



## 'Thermodynamic assessment of the Ag-Zr and Cu-Zr binary systems



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### ABSTRACT

The Ag-Zr and Cu-Zr binary systems are thermodynamically reassessed in this study. Not only phase diagrams, but also thermodynamic properties, such as enthalpy of formation for solids, activity for liquid, and enthalpy of mixing for liquid, are all calculated and compared with available experimental data to assure the accuracy of the assessment.  $\text{Cu}_2\text{Zr}$  and  $\text{Cu}_{24}\text{Zr}_{13}$  phases are considered as meta-stable phases, which would not exist in the Cu-Zr equilibrium phase diagram. The artifact of liquid miscibility gap at high temperature is avoided in the presently calculated phase diagrams.

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### 1. Introduction

The Cu-Zr-based alloys are of great interest because of their easy formation of amorphous metallic glasses, in other words, high glass-forming ability (GFA) in this system [1,2]. With the addition of Ag element, the stability of supercooled liquid and GFA would be increased; also, the mechanical properties were improved [3]. Hence, the understanding of Ag-Cu-Zr system is important for industrial application. Furthermore, by using the thermodynamic dataset, the formation region of bulk metallic glasses (BMGs) could be predicted and later verified by experimental methods, such as copper mold or roller melt-spinning methods [4–6]. The experimental number of samples could be reduced in a large amount due to thermodynamic prediction based on reliable and consistent thermodynamic description of Ag-Cu-Zr ternary system, which first requires reliable modeling of binary Ag-Zr and Cu-Zr sub-systems. The Ag-Cu system was assessed several times [7–11] and not discussed in this work.

The phase diagram of Ag-Zr system was reviewed and established by Karakaya and Thompson [12]. There were two intermetallic phases,  $\text{AgZr}$  and  $\text{AgZr}_2$ , existing in this system after assessment and calculation. The Ag-Zr system was optimized by Karakaya et al. [12], He et al. [13], and Kang et al. [14]. But in Ref. [12], the experimental data from Zhang et al. [15] were not considered. Thermodynamic description of Ref. [13] resulted in a liquid miscibility gap at high temperature. Kang et al. [14] used

Modified Quasichemical Model and FactSage to assess the system in 2010. However, the quasichemical model can be only applied in FactSage and is not compatible with Pandat and ThermoCalc.

The Cu-Zr system, on the other hand, was thermodynamically assessed by several authors [14,16–21]. There were several contradictions in the results of these thermodynamic descriptions. The first question was whether the copper-rich intermetallic compound has  $\text{Cu}_9\text{Zr}_2$  or  $\text{Cu}_5\text{Zr}$  stoichiometry. The second one was whether  $\text{Cu}_5\text{Zr}_8$ ,  $\text{Cu}_2\text{Zr}$ , and  $\text{Cu}_{24}\text{Zr}_{13}$  phases claimed by Kneller et al. [22] and Braga et al. [23] are stable or not. In this work, we thermodynamically reassess the Ag-Zr and Cu-Zr binary systems taking into account all the available experimental data.

### 2. Critical review of experimental literature data

#### 2.1. Ag-Zr binary system

##### 2.1.1. Solid phases

The  $\text{AgZr}$  intermetallic phase in the Ag-Zr system was confirmed through X-ray analysis by Raub et al. [24] and Karlsson [25]. Later, the  $\text{AgZr}_2$  phase was identified as the BCT structure with lattice parameter  $c = 398$  pm by Betterton and Easton [26], which is different from the results of Nevitt and Downey [27] who proposed  $c = 1200.37$  pm. Karlsson [25] reported that  $\text{AgZr}_3$  phase existed in the composition range of 70–80 at% Zr. This intermetallic phase was not taken into consideration in this study, mainly based on other experimental results which indicated existence of  $\text{AgZr}_2$  phase [15,26–28]. Raub et al. [24] first reported that  $\text{AgZr}$  had a small homogeneity range. In Ref. [25] the homogeneity range of

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**Table 1**  
Solid phases in the Ag-Zr and Cu-Zr systems.

Phase name / Temperature range (°C)	Pearson symbol /Space group/ Prototype	Lattice para- meters (pm)	Reference
(Ag) ≤ 961.93	cF4 <i>Fm-3m</i> Cu	$a = 408.61$	[63] (1981 King)
(Cu) ≤ 1084.87	cF4 <i>Fm-3m</i> Cu	$a = 361.46$	[63] (1981 King)
(βZr) 1855–863	cI2 <i>Im-3 m</i> W	$a = 360.90$	[64] (1982 King) [65] (1973 Metals)
(αZr) ≤ 863	hP2 <i>P6<sub>3</sub>/mmc</i> Mg	$a = 323.17$ $c = 514.76$	[64] (1982 King) [65] (1973 Metals)
AgZr ≤ 468	tP4 <i>P4/nmm</i> γ-CuTi	$a = 346.8\text{--}347.6$ $c = 660.3\text{--}662.9$	[25] (1952 Karlssen)
AgZr <sub>2</sub> ≤ 834	tl6 <i>I4/mmm</i>  MoSi <sub>2</sub>	$a^* = 325$ $c^* = 398$ or $a^\dagger = 324.64$ $c^\dagger = 1200.37$	*[26] (1958 Bet- terton), BCT structure †[27] (1962 Nevitt)
Cu <sub>9</sub> Zr <sub>2</sub> ≤ 1012	F-43 m	$a = 685.6$ $c = 688.2$	[35] (1985 Glimois) [37] (2001 Saitoh)
Cu <sub>51</sub> Zr <sub>14</sub> ≤ 1115	hP65  <i>P6/m</i> Ag <sub>51</sub> Gd <sub>14</sub>	$a = 1124.44$ $c = 828.15$	[66] (1975 Gabathuler) [67] (1975 Bsenko)
Cu <sub>8</sub> Zr <sub>3</sub>	oP44 <i>Pnma</i> Cu <sub>8</sub> Hf <sub>3</sub>	$a = 786.93$ $b = 815.47$ $c = 998.48$	[67] (1975 Bsenko)
Cu <sub>10</sub> Zr <sub>7</sub>	oC68 <i>C2ca</i> Ni <sub>10</sub> Zr <sub>7</sub>	$a = 1267.29$ $b = 931.63$ $c = 934.66$	[67] (1975 Bsenko)
CuZr 960–725**	cP2 <i>Pm-3 m</i> CsCl	$a = 325.87$	[50] (1980 Carvalho) **[23] (1998 Braga)
CuZr <sub>2</sub> 1025–950***	tl6 <i>I4/mmm</i> MoSi <sub>2</sub>	$a = 322.04$ $c = 1118.32$	[27] (1962 Nevitt) ***[22] (1986 Kneller) and [23] (1998 Braga)

AgZr is given to be less than 3 at%. Zhang et al. [15] observed that the AgZr and AgZr<sub>2</sub> phases at 900 °C were homogeneous in the range from 47.5 to 51.0 at% Ag and from 31.3 to 34.0 at% Ag, respectively. For simplicity, this work set AgZr and AgZr<sub>2</sub> phases as stoichiometric compounds.

### 2.1.2. Thermodynamic data

Only Fitzner and Kleppa [29] reported values of enthalpy of formation of intermetallic AgZr and AgZr<sub>2</sub> phases at 298 K. These values were obtained from observed heats of reaction at 1473 K, and then they transferred the measured heat effect to standard enthalpy of formation at 298 K. Hence, the values presented in Ref. [29] are not reliable; even the authors marked that these values were uncertain. There is no experimental measurement of heat capacities and entropies of AgZr and AgZr<sub>2</sub> phases.

### 2.1.3. Phase equilibrium data

The experimental data for the Ag-Zr phase equilibria were mainly from Karakaya et al. [12]. For the Ag-Zr system, Raub and Engel [24] measured the liquidus and solidus temperatures for a composition range from 4 to 51 at% Zr and found the eutectic

**Table 2**

Experimental and calculated standard enthalpy of formation of the Cu-Zr compounds,  $\Delta_f H^\circ$ , at 298 K. Reference state of calculated values is fcc-(Cu) and hcp-(αZr).

