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

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Synopsis

Work is being done at Mintek and at Leeds University to build up a 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 to obtain 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 a later stage of the research 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.

Parallel work at the University of Bayreuth, Germany, entails the creation of a Pt-Al-Cr-Ni database using a slightly different approach that utilizes more data from *ab initio* calculations and more complex models. The Cr-Pt binary phase diagram has been reassessed, and the latest results of thermodynamic modelling are presented.

Keywords: Pt-based alloys, phase diagram calculations.

Introduction

Work is being done to build a thermodynamic database for the prediction of phase equilibria in Pt-based superalloys[1–4]. These alloys are being developed for high temperature applications in aggressive environments. The database will aid the design of alloys by enabling of the composition and proportions of phases present in alloys of different compositions to be calculated. 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 seen[1], 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 this project to facilitate further alloy development and also provide 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 therefore more data and accepted phase diagrams have been published. For the Pt-based database, there are fewer commercial alloys, experimental data, and very few accepted ternary systems. Even some of the

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binary systems are problematic. Thus, part of this work has included the study of phase diagrams to address the lack of data, and to use the data elicited to compile a thermodynamic database. Since the basis of the alloys is the Pt_{84}:Al_{11}:Ru_2:Cr_3 alloy, the thermodynamic database will be built on the Pt-Al-Cr-Ru system. The Scientific Group Thermodata Earth (SGTE) database[5] has all the stable elements and describes 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-Ru[6]. 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 or all the places of interest to this study. 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 in a different way.

The phase diagram programmes (e.g. Thermo-Calc™, MTDATA and Pandat) comprise the programme 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 do not include the intermetallic phases in the Al-Ru and Pt-Al systems. 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 of 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. Prior to building a database, it must be established which phases need description. The elemental information, and any phase that is already included in the SGTE database[5], can be accessed from that source. For phases that are not represented, 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 crystallography. This information is usually derived from (XRD) structural information and composition ranges, and is usually made as simple as possible. Next, values have to be obtained for the interaction parameters. These can be guessed for an initial value or set to zero, and the user can decide which parameter can be changed during optimization, in which, experimental data are compared against the thermodynamic description, which is adjusted to best fit the experimental data. However, optimization can only be conducted only after a 'pop' file which contains the experimental data has been created. (These can include phase compositions in equilibrium with each other at known temperatures, reaction information, and enthalpies). However, optimization can be conducted only after 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 module[9] of the Thermo-Calc software10. Using 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-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 Pt_3Al phases. Since these are crucial to the project, they have to be modelled satisfactorily, before incorporation into the main database. Once each binary system is modelled satisfactorily, it 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 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]), Mintek (for Pt-Cr-Ru[15–16] and Pt-Al-Cr[17], Pt-Al-Ru[18]) or the CSIR and Mintek (for Pt-Al-Ru[19]). Only once finalized can the ternaries be combined for the Pt-Al-Cr-Ru quaternary. The Thermo-CalcTM database will then be optimized 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 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 ~Pt_3Al, (Pt), ~Pt_2Al and (Ru).

The Pt-Al-Cr-Ru system is optimized 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 (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 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[20].) 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.

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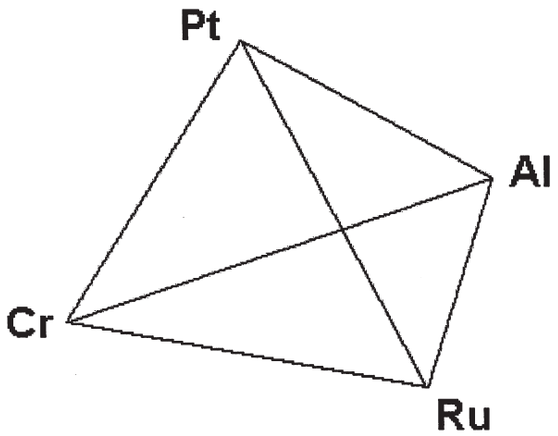


Figure 1—Schematic diagram of the Pt-Al-Cr-Ru system, showing four ternary systems and six binary systems

