RARE METALS Vol. 25, No. 5, Oct 2006, p. 597

# Development of a database for the prediction of phases in Pt-based Superalloys: Cr-Pt-Ru

A. Watson<sup>1)</sup>, L.A. Cornish<sup>2,3)</sup>, and R. Süss<sup>2,3,4)</sup>

1) Institute for Materials Research, School of Process, Materials and Environmental Engineering, University of Leeds, Leeds, UK 2) Advanced Materials Division, Mintek, Private Bag X3015, Randburg, 2125, South Africa

3) DST/NRF Centre of Excellence for Strong Materials, University of the Witwatersrand, Johannesburg, 2025, South Africa

4) School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, 2025, South Africa

(Received 2006-06-01)

**Abstract:** Work has been ongoing in building a thermodynamic database for the prediction of phase equilibria in Pt-based superalloys. The alloys are being developed for high temperature applications in aggressive environments. The database will aid the design of alloys by enabling the calculation of the composition and proportions of phases present in alloys of different compositions. In order to extend this database, a preliminary assessment of the Cr-Pt-Ru system has been undertaken, using a combination of Pandat and *MTDATA* software. As a first step, it was necessary to provide thermodynamic models for the three associated binary systems. Owing to a lack of thermodynamic information for these systems, the binary assessments were based on phase diagrams available in the literature. Using recent experimental phase equilibria data for the ternary system, a preliminary assessment of the Cr-Pt-Ru system has been produced. In this preliminary assessment, simplified models were employed for the L1<sub>2</sub> and sigma phases with a view to extending the descriptions as new experimental information becomes available.

Key words: Cr-Pt-Rh; thermodynamics; assessment; phase diagram

[The work was financially supported by EPSRC platform grant GR/R95798, "The Platinum Development Initiative", and the Department of Science and Technology, South Africa.]

# 1. Introduction

Alloys based on the platinum group metals are becoming increasingly attractive for high-temperature applications, for example, as possible alternatives to nickel-based superalloys used in aerospace applications [1]. At appropriate compositions, alloys based on the Pt-Al binary system exhibit  $\gamma/\gamma'$  microstructures analogous to those of the Ni-Al system where the ordered Ni<sub>3</sub>Al L1<sub>2</sub> intermetallic phase ( $\gamma'$ ) is precipitated in a disordered fcc matrix ( $\gamma$ ). It is the coherent  $\gamma'$  phase that is the primary strengthening phase in the alloy. A close match in lattice parameter between the precipitate and the matrix (<1%) allows the  $\gamma'$  to precipitate homogeneously throughout the matrix. Typically, aero engines utilising nickelbased superalloys can maintain their strength at operating temperatures of up to around 1000°C, but they are susceptible to corrosion. On the other hand, using alloys based on platinum would enable a significant increase in operating temperatures (to around 1300°C) owing to their higher melting point and improved corrosion resistance over nickel-based materials. This would lead to increased efficiency, lower fuel costs and reduced emissions.

Alloy development can be expensive both in time and financially. The costs can be significantly reduced by employing computational thermodynamics where by using appropriate thermodynamic databases, multiphase multicomponent equilibria can be predicted relatively easily [2]. The present work describes a contribution to a thermodynamic database

Corresponding author: A. Watson E-mail: A.Watson@leeds.ac.uk

© 1994-2007 China Academic Journal Electronic Publishing House. All rights reserved. http://www.cnki.net

for development of Pt-based superalloys through a modelling of the Cr-Pt-Ru system.

## 2. Methodology

The basic methodology of thermodynamic database design and construction has been described in detail many times, for example in Ref. [2]. The basis for the construction of the database is the provision of reliable thermodynamic models for the unary and binary systems within the database. This relies on critical assessment of the experimental information available for each system, and by the application of appropriate models for each of the phases involved, model parameters are derived which allow the phase equilibria and thermodynamic properties of the systems to be reproduced through calculation to a reasonable degree of accuracy. It is often necessary to critically assess the higher order systems as well, typically the ternary systems and on occasion, quaternary systems should such information be available.

Unary Gibbs energy data for the elements used in the present work are taken from the SGTE unary database v4.4. These data form the basis of the critical assessment of the constituent binary systems, as for the ternary Cr-Pt-Ru system.

