Thermochemistry of Binary Alloys of Transition Metals: The Me-Ti, Me-Zr, and Me-Hf(Me = Ag, Au) Systems

K. FITZNER and O.J. KLEPPA

The standard enthalpies of formation of congruently melting intermetallic compounds in the (Ag, Au)-(Ti, Zr, Hf) binary systems were determined by high-temperature direct synthesis calorimetry at 1473 ± 2 K. The enthalpies of mixing for the liquid alloys in the same systems have been measured by the same technique in the range of compositions available for experiments at 1473 ± 2 K. The results obtained are compared with estimated values from Miedema's semiempirical model.

I. INTRODUCTION

DURING recent years, a systematic study of the thermochemistry of the liquid alloys of copper, silver, and gold with transition metals has been pursued in this laboratory.[1-6] Most recently, we studied the alloys of silver and gold with the group IIIA metals[7] at 1473 K. In the present article, our study is extended to the alloys of silver and gold with the IVA metals titanium, zirconium, and hafnium. A further extension to the alloys with the VA metals vanadium, niobium, and tantalum has been initiated.

The equilibrium phase diagrams of the binary alloys of silver and gold with titanium, zirconium, and hafnium are not well established. Although the recent phase diagram evaluation presented in Reference 8 to some extent clarifies the phase relations, the knowledge of high-temperature equilibria is still very incomplete. While the system Au-Ti has three compounds with reported congruent melting points, Au-Zr and Au-Hf both exhibit a number of phases with unknown melting points. Also, their phase equilibria are very ill-defined.

Since there are virtually no data for Ag-Hf, we have assumed that this system is analogous to Ag-Zr. In spite of many uncertainties, we found that some phases, such as, e.g., the equiatomic compounds, are found in most of the considered binary systems.

In the present investigation, the standard enthalpies of formation of congruently melting compounds in the Ag-Zr, Ag-Hf, Au-Ti, Au-Zr, and Au-Hf systems were determined. We also measured the enthalpies of mixing for the liquid alloys in the range of compositions available for experiments at 1473 K. As far as we know, there are no thermodynamic data reported in the literature for the considered alloys. However, we will compare our results with values estimated from Miedema's semiempirical model.[9]

II. EXPERIMENTAL

A. General

The direct synthesis method was used for a series of intermetallic compounds as well as for the liquid solu-

K. FITZNER, Associate Professor, is with the Institute of Metals Research, Polish Academy of Sciences, 30-059 Krakow, Poland. O.J. KLEPPA, Emeritus Professor, is with the James Franck Institute, University of Chicago, Chicago, IL 60637.
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tions. The calorimetric measurements were carried out at 1473 ± 2 K in our modified Setaram-type calorimeter. Details of the construction of this unit as well as of the "liner" assembly were given previously.[10]

In direct synthesis calorimetry, pellets made from pressed, metallic powders are dropped from room temperature into the high-temperature calorimeter where they are brought to chemical reaction. The heat effect produced inside the crucible is then picked up by the calorimeter. The reaction chamber consists of a thin-walled BN crucible, which protects the Pt20Rh liner from the contents of a 15-mm diameter BeO crucible, in which the reaction takes place. All experiments were performed in an atmosphere of purified argon, which was passed over titanium chips at about 1173 K.

Calibration of the calorimeter was achieved by dropping small pieces of 2-mm diameter high-purity copper wire from room temperature into the calorimeter. The enthalpy of pure copper was taken from Hultgren et al.[11] (46,465 J mol^{-1} at 1473 K). The results of the calibrations were reproducible within ±1.5 pct.

B. Materials

(1) Silver powder of 99.9 pct purity used in this study was obtained from Johnson-Matthey, AESAR Group, Seabrook, NH (Lot #16996). We also used some 2-mm diameter silver wire of comparable purity.
(2) Gold powder of 99.95 pct purity was obtained from Johnson-Matthey, AESAR Group (Lot #124538). Gold wire of 2-mm diameter was obtained from Engelhard, Carteret, NJ.
(3) Titanium powder of 99.9 pct purity was obtained from Johnson-Matthey.
(4) Zirconium rod of 99.5 pct purity was purchased from Johnson-Matthey. The metal was machined on a mill into a powder suitable for the experiments.
(5) Hafnium powder of 99.6 pct purity was obtained from Johnson-Matthey, AESAR Group. It contained ~2 pct zirconium. Some hafnium powder was also prepared by machining on a lathe.
(6) Solid alloys. Most of the reacted alloy pellets were recovered from the crucible of the calorimeter and then used in a second series of measurements in order to determine their heat contents. Only three alloys, namely, AgZr, AgZr$_2$, and AuZr$_2$, were prepared by arc-melting from the pure elements. These compounds form liquid solutions at the temperature of our measurements.

