

# Building a Thermodynamic Database for Platinum-Based Superalloys: Part II

## USE OF MODELS REQUIRING FEWER PARAMETERS

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*Work is being done at Mintek, the University of Leeds and the University of Bayreuth to build up a platinum-aluminium-chromium-ruthenium (Pt-Al-Cr-Ru) database for the prediction of phase diagrams for further alloy development by obtaining good thermodynamic descriptions of all of the possible phases in the system. Binary descriptions were combined, allowing extrapolation into the ternary systems, and experimental phase equilibrium data were compared with calculated results. Very good agreement was obtained for the Pt-Al-Ru system, as described in Part I of this series of papers (1). This paper (Part II) addresses the Pt-Cr-Ru system, with equally encouraging results. The final paper in the series (Part III, to be published in a future issue of Platinum Metals Review) will deal with work on the platinum-aluminium-chromium-nickel (Pt-Al-Cr-Ni) database at the University of Bayreuth. The Pt-Al-Cr-Ru and Pt-Al-Cr-Ni databases will eventually be merged.*

Work has been ongoing in building a thermodynamic database for the prediction of phase equilibria in Pt-based superalloys (1–5). 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. Currently, the database contains the elements platinum, aluminium, chromium and ruthenium. This paper is a revised account of work presented at the conference: Southern African Institute of Mining and Metallurgy 'Platinum Surges Ahead' at Sun City, South Africa, from 8th to 12th October 2006 (5).

Part I, describing initial results for the Pt-Al-Ru system from the compound energy formalism model, was published in the July 2007 issue of *Platinum Metals Review* (1).

For the Ru-Al system, very good agreement has been obtained between experimental phase equilibrium data and calculations based on a version of the compound energy formalism model (1). However, for the other binary and ternary systems, there are insufficient data to obtain good results by this method, since more phases are represented in each system. This paper (Part II) describes the different approach which was needed, with simpler representation to allow for sparse data.

Part III will complete the series by describing work at the University of Bayreuth on the platinum-aluminium-chromium-nickel (Pt-Al-Cr-Ni) database, which is eventually to be merged with the Pt-Al-Cr-Ru database.

## Simple Phase Representation: General Considerations

Concerning the (Pt) and Pt<sub>3</sub>Al phases, there is disagreement on which particular model should be used. These phases are similar to (Ni) and Ni<sub>3</sub>Al respectively. (Here, (Pt) and (Ni) denote combinations of four atoms of the elements in the four-compound sublattice formalism (CSF); arithmetically, Pt<sub>4</sub> and Ni<sub>4</sub> respectively.) One school of thought states that as all four phases are based on the f.c.c. lattice, then Ni<sub>3</sub>Al, which can be viewed as an ordered f.c.c. phase, should be included as the f.c.c. phase in modelling (Pt) and Pt<sub>3</sub>Al. On the other hand, another school of thought stipulates that, since (Pt) and Pt<sub>3</sub>Al solidify separately, they should be modelled separately. The second school of thought would allow for Pt<sub>3</sub>Cr and PtCr to be modelled as part of (Pt), since they form by ordering within the (Pt) phase field at lower temperatures. This might be considered as anomalous in that Pt<sub>3</sub>Al would not be incorporated in the f.c.c. model, whereas Pt<sub>3</sub>Cr would be. However, given that phases should be modelled in the same way only if they are likely to be contiguous, this would not be a problem unless Pt<sub>3</sub>Al is likely to be contiguous with Pt<sub>3</sub>Cr. At the moment, this is not likely. A similar argument can be made for Pt<sub>3</sub>Al, which just like Ni<sub>3</sub>Al, solidifies as a separate phase from (Pt), and is not formed within.

