr_3, Cu_2Zr, $Cu_{10}Zr_7$, CuZr, Cu_5Zr_7, $CuZr_2$ and liquid. Information about crystal structures is gathered in Table 1. The intermetallic compounds do not show homogeneity range and in that case were treated as line compounds in this work.

Table 1
Crystal structures of phases in the binary Cu–Zr system.

Phase	Strukturbericht designation	Pearson symbol	Space group
(Cu)	A1	*cF*4	$Fm\bar{3}m$
Cu_9Zr_2	–	*tP*24	$P4/m$
$Cu_{51}Zr_{14}$	–	*hP*65	$P6/m$
Cu_8Zr_3	–	*oP*44	*Pnma*
Cu_2Zr	–	–	...
$Cu_{10}Zr_7$	–	*oC*68	...
CuZr	B2	*cP*2	$Pm\bar{3}m$
Cu_5Zr_7	–	*o*	...
$CuZr_2$	A6	*tI*6	$I4/mmm$
(βZr)	A2	*cI*2	$Im\bar{3}m$
(αZr)	A3	*hP*2	$P6_3/mmc$

3.1. Pure elements

The Gibbs free energies of pure elements with respect to temperature ${}^0G_i(T) = G_i(T) - H_i^{SER}$ are represented by Eq. (1):

$$ {}^0G_i(T) = a + bT + cT\ln(T) + dT^2 + eT^{-1} + fT^3 + iT^4 + jT^7 + kT^{-9} \tag{1}$$

The ${}^0G_i(T)$ data refers to the constant enthalpy value of the standard element reference H_i^{SER} at 298.15 K and 1 bar as recommended by Scientific Group Thermodata Europe (SGTE) [40]. The reference states are: FCC_A1 (Cu), HCP_A3 (Zr). The ${}^0G_i(T)$ expression may be given for several temperature ranges, where the coefficients *a, b, c, d, e, f, i, j, k* have different values. The ${}^0G_i(T)$ functions are taken from SGTE Unary (Pure elements) TDB v.4.4 [40].

Solutions (FCC_A1,HCP_Zn, BCC_A2, Liquid):

Solid and liquid solution phases are described by the substitutional solution model [33]:

$$G_m(T) = \sum_i x_i {}^0G_i(T) + RT\sum_i x_i \ln(x_i) + \sum_i \sum_{j>1} x_i x_j \left(\sum_\nu {}^\nu L_{ij}(x_i - x_j)^\nu \right) \tag{2}$$

where the $\sum_i \sum_{j>i} x_i x_j \left(\sum_\nu {}^\nu L_{ij}(x_i - x_j)^\nu \right)$ part is the Redlich–Kister polynomial for excess Gibbs free energy. The parameters ${}^\nu L_{ij}$ have a form ${}^\nu A + {}^\nu BT + {}^\nu CT\ln(T)$. Using parameter *C* is depending on the thermodynamic characteristic of the phase. In case of temperature dependency of enthalpy of mixing of the phase the parameter *C* should be used.

Intermetallic compounds Cu_9Zr_2, $Cu_{51}Zr_{14}$, Cu_8Zr_3, Cu_2Zr, $Cu_{10}Zr_7$, CuZr, Cu_5Zr_7, $CuZr_2$.

Since the intermetallic compounds do not show homogeneity range, the phases were treated as the line compounds. In this case, the Gibbs energy is described as follows:

$$G_m^{Cu_iZr_j}(T) = x_{Cu}{}^0G_{Cu} + x_{Zr}{}^0G_{Zr} + {}^{xs}G_m^{Cu_iZr_j} \tag{3}$$

where ${}^0G_{Cu}$ and ${}^0G_{Zr}$ are Gibbs energies of Cu and Zr in the crystal structure stable at 298.15 K under pressure 1 bar (i.e. functions GHSER), respectively. The Gibbs energy ${}^{xs}G_m^{Cu_iZr_j}$ is the excess Gibbs energy of the phase Cu_iZr_j and it is given by a function *A* + *BT*.

