Journal of Alloys and Compounds, 189 (1992) 97–100
JALCOM 340

A computer assessment of the molybdenum–rhodium phase diagram

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(Received April 24, 1992)

Abstract

An optimized phase diagram of the Mo–Rh system was calculated using thermodynamic coefficients derived by the assessment of available experimental phase diagram and thermodynamic data. The excess Gibbs free energies of the phases are described employing the ordinary polynomial expressions. The temperatures of various transitions and the composition limits of the phases are reproduced closely.

1. Introduction

The present assessment was undertaken as part of a computer calculation of the ternary Mo–Pd–Rh system. There have been no such calculations published previously on the binary Mo–Rh system except for the attempt by Kaufman and Bernstein [1]. They used estimated Gibbs excess energy coefficients to draw the phase diagram. The present assessment was therefore undertaken to permit a more complete assessment of the system using available experimental phase diagram and thermodynamic data in order to obtain the best coefficients for use in the computer calculation of the system. The Lukas optimization program [2] was used to obtain the set of coefficients describing the thermodynamic properties in the manner most consistent with existing thermodynamic and phase diagram data.

2. Experimental phase diagram and thermodynamic data

2.1. Phase diagram information

The phase diagram, above 1100 °C, has been established fairly completely. There are large solid solubilities of rhodium in molybdenum, Mo(Rh), and molybdenum in rhodium, Rh(Mo) [3–5]. The limit of the terminal molybdenum-rich phase is very temperature dependent whereas the variation with temperature of the limit of the rhodium-rich f.c.c. phase is slight. The maximum solid solubility of rhodium in molybdenum was reported by Haworth and Hume-Rothery [5] as 20 at.% rhodium at the eutectic temperature, at 1940 ± 5 °C. The rhodium-rich f.c.c. phase is produced by the peritectic reaction, liquid + ϵ(h.c.p.) = f.c.c. Rh(Mo), at 85 at.% rhodium and 2000 ± 10 °C [5]. The very extensive composition range high-temperature h.c.p. intermediate phase formed congruently from the liquid at 67 at.% rhodium and at 2075 ± 10 °C dominates the middle of the system [5]. The composition limits of this phase have been reported to extend approximately from 48 to 85 at.% rhodium at all temperatures between 1140 and 1300 °C [3–6]. It is stable down to 1100 °C and its limits are shown as only slightly temperature dependent. Low temperature order–disorder transformations of the disordered h.c.p. phase to ordered MoRh and $MoRh_3$ phases have been reported [5, 7]. In assessment of the Mo–Rh system by Brewer and Lamoreaux [8], the order–disorder transformation temperatures are given as 1050 ± 75 °C for MoRh and 1200 ± 200 °C for $MoRh_3$. Both of these intermetallic phase fields are thought to extend about 1 at.% either side of their stoichiometric compositions. However, the system has recently been re-examined by the authors [9] between 1100 and 1000 °C using ultra rapidly solidified as well as conventionally melted alloys. Very limited solid solubility of 1.25 at.% rhodium in molybdenum at 1100 °C is confirmed. The range of the h.c.p. phase was found to be from approximately 52 to 81 ± 1 at.% rhodium at this temperature. No trace of the phase MoRh was found at 1100 ± 5 °C, in agreement with previous findings of Raub [3]; however, there is still a possibility of its existence below this temperature. Detailed investigation of alloys with compositions near the second reported intermediate phase $MoRh_3$ at temperatures between

0925-8388/92/$5.00

TABLE 1. Partial Gibbs free energies of molybdenum at 1273 K (J mol^{-1})

x_{Rh}	0.50	0.70	0.80	0.85
Phase	h.c.p.(?)	h.c.p.	h.c.p.+f.c.c.	h.c.p.+f.c.c.
$\Delta\bar{G}_{Mo}$ (J mol^{-1})	−2550	−15062	−66944	−75312

1100 and 1000 °C showed only the normal h.c.p. phase and did not confirm the existence of this phase.