III. RESULTS

Silver and gold are liquid at our experimental temperature of 1473 K. Thus, it was expected that they might react with metal powders (metal = Ti, Zr, Hf) to form compounds in direct synthesis experiments. The standard molar enthalpies of formation can be obtained from the heat effects associated with the following two reactions:

$$xA(s, 298) + yB(s, 298) \rightarrow A_xB_y(s, 1473) \qquad [1]$$

$$A_xB_y(s, 298) \rightarrow A_xB_y(s, 1473) \qquad [2]$$
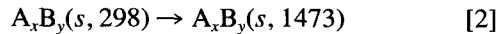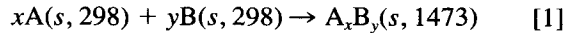
Here, A denotes silver or gold and B the group IVA metal.

From Eqs. [1] and [2], one obtains

$$xA(s, 298) + yB(s, 298) \rightarrow A_xB_y(s, 298) \qquad [3]$$
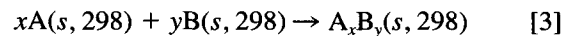
Consequently, the standard molar enthalpy of formation, $\Delta H^\circ_{f,298}$, is obtained from the measured heat effects for Reactions [1] and [2]:

$$\Delta H^\circ_{f,298} = \Delta H_{(1)} - \Delta H_{(2)} \qquad [4]$$

Our experimental results are summarized in Table I and are shown graphically in Figure 1. In this figure, they are compared with the values predicted by the semi-empirical theory of de Boer et al.[9]

The heats of mixing of the liquid alloys were also measured at 1473 ± 2 K. In a typical series of

Table I. Observed Heats of Reaction, Average Heat Contents at 1473 K, and Calculated Enthalpies of Formation (in kJ/g atom)*

Compound	$\Delta H_{observed}$	$H^\circ_{1473} - H^\circ_{298}$	$\Delta H^\circ_{f,298}$
AgZr	46.49 ± 0.36 (3)	49.61 ± 3.11 (4)	[− 3.12 ± 3.13]
AgZr$_2$	44.91 ± 0.70 (6)	46.38 ± 2.80 (5)	[− 1.47 ± 2.89]
AgHf	22.25 ± 0.77 (5)	32.99 ± 1.85 (6)	[−10.74 ± 2.00]
Au$_2$Ti	−12.37 ± 0.93 (6)	33.56 ± 1.80 (5)	−45.93 ± 2.03
AuTi	− 8.78 ± 0.51 (5)	35.42 ± 1.40 (6)	−44.20 ± 1.49
AuTi$_3$	3.64 ± 0.38 (5)	35.03 ± 0.33 (6)	−31.39 ± 0.50
Au$_3$Zr	−19.64 ± 1.59 (6)	31.77 ± 2.46 (5)	−51.41 ± 2.93
Au$_2$Zr	−26.16 ± 1.83 (6)	34.84 ± 1.46 (5)	−61.00 ± 2.34
Au$_4$Zr$_5$	−13.27 ± 1.07 (6)	33.88 ± 2.85 (5)	−47.15 ± 3.04
AuZr$_3$	15.40 ± 1.31 (6)	45.47 ± 1.40 (4)	−30.07 ± 1.92
Au$_3$Hf	−21.75 ± 2.31 (6)	33.02 ± 1.27 (6)	−54.77 ± 2.64
Au$_2$Hf	−29.46 ± 2.04 (6)	32.52 ± 0.55 (5)	−61.98 ± 2.11
AuHf	−21.49 ± 0.94 (6)	35.54 ± 0.88 (5)	−57.03 ± 1.29
AuHf$_2$	− 6.10 ± 4.06 (4)	34.66 ± 0.80 (6)	[−40.76 ± 4.14]