Phases	Method	$\Delta_f H^\circ$ , kJ/mol-atoms	Reference
Cu <sub>9</sub> Zr <sub>2</sub>	Measured	$-8.7 \pm 1.9^a$ $-10.389 \pm 0.077$ $-23.8$ $-9.0597$	[43] (1989Sommer) [40] (2003Zaitsev) [19] (2008Yamaguchi) [14] (2010Kang)
	Calphad	$-9.93153$	This work
Cu <sub>51</sub> Zr <sub>14</sub>	Measured	$-14.07 \pm 1.24^b$ $-14.3 \pm 0.3$ $-11.241 \pm 0.076$ $-24.3 \pm 2.2$ $-25.2$	[41] (1982Kleppa) [45] (1996Weihs) [40] (2003Zaitsev) [68] (2003Meschel) [19] (2008Yamaguchi)
	Calphad	$-12.97558$ $-12.601$ $-20.252$ $-9.6663$ $-12.2164$	[16] (1994Zeng) [18] (2008Turchanin) [20] (2010Zhou) [14] (2010Kang) This work
Cu <sub>8</sub> Zr <sub>3</sub>	Measured	$-13.129 \pm 0.083$ $-16.2$	[40] (2003Zaitsev) [19] (2008Yamaguchi)
	Calphad	$-13.46029$ $-14.788$ $-18.55966$ $-11.135$ $-13.1058$	[16] (1994Zeng) [18] (2008Turchanin) [20] (2010Zhou) [14] (2010Kang) This work
Cu <sub>10</sub> Zr <sub>7</sub>	Measured	$-12.31 \pm 0.24^b$ $-22.004 \pm 0.259$ $-22.9$	[41] (1982Kleppa) [40] (2003Zaitsev) [19] (2008Yamaguchi)
	Calphad	$-14.22059$ $-20.466$ $-16.133$ $-18.994$ $-15.353$	[16] (1994Zeng) [18] (2008Turchanin) [20] (2010Zhou) [14] (2010Kang) This work
CuZr	Measured	$-9.05 \pm 1.18$ $-24.4 \pm 0.96$ $-24 \pm 2$ $-17.9 \pm 2.8$ $-17.282 \pm 0.309$	[41] (1982Kleppa) [42] (1982Ansara) [44] (1989Sidero) [47] (1996Turchanin) [40] (2003Zaitsev)
	Calphad	$-10.05212$ $-17.014$ $-12.44168$ $-13.626$ $-9.38877$	[16] (1994Zeng) [18] (2008Turchanin) [20] (2010Zhou) [14] (2010Kang) This work
CuZr <sub>2</sub>	Measured	$-10.95 \pm 0.69$ $-17.3 \pm 0.84$ $-19.797 \pm 0.357$ $-16.6$	[41] (1982Kleppa) [42] (1982Ansara) [40] (2003Zaitsev) [19] (2008Yamaguchi)
	Calphad	$-14.63467$ $-23.635$ $-13.84$ $-14.923$ $-12.4512$	[16] (1994Zeng) [18] (2008Turchanin) [20] (2010Zhou) [14] (2010Kang) This work

<sup>a</sup> In [43] (1989Sommer), Cu<sub>9</sub>Zr<sub>2</sub> was designated as Cu<sub>4</sub>Zr.

<sup>b</sup> In [41] (1982Kleppa), Cu<sub>51</sub>Zr<sub>14</sub> and Cu<sub>10</sub>Zr<sub>7</sub> were designated as Cu<sub>3</sub>Zr and Cu<sub>3</sub>Zr<sub>2</sub>, respectively.

reaction  $L \leftrightarrow (\text{Ag}) + \text{AgZr}$  at 955 °C. Betterton et al. [26] investigated the Zr-rich part (up to 36 at% Ag) of the Ag-Zr system and determined the formation of AgZr and AgZr<sub>2</sub> intermetallic phases. The eutectoid reaction, in which the (βZr) solid solution decomposed into (αZr) and AgZr<sub>2</sub> phases, was determined. They also found that the solubility of Ag in (βZr) at peritectic temperature of 1190 °C was about 20 at%. The solubility of Ag in (αZr) was found to be about 0.1 at% at the eutectoid temperature 823 °C [26]. Later, Loboda et al. [28] used DTA for analysis of Ag-Zr alloys in a composition range from 30 to 70 at% Zr and obtained peritectic reactions of formation of AgZr at 1135 °C and AgZr<sub>2</sub> at 1170 °C. The melting temperatures were chosen from onset

**Table 3**

Experimental, assessed and calculated congruent melting point of intermetallic compounds in the Cu-Zr system.

Compound	Method	Temperature (°C)	Composition of compound, at% Zr	Reference
Cu <sub>51</sub> Zr <sub>14</sub>	Measured	1112	22.8	[24] (1948Raub), Cu <sub>51</sub> Zr <sub>14</sub> was designated as Cu <sub>3</sub> Zr
		1100	21.6	[51] (1953Lundin)
		1113	20.49	[30] (1972Perry), Cu <sub>51</sub> Zr <sub>14</sub> was designated as Cu <sub>4</sub> Zr
		1104	22.2	[34] (1978Kuznetsov), Cu <sub>51</sub> Zr <sub>14</sub> was designated as Cu <sub>7</sub> Zr <sub>2</sub>
		1115	–	[35] (1985 Glimois)
	Assessed	1120 ± 6	–	[19] (2008Yamaguchi)
		1115	21.54	[38] (1990Arias)
		1122	21.54	[69] (1985Saunders)
		1113	21.54	[16] (1994Zeng)
		1122	21.54	[13] (2006He)
		1116	21.5	[17] (2006Wang)
		1109	21.54	[18] (2008Turchanin)
		1111	21.54	[14] (2010Kang)
		1109	21.54	[20] (2010Zhou)
		1114	21.54	This work
Cu <sub>10</sub> Zr <sub>7</sub>	Measured	895	41.25	[51] (1953Lundin), Cu <sub>10</sub> Zr <sub>7</sub> was designated as Cu <sub>3</sub> Zr <sub>2</sub>
		912 ± 3	–	[19] (2008Yamaguchi)
	Assessed	895	41.18	[38] (1990Arias)
	Calculated	891	41.18	[16] (1994Zeng)
		891	41.18	[13] (2006He)
		927	41.0	[17] (2006Wang)
		892	41.18	[18] (2008Turchanin)
		931	41.18	[20] (2010Zhou)
CuZr	Measured	935	49.75	[51] (1953Lundin)
		933	50.0	[19] (2008Yamaguchi)
	Assessed	935	50.0	[38] (1990Arias)
	Calculated	928	50.0	[69] (1985Saunders)
		936	50.0	[16] (1994Zeng)
		936	50.0	[13] (2006He)
		953	50	[17] (2006Wang)
		938	50.0	[18] (2008Turchanin)
		935	50.0	[20] (2010Zhou)
		947	50	This work
CuZr <sub>2</sub>	Measured	1000	64.97	[51] (1953Lundin)
		1006	–	[19] (2008Yamaguchi)
	Assessed	1000	66.67	[38] (1990Arias)
	Calculated	1011	66.67	[69] (1985Saunders)
		1002	66.67	[16] (1994Zeng)
		1002	66.67	[13] (2006He)
		1013	66.7	[17] (2006Wang)
		1009	66.67	[18] (2008Turchanin)
		1011	–	[14] (2010Kang)
		1002	66.67	[20] (2010Zhou)
		1002	66.67	This work

temperatures of a DTA curve. For one alloy composition, they prepared three samples for experiment. Each sample was only heated once with a heating rate of 40 K/min, which is considered to be too fast for the DTA experiment. Zhang et al. [15], which by means of DTA and metallographic methods, found three invariant reactions: eutectic  $L \leftrightarrow (Ag) + AgZr$  at 953 °C,  $L \leftrightarrow (\beta Zr) + AgZr_2$  at 1149 °C, and peritectic  $L + AgZr_2 \leftrightarrow AgZr$  at 1153 °C. The three-phase region of Ag-Zr phase diagram, which consisted of ( $\alpha$ Zr), ( $\beta$ Zr), and AgZr<sub>2</sub> phases, revealed by Betterton and Easton [26] was not considered in this work due to its inconsistency with other experimental data.

