Phase Diagram of the Rhenium-Rhodium System: State of the Art

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The available experimental data for metallic solid solutions in the rhenium-rhodium binary metallic system are incomplete. This paper reviews recent data on the Re-Rh system which enables the solidus parts of the equilibrium phase diagram to be constructed. Experimental data for solid solutions prepared by different techniques and theoretical modelling show that the single phase regions are wider than previously reported. The maximum solid phase solubility of Re in Rh is 15 at%, and that of Rh in Re is 75 at%. In this paper, a phase diagram for the Re-Rh system which serves as a reliable model for the representation of the available experimental data is proposed.

Introduction

Polymetallic compositions containing platinum group metals (pgms) and rhenium are widely used in industry as high-temperature materials, in superalloys and as catalysts (1). Re-Rh solid solutions are used in high-temperature thermocouples (2), as coatings with high thermal, mechanical and chemical stability (3) and in applications where high hardness is required (4).

The properties of solid solutions depend on the composition, the preparation conditions and particularly on the presence of impurities in the alloy. Metallic phase behaviour is most commonly predicted using the relationship between composition or temperature and properties. However, the information currently available about the Re-Rh system is poor and contradictory due to the difficulties that arise during the preparation of solid solutions. This, together with the high cost of the materials, limits the practical applications of Re-Rh solid solutions and composites. Construction of the correct equilibrium phase diagram would provide a firm foundation for future investigations of chemical, physical and material properties of Re-Rh solid solutions and could enable their usefulness to be extended. Comprehensive knowledge of two-component systems is also essential for the construction of ternary and quaternary phase diagrams. The collection of equilibrium data is made

difficult by the extremely high melting points of the metal components. The present paper aims to critically analyse recent experimental data on Re-Rh solid solutions and calculate the equilibrium phase diagram for the Re-Rh system using the regular solution model.

The Rhenium-Rhodium System

In the early 1960s, the first experimental data on the Re-Rh system was obtained using high-temperature melting and annealing of fine metallic powders in vacuum. The first phase diagram was constructed based on the analysis of bimetallic solid solutions prepared at a wide range of concentrations (5). As shown in **Figure 1**, the peritectic phase diagram has three regions in the solid state: face-centred cubic (fcc) solid solutions in the Rh part, hexagonal close-packed (hcp) solid solutions in the Re part and a two-phase region between the single phase sections. According to published data, this two-phase region is wide. The maximum solubility at 1000ºC of Re in Rh has been estimated as 15 at% and that of Rh in Re as 24 at%, and the peritectic temperature was determined to be 2620ºC.

Kaufman later calculated the two-component phase diagrams for Re with all pgms, using the regular solution model (6). Further measurements of mixing volumes and formation enthalpy for high melting point metallic systems confirmed the accuracy of this model. Although Kaufman's calculations were partly based on non-validated thermodynamic data, they were in tolerable concordance with the experimental diagrams. The calculated and experimentally obtained phase diagrams were adequate for the majority of metallic systems, but not for Re-Rh. This may be explained by the inapplicability of the model or by the inaccuracy of the corresponding experimental data. Direct thermodynamic measurements for a binary Re-Rh system could help to improve the usefulness of the model in this case. This information is available for pure pgms and pure Re (7–10), and for some of the bimetallic solid solutions. The criteria for analysing the accuracy of data used to construct experimental and calculated phase diagrams were discussed by Schmid-Fetzer *et al*. in 2005 (11). Based on these criteria, the available experimental phase diagram for the binary Re-Rh system (5) seems to be incorrect, at least in the liquidus part (hcp ↔ liquid).
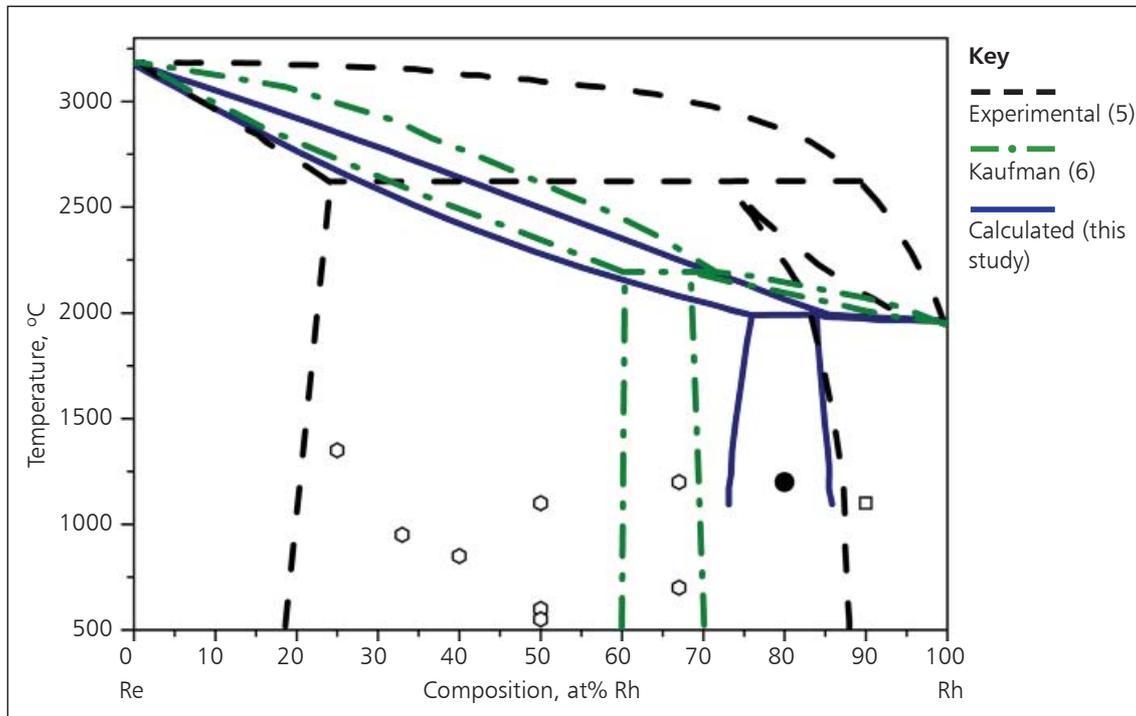