*Numbers in parentheses indicate numbers of experiments averaged. Results in square brackets are considered to be uncertain.
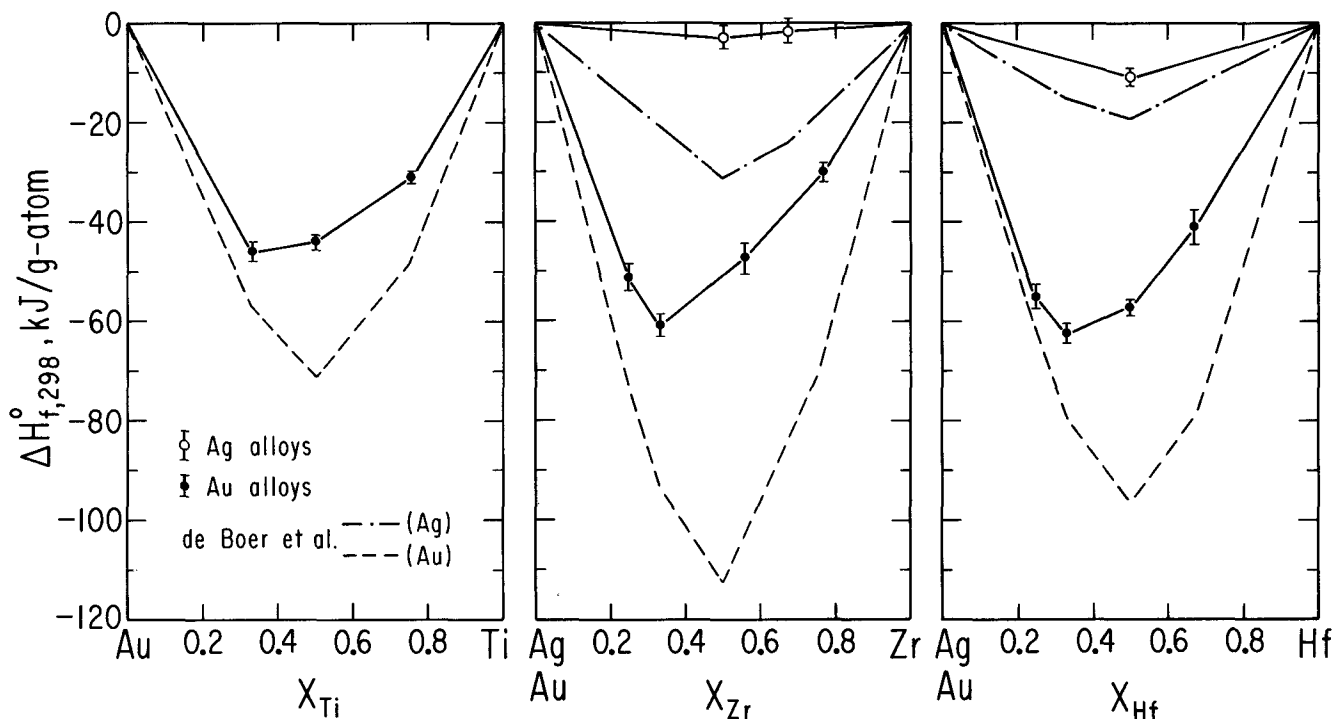

Fig. 1—Comparison of the standard enthalpies of formation obtained for A_xB_y(A $\equiv$ Ag, Au and B $\equiv$ Ti, Zr, Hf) alloys with values predicted from Miedema's model.[9]

experiments, the initial drops into the calorimeter consisted of either pure metal (silver or gold) or a mixture of the transition element with silver or gold in the form of a pellet. Several consecutive additions were then made in order to vary the composition of the alloy. The heat effects associated with each drop were determined and added up in order to allow the heat of mixing for each alloy composition to be calculated. For all pure elements, we adopted the enthalpies at 1473 K given by Hultgren et al.[11] The enthalpies of fusion of Ti, Zr, and Hf were taken from Barin and Knacke[12] and were assumed to be independent of temperature between the melting points of the transition metal and 1473 K.

The experimental values of the heats of mixing, ΔH_{l-l}^M, are summarized in Tables IIa through IIe and are plotted in Figures 2 through 5. The heat of mixing curves may be described by the equation:

$$\Delta H_{l-l}^M = \lambda x(1 - x) \qquad [5]$$

where x is the mole fraction of the transition metal. The interaction parameter, λ, may, in general, vary with composition. In view of the limited amount of data for the considered binary systems, we assumed the simplest, i.e., a linear, concentration dependence: $\lambda = a + bx$. However, for Au-Zr and Au-Hf alloys, constant values of λ were adopted due to the limited range of compositions covered by the experiments. In the case of the Ag-Zr solutions, the dependence of λ on x apparently is nonlinear, since a least-squares fit of λ against x cannot reproduce the measured composition dependence of the heat of mixing.

The results of the least-squares fits for the considered systems are gathered in Table III. In this table, we also give the predicted values of the partial heats of solution of the liquid transition metals at infinite dilution, as derived by de Boer et al.[9] from their semiempirical model. The experimental and predicted values are plotted in Figure 6.

Table IIa. Enthalpies of Mixing for Ag(l) + Ti(l) Alloys at 1473 K

Series Number	n_{Ag} (m/mol)	n_{Ti} (m/mol)	Σn_i (m/mol)	X_{Ti}	ΔH_{l-l}^M (kJ/mol)
1	5.4681*	5.5073*	10.9754*	0.50	−8.33 ± 1.63**
	6.9648	—	17.9402	0.31	−4.93
2	1.8656	0.3278	2.1934	0.15	−2.66
	1.8499	0.3278	4.3711	0.15	−2.96
	1.8832	0.3445	6.5988	0.15	−3.43
	3.4064	—	10.0052	0.10	−2.22
3	1.7757	0.1587	1.9344	0.08	−1.66
	1.8063	0.1628	3.9035	0.08	−1.65
	1.7998	0.1608	5.8641	0.08	−2.09
	3.7674	—	9.6315	0.05	−1.44
	1.3754	0.0772	11.0841	0.05	−1.93
4	1.9222	0.0418	1.9640	0.02	−0.54
	1.7748	0.0355	3.7743	0.02	−1.25
	1.4273	0.2443	5.4459	0.05	−2.10
	1.4671	0.0772	6.9902	0.05	−2.48

*Total of four experiments.
**Average of four experiments.