Building the database

Using the compound energy formalism model

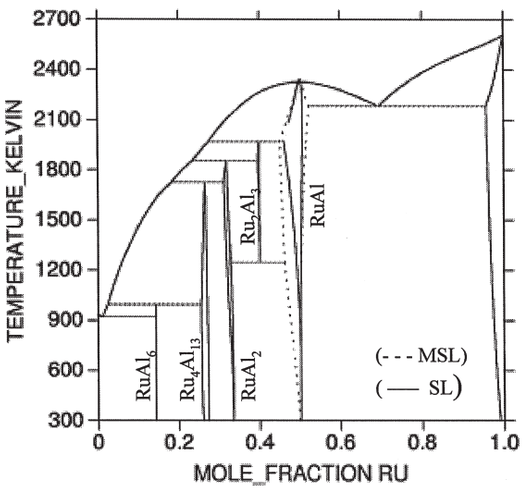
Introduction

At the beginning, it was assumed that the six binary phase diagrams reported by Massalski[21] were correct, but it was realized 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] and Pt-Al-Ru[18–19], and is nearly complete for Pt-Al-Cr[17]. Some quaternary alloys have already been done[3–4], 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 Leeds[22], for optimization. There will also be inputs from *ab initio* work from the University of Limpopo on enthalpies of formation for the Pt_3Al[23] and Cr-Ru[24] phases. Additionally, the transmission electron microscopy (TEM) results will be utilized in changes to modelling, especially of the ~Pt_3Al phase[25–27]. 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 the programmes. Only then can the other elements be added to the database descriptions. These elements, which will include at least cobalt and nickel, added in smaller proportions to 'tweak' the properties.

Experimental work has included the phase investigations alluded to above. Studies of as-cast alloys were done to determine the solidification reactions[13–15,19]. These reactions and the temperatures at which they occur (found by differential thermal analysis or DTA) are important inputs to the phase diagram programmes. The samples were also heat-treated at 600° and 1 000°C[16], then analyzed so that the phase compositions at known temperatures could be input.

Ru-Al

Initially, a simplified version of the four compound sublattice formalism (4CSF), a version of the compound energy formalism model[28], which models different combinations of the atoms, was used for the RuAl phase[11]. This worked very well for the Al-Ru system, shown in Figure 2, where the calculated diagram is compared both with that of Boniface and Cornish[29–30] and a phase diagram by Mücklich and Ilić[31], which was published subsequent 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 $RuAl_6$ phase was described as a stoichiometric phase (i.e. a 'line compound', with no composition range), and the other intermetallic phases (Ru_4Al_{13}, RuA_{l2} and Ru_2Al_3) were modelled with the sublattice model. The solubility of Ru in (Al) was considered negligible. The coeffi-



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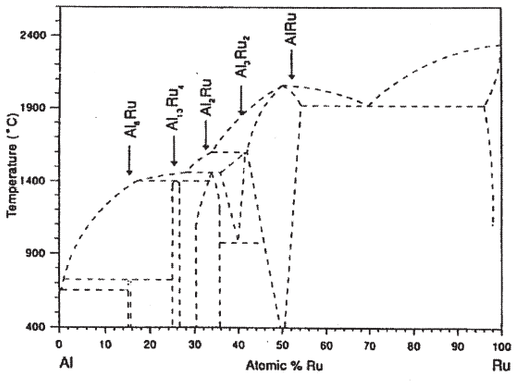


(b)

Figure 2—Comparison of the Al-Ru phase diagrams: (a) Calculated[11]; (b) Experimental from Boniface and Cornish[30]; (c) Experimental by Mücklich and Ilić[31]

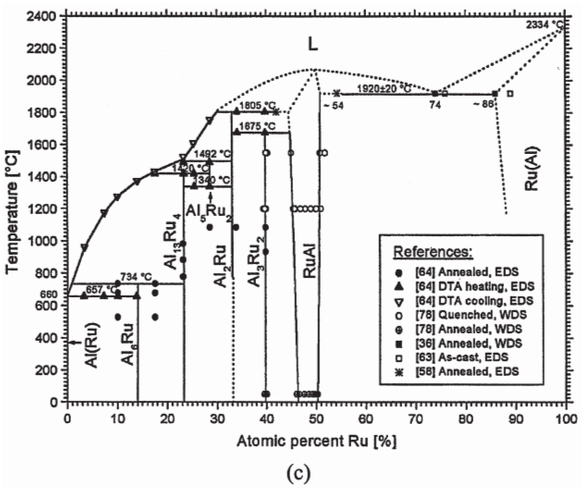


Figure 2 (continued)—Comparison of the Al-Ru phase diagrams: (a) Calculated[11]; (b) Experimental from Boniface and Cornish[30]; (c) Experimental by Mücklich and Ilić[31]

cients were also within a 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 impurities[32]. Differences in the experimental phase diagrams are due to the use of different techniques. Boniface and Cornish[29–30] studied both as-cast and annealed samples, and the as-cast specimens showed that Ru_3Al_2 solidified at higher temperatures than $RuAl_2$. Annealed samples[31] 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, they can usually be explained by the inflexibility of the mathematical mode, or sometimes by the diagram's having 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 Kahan[33] and Oya *et al.*[34]. The major difference, which was very important to the development of the Pt-based alloys using the ~Pt_3Al precipitates in a (Pt) solid solution, was the phase transformations in the ~Pt_3Al (γ') phase, and the number of types of the ~Pt_3Al (γ') phase. McAlister and Kahan[33] reported one transformation of the high-temperature Pt_3Al phase from $L1_2$ (γ') to a tetragonal low temperature variant (designated D0'c) (γ'_1) at ~1280°C. However, Oya *et al.*[34] had the highest transformation $\gamma' \rightarrow \gamma'_1$ at ~340°C, and gave an additional transformation $\gamma'_1 \rightarrow \gamma'_2$ at 127°C. Previous attempts to solve 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 DTA[35]. Recent work[4] using an *in situ* heating in a TEM showed that the Oya *et al.*[34] 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 Jin[36] using the CALPHAD method, but there was a need for re-assessment[12] 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 (as 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[18,35]. Experimental work on the Pt-Al-Ru ternary confirmed the presence of the β phase in the Al-Pt binary[19].

