Building a Thermodynamic Database for Platinum-Based Superalloys: Part I

INTRODUCTION, AND INITIAL RESULTS FROM THE COMPOUND ENERGY FORMALISM MODEL

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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. The available databases do not cover all of the phases, and these had to be gleaned from literature, or modelled using experimental data. Similarly, not all of the experimental data were known, and where there were gaps or inconsistencies, experiments had to be undertaken. A preliminary version of the database was constructed from assessed thermodynamic data-sets for the binary systems only. The 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 and Pt-Cr-Ru systems, which was encouraging and confirmed that the higher-order systems could be calculated from the binary systems with confidence. Since some of the phase models in earlier databases were different, these phases had to be remodelled. However, more work is ongoing for information concerning the ternary phases present in the Al-Cr-Ru, Pt-Al-Ru (two ternary compounds in each) and Pt-Al-Cr (possibly more than three ternary compounds) systems. Later in the work, problems with the thermodynamic descriptions of the Cr-Ru and Pt-Cr binary systems were found, and a programme of experimental work to overcome these has been devised, and is being undertaken.

Work has been ongoing in building a thermodynamic database for the prediction of phase equilibria in Pt-based superalloys (1–4). 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
Ever since the possibility of basing a new series of alloys on platinum was seen (1), work has been ongoing at Mintek, Fachhochschule Jena and Bayreuth University, Germany, with input from the National Institute for Materials Science (NIMS), Japan. Experimental work in this field is time-consuming and very expensive in terms of equipment, materials and expertise. A number of important commercial alloy systems, such as steels, nickel-based alloys, and aluminium alloys now have thermodynamic databases which have been derived from copious experimental results published by experts. These databases can be used with appropriate software to calculate phase diagrams, phase proportion diagrams, and Pourbaix diagrams. They can be used instead of experimentation, saving both time and money. A similar database is being derived within this programme, so that it will facilitate further alloy development, and also be a tool to help designers to select alloy compositions and conditions in the future. However, steels, nickel-based and aluminium alloys have been used extensively, and there are more data and accepted phase diagrams for these systems than for Pt alloys. As inputs to the Pt-based database, there are fewer commercial alloys, experimental data, and very few accepted ternary systems. There are problems even with some of the binary systems. Thus, part of this work included the study of phase diagrams to address the lack of data, and to use these data to compile a thermodynamic database. Since the basis of the alloys is the Pt₈₄:Al₁₁:Cr₃:Ru₂ alloy, the thermodynamic database will be built on the Pt-Al-Cr-Ru system. The Scientific Group Thermodata Europe (SGTE) database (5) includes all the elements and some of the most commonly used phases, i.e. those that are industrially important, but contains few of the required Pt phases. Additionally, the ruthenium data have been updated to capture Ansara’s modification, to obtain a better estimate of the calculated melting temperature for (hypothetical) b.c.c.-Ru (6) than hitherto. Although there is a database for precious metals (7) it is not sufficiently complete for the purposes of this investigation, and does not contain all the elements of interest to this study, or all the phases. Additionally, not all the phase descriptions necessary are present in Spencer’s database. The Al-Cr system has also been independently assessed (8), although some of the phases might ultimately be modelled a different way by this group.