Table IIb. Enthalpies of Mixing for Ag(l) + Zr(l) Alloys at 1473 K

Series Number	n_{Ag} (m/mol)	n_{Zr} (m/mol)	Σn_i (m/mol)	X_{Zr}	ΔH_{l-l}^M (kJ/mol)
1	5.0194*	10.0405*	15.0599*	0.67	−10.93 ± 0.7**
	5.0211	—	20.0810	0.50	− 7.23
2	0.9981	0.9912	1.9893	0.50	− 6.54
	0.9370	0.9287	3.8550	0.50	− 6.69
3	1.3716	0.9046	2.2762	0.40	− 4.90
	1.3957	0.9331	4.6050	0.40	− 5.82
	1.5125	—	6.1175	0.30	− 3.29
	1.4013	0.5987	8.1175	0.30	− 3.50
4	1.1390	0.2895	1.4285	0.20	− 5.47
	1.2873	0.3224	3.0382	0.20	− 3.42
	4.2187	0.1250	7.3819	0.10	− 1.68

*Total of six experiments.
**Average of six experiments.

Table IIc. Enthalpies of Mixing for Ag(l) + Hf(l) Alloys at 1473 K

Series Number	n_{Ag} (m/mol)	n_{Hf} (m/mol)	Σn_i (m/mol)	X_{Hf}	ΔH^M_{l-l} (kJ/mol)
1	8.4652*	3.6276*	12.0928*	0.30 (two-phase field)	-19.23 ± 1.3**
2	1.9027	0.4773	2.3800	0.20	-10.18
	1.8119	0.4515	4.6434	0.20	-13.44
4.6339		—	9.2773	0.10	-4.63
	1.8489	0.2045	11.3307	0.10	-5.61
11.3485		—	22.6792	0.05	-1.08
3	5.1455	—	5.1455	0.00	—
	1.8007	0.3664	7.3126	0.05	-3.46
	1.4087	0.0829	8.8042	0.05	-0.79
	1.7164	1.3277	11.8483	0.15	-9.63
	1.3874	0.2426	13.4783	0.15	-8.87

*Total of six experiments.
**Average of six experiments.

Table IId. Enthalpies of Mixing for Au(l) + Zr(l) Alloys at 1473 K

Series Number	n_{Au} (m/mol)	n_{Zr} (m/mol)	Σn_i (m/mol)	X_{Zr}	ΔH^M_{l-l} (kJ/mol)
1	2.1719*	6.4791*	8.6510*	0.75	-41.78 ± 1.31**
2	1.7393	—	1.7393	0.00	—
	0.5722	0.1217	2.4332	0.05	-10.91
	0.7133	0.0395	3.1860	0.05	-15.92
3	2.2882	—	2.2882	0.00	—
	0.7595	0.0932	3.1409	0.03	-4.46
	0.7412	0.0296	3.9117	0.03	-5.16
	0.5676	0.1491	4.6284	0.07	-11.55

*Total of six experiments.
**Average of six experiments.

Table IIe. Enthalpies of Mixing for Au(l) + Hf(l) Alloys at 1473 K

Series Number	n_{Au} (m/mol)	n_{Hf} (m/mol)	Σn_i (m/mol)	X_{Hf}	ΔH^M_{l-l} (kJ/mol)
1	1.4406	—	1.4406	0.00	—
	0.7021	0.1137	2.2564	0.05	-11.39
	1.0169	0.0678	3.3411	0.05	-15.25
2	3.4965	0.2835	3.7799	0.075	-16.75
	1.1936	0.0975	5.0710	0.075	-20.96
	6.8818	0.0392	11.9920	0.030	-9.50

IV. DISCUSSION

The standard enthalpies of formation of 13 congruently melting intermetallic compounds were determined from direct-synthesis experiments followed by heat content measurements. Since the evolved exothermic effects were not large enough to raise the temperature of the sample above its melting point, the reactions in the solid state were mainly governed by interdiffusion of the two components. Consequently, to prove that the obtained results represent real values of the heat of formation, one must show that the synthesis reactions go to completion. For this reason, after the experiments, the solidified alloys were examined by X-ray powder diffraction and by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. The resulting observations can be summarized as follows.

