

Thermodynamic assessment of Au-Zr system

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Abstract: Au-Zr binary system was reassessed by using the calculation phase diagram (CALPHAD) technique based on experimental thermodynamic data and newly reported phase diagrams. The excess Gibbs energies of the three terminal solutions and the liquid phases were formulated with Redlich-Kister polynomial. All the intermetallic phases were treated as stoichiometric compounds with the exception of ZrAu which is modeled by a two-sublattice model, $(\text{Au}, \text{Zr}) : (\text{Au}, \text{Zr})$. The results show that there exist seven intermetallics; Zr_3Au , Zr_2Au , Zr_5Au_4 , $\text{Zr}_7\text{Au}_{10}$, ZrAu_2 , ZrAu_3 , and ZrAu_4 in the system. The eutectoid reaction: $\beta(\text{Zr}) \rightarrow \alpha(\text{Zr}) + \text{Zr}_3\text{Au}$ takes place at 1 048 K and the maximal solubility of Au in α -Zr is 4.7% (mole fraction). The maximal solubility of Zr in Au is 6.0% (mole fraction) at 1 347 K. The homogeneity range of ZrAu phase is about 44.5%-52.9% (mole fraction) of Au. The present assessment fits experimental data very well.

Key words: Au-Zr system; CALPHAD; two-sublattice model

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1 INTRODUCTION

Chemical vapor deposition (CVD) diamond holds great promise in solving thermal management problem in high performance multi-chip modules (MCMs). However, this material does present some technological challenges, one being the development of reliable metallization systems^[1]. The desirable characteristics of a metallization system are good adhesion to the substrate, low stress, good electrical conductivity and minimal reactions at subsequent processing temperatures (up to 400°C)^[2]. Gold is usually chosen as the metal for the conductive layer for its superior electrical conductivity and ease of deposition. Zirconium is easy to form carbides with diamond and to combine with gold at high temperature. So Au-Zr system is an ideal metalization system for CVD diamond.

Recently, SU Xu-ping et al^[3] has made evaluation of this system by employing CALPHAD method and good fitting has been realized between the calculated and most experimental data. However, some disadvantages of their phase diagrams should be pointed out. Firstly, they treated ZrAu phase as a line compound which actually has a homogeneity range from 45% to 53% of Au (mole fraction)^[4]. Such simplification may cause problem

when extrapolating to higher order system, such as Au-Zr-Ti. Secondly, the angle between hcp(Zr) and bcc(Zr) was calculated to be too small compared with the experimental data. In view of these, reassessment is performed in this paper.

2 EVALUATION OF EXPERIMENTAL INFORMATION

2.1 Phase diagram

Much investigation about Au-Zr system has been made by different research groups. E. Raub and M. Engel measured the Au-rich side of the phase diagram of Zr-Au system up to 45.5% Zr^[5]. E. Stolz and K. Schubert^[6] reported seven intermetallic compounds Zr_3Au , Zr_2Au , Zr_5Au_4 , $\text{Zr}_7\text{Au}_{10}$, ZrAu_2 , ZrAu_3 , and ZrAu_4 in Au-Zr system. But neither their type of formation nor their stability ranges were defined. T. B. Massalski et al^[7] summarized the work done before 1985. More recently, M. Lomello-Tafin et al^[4] remeasured this system by means of differential thermal analysis (DTA), X-ray diffraction (XRD) and electron probe microanalyses (EPMA), and two new compounds Zr_3Au_2 and ZrAu were discovered. According to the experiment, the compound Zr_5Au_4

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reported by E. Stolz and K. Schubert is not a line compound but the Zr-rich limit of $ZrAu$ ^[6]. The experimental phase diagram is shown in Fig. 1, which is the basis of the present optimization.