Initially, the four-compound sublattice formalism (4CSF) method was applied. 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) and Pt_3Al phases[12], because this model had used in the development of the nickel-based superalloy database[37–38].

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 $Pt_{21}Al_5$, $Pt_{21}Al_8$, $PtAl_2$, 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 $Pt_{52}Al_{48}$. The phase diagram shown in Figure 3 appears to agree with that of Massalski[21], which is actually derived from McAlister and Kahan[33], but the 4CSF model did not produce 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.

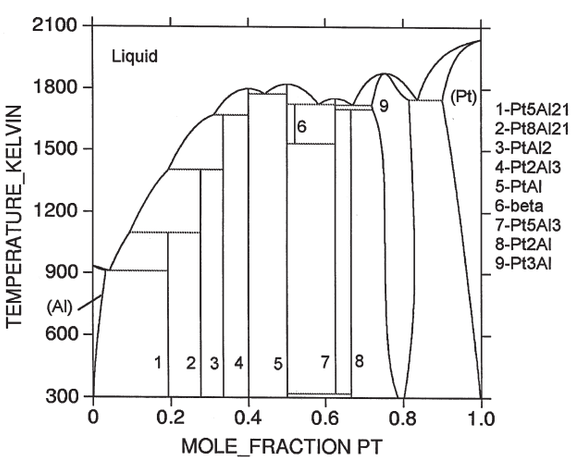
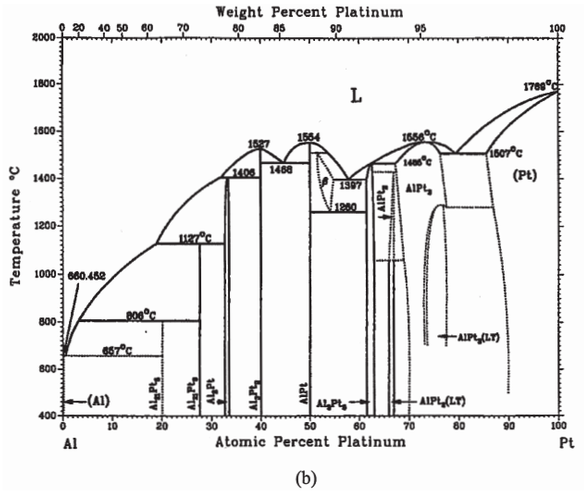


Figure 3—Comparison of Al-Pt phase diagrams: (a) Calculated[12]; (b) Experimental from Massalski[21] (McAlister and Kahan[33]); (c) Experimental from Oya *et al.*[34]



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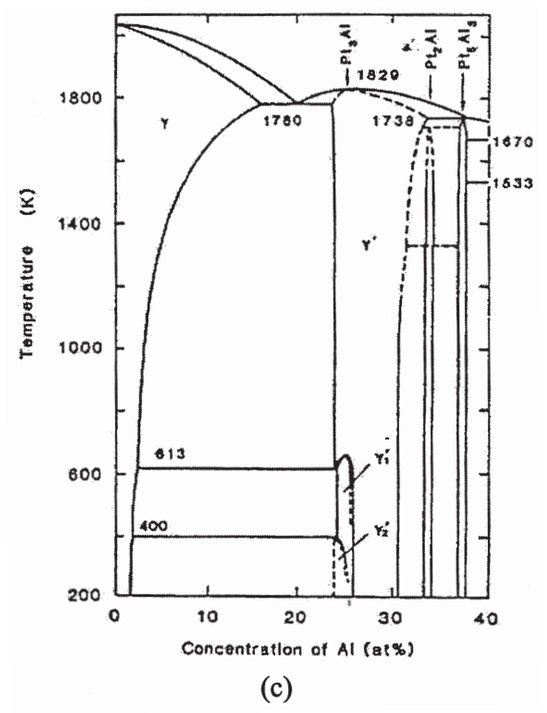