A. Solid Silver Alloys

1. AgZr, AgZr$_2$

Since these compounds were liquid at 1473 K, we were unable to remove them from the BeO crucibles. Hence, both of these compounds used for the heat content measurements were prepared by arc-melting. A recently published Ag-Zr phase diagram[13] suggests that AgZr$_2$ is the congruently melting compound and that AgZr melts incongruently. However, our results indicate that AgZr
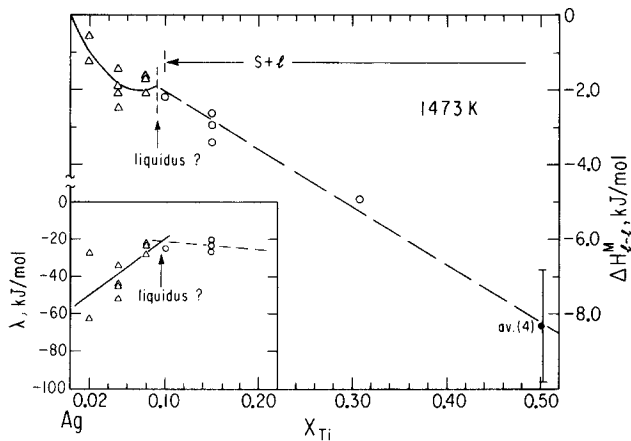
Fig. 2—Plots of ΔH_{l-l}^M and λ for liquid alloys of silver + titanium at 1473 K.

may be more stable. Unfortunately, the data are not precise enough to settle this question. Also, SEM and EDX analysis showed that our $AgZr_2$ sample consisted of a mixture of AgZr and $AgZr_2$, with AgZr being a significant phase. A similar analysis of the AgZr sample showed that AgZr had a small amount of silver. However, X-ray diffraction did not show free silver.

2. AgHf

Since the phase relations in the Ag-Hf system are not known, only a single phase, AgHf, was studied. The lack of powder diffraction data in the literature prevented us from identifying this compound. Our own powder diffraction study showed a new structure but also some very weak hafnium lines. Scanning electron microscopy and EDX analysis confirmed formation of the AgHf phase with some hafnium present in the sample. The estimated amount of free hafnium was 1 to 2 pct by volume.
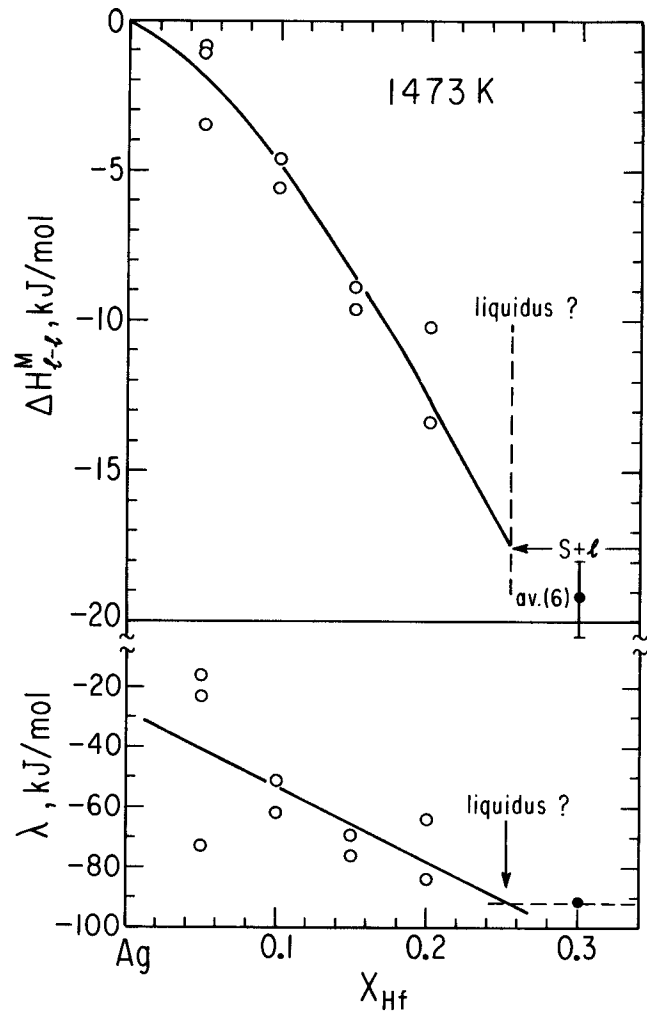

