

Building a database for the prediction of phases in Pt-based superalloys

L.A. CORNISH*, R. SÜSS*, A. WATSON† and S.N. PRINS§

**Advanced Materials Division, Mintek, South Africa.*

DST/NRF Centre of Excellence for Strong Materials, Johannesburg, South Africa

†Institute for Materials Research, University of Leeds, UK

§CSIR-NML, Pretoria, South Africa

The work is being done using the Thermo-Calc™ software, and the database is being built up by obtaining good thermodynamic descriptions of all of the possible phases in the system. The database supplied did 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 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. At later stage of the work, problems with the thermodynamic descriptions of the Cr-Ru and Pt-Cr binary systems were found. A programme of experimental work to overcome these has been devised, and is being undertaken.

Keywords: Pt-based alloys, phase diagram calculations.

Introduction

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. Currently, the database contains the elements platinum, aluminium, chromium and ruthenium.

Ever since the possibility of basing a new series of alloys on platinum was seen¹, work has been ongoing at Mintek, Fachhochschule Jena and Bayreuth University, Germany, with input from NIMS, Japan. Undertaking experimental work 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, which can be used instead of experimentation. This saves both time and money. A similar database is being derived within the project 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 the Pt-based database, there are fewer commercial alloys, and experimental data, and few accepted ternary systems. Even some of the binary systems have problems. 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:Ru₂:Cr₃ alloy, the thermodynamic database will be built on the Pt-Al-Cr-Ru system. The Scientific Group Thermodata Europe (SGTE) database² has 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) bcc-Ru³. Although there is a database for precious metals⁴ 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

assessed⁵, although some of the phases might ultimately be modelled a different way.

The Thermo-Calc™ programme comprises the program itself, accessed in modules through a main module, 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 databases cover the phases of only the most common and well-known systems and all the stable elements². The intermetallic phases in the Al-Ru and Pt-Al systems are not included in the SGTE database. Providing that the elements are in the 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. The database can be modified to include new phases, or run in conjunction with another database. The aim of this project 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. The elemental information, and any phase that is already included in the SGTE database², 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 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 in actual crystallography. This information is usually derived from (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. The interaction parameters can be guessed for an initial value or set to zero, and the user can decide which parameter can be changed during optimization. In optimization, experimental data are compared against the thermodynamic description, which is adjusted to best fit the experimental data. A 'pop' file has to be created which contains the experimental data (these can include phase compositions in equilibrium with each other at known temperatures, reaction information, enthalpies, etc.) Then optimization 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 changed) 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.

Optimization is the iterative process in which selected expressions of the thermodynamic descriptions are allowed to change so that agreement with the experimental results is improved. The optimization was carried out with the Parrot module⁶ of the Thermo-Calc software⁷. With this module, the Gibbs energy functions can be derived by fitting experimental data by a least squares method. Different types of experimental data can be used and the weights can be assigned to the data based on 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 rationalized, the base systems will be complete. Selected important binaries were optimized first, for example, Al-Ru⁸ and Al-Pt⁹. 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 project, they have to be modelled satisfactorily, before incorporation into the main database. Once each binary system is modelled satisfactorily, they can be added into the ternary systems, after which each ternary system must be optimized individually. This is done using the experimental data gleaned either from literature, or, as was mostly the case, derived experimentally within the programme at the University of the Witwatersrand and Mintek (for Al-Cr-Ru^{10,11}), Mintek (for Pt-Cr-Ru^{12,13} and Pt-Al-Cr¹⁴, Pt-Al-Ru¹⁵) or the CSIR and Mintek (for Pt-Al-Ru¹⁶). Only once finalised can the ternaries be combined for the Pt-Al-Cr-Ru quaternary. The Thermo-Calc™ database will then be optimized against some quaternary alloys which have already been made for the alloy development work^{17,18,19}. Once this stage is complete, then the other small additions, to improve the properties (as in nickel-based superalloys), can be included in the optimization. It is envisaged that the very final stage will be focused on the optimization of only the important phases: at least the cubic and tetragonal structures of ~Pt₃Al, (Pt), ~Pt₂Al and (Ru).

The Pt-Al-Cr-Ru system is optimized in Thermo-Calc™ by studying the four component ternary systems. The reason for undertaking an optimization of whole ternaries rather than portions of them is that there are very little 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 optimized (e.g. the region between the (Ni) and Ni₃Al 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 able to converge 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.) Thus, the ternary systems for the Pt-Al-Cr-Ru quaternary will be studied in full to provide a sound basis for the Thermo-Calc™ database. The Pt-Al-Cr-Ru system is shown schematically in Figure 1.

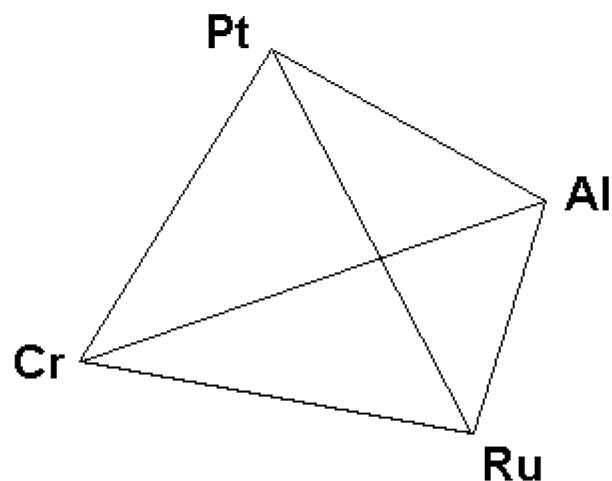


Figure 1. Schematic diagram of the Pt-Al-Cr-Ru System, showing four ternary systems and six binary systems

Building the database

Using the Compound Energy Formalism model

Introduction

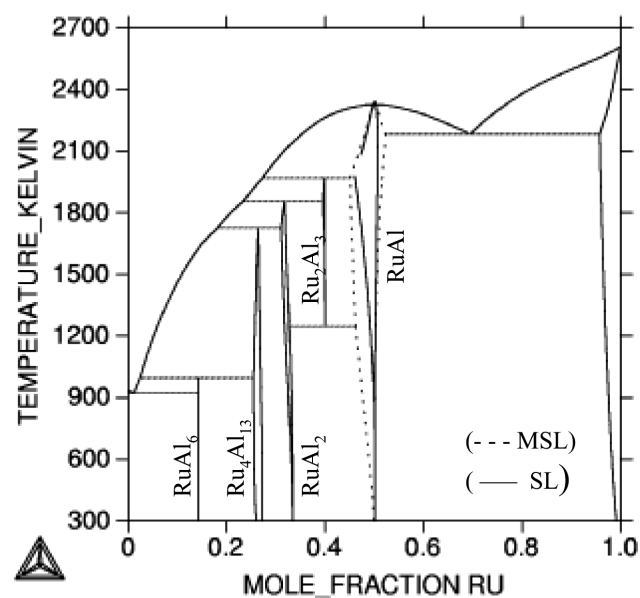
At the beginning, it was assumed that the six binary phase diagrams reported by Massalski²⁰ were correct, but it was realised after subsequent ternary work that this assumption was wrong. For the ternary systems, experimental work has already been completed for Al-Cr-Ru^{10,11}, Pt-Cr-Ru^{12,13}, Pt-Al-Ru^{15,16}, and is nearly complete for Pt-Al-Cr¹⁴. Some quaternary alloys have already been done^{18,19}, but any new alloys will probably be 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 Leeds²¹, to Thermo-CalcTM for optimization. There will also be inputs from *ab initio* work from the University of Limpopo on enthalpies of formation for the Pt₃Al²² and Cr-Ru²³ phases. Additionally, the transmission electron microscopy (TEM) results will be utilized in changes to modelling, especially of the ~Pt₃Al phase²⁴⁻²⁶.