The phase diagram programs (e.g. Thermo-Calc™, MTDATA and Pandat) comprise the software itself, accessed in modules through a main interface, and a series of databases where the structural and thermodynamic data are stored. In these databases, each phase is described by a series of parameters. The SGTE database covers the phases of only the most common and well known systems, and all the stable elements (5). The intermetallic phases in the Al-Ru and Pt-Al systems are not included in the SGTE database. Providing that the elements are available in a database (and all of the stable elements are in the SGTE database, or other available databases), a phase diagram can be calculated and drawn. However, if there is no description for a particular phase, then the calculated phase diagram cannot include it. A given database can be modified to include new phases, or run in conjunction with another database. The aim of this programme is to develop a database specifically for the Pt-rich alloys in this investigation. Prior to building a database, it must be known which phases need descriptions. Information on the elements, and on any phase that is already included in the SGTE database (5), can be accessed from that database. For phases that are not represented by the SGTE database, a number of factors must be taken into consideration. Firstly, the structure of the phase has to be decided, including the number of lattice sites for the atoms, and which particular atoms fit on the sites. Each phase is modelled with sublattices, and each sublattice usually corresponds with a type of atom position. Elements allowed in a particular sublattice are those actually found in those positions by crystallographic measurement. This information is usually derived from X-ray diffraction (XRD) structural information and composition ranges,
and is usually made to be as simple as possible. Next, some values have to be obtained for the interaction parameters. Initial values may be guessed, or the parameters set to zero, and the user can decide which parameter can be varied during optimisation. In preparing for optimisation, experimental data are compared against the thermodynamic description, which is adjusted to best fit the experimental data. A ‘pop’ file is created which contains the experimental data (these can include phase compositions in equilibrium with each other at known temperatures, reaction information, enthalpies, etc.). Then optimisation can be conducted. Thermo-Calc™ uses the information in the pop file and, through iteration, calculates the parameters required (those that were set to be varied) to best fit the data in the pop file. The result of this process is the incorporation of new phases, which now have parameters that can be used to calculate a phase diagram that agrees with the input data.

Optimisation is the iterative process in which selected expressions of the thermodynamic descriptions are allowed to vary so that agreement with the experimental results is improved. The optimisation was carried out with the PARROT module (for the assessment of experimental data, and establishment of thermodynamic coefficients) (9) of the Thermo-Calc™ software (10). With this module, the Gibbs energy functions can be derived by a least-squares fit to experimental data. Different types of experimental data can be used, with weightings assigned on the basis of the uncertainties associated with the original data. Once calculated phase diagrams that agree with the experimental data are obtained, and the thermodynamic descriptions have been rationalised, the base systems will be complete. Selected important binaries were optimised first, for example, Al-Ru (11) and Al-Pt (12). More work has to be carried out on the Al-Pt system because there is no description for the two major Pt₃Al phases. Since these phases are crucial to the programme, they have to be modelled satisfactorily, before incorporation into the main database. Once each binary system has been modelled satisfactorily, it can be added into the ternary systems, after which each ternary system must be optimised individually. This is done using the experimental data, either drawn from the literature, or, as was mostly the case, derived experimentally within the programme at the University of the Witwatersrand and Mintek (for Al-Cr-Ru (13, 14), Pt-Cr-Ru (15, 16), Pt-Al-Cr (17, 18) and Pt-Al-Ru (19)) or the CSIR and Mintek (for Pt-Al-Ru (20)). Only once the ternaries have been finalised can they be combined for the Pt-Al-Cr-Ru quaternary. The Thermo-Calc™ database will then be optimised against some quaternary alloys that have already been made for the alloy development work (2–4).

Once this stage is complete, then the other small additions, to improve the properties (as in nickel-based superalloys), can be included in the optimisation. It is envisaged that the very final stage will be focused on the optimisation of only the important phases: at least the cubic and tetragonal structures of ~ Pt₃Al, (Pt), ~ Pt₂Al and (Ru). Here, (Pt) and (Ru) denote combinations of four atoms of the elements in the four-compound sublattice formalism (4CSF); arithmetically, Pt₄ and Ru₄, respectively.

The Pt-Al-Cr-Ru system is optimised by studying the four-component ternary systems. The reason for undertaking an optimisation of whole ternaries rather than portions of them is that there are very few data available for the system, and any thermodynamic model needs to be valid over the complete range of compositions in the base system before the minor components can be added. If only a small region is to be optimised (e.g. the region between the (Pt) and Pt₃Al phases only), then it is likely that although the model would be sufficiently good locally, the fit would either be very erratic or the calculations would not be capable of converging when new elements were added, or other elements added beyond their original compositions. (This phenomenon is well known for Thermo-Calc™ and has been experienced at Mintek for copper additions in duplex stainless steels (21).) Thus, the ternary systems for the Pt-Al-Cr-Ru quaternary will be studied in full to provide a sound basis for the computer database. The Pt-Al-Cr-Ru system is shown schematically in Figure 1.
Using the Compound Energy Formalism Model