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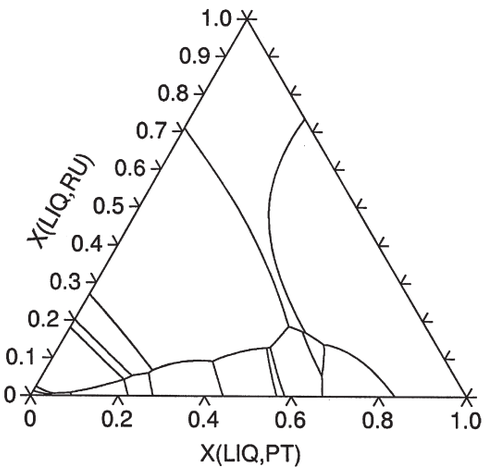
Figure 3—Comparison of Al-Pt phase diagrams: (a) Calculated[12]; (b) Experimental from Massalski[21] (McAlister and Kahan[33]); (c) Experimental from Oya *et al.*[34]

The congruent formation of the Pt_3Al phase and L → Pt_3Al + (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 as forming 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 $PtAl_3$ ($L1_2$) and Pt_2Al_2 ($L1_0$) 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[39]. The data from these alloys will be used to optimize the Pt_3Al phase in the Pt-Al binary.

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 data[40]. There were problems in the calculation of isothermal sections, which arose because the current models were not sufficiently



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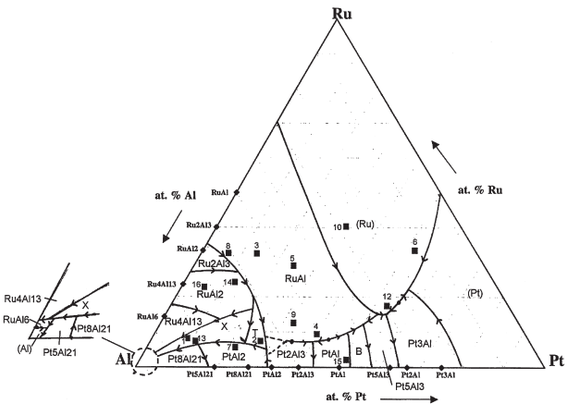

(b)

Figure 4—Comparison of Pt-Al-Ru liquidus surface projections: (a) Calculated by Prins *et al.*[40]; (b) Experimental by Prins *et al.*[19]

robust to allow for extension into the ternary. However, the liquidus projection showed very good agreement with the experimental projection (see Figure 4). Obviously, the two ~$Pt_{18}Al_{18}Ru_{64}$ and ~$Pt_{12}Al_{15}Ru_{73}$ ternary phases[19] 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 of the inadequacies in modelling the phases, which allowed Pt_2Al to be too stable.

Cr-Pt

An assessment by Oikawa *et al.*[41] showed that the two eutectic temperatures in the Cr-Pt binary should be reversed when compared with Massalski[21], as shown in Figure 5. This was initially thought to be wrong, even considering that the original data were very close (within 30±10°C). Thus, when work began on the Cr-Pt system, the work of Oikawa *et al.*[41] was ignored and the 4CSF model was used on the (Pt), Pt_3Cr and PtCr ordered phases[42]. However, the 4CSF model needed more data than were available, and consequently the fit was very poor[21]. 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.*[41], and those parameters are being used until subsequent experimental work indicates that a revision is necessary.

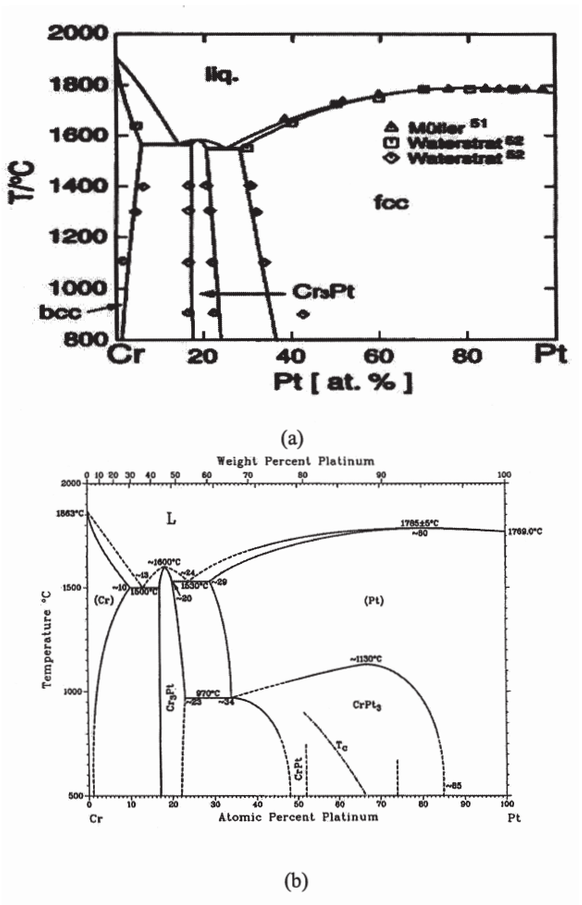

Figure 5—Comparison of Cr-Pt phase diagrams: (a) Calculated by Oikawa *et al.*[41]; (b) Experimental[21]

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. Further work and an extrapolation of the Pt-Cr, Cr-Ru and Pt-Ru binaries (the latter from Spenser's database[7]) demonstrated also that the calculations were poor[43], 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 discovered[44] that there were problems with Massalski's[21] 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 (owing to large atoms and high melting points), and Cr oxidizes easily on protracted annealing, despite precautions. However, this work is ongoing.