The Pt-Al-Cr-Ru system needed to be thoroughly researched through actual 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 optimized using Thermo-CalcTM. 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 properties. These will include at least cobalt and nickel.

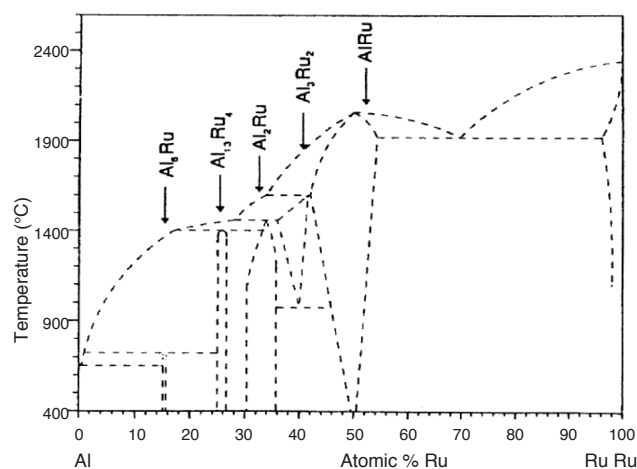
Experimental work has included the phase investigations alluded to above. Studies of as-cast alloys were done to determine the solidification reactions^{10,11,12,16}. The solidification reactions and their temperatures (found by differential thermal analysis or DTA) are important inputs to Thermo-CalcTM. The samples were also heat-treated at 600° and 1 000°C¹³, then analysed so that the phase compositions at known temperatures could be input into Thermo-CalcTM.

Ru-Al

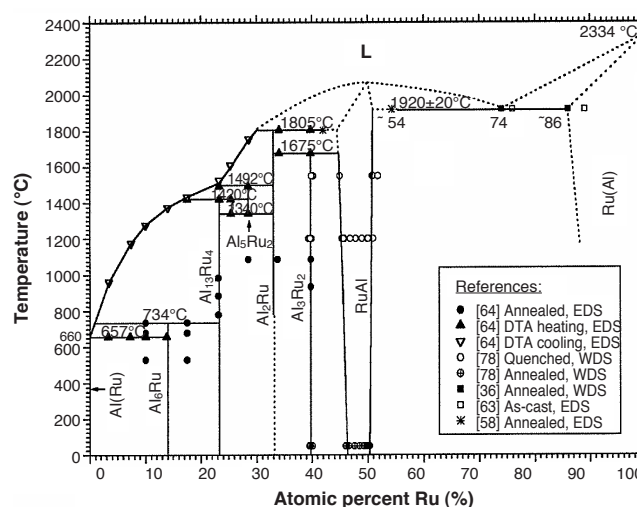
Initially, a simplified version of the four compound sublattice formalism (4CSF), a version of the compound energy formalism model²⁷, which models different combinations of the atoms, was used for the RuAl phase⁸. This worked very well for the Al-Ru system, as is shown in Figure 2, where the calculated diagram is compared both with that of Boniface and Cornish³¹ and a phase diagram by Mücklich and Ilic³² 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 nearer to experimental findings. The RuAl₆ phase was described as a stoichiometric phase (i.e. 'line compound'), and the other intermetallic phases (Ru₄Al₁₃, RuAl₂ and Ru₂Al₃) were modelled with the sublattice model. The solubility of Ru in (Al) was considered negligible. The coefficients were also within



(a)



(b)



(c)

Figure 2. Comparison of the Al-Ru phase diagrams: a) Calculated⁸; b) Experimental from Boniface and Cornish³¹; c) Experimental by Mücklich and Ilic³².

range comparable with 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 Ru_2Al_3 phase, and the appearance of the Ru_2Al_5 phase. Boniface had observed a similar phase, but attributed it to being a ternary phase because it was found only with zirconium and silicon impurities³³. Differences in the experimental phase diagrams are due to the use of different techniques. Boniface and Cornish³⁰ studied both as-cast and annealed samples, and the as-cast specimens showed that Ru_3Al_2 solidified at higher temperatures than Ru_2Al . Annealed samples³² are less likely to show this. Since data from the experimental diagram are used to optimize 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.

Pt-Al

At the outset of the programme, there were two conflicting phase diagrams: those of McAlister and Kahan³⁴ and Oya *et al.*³⁵. The major difference, which was very important to the development of the Pt-based alloys using the $\sim\text{Pt}_3\text{Al}$ precipitates in a (Pt) solid solution, was the phase transformations in the $\sim\text{Pt}_3\text{Al}$ (γ) phase, and the number of types of the $\sim\text{Pt}_3\text{Al}$ (γ) phase. McAlister and Kahan³⁴ reported one transformation of the high-temperature Pt_3Al phase from L1_2 (γ') to a tetragonal low temperature variant (designated $\text{D0}'\text{c}$) (γ'_1) at ~ 1 280°C. However, Oya *et al.*³⁵ had the highest transformation $\gamma' \rightarrow \gamma'_1$ at $\sim 340^\circ\text{C}$, and gave an additional transformation $\gamma'_1 \rightarrow \gamma'_2$ at 127°C. Previous attempts to resolve this conundrum by SEM, XRD and DTA had been unsuccessful, although Biggs found peaks at 311–337°C and 132°C for different composition samples using DTA³⁶. Recent work¹⁹ using an *in situ* heating in a TEM showed that the Oya *et al.*³⁵ diagram 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 Jin³⁷ using the CALPHAD method, but there was a need for re-assessment⁹ because they had only one Pt_3Al phase, i.e. they did not reflect the ordering in the Pt_3Al phases. This needs to be done using a model that allows ordering to be calculated (described below). They did not include the PtAl_2 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 Pt_2Al phase^{15,36}. Experimental work on the Pt-Al-Ru ternary confirmed the presence of the β phase in the Al-Pt binary¹⁶.

Initially, the four-compound sublattice formalism (4CSF), a version of the compound energy formalism model²⁷, was used. This models different combinations of four atoms of two different elements, for example: (A) (mathematically A_4), A_3B , AB (mathematically A_2B_2), AB_3 , and (B) (mathematically B_4) where at least two of these appear in a system. This method was used for the (Pt)⁹ and Pt_3Al ⁹ phases, because this model had used in the development of the nickel-based superalloy database^{29,30}.