## 2.2. Cu-Zr binary system

### 2.2.1. Solid phases

There are several intermetallic phases, such as Cu<sub>9</sub>Zr<sub>2</sub>, Cu<sub>51</sub>Zr<sub>14</sub>, Cu<sub>8</sub>Zr<sub>3</sub>, Cu<sub>10</sub>Zr<sub>7</sub>, CuZr, and CuZr<sub>2</sub>, existing in the Cu-Zr binary system. The existence of Cu<sub>9</sub>Zr<sub>2</sub> or Cu<sub>5</sub>Zr phase is disputable in the literature. In Refs. [30–32], they considered that the first Cu-rich phase should be Cu<sub>5</sub>Zr. Furthermore, the DTA investigations had been done by Braga et al. [23] for entire Cu-Zr system, and results

for a composition range from 0 to 20 at% Zr were consistent with data published by Kneller et al. [22]. Both works supposed that the first Cu-rich intermetallic phase was Cu<sub>5</sub>Zr. However, Vitek used an electron microprobe to obtain that one phase had a composition range between Cu<sub>9</sub>Zr<sub>2</sub> and Cu<sub>4</sub>Zr [33]. Kuznetsov et al. [34] observed that one phase consisting of 18 at% Zr should be Cu<sub>9</sub>Zr<sub>2</sub> phase by thermal analysis, which reacted peritectically with liquid and Cu<sub>7</sub>Zr<sub>2</sub> at 1010 °C. In 1985, Glimois et al. [35] investigated the copper-rich side of the phase diagram of Cu-Zr system by X-ray diffraction, metallography, and differential thermal analysis. They confirmed the existence of the incongruently melting intermetallic compound Cu<sub>9</sub>Zr<sub>2</sub>, and presented the crystal structure information, which is shown in Table 1. Taguchi et al. committed solid-state diffusion reaction between pure Cu and Zr metals at 700–883 °C [36]. The Cu<sub>9</sub>Zr<sub>2</sub> phase with the composition of 81.8 at% Cu was determined by Electron Probe Micro-Analysis (EPMA) in their work [36]. In the most recent study, Saitoh et al. [37] prepared the Cu-8.9 at% Zr alloy, which is eutectic composition point at 972 °C in the Cu-Zr system assessed by Arias and Abriata [38], being annealed at 750 °C, 850 °C, and 950 °C to examine the microstructure in the Cu + Cu<sub>9</sub>Zr<sub>2</sub> two-phase region by X-ray diffraction

**Table 4**

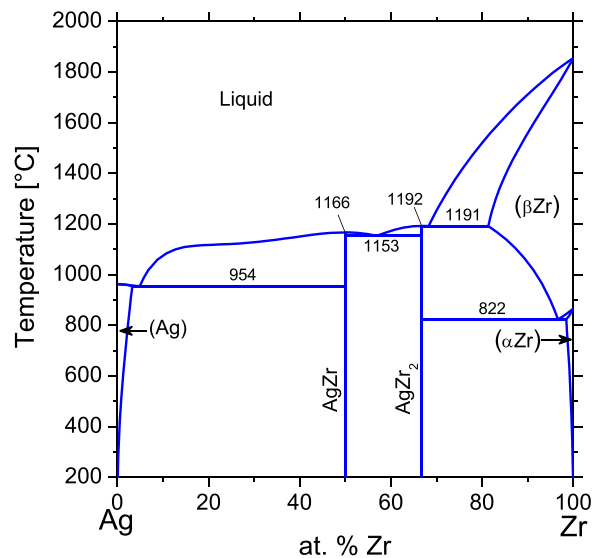
Phase designations, models (sublattice formula) and parameters of the Gibbs energy equations optimized in present work for the Ag-Zr system. Gibbs energy is given in J mol-atoms<sup>-1</sup> and temperature (T) is given in Kelvin. The Gibbs energy equations for the phases of pure elements are adopted from the SGTE compilation [58].

Liquid; LIQUID; (Ag, Zr) <sub>1</sub>
$L_{Ag,Zr}^{0,Liq} = -23481.8 + 16.7326 \times T$
$L_{Ag,Zr}^{1,Liq} = +16991.4 + 1.8009 \times T$
(Ag); FCC; (Ag, Zr) <sub>1</sub>
$L_{Ag,Zr}^{0,fcc} = +3981.04 + 10.6628 \times T$
(βZr); BCC; (Ag, Zr) <sub>1</sub>
$L_{Ag,Zr}^{0,bcc} = +25220.7 - 11.613 \times T$
(αZr); HCP; (Ag, Zr) <sub>1</sub>
$L_{Ag,Zr}^{0,hcp} = +10944.9 + 9.21728 \times T$
AgZr; AGZR; (Ag) <sub>0.5</sub> (Zr) <sub>0.5</sub>
$G_{Ag,Zr}^{0,AgZr} = -5500 - 0.730238 \times T + 0.5 \times G_{Ag}^{0,fcc} + 0.5 \times G_{Zr}^{0,hcp}$
AgZr <sub>2</sub> ; AGZR <sub>2</sub> ; (Ag) <sub>0.333333</sub> (Zr) <sub>0.666667</sub>
$G_{Ag,Zr}^{0,AgZr_2} = -3617.36 - 1.93893 \times T + 0.333333 \times G_{Ag}^{0,fcc} + 0.666667 \times G_{Zr}^{0,hcp}$

**Table 5**

Phase designations, models (sublattice formula) and parameters of the Gibbs energy equations optimized in present work for the Cu-Zr system. Gibbs energy is given in J mol-atoms<sup>-1</sup> and temperature (T) is given in Kelvin. The Gibbs energy equations for the phases of pure elements are adopted from the SGTE compilation [58].

Liquid; LIQUID; (Cu, Zr) <sub>1</sub>
$L_{Cu,Zr}^{0,Liq} = -67897.6 + 18.0843 \times T$
$L_{Cu,Zr}^{1,Liq} = -5634.86 + 3.3207 \times T$
(Cu); FCC; (Cu, Zr) <sub>1</sub>
$L_{Cu,Zr}^{0,fcc} = +4193.48$
(βZr); BCC; (Cu, Zr) <sub>1</sub>
$L_{Cu,Zr}^{0,bcc} = -3804.59$
(αZr); HCP; (Cu, Zr) <sub>1</sub>
$L_{Cu,Zr}^{0,hcp} = +16,507$
Cu <sub>9</sub> Zr <sub>2</sub> ; CU9ZR2; (Cu) <sub>0.818182</sub> (Zr) <sub>0.181818</sub>
$G_{Cu,Zr}^{0,Cu_9Zr_2} = -9931.53 - 0.5372 \times T + 0.818182 \times G_{Cu}^{0,fcc} + 0.181818 \times G_{Zr}^{0,hcp}$
Cu <sub>51</sub> Zr <sub>14</sub> ; CU51ZR14; (Cu) <sub>0.784615</sub> (Zr) <sub>0.215385</sub>
$G_{Cu,Zr}^{0,Cu_{51}Zr_{14}} = -12216.4 - 0.115 \times T + 0.784615 \times G_{Cu}^{0,fcc} + 0.215385 \times G_{Zr}^{0,hcp}$
Cu <sub>8</sub> Zr <sub>3</sub> ; CU8ZR3; (Cu) <sub>0.727273</sub> (Zr) <sub>0.272727</sub>
$G_{Cu,Zr}^{0,Cu_8Zr_3} = -13105.8 + 0.0319 \times T + 0.727273 \times G_{Cu}^{0,fcc} + 0.272727 \times G_{Zr}^{0,hcp}$
Cu <sub>10</sub> Zr <sub>7</sub> ; CU10ZR7; (Cu) <sub>0.588235</sub> (Zr) <sub>0.411765</sub>
$G_{Cu,Zr}^{0,Cu_{10}Zr_7} = -15,353 + 1.335 \times T + 0.588235 \times G_{Cu}^{0,fcc} + 0.411765 \times G_{Zr}^{0,hcp}$
CuZr; CUZR; (Cu) <sub>0.5</sub> (Zr) <sub>0.5</sub>
$G_{Cu,Zr}^{0,CuZr} = -9388.77 - 4.0134 \times T + 0.5 \times G_{Cu}^{0,fcc} + 0.5 \times G_{Zr}^{0,hcp}$
CuZr <sub>2</sub> ; CUZR2; (Cu) <sub>0.333333</sub> (Zr) <sub>0.666667</sub>
$G_{Cu,Zr}^{0,CuZr_2} = -12451.2 + 0.380966 \times T + 0.333333 \times G_{Cu}^{0,fcc} + 0.666667 \times G_{Zr}^{0,hcp}$



**Fig. 1.** Calculated phase diagram of the Ag-Zr system using thermodynamic description of this work; the inverted miscibility gap does not occur in the liquid phase up to 9000 °C.

and TEM methods. They concluded that the Cu<sub>9</sub>Zr<sub>2</sub> phase was a stable phase and determined the crystal structure as shown in Table 1.

