Phase Diagram Calculations for High-Temperature Structural Materials [and Discussion]

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Phase diagram calculations for high-temperature structural materials

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Materials in use at high temperatures can reach states which are close to equilibrium and knowledge of the stable phase structure at fabrication and working temperatures can therefore be very important. The field of high-temperature structural materials provided one of the areas where thermodynamic phase diagram calculations were first used some two to three decades ago. However, although some general features of phase equilibria were predicted reasonably well, the early attempts were not able to provide sufficient accuracy for more general, practical use. Recent work has now shown that it is possible to make very accurate predictions for phase equilibria in a number of high-temperature structural materials and it is possible to demonstrate that predictions for phase equilibria in 'real' multicomponent alloys provide results close to those which are measured experimentally. This paper will present typical results which can now be obtained for γ-TiAl-based intermetallics and Ni-based superalloys and some specific examples of usage will be shown. A further advantage of the CALPHAD (calculation of phase diagrams) route is that other properties can be predicted using input data from the calculations, for example non-equilibrium solidification phenomena, time-temperature-transformation diagrams, antiphase domain boundary and stacking fault energies. This extension of the CALPHAD method will be briefly discussed.

1. Introduction

The calculation of phase equilibria using what has become known as the CALPHAD (calculation of phase diagrams) method is becoming increasingly popular. The method requires firstly a mathematical description of the thermodynamic properties of the system of interest. If the phases of interest are stoichiometric compounds, e.g. NaCl, the composition is defined and a mathematical formula is then used to describe fundamental properties such as enthalpy and entropy. Where phases exist over a wide range of stoichiometries, which is the usual case for metallic materials, other mathematical models are used which account for the effect of composition changes on free energy. All types of models require input of coefficients which uniquely describe the properties of the various phases and these coefficients are held in databases which are either in the open literature or are proprietary.

Once the thermodynamics of the various phases are defined, an applications

software package which performs a series of calculations based on the thermodynamic data is then used to calculate phase equilibria. This is usually done via a Gibbs free energy minimization process. There are now a variety of such software packages available which can perform complex multicomponent calculations and for more information the recent review by Bale & Eriksson (1990) provides a fairly comprehensive coverage of these.

The field of high-temperature structural materials provided one of the earliest testing grounds for phase diagram calculations of the CALPHAD type. Early work by Kaufman and co-workers (see, for example, Kaufman & Nesor 1974*a*, *b*, 1975) showed that it was possible to provide some guidance in the search for high-temperature eutectic reactions in Ni-based ternary alloys. This information could then be used in the search for directionally solidified eutectic materials. However, although Kaufman and co-workers produced datasets which could be used for calculations in a wide number of ternary systems, it has became increasingly clear that the assumptions made in their simple model types, i.e. regular and subregular solution, inherently limit accuracy and general applicability.

As newer models and software packages have come to the fore the CALPHAD method has advanced to the stage where it can be legitimately expected that predictions for phase equilibria in multicomponent systems should provide answers close to that which would be measured experimentally. An example of such work is the effort devoted over the last two decades to multicomponent ferrous alloys by the Scientific Group Thermodata Europe (Ansara & Sundman 1987), and in particular by the Royal Institute of Technology, Stockholm, Sweden, a member of this group. Results have clearly demonstrated the excellent levels of accuracy that can now be attained which in turn allows design engineers to model materials of this type with confidence.

Unfortunately, until very recently there have been very few, if any, databases of equivalent accuracy currently in existence for other material types. This has presented severe problems for CALPHAD calculations with high-temperature materials of current usage, for example Ni-based superalloys, Ti alloys and γ-TiAl-based alloys. The present paper discusses new work in the field of Ti- and Ni-based alloys and demonstrates that high levels of accuracy can be achieved in predicted equilibria for multicomponent alloys of these types. Furthermore, the same database which is used for equilibrium predictions can be used for the prediction of other effects not normally associated with CALPHAD type calculations: (i) non-equilibrium solidification behaviour of superalloys during casting, providing results for fraction of solid transformation as a function of temperature, microsegregation, formation of interdendritic phases, heat evolution, etc.; (ii) time-temperature-transformation (TTT) diagrams for σ-phase growth; (iii) antiphase domain boundary energies in γ' and stacking fault energies in γ.