Another source of contention is that in the model being developed here, many parameters are needed to describe the phase. For the Ni-Al system, it could be argued that there are many data points and that the large number of parameters is justified. However, for Pt-Al, not only are there fewer data points, but there is also much greater uncertainty in the binary phase diagram regarding the reaction temperatures involving Pt<sub>3</sub>Al, and even the type of ordering. Thus, a much simpler model is prescribed for the Pt<sub>3</sub>Al phase, both because of a dearth of data (as compared with

Ni<sub>3</sub>Al), and also because the Pt<sub>3</sub>Al and (Pt) phases solidify separately. All the information regarding ordering needs to be gathered before any incorporation into modelling is attempted. However, it must be noted that in the Dupin database (6), the Ni<sub>3</sub>Al phase is modelled as ordered f.c.c., even though it solidifies separately. The latest database from Dupin (6) was used to draw the Ni-Al phase diagram, and the  $\gamma/\gamma'$  boundary did not agree well with that in the experimental phase diagram, so it is questionable whether Dupin's complex modelling is really worthwhile.

It is best to adopt the most appropriate model for each phase in the system on the basis of its crystal structure and the available experimental data. Simple substitutional solid solutions can be modelled with two sublattices; one sublattice of sites of mixed occupancy (by the substituting elements) and one of interstitial sites. Ordered phases have a more complex crystallography in that atoms have preferential site occupancy. These phases are modelled with a more complex sublattice model comprising multiple sublattices with mixing of a number of different elements on each, depending on the crystallography. Although a multiple sublattice model is more complex than a simple two-sublattice model, it is easier to use the former to describe phases with a limited homogeneity range. In the extreme case, a stoichiometric phase is thus modelled with a single component on each sublattice. It is often useful to model an ordered phase along with its disordered 'parent' phase, for example b.c.c.\_B2 and b.c.c.\_A2, or f.c.c.\_L12 and f.c.c.\_A1, with a single Gibbs energy description enabling the ordering transition to be modelled. This modelling is quite complex, and whether such complications should be included depends on the application of the database.

There are databases being developed without such complex modelling and these are very useful. One example is the COST 531 lead-free solders database (7), comprising assessed thermodynamic data for binary and ternary systems based on eleven elements associated with lead-free solder materials. Thus, it might be questioned whether the current pgm database should be concerned with order/disorder reactions. The answer should be positive, of

course, because the ordered Pt<sub>3</sub>Al phase, which is an ordered f.c.c. phase, is the basis of the alloys. However, if there are too few experimental data available, modelling the Pt<sub>3</sub>Al and f.c.c.\_Al phase with a single Gibbs energy description will be difficult. If a model requiring many parameters is optimised with few data points, the parameters themselves become meaningless and the results are highly unlikely to be representative. Thus, in the current work, it was decided to model such ordered phases separately and then extend the database subsequently if there is both sufficient need and the experimental data become available. In this way, the database grows with the available experimental data, and at any time, the database is the optimum that can be achieved. Currently, the database is being developed so that the phase equilibria between the phases on solidification can be derived. As more work is done on developing the alloys for application, the order/disorder reactions will become increasingly important, especially for the Pt<sub>3</sub>Al phase. A combination of Thermo-Calc<sup>TM</sup> (8), Pandat (9) and MTDATA (10) software was used for the present work.

### Chromium-Platinum

Until experimental results show otherwise, the assessment of Oikawa *et al.* (11) will be used, extrapolated into the ternary, and will then be reoptimised with experimental values from the Pt-Cr-Ru system. The assessment of Oikawa *et al.* (11)

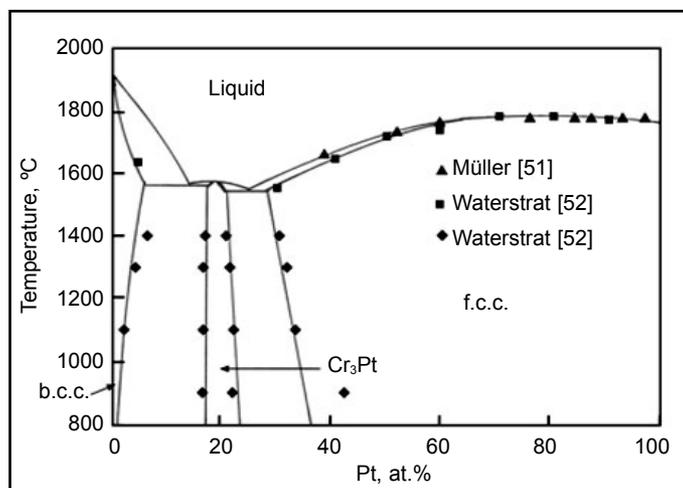
is shown in Figure 1. However, it was necessary to derive Gibbs energy parameters for the metastable h.c.p. phase in the binary system. The metastable phase was initially allocated the same set of Gibbs energy values as for the f.c.c. phase, but the parameters were optimised using the ternary data (described below).

