Au – Zr (Gold – Zirconium)

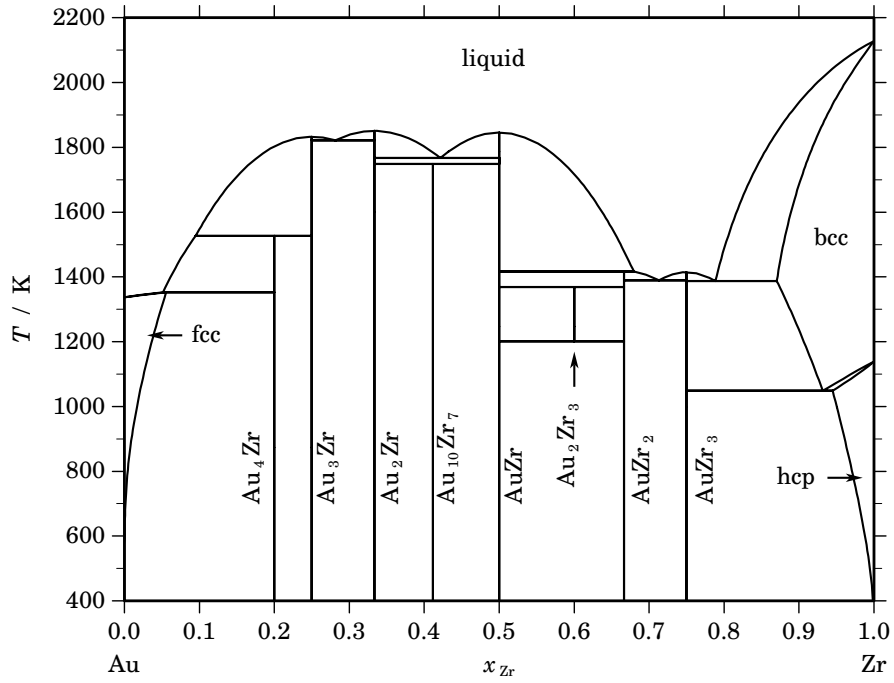

Fig. 1. Calculated phase diagram for the system Au-Zr.