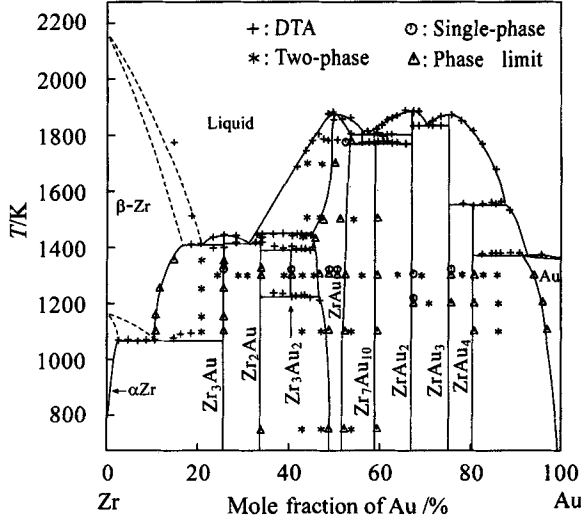


Fig. 1 Experimental phase diagram by M. Lomello-Tafin et al.^[8]

2.2 Thermodynamic property

K. Fitzner and O. J. Kleppa^[9] measured the standard enthalpies of formation for the congruently melting compounds at 298.15 K and the enthalpies of mixing for solid Zr in liquid Au by their modified Setaram-type calorimeter. Later, enthalpies of mixing for liquid alloys and the enthalpies of formation for the compounds at high temperatures were determined by M. Lomello-Tafin et al.^[8] with direct reaction calorimeter. Both sets of thermodynamic data were used in this optimization.

3 THERMODYNAMIC MODEL

3.1 β -Zr, α -Zr, Au(fcc) and Liquid

The three solid solution phases β Zr(bcc), α Zr(hcp) and Au(fcc) as well as liquid, are described with a substitutional solution model for which the Gibbs energy expression is

$$G^{\theta}(x, T) = \sum_{i=1}^2 x_i G_i^{\theta}(T) + RT \sum_{i=1}^2 x_i \ln x_i + {}^E G^{\theta}$$

where G^{θ} is Gibbs energy of the liquid, α -Zr, β -Zr and Au(fcc), respectively, x_i denotes the mole fraction of Au or Zr, and ${}^E G^{\theta}$ is the excess Gibbs energy, expressed by a Redlich-Kister polynomial^[10] as

$${}^E G^{\theta} = x_1 x_2 \sum_{j=0}^n L_{Au,Zr}^{\theta}(x_1 - x_2)^j$$

where $({}^j L_{Au,Zr}^{\theta} = A_j + B_j T)$, A_j and B_j are the parameters to be optimized.

3.2 Stoichiometric phases

The intermetallic compounds Zr_3Au , Zr_2Au , Zr_3Au_2 , Zr_7Au_{10} , $ZrAu_2$, $ZrAu_3$, and $ZrAu_4$ are stoichiometric phases. With assumption of Neumann-Kopp rule^[10], Gibbs free energies of these phases are calculated using the following expression:

$$G^{A,B} = a^{\circ} G_{Au}^{fcc} + b^{\circ} G_{Zr}^{hcp} + C + DT$$

where ${}^{\circ} G_{Zr}^{fcc}$ and ${}^{\circ} G_{Au}^{fcc}$ are the Gibbs energies of the respective pure elements, C and D are also constants to be optimized.

3.3 ZrAu phase

The structure of ZrAu has not been clearly determined until now. M. Lomello-Tafin et al.^[4] pointed out that most of the equiatomic Zr-platinum elements are congruent melting compounds and have CsCl-type structure at higher temperature. It should be noticed that the atomic radius of Zr is 206 pm, which is almost equal to that of Hf, 208 pm, but differs greatly from that of Ti, 176 pm. And, what is more, the electronegativities of Zr and Hf are similar. So it is more reasonable to conclude that AuZr has the same structure as Au-Hf. Because the structure of AuHf is CuTi type, according to the atomic location of CuTi^[11], a two-sublattice model, (Au,Zr):(Au,Zr) is used to describe ZrAu. Thus the Gibbs energy of ZrAu is expressed as

$$G_{Au,Zr}^{ZrAu} = \sum_i \sum_j y_i^I y_j^{II} {}^{\circ} G_{i,j}^{ZrAu} + 0.5RT \left[\sum_i y_i^I \ln y_i^I + \sum_j y_j^{II} \ln y_j^{II} \right] + {}^E G^{ZrAu}$$

where ${}^E G^{ZrAu}$ is the excess Gibbs energy:

$${}^E G^{ZrAu} = y_{Au}^I y_{Zr}^I y_{Au}^{II} L_{Au,Zr}^{ZrAu} + y_{Au}^I y_{Zr}^I y_{Zr}^{II} L_{Au,Zr}^{ZrAu} + y_{Au}^I y_{Au}^{II} y_{Zr}^{II} L_{Au,Zr}^{ZrAu} + y_{Zr}^I y_{Au}^{II} y_{Zr}^{II} L_{Zr,Au}^{ZrAu} + y_{Au}^I y_{Zr}^I y_{Au}^{II} y_{Zr}^{II} L_{Au,Zr}^{ZrAu}$$