### Platinum-Ruthenium

It was initially thought that the description of Pt-Ru in the Spencer database (12) version of Pt-Ru would be the same as that in the Scientific Group Thermodata Europe (SGTE) database (13). However, this was not so. The phase diagram from Spencer is a eutectic, with a maximum in (Pt) and ~10°C between the maximum and eutectic temperature, whereas that from SGTE is peritectic, which is consistent with available literature (14, 15) and experimental work at Mintek.

Optimising with data from Hutchinson (14) gave a good fit and convincing coefficients. While plotting the free energy curves demonstrated that Ru had an unusual energy curve, it would be unwise to change this feature, because it originated from the Ru unary data, is set across the entire database, and represents a best-fit value for many systems. One solution to this anomaly would be to add an interaction parameter, but it must be remembered that there are too few data available. However, it was found that the most reasonable fit to the phase boundaries of the (Pt) + (Ru) two-phase field,

Fig. 1 Cr-Pt phase diagram calculated by Oikawa *et al.* (11) (Courtesy of Elsevier Science; reference numbers are as cited in Reference (11))



where a few compositions had been measured experimentally, resulted in the appearance of a very shallow eutectic reaction. The phase diagram, optimised using WinPhaD and calculated using Pandat, is given in Figure 2, and may be compared with the experimental diagram in Figure 3.

## Chromium-Ruthenium

This system contains two intermetallic compounds:  $\text{Cr}_2\text{Ru}$  ( $\sigma$ ) and  $\text{Cr}_3\text{Ru}$ . The accepted models

have three sublattices, so this format would be followed for the Cr-Ru system despite the fact that, especially given such limited data, it would be difficult to have mixing on all three sublattices – many end-members would be needed. It was therefore decided that Cr only would be located on one sublattice, and the remaining two would have mixing; this is normal practice. The current model of choice for the  $\sigma$  phase is 10:16:4 (where the notation shows the numbers of atoms on each of the three