2. The CALPHAD approach

The basis of the CALPHAD approach is the mathematical description of the free energy of the various chemically distinct phases in an alloy system. There are now a variety of models available to describe the thermodynamic properties of phases which can be, for example, stoichiometric compounds, solution phases, gaseous species, ionic materials, intermetallic compounds, ceramic types, etc. Several these models are listed by Hillert (1986) and Eriksson & Hack (1989).

The integral free energy of formation (ΔG) of a pure species or stoichiometric compound is given simply by the equation

$$\Delta G = \Delta H + T\Delta S, \tag{2.1}$$

where ΔH is the enthalpy of formation, T is the temperature and ΔS is the entropy of formation. For the case of a 'solution' phase where mixing of the various components takes place its free energy (ΔG) can be written generally as

$$\Delta G = \Delta G^{\circ} + \Delta G_{\mathrm{mix}}^{\mathrm{ideal}} + \Delta G_{\mathrm{mix}}^{\mathrm{xs}}, \tag{2.2}$$

where ΔG° is the free energy contribution of the pure components of the phase, $\Delta G_{\mathrm{mix}}^{\mathrm{ideal}}$ is the ideal mixing term and $\Delta G_{\mathrm{mix}}^{\mathrm{xs}}$ is the excess free energy on mixing of the components. There are also terms associated with (2.1) the effect of pressure which is important to geological systems and (2.2) the effect of magnetism which is important to ferrous alloys. It is not the purpose of this paper to describe in detail the various models which are used to describe the thermodynamic properties of phases, but it is useful to briefly discuss some of the models which are available and where they are applied.

(*a*) Ideal solution model

The simplest model is the ideal solution model where interactions between components in the phase of interest are considered to be negligible and the free energy of mixing is given by

$$\Delta G_{\mathrm{m}} = x_i \sum_i \Delta G_i^{\circ} + RT \sum_i \ln x_i, \tag{2.3}$$

where x_i is the mole fraction of component i, ΔG_i° defines the free energy of the phase in the pure component i and R is the gas constant. In gases, ideal mixing is often assumed and this assumption is usually quite reasonable. However, in solid phases the interactions between components are far more significant and cannot usually be ignored.

(*b*) Non-ideal solution models

To deal with non-ideal interactions a further term is added to (2.3) which becomes

$$\Delta G_{\mathrm{m}} = x_i \sum_i \Delta G_i^{\circ} + RT \sum_i \ln x_i + \sum_i \sum_{j>1} x_i x_j \sum_v \Omega_v (x_i - x_j)^v. \tag{2.4}$$

The final term is based on a Redlich–Kister–Muggianu (RKM) equation which considers the free energy of a many-component solution phase to be a product of the summed binary interactions and Ω_v is an interaction parameter dependent on the value of v. In practice the value for v does not usually rise above 3. Equation (2.4) assumes higher-order interactions are small in comparison to those which arise from the binary terms but this may not be always the case. Ternary interactions are often considered but there is little evidence of the need for interaction terms of a higher order than this. Various polynomial expressions for the excess term have been considered other than the RKM equation (see, for example, the reviews by Ansara (1979) and Hillert (1980)). However, all are based on predicting the properties of the higher-order system from the properties of the lower-component systems.

Equation (2.2) is normally used in metallic systems for substitutional phases such as liquid, BCC, FCC, etc., and in this mode its use is extensive. It can also be used to a limited extent for ceramic systems and useful predictions could be found in the case of quasi-binary and quasi-ternary oxide (Kaufman & Nesor 1978) systems. However, for phases where components occupy preferential sites on crystallographic sublattices such as interstitial solutions, ordered intermetallics, ceramic compounds, etc., simple substitutional models are not generally adequate and sublattice models are now becoming increasingly popular.