2.2 *Thermodynamic data*

Yamawaki *et al.* [10] studied the system using a calcia–zirconia solid electrolyte e.m.f technique over the temperature range 1200–1300 K. The partial free energies, enthalpies and entropies of solution of molybdenum were calculated at 1273 K. However, the uncertainties are very large for all these thermodynamic properties. The partial quantities for rhodium were derived at 1273 K, so as to be consistent with the phase diagram of Shunk [11]. The partial Gibbs free energies of molybdenum were only input into the data set used in the assessment and are given in Table 1. The reported partial molar enthalpy values were not used because of the very large error limits attached to them.

A set of estimated equations was also obtained by Brewer and Lamoreaux [8] to describe the partial thermodynamic quantities for the phases of the system. Since experimental data are available these estimated values were not utilized in the assessment.

3. Thermodynamic modelling

In the Lukas program the lattice stabilities of the pure elements are described by the equation

$$^{\circ}G=A-BT+CT(1-\ln T)-1/2DT^2-1/2ET^{-1}-1/6FT^3$$

In the present calculation the equations were limited to the first two terms and the coefficients are given in Table 2. Lattice stability values of Kats *et al.* [12] were used for the rhodium and the molybdenum lattice stability values were those of Andersson *et al.* [13], except for the molybdenum (liquid) lattice stability value. For this, in order to obtain a format convenient to employ in the Lukas optimization program, a best fit linear equation was derived using values obtained from Andersson's original equation which is of the form $41616.767-14.6985+4.035826.10^{-22}T^7$ [13].

The excess properties of all the phases except for liquid were described using the sub-regular model. The ordinary polynomial expression was employed for the composition dependence of the phases and the Gibbs energies are given by the following expression:

$$G_m=(1-x)_{Mo}{}^{\circ}G_{Mo}+x_{Rh}G_{Rh}$$
$$+RT[(1-x)_{Mo}\ln(1-x)_{Mo}+x_{Rh}\ln x_{Rh}]+{}^{E}G_m$$

TABLE 2. Gibbs energies of transformations of elements (in joules per mole) and the assessed Gibbs excess free energy coefficients and composition dependence for the phases in the Mo–Rh system (reference states are pure solid Mo(b.c.c.) and Rh(f.c.c.))

Element, Mo	Temperature dependence		Element, Rh	Temperature dependence	
	1	$-T$		1	$-T$
G^{liq}–G^{bcc}	41402.91	14.2966	G^{liq}–G^{fcc}	26568.0	11.88
G^{bcc}–G^{bcc}	0.0	0.0	G^{bcc}–G^{fcc}	6904.0	−4.39
G^{fcc}–G^{bcc}	15200.0	−0.63	G^{fcc}–G^{fcc}	0.0	0.0
G^{hcp}–G^{bcc}	11550.0	0.0	G^{hcp}–G^{fcc}	628.0	−0.63

Phase	Temperature dependence		Composition dependence
	1	$-T$	
Liquid	−60261.04	−18.39	$(1-x)_{Mo}x_{Rh}$
	−84654.63	−44.16	$(1-x)_{Mo}x_{Rh}(x_{Rh})$
	−27.78	−0.22	$(1-x)_{Mo}x_{Rh}(x_{Rh}^2)$
B.c.c.	22507.43	5.48	$(1-x)_{Mo}x_{Rh}$
	−41776.92	7.67	$(1-x)_{Mo}x_{Rh}(x_{Rh})$
F.c.c	110113.559	65.004	$(1-x)_{Mo}x_{Rh}$
	−199401.5	−99.42	$(1-x)_{Mo}x_{Rh}(x_{Rh})$
H.c.p.	−8453.152	5.495	$(1-x)_{Mo}x_{Rh}$
	−60006.5	−25.872	$(1-x)_{Mo}x_{Rh}(x_{Rh})$