#### 3. Binary systems

# 3.1. Cr-Pt

Of the three binary systems comprising the Cr-Pt-Ru ternary system, the Cr-Pt is the best known. Nevertheless, little experimental study of this system has taken place. The phase diagram given by Ref. [3] is based primarily on experimental investigations by Refs. [4] and [5]. The system comprises terminal solid solutions based on the components and the Cr<sub>3</sub>Pt intermediate phase, which has the A15 crystallographic structure and is shown to melt congruently. The A15 phase, however, does not lie at its stoichiometric composition, having a maximum Pt-content of 23 at.% at 970°C. The wide (Pt) terminal solid solution exhibits both L1<sub>2</sub> (CrPt<sub>3</sub>) and L1<sub>0</sub> (CrPt) ordering. Ref. [3] indicates two eutectic reactions;  $L \equiv (Cr) + Cr_3Pt$  (at 1500°C) and L

 $\equiv$  Cr<sub>3</sub>Pt + (Pt) (at 1530°C). A maximum in the liquidus and the fcc solidus appears at around 1785°C and ~80 at.% Pt. The phase diagram is given in Fig. 1. A thermodynamic assessment of the Cr-Pt system has been conducted [6]. However, they neglected to model the ordering of the (Pt) solid solution giving the L1<sub>2</sub> and L1<sub>0</sub> structures. Also, in their assessed phase diagram, the Cr-rich eutectic has a higher temperature than the Pt-rich. This is contrary to Ref. [3], although there is recent experimental evidence to support this. Solidification microstructures of alloys in the Cr-Pt-Ru [7], Al-Cr-Pt [8], and Cr-Ni-Pt [9] ternary systems show that the temperature order of the eutectics in the Cr-Pt system is more likely to be as given in Ref. [6] than that in Ref. [3]. The calculated phase diagram given by Ref. [6] is given in Fig. 2. Crystallographic data for the phases are given in Table 1 and invariant temperatures are given in Table 2.



#### 3.2. Cr-Ru

The Cr-Ru system is reasonably well established, although there is some speculation regarding the intermediate phases. Fig. 3 shows the assessed phase diagram [3]. This is based on phase diagram studies conducted by Refs. [10-15]. The system comprises large terminal solid solutions of chromium and ruthenium ((Cr) & (Ru)) and associated with them is a eutectic reaction at 1610°C. Two intermediate phases are stable in the system. A sigma phase is stable over the temperature range from approximately 800°C to just below the eutectic temperature, at 1580°C. The homogeneity range of the sigma phase field is approximately 4 at.%, centred at a Ru composition of 33 at.%. The stability range of the Cr<sub>3</sub>Ru phase is less certain. It has a narrow homogeneity range, appearing in the phase diagram as a line compound. The phase is drawn on the phase diagram of Ref. [3], at a composition of ~32 at.% Ru, in agreement with Ref. [15]. However, it should lie at a composition of 25 at.% Ru to be consistent with the text of the article, and the fact that this region of the phase diagram is constructed with dashed lines would suggest that this part of the diagram is still uncertain. Interestingly, its crystal structure is the same as the Cr<sub>3</sub>Pt phase, A15, suggesting the possibility of mutual solubility in the ternary Cr-Pt-Ru system. It exists over a narrow temperature range: 750-1000°C, but this is by no means certain as indicated in the published phase diagram by a dashed line. Crystallographic data and invariant temperatures are given in Tables 1 and 2, respectively.



Fig. 2. Assessed Cr-Pt phase diagram [6].

System	Reaction	at.% of	omposition f the 2 <sup>nd</sup> ele	n ement	Temperature / °C	Reaction type	Reference
Cr-Pt	$L \equiv Cr$		0		1863	Melting	[3]
	$L \equiv Cr_3Pt$		~18			Congruent	[3]
			18.5		1582		[6]
	$L \equiv Cr_3Pt + (Cr)$	~13	~17	~13	1500	Eutectic	[5]
		14	17	6	1565	Eutectic	[6]
	$L \equiv Cr_3Pt + (Pt)$	~24	~20	~29	1530	Eutectic	[5]
		25	20.5	28	1548	Eutectic	[6]
	$(Pt) \equiv Cr_3Pt$		~67		~1130	Congruent	[3]
	$(Pt) \equiv Cr_3Pt + CrPt_3$	~34	~23	-	970	Eutectoid	[3]
	$L \equiv (Pt)$		~80		1785	Congruent	[3]
Cr-Ru	$\mathbf{L} \equiv (\mathbf{Cr}) + (\mathbf{Ru})$	~37	~32	~48	1610	Eutectic	[3]
		37.2	32.9	48.5	1611	Eutectic	This work
	$(Cr) + (Ru) \equiv Cr_2Ru$	~32	~48	~33	1580	Peritectoid	[3]
		32.4	48.4	33.3	1578	Peritectoid	This work
	$(Cr) + Cr_2Ru \equiv Cr_3Ru$	~23	~33	~32*	~1000	Peritectoid	[3]
		22.1	33.3	26	985.9	Peritectoid	This work
	$Cr_2Ru \equiv Cr_3Ru + (Ru)$	~33	~32*	~50	~800	Eutectoid	[3]
		33.3	25.7	50.6	803.7	Eutectoid	This work
	$Cr_3Ru \equiv (Cr) + (Ru)$	~32*	~18	~51	~750	Eutectoid	[3]
		25.6	19	51.2	751	Eutectoid	This work
Pt-Ru	$L \equiv (Pt) + (Ru)$	73.5	72.6	80.9	2127.6	Eutectic	This work
	L≡(Pt)		~69.5		~2129.4	Congruent	This work

Table 1.	Invariant eq	uilibria in	the	Cr-Pt.	Cr-Ru.	and Pt-Ru	binarv	systems
----------	--------------	-------------	-----	--------	--------	-----------	--------	---------

Note: \* Incorrectly marked on the diagram-see above.