However, when the 4CSF model was applied to the Pt-Al system⁹, the results were less successful, mainly because there were very few data, and the system was more

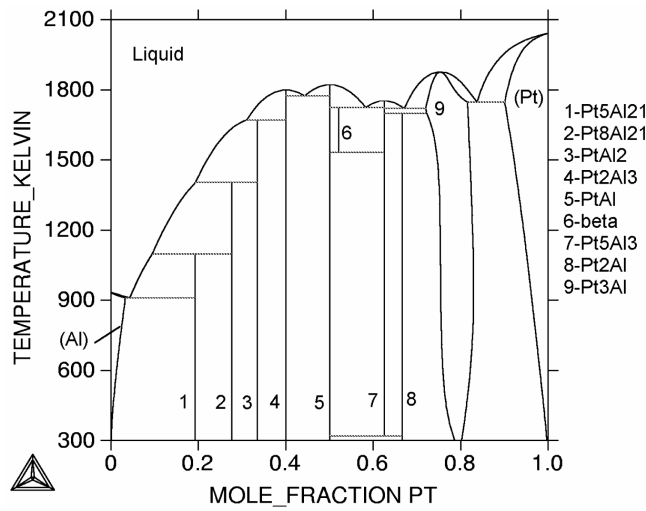
complex. The intermetallic compounds $\text{Pt}_{21}\text{Al}_5$, $\text{Pt}_{21}\text{Al}_{18}$, PtAl_2 , Pt_2Al_3 , PtAl , Pt_5Al_3 and Pt_2Al were treated as stoichiometric compounds. The β phase was assumed to be stoichiometric, since very little experimental information was available, and was treated as $\text{Pt}_{52}\text{Al}_{48}$. The phase diagram shown in Figure 3 appears to agree with that of Massalski²⁰, which is actually from McAlister and Kahan³⁴, but the 4CSF model did not give the different Pt_3Al phases. The calculated compositions and temperatures for the invariant reactions of the intermetallic phases are in generally good agreement with the experimentally reported compositions and temperatures. However, there are some areas in less good agreement, in most cases because of the models being used.

The congruent formation of the Pt_3Al phase and $\text{L} \rightarrow \text{Pt}_3\text{Al} + (\text{Pt})$ 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_3Al is fixed at 75 at. %, while it has been reported in the literature to form congruently at 73.2 at. %. This off-stoichiometry formation cannot be described with the model, and subsequently had an influence on the temperature as well as the enthalpy of formation for the Pt_3Al phase. The symmetry and fixed compositions of 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 Pt_3Al phase is acceptable. However, the Pt_3Al phase is ordered throughout its phase area. The unstable PtAl_3 (L12) and Pt_2Al_2 (L10) phases, which are introduced through the 4CSF model, are not stable at any composition or temperature in the phase diagram, which is correct.

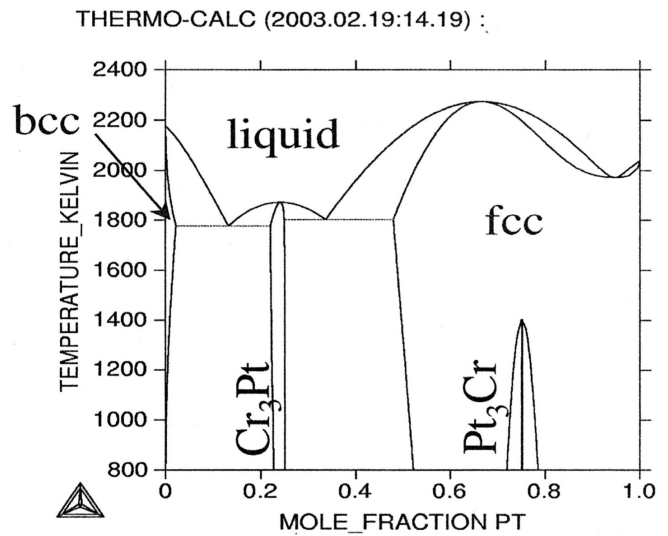
Further work on this system was postponed until more data to describe the (Pt) and Pt_3Al phases had been obtained. Currently, the Pt-Al binary is being investigated with the advent of Mintek's new Nova NANOSEM, and good results are being obtained. The data from these alloys will be used to optimize the Pt_3Al phase in the Pt-Al binary.

Cr-Pt

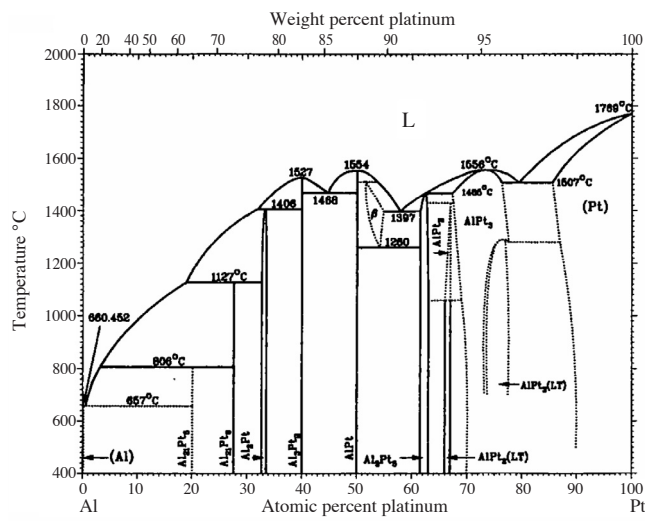
An assessment by Oikawa *et al.*³⁸ showed that the temperatures of the two eutectic temperatures in the Cr-Pt binary should be reversed when compared with Massalski²⁰. This was initially thought to be wrong, even considering that the original data were very close (within $30 \pm 10^\circ\text{C}$). Thus, when work began on the Cr-Pt system, the work of Oikawa *et al.*³⁸ was ignored and the 4CSF model was used on the (Pt), Pt_3Cr and PtCr ordered phases²⁸. There were many problems with using the 4CSF model, mostly because the model is complex and requires data that might be probable for the different phase types. If the phases do not exist naturally, the only way that these data can be obtained is by *ab initio* techniques. (Subsequent to this work, very good progress has been made by Preussner with the 4CSF and using the end points calculated using *ab initio* techniques³⁹.) The problem was that the 4CSF model needed more data than were available, and consequently the fit was very poor, as shown in Figure 4, which compares the calculated⁴⁰ and experimental phase diagrams²⁰. Subsequently, 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.*³⁸, and those parameters are being used until subsequent experimental work indicates that a revision is necessary.