Fig. 1. Proposed phase diagram for the rhenium-rhodium system according to data from experiment (5), Kaufman (6) and the present study. A two-phase sample with 80 at% Rh is shown as a black circle. Other compositions and preparatory temperatures are given in Table I

Korenev and coauthors developed the 'single source precursor strategy' for the preparation of solid solutions of pgms under mild conditions using bimetallic double complex salts as precursors (12). This approach allows the reproducible preparation of a broad range of pgm solid solutions with precise compositions. Heating the obtained metallic solid solutions up to the melting point does not change the phase composition and cell parameters; in other words, the phases prepared are thermodynamically stable and in equilibrium. The working temperatures are usually below 800ºC. This approach has also been applied to the preparation of Re-Rh solid solutions (13–18). For example, the $Re_{0.50}Rh_{0.50}$ solid solution can be obtained by thermal decomposition of $[Rh(NH_3)_5Cl][ReCl_6]$ in a hydrogen or argon stream at 600ºC (16). The variation of the precursor composition and preparatory conditions results in different metallic materials based on polymetallic nanoparticles, which can be also prepared on porous supports for catalytic applications (19). To improve the accuracy of the data used to construct the phase diagrams, Re-Rh solid solutions were also synthesised by heating fine powders of the highly pure metals at 1000–1100ºC under vacuum for 100–200 h (20, 21) as well as using the thermobaric treatment (2000ºC, 4 GPa) (22). The solid solutions obtained were characterised by powder X-ray diffraction (XRD), elemental analysis and scanning electron microscopy (SEM), with the measurements of the cell parameters and atomic volumes taken for all phases. The crystallographic characteristics and preparatory conditions for all known Re-Rh solid solutions are summarised in **Table I**. According to the data obtained, the two phase region in the Re-Rh phase diagram at 1000ºC should be placed between $Re_{0.15}Rh_{0.85}$ (fcc) and $Re_{0.25}Rh_{0.75}$ (hcp), indicating that the maximum solid phase solubility of Re in Rh is 15 at%, and that of Rh in Re is 75 at%.

To analyse the hcp-fcc bimetallic system, the atomic volume, V/Z (where V is the volume of the elemental cell and Z corresponds to the number of atoms in the elemental cell, with $Z = 6$ for hcp and $Z = 4$ for fcc), is plotted against the composition of the obtained metallic phase according to Zen's law (25, 26). All solid solutions in the Re-Rh system show a nearly linear dependence of V/Z on composition, with a negative deflection of no more than 2% (**Figure 2**), which roughly reflects the idealness of the system. Reported values for the cell parameters of the cubic solid solution $Re_{0.12}Rh_{0.88}$ ($a = 3.64$ Å, $V/Z = 12.06$ Å³), prepared by melting the pure metals at 2500ºC (5), appear to

be incorrect since the atomic volume is less than that of pure Rh. This solid solution was therefore not considered in the present study. The V/Z dependence can be fitted by the second-order polynomial (Equation (i)):

$$V/Z = 14.75 - 15.4 \times 10^{-3} \times X_{Rh} + 5.45 \times 10^{-5} \times X_{Rh}^2 \quad \text{(i)}$$

where X_{Rh} is the at% of Rh in a binary solution. The phases were prepared by melting and the thermal decomposition of bimetallic compounds follows a standard curve, indicating that solid solutions prepared by thermal decomposition of single source precursors are nearly in equilibrium. This polynomial curve can be used for estimating the composition of Re-Rh solid solutions with known cell parameters.