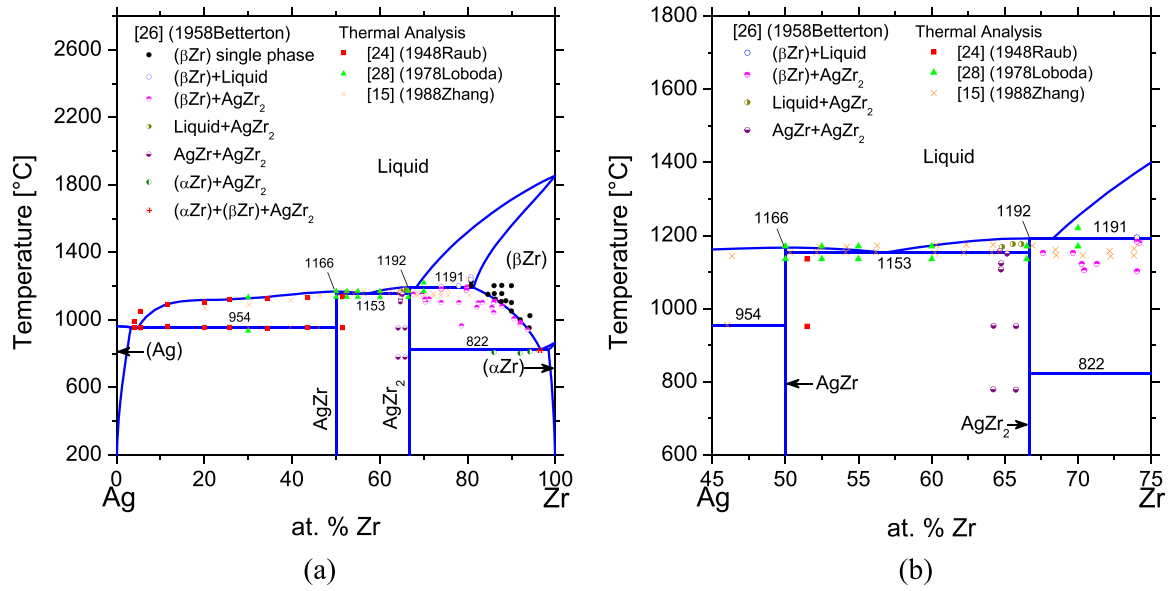
In the thermodynamic modeling of the Cu-Zr system, some authors adopted that the first Cu-rich intermetallic phase was Cu<sub>9</sub>Zr<sub>2</sub> [14,17,19,21,39], while others considered that it would be Cu<sub>5</sub>Zr phase [16,18,20]. In the present work, we accept it as the Cu<sub>9</sub>Zr<sub>2</sub> phase based on the experimental results of Refs. [36,37], in which the given stoichiometry was carefully determined by the EPMA measurement.

Kneller et al. investigated the Cu-Zr system by thermal and X-ray analyzes. They reported that new phases, i.e. Cu<sub>5</sub>Zr<sub>8</sub>, Cu<sub>2</sub>Zr, and Cu<sub>24</sub>Zr<sub>13</sub>, had been found [22]. Braga et al. [23] also found that in the composition range of Zr from 27.3 to 33.5 at%, at least one phase (Cu<sub>24</sub>Zr<sub>13</sub> or Cu<sub>2</sub>Zr) is stable at 1190–1300 K. Nevertheless, in the opinion of Arias et al. [38], the annealing times at such low temperature in the experiment of Kneller et al. [22] were not sufficient to allow samples to reach equilibrium. Moreover, a significant oxygen contamination was concerned in this experiment. Braga et al.'s [23] DTA results were strongly scattered. Hence, results of last two papers have not been considered in this work.

In this study, we also do not consider the results published by Zaitsev et al. [39,40] obtained by means of Knudsen cell mass spectrometry. Their determination of phases was mainly based on the results from Kneller et al. [22] and Braga et al. [23]. The crystallographic data of solid phases in Ag-Zr and Cu-Zr systems are summarized in Table 1.

## 2.2.2. Thermodynamic data

Kleppe and Watanabe [41] measured enthalpies of mixing of liquid copper with solid zirconium at 1373 K. The enthalpies of formation of Cu<sub>10</sub>Zr<sub>7</sub> (designated as Cu<sub>3</sub>Zr<sub>2</sub> in the original paper), CuZr, and CuZr<sub>2</sub> compounds were evaluated using results on heat content measurements, and the values of Cu<sub>51</sub>Zr<sub>14</sub> (designated as Cu<sub>3</sub>Zr) were calculated from heats of dissolution. The formation enthalpies of CuZr and CuZr<sub>2</sub> compounds were determined by a dissolution calorimetry using liquid Al bath at 1030 K and 1040 K, respectively [42]. The reference state of Zr in Ref. [42] should be hcp-(αZr). Sommer and Choi [43] measured the enthalpy of formation of Cu<sub>9</sub>Zr<sub>2</sub> compound, which was designated as Cu<sub>4</sub>Zr in their report, in high temperature calorimeter at 1473 K. In Ref. [44], they committed high temperature calorimetric experiment in



**Fig. 2.** Calculated phase diagram of the Ag-Zr system using present thermodynamic description compared with available experimental data [15,24,26,28]: (a) full scale and (b) enlarged part.

**Table 6**

Comparison of experimental and calculated invariant reactions for the Ag-Zr system.

Reaction	Type	Method	Temperature (°C)	Composition of respective phases, at% Zr			Reference/comments
				1st	2nd	3rd	
L + (βZr) ↔ AgZr <sub>2</sub>	Peritectic	Measured	1191	64	80	67	[26] (1958 Betterton)
			1170	–	–	66.5	[28] (1978 Loboda)
		Assessed	1190	63.5	80.2	66.7	[12] (1992 Karakaya)
		Calculated	1195	62.3	–	–	[13] (2006 He)
L ↔ (βZr) + AgZr <sub>2</sub>	Eutectic	Measured	1149	70.5	–	–	[15] (1988 Zhang)
			1146	72.2	–	–	[14] (2010 Kang)
		Calculated	1191	68.26	81.36	66.67	This work
L + AgZr <sub>2</sub> ↔ AgZr	Peritectic	Measured	1135	30	66.5	50	[28] (1978 Loboda)
			1153	–	–	–	[15] (1988 Zhang)
		Assessed	1136	46.5	66.0	50.0	[12] (1992 Karakaya)
		Calculated	1123	48.8	–	–	[13] (2006 He)
L ↔ AgZr <sub>2</sub> + AgZr	Eutectic	Calculated	1154	57.5	–	–	[14] (2010 Kang)
			1153	56.85	66.67	50.0	This work
L ↔ (Ag) + AgZr	Eutectic	Measured	955	2.5	–	50	[24] (1948 Raub)
			935	–	–	50	[28] (1978 Loboda)
			953	–	–	–	[15] (1988 Zhang)
		Assessed	940	2.5	0.1	48.5	[12] (1992 Karakaya)
			941	5.6	–	–	[13] (2006 He)
			956	6.9	–	–	[14] (2010 Kang)
		Calculated	954	4.90	3.26	50.0	This work
(βZr) ↔ (αZr) + AgZr <sub>2</sub>	Eutectoid	Measured	823	96.3	99.9	66.7	[26] (1958 Betterton)
			821	–	–	66.5	[28] (1978 Loboda)
		Assessed	820	96.1	97.8	67.0	[12] (1992 Karakaya)
			817	94.7	–	–	[13] (2006 He)
		Calculated	817	96.3	–	–	[14] (2010 Kang)
			822	96.62	98.45	66.67	This work

He atmosphere at 1873 K and calculated the enthalpy of formation of solid Cu<sub>0.5</sub>Zr<sub>0.5</sub> alloy at 298 K. The enthalpy of formation of Cu<sub>51</sub>Zr<sub>14</sub> compound was measured by Weihs et al. [45] using Cu-Zr multilayer foils, the values of which agreed with Klippa et al.'s results [41]. All experimental enthalpies of formation data are shown in Table 2.

The activity of copper in liquid Cu-Zr alloys at 1499 K was measured by the Knudsen effusion method [43]. The same method was also used by Berezhitskii to measure the activity of Cu at 1623 K [46]. Zaitsev et al. [40] used Knudsen cell mass

spectrometry to measure the vapor pressure of Cu and evaluated the activity of Cu in the composition range of 5–85 at% Zr at 918–1550 °C. Experimental data of these three works are used for optimization. The enthalpy of dissolution of solid zirconium in liquid copper had been measured by high-temperature calorimetry at 1373 K [41]. The authors used the enthalpy of fusion of Zr (equal to 15,330 J/mol) to obtain the enthalpy of mixing for liquid by calculation [41]. The enthalpy of mixing of liquid Cu-rich (3–50 at% Zr) Cu-Zr alloys at 1473 K had been calorimetrically determined by Sommer and Choi [43]. Turchanin et al. [47] and Witusiewicz et al.