3.2. Optimization procedure

The thermodynamic parameters for all phases in the system were optimized using ThermoCalc v. S software [41], and the results

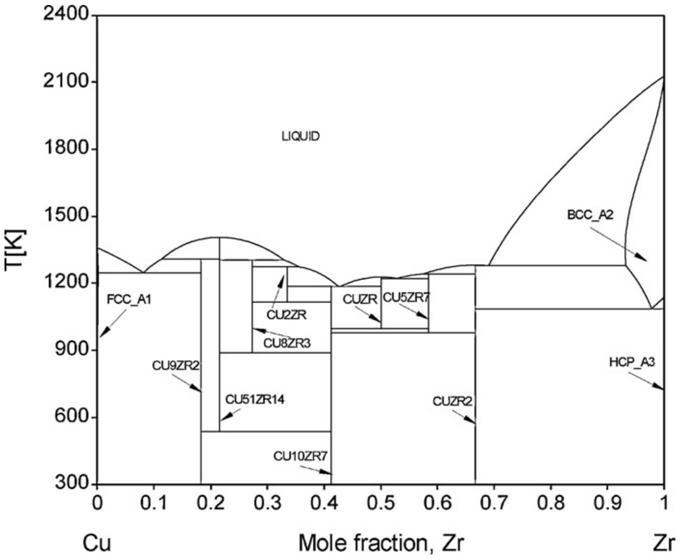

Fig. 1. Calculated phase diagram of the binary Cu–Zr.

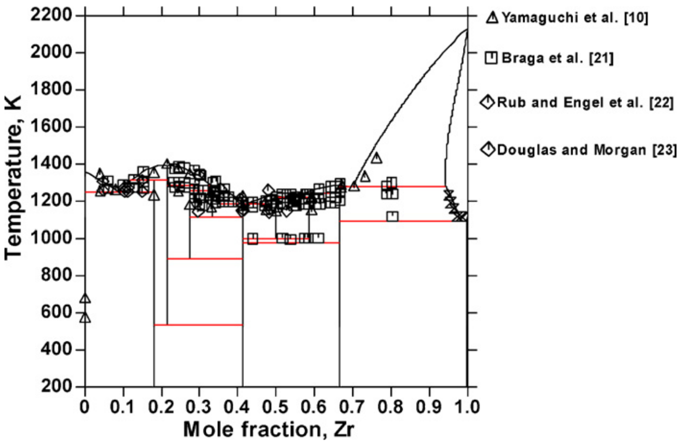

Fig. 2. Calculated phase diagram of the binary Cu–Zr system superimposed with experimental data.

were checked additionally using Pandat v.8 software [42]. For this optimization, thermodynamic data for the liquid and IMCs, invariant reactions and liquidus data were used. Each piece of the selected information was given a certain weight based on personal judgment. The optimization was carried out, step by step, in agreement with the guidelines given by Schmid-Fetzer et al. [43]. First, the optimization of the liquid phase using associate solution model was performed, and then the other phases were assessed. All parameters were finally evaluated together to provide the best description of the system. The calculated interaction parameters are shown in Table 2.

4. Results and discussion

Fig. 1 illustrates calculated phase diagrams with description of the phases involved in this optimization. Due to making this picture

Table 2
Gibbs energies of phases in binary Cu–Zr system.