Phase	Composition	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Cr) – bcc	0-10 at.% Pt	cI2	Im-3m	A2	W
	0-32 at.% Ru				
Cr <sub>3</sub> Pt	17-~23 at.% Pt	cP8	Pm-3n	A15	Cr <sub>3</sub> Si
CrPt	~48-~52 at.% Pt	tP2	P4/mmm	$L1_0$	AuCu
CrPt <sub>3</sub>	~34-85 at.% Pt	cP4	Pm-3m	$L1_2$	AuCu <sub>3</sub>
(Pt) - fcc	0-~71 at.% Cr	cF4	Fm-3m	A1	Cu
	0-~70 at.% Ru				
Cr <sub>3</sub> Ru	~25 at.% Ru	cP8	Pm-3n	A15	Cr <sub>3</sub> Si
Cr <sub>2</sub> Ru	32-36 at.% Ru	<i>tP</i> 30	$P4_2/mnm$	D8 <sub>b</sub>	σCrFe
(Ru) – hcp	0-52 at.% Cr	hP2	$P6_3/mmc$	A3	Mg

Table 2. Crystallographic data of the phases [3]



3.3. Pt-Ru

Little experimental data exist for this system. The assessed diagram from Ref. [3] is given in Fig. 4. The phase diagram comprises two terminal solid solutions, (Pt) and (Ru), associated with a peritectic reaction, although this is uncertain as indicated by the dashed lines in the phase diagram.

## 4. Cr-Pt-Ru ternary phase diagram

Only two investigations of the ternary system have been conducted. Zhao [16] presents a comprehensive isothermal section for 1200°C. Diffusion multiples were prepared and underwent a HIPping treatment at 1200°C for 40 h. Studies incorporating EPMA and EBSD analysis were employed to locate the fcc, hcp, bcc, and A15 phase boundaries. The results indicate quite a large extension of the  $Cr_3Pt$  phase into the ternary system at this temperature. It does not meet the Cr-Ru binary, of course, as the A15 phase is not stable in the Cr-Ru system at this temperature. Interestingly, the direction of this extension is towards compositions richer in Ru than the Cr<sub>3</sub>Ru stoichiometry at the Cr-Ru binary edge which would tend to agree with the findings of Ref. [15]. The isothermal section given by Ref. [16] is reproduced in Fig. 5. Isothermal sections for 1000 and 600°C have been presented [17]. Phase boundaries were determined by annealing alloys of different compositions for 1000 h or 600 h before examination using SEM/EDX.





Fig. 5. Experimental isothermal section for 1200°C [16].

# 5. Optimisation

In the optimisation process, the parameters to the Gibbs energy expressions for each of the phases are adjusted in order that they can be used to calculate phase equilibria, which agree with the experimental information used. This is achieved by using appropriate software that performs a least squares analysis of the calculated and experimental data. The software then adjusts the parameters in order to minimise the sum of the squares of the errors between the calculated and experimental data. The software used in this work was WinPhad, Pandat [18] and *MTDATA* [19].

#### 5.1. Choice of Models

The temperature dependence of the Gibbs energy was described by:

$$G(T) = A + BT + CT \ln T + \sum DT^{n}$$
(1)

where *A*-*D* are adjustable parameters. The compositional dependence of a binary substitutional solution phase (for example, the liquid phase)  $\phi$ , of components *i* and *j* is given by:

$$G_{\rm m}^{\phi} = x_i G_i^{\Theta,\phi} + x_j G_j^{\Theta,\phi} + RT(x_i \ln x_i + x_j \ln x_j) + G_{\rm m}^{\rm E}$$
(2)

where the  $G^{\oplus}$  terms are the 'so-called' lattice stability terms and the  $G^{E}$  term is the excess Gibbs energy of mixing. The excess Gibbs energy is described by the 'Redlich-Kister' polynomial [20]:

$$G_{\rm m}^{\rm E} = x_i x_j \sum_{n=0}^{n} L (x_i - x_j)^n$$
(3)

where  ${}^{n}L$  are adjustable parameters. Extrapolation of the binary Gibbs energies into the ternary system was carried out using the method of Muggianu [21].