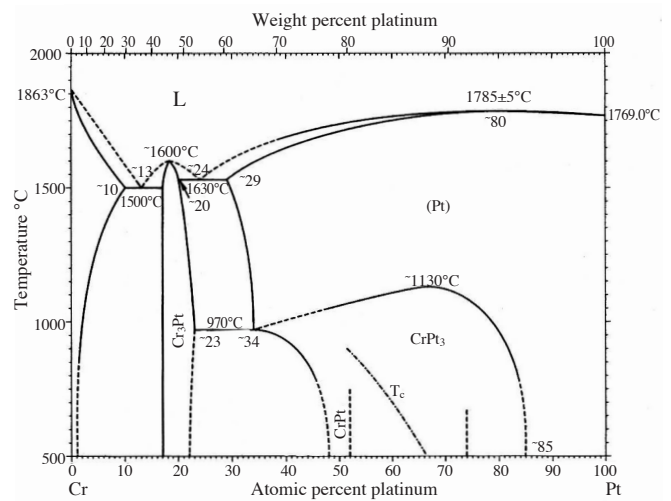
(a)



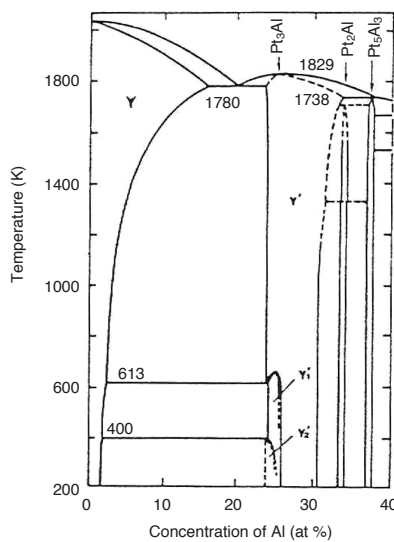
(a)



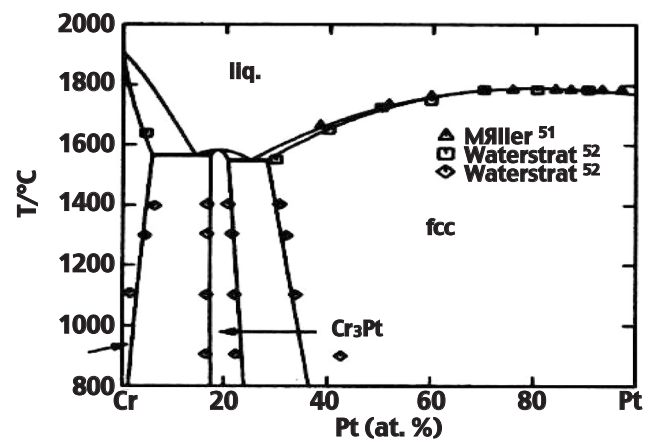
(b)



(b)



(c)



(c)

Figure 3. Comparison of Al-Pt phase diagrams: a) Calculated⁹; b) Experimental from Massalski²⁰ (McAlister and Kahan³⁴); c) Experimental from Oya *et al.*³⁵

Figure 4. Comparison of Cr-Pt phase diagrams: a) Calculated initially by Glatzel and Prins²⁸; b) Experimental²⁰; c) Calculated by Oikawa *et al.*³⁸

Cr-Ru

For the Cr-Ru system, there was no previous assessment, and the first calculation once again used the 4CSF model with poor reproducibility because the model was too complex for the data available (Figure 5). Further work and an extrapolation of the Pt-Cr, Cr-Ru and Pt-Ru binaries (the later from Spenser's database⁴) demonstrated further that the calculations were poor⁴⁰ although the fit with the ternary Pt-Cr-Ru liquidus was good⁴¹, as shown in Figure 6. It was evident that another form of modelling was required. Subsequently, it was revealed⁴² that there were problems with Massalski's²⁰ 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 slow (large atoms and high melting points), and Cr oxidises easily on protracted annealing, despite precautions.

Pt-Al-Ru

The resulting database files from the Ru-Al, Pt-Al and Pt-Ru were added and the phase diagram was plotted, as an

extrapolation from the binary systems, without any ternary interaction parameters or optimization with ternary data⁴³. There were problems in the calculation of isothermal sections, which 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 (Figure 7). Obviously, the two $\sim\text{Pt}_{18}\text{Al}_{18}\text{Ru}_{64}$ and $\sim\text{Pt}_{12}\text{Al}_{15}\text{Ru}_{73}$ ternary phases¹⁶ were not calculated, because data for these were not input. The stability of the Pt_2Al phase was 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 the inadequacies of modelling the phases, which allowed Pt_2Al to be too stable.

Using simpler models

General considerations

There is disagreement on which particular model should be used for (Pt) and Pt_3Al , which is similar to (Ni) and Ni_3Al . One school of thought states that as both are based on fcc,

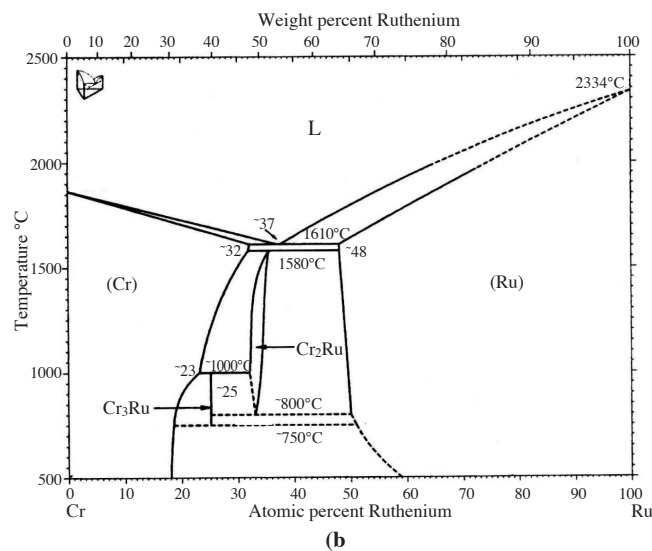
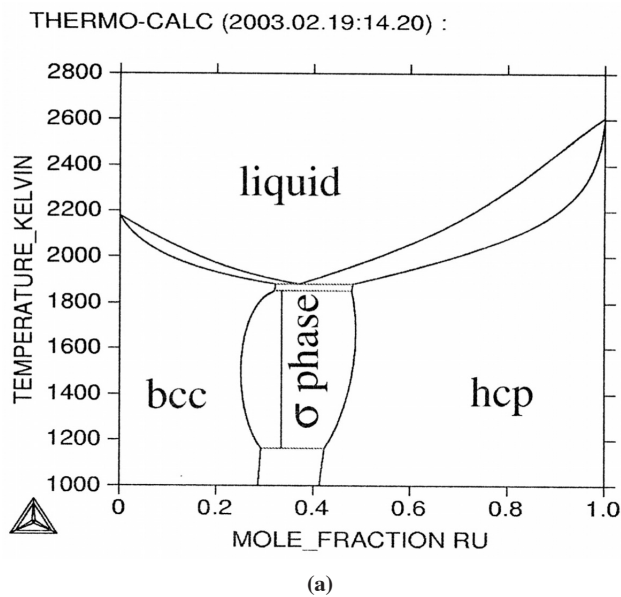


Figure 5. Comparison of Cr-Ru phase diagrams: a) Calculated by Glatzel and Prins²⁸; b) Experimental from Massalski²⁰