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 holds that as both are based on fcc, 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 argues 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 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 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 with 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 database[45], the Ni_3Al phase is modelled as ordered fcc, even though it solidifies separately. The latest database from Dupin[45] was used to draw the Ni-Al phase diagram, and the/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 modeling 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 if the data become available. A combination of Thermo-Calc™[46], Pandat[47] and MTDATA[48] software was used for the current database.

Pt-Cr

Until experimental results show otherwise, the assessment of Oikawa *et al.*[41] will be used, extrapolated into the ternary, and will then be re-optimized with experimental values from the Pt-Cr-Ru system. The assessment of Oikawa *et al.*[41] is shown in Figure 5. However, it was necessary to derive Gibbs energy parameters for the metastable hcp phase in the binary system. This was initially set to the same set of values as for the fcc phase, but the parameters were optimized using the ternary data described below.

Pt-Ru

It was initially thought that the Spencer database[7] 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 ~10°C between the maximum and the eutectic temperature, whereas that from SGTE is peritectic, which is consistent with available literature[49] and experimental work at Mintek.

Optimizing with data from Hutchinson[49] gave a good fit and reasonable coefficients. However, plotting the free energy curves demonstrated that Ru had an unusual 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. However, it was found that the most reasonable fit to the phase boundaries of the (Pt)+(Ru) two-phase field, where a few compositions had been measured, resulted in the appearance of a very shallow eutectic reaction. The phase diagram, optimized using WinPhad and calculated using Pandat, is given in Figure 6.

Cr-Ru

This system contains two intermetallic compounds: Cr_2Ru (sigma) 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, which is normal practice. The current model of choice for sigma is 10:16:4 (where the numbers denote numbers of atoms on each of the three sublattices, and the previous model was 8:18:4), which was in the Glatzel assessment[42], 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 (sigma) and Cr_3Ru would be line compounds. The Ru and Cr unary data were derived from Kaufman[50]. Since the reported reaction temperatures involving Cr2Ru (sigma) and Cr_3Ru were suspiciously convenient: ~750, ~800 and ~1 000°C, it was realised that there were problems with the system, and the rounded data represented the best that could be obtained from previous workers[21]. However, with no other data available, these had to be used. Attempts to measure these temperatures with a DTA were inconclusive[51]. The phase diagram gave a very good fit, as shown in Figure 7, compared with the experimental diagram[21].

Pt-Cr-Ru

Experimental results of the A15 Cr_3Ru and Cr_3Pt phases were not conclusive in showing whether the phases are

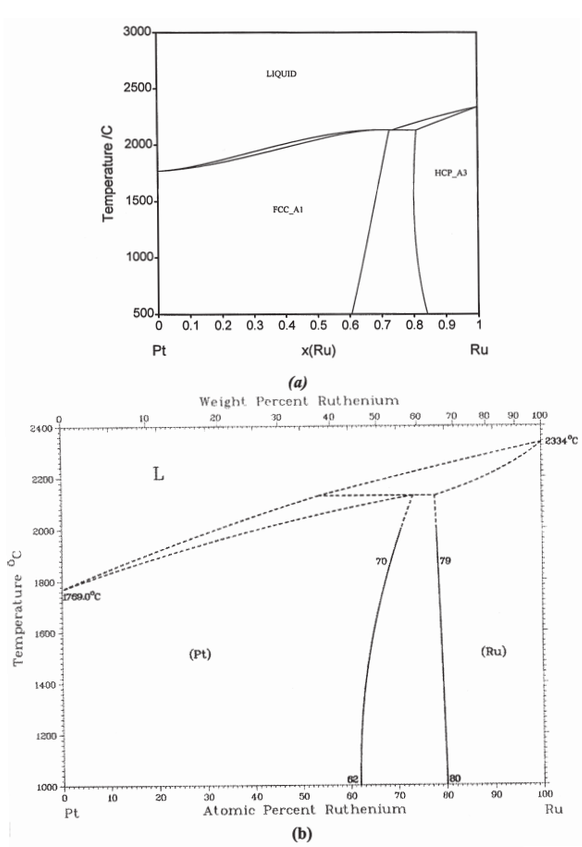

Figure 6—(a) Best calculated Pt-Ru phase diagram to date; (b) Experimental Pt-Ru phase diagram[21]