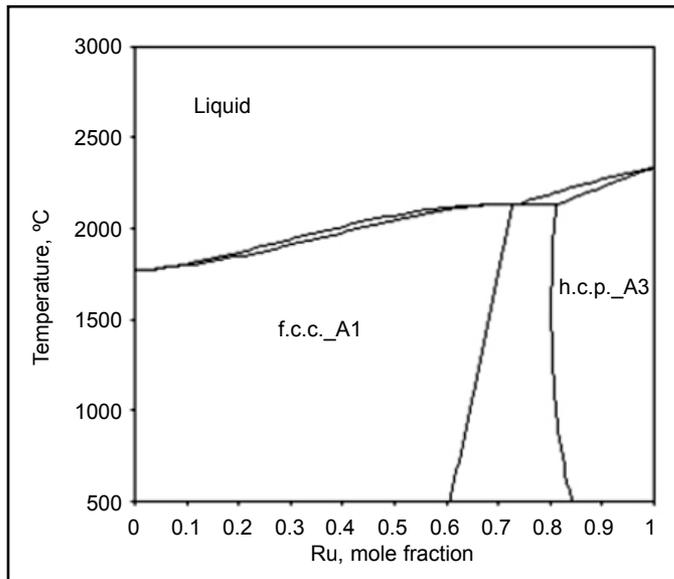


Fig. 2 Pt-Ru phase diagram: Best calculated diagram to date

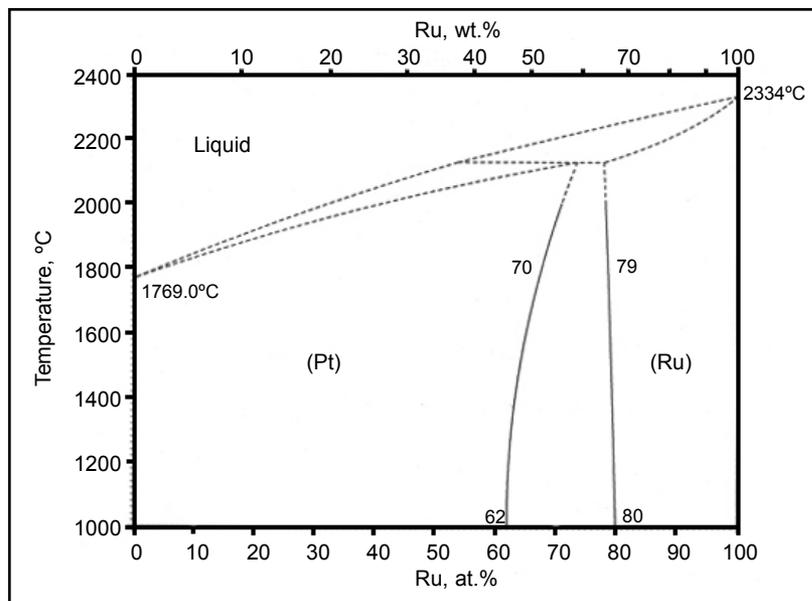


Fig. 3 Pt-Ru phase diagram: Experimental from (15) (Courtesy of ASM International)

sublattices; the previous model was 8:18:4). The previous model featured in the Glatzel assessment (16), although with mixing on all three sublattices. Elements are usually mixed on many sublattices only where there is a very wide range of phase stability. In this case, there is a narrow phase stability range, so the degree of mixing needs to be reduced.

The approach used was to build up the system with the most simple phase diagram descriptions possible: thus  $\text{Cr}_2\text{Ru}$  ( $\sigma$ ) and  $\text{Cr}_3\text{Ru}$  would be line compounds. The Ru and Cr unary data were derived from Kaufman (17). Since Kaufman's (17) reported reaction temperatures involving  $\text{Cr}_2\text{Ru}$  ( $\sigma$ ) and  $\text{Cr}_3\text{Ru}$  were suspiciously convenient:  $\sim 750$ ,  $\sim 800$  and  $\sim 1000^\circ\text{C}$ , it was realised that there were problems with the system, and the rounded data are the best that were obtained from the literature (15). These had to be used, as there are no other data available. Attempts to measure the reaction temperatures by differential thermal analysis (DTA) were inconclusive (18). The phase diagram gave a very good fit, as shown in Figure 4, compared with the experimental diagram (Figure 5) (15).

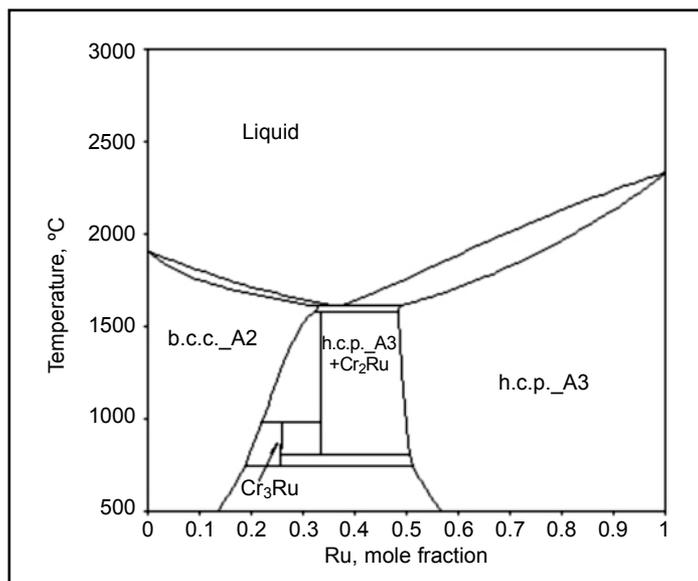
### Platinum-Chromium-Ruthenium

Experimental results of the A15  $\text{Cr}_3\text{Ru}$  and  $\text{Cr}_3\text{Pt}$  phases were not conclusive in showing whether the phases are contiguous, despite two