At the beginning of the programme, it was assumed that the six binary phase diagrams reported by Massalski (22) were correct, but it was realised after subsequent ternary work that this assumption was wrong. For the ternary systems, experimental work has already been completed for Al-Cr-Ru (13, 14), Pt-Cr-Ru (15, 16), Pt-Al-Ru (19, 20), and is nearly complete for Pt-Al-Cr (17, 18). Some quaternary alloys have already been addressed (3, 4), but any new alloys chosen will probably be located only within the Pt-rich corner. The aim is to input results from the phase diagram work, together with enthalpies from the single-phase or near single-phase compositions from the University of Leeds (23), for optimisation. There will also be inputs from ab initio work from the University of Limpopo, South Africa, on enthalpies of formation for the Pt3Al (24) and Cr-Ru (25) phases. Additionally, the transmission electron microscopy (TEM) results will be utilised in changes to modelling, especially of the ~ Pt3Al phase (26–28). The Pt-Al-Cr-Ru system needed to be thoroughly researched through experimental work, so that the phases could be realistically described (to be as true to their crystallographic form as possible, so that any additional elements could be correctly incorporated) and then optimised using the software. Only then can the other elements be added to the database descriptions. These will be the additional elements, added in smaller proportions to ‘tweak’ the metallurgical properties of the systems. These will include at least cobalt and nickel. Experimental work has included the phase investigations alluded to above. Studies of as-cast alloys were done to determine their solidification reactions (13–15, 20). The solidification reactions and the temperatures at which they occur (found by differential thermal analysis (DTA)) are important inputs to the phase diagram programs. The as-cast alloy samples were also heat-treated at 600°C and 1000°C (16), then analysed so that the phase compositions at known temperatures could be input.

Ruthenium-Aluminium

Initially, a simplified version of the four-compound sublattice formalism (4CSF), a version of the compound energy formalism model (29), which models different combinations of the atoms, was used for the RuAl phase (11). This worked very well for the Al-Ru system, as is shown in Figures 2(a)–(c), where the calculated diagram is compared both with that of Boniface and Cornish (30, 31) and with a phase diagram by Mücklich and Ilic (32) which was published subsequently to the calculated work. The RuAl (B2) phase was actually described by two different models: the compound energy formalism (CEF), which is a simplified form of the 4CSF model, and is designated SL (for sublattice model) in Figure 2, as well as the modified sublattice formalism (MSL), which describes the order-disorder transformation with one Gibbs energy function. The MSL model allowed a wider RuAl phase field (by giving more flexibility in atom positions), which is closer to experimental findings. The RuAl phase was described as a stoichiometric phase (i.e. ‘line compound’, with no composition range), and the other intermetallic phases (Ru5Al3, RuAl2 and Ru2Al3) were modelled with the sublattice model. The solubility of Ru in (Al) was considered negligible. The coefficients were also within a range comparable to those of other phases in other systems.

It will be noticed that the two experimental phase diagrams are very similar, except for the stability of the Ru2Al3 phase, and the appearance of the Ru3Al phase. Boniface had observed a similar phase, but attributed it to being a ternary phase because it was found only with zirconium and...
silicon impurities (33). Differences in the experimental phase diagrams are due to the use of different techniques. Boniface and Cornish (30, 31) studied both as-cast and annealed samples, and the as-cast specimens showed that Ru$_3$Al$_2$ solidified at higher temperatures than RuAl$_2$. Annealed samples (32) are less likely to show this feature. Since data from the experimental diagram are used to optimise the calculated phase diagram, the latter should agree with the former. Where there are differences, this is usually due to the mathematical model not allowing flexibility, or sometimes too much flexibility for complex models with limited data. In some cases, simpler models have to be used because there are insufficient data for all the parameters required by a more complex (but potentially more accurate) model.