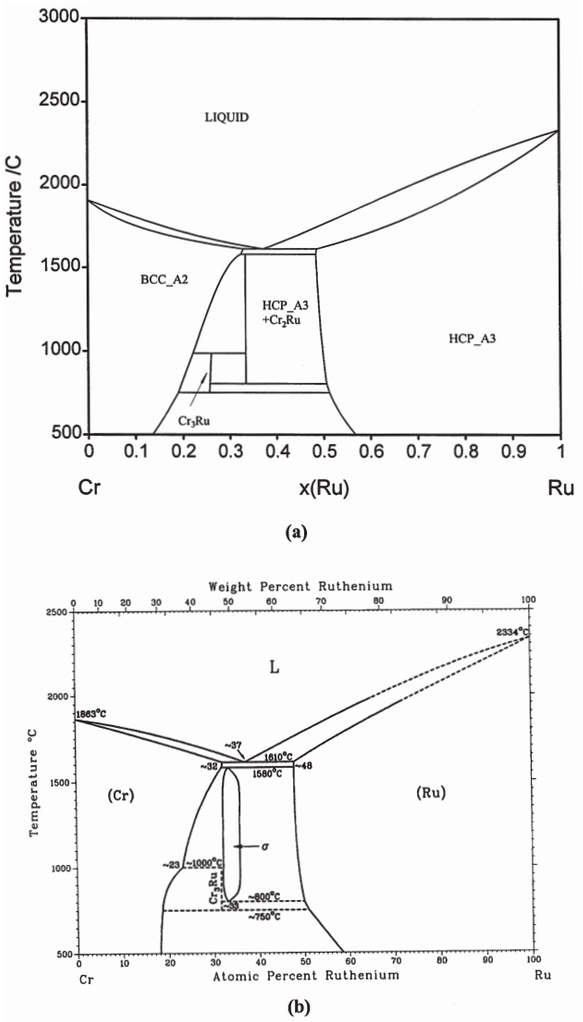

Figure 7—(a) Best calculated Cr-Ru phase diagram to date; (b) Experimental Cr-Ru phase diagram[21]

contiguous, despite the making of two more samples of intermediate compositions between Cr_3Ru and Cr_3Pt. These samples are currently being annealed at ~850°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 phase[52] 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[52] 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 (giving 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, an interaction parameter to increase the phase extensions into the ternary was found for hcp PtCr. The projected liquidus surface is shown in Figure 8. It is an improvement on the assessment by Glatzel *et al.*[42], 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 previously[42], and agrees better with the experimental results.

The thermodynamic description of the ternary system was optimized using the experimental data of Zhao[54], as this set

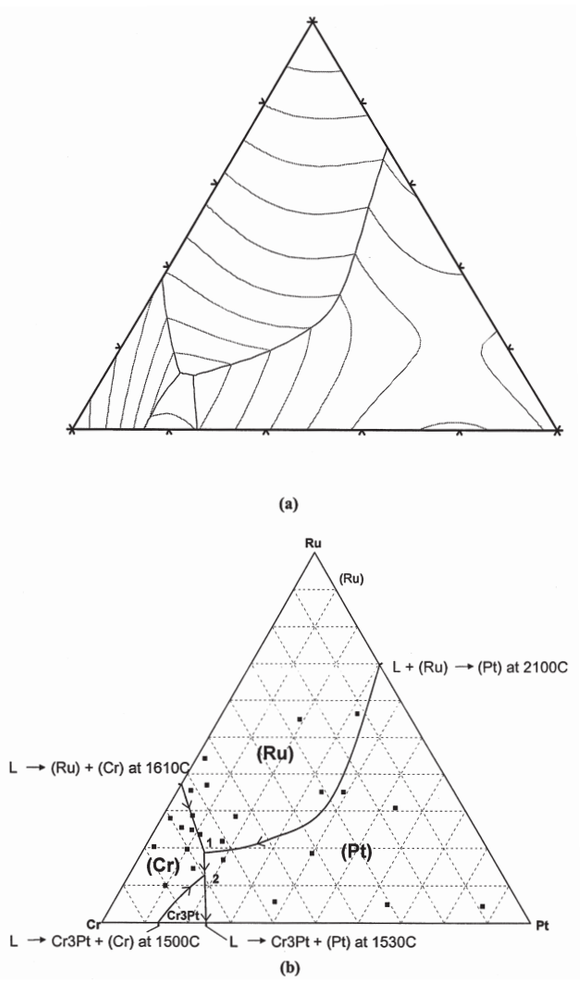

Figure 8—(a) Best calculated liquidus surface to date for the Pt-Cr-Ru system; (b) Experimental liquidus surface for Pt-Cr-Ru[15,53]

of data seemed to be more complete and self-consistent, and Mintek's data[15–16] was affected by coring. The assessment module of MTDATA was used to perform the optimization. During the optimization process it was found that it was necessary to adjust only the Gibbs energy description of the metastable hcp-phase in the Cr-Pt binary in order to get a reasonable fit with the experimental phase diagram data for the fcc and hcp phase boundaries. No ternary interactions were required for these phases[55].