A powerful tool for understanding the properties of metals with extremely high melting points is the thermodynamic modeling of the binary phase diagrams in equilibrium, which gives information about the possible solubility limits and peritectic temperature. The technique can also be used for materials design and industrial process optimisation. For the present study, the phase diagram was calculated using the PANDAT 8 software (27) based on the CALPHAD method (28) and using the Scientific Group Thermodata Europe (SGTE) v. 4.4 thermodynamic database (29). **Figure 1** shows that the calculated solid solubility limits are inconsistent with the existing experimental phase diagram (5). However, there is good compatibility between the theoretical phase diagram and recently obtained experimental data for the Re-Rh solid solutions. The comparison clearly shows that the previous experimental phase diagram for the Re-Rh system should be reconsidered and corrected below the peritectic temperature. The Rh part (fcc solid solutions) of the experimental phase diagram seems to be accurate, whereas the Re part (hcp solid solutions) requires correction.

Conclusion and Further Work

In conclusion, the proposed phase diagram for the Re-Rh system serves as a reliable model for representing the experimental data which are available to date. Further thermodynamic studies of solid solutions derived from high purity metals are recommended in order to improve the phase diagram. A critical analysis of the available experimental data on the solid solutions of pgms and rhenium should be carried out to construct a consistent set of thermodynamic data and phase diagrams for these systems.

Table I. Crystallographic Data on Known Phases in the Rhenium-Rhodium System

Composition (Reference)	Cell parameters, a, Å; c, Å	Cell parameters, c/a	Space group	Density, D_x, g cm^{-3}	Atomic volume, V/Z, Å^3	Preparation conditions
Re (23, No. 5-702)	2.760; 4.458	1.615	$P6_3/mmc$	21.026	14.705	Melting point 3180°C
Re$_{0.75}$Rh$_{0.25}$ (20, 21)	2.753(1); 4.396(2)	1.597	$P6_3/mmc$	19.098	14.43(2)	Annealing in vacuum (1250°C, 80 h)
Re$_{0.75}$Rh$_{0.25}$ (13)	2.749(2); 4.395(3)	1.599	$P6_3/mmc$	19.094	14.38(4)	Thermal decomposition in He of [Rh(NH$_3$)$_5$Cl]$_2$[Re$_6$S$_8$(CN)$_6$] · 3H$_2$O (1200°C, 1 h)
Re$_{0.67}$Rh$_{0.33}$ (20, 21)	2.746(1); 4.387(2)	1.598	$P6_3/mmc$	18.380	14.34(2)	Annealing in vacuum (950°C, 450 h)
Re$_{0.67}$Rh$_{0.33}$ (14)	2.746(1); 4.387(2)	1.598	$P6_3/mmc$	18.398	14.32(2)	Thermal decomposition in H$_2$ of [Rh(NH$_3$)$_5$Cl](ReO$_4$)$_2$ (950°C, 400 h)
Re$_{0.60}$Rh$_{0.40}$ (15)	2.7473(2); 4.3886(4)	1.597	$P6_3/mmc$	17.704	14.34(4)	Thermal decomposition in H$_2$ of [Rhpy$_4$Cl$_2$]$_4$[Re$_6$S$_8$(CN)$_6$] · 1.5H$_2$O (850°C, 1 h)
Re$_{0.50}$Rh$_{0.50}$ (20, 21)	2.730(1); 4.354(2)	1.595	$P6_3/mmc$	17.082	14.05(2)	Annealing in vacuum (1100°C, 200 h)
Re$_{0.50}$Rh$_{0.50}$ (16)	2.733(5); 4.364(6)	1.597	$P6_3/mmc$	17.006	14.11(8)	Thermal decomposition in H$_2$ of [Rh(NH$_3$)$_5$Cl][ReCl$_6$] (600°C, 1 h)

(Continued)