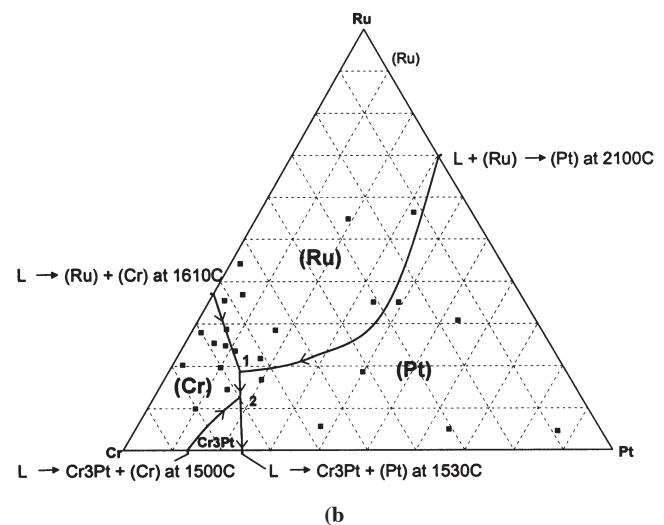
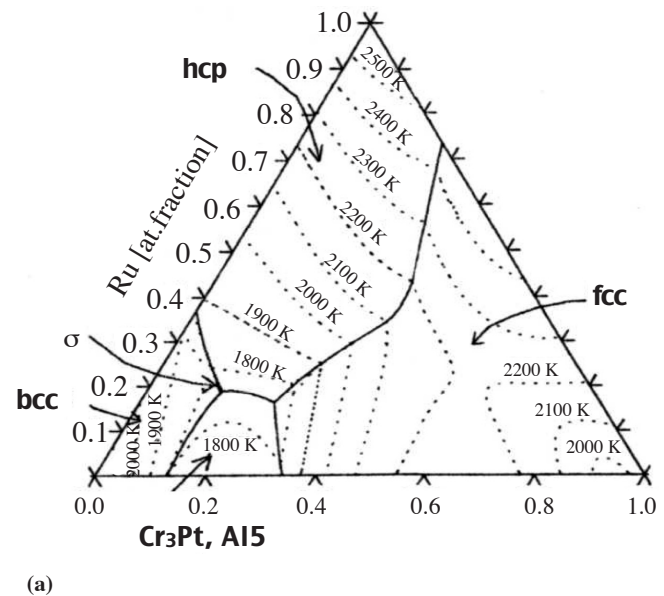


Figure 6. Comparison of liquidus surfaces of the Pt-Cr-Ru system: a) Calculated^{40,41}; b) Experimental^{12,41}

then Ni_3Al , which can be viewed as an ordered fcc phase, should be included as the fcc phase. On the other hand, another school of thought stipulates that, since both solidify separately, they should be modelled separately. The second school of thought would allow for Pt_3Cr and PtCr to be modelled as part of (Pt), since they form by ordering within the (Pt) phase field at lower temperatures. However, this could then cause problems in that Pt_3Al would not be incorporated in the fcc model, whereas Pt_3Cr would be. However, given that phases should be modelled the same way only if they are likely to be contiguous, this would not be a problem unless Pt_3Al is likely to be contiguous with Pt_3Cr . At the moment, this is not likely. A similar argument can be made for Pt_3Al , which just like Ni_3Al , solidifies as a separate phase from (Pt), and is not formed within.

Another source of contention is that in the current model, many parameters are needed to describe the phase. For the Ni-Al system, it could be argued that there are many data and 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

itself regarding the reaction temperatures involving Pt_3Al and even the type of ordering. Thus, a much simpler model is prescribed for the Pt_3Al phase, both because of a dearth of data (as compared to Ni_3Al), and also because the Pt_3Al 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 database⁴⁴, the Ni_3Al phase is modelled as ordered fcc, even though it solidifies separately. The latest database from Dupin⁴⁴ was used to draw the Ni-Al phase diagram, and the γ / γ' boundary did not agree well with the experimental phase diagram, so it is questionable whether the complex modelling is really worthwhile.

In general, it is best to have the simplest models possible, because then fitting is easier and probably more meaningful. This is especially so when the data are limited. There are commercial databases available with very simple modelling, and these are very useful. One example of this is the lead-free solders database, which comprises the Ag-Cu-Sn-Ni-Au-Pd database, which was derived by modelling ternary Ag-Cu-Si, then adding Ni, Au and Pd. Here, the line compounds are used for many of the intermetallic compounds, and ordering is not considered because it is not worth the effort for the application required. Thus, the question could be asked whether the current database should be concerned with ordering. The answer could be positive, of course, because the ordered Pt_3Al phase is the basis of the alloys. However, if there are few data available, then they will be difficult to order meaningfully in any case. It would be valid to model very simply, then extend the database subsequently if there is sufficient need, and the data become available.

The sections below describe how the work was done. Most of the problems arise from lack of data, especially thermodynamic values. The computer programmes used were Winphad and Pandat, mainly because they are so much easier to use than Thermo-CalcTM.

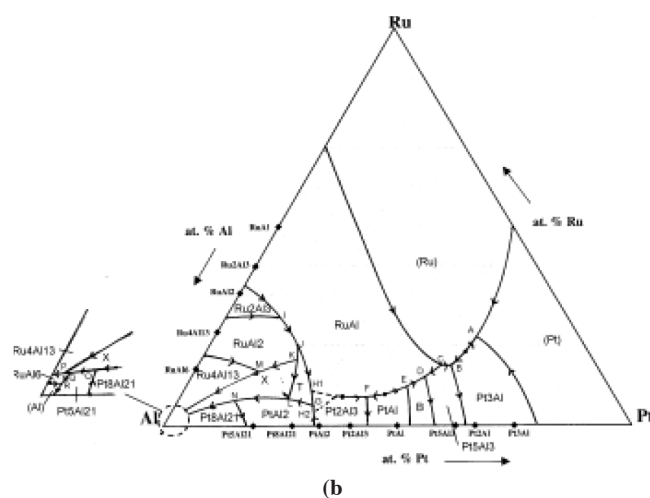
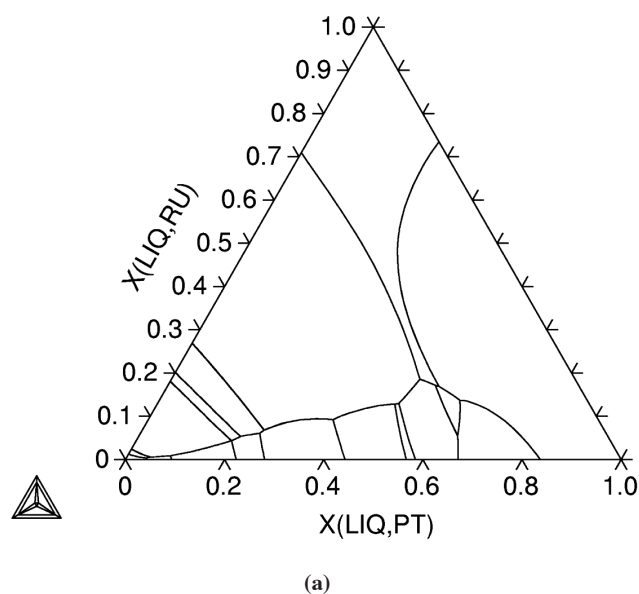


Figure 7. Comparison of Pt-Al-Ru liquidus surface projections: a) Calculated by Prins *et al.*⁴³; b) Experimental by Prins *et al.*¹⁶

Pt-Cr

The first Pt-Cr assessment done within this work²⁸ built on the original assessment of Oikawa *et al.*³⁸, and incorporated the Compound Energy Formalism (CEF) model to the fcc phases, (Pt), Pt_3Cr and PtCr to give a worse fit²⁸ to the currently accepted phase diagram than the work of Oikawa *et al.*³⁸, and was criticised at the 2004 CALPHAD conference⁴⁰. Part of the problem was identified as the many parameters being fitted by very few data points. In fact, in the *.pop file there were five data points for many more parameters!