more samples of intermediate compositions between  $\text{Cr}_3\text{Ru}$  and  $\text{Cr}_3\text{Pt}$  being prepared at Mintek. These samples were annealed at  $\sim 850^\circ\text{C}$ , because if the phases are contiguous, they should meet at this temperature for the sample compositions chosen. Depending on how the phases extend into the ternary, the sublattice on which substitution is occurring can be determined. For  $\text{Cr}_3\text{Ru}$ , if Ru is constant, then Pt substitutes for Cr; and for  $\text{Cr}_3\text{Pt}$ , if Cr is constant, Ru substitutes for Pt. It must, however, be remembered that the original samples were not in equilibrium, and the latest samples were annealed for longer, to promote equilibrium.

It should be noted that Waterstrat's  $\text{Cr}_3\text{Pt}$  phase (19) was more narrow (almost stoichiometric) and did not decompose at lower temperature (which is what was calculated at one stage in the present work). A likely model for this case (19) would be Cr on one sublattice and Pt + Cr on the other, but this depends on the atomic sizes. These can be measured in different ways (giving different results) and the most appropriate method should be used for the mode of bonding of the particular atom. Pt and Ru show similar covalent radii. This being so, they could sit on the same sublattice. However, it is recommended that other A15 phases be researched to see how they would best be modelled, especially for the composition

Fig. 4 Cr-Ru phase diagram: Best calculated diagram to date



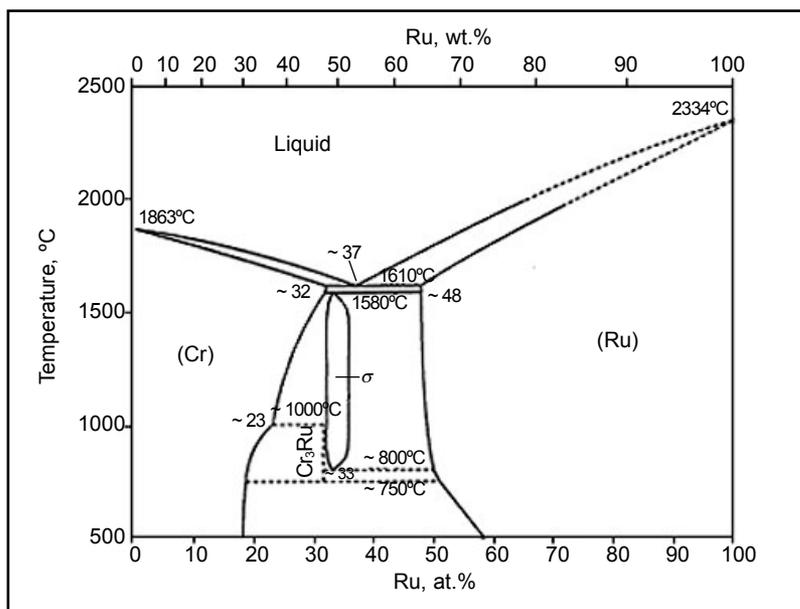


Fig. 5 Cr-Ru phase diagram: Experimental from (15) (Courtesy of ASM International)

ranges (i.e. the spread on both sides from mole fraction  $X = 0.25$ ). For the representation of  $\text{Cr}_3\text{Pt}$  within the ternary (and higher-order phase diagrams), the model would be much simpler (and have fewer end members) if the lattice components could be described as (Cr, Cr) (Cr, Pt, Ru).