Owing to the general lack of experimental information available regarding the  $L1_2$  and  $L1_0$  phases in the ternary system, it was decided that the ordering would not be modelled on this occasion. This makes the modelling of the ternary system considerably easier and also means that the optimisation of the Cr-Pt system given by Ref. [6] could be used directly without any modification. Another simplification was introduced by treating the Cr<sub>2</sub>Ru sigma phase as stoichiometric, as from the experimental information available, its extension into the ternary systems seems to be small. On the other hand, the Cr<sub>3</sub>Ru A15 phase was treated in the same manner as the Cr<sub>3</sub>Pt A15 phase to enable the phase to extend well across the ternary system from the Cr-Pt binary edge. The model used for this phase was the compound energy model incorporating two sublattices with components mixing on each sublattice. The compositional dependence in such a model is given by:

$$G_{\rm m} = \sum_{i} \sum_{j} y_i^1 y_j^2 G_{ij}^{\Theta} + RT \sum_{s} a^s \sum_{i} y_i^s \ln y_i^s + G_{\rm m}^{\rm E}$$

$$\tag{4}$$

where *a* is the stoichiometry of each sublattice *s* and the *y* terms are site fractions. The  $G_{ij}^{\Theta}$  terms are the Gibbs energies of formation of the 'virtual' compounds associated with the phase, where each sublattice is occupied completely by a single component. The excess Gibbs energy related to mixing on the different sublattices is given by:

$$G_{\rm m}^{\rm E} = \sum_{i_1} \sum_{i_2} \sum_{j} y_{i_1}^1 y_{i_2}^1 y_{j_2}^2 L_{i_1,i_2:j} + \sum_{i} \sum_{j_1} \sum_{j_2} y_{i_1}^1 y_{j_1}^2 y_{j_2}^2 L_{i:j_1,j_2} + \sum_{i_1} \sum_{i_2} \sum_{j_1} \sum_{j_2} y_{i_1}^1 y_{i_2}^1 y_{j_1}^2 y_{j_2}^2 L_{i_1,i_2:j_1j_2}$$
(5)

Details of the modelling used for each of the individual phases are given in Table 3.

#### Table 3. Models and optimised parameters

Component Unary Data

Cr

```
G(\text{LIQUID},\text{Cr};0) = 15483.015 + 146.059775*T - 26.908*T \ln(T) + 1.89435E - 3*T^2 - 1.47721E - 6*T^3 + 139250/T + 1.47721E - 6*T^3 + 1.4772E - 
237.615E-23*T<sup>7</sup>
(298.15<T<2180K)
-16459.984+335.616316*T-50*T\ln(T)
(2180<T<6000K)
G(\text{BCC},\text{Cr:Va;0}) = -8856.94 + 157.48 \times T - 26.908 \times T \ln(T) + 1.89435 \text{E} - 3 \times T^2 - 1.47721 \text{E} - 6 \times T^3 + 139250/T
(298.15<T<2180K)
-34869.344+344.18*T-50*Tln(T)-2885.26E29/T<sup>9</sup>
(2180<T<6000K)
TC(BCC,Cr:Va;0) = -311.5, BMAGN(BCC_A2,CR:VA;0) = -0.008
(298.15<T<6000K)
G(\text{FCC,Cr:Va;0}) = -1572.94 + 157.643 * T - 26.908 * T \ln(T) + 1.89435 \text{E} - 3 * T^2 - 1.47721 \text{E} - 6 * T^3 + 139250/T
(298.15<T<2180K)
-27585.344+344.343*T-50*T\ln(T)-2885.26E29/T^9
(2180<T<6000K)
TC(FCC,Cr:Va;0) = -1109, BMAGN(FCC_A1,CR:VA;0) -2.46,
(298.15<T<6000K)
G(\text{HCP,Cr:Va;0}) = -4418.94 + 157.48 * T - 26.908 * T \ln(T) + 1.89435 \text{E} - 3 * T^2 - 1.47721 \text{E} - 6 * T^3 + 139250/T
(298.15<T<2180K)
-30431.344+344.18*T-50*T\ln(T)-2885.26E29/T^{9}
(2180<T<6000K)
TC(HCP,Cr:Va;0) = -1109, BMAGN(HCP_A3,CR:VA;0) = -2.46
(298.15<T<6000K)
Pt
G(\text{LIQUID},\text{Pt};0) = 12518.385 + 115.113092*T - 24.5526*T \ln(T) - 2.48297 \text{E} - 3*T^2 - 0.020138 \text{E} - 6*T^3 + 7974/T
(298.15<T<600K)
19023.491+32.94182*T-12.3403769*T\ln(T)-11.551507E-3*T^{2}+0.931516E-6*T^{3}-601426/T
(600<T<2041.5K)
1404.468+205.858962*T-36.5*Tln(T)
(2041.5<T<4000K)
G(\text{BCC},\text{Pt:Va;0}) = 7404.369 + 121.988275 * T - 24.5526 * T \ln(T) - 2.48297 \text{E} - 3 * T^2 - 0.020138 \text{E} - 6 * T^3 + 7974/T
(298.15<T<1300K)
5746.826+159.129615*T-30.2527*Tln(T)+2.321665E-3*T<sup>2</sup>-0.656946E-6*T<sup>3</sup> -272106/T
(298.15<T<2041.5K)
-207048.216+1016.95892*T-136.192996*T \ln(T)+20.454938 E-3*T^2-0.759259 E-6*T^3+7153902/T
(2041.5<T<4000K)
G(\text{FCC},\text{Pt:Va;0}) = -7595.631 + 124.388275 * T - 24.5526 * T \ln(T) - 2.48297 \text{E} - 3 * T^2 - 0.020138 \text{E} - 6 * T^3 + 7974/T
(298.15<T<1300K)
```