A new approach was initiated. The phase diagram of Oikawa *et al.*³⁸ is to be recreated, and this assessment changed only when there are good experimental reasons for doing so. Until experimental results show otherwise, the assessment of Oikawa *et al.*³⁸ will be used, extrapolated into the ternary, and will then be re-optimized with Mintek's experimental values from the Pt-Cr-Ru system. The assessment of Oikawa *et al.*³⁸ is shown in Figure 4.

Pt-Ru

It was initially thought that the Spencer database⁴ version of Pt-Ru would be the same as the SGTE database. However, this was not so, and the phase diagram from Spencer is a eutectic, with a maximum in (Pt) and $\sim 10^\circ\text{C}$ between the maximum and the eutectic temperature, whereas that from

SGTE is peritectic, which is consistent with available literature. Experimental work at Mintek also showed that the reaction is peritectic in nature.

When the phase diagram was initially calculated, at low temperatures the Pt solubility (i.e. the extent of the (Pt) phase field) suddenly decreased. This looked unrealistic, and could be attributed to a lack of data at low temperatures. The free energy curves were plotted, and the curve for Ru was very unusual, showing a distinct slope rather than a parabola.

The first attempt at improving the parameters through optimizing was to try and destabilise the fcc (Pt) phase by making the enthalpy interaction parameter less negative. This reduced the temperature difference between the fcc maximum and the eutectic temperature but also added a miscibility gap in fcc, which has not been reported. Next, the temperature-dependent term (entropy) was made less negative (-1.5). Eventually, this gave a peritectic reaction at 2 134°C (compared with Massalski's temperature of 2 130°C²⁰ which was obtained from Hutchinson⁴⁵ at 2 126°C using the experimental data). However, there was also a small miscibility gap. The two-phase regions were too Pt-rich, and the free energy curves were drawn in an attempt to ascertain why, because the phase diagram depends on the shape of these curves. The Ru curve was most likely to cause this problem, but it has to be remembered that there are few data. Part of the problem was deemed to be the unusual Ru energy curve. However, as this originated from the Ru unary data, and is set across the entire database, it would be unwise to change it because it represents a best fit value for many systems. One solution would be to add an interaction parameter, but it must be remembered that there are too few data available.

Since the solid data were reasonable, the problem seemed to be with the liquid data, so optimization was undertaken using L + hcp tie-line data extrapolated from the phase diagram⁴⁵. This gave coefficients that were too large, although a peritectic reaction was obtained. However, since the liquidus composition was very close to the fcc values, some L + fcc tie lines (again, extrapolated from the phase diagram⁴⁵) were input for optimization. This attempt was reasonable. The liquid free energy curve was sensible, and there is obviously a change in c_p at ~600°C. The phase diagram is shown in Figure 8. Additionally, to confirm the

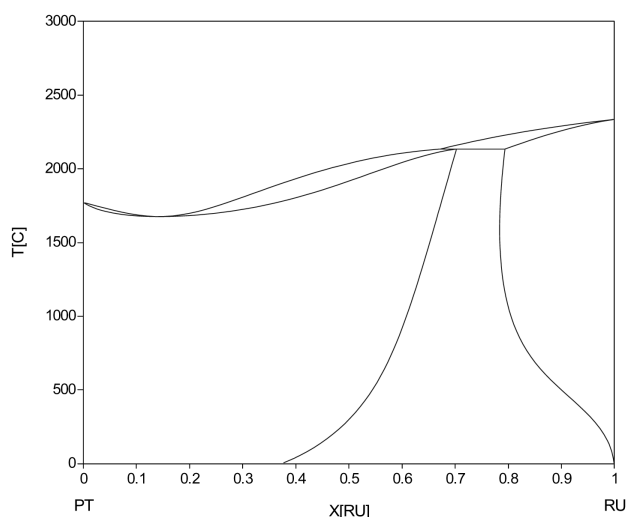


Figure 8. Best calculated Pt-Ru phase diagram to date

liquidus temperature, it was decided to run an experimental sample at ~15 at.% Ru in the DTA. The calculated peritectic temperature is 1 667°C, which should have been in the range of a 1 750°C rod. However, the DTA became unavailable.

Cr-Ru

This system contains two intermetallic compounds: Cr_2Ru (σ) and Cr_3Ru . The accepted models have three sublattices, so this format would be followed for the Cr-Ru system. However, especially given such limited data, it would be difficult to have mixing on all three sublattices, with many end-members needed, so it was decided that Cr only would be on one sublattice, and the remaining two would have mixing. (This is normal practice.) The current model of choice for σ is 10:16:4 (the previous model was 8:18:4), which was in the Glatzel assessment²⁸, 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 mixing needs to be reduced.

The approach used was to build up the system with the most simple phase diagram descriptions possible: thus Cr_2Ru (σ) and Cr_3Ru would be line compounds. The Ru and Cr unary data were derived from Kaufman⁴⁶.

The first stage was to use ideal solid solutions for the L, bcc and hcp phases: elemental data only. A eutectic was produced, but it was too near Cr. Moving away from the ideal solid solution, an L_0 enthalpy coefficient was input and optimized, using the 'real' eutectic at 1 610°C as a datum point, which improved the phase diagram. Data for tie-lines between the terminal solid solution were obtained from the best experimental diagram²⁰ and input for optimization. The intermetallic compounds were ignored. Then σ formation and decomposition temperatures were added, and a value for (Cr) was invented, since Cr_3Ru was in the way.