The alloy systems or intermetallic compounds composed of Zr and Au have attracted much attention for the theoretical study of the solid state and for many industrial purposes such as the use of amorphous Au-Zr alloys as catalysts for CO hydrogenation and oxidation. The Au-rich side of the Au-Zr phase diagram was studied by [1948Rau]. [1997Lom] reexamined this system by means of differential thermal analysis, x-ray diffraction and electron probe microanalysis, and established the phase diagram in its present form. He suggested that the compounds $AuZr_3$, AuZr, Au_2Zr and Au_3Zr melt congruently. $AuZr_2$ and Au_4Zr form peritectically. Au_2Zr_3 and $Au_{10}Zr_7$ are formed by peritectoid reactions. The maximum solid solubility of Au in βZr is 16 at.% Au. The αZr has a narrow homogeneity range. The maximum solid solubility of Zr in Au is about 8 at.% Zr. This value agrees with that of [1948Rau]. A literature review was presented by [1999Oka]. According to [1999Oka], Au_4Zr_5 does not exist. The experimental standard enthalpies of formation of the congruently melting compounds $AuZr_2$, Au_4Zr_5, Au_2Zr, Au_3Zr were determined by [1992Fit], those of the compounds $AuZr_3$, $AuZr_2$, Au_4Zr_5, AuZr, $Au_{10}Zr_7$, Au_2Zr, Au_3Zr, Au_4Zr were determined by [1998Lom]. The enthalpies of mixing of solid Zr in liquid Au and the enthalpies of mixing for the liquid alloys were also measured by [1998Lom] and [1992Fit], respectively. The thermodynamic evaluation of the Au-Zr system was made by [2000Su]. The terminal solid solutions bcc, hcp, fcc and the liquid phase were described by a substitutional solution model using the Redlich-Kister equation. The intermetallic compounds $AuZr_3$, $AuZr_2$, Au_2Zr_3, AuZr, $Au_{10}Zr_7$, Au_2Zr, Au_3Zr, Au_4Zr are modelled as stoichiometric phases. The calculated phase diagram is in good agreement with the experiments reported by [1998Lom]. All invariant equilibria in the system are reproduced well. The assessed terminal solubilities of Zr in Au, and of Au in Zr do not agree well with the experimental data, but the review of [1999Oka] showed a thermodynamic improbability. The assessed enthalpies of formation agree well with experimental data. The calculated partial and integral molar enthalpies of mixing of solid Zr in liquid is good below 11 at.% Zr; above this composition, the measurements of the enthalpies of mixing are not accurate due to the occurrence of solid Au_4Zr at the experimental temperature. More experimental work on the liquid/βZr and βZr/αZr boundaries may be necessary to improve the description.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Au,Zr)_1$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Au,Zr)_1$
Au_4Zr	$\cdots$	$AuZr_4$	$oP20$	$Pnma$	AU4ZR	Au_4Zr_1
Au_3Zr	$D0_a$	βCu_3Ti	$oP8$	$Pmmn$	AU3ZR	Au_3Zr_1
Au_2Zr	$C11_b$	$MoSi_2$	$tI6$	$I4/mmm$	AU2ZR	Au_2Zr_1
$Au_{10}Zr_7$	$\cdots$	$\cdots$	$tI34$	$\cdots$	AU10ZR7	$Au_{10}Zr_7$
AuZr	$\cdots$	$\cdots$	$\cdots$	$\cdots$	AUZR	Au_1Zr_1
Au_2Zr_3	$\cdots$	$\cdots$	$\cdots$	$\cdots$	AU2ZR3	Au_2Zr_3
$AuZr_2$	$C11_b$	$MoSi_2$	$tI6$	$I4/mmm$	AUZR2	Au_1Zr_2
$AuZr_3$	$A15$	Cr_3Si	$cP8$	$Pm3n$	AUZR3	Au_1Zr_3
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Au,Zr)_1$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(Au,Zr)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Zr}			$\Delta_r H$ / (J/mol)
liquid $\rightleftharpoons$ Au_2Zr	congruent	1850.8	0.333	0.333		−30587
liquid $\rightleftharpoons$ AuZr	congruent	1845.5	0.500	0.500		−25408
liquid $\rightleftharpoons$ Au_3Zr	congruent	1833.0	0.250	0.250		−29297
liquid $\rightleftharpoons$ Au_3Zr + Au_2Zr	eutectic	1821.4	0.282	0.250	0.333	−29490
liquid $\rightleftharpoons$ Au_2Zr + AuZr	eutectic	1767.1	0.422	0.333	0.500	−26518
Au_2Zr + AuZr $\rightleftharpoons$ $Au_{10}Zr_7$	peritectoid	1749.0	0.333	0.500	0.412	−2
liquid + Au_3Zr $\rightleftharpoons$ Au_4Zr	peritectic	1527.1	0.095	0.250	0.200	−5907
AuZr + liquid $\rightleftharpoons$ $AuZr_2$	peritectic	1416.3	0.500	0.680	0.667	−18469
liquid $\rightleftharpoons$ $AuZr_3$	congruent	1414.5	0.750	0.750		−14774
liquid $\rightleftharpoons$ $AuZr_2$ + $AuZr_3$	eutectic	1389.8	0.713	0.667	0.750	−16664
liquid $\rightleftharpoons$ $AuZr_3$ + bcc	eutectic	1387.1	0.788	0.750	0.870	−11324
AuZr + $AuZr_2$ $\rightleftharpoons$ Au_2Zr_3	peritectoid	1368.8	0.500	0.667	0.600	−6
liquid + Au_4Zr $\rightleftharpoons$ fcc	peritectic	1352.3	0.052	0.200	0.056	−10372
Au_2Zr_3 $\rightleftharpoons$ AuZr + $AuZr_2$	eutectoid	1200.8	0.600	0.500	0.667	−5
bcc $\rightleftharpoons$ $AuZr_3$ + hcp	eutectoid	1049.0	0.932	0.750	0.945	−4531

Table IIIa. Integral quantities for the liquid phase at 2200 K.

x_{Zr}	ΔG_{m} [J/mol]	ΔH_{m} [J/mol]	ΔS_{m} [J/(mol·K)]	$G_{\mathrm{m}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{m}}^{\mathrm{E}}$ [J/(mol·K)]	ΔC_P [J/(mol·K)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−18209	−16976	0.561	−12263	−2.142	0.000
0.200	−30826	−30591	0.107	−21673	−4.054	0.000
0.300	−39452	−40691	−0.564	−28278	−5.643	0.000
0.400	−44436	−47122	−1.221	−32125	−6.817	0.000
0.500	−45943	−49729	−1.721	−33264	−7.484	0.000
0.600	−44052	−48358	−1.957	−31741	−7.553	0.000
0.700	−38780	−42854	−1.852	−27606	−6.931	0.000
0.800	−30058	−33062	−1.365	−20905	−5.526	0.000
0.900	−17633	−18829	−0.544	−11687	−3.246	0.000
1.000	0	0	0.000	0	0.000	0.000

Reference states: Au(liquid), Zr(liquid)

Table IIIb. Partial quantities for Au in the liquid phase at 2200 K.