and y_i^I and y_j^{II} are the mole fraction of Au, Zr in sublattice I and II, respectively. In order to reduce the number of variables to be optimized, assume that ${}^{\circ} L_{Au,Zr}^{ZrAu} = {}^{\circ} L_{Au,Zr}^{ZrAu} = {}^{\circ} L_{Au}^{ZrAu} = {}^{\circ} L_{Zr}^{ZrAu}$, and the parameter ${}^{\circ} L_{Au,Zr}^{ZrAu}$ is set to zero.

4 RESULTS AND DISCUSSION

Using the assembled lattice stabilities of Au and Zr established by A. T. Dinsdale^[12], the phase

diagram of Au-Zr has been optimized using Thermo-calc software, which applied a least square algorithm to fit various experimental data^[13], and as shown in Table 1, all parameters are numerically acceptable.

Table 1 Thermodynamic parameters evaluated in the present work

Liquid (1 sublattice, site: 1.0, constituents: Au,Zr)
${}^0L_{\text{Au,Zr}}^{\text{liq}} = -201\,982.44 + 25.332\,274T$
${}^1L_{\text{Au,Zr}}^{\text{liq}} = 10\,471.25 - 7.998\,875T$
$\alpha\text{-Zr (hcp)}$ (2 sublattice, site: 1.0 : 0.5, constituents: Au,Zr : Va)
${}^0L_{\text{Au,Zr}}^{\text{hcp}} = -123\,674.45$
$\beta\text{-Zr (bcc)}$ (2 sublattice, site: 1.0 : 3.0, constituents: Au,Zr : Va)
${}^0L_{\text{Au,Zr}}^{\text{bcc}} = -181\,067.16 + 16.646\,143T$
${}^1L_{\text{Au,Zr}}^{\text{bcc}} = -37\,200.00$
Au(fcc) (2 sublattice, site: 1.0 : 1.0, constituents: Au,Zr : Va)
${}^0L_{\text{Au,Zr}}^{\text{fcc}} = -170\,440.90 + 0.277\,674T$
Zr ₂ Au (2 sublattice, site: 2.0 : 1.0, constituents: Zr : Au)
${}^0G_{\text{Zr}^2\text{Au}}^{\text{Zr}^2\text{Au}} - 2 {}^0G_{\text{Zr}}^{\text{hcp}} - {}^0G_{\text{Au}}^{\text{fcc}} = -143\,990.78 + 14.553\,000T$
Zr ₃ Au (2 sublattice, site: 3.0 : 1.0, constituents: Zr : Au)
${}^0G_{\text{Zr}^3\text{Au}}^{\text{Zr}^3\text{Au}} - 3 {}^0G_{\text{Zr}}^{\text{hcp}} - {}^0G_{\text{Au}}^{\text{fcc}} = -148\,517.65 + 8.902\,574T$
Zr ₃ Au ₂ (2 sublattice, site: 3.0 : 2.0, constituents: Zr : Au)
${}^0G_{\text{Zr}^3\text{Au}_2}^{\text{Zr}^3\text{Au}_2} - 3 {}^0G_{\text{Zr}}^{\text{hcp}} - 2 {}^0G_{\text{Au}}^{\text{fcc}} = -256\,352.16 + 18.235\,905T$
Zr ₇ Au ₁₀ (2 sublattice, site: 7.0 : 10.0, constituents: Zr : Au)
${}^0G_{\text{Zr}^7\text{Au}_{10}}^{\text{Zr}^7\text{Au}_{10}} - 7 {}^0G_{\text{Zr}}^{\text{hcp}} - 10 {}^0G_{\text{Au}}^{\text{fcc}} = -1\,008\,102.40 + 92.476\,753T$
ZrAu (2 sublattice, site: 1.0 : 1.0, constituents: Au,Zr : Au,Zr)
${}^0G_{\text{ZrAu}}^{\text{ZrAu}} - 2 {}^0G_{\text{Au}}^{\text{fcc}} = 1000$
${}^0G_{\text{Zr}^1\text{Au}}^{\text{Zr}^1\text{Au}} - {}^0G_{\text{Zr}}^{\text{hcp}} - {}^0G_{\text{Au}}^{\text{fcc}} = -115\,649.60 + 7.357\,727T$
${}^0G_{\text{Zr}^1\text{Au}}^{\text{Zr}^1\text{Au}} - {}^0G_{\text{Au}}^{\text{fcc}} - {}^0G_{\text{Zr}}^{\text{hcp}} = 0$
${}^0G_{\text{Zr}^1\text{Au}}^{\text{Zr}^1\text{Au}} - 2 {}^0G_{\text{Zr}}^{\text{hcp}} = 32\,000.00$
${}^0L_{\text{Au,Zr}}^{\text{ZrAu}} = -68\,000.00 + 13.827\,498T$
${}^0L_{\text{Au,Zr}}^{\text{ZrAu}} = -68\,000.00 + 13.827\,498T$
${}^0L_{\text{Au,Zr}}^{\text{ZrAu}} = -68\,000.00 + 13.827\,498T$
${}^0L_{\text{Zr,Au}}^{\text{ZrAu}} = -68\,000.00 + 13.827\,498T$
ZrAu ₂ (2 sublattice, site: 1.0 : 2.0, constituents: Zr : Au)
${}^0G_{\text{Zr}^2\text{Au}}^{\text{Zr}^2\text{Au}} - {}^0G_{\text{Zr}}^{\text{hcp}} - 2 {}^0G_{\text{Au}}^{\text{fcc}} = -173\,810.28 + 17.175\,849T$
ZrAu ₃ (2 sublattice, site: 1.0 : 3.0, constituents: Zr : Au)
${}^0G_{\text{Zr}^3\text{Au}}^{\text{Zr}^3\text{Au}} - {}^0G_{\text{Zr}}^{\text{hcp}} - 3 {}^0G_{\text{Au}}^{\text{fcc}} = -204\,019.82 + 21.130\,226T$
ZrAu ₄ (2 sublattice, site: 1.0 : 4.0, constituents: Zr : Au)
${}^0G_{\text{Zr}^4\text{Au}}^{\text{Zr}^4\text{Au}} - {}^0G_{\text{Zr}}^{\text{hcp}} - 4 {}^0G_{\text{Au}}^{\text{fcc}} = -203\,193.94 + 17.360\,239T$