Table I. (Continued)

| Composition (Reference)	Cell parameters, a, Å c, Å	Cell parameters, c/a	Space group	Density, D_x, g cm^{-3}	Atomic volume, V/Z, Å^3	Preparation conditions
Re$_{0.50}$Rh$_{0.50}$ (16)	2.727(5) 4.352(6)	1.596	P6$_3$/mmc	17.128	14.01(8)	Thermal decomposition in Ar of [Rh(NH$_3$)$_5$Cl][ReBr$_6$], (550°C, 1 h)
Re$_{0.50}$Rh$_{0.50}$ (16)	2.730(5) 4.355(6)	1.595	P6$_3$/mmc	17.078	14.05(8)	Thermal decomposition in H$_2$ of [Rhpy$_4$Cl$_2$]ReO$_4$, (470°C, 1 h)
Re$_{0.33}$Rh$_{0.67}$ (20, 21)	2.721(1) 4.348(2)	1.598	P6$_3$/mmc	15.533	13.94(2)	Annealing in vacuum (1200°C, 145 h)
Re$_{0.33}$Rh$_{0.67}$ (18)	2.722(5) 4.350(6)	1.598	P6$_3$/mmc	15.514	13.96(8)	Thermal decomposition in H$_2$ of [Rh(NH$_3$)$_5$Cl]$_2$[ReCl$_6$]Cl$_2$ (700°C, 1 h)
Re$_{0.30}$Rh$_{0.70}$ (20, 21)	2.721(1) 4.348(2)	1.599	P6$_3$/mmc	15.257	13.94(2)	Annealing in vacuum (1100°C, 200 h)
Re$_{0.20}$Rh$_{0.80}$ (20, 21)[a]	2.716(1) 4.350(2)	1.599	P6$_3$/mmc	–	13.89(2)	Annealing in vacuum (1200°C, 75 h)
	3.814(1)	–	Fm$\bar{3}$m	–	13.86(1)	
Re$_{0.10}$Rh$_{0.90}$ (20, 21)	3.810(1)	–	Fm$\bar{3}$m	13.358	13.83(3)	Annealing in vacuum (1100°C, 200 h)
Rh (23, No. 5-685) and (24)	3.8031	–	Fm$\bar{3}$m	12.425	13.752	Melting point 1960°C

[a]*Mixture of hcp and fcc solid solutions*
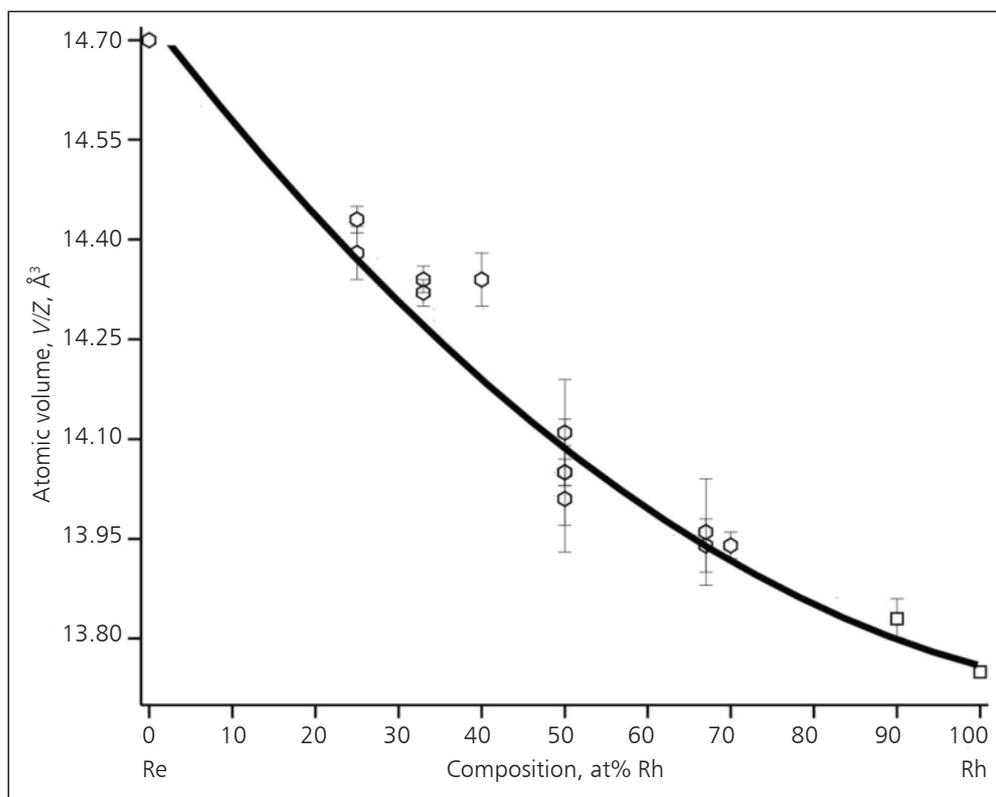
Fig. 2. Atomic volumes for known hcp (hexagons) and fcc (squares) Re-Rh solid solutions. The corresponding compositions and atomic volumes, V/Z, are given in Table I

Improved data on binary systems will enable ternary and quaternary phase diagrams to be predicted with greater accuracy. Investigation of the physical properties of Re-Rh solid solutions such as their hardness, electrical and thermal conductivity and thermoelectric characteristics will improve the practical usefulness of this system.

Acknowledgement

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