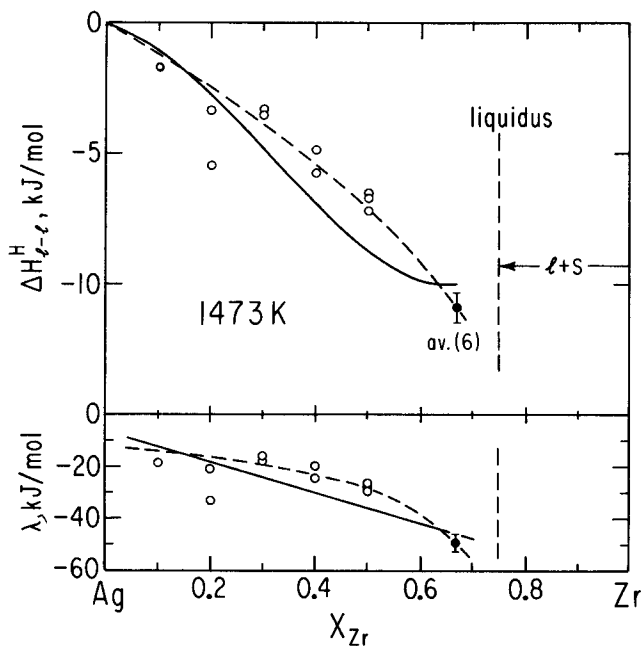Fig. 3—Plots of ΔH_{l-l}^M and λ for liquid alloys of silver + zirconium at 1473 K.

Fig. 4—Plots of ΔH_{l-l}^M and λ for liquid alloys of silver + hafnium at 1473 K.

B. Solid Gold Alloys

1. AuTi, Au_2Ti, and $AuTi_3$

X-ray power diffraction confirmed the formation of the Au_2Ti and $AuTi_3$ phases. Neither free titanium nor free gold was detected in the samples. Results for the powder diffraction of the AuTi sample were inconclusive, since it was very difficult to prepare a powder of this phase. Scanning electron microscopy and EDX analysis showed AuTi as the major phase accompanied by small amounts of Au_2Ti and $AuTi_3$ compounds.

2. Au_3Zr, Au_2Zr, Au_4Zr_5, and $AuZr_3$

X-ray powder diffraction of the Au_3Zr sample showed no free zirconium. Scanning electron microscopy and EDX analysis confirmed the formation of only one phase, namely, Au_3Zr. X-ray powder diffraction also confirmed the formation of the Au_2Zr phase, for which powder diffraction file data are available. However, SEM and EDX analysis showed that two phases were present in this sample: Au_3Zr and Au_2Zr, with Au_2Zr being the major phase.

The X-ray powder diffraction of the Au_4Zr_5 sample showed no free zirconium metal. Scanning electron
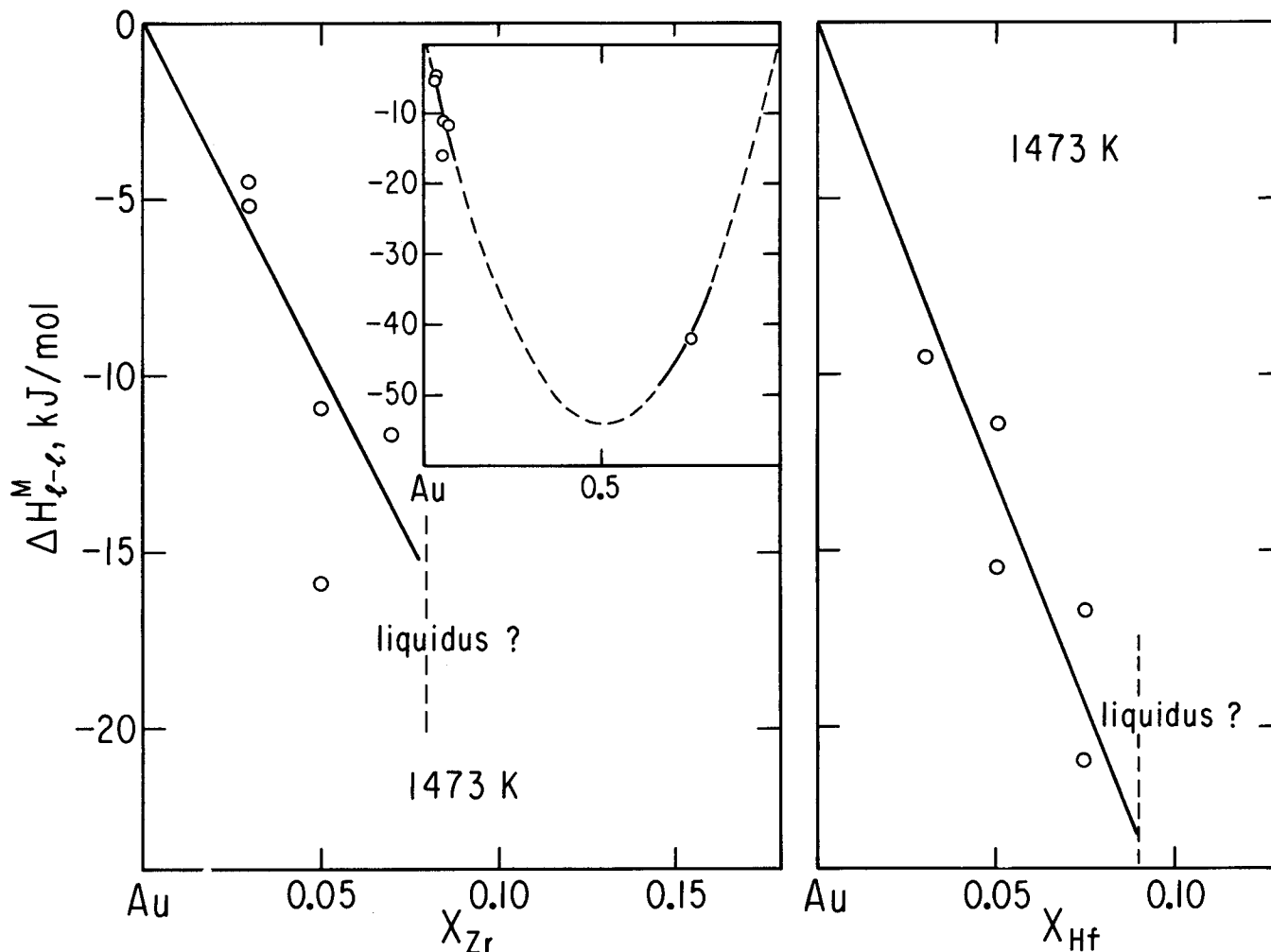
Fig. 5—Liquid-liquid enthalpies of mixing of Au(l) + Zr(l) and Au(l) + Hf(l) alloys at 1473 K.