The experimental data for the A15 phase fitted reasonably well, although this was little improved by allowing the optimization to give a Gibbs energy description for the metastable Pt_3Ru A15 phase. The A15 phase extends from the Cr-Pt edge as required, but too far into the ternary. Also, the A15 phase field is not wide enough as it extends into the ternary, which is probably because the phase is modelled with a very narrow homogeneity range in the Cr-Ru system. Improvement to the modelling of this phase in the binary system would undoubtedly improve the overall modelling of this phase, but this would require further experimental study of its stability range. However, the fit to the experimental bcc phase diagram data is very good. The calculated phase diagram for 1 200°C showing the experimental data is given in Figure 9. The fit with the experimental data from Süss *et al.*[16] is not so good, particularly with respect to the (Ru) hcp phase boundary, but this could be due to coring effects. Again, this could be improved by a better description of the A15-phase. The calculated diagram for 1 000°C is given in Figure 10.

Work on the Pt-Al-Cr-Ni database at the University of Bayreuth

First-principle calculations

At the University of Bayreuth, a different approach was used to compensate for the lack of data using first principles or *ab initio* calculations for the enthalpy of formation of compounds can be calculated. These calculations are complex and time-consuming, and are based on density functional theory as described by Kohn and Sham[56]. As these results are often hard to determine experimentally, this technique is quite powerful. The results can be directly used in a thermodynamic description of the alloy systems[57]. The programme VASP[58] has been used to calculate the enthalpies of formation of the ordered compounds. At this stage no magnetic contribution has been added to the calculations since there is some discrepancy; for the $L1_2$-ordered $CrPt_3$ Kussmann *et al.*[59] observed ferromagnetic behaviour, while Pickard *et al.*[60] observed ferrimagnetic behaviour. The total energies of the pure elements were compared with those obtained by Wang *et al.*[61] with very good agreement.

Resulting Cr-Pt phase diagram

The phase diagram after a thermodynamic optimization process is shown in Figure 11[62]. The calculated phase diagram shows a very good agreement with experimental data. The modelled eutectic temperatures are within the stated experimental errors and agree with Venkatraman and Neumann[63] (the basis of Massalski[21]), rather than Oikawa *et al.*[41]. The ordering reaction still needs to be modelled correctly. A later version of the Pt-Cr phase diagram is promising[64]. The missing $L1_2$ Pt_3Cr phase at low temperatures may be because the magnetic properties have not yet been taken into account. Since all the Gibbs energies have now been modelled, it is possible to calculate further thermodynamic data. Figure 12 shows a comparison between the calculated and the experimental chemical activities[65,67]. Using the first principle calculations in the thermodynamic model produced $L1_2$ Cr_3Pt at low temperatures, and indicates that the platinum-rich side of the phase diagram should be further examined, probably using the diagram from Zhao[64].

The Pt-Al-Cr-Ni system

The thermodynamic assessment of the Cr-Pt system has already shown that many regions of the binary phase diagram are relatively unknown. The *ab initio* calculations

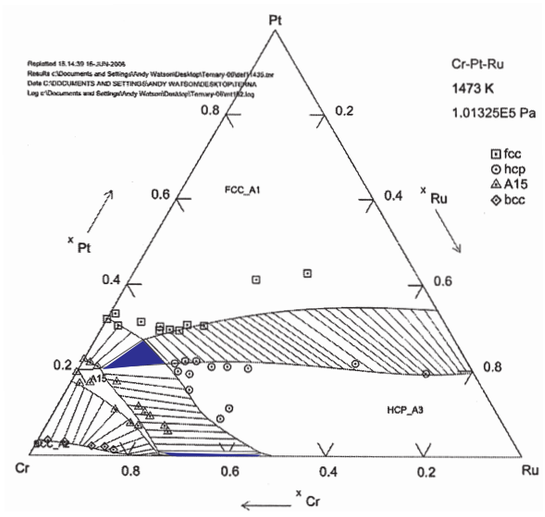

Figure 9—Calculated isothermal section for the Cr-Pt-Ru system for 1200°C with experimental data from Zhao[54]

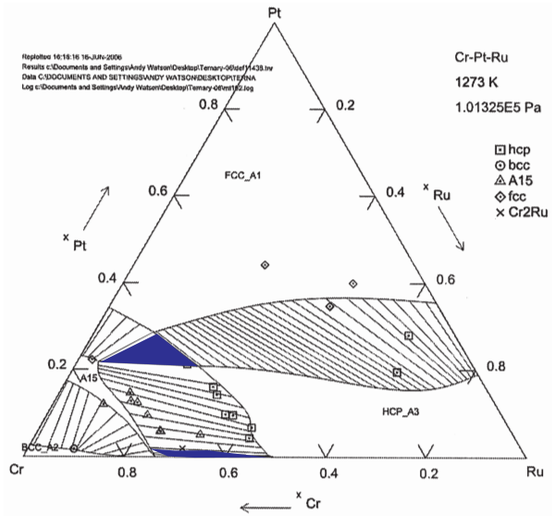

Figure 10—Calculated isothermal section for the Cr-Pt-Ru system for 1000°C with experimental data from Süss *et al.*[16]