 $-9253.174 + 161.529615 * T - 30.2527 * T \ln(T) + 2.321665 \text{E} - 3 * T^2 - 0.656946 \text{E} - 6 * T^3 - 272106/T$ 

602

Watson A. et al., Development of a database for the prediction of phases in Pt-based superalloys...

(1300 < K < 2041.5K)  $-222048.216 + 1019.35892 * T - 136.192996 * T \ln(T) + 20.454938E - 3 * T^{2} - 0.759259E - 6 * T^{3} + 71539020/T$  (2041.5 < T < 4000K)

$$\begin{split} G(\text{HCP,Pt:Va;0}) &= -5095.631 + 124.488275*T - 24.5526*T \ln(T) - 2.48297\text{E} - 3*T^2 - 0.020138\text{E} - 6*T^3 + 7974/T \\ (298.15 < T < 1300\text{K}) \\ &- 6753.174 + 161.629615*T - 30.2527*T \ln(T) + 2.321665\text{E} - 3*T^2 - 0.656946\text{E} - 6*T^3 - 272106/T \\ (1300 < T < 2041.5\text{K}) \\ &- 219548.216 + 1019.45892*T - 136.192996*T \ln(T) + 20.454938\text{E} - 3*T^2 - 0.759259\text{E} - 6*T^3 + 71539020/T \\ (2041.5 < T < 4000\text{K}) \end{split}$$

Ru

$$\begin{split} G(\text{LIQUID}, \text{Ru}; 0) &= 19918.743 + 119.467485 * T - 22.9143287 * T \ln(T) - 4.062566\text{E} - 3 * T^2 + 0.17641\text{E} - 6 * T^3 + 56377/T \\ (298.15 < T < 800\text{K}) \\ &= 50827.232 - 179.818561 * T + 19.539341 * T \ln(T) - 26.524167\text{E} - 3 * T^2 + 1.667839\text{E} - 6 * T^3 - 3861125/T \\ (800 < T < 2607\text{K}) \\ &= -17161.807 + 349.673561 * T - 51.8816 * T \ln(T) \\ (2607 < T < 4500) \end{split}$$

$$\begin{split} G(\text{BCC}, \text{Ru:Va;0}) &= 18938.127 + 121.666233 * T - 22.9143287 * T \ln(T) - 4.062566\text{E} - 3 * T^2 + 0.17641\text{E} - 6 * T^3 + 56377/T \\ (298.15 < T < 1500\text{K}) \\ &- 32948.103 + 483.316214 * T - 72.3241219 * T \ln(T) + 18.726245\text{E} - 3 * T^2 - 1.952433\text{E} - 6 * T^3 + 11063885/T \\ (1500 < T < 2607\text{K}) \\ &- 38562273 + 168604.317 * T - 21329.705 * T \ln(T) + 5221.639\text{E} - 3 * T^2 - 240.245985\text{E} - 6 * T^3 + 130.829926\text{E}8/T \\ (2607 < T < 2740\text{K}) \\ &- 29268.304 + 358.282314 * T - 51.8816 * T \ln(T) \\ (2740 < T < 4500\text{K}) \end{split}$$