Phase	Temperature range	Function
Liquid	$298.15<T<1357.77$	${}^0G_{\mathrm{Cu}}^{\mathrm{Liquid}}=+5194.277+120.973331T-24.112392T\times\ln(T)-.00265684T^2+1.29223\mathrm{E}-07\times T^3+52478T^{-1}-5.8489\mathrm{E}-21\times T^7$
	$1357.77<T<3200.00$	${}^0G_{\mathrm{Cu}}^{\mathrm{Liquid}}=-46.545+173.881484T-31.38T\times\ln(T)$
	$298.15<T<2128.00$	${}^0G_{\mathrm{Zr}}^{\mathrm{Liquid}}=+10320.095+116.568238T-24.1618T\times\ln(T)-.00437791T^2+34971T^{-1}+1.6275\mathrm{E}-22T^7$
	$2128.00<T<6000.00$	${}^0G_{\mathrm{Zr}}^{\mathrm{Liquid}}=-8281.26+253.812609T-42.144T\times\ln(T)$
	$298.15<T<3000.00$	${}^0L_{\mathrm{Cu:Zr}}^{\mathrm{Liquid}}=-140638.632+444.1606T-51.3121T\times\ln(T)$
	$298.15<T<3000.00$	${}^1L_{\mathrm{Cu:Zr}}^{\mathrm{Liquid}}=-22066.212+84.9923T-9.6125T\times\ln(T)$
	$298.15<T<3000.00$	${}^2L_{\mathrm{Cu:Zr}}^{\mathrm{Liquid}}=56633.154-307.3817T+36.8512T\times\ln(T)$
	$298.15<T<3000.00$	${}^3L_{\mathrm{Cu:Zr}}^{\mathrm{Liquid}}=-22368.721+119.5438T-13.6488T\times\ln(T))$
FCC_A1	$298.15<T<1357.77$	${}^0G_{\mathrm{Cu}}^{\mathrm{FCC\_A1}}=-7770.458+130.485235T-24.112392T\times\ln(T)-.00265684T^2+1.29223\mathrm{E}-07T^3+52478T^{-1}$
	$1357.77<T<3200.00$	${}^0G_{\mathrm{Cu}}^{\mathrm{FCC\_A1}}=-13542.026+183.803828T-31.38T\times\ln(T)+3.64167\mathrm{E}+29T^{-9}$
	$298.15<T<2128.00$	${}^0G_{\mathrm{Zr}}^{\mathrm{FCC\_A1}}=-227.595+124.74905T-24.1618T\times\ln(T)-.00437791T^2+34971T^{-1}$
	$2128.00<T<6000.00$	${}^0G_{\mathrm{Zr}}^{\mathrm{FCC\_A1}}=-18485.921+261.824183T-42.144T\times\ln(T)-1.342896\mathrm{E}+31T^{-9}$
	$298.15<T<3000.00$	${}^0L_{\mathrm{Cu:Zr}}^{\mathrm{FCC\_A1}}=8254.852$
BCC_A2	$298.15<T<1357.77$	${}^0G_{\mathrm{Cu}}^{\mathrm{BCC\_A2}}=-3753.458+129.230235T-24.112392T\times\ln(T)-.00265684T^2+1.29223\mathrm{E}-07T^3+52478T^{-1}$
	$1357.77<T<3200.00$	${}^0G_{\mathrm{Cu}}^{\mathrm{BCC\_A2}}=-9525.026+182.548828T-31.38T\times\ln(T)+3.64167\mathrm{E}+29T^{-9}$
	$298.15<T<2128.00$	${}^0G_{\mathrm{Zr}}^{\mathrm{BCC\_A2}}=-525.539+124.9457T-25.607406T\times\ln(T)-3.40084\mathrm{E}-04T^2-9.729\mathrm{E}-09T^3+25233T^{-1}-7.6143\mathrm{E}-11T^4$
	$2128.00<T<6000.00$	${}^0G_{\mathrm{Zr}}^{\mathrm{BCC\_A2}}=-30705.955+264.284163T-42.144T\times\ln(T)+1.276058\mathrm{E}+32T^{-9}$
	$298.15<T<3000.00$	${}^0L_{\mathrm{Cu:Zr}}^{\mathrm{BCC\_A2}}=356.954-5.5499T$
HCP_A3	$298.15<T<1357.77$	${}^0G_{\mathrm{Cu}}^{\mathrm{HCP\_A3}}=-7170.458+130.685235T-24.112392T\times\ln(T)-.00265684T^2+1.29223\mathrm{E}-07T^3+52478T^{-1}$
	$1357.77<T<3200.00$	${}^0G_{\mathrm{Cu}}^{\mathrm{HCP\_A3}}=-12942.026+184.003828T-31.38T\times\ln(T)+3.64167\mathrm{E}+29T^{-9}$
	$130.00<T<2128.00$	${}^0G_{\mathrm{Zr}}^{\mathrm{HCP\_A3}}=-7827.595+125.64905T-24.1618T\times\ln(T)-.00437791T^2+34971T^{-1}$
	$2128.00<T<6000.00$	${}^0G_{\mathrm{Zr}}^{\mathrm{HCP\_A3}}=-26085.921+262.724183T-42.144T\times\ln(T)-1.342896\mathrm{E}+31T^{-9}$
	$298.15<T<3000.00$	${}^0L_{\mathrm{Cu:Zr}}^{\mathrm{HCP\_A3}}=-52576.592+70.9696T$
Cu_9Zr_2	$298.15<T<3000.00$	${}^0G_{\mathrm{Cu:Zr}}^{\mathrm{Cu_9Zr_2}}=-9410.421-0.40907T+.818\mathrm{GHSERCU}+.182\mathrm{GHSERZR}$
$Cu_{51}Zr_{14}$	$298.15<T<3000.00$	${}^0G_{\mathrm{Cu:Zr}}^{\mathrm{Cu_{51}Zr_{14}}}=-10184.262-1.0260T+.785\mathrm{GHSERCU}+.215\mathrm{GHSERZR}$
Cu_8Zr_3	$298.15<T<3000.00$	${}^0G_{\mathrm{Cu:Zr}}^{\mathrm{Cu_8Zr_3}}=-11925.337-0.43889T+.727\mathrm{GHSERCU}+.273\mathrm{GHSERZR}$
Cu_2Zr	$298.15<T<3000.00$	${}^0G_{\mathrm{Cu:Zr}}^{\mathrm{Cu_2Zr}}=-11425.463-1.4755T+.666\mathrm{GHSERCU}+.334\mathrm{GHSERZR}$
$Cu_{10}Zr_7$	$298.15<T<3000.00$	${}^0G_{\mathrm{Cu:Zr}}^{\mathrm{Cu_{10}Zr_7}}=-20463.114+5.8825T+.588\mathrm{GHSERCU}+.412\mathrm{GHSERZR}$
CuZr	$298.15<T<3000.00$	${}^0G_{\mathrm{Cu:Zr}}^{\mathrm{CuZr}}=-14836.032+0.8587T+.5\mathrm{GHSERCU}+.5\mathrm{GHSERZR}$
Cu_5Zr_7	$298.15<T<3000.00$	${}^0G_{\mathrm{Cu:Zr}}^{\mathrm{Cu_5Zr_7}}=-15186.254+1.8103T+.416\mathrm{GHSERCU}+.584\mathrm{GHSERZR}$
$CuZr_2$	$298.15<T<3000.00$	${}^0G_{\mathrm{Cu:Zr}}^{\mathrm{CuZr}}=-17045.108+4.2935T+.334\mathrm{GHSERCU}+.666\mathrm{GHSERZR}$