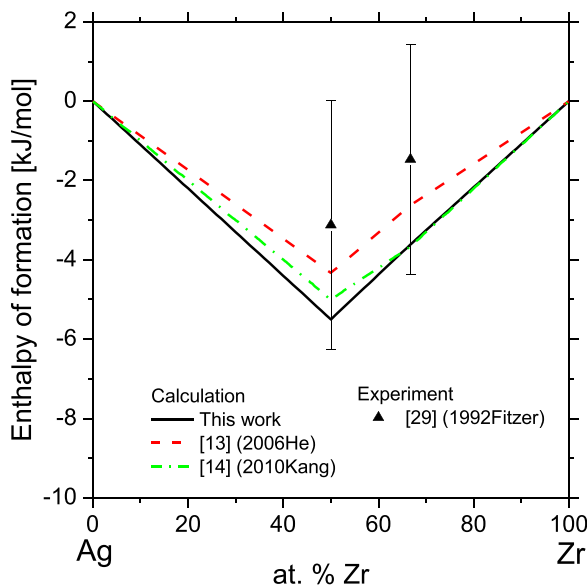


Fig. 3. Calculated enthalpies of formation of solid phases at 298 K for the Ag-Zr system using thermodynamic description of this work compared with experimental data [29] and previous calculations [13,14]. Reference states are fcc-(Ag) and hcp-(Zr).

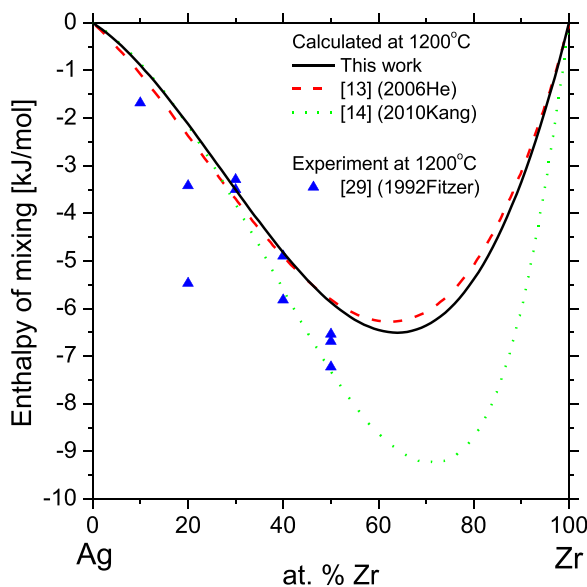


Fig. 4. Calculated enthalpy of mixing for liquid phase at 1200 °C for the Ag-Zr system compared with experimental data [29] and previous calculations [13,14]. Reference states are liquid Ag and liquid Zr.

[48] measured enthalpies of dissolution of solid zirconium in liquid copper by high temperature calorimetry for Cu-Zr system at 1873 K and 1467–1485 K, respectively. Since the data published by Turchanin et al. in 1998 [49] were almost the same as in 1996 [47], we only took the data from Ref. [47] for consideration. The enthalpies of mixing in the liquid phase of the Cu-Zr system at 1443 K were measured by Yamaguchi et al. using high temperature reaction calorimeter [19] in  $X_{Zr}$  range from 0.182 to 0.667.

Experimental  $C_p$  values were only reported by Yamaguchi et al. [19]. The heat content of alloys with compositions  $X_{Zr}=0.04, 0.081, 0.181, 0.215, 0.273, 0.412, 0.667$  were investigated by using a drop calorimeter. However, Yamaguchi et al. [19] did not consider obtained values seriously in their optimization. This work also considers such values to be less important than solidus and liquidus temperatures data, which was determined by the same authors

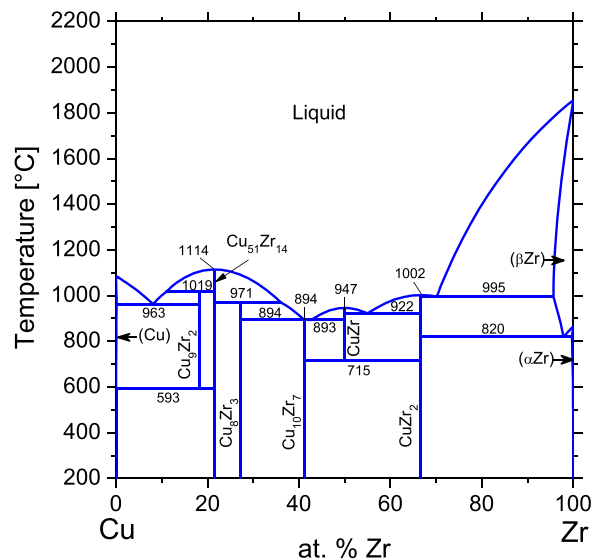


Fig. 5. Calculated phase diagram of the Cu-Zr system using thermodynamic description of this work.

and discussed in Section 2.2.3.

### 2.2.3. Phase equilibrium data

For the Cu-Zr entire system, the phase equilibria data were assessed by Arias et al. [38] in 1990 based on experimental results of Refs. [24,30,34,35,50,51]. The newer experimental data published by Zhou et al. [20] and Yamaguchi et al. [19] are considered in this work as well. For the Zr-rich side of the Cu-Zr system, experimental data were mainly established by Lundin et al. [51] using metallographic examination of Zr-Cu alloys in the composition range from 0.1 to 4 wt% Cu at 600–980 °C. On the other hand, the Cu-rich side of the Cu-Zr system was investigated by several authors [20,52–56], and it mainly focused on the solubility of Zr in Cu.

The congruent melting point of intermetallic phases in the Cu-Zr system was investigated by several researchers [19,24,30,34,35,51]. In accordance with Lundin et al. [51], the CuZr phase melted congruently at 935 °C. Later, Hillmann and Hofmann reported the formation of CuZr phase when the pure Cu/Zr diffusion couple was annealed at 650 °C [57]. Table 3 shows experimental congruent melting points for  $Cu_{51}Zr_{14}$ ,  $Cu_{10}Zr_7$ , CuZr, and  $CuZr_2$  phases. Obviously, the congruent melting temperatures for  $Cu_{51}Zr_{14}$  and  $Cu_{10}Zr_7$  differ by about 10 K. The stoichiometries of these two phases in Refs. [24,30,34,51] were designated differently, however, in this work we consider them as  $Cu_{51}Zr_{14}$  and  $Cu_{10}Zr_7$  phases.