$$\begin{split} G(\text{FCC}, \text{Ru:Va;0}) &= 4938.127 + 125.466233*T - 22.9143287*T \ln(T) - 4.062566\text{E} - 3*T^2 + 0.17641\text{E} - 6*T^3 + 56377/T \\ (298.15 < T < 1500\text{K}) \\ &- 46948.103 + 487.116214*T - 72.3241219*T \ln(T) + 18.726245\text{E} - 3*T^2 - 1.952433\text{E} - 6*T^3 + 11063885/T \\ (1500 < T < 2607\text{K}) \\ &- 38576273 + 168608.117*T - 21329.705*T \ln(T) + 5221.639\text{E} - 3*T^2 - 240.245985\text{E} - 6*T^3 + 130.829926\text{E}8/T \\ (2607 < T < 2740\text{K}) \\ &- 43268.304 + 362.082314*T - 51.8816*T \ln(T) \\ (2740 < T < 4500\text{K}) \end{split}$$

```
\begin{split} G(\text{HCP}, \text{Ru:Va;0}) &= -7561.873 + 127.866233 * T - 22.9143287 * T \ln(T) - 4.062566E - 3 * T^2 + 0.17641E - 6 * T^3 + 56377/T \\ (298.15 < T < 1500 \text{K}) \\ &-59448.103 + 489.516214 * T - 72.3241219 * T \ln(T) + 18.726245E - 3 * T^2 - 1.952433E - 6 * T^3 + 11063885/T \\ (1500 < T < 2607 \text{K}) \\ &-38588773 + 168610.517 * T - 21329.705 * T \ln(T) + 5221.639E - 3 * T^2 - 240.245985E - 6 * T^3 + 130.829926E8/T \\ (2607 < T < 2740 \text{K}) \\ &-55768.304 + 364.482314 * T - 51.8816 * T \ln(T) \\ (2740 < T < 4500 \text{K}) \end{split}
```

(continued Table 3)

Phase	Constitution	Parameter	Value	Source
Liquid	(Cr,Pt,Ru)	$^{0}L(Cr,Pt)$	-135800	[6]
		$^{1}L(Cr,Pt)$	5500	[6]
		$^{0}L(Cr,Ru)$	-17386.332	This work
		$^{0}L(Pt,Ru)$	-28071.046 - 11.515654T	This work
		$^{1}L(\text{Pt,Ru})$	-11369.048	This work
bcc	(Cr,Pt,Ru):(Va) <sub>3</sub>	$^{0}L(Cr,Pt)$	-105000	[6]
		$^{0}L(Cr,Ru)$	-22426.461 + 1.950073T	This work
		$^{1}L(Cr,Ru)$	8866.523	This work
fcc	(Cr,Pt,Ru):(Va)	$^{0}L(Cr,Pt)$	-146232.35	[6]
		$^{1}L(Cr,Pt)$	3437.65	[6]
		$^{0}L(Cr,Ru)$	1988.662 - 2.83672T	This work
		$^{1}L(Cr,Ru)$	390.321	This work
		$^{0}L(Pt,Ru)$	-67966.086 + 0.455942T	This work
		$^{1}L(\text{Pt,Ru})$	-13113.006 + 7.827195T	This work
hcp	(Cr,Pt,Ru):(Va) <sub>0.5</sub>	$^{0}L(Cr,Pt)$	-137981 - 0.058413T	[6]
		$^{1}L(Cr,Pt)$	9551.99 – 0.001652 <i>T</i>	[6]
		$^{0}L(Cr,Ru)$	1988.662 - 2.83672T	This work
		$^{1}L(Cr,Ru)$	390.321	This work
		$^{0}L(Pt,Ru)$	-28869.113 - 7.889606T	This work
		$^{1}L(\text{Pt,Ru})$	-7333.888 + 0.682843T	This work
A15	(Cr,Pt,Ru) <sub>0.75</sub> :(Cr,Pt,Ru) <sub>0.25</sub>	<i>G</i> (A15,Cr:Cr)	15000 + <i>G</i> (bcc,Cr;0)	[6]
		<i>G</i> (A15,Pt:Pt)	10000 + G(fcc,Pt;0)	[6]
		<i>G</i> (A15,Ru:Ru)	25000 + <i>G</i> (hcp,Ru;0)	This work
		G(A15,Cr:Pt)	-28500 + 0.75G(bcc,Cr;0) + 0.25G(fcc,Pt;0)	[6]
		<i>G</i> (A15,Pt:Cr)	10000 + 0.75 <i>G</i> (fcc,Pt;0) + 0.25 <i>G</i> (bcc,Cr;0)	[6]
		<i>G</i> (A15,Cr,Ru)	2556.077 - 5.24126T + 0.75G(bcc,Cr;0) + 0.25G(hcc,Ru;0)	This work
		<i>G</i> (A15,Ru:Cr)	37443.92 + 5.24126 <i>T</i> + 0.75 <i>G</i> (hcp,Ru;0) + 0.25 <i>G</i> (bcc,Cr;0)	This work
		<i>L</i> (A15,Cr,Pt:Cr)	1250	[6]
		L(A15,Cr,Pt:Pt)	1250	[6]
		L(A15,Cr:Cr:Pt)	-25250	[6]
		L(A15,Pt:Cr:Pt)	1250	[6]
		<i>L</i> (A15,Cr:Pt,Ru)	-1.709 + 0.00479T	This work
		L(A15,Pt:Cr,Ru)	5450.82 + 6.65232T	This work

# 5.2. Cr-Pt

As indicated in the previous section, the optimisation by Ref. [6] was accepted in this work. The optimised phase diagram is given in Fig. 2 and the Gibbs energy parameters are given in Table 3. However, it was necessary to derive Gibbs energy parameters for the metastable hcp phase in the bi-

nary system. This was initially set to the same set of values as for the fcc phase but the parameters were later optimised using the ternary data (see below).