To model the ternary system, an interaction parameter, added to increase the phase extensions into the ternary, was determined for the h.c.p. phase. The projected liquidus surface, shown in Figure 6, is an improvement on the assessment by Glatzel *et al.* (16). However, the invariant reactions are still incorrect, because Figure 6 shows the liquidus surfaces for (Ru) and  $\text{Cr}_3\text{Pt}$  abutting, by contrast with the experimental results in Figure 7. Those for (Cr) and (Pt) should in fact abut, because of the (Pt) + (Cr) eutectic observed in the ternary samples (20, 21). However, the junction between the incorrect surfaces of primary solidification is smaller than was calculated previously (16), and agrees more closely with the experimental results.

The thermodynamic description of the ternary system was optimised using the experimental data of Zhao (22), as this set of data seemed to be more complete and self-consistent, and Mintek's data (20, 23) were affected by coring. 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 h.c.p. phase in the Cr-Pt binary in order to get a reasonable fit to the experimental phase diagram data for the f.c.c. and h.c.p. phase boundaries. No ternary interactions were required for these phases (24).

The experimental data for the A15 phase fitted reasonably well, although the fit was little improved by allowing the optimisation to give a Gibbs energy description for the metastable  $\text{Pt}_3\text{Ru}$  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. This feature is probably due to the fact that the phase is modelled with a very narrow homogeneity range in the Cr-Ru system. Better modelling of the A15 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 b.c.c. phase diagram data is, however, very good. The calculated phase diagram for 1200°C, showing the experimental data, is given in Figure 8. The fit with the experimental data from Süss *et al.* (23) is not so good, particularly with respect to the (Ru) h.c.p. phase boundary, but this could be due to coring effects. Again, this could be improved by a better description of the A15 phase.