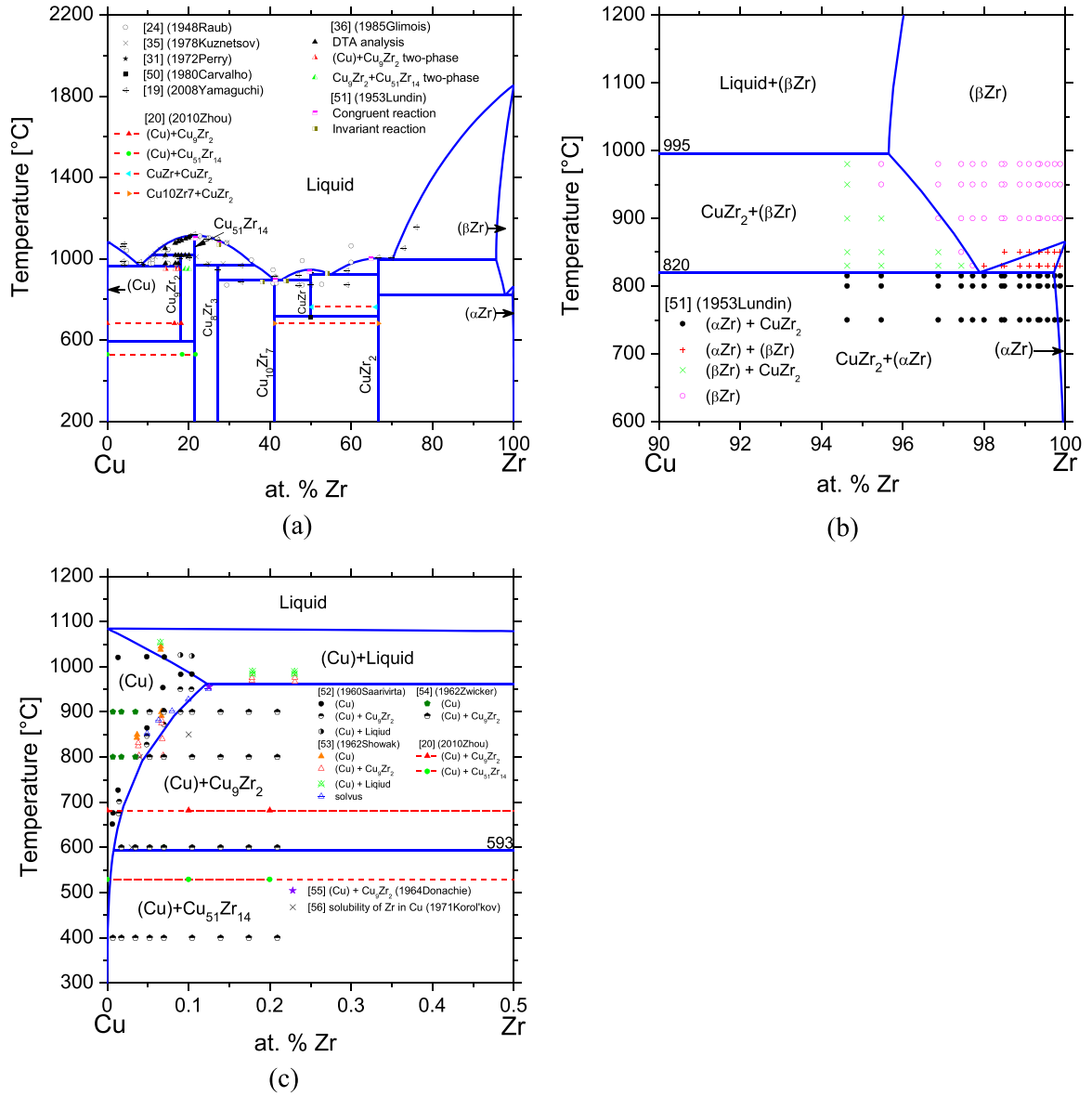
## 3. Thermodynamic modeling

### 3.1. Pure elements

The Gibbs energy for pure element  $i$  ( $i = \text{Ag, Cu, or Zr}$ ) in any phase  $\phi$  is described by the following equation:

$$G_i^{\phi}(T) = G_i^{\phi}(T) - H_i^{SER} = a + bT + cT \ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \quad (1)$$

where  $G_i^{\phi}(T)$  is the Gibbs energy for element  $i$  in phase  $\phi$  and  $H_i^{SER}$  is the molar enthalpy of element  $i$  at 298.15 K and 1 bar in its standard element reference (SER) state, which is fcc for Ag and Cu and hcp for Zr. The Gibbs energy functions for Ag, Cu, and Zr are taken from the SGTE (Scientific Group Thermodata Europe)



**Fig. 6.** Calculated phase diagrams of the Cu-Zr system using thermodynamic description of this work compared with experimental data [19,20,24,31,35,36,50–56]: (a) full scale, (b) enlarged Zr-rich and (c) Cu-rich sides. Reference states are fcc-(Cu) and hcp-(αZr).

database compilation by Dinsdale [58].

### 3.2. Solution phases

The Gibbs energies for liquid, fcc, bcc, and hcp solution phases in Ag-Zr and Cu-Zr systems are described by the substitution solution model, in which Gibbs energy was described as follows:

$$G^\phi = \sum_{i=1}^2 x_i G_i^{0,\phi} + RT \sum_{i=1}^2 x_i \ln x_i + \sum_{i=1}^2 \sum_{j>1}^2 x_i x_j \sum_{\nu=0}^1 L_{ij}^{\nu,\phi} (x_i - x_j)^\nu \quad (2)$$

where  $x_i$  and  $x_j$  represent the mole fractions of the components for Ag and Zr or Cu and Zr in Ag-Zr and Cu-Zr systems, respectively.  $R$  is the gas constant,  $L_{ij}^{0,\phi}$  is the regular and  $L_{ij}^{1,\phi}$  is the sub-regular solution parameters of the interaction between elements Ag and Zr or Cu and Zr.

### 3.3. Intermetallic phases

AgZr and AgZr<sub>2</sub> phases in Ag-Zr system and Cu<sub>9</sub>Zr<sub>2</sub>, Cu<sub>51</sub>Zr<sub>14</sub>,

Cu<sub>8</sub>Zr<sub>3</sub>, Cu<sub>10</sub>Zr<sub>7</sub>, CuZr, and CuZr<sub>2</sub> phases in Cu-Zr system are treated as stoichiometric phases in the present modeling. Take CuZr<sub>2</sub> phase, for example, the Gibbs energy is expressed as follows:

$$G^{\text{CuZr}_2} = a + b \cdot T + 0.333333 \cdot G_{\text{Cu}}^{0,\text{fcc}} + 0.666667 \cdot G_{\text{Zr}}^{0,\text{hcp}} \quad (3)$$

where  $a$  and  $b$  are parameters of the Gibbs energy of formation optimized in this study.

### 3.4. Parameter optimization

For Ag-Zr binary system, the parameters of liquid and fcc phases in thermodynamic description published by He et al. [13],  ${}^0L_{\text{Ag,Zr}}^{\text{Liq}}$  and  ${}^0L_{\text{Ag,Zr}}^{\text{fcc}}$ , included  $T \ln T$  terms. They were eliminated in the present work because of the lack of  $C_p$  experimental data. The initial values for these two parameters are considerably taken from the results of Kang et al. [14] and then further optimized.

Contrary to Ag-Zr system, the Cu-Zr binary system was thermodynamically assessed several times by various authors [14,16–21]. But every result had their insight and different consequences.

**Table 7**

Comparison of experimental and calculated invariant reactions for the Cu-Zr system.