**Platinum-Aluminium**

At the outset of the programme, there were two conflicting phase diagrams: those of McAlister and Kahan (34) and Oya et al. (35). The major difference, which was very important to the development of the Pt-based alloys using the ~ Pt$_3$Al precipitates in a (Pt) solid solution, was the phase transformations in the ~ Pt$_3$Al (γ') phase, and the number of types of the ~ Pt$_3$Al (γ') phase. McAlister and Kahan (34) reported one transfor-

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**Fig. 2** Comparison of the Al-Ru phase diagrams: (a) calculated (11) (Courtesy of CALPHAD; MSL: modified sublattice model; SL: sublattice model)

**Fig. 2(b)** Comparison of the Al-Ru phase diagrams: Experimental from Boniface and Cornish (31) (Courtesy of Elsevier Science)
mation of the high-temperature Pt₃Al phase from L₁₂ (γ′) to a tetragonal low-temperature variant (designated D₀′₈) (γ′₁) at ~ 1280ºC. However, Oya et al. (35) observed the highest transformation γ′ → γ′₁ at ~ 340ºC, and gave an additional transformation γ′₁ → γ′₂ at 127ºC. Previous attempts to resolve this conundrum by scanning electron microscopy (SEM), XRD and DTA had been unsuccessful, although Biggs found peaks at 311 to 337ºC and 132ºC for different composition samples using DTA (36). Recent work (4) using in situ heating in a TEM showed that the diagram of Oya et al. (35) was more correct, although there is a possibility that very minor impurities are responsible, since the different workers sourced their raw material differently. The Pt-Al system had been calculated by Wu and Jin (37) using the CALPHAD method, but there was a need for reassessment (12) because they considered only one Pt₃Al phase, i.e. they did not reflect the ordering in the Pt₃Al phases. This needs to be done using a model that allows ordering to be calculated (described below). Wu and Jin did not include the Pt₅Al₂ or β phases, owing to a lack of experimental data. A study of Pt-Al-X ternaries (where X = Ru, Ti, Cr, Ni) confirmed the presence of the Pt₅Al phase (19, 36). Experimental work on the Pt-Al-Ru ternary confirmed the presence of the β phase in the Al-Pt binary (20).

Initially, the four-compound sublattice formalism (4CSF) was applied. This models different combinations of four atoms of two different elements, for example: (A) (arithmetically A₄), AB, AB (arithmetically A₄B₄), AB₂, and (B) (arithmetically B₄) where at least two of these appear in a system. This method was used for the (Pt) and Pt₃Al phases (12), because this model had been used in the development of the nickel-based superalloy database (38, 39).

However, when the 4CSF model was applied to the Pt-Al system (12), the results were less successful, mainly because there were very few data, and the system was more complex. The intermetallic compounds Pt₅Al₁₃, Pt₅Al₂₁, Pt₅Al₁₁, Pt₅Al₈, Pt₅Al₅ and Pt₅Al were treated as stoichiometric compounds. The β phase was assumed to be stoichiometric, since very little experimental information was available, and was treated as Pt₅Al₈. The phase diagram shown in Figures 3(a)–(c) appears to agree with that of Massalski (22), which is actually from McAlister and Kahan (34), but the 4CSF model did not produce the different Pt₅Al phases. The calculated compositions and temperatures for the invariant reactions of the
Intermetallic phases are generally in good agreement with those reported from experiment. However, there are some areas in less good agreement, in most cases for reasons inherent in the models being used.

Calculated results for the congruent formation of the Pt$_3$Al phase and $L \rightarrow$ Pt$_3$Al + (Pt) eutectic reactions are not in very good agreement with the experimental diagram, as both reactions are shifted to lower platinum compositions in the calculated system. The 4CSF model is such that the formation composition of Pt$_3$Al is fixed at 75 at.%, whereas the phase has been reported in the literature to form congruently at 73.2 at.%. This non-stoichiometric formation cannot be described with the model,
and had consequences for the temperature as well as the enthalpy of formation for the Pt₃Al phase. The symmetry and fixed compositions assumed in the 4CSF model also made it difficult to fix the eutectic reaction to lower Pt contents in the calculation. Furthermore, the phase area of the (Pt) solid solution is too narrow, especially at lower temperatures, although the phase area for the Pt₃Al phase is acceptable. However, the Pt₃Al phase is ordered throughout its phase area. The unstable PtAl₃ (L¹₁) and Pt₂Al₂ (L₁₀) phases, which are introduced through the 4CSF model, are not stable at any composition or temperature in the phase diagram, which is correct. Further work on this system was postponed until more data to describe the (Pt) and Pt₃Al phases had been obtained. Currently, the Pt-Al binary is being investigated at Mintek using the Nova NanoSEM, and good results are being obtained (40). The data from these alloys will be used to optimise the Pt₃Al phase in the Pt-Al binary.