It was noticed that the reaction temperatures for Cr_2Ru (σ) and Cr_3Ru were suspiciously convenient: ~750, ~800 and ~1 000°C. However, with no other data available, these had to be used. It was essential that DTA was undertaken on two samples to establish these reaction temperatures. This was tried⁴⁷, but the results were inconclusive because the Ru and Cr atoms are very slow to diffuse (being large and having high melting points), and the DTA scan rate needs to be extremely slow to allow for equilibrium. Further attempts to equilibrate samples with Cr failed because the samples oxidized. The enthalpy term only for L_0 was optimized for the liquid, bcc and fcc phases, with reasonable results. Next, some tie-lines were used from the best experimental phase diagram and these were used to optimize the L_0 entropy and L_1 enthalpy, but the results were not good. In order to try to improve these results, only the L_0 enthalpy and entropy were optimized, and the results were better. Next, the σ phase was added, together with data on the formation and dissolution, but the σ phase did not appear on the phase diagram. The free energy curves were checked, and although σ was present (with a small range because it was made stoichiometric), it was not stable. Only the enthalpy term was used and optimized, resulting in the phase being stable at too low temperatures. The enthalpy was consistent with the Gibbs free energy at that temperature. A slightly different approach for σ was used: inputting and

optimising enthalpy and entropy for L_0 . The phase diagram appeared good, but it must be remembered that the values are not representative without experimental thermodynamic results.

The sigma was held constant and Cr_3Ru was added, and the L_0 enthalpy term only was input and optimized. The Cr_3Ru phase was stable below the lowest stable temperature (just as sigma was initially). An entropy term was added, and both the enthalpy and entropy terms were optimized. The phase was still stable below its temperature range, but it was now stable just below the bcc solidus, although in the right temperature range.

The next combination was to allow both the enthalpy and the entropy of Cr_2Ru but only the entropy for Cr_3Ru to vary. This gave a phase diagram which agreed with the input data, except for the decomposition of Cr_3Ru . The terminal solid solutions (bcc and hcp) were not stable enough at low temperatures and ran almost parallel to the vertical axes. Everything was now optimized, keeping all the relevant data points, and a good fit was obtained. This optimization was repeated, and became even better (the parameters were very similar to the very best subsequently obtained). The parameters for liquid, bcc and hcp were sensible, so these were fixed, and the intermetallic phase compositions were optimised. The new values were reasonable, although there was a positive heat of formation, but this could still give a compound that was stable at low temperature. The next stage was to optimize everything for the compounds, and the phase diagram gave a very good fit, as shown in Figure 9, compared with the experimental diagram shown in Figure 5.

Pt-Cr-Ru

In theory, once the binary systems were finished, the database files should have been copied into a single file, and the ternary database would be complete. However, it must be remembered that Cr_3Ru and Cr_3Pt have the same A15 structure and so these should be modelled the same, in case the phase is actually contiguous across the ternary. Currently, Cr_3Ru is a stoichiometric line compound, whereas Cr_3Pt has two sublattices, and both elements are

mixed on both.

The experimental results of the A15 Cr_3Ru and Cr_3Pt phases are not conclusive in showing whether the phases are contiguous, despite two more samples of intermediate compositions between Cr_3Ru and Cr_3Pt being made. These samples are currently being 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 Cr_3Ru , if Ru is constant, then Pt substitutes for Cr; and for Cr_3Pt , if Cr is constant, Ru substitutes for Pt. However, it must 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 Cr_3Pt phase⁴⁸ 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 case⁴⁸ would be Cr on one sublattice and Pt + Cr on the other, but this depends on the atomic sizes. The atom sizes can be measured in different ways (to give different answers) and the most appropriate measurement should be used for how the atom will be bonded. The covalent radii show that Pt and Ru are similar, and this being so, they could sit on the same sublattice. However, it is recommended that other A15 phases are researched to see how their modelling is undertaken, especially for the composition ranges (i.e. the spread on both sides from $x = 0.25$). For the representation of Cr_3Pt within the ternary (and higher order phase diagrams), the model would be much simpler (and have fewer end members) if the lattices could be (Cr, Cr) (Cr, Pt, Ru).

To model the ternary system, the three binary phase diagrams were added in own database. An interaction parameter was found for hcp PtCr, and the effect of this needs to be re-checked in the boundaries. Also, the extent of coring has to be established, or interpreted, in order to add interaction parameters. The best way to check the 'full' database is to recalculate the binary phase diagrams from it, which has been successfully accomplished. In the ternary database, a ternary interaction parameter was added to increase the phase extensions into the ternary. Three had to be added to maintain the symmetry; all were $-5\ 000$, but more work was needed on these, and is under way⁴⁹. The projected liquidus surface is shown in Figure 10. It is an improvement on the assessment by Glatzel *et al.*²⁸ in that it does not show primary sigma, but the invariant reactions are still incorrect, because the liquidus surfaces for (Ru) and Cr_3Pt abut, whereas those for (Cr) and (Pt) should, because of the (Pt) + (Cr) eutectic observed in the ternary samples. However, the junction between the wrong surfaces of primary solidification is smaller than was calculated previously²⁸, and agrees more with the experimental results. Obviously, there is more work needed on the system with interaction parameters and phase boundaries.

The isothermal section at $1\ 000^\circ\text{C}$ is shown in Figure 11. It shows some solubility of Cr and Pt in (Ru), (Pt) and (Cr), but much less than in the experimental isothermal section. This shows that more work is needed on the interaction parameters for the (Pt) and (Cr) phases. There is a miscibility gap in (Pt), which is not seen experimentally, but is probably related to the limited extent of the calculated phase, or possibly ordering. More work is also needed here. Both intermetallic phases are present, with no extension into the ternary because they were input as line