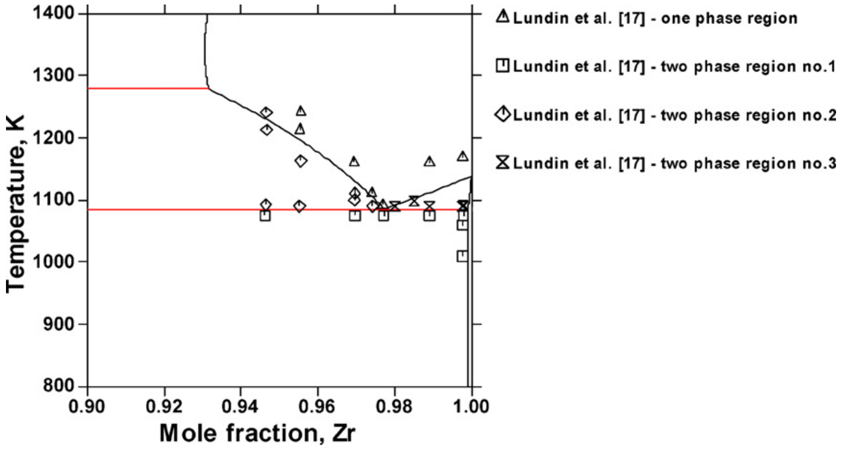

Fig. 3. Zoomed in Zr–reach part of the Cu–Zr phase diagram.