Reaction	Type	Method	Temperature (°C)	Composition of respective phases, at% Zr			Reference/comments
				1st	2nd	3rd	
L ↔ (Cu) + Cu <sub>9</sub> Zr <sub>2</sub>	Eutectic	Measured	977	10.0	–	–	[24] (1948Raub)
			971	8.85	–	16.0	[30] (1972Perry), Cu <sub>9</sub> Zr <sub>2</sub> was designated as Cu <sub>5</sub> Zr
			977	–	–	–	[35] (1985 Glimois)
		Assessed	972	8.6	0.12	18.18	[38] (1990Arias)
		Calculated	968	7.69	0.11	16.67	[16] (1994Zeng), Cu <sub>9</sub> Zr <sub>2</sub> was designated as Cu <sub>5</sub> Zr
			1003	7.73	–	18	[17] (2006Wang)
			980	8.2	0.13	16.67	[18] (2008Turchanin), Cu <sub>9</sub> Zr <sub>2</sub> was designated as Cu <sub>5</sub> Zr
			980	8.1	–	–	[14] (2010Kang)
			979	7.2	0.1	16.67	[20] (2010Zhou), Cu <sub>9</sub> Zr <sub>2</sub> was designated as Cu <sub>5</sub> Zr
			978	8.1	–	18.2	[21] (2011Gierlotka)
			963	8.11	0.12	18.18	This work
Cu <sub>9</sub> Zr <sub>2</sub> ↔ (Cu) + Cu <sub>51</sub> Zr <sub>14</sub>	Eutectoid	Measured	529–682	–	–	–	[20] (2010Zhou), Cu <sub>9</sub> Zr <sub>2</sub> was designated as Cu <sub>5</sub> Zr
		Calculated	591	16.7	–	21.5	[20] (2010Zhou), Cu <sub>9</sub> Zr <sub>2</sub> was designated as Cu <sub>5</sub> Zr
			593	18.18	0.0077	21.54	This work
L + Cu <sub>51</sub> Zr <sub>14</sub> ↔ Cu <sub>9</sub> Zr <sub>2</sub>	Peritectic	Measured	1010	–	22.2	18.0	[34] (1978Kuznetsov), Cu <sub>51</sub> Zr <sub>14</sub> was designated as Cu <sub>7</sub> Zr <sub>2</sub>
		Assessed	1014	–	–	–	[35] (1985 Glimois)
			1012	11.5	21.54	18.18	[38] (1990Arias)
			1014	10.7	21.54	16.67	[16] (1994Zeng), Cu <sub>9</sub> Zr <sub>2</sub> was designated as Cu <sub>5</sub> Zr
			1038	10.7	21.5	18	[17] (2006Wang)
			1007	10.3	21.54	16.67	[18] (2008Turchanin), Cu <sub>9</sub> Zr <sub>2</sub> was designated as Cu <sub>5</sub> Zr
			1017	18.2	21.54	–	[14] (2010Kang)
			1013	9.8	21.54	16.7	[20] (2010Zhou), Cu <sub>9</sub> Zr <sub>2</sub> was designated as Cu <sub>5</sub> Zr
			1036	11.3	21.5	18.2	[21] (2011Gierlotka)
			1018	11.07	21.54	18.18	This work
L + Cu <sub>51</sub> Zr <sub>14</sub> ↔ Cu <sub>8</sub> Zr <sub>3</sub>	Peritectic	Measured	1070	30.8	21.6	27.5	[51] (1953Lundin)
		Assessed	975	–	22.2	–	[34] (1978Kuznetsov), Cu <sub>51</sub> Zr <sub>14</sub> and Cu <sub>8</sub> Zr <sub>3</sub> were designated as Cu <sub>7</sub> Zr <sub>2</sub> and Cu <sub>5</sub> Zr <sub>2</sub> , respectively
			975	36.0	21.54	27.27	[38] (1990Arias)
			922	38.8	21.54	27.27	[16] (1994Zeng)
			1032	31.6	21.5	27	[17] (2006Wang)
			971	34.3	21.54	27.27	[18] (2008Turchanin)
			1012	27.3	–	–	[14] (2010Kang)
			985	32.8	21.5	27.3	[21] (2011Gierlotka)
			971	36.01	21.54	27.27	This work
		Calculated	922	38.8	21.54	27.27	[16] (1994Zeng)
			1032	31.6	21.5	27	[17] (2006Wang)
L ↔ Cu <sub>8</sub> Zr <sub>3</sub> + Cu <sub>10</sub> Zr <sub>7</sub>	Eutectic	Measured	885	38.19	27.54	41.25	[51] (1953Lundin)
		Assessed	885	38.2	27.27	41.18	[38] (1990Arias)
		Calculated	891	40.8	27.27	41.18	[16] (1994Zeng)
			888	39.1	27.27	41.18	[18] (2008Turchanin)
			894	41.18	27.27	41.18	This work
L ↔ Cu <sub>10</sub> Zr <sub>7</sub> + CuZr	Eutectic	Measured	890	43.99	41.25	49.75	[51] (1953Lundin)
		Assessed	890	44	41.18	50.0	[38] (1990Arias)
		Calculated	890	42.5	41.18	50.0	[16] (1994Zeng)
			916	44.7	41	50	[17] (2006Wang)
			888	43.3	41.18	50.0	[18] (2008Turchanin)
			920	45.6	41.18	50.0	[20] (2010Zhou)
			907	42.8	41.2	50	[21] (2011Gierlotka)
			893	42.74	41.18	50.0	This work
CuZr ↔ Cu <sub>10</sub> Zr <sub>7</sub> + CuZr <sub>2</sub>	Eutectoid	Measured	712	–	–	–	[50] (1980 Carvalho)
		Assessed	715	50.0	41.18	66.67	[38] (1990Arias)
			704	50.0	41.18	66.67	[16] (1994Zeng)
			712	50.0	41.18	66.67	[18] (2008Turchanin)
			729	50.0	41.18	66.67	[20] (2010Zhou)
			715	50.0	41.18	66.67	This work
L ↔ CuZr + CuZr <sub>2</sub>	Eutectic	Measured	928	54.26	49.75	64.97	[51] (1953Lundin)
		Assessed	928	54.3	50.0	66.67	[38] (1990Arias)
		Calculated	924	53.8	50.0	66.67	[16] (1994Zeng)
			921	54.1	50.0	66.67	[18] (2008Turchanin)
			912	43.5	50.0	66.67	[14] (2010Kang)
			922	54.3	50.0	66.67	[20] (2010Zhou)
			922	54.98	50.0	66.67	This work
L ↔ CuZr <sub>2</sub> + (βZr)	Eutectic	Measured	995	72.38	64.97	94.63	[51] (1953Lundin)
		Assessed	995	72.4	66.67	94.3	[38] (1990Arias)
		Calculated	996	70.0	66.67	94.7	[16] (1994Zeng)



Table 7 (continued)

Reaction	Type	Method	Temperature (°C)	Composition of respective phases, at% Zr			Reference/comments
				1st	2nd	3rd	
			998	70.9	66.67	95.0	[18] (2008Turchanin)
			1008	69.8	–	–	[14] (2010Kang)
			995	70.2	66.67	94.6	[20] (2010Zhou)
			1003	69.2	66.6	–	[21] (2011Gierlotka)
			995	70.12	66.67	95.65	This work
$(\beta\text{Zr}) \leftrightarrow \text{CuZr}_2 + (\alpha\text{Zr})$	Peritectoid	Measured	822	97.7	64.97	99.71	[51] (1953Lundin)
		Assessed	822	97.8	66.67	99.8	[38] (1990Arias)
		Calculated	816	97.6	66.67	99.6	[16] (1994Zeng)
			818	97.8	66.7	–	[17] (2006Wang)
			824	98.3	66.67	99.96	[18] (2008Turchanin)
			826	97.6	–	–	[14] (2010Kang)
			846	96.9	66.67	97.7	[20] (2010Zhou)
			813	–	66.6	–	[21] (2011Gierlotka)
			820	97.89	66.67	99.72	This work

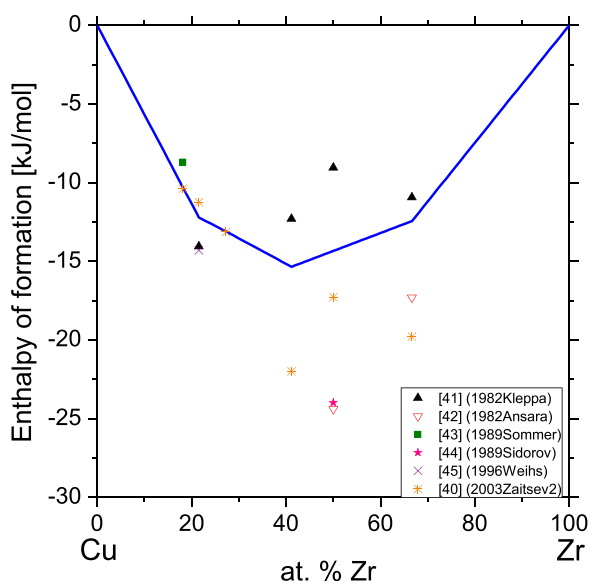


Fig. 7. Calculated enthalpies of formation of solid phases at 298 K using thermodynamic description of this work compared with experimental data [40–45].

The property of high and low temperature for  $\text{CuZr}_2$ , which were named  $\text{CuZr}_2\text{-H}$  and  $\text{CuZr}_2\text{-L}$  by Wang et al. [17], was not considered in this study. The optimization was initially based on the parameters of Zeng et al. [16], and experimental data published by Zhou et al. [20] were considered as important for parameters optimization.

All thermodynamic calculations and optimization of parameters are performed by the Pandat software ([www.compuTherm.com](http://www.compuTherm.com)) with PanOptimizer [59]. The parameters of Gibbs energies optimized in this work are given in Tables 4 and 5 for the Ag–Zr and Cu–Zr systems, respectively.

## 4. Results and discussion

### 4.1. Ag–Zr binary system

#### 4.1.1. Phase diagram

Fig. 1 shows the calculated phase diagram of Ag–Zr binary system using thermodynamic description of present work. Although this diagram has only shown a temperature range of 200–2000 °C, our check calculation was carried out up to temperature

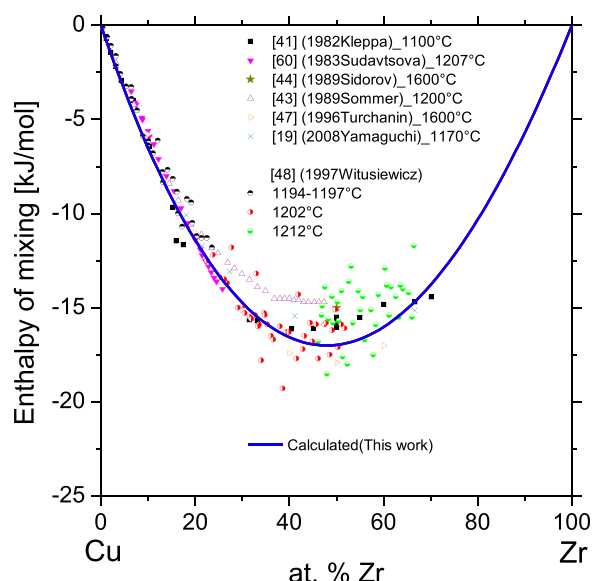


Fig. 8. Calculated enthalpy of mixing for liquid phase using present thermodynamic description (temperature independence) in comparison with available experimental data [19,41,43,44,47,48,60]. Reference states are liquid Cu and liquid Zr.

as high as 9000 °C, and no inverted miscibility gap appears in the liquid phase at high temperature. The calculated temperatures of the invariant reactions are also given in Fig. 1.