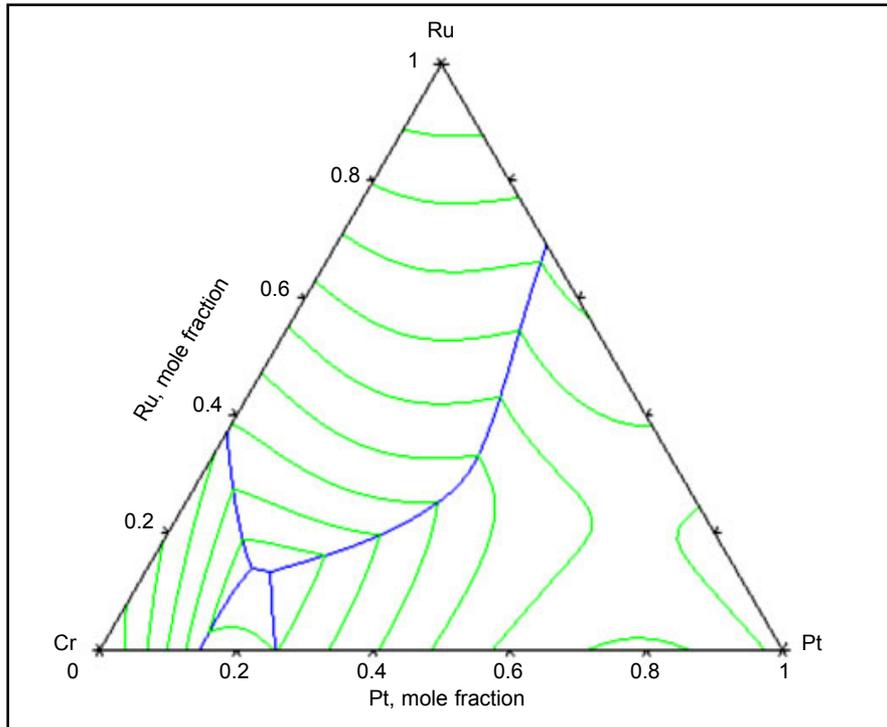


Fig. 6 Liquidus surface for the Pt-Cr-Ru system: Best calculated surface to date

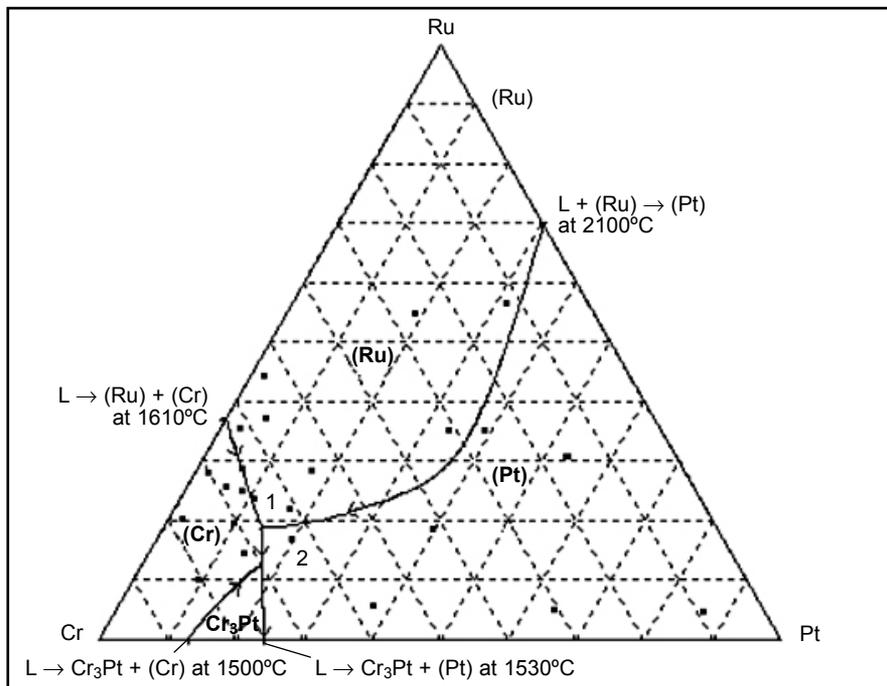


Fig. 7 Liquidus surface for the Pt-Cr-Ru system: Experimental from (20, 21) (Courtesy of Elsevier Science and the African Materials Research Society). Reaction 1:  $L + (Ru) \leftrightarrow (Pt) + (Cr)$ ; Reaction 2:  $L + (Cr) \leftrightarrow (Pt) + Cr_3Pt$

The calculated phase diagram for 1000°C is given in Figure 9.

## Conclusion

The latest developments to the Pt-Al-Cr-Ru database have improved the agreement with the experimental phase diagrams, and especially with diffusion data. The models of the f.c.c., Cr<sub>3</sub>Ru and Cr<sub>2</sub>Ru ( $\sigma$ ) phases were changed, and the new models were selected so that fewer parameters were necessary. However, the order/disorder reactions of the f.c.c. phases have yet to be modelled successfully, and before this can be realised more experimental data are needed. The A15 phase needs to be modelled in order to produce a wider phase range within the ternary. Once again, more experimental data are needed to confirm whether the A15 phases in the Cr-Pt and Cr-Ru systems are contiguous. More samples between the two binary phases had been manufactured, annealed at intermediate temperatures and analysed, but the results were not conclusive. Thus, future work on the

database can only be undertaken once more experimental data have been acquired.

Work is in hand at the University of Bayreuth on the platinum-aluminium-chromium-nickel (Pt-Al-Cr-Ni) database, which is eventually to be merged with the Pt-Al-Cr-Ru database. Part III of this series of papers, to be published in a future issue of *Platinum Metals Review*, will describe this work.