x_{Au}	ΔG_{Au} [J/mol]	ΔH_{Au} [J/mol]	ΔS_{Au} [J/(mol·K)]	$G_{\mathrm{Au}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Au}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Au}	γ_{Au}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−3362	−1655	0.776	−1435	−0.100	0.832	0.925
0.800	−9756	−6824	1.333	−5674	−0.523	0.587	0.733
0.700	−19147	−15818	1.514	−12623	−1.452	0.351	0.502
0.600	−31529	−28944	1.175	−22185	−3.072	0.178	0.297
0.500	−46943	−46512	0.196	−34264	−5.567	0.077	0.154
0.400	−65525	−68830	−1.502	−48764	−9.121	0.028	0.070
0.300	−87612	−96208	−3.907	−65589	−13.917	0.008	0.028
0.200	−114083	−128954	−6.759	−84643	−20.141	0.002	0.010
0.100	−147949	−167377	−8.831	−105831	−27.976	0.000	0.003
0.000	$-\infty$	−211786	∞	−129055	−37.605	0.000	0.001

Reference state: Au(liquid)

Table IIIc. Partial quantities for Zr in the liquid phase at 2200 K.

x_{Zr}	ΔG_{Zr} [J/mol]	ΔH_{Zr} [J/mol]	ΔS_{Zr} [J/(mol·K)]	$G_{\mathrm{Zr}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Zr}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Zr}	γ_{Zr}
0.000	$-\infty$	−186046	∞	−137056	−22.268	0.000	0.001
0.100	−151838	−154867	−1.377	−109719	−20.522	0.000	0.002
0.200	−115107	−125659	−4.796	−85668	−18.178	0.002	0.009
0.300	−86828	−98730	−5.410	−64805	−15.420	0.009	0.029
0.400	−63797	−74390	−4.815	−47036	−12.434	0.031	0.076
0.500	−44943	−52947	−3.638	−32264	−9.401	0.086	0.171
0.600	−29737	−34709	−2.260	−20393	−6.508	0.197	0.328
0.700	−17851	−19987	−0.971	−11327	−3.937	0.377	0.538
0.800	−9052	−9089	−0.017	−4970	−1.872	0.610	0.762
0.900	−3154	−2324	0.377	−1227	−0.499	0.842	0.935
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Zr(liquid)

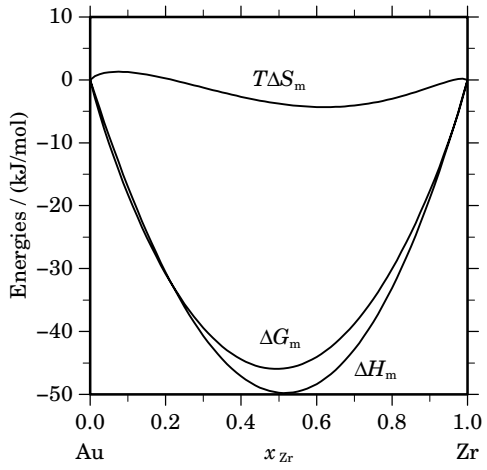

Fig. 2. Integral quantities of the liquid phase at T=2200 K.

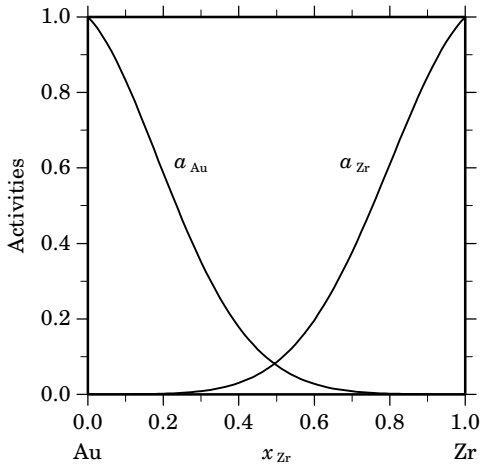

Fig. 3. Activities in the liquid phase at T=2200 K.

Table IV. Standard reaction quantities at 298.15 K for the compounds per mole of atoms.

Compound	x_{Zr}	$\Delta_f G^\circ$ / (J/mol)	$\Delta_f H^\circ$ / (J/mol)	$\Delta_f S^\circ$ / (J/(mol·K))	$\Delta_f C_P^\circ$ / (J/(mol·K))
Au_4Zr_1	0.200	−40169	−41759	−5.335	0.000
Au_3Zr_1	0.250	−49395	−51453	−6.903	0.000
Au_2Zr_1	0.333	−57045	−59445	−8.050	0.000
$Au_{10}Zr_7$	0.412	−57473	−59624	−7.217	0.000
Au_1Zr_1	0.500	−57951	−59823	−6.278	0.000
Au_2Zr_3	0.600	−51184	−53114	−6.472	−0.063
Au_1Zr_2	0.667	−46730	−48743	−6.754	0.000
Au_1Zr_3	0.750	−35657	−36536	−2.950	0.000

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