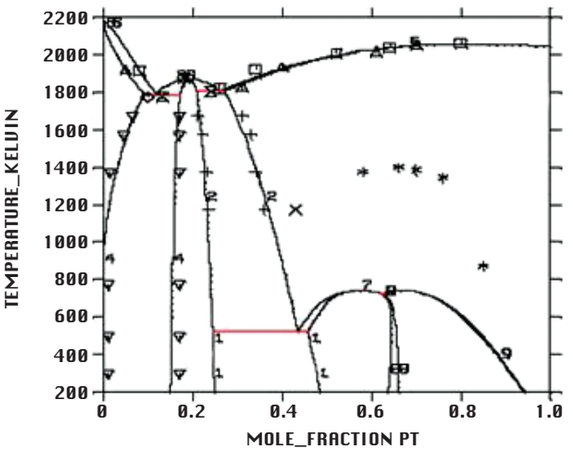

Figure 11—Cr-Pt phase diagram calculated using ab initio values. Symbols denote experimental values[63,65]

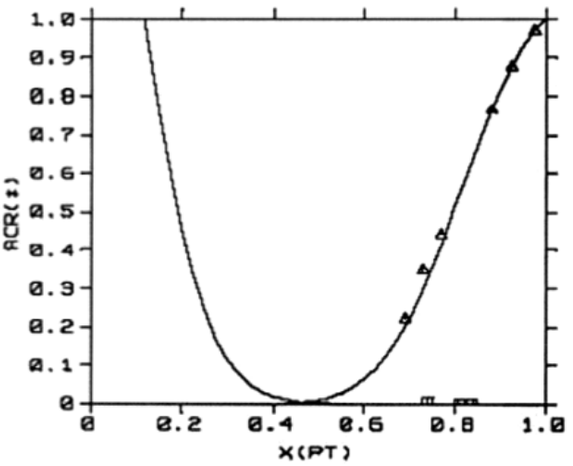

Figure 12—Calculated activity of Cr and Pt at 1500°C (with respect to the pure phases at 1500°C) compared with experimental results[66–67]

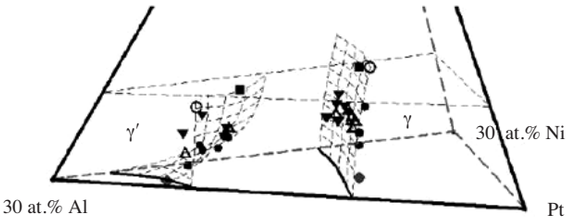

Figure 13—Pt-Al-Cr-Ni phase diagram of the Pt rich side[70]

used here show that a stable Cr_3Pt-$L1_2$ structure is achieved (Figure 11). Greenfield and Beck[68] discovered a stable $L1_2$ structure at 63 at.% Cr, although it is not shown in experimental phase diagrams[63]. More experimental work using rigorous X-ray diffraction techniques needs to be done to substantiate the $L1_2$ and $L1_0$ phase regions. Many experiments on the Pt-rich side of the Pt-Al-Cr-Ni system have already been carried out[69], and Ni additions increase the curvature of the γ' solvus, as shown in Figure 13[70]. However, only when the experimental work is completed can a database for the Pt-Al-Cr-Ni system be created.

Conclusions

There have been some problems in the binary systems attributable to a lack of data. These are most notable in Pt-Al, because of the modelling and the uncertainty of the Pt_3Al 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. Any binary system which contains uncertainties is experimentally difficult for a variety of reasons. The most accurate data relate to systems that are commercially important. Good models can be very simple, and more complex models need a greater number of data. Many of the problems were due to insufficiently tested 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.

Currently, the Cr-Ru and Pt-Ru systems have been modelled using the experimental phase diagram data published in the literature. The descriptions for these binary systems have been combined with those for the Cr-Pt system from Oikawa *et al.*[41] to calculate isothermal sections of the ternary system. It was found that a reasonable fit to the ternary experimental data provided in the literature could be achieved by producing a suitable description for the metastable binary Cr-Pt hcp phase. Further work is required to improve the fit of experimental phase diagram data for the A15-phase.

Work has already started on the Pt-Al-Cr-Ni database at the University of Bayreuth in Germany, using data calculated from *ab initio* techniques as additional inputs. It is planned that the Pt-Al-Cr-Ru and Pt-Al-Cr-Ni databases will be merged, and work is already being done for this purpose.

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