Table III. Summary of Enthalpy of Mixing Data at 1473 ± 2 K in kJ/mol

System	Interaction Coefficient, λ^*	$\Delta \bar{H}^{\circ}_{Me}$	
		This Work	de Boer et al.[9]
Ag-Ti	$-56.7 + 372.0\ X_{Ti}$	-56.7	-6.0
Ag-Zr	$-6.1 - 58.3\ X_{Zr}$	-13^{**}	-87.0
Ag-Hf	$-27.5 - 258.7\ X_{Hf}$	-27.5	-53.0
Au-Zr	-216.0	-216.0	-303.0
Au-Hf	-286.2	-286.2	-257.0

$\Delta \bar{H}^{\circ}_{Me}$ denotes the partial heat of solution of the liquid transition element at infinite dilution in silver or gold.
*Valid only in the range of concentrations covered in this study.
**Extrapolated value along broken line for λ in Fig. 3.

microscopy and EDX analysis showed only one phase, Au₄Zr₅. The AuZr₃ compound was found to be liquid at 1473 K. Scanning electron microscopy and EDX analysis of an arc-melted sample showed that in addition to AuZr₃, a small amount of AuZr₂ was also present.

3. *Au₃Hf, Au₂Hf, AuHf, and AuHf₂*

X-ray powder diffraction of the Au₃Hf and Au₂Hf samples did not show free hafnium metal. Scanning

electron microscopy and EDX analysis confirmed that these were single-phase samples, namely, Au₃Hf and Au₂Hf. Similar analysis performed on the AuHf sample showed that in addition to the AuHf phase, AuHf₂ was present. In turn, the AuHf₂ sample showed the presence of the Au₅Hf₄ compound and a small amount of free hafnium metal. This implies that the reaction was not complete for this particular compound.
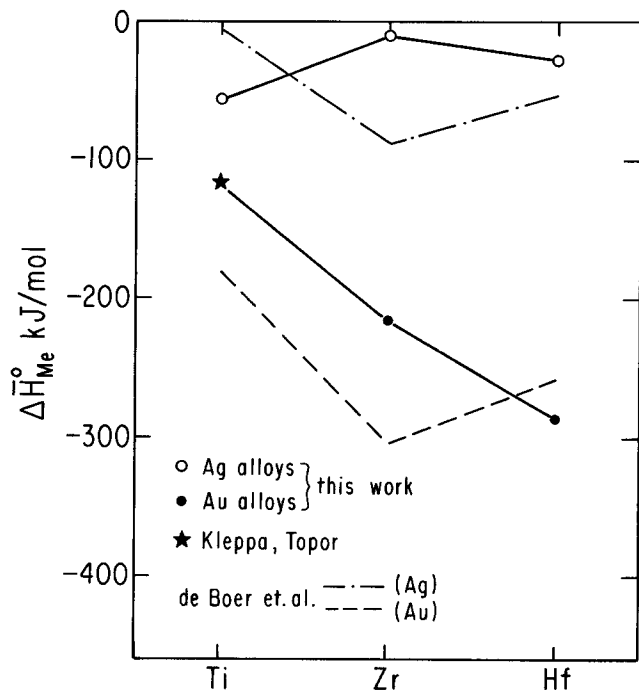
It is apparent from this discussion that for several

Fig. 6—Limiting partial enthalpies of solution of Me(l) (Me = Ti, Zr, Hf) in Ag(l) and Au(l).

compounds, the analysis of the samples indicates a phase mixture with one dominant phase rather than a single phase. In spite of this, we believe all of the results with the possible exception of AgZr and AgZr$_2$ are meaningful. It was recently noted by Hertz and Gachon[14] that studying the same transition metal intermetallic compounds by solute-solvent drop calorimetry[15] and by the direct reaction technique[16,17,18] generally led to very similar results.