**Platinum-Aluminium-Ruthenium**

The resulting database files from the Ru-Al, Pt-Al and Pt-Ru systems were added and the phase diagram was plotted, as an extrapolation from the binary systems, without any ternary interaction parameters or optimisation with ternary data (41). There were problems in the calculation of isothermal sections; these arose because the current models were not sufficiently robust to allow for extension into the ternary. However, the liquidus projection showed very good agreement with the experimental projection (Figures 4(a)–(b)). Obviously, the two ~ Pt₁₃Al₁₈Ru₆₄ and ~ Pt₁₂Al₁₇Ru₃₃ ternary phases (20) were not calculated, because data for these were not input. The stability of the Pt₃Al phase was calculated as too high in the ternary, because it solidified from the melt as a primary phase, which rendered the liquidus inaccurate for that region. This was probably because of the inadequacies of modelling the phases, which resulted in Pt₃Al being shown as too stable.
Chromium-Platinum

An assessment by Oikawa et al. (42) showed that the values for the two eutectic temperatures in the Cr-Pt binary should be reversed when compared with those results (22), as shown in Figure 5. Oikawa et al.'s conclusion was initially thought to be wrong, even considering that the original temperature data were very close (within 30 ± 10ºC). Thus, when work began on the Cr-Pt system, the work of Oikawa et al. (42) was ignored and the 4CSF model was used on the (Pt), Pt3Cr and PtCr ordered phases (43). However, more data were

Fig. 4 Comparison of Pt-Al-Ru liquidus surface projections: (a) calculated by Prins et al. (41) (Courtesy of CALPHAD; X = mole fraction)

Fig. 4(b) Experimental by Prins et al. (20) (Courtesy of Elsevier Science; X ~ Ru3Pt15Al75; T ~ Ru3Pt15Al75)
required for the 4CSF model than were available, and consequently the fit was very poor (22). Subsequently, results from experimental work on the Cr-Pt-Ru, Al-Cr-Pt and Cr-Ni-Pt ternary systems also agreed with the findings of Oikawa et al. (42), and those parameters are being used until subsequent experimental work indicates that a revision is necessary.

**Chromium-Ruthenium**

For the Cr-Ru system, there was no previous assessment, and the first calculation once again used the 4CSF model. Reproducibility was poor because the model was too complex for the data available. Further work and an extrapolation of the Pt-Cr, Cr-Ru and Pt-Ru binaries (the latter from Spencer’s database (7)) demonstrated rather that the calculations were poor (44) although the fit with the ternary Pt-Cr-Ru liquidus was reasonable. It was evident that another form of modelling was required. Subsequently, it was revealed (45) that there were problems with Massalski’s (22) phase diagram, and two alloys were manufactured to study the sequence of reactions in the Cr-Ru binary. The Cr-Ru system is very difficult to study experimentally because the diffusion rates are very low (large atoms and high melting points), and Cr oxidised easily on

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*Fig. 5 (a) Comparison of Cr-Pt phase diagrams: (a) calculated by Oikawa et al. (42) (Courtesy of Elsevier Science; reference numbers are as cited in Reference (42)).

*Fig. 5 (b) Experimental (22) (Courtesy of ASM International; $T_c$ is the critical temperature).
protracted annealing, despite precautions. However, this work is ongoing.

Conclusion

Although good results were obtained for Ru-Al using the 4CSF representation for RuAl, there were insufficient data to obtain good results for the other systems since more phases were represented in each system. A different approach was needed for other systems since more phases were represented. The use of simpler thermodynamic models to treat binary and ternary alloys will be reported in Part II of this series of papers, to be published in a future issue of *Platinum Metals Review*.

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