clear for reading, the experimental information was not included in this figure. Fig. 2 shows calculated phase diagram superimposed with experimental data obtained by several researchers. Taking into account that a density of experimental information could make this picture unclear we decided to show data obtained by Yamaguchi et al. [10], by Braga et al. [21], by Raub and Engel [22] and by Douglas and Morgan [23]. The phase diagram reproduces experimental data well. The small discrepancy can be found for liquidus line of the region Zr-BCC; however,the equilibrium between Zr-BCC and $CuZr_2$ is in very good agreement with the data obtained by Douglas and Morgan [23]. Fig. 3 shows zoomed in Zr-rich part of the phase diagram together with experimental data obtained by Lundin et al. [17]. This picture exhibits very good agreement between calculation and one-phase and two-phase regions determined experimentally. Calculated invariant reactions compared to experimental data obtained by different researchers are gathered in Table 3. Information collected in this table shows big discrepancy between temperatures of reactions obtained by different authors; however, calculated results lay inside a span of experimental data. Fig. 4 shows calculated enthalpy of mixing of liquid Cu–Zr alloy at 1000 K and at 1473 K superimposed with experimental data obtained by Yamaguchi et al. [10], by Abe et al. [35] by Sommer and Choi [6] and by Kleppa and Watanabe [8]. From this picture one can see that proposed substitional model described well temperature dependency of enthalpy of mixing of liquid phase. In Fig. 5 one can see calculated activity of Cu at 1673 K together with experimental data obtained by Zaitsev et al. [12] and by Sommer and Choi [6] at 1673 K and at 1623 K, respectively. This Figure also shows very good agreement between calculation and experimental information. As it was mentioned earlier, in opposite to Abe et al. [35] we did not use liquid associate Cu_2Zr in our description. There are two reasons for this treatment of the liquid phase. First one is that shape of enthalpy of mixing of the liquid phase does not exhibit sharp extreme; the second reason is that a solid intermetallic compound Cu_2Zr decomposes by peritectic reaction at 1114 K and because of that should not be stable as an associate in the liquid phase. Fig. 6 shows calculated chemical potential of Zr in various phases at the function of temperature superimposed with experimental data obtained by Zaitsev et al. [12] by electromotive force measurement. Interesting comparison between chemical potential of zirconium obtained by Zaitsev et al. [12] and previous optimization can be found in Kang and Jung [38] work. From Fig. 6 one can find that our proposition of the description of the Cu–Zr system agrees well with Zaitsev et al. [12] experimental work. Fig. 7 exhibits calculated heat of dissolution of Zr in BCC_A2 structure in the liquid at 1443 K superimposed with experimental data obtained by Yamaguchi et al. [10]. Generally speaking, the calculation reproduces experiment well, only for a concentration of Zr equal 0.4 mole fraction modeled function is more negative than experiment. Summarizing comparison of the calculation and experimental data, one can say that proposed a new set of Gibbs energy functions reproduce well thermodynamic properties and phase diagram of the binary Cu–Zr system.

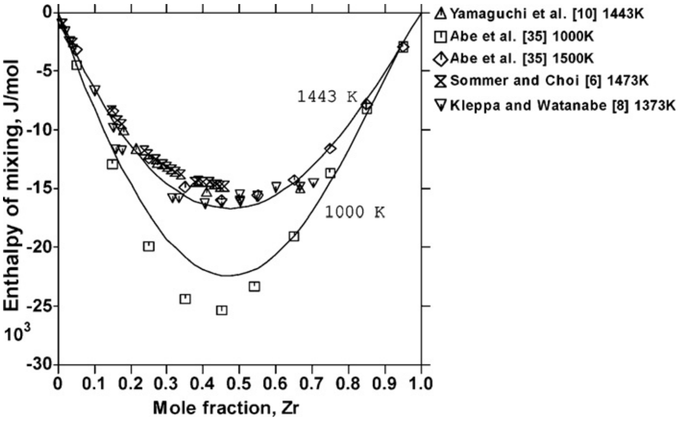

Fig. 4. Calculated enthalpy of mixing of the liquid phase at 1473 K and 1000 K superimposed.