4.1 Phase diagram

The calculated phase diagram of Au-Zr system is plotted in Fig. 2 in comparison with the experimental data. In combination to the invariant equilibria listed in Table 2, it is obvious that the presently calculated phase diagram agrees reasonably with that of the formerly reported. The boundaries of AuZr have also been well fitted.

4.2 Thermodynamic property

Fig. 3 shows good fit between the calculated and experimental enthalpies of mixing (ΔH_{mix}) of

liquid alloys at 1 473 K. Also the enthalpies of formation of some compounds at different temperature have been optimized, which are consistent with the experimental data.

4.3 Comparison between assessed and experimental data

As shown in Fig. 2, ZrAu phase is well optimized with a homogeneity range. The fitting of liquid lines in Au-rich part is better than those by SU Xu-ping et al^[3], and the terminal phase boundaries of Zr(hcp) are close to the experimental data than those by SU Xuping et al^[3].

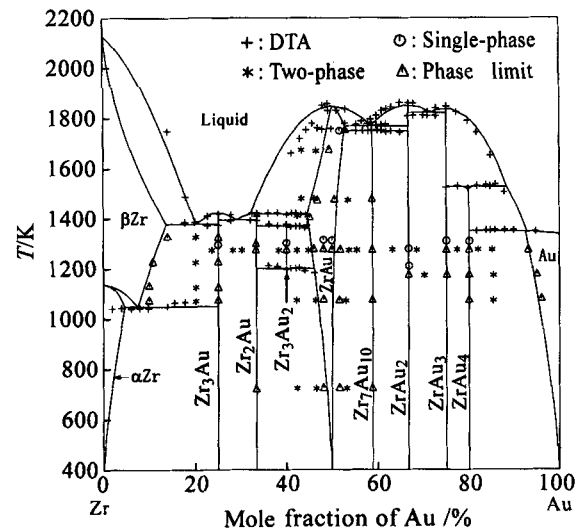


Fig. 2 Calculated phase diagram of Au-Zr system in comparison with experimental data