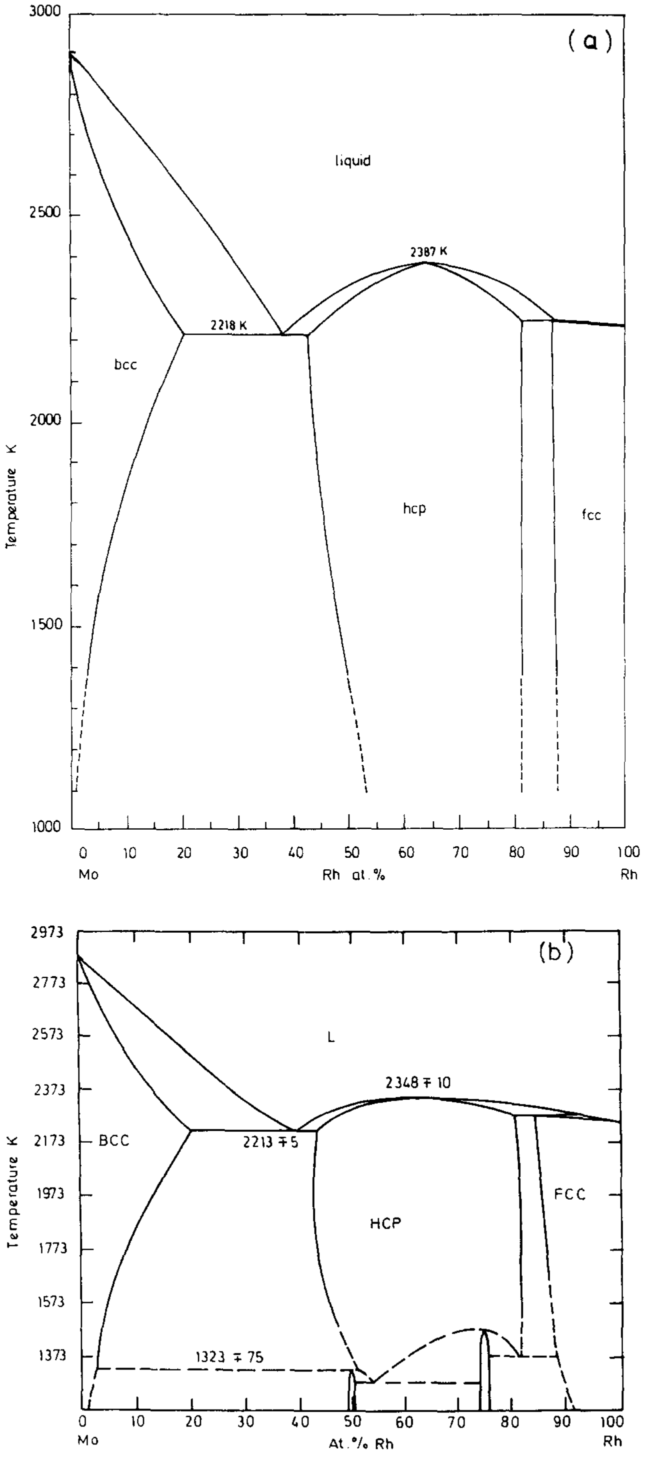

Fig. 1. Phase diagrams above 1100 K, (a) plotted using assessed coefficients and (b) plotted using experimental data.

where the excess free energy is described as

$$ {}^{E}G_m = (1-x)_{Mo}x_{Rh}(A_0 + A_1x_{Rh}) $$

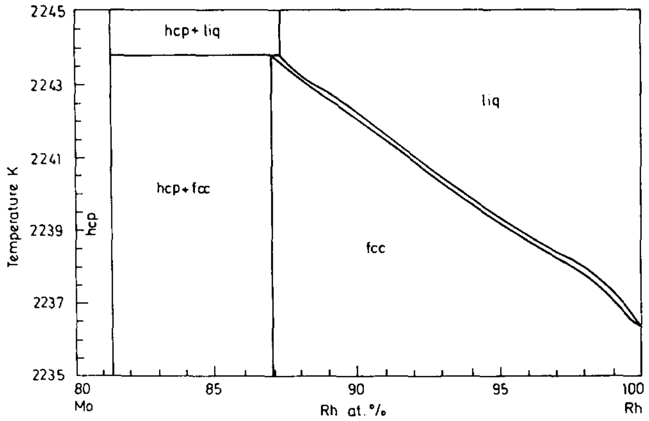

Fig. 2. Peritectic region of the phase diagram shown in more detail.