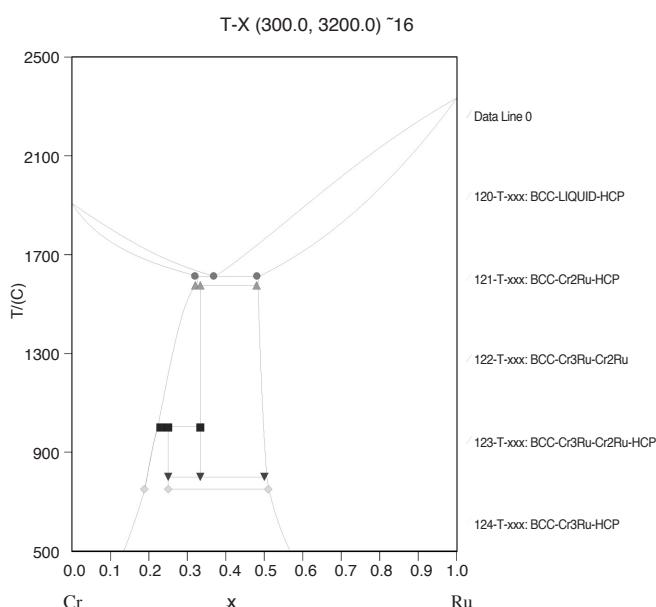


Figure 9. Best calculated Cr-Ru phase diagram to date

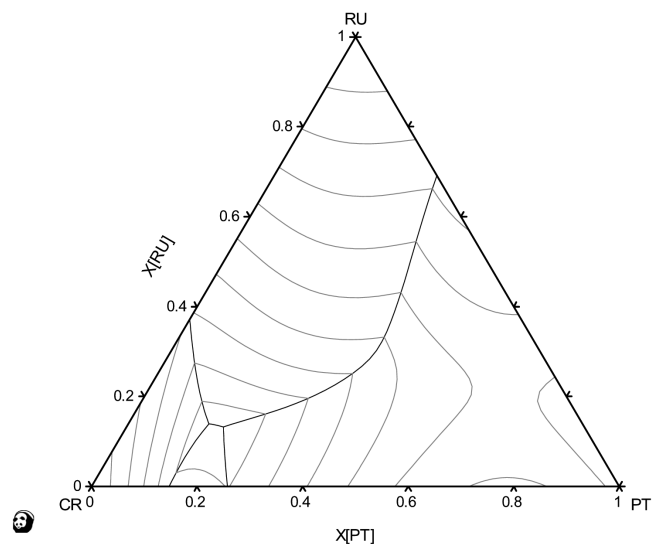
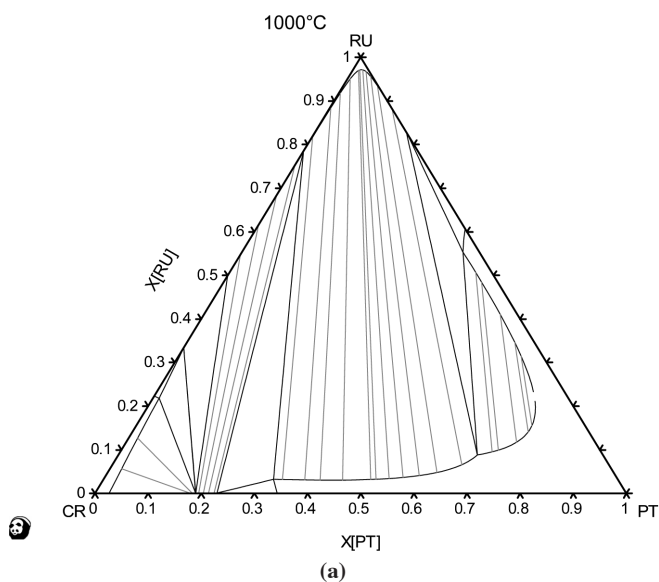
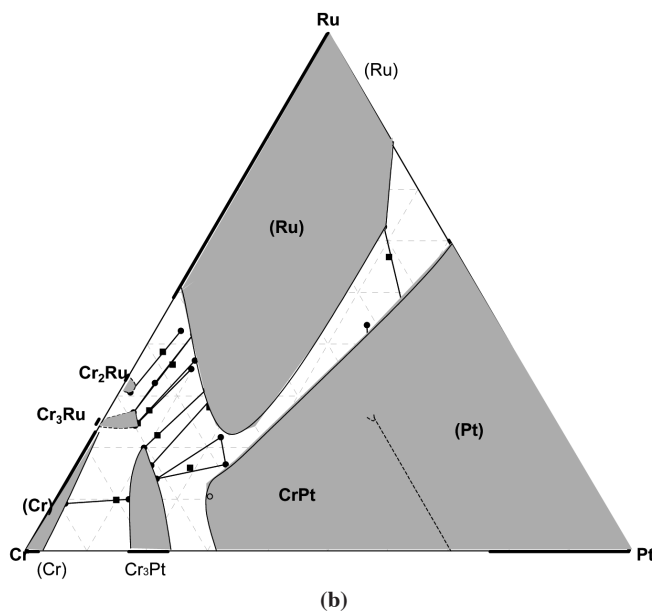


Figure 10. Best calculated liquidus surface to date for the Pt-Cr-Ru system



(a)



(b)

Figure 11. 1000°C isothermal section for the Pt-Cr-Ru system: a) Calculated; b) Experimental from Süss *et al.*¹³.

compounds.

The isothermal section at 600°C was similar to that in Figure 11 in that it showed a miscibility cap in (Pt), and the solubilities are much less in (Pt) and (Ru) than was observed experimentally¹³. The two intermetallic phases are absent, which is correct in the current understanding of the diagram (which might change with more experimental work).

Overall, the results for the ternary are very good, considering that they are just an extrapolation of the binaries. Once again they demonstrate the validity of the whole CALPHAD technique in calculating higher-order systems from lower-order systems. However, the match between the calculated and experimental diagrams could be improved and more work is necessary. Some of it is already under way. This work includes:

- obtaining an *ab initio* enthalpy of formation for Cr₂Ru, although, neither intermetallic phase is stable at 0K, which might pose a problem
- preparing a Cr₃Ru sample for calorimetry by mixing powders and heating to 980°C for 20 min, quenching and examining by SEM
- undertaking slow scan DTA for temperatures of formation and dissolution for the intermetallic compounds, especially in the Cr-Ru system, and for the reactions in the Cr-Pt system
- adding and optimizing interaction parameters for the (Pt) and (Ru) phases especially ((Cr) has a better fit)
- undertaking a DTA measurement of Pt₈₅:Ru₁₅ for the liquidus temperature, to ascertain the possible minimum
- modelling the Cr₃Ru and Cr₃Pt phases the same way because they have the same structures and might possibly be contiguous
- verifying experimentally whether Cr₃Ru and Cr₃Pt are contiguous to see how they extend in the ternary, which will determine the mixing allowed on the individual sublattices, if they are contiguous, in which case an attempt will be made to model Pt-Ru on one sublattice only and Cr on the other sublattice, to simplify and reduce the number of end-members, i.e. coefficients
- using the sigma model for Cr₂Ru.

Although there is still much work to be done, some of which is experimental, once the Pt-Cr and Cr-Ru binary phase diagrams are confirmed more rigorously, the calculated phase diagrams can be worked on with more confidence. Currently, it would be a waste of time to optimize the database for the intermetallic phases because there are too many unknowns. This experimental work is under way. Two of the challenges are that high temperature DTA is needed for Pt-Cr, and the Cr-Ru samples are very difficult to homogenise. The probable reason that the Cr-Ru phase diagram is not confirmed must be that other workers have also experienced the same problems.

Conclusions

The Pt-Al-Cr-Ru database is progressing well, and there has been good agreement for the Pt-Cr-Ru and Pt-Al-Cr phase diagrams when they were extrapolated from the binaries, which was encouraging and confirmed that the higher order systems could be calculated from the binary systems with confidence. However, more work needs to be done on the interaction parameters of the (Pt) and (Ru) phases, as these do not extend sufficiently into the ternary, compared to the experimental results for the Pt-Cr-Ru system. The models

of the Pt₃Al and Pt₂Al phases need to be re-assessed, and if good *ab initio* data became available, it might be worthwhile to model these phases in a more complex manner. Currently, the best results have been obtained using very simple models.

There have been some problems in the binary systems, notably Pt-Al because of the modelling and the uncertainty of the Pt₃Al phase types, and Cr-Ru, which is very difficult experimentally because the diffusion rates of Cr and Ru are so slow. Annealing is also problematic because alloys with substantial Cr oxidise very easily.

There have been some hard lessons learned in the creation of the database, and these include the fact that any binary system which has uncertainties is experimentally difficult for a variety of reasons, and the most accurate data belong to systems that are commercially important. Good models can be very simple, and more complex models need many data. Many of the problems were due to insufficient good data, but work is being done within the programme to generate reliable phase data to build the thermodynamic database and hence to aid the application of high temperature alloys.

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