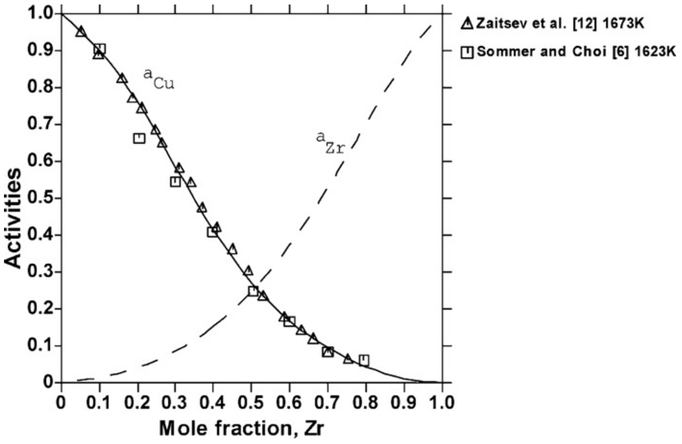

Fig. 5. Calculated activities of copper and zirconium at 1673 together with experimental data.

Table 3
Invariant reactions in the binary Cu–Zr system.

Reaction	Temperature	x_{Zr}(Liquid)	Method	Reference
Liquid = FCC_A1+Cu_9Zr_2	1251	0.081	Calculated	This work
	1238	0.065	Measured	[17]
	1271	0.106	Measured	[21]
	1241	0.0769	Calculated	[32]
	1245	0.086	Calculated	[12]
	1276	0.073	Calculated	[37]
	1253	0.081	Calculated	[38]
Liquid + $Cu_{51}Zr_{14}$ = Cu_9Zr_2	1309	0.113	Calculated	This work
	1283	0.107	Measured	[20]
	1287	–	Measured	[18]
	1311	0.125	Measured	[21]
	1288	0.107	Calculated	[32]
	1285	0.11	Calculated	[12]
	1311	0.107	Calculated	[37]
	1290	0.182	Calculated	[38]
Liquid + $Cu_{51}Zr_{14}$ = Cu_8Zr_3	1258	0.328	Calculated	This work
	1248	–	Measured	[20]
	1343	0.308	Measured	[17]
	1305	0.34	Measured	[21]
	1195	0.388	Calculated	[31]
	1283	0.326	Calculated	[12]
	1305	0.316	Calculated	[37]
	1285	–	Calculated	[38]
Cu_8Zr_3 = $Cu_{51}Zr_{14}$+$Cu_{10}Zr_7$	888	–	Calculated	This work
	885	–	Measured	[31]
	883	–	Calculated	[12]
	886	–	Calculated	[37]
	886	–	Calculated	[38]
Liquid = $CuZr_2$+BCC_A2	1276	0.692	Calculated	This work
	1268	0.724	Measured	[17]
	1293	–	Measured	[21]
	1284	0.685	Calculated	[37]
	1281	0.697	Calculated	[38]
Liquid + Cu_8Zr_3 = Cu_2Zr	1253	0.354	Calculated	This work
	1269	–	Measured	[21]
	1269	0.347	Calculated	[37]
	1256	–	Calculated	[38]
Liquid + $CuZr_2$ = Cu_5Zr_7	1242	0.574	Calculated	This work
	1238	–	Measured	[31]
	1220	0.57	Measured	[21]
	1237	0.576	Calculated	[12]
	1218	0.565	Calculated	[37]
	1182	–	Calculated	[38]
Liquid = Cu_5Zr_7 + CuZr	1221	0.528	Calculated	This work
	1186	0.56	Measured	[21]
	1200	0.526	Calculated	[12]
	1200	0.545	Calculated	[37]
	1207	–	Calculated	[38]
Liquid + Cu_2Zr = $Cu_{10}Zr_7$	1184	0.424	Calculated	This work
	1177	0.355	Measured	[31]
	1200	–	Measured	[21]
	1199	0.399	Calculated	[37]
	1234	–	Calculated	[38]
Liquid = $Cu_{10}Zr_7$ + CuZr	1180	0.428	Calculated	This work
	1164	0.44	Measured	[17]
	1163	0.475	Measured	[31]
	1178	–	Measured	[21]
	1167	0.432	Calculated	[12]
	1189	0.447	Calculated	[37]
	1207	–	Calculated	[38]
Cu_2Zr = Cu_8Zr_3 + $Cu_{10}Zr_7$	1114	–	Calculated	This work
	1160	–	Measured	[31]
	1184	–	Measured	[21]
	1104	–	Calculated	[12]
	1160	–	Calculated	[37]
	1104	–	Calculated	[38]
BCC_A2 = $CuZr_2$ + HCP_A3	1086		Calculated	This work
	1189		Measured	[6]
	1095		Measured	[17]
	1091		Calculated	[37]
	1099		Calculated	[38]
CuZr = $Cu_{10}Zr_7$ + Cu_5Zr_7	995		Calculated	This work
	985		Measured	[31]
	1004		Measured	[21]
	987		Calculated	[12]
	1003		Calculated	[37]
	994		Calculated	[38]
Cu_5Zr_7 = $Cu_{10}Zr_7$ + $CuZr_2$	978		Calculated	This work
	970		Measured	[31]
	972		Calculated	[12]
	985		Calculated	[37]
	950		Calculated	[38]
$Cu_{51}Zr_{14}$ = Cu_9Zr_2 + $Cu_{10}Zr_7$	534		Calculated	This work