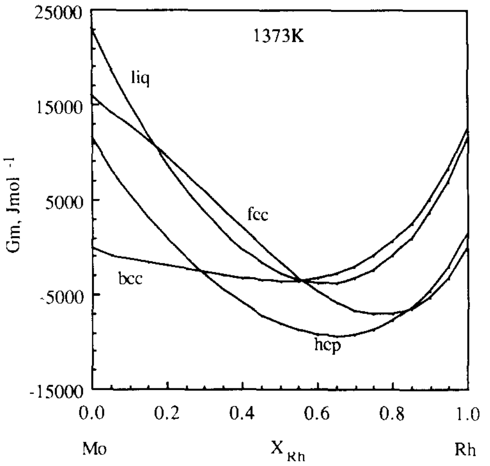

Fig. 3. Gibbs free energy curves of phases produced by optimization at 1373 K.

$(1-x)$ and x are the molar fractions of individual components, ${}^{\circ}G_i$ are the lattice stability values of pure elements and A_i are the binary polynomial coefficients which are temperature dependent.

4. Optimization

The phase diagram data points above 1373 K, from the diagram as assessed by Brewer and Lamoreaux [8], were adopted as the main sources of phase diagram data. The results of our constitutional investigation [9] were also used as input. Partial free energies of the elements at 1273 K reported by Yamawaki *et al.* [10] for three alloy compositions at 70 at.% rhodium, 80 at.% rhodium and 85 at.% rhodium were also included in the data set. The partial free energies of the alloy with 50 at.% rhodium was not employed because it was thought that the possible existence of the reported $Mo_{50}Rh_{50}$ ordered phase [7] might affect the reported measurement at 1273 K.

Initially Rand and Potter's [14] lattice stabilities for the elements combined with the phase diagram and thermodynamic data were input into the Lukas program and various descriptions including regular, sub-regular and more composition dependent terms were tried in an effort to obtain the best coefficients producing a realistic phase diagram. All these attempts were unsatisfactory since the f.c.c. phase reappeared in the molybdenum-rich part of the diagram above 1700 K. It was found that the f.c.c. phase was stable relative to the b.c.c. phase and the h.c.p. phases above 1700 K. When the f.c.c. phase was removed from the calculation the b.c.c., the liquid and the h.c.p. equilibrium were well reproduced, thus suggesting that the molybdenum f.c.c. phase stability term was causing the problem. The molybdenum lattice stabilities from Andersson *et al.* [13] were therefore tried after modification of the format of the molybdenum (liquid) phase stability equation. These stabilities proved to be satisfactory and after some attempts the coefficients describing the phase diagram best were obtained. These coefficients are shown in Table 2.

5. Results and discussion

The diagram above 1100 K, plotted using the assessed coefficients is shown in Fig. 1(a). As can be seen, agreement with the experimental diagram (Fig. 1(b)) is generally very satisfactory. The peritectic region is given in more detail in Fig. 2. Gibbs free energy curves of the phases produced by the optimization at 1373 K are given in Fig. 3.

The temperature of the eutectic reaction is calculated as 2218 K within the accuracy limit reported. The temperature dependence of the b.c.c. and f.c.c. phase limits are reproduced quite well. The solid solubility limits of the h.c.p. phase are calculated to decrease approximately linearly with falling temperature. The only major differences from the experimental diagram are in the calculated values of the congruent melting point of the h.c.p. phase (approximately 29 K less), the peritectic temperature (approximately 19 K less) and the liquid composition of the peritectic reaction (5 at.% rhodium less). These major discrepancies could probably be reduced if experimental thermodynamic data were available for the liquid phase.

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