#### 5.3. Cr-Ru

Gibbs energy parameters for the bcc, hcp, sigma, and A15 phases were optimised using WinPhad together with the invariant temperatures and compositions given in Table 1, taken from Ref. [3]. The phase diagram calculated using Pandat is given in Fig. 6. The fit of the calculated phase diagram to the experimental invariants is very good, with only slight deviation occurring for the A15 phase. This is acceptable in this case as the experimental data for the stability of this phase have a degree of uncertainty. But more importantly, the model used is compatible with that used for the  $Cr_3Pt$  A15 phase.



Fig. 6. Assessed Cr-Ru phase diagram.

# 5.4. Pt-Ru

Optimisation of this system was particularly difficult in that there are very few experimental data. The equilibria involving the liquid phase are unknown and the nature of the invariant reaction is uncertain. Massalski [3] assumes a peritectic reaction takes place in this system, using experimental data from Ref. [22]. But, it was found that the most reasonable fit to the phase boundaries of the (Pt) + (Ru) two-phase field, where a few compositions had been measured, resulted in the appearance of a very shallow eutectic reaction. The phase diagram, optimised using WinPhad and calculated using Pandat, is given in Fig. 7. The optimised parameters are given in Table 3.



Fig. 7. Assessed Pt-Ru phase diagram.

#### 5.5. Cr-Pt-Ru ternary system

The thermodynamic description of the ternary system was optimised using the experimental data of Ref. [16] as this set of data seemed to be more complete and self-consistent. The assessment module of *MTDATA* was used to perform the optimisation. During the optimisation process it was found that it was necessary to adjust only the Gibbs energy description of the metastable hcp phase in the Cr-Pt binary in order to get a reasonable fit to the experimental phase diagram data for the fcc and hcp phase boundaries. No ternary interactions were required for these phases.

The experimental data for the A15 phase fitted reasonably well although this was a little improved by allowing the optimisation to give a Gibbs energy description for the metastable Pt<sub>3</sub>Ru A15 phase. The A15 phase extends from the Cr-Pt edge as required but too far into the ternary. Also, the A15 phase field is not wide enough as it extends into the ternary, which is probably due to the fact the phase is modelled with a very narrow homogeneity range in the Cr-Ru system. Improvement to the modelling of this phase in the binary system would undoubtedly improve the overall modelling of this phase, but this would require further experimental study of its stability range. The fit to the experimental bcc phase diagram data, however, is very good. The calculated

phase diagram for 1200°C, along with the experimental data is given in Fig. 8. The fit of the experimental data from Ref. [17] is not so good, particularly with respect to the hcp phase boundary. Again, this could be improved by a better description of the A15 phase. The calculated diagram for 1000°C is given in Fig. 9.



Fig. 8. Calculated isothermal section for the Cr-Pt-Ru system for 1200°C with experimental data from Ref. [16].



Fig. 9. Calculated isothermal section for the Cr-Pt-Ru system for 1000°C with experimental data from Ref. [17].

# 6. Discussion

It is interesting that a good fit to the fcc and hcp experimental data for 1200°C can be achieved just by adjusting the metastable hcp interactions in the Cr-Pt binary system. Only two fcc data points at this temperature do not fit the calculated phase boundary. Introducing a ternary interaction parameter for both the fcc and hcp phases can improve the fit to these data points, but bearing in mind that this applies to only two experimental data points, it is probably better to have a simpler description for the system as a whole. Most improvement to the calculated diagram would be achieved by improvement to the description of the A15 phase. Destabilising the Cr<sub>3</sub>Ru A15 phase in the Cr-Ru binary would have the effect of reducing the extension of the A15 phase into the ternary, which is desirable, but this would of course, have implications with respect to the Cr-Ru phase diagram. In any case, the Cr-Ru binary system in the stability region of the Cr<sub>3</sub>Ru A15 phase is still uncertain and should be investigated further in order that the binary system could be better described.