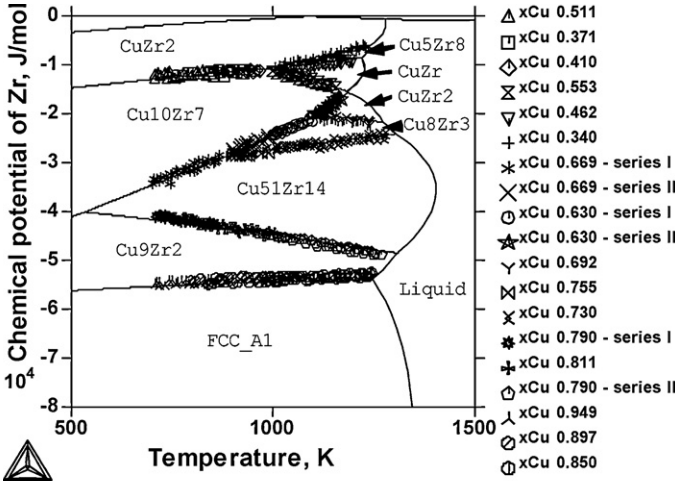

Fig. 6. Calculated chemical potential of zirconium superimposed with data obtained by Zaitsev et al. [12].

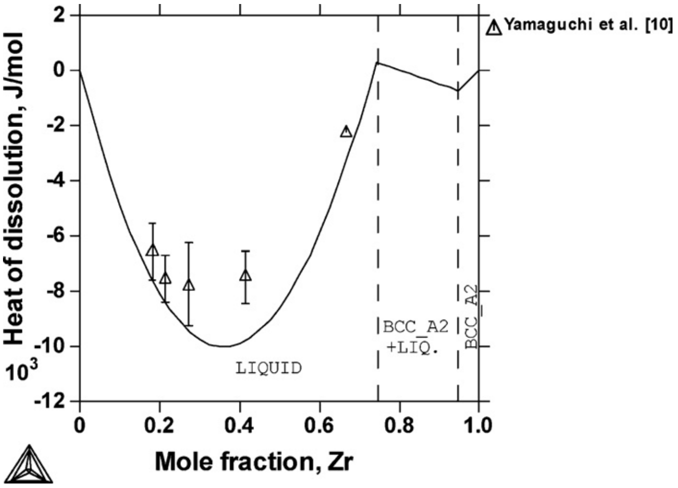

Fig. 7. Calculated heat of dissolution solid Zr in BCC_A2 structure in liquid at 1443 K superimposed with experimental data.

5. Conclusions

A new thermodynamic description of the binary Cu–Zr system was proposed in this work. The functions of Gibbs energies of the phases reproduce well phase diagram and thermodynamic properties of liquid and solid phase. The enthalpy of mixing of the liquid phase was modeled using substitutional solution as a function of temperature. Based on thermodynamic properties of the liquid obtained by several experimental techniques we did not find any reason for using more complicated mathematical description of the liquid behavior. Using the substitional solution model allows for easy extrapolation to higher-ordered systems.

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