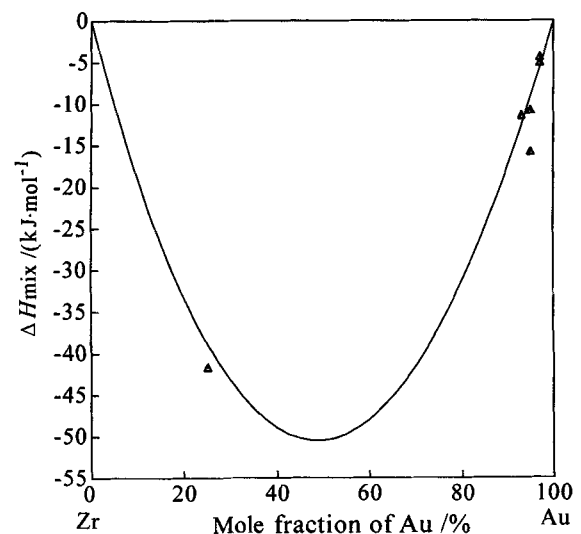


Fig. 3 Mixing enthalpies of liquid at 1 473 K

Table 2 Invariant reactions in Au-Zr system

Equilibrium	T/K		Phase	Mole fraction of Au / %	
	Present	Ref. [4]		Present	Ref. [4]
LIQ→β-Zr + Zr ₃ Au	1 378	1 378±8	LIQ	0.2	
			β-Zr	13.7	≈0.1
β-Zr→α-Zr + Zr ₃ Au	1 048	1 049±10	β-Zr	≈10.0	
			α-Zr	4.07	<2.0
LIQ→Zr ₃ Au	1 423	1 416			
LIQ→Zr ₃ Au+ Zr ₂ Au	1 393	1 393±4	LIQ	29.00	30
LIQ+ ZrAu→Zr ₂ Au	1 419	1 419±3	LIQ	32.00	32.0
			ZrAu	44.50	≈45.0
ZrAu+ Zr ₂ Au→ Zr ₃ Au ₂	1 370	1 370±5	ZrAu	44.90	≈45.0
Zr ₃ Au ₂ → ZrAu+ Zr ₂ Au	1 200	1 200±6	ZrAu	46.10	≈47.0
LIQ→ ZrAu	1 848	1 848	LIQ	50.30	50.0
LIQ→ ZrAu+ ZrAu ₂	1 768	1 763±10	LIQ	58.50	55.0
			ZrAu	52.90	≈53.0
ZrAu+ ZrAu ₂ →Zr ₇ Au ₁₀	1 749	1 749±4	ZrAu		
LIQ→ZrAu ₂	1 851	1 860±4			
LIQ→ZrAu ₂ + ZrAu ₃	1 822	1 808±4	LIQ	71.40	70.0
LIQ→ZrAu ₃	1 839	1 845			
LIQ+ ZrAu ₃ →ZrAu ₄	1 528	1 527±5	LIQ	89.70	≈87.0
LIQ+ ZrAu ₄ → Au(fcc)	1 347	1 350±3	LIQ	95.80	92.0-95.0
			fcc	94.00	≈92.0

Table 3 Enthalpies at different temperatures ($\Delta H_f / (\text{kJ} \cdot \text{mol}^{-1})$)

Phase	high temperature		298.15 K	
	Ref. [9]	Present	Ref. [8]	Present
Zr ₃ Au	-39.7(1 273 K)	-39.55	-30.07	-37.13
Zr ₂ Au	-49.4(1 273 K)	-50.15		
ZrAu	-59.7(1 373 K)	-58.98		
Zr ₇ Au ₁₀	-60.6(1 273 K)	-60.63		
ZrAu ₂	-59.0(1 273 K)	-59.01	-61.00	-57.94
ZrAu ₃	-54.7(1 573 K)	-51.27	-51.41	-51.10
ZrAu ₄	-38.0(1 173 K)	-41.42		

5 CONCLUSIONS

1) Au-Zr system is reassessed by using the CALPHAD technique, in which AuZr phase is modeled by a two-sublattice model. The calculated phase diagram fits experimental data very well.

2) The new thermodynamic data of Au-Zr system are well established by using CALPHAD technique, which contributes to building the systematic thermodynamic database of Au-III A (Ti, Zr, Hf) systems.

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