C. Liquid Alloys

Heat of mixing data for fairly dilute solutions of titanium in gold were previously reported by Topor and Kleppa.[6] With this exception, the thermodynamic properties of the considered liquid alloys have been unknown. Our results may, to some extent, fill this gap and may also shed some light on some features of the phase diagrams. The interaction parameters, λ, which characterize the heats of mixing, are summarized in Table III.

1. Ag-Ti

The heat of mixing curve in Figure 2 was recalculated using the interaction parameter, λ, given in Table III. It intersects the values of λ extrapolated from the two-phase region at $X_{Ti} \cong 0.09$, which is the liquidus composition at 1473 K.

2. Ag-Zr and Ag-Hf

As mentioned above, it is possible that the AgZr phase may be more stable than AgZr$_2$ and that AgZr accordingly may be the congruent melting compound. In contrast to the Ag-Zr system, the phase diagram for the Ag-Hf system is unknown. Our experiments performed on alloys below $X_{Hf} = 0.2$ reflect one liquid phase, while

Ag$_{0.7}$Hf$_{0.3}$ showed two phases; hence, the liquidus is certainly below $X_{Hf} = 0.3$. Visual examination of the AgHf samples shows that the melting point of this compound is above 1473 K.

3. Au-Zr and Au-Hf

It was found during experiments on these systems that on reaching the composition $X_{Zr} = X_{Hf} = 0.10$, we observed a change in the sign of the heat effect, presumably due to compound formation (precipitation). Hence, we infer that the liquidus compositions at 1473 K lie below mole fraction 0.10 in these two systems. The heats of mixing calculated with a constant value of λ follow the trend toward $X_{Zr} = X_{Hf} = 0.08$. We conclude that for these systems, the liquidus compositions lie between $X_{Me} = 0.08$ and 0.10. However, we have also found that the composition AuZr$_3$($X_{Zr} = 0.75$) produced a liquid phase. The melting point of this phase accordingly falls below 1473 K.

Finally, we compared our results with Miedema's semiempirical model[9] in Figures 1 and 6. It is apparent that the model significantly overestimates the magnitude of the negative enthalpy effects.

ACKNOWLEDGMENTS

REFERENCES

1. S. Sato and O.J. Kleppa: Metall. Trans. B, 1979, vol. 10B, pp. 63-66.
2. H. Yokokawa and O.J. Kleppa: J. Chem. Thermodyn., 1981, vol. 13, pp. 703-15.
3. O.J. Kleppa and S. Watanabe: Metall. Trans. B, 1982, vol. 13B, pp. 391-401.
4. S. Watanabe and O.J. Kleppa: Metall. Trans. B, 1984, vol. 15B, pp. 357-68.
5. L. Topor and O.J. Kleppa: Metall. Trans. B, 1984, vol. 15B, pp. 573-80.
6. O.J. Kleppa and L. Topor: Metall. Trans. A, 1985, vol. 16A, pp. 93-99.
7. K. Fitzner, W.-G. Jung, and O.J. Kleppa: Metall. Trans. A, 1991, vol. 22A, pp. 1103-11.
8. Binary Alloy Phase Diagrams, 2nd ed., T.B. Massalski, ed., ASM INTERNATIONAL, Metals Park, OH, 1990.
9. F.R. de Boer, R. Boom, W.C.M. Mattens, A.R. Miedema, and A.K. Niessen: Cohesion in Metals, Transition Metal Alloys, North-Holland, Amsterdam, 1988.
10. O.J. Kleppa and L. Topor: Thermochim. Acta, 1989, vol. 139, pp. 291-97.
11. R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley, and D.D. Wagman: Selected Values of the Thermodynamic Properties of the Elements, ASM, Metals Park, OH, 1973.
12. I. Barin and O. Knacke: Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin, 1977.
13. K. Zhang, H. Zhao, and Y. Zhou: J. Less-Common Met., 1988, vol. 138, pp. 173-77.
14. J. Hertz and J.C. Gachon: Anales Fisica, Ser. B, 1990, vol. 86, pp. 1-22.
15. L. Topor and O.J. Kleppa: J. Less-Common Met., 1989, vol. 155, pp. 61-73.
16. J.C. Gachon: J. Phys. Chem. Solids, 1988, vol. 49, pp. 99-113.
17. J.L. Jorda, J.C. Gachon, J. Charles, and J. Hertz: J. Therm. Anal., 1988, vol. 34, pp. 551-57.
18. N. Selhaoui: Ph.D. Thesis, University of Nancy, Nancy, France, 1990.