Fig. 2 shows the comparison of the calculated phase diagram and experimental data [15,24,26,28] for Ag–Zr system. Most of the calculated phase equilibria are consistent with the experimental data [15,24,26,28]. Betterton et al. [26] found three-phase region,  $(\beta\text{Zr}) + (\alpha\text{Zr}) + \text{AgZr}_2$ , existing at 819 °C and Zr composition of 96.8 at%, which is close to the present optimized eutectoid reaction  $(\beta\text{Zr}) \leftrightarrow (\alpha\text{Zr}) + \text{AgZr}_2$  at 822 °C and Zr composition of 96.6 at%. Fig. 2(b) represents the central part of the Ag–Zr phase diagram. The optimization resulted in congruent melting temperatures of 1166 °C and 1192 °C of the AgZr and  $\text{AgZr}_2$  phases, respectively. This is consistent with the finding of Zhang et al. [15]. Some other researchers [26] proposed that AgZr and  $\text{AgZr}_2$  phases melt incongruently, but it is difficult to experimentally distinguish that, with considering the calculated temperature of eutectic  $\text{L} \leftrightarrow \text{AgZr}_2 + (\beta\text{Zr})$  at 1191 °C and congruent melting point of  $\text{AgZr}_2$  phase at 1192 °C. Table 6 shows the comparison of experimental, assessed, and calculated invariant reactions.

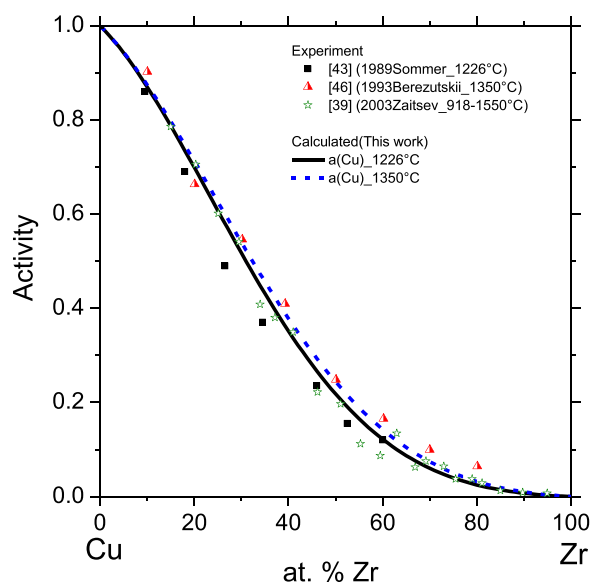


Fig. 9. Calculated activities of Cu in liquid phase at 1226 °C and 1350 °C (referred to liquid state) compared with experimental results [39,43,46].

#### 4.1.2. Thermodynamic properties of solid and liquid phases

Limited experimental work is available in the literature for the thermodynamic properties of the solid and liquid phases of Ag-Zr system. Up to now, only Fitzner and Kleppa [29] measured the enthalpy of mixing of the liquid phase using high-temperature calorimeter, and derived the enthalpy of formation at 298 K with a large error bar. The calculated enthalpy of formation shown in Fig. 3 is compared with previous Calphad calculations [13,14] and the re-calculated experimental data for the AgZr and AgZr<sub>2</sub> phases [29]. In the present work, the optimized enthalpy of formation of the AgZr phase is  $-5.5$  kJ/mol-atoms. Coincidentally, the optimized enthalpy of formation of the AgZr<sub>2</sub> phase is  $-3.62$  kJ/mol-atoms, which is close to the value of  $-3.67$  kJ/mol-atoms on the convex hull of the AgZr phase. The present optimized results are within the large error bar of the single available experimental dataset [29].

Fig. 4 represents the calculated enthalpies of mixing for liquid phase at 1200 °C for Ag-Zr system in the present work compared with previous Calphad calculations [13,14] and the only experimental data from Ref. [29]. The calculation of this study is close to the results of He et al. [13], and the calculated value for minimum is 3 kJ/mol less negative than the result of Kang et al. [14].

### 4.2. Cu-Zr binary system

#### 4.2.1. Phase diagram

Fig. 5 shows the calculated phase diagram of this study after optimization for the Cu-Zr system. Fig. 6 is the comparison of calculated and experimental data for phase equilibria of Cu-Zr system. The optimized phase diagram in this study differs from published and calculated ones [14,17–21], mainly in Cu-rich area and definition of solid phases. As shown in Fig. 6(c), there exists a two-phase region, (Cu) + Cu<sub>51</sub>Zr<sub>14</sub>, below 593 °C according to present description. This optimization result is consistent with the data of Zhou et al. [20], who concluded that (Cu) + Cu<sub>51</sub>Zr<sub>14</sub> two-phase field exists at 529 °C in the composition range of 0–21.71 at% Zr. However, this differs from the data of Zwicker et al. [54] supposing existence of Cu + Cu<sub>9</sub>Zr<sub>2</sub> two-phase field below 400 °C in the composition range of 0.007–0.209 at% Zr.

Table 7 shows the comparison of experimental and calculated invariant reactions for Cu-Zr system. The invariant reaction, Cu<sub>9</sub>Zr<sub>2</sub>  $\leftrightarrow$  (Cu) + Cu<sub>51</sub>Zr<sub>14</sub>, is the optimized result of this study, which is

not shown in other assessments [14,17–19,21]. This outcome is consistent with the experimental data of Zhou et al. [20]. Other invariant reactions calculated from this study are well consistent with the available experimental data.

#### 4.2.2. Thermodynamic properties of solid phases

Fig. 7 shows the comparison of calculated and experimental enthalpies of formation of solid phases at 298 K in the Cu-Zr system [40–45]. The experimental data and calculated results are also collected in Table 2. The available experimental data are scattering. In the present work, the calculated enthalpies of formation of Cu<sub>51</sub>Zr<sub>14</sub> and Cu<sub>10</sub>Zr<sub>7</sub> are, respectively,  $-12.22$  kJ/mol-atoms and  $-15.35$  kJ/mol-atoms, which are located between the experimental values of Refs. [40,41]. The calculated value of Cu<sub>8</sub>Zr<sub>3</sub> phase in this work is  $-13.11$  kJ, which is also coincidentally close to the value of  $-13.12$  on the convex hull connecting Cu<sub>51</sub>Zr<sub>14</sub> and Cu<sub>10</sub>Zr<sub>7</sub> phases.

The calculated congruent melting points for Cu<sub>51</sub>Zr<sub>14</sub>, Cu<sub>10</sub>Zr<sub>7</sub>, CuZr, and CuZr<sub>2</sub> phases are shown in Table 3 to compare with the experimental data. The optimized results are consistent with published experimental and calculated values.

#### 4.2.3. Thermodynamic properties of the liquid phase

Fig. 8 shows the comparison of calculated and experimental enthalpies of mixing for liquid phase at various temperatures for Cu-Zr system [19,41,43,44,47,48,60]. The experimental data for compositions exceeding 20 at% Zr are scattered, but the optimized results of this study are within the variation. Some authors, such as Gierlotka et al. [21] and Turchanin et al. [61], have modeled enthalpy of mixing for liquid phase as being temperature-dependent. However, there are no obvious experimental evidences to support these assumptions. Therefore, the enthalpy of mixing for liquid is modeled as being temperature-independent. Fig. 9 compares the calculated and experimental data on activity of Cu and Zr in liquid phase for Cu-Zr system [43,46,62]. The presented results are consistent.

## 5. Conclusion

The thermodynamics of Ag-Zr and Cu-Zr systems are re-assessed in this study. The enthalpies of mixing for liquid phase of both systems are modeled as being temperature-independent. All calculated results, such as phase diagrams and the thermodynamic properties for liquid and solid phases of both binaries, are compared with the available experiments and proved to be physically reasonable. The obtained set of optimized parameters avoids liquid miscibility gap at high temperature for both systems.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.calphad.2016.08.001>.

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