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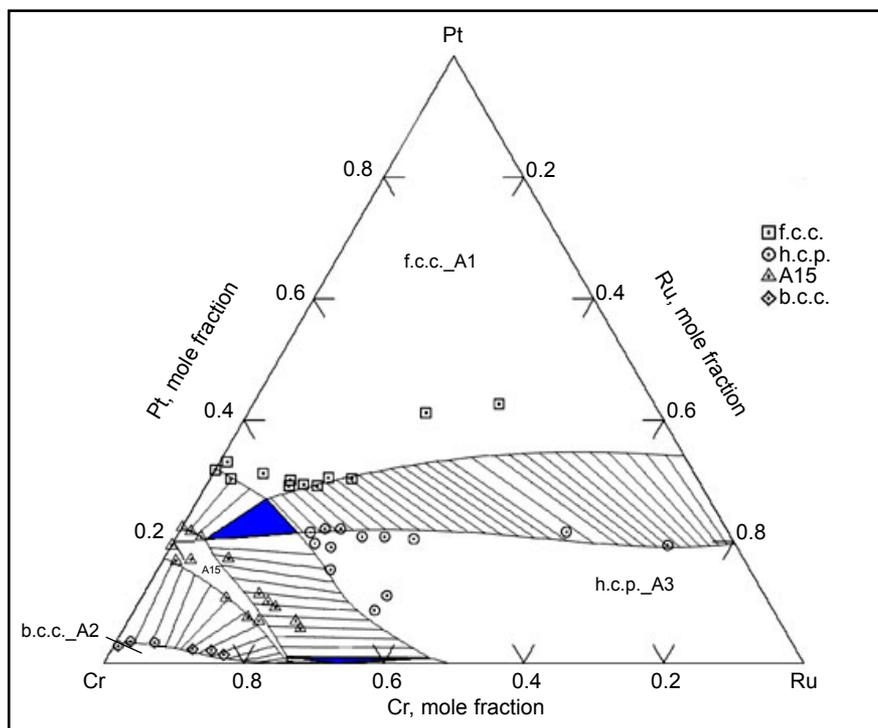


Fig. 8 Calculated isothermal section for the Pt-Cr-Ru system for 1200°C with experimental data from Zhao (22) (Courtesy of Springer)

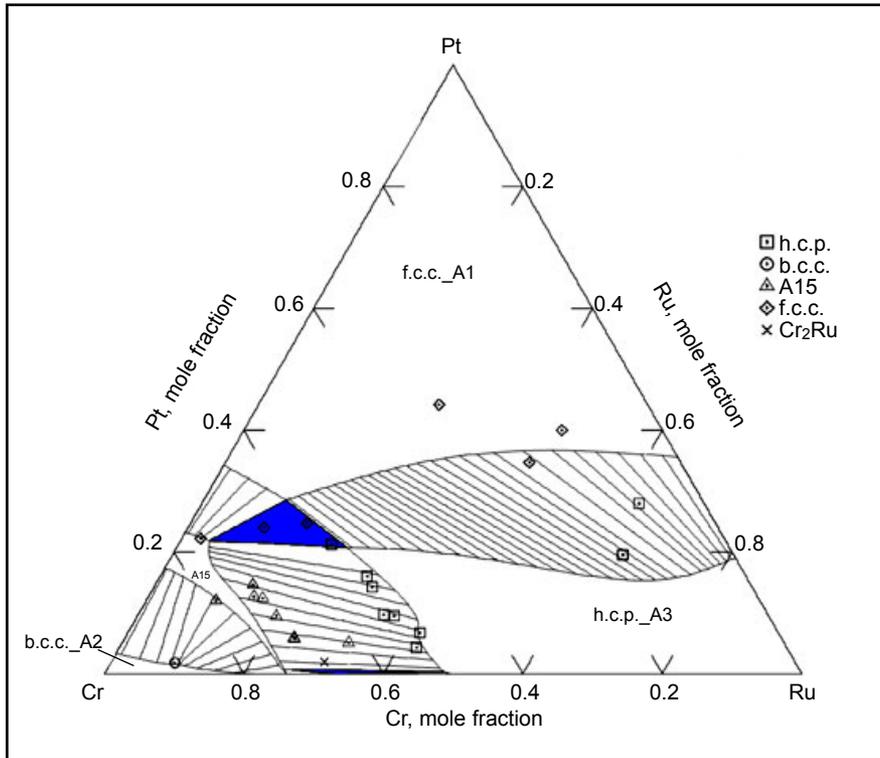


Fig. 9 Calculated isothermal section for the Pt-Cr-Ru system for 1000°C with experimental data from Süss et al. (23) (Courtesy of Elsevier Science)

provision of the WinPhaD, Pandat and MTDATA software. This paper is published with the permission of Mintek and the Southern African Institute of Mining and Metallurgy.

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