# 7. Conclusions

The Cr-Ru and Pt-Ru systems have been modelled using experimental phase diagram data available in the literature. The descriptions for these binary systems have been combined with that for the Cr-Pt system from Ref. [6] to calculate isothermal sections of the ternary system. It was found that a reasonable fit to the ternary experimental data available in the literature could be achieved by producing a suitable description for the metastable binary Cr-Pt hcp phase. Further work is required to improve the fit of experimental phase diagram data for the A15 phase.

# Acknowledgements

The authors would like to thank CompTherm LLC Wisconsin, USA, for the provision of the WinPhad and Pandat, and the NPL, Teddington, UK for the *MTDATA* software.

# References

- Wolff I.M. and Hill P.J., Platinum metals-based intermetallics for high temperature service, *Platinum Met. Rev.*, 2000, 44 (4): 158.
- [2] Schmid-Fetzer R., Andersson D., Chevalier P.Y., Eleno L., Fabrichnaya O., Kattner U.R., Sundman B., Wang C., Watson A., Zabdyr L., and Zinkevich M., Assessment techniques, database design and software facilities for thermodynamics and diffusion, *Calphad*, in press, 2006.
- [3] Massalski T.B., *Binary Alloy Phase Diagrams*, ASM, Metals Park, Ohio, 1990.
- [4] Müller L., Melting points of platinum alloys, *Ann. Phys.* (in German), 1930, 7 (1): 9.
- [5] Waterstrat R.M., The chromium-platinum constitution diagram, *Metall. Trans.*, 1973, **4** (6): 1585.
- [6] Oikawa K., Qin G.W., Ikeshoja T., Kitakami O., Shimada Y., Ishida K., and Fukamichi K., Thermodynamic calculations of phase equilibria of Co-Cr-Pt ternary system and magnetically induced phase separation in the FCC and HCP phases, *J. Magn. Magn. Mater.*, 2001, **236**: 220.
- [7] Süss R., Cornish L.A., and Witcomb M.J., Investigation of as-cast alloys in the Pt-Cr-Ru system, J. Alloys Compd., 2006, 416 (1-2): 80.
- [8] Süss R. and Cornish L.A., unpublished work, Mintek, 2005.
- [9] Nzula M. and Cornish L.A., Solidification and hardness studies in selected Cr-Ni-Pt alloys, [in] *Proc. Microsc. Soc. South. Afr.*, Kwa-Zulu Natal, South Africa, 2005, 25: 8.
- [10] Raub E. and Mahler W., Alloys of chromium with platinum, iridium, rhodium, and ruthenium, Z. *Met-allkde.*, 1955, 46: 210.
- [11] Greenfield P. and Beck P.A., Intermediate phases in binary systems of certain transition elements, *Trans.*

*AIME.*, 1956, **206**: 265.

- [12] Savitskii E.M., Terekhova V.F. and Birun N.A., *Russ. J. Inorg. Chem.*, 1961, 6 (8): 1002.
- [13] Shurin A.K. and Dmitrieva G.P., Sb. Nauchn. Rab. Inst. Metallofiz. Akad. Nauk. Ukr. SSR., 1964, (18): 170.
- [14] Wopersnow W. and Raub C.J., *Metall. Berlin*, 1979, 33 (12): 1261.
- [15] Waterstrat R.M., Analysis of selected alloys in the systems Cr-Pd, Cr-Ru, V-Pd, and Ta-Pt, J. Less Common Met., 1981, 80: 31.
- [16] Zhao J.C., Reliability of the diffusion-multiple approach for phase diagram mapping, *J. Mater. Sci.*, 2004, **39**: 3913.
- [17] Süss R., Cornish L.A., and Witcomb M.J., Investigation of isothermal sections at 1000°C and 600°C in the Pt-Cr-Ru system, to be submitted to *J. Alloys Compd.*
- [18] Chen S.L., Daniel S., Zhang F., Chang Y.A., Yan X.Y., Xie F.Y., Schmid-Fetzer R., and Oates W.A., The PANDAT software package and its applications, *Calphad*, 2002, **26** (2): 175.
- [19] Davies R.H., AT Dinsdale, JA Gisby, JAJ Robinson and SM Martin, "MTDATA - thermodynamic and phase equilibrium software from the national physical laboratory", *Calphad*, 2002, **26** (2): 229.
- [20] Redlich O. and Kister A.T., *Ind. Eng. Chem.*, 1948, (2): 345.
- [21] Muggianu Y.M., Gambino M., Bros J.P., Enthalpies of formation of liquid bismuth-gallium-tin alloys at 723 K. Choice of an analytical representation of integral and partial thermodynamic functions of mixing, *J. Chim. Phys. Phys.-Chim. Biol.* (France), 1975, **72** (1): 83.
- [22] Hutchinson J.M., Solubility relationships in the Ru-Pt System, *Platinum Met. Rev.*, 1972, 16: 88.