(c) *Sublattice models*

One of the earliest treatments of phases with distinct sublattice occupation was by Hillert & Staffansson (1970) who considered the case of a phase with two sublattices. The sublattice occupancy is shown schematically below:

$$(A, B)_u (C, D)_v.$$
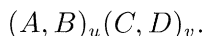
For the two sublattice model ΔG° is written as

$$\Delta G^\circ = y_A^1 y_C^2 \Delta G_{A:C} + y_A^1 y_D^2 \Delta G_{A:D} + y_B^1 y_C^2 \Delta G_{B:C} + y_B^1 y_D^2 \Delta G_{B:D}, \qquad (2.5)$$

where

$$y_i^{\mathrm{s}} = n_i^{\mathrm{s}} / \sum_i n_i^{\mathrm{s}} \qquad (2.6)$$

and

$$\sum_i y_i^{\mathrm{s}}. \qquad (2.7)$$

The ideal entropy of mixing is written as

$$\Delta G_{\mathrm{mix}}^{\mathrm{ideal}} = RT[u(y_A^1 \ln y_A^1 + y_B^1 \ln y_B^1) + v(y_C^2 \ln y_C^2 + y_D^2 \ln y_D^2)]. \qquad (2.8)$$

The $\Delta G_{\mathrm{mix}}^{\mathrm{xs}}$ term considers the interactions between the components on the sublattice and can be quite complex, see for example Ansara *et al.* (1988). More recently Sundman & Ågren (1981) extended this model to take into account multiple sublattices and their model is used extensively in the present work.

3. Results and discussion

(a) Ti–Al–X *systems*

The α_2-Ti$_3$Al and γ-TiAl compounds have been the centre of considerable interest as a material which would extend the applicability of Ti-based alloys to higher temperature regimes and areas where good oxidation and burn resistance are important. Initially, materials based on Ti$_3$Al, the so-called super-α_2 class of alloys, were seen as new generation materials. They are potentially stronger than the γ-TiAl-based alloys and can be made more ductile. However, the superior oxidation resistance and comparable fracture toughness of the γ-TiAl based alloys has seen these materials come to the fore.

Similarly to conventional Ti-alloys, the properties of γ-TiAl based alloys are strongly controlled by their microstructure. The various microstructure types and their effect on mechanical properties are now well documented (Kim 1994). Basically this can be understood from the Ti–Al phase diagram (figure 1). Levels of Al usually lie in the range 45–50 at.% where it is possible to anneal at high temperatures to produce a structure that is fully α(HCP). The high temperature α decomposes both by precipitating γ in the $\alpha + \gamma$ two-phase region and
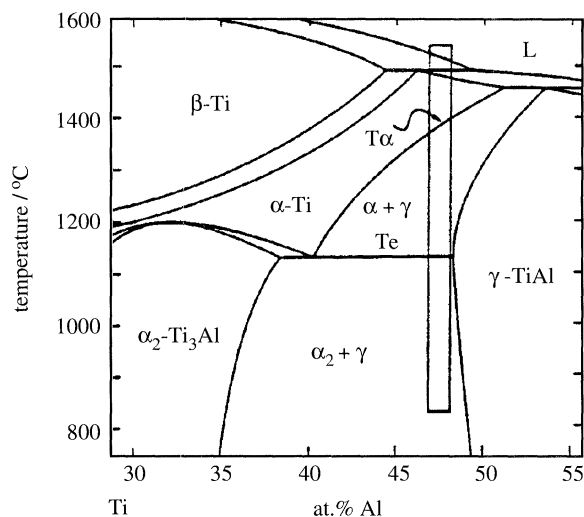
Figure 1. Ti–Al phase diagram (Kim 1991). Shaded area indicates Al composition of early γ-TiAl alloys.

importantly through decomposition by a eutectoid reaction to α_2 and γ. The microstructure then is a mixture of γ formed at high temperatures in the $\alpha + \gamma$ two-phase region and a lamellar structure of $\alpha_2 + \gamma$. By quenching from the α region it is also possible to by-pass the precipitation of γ-TiAl and produce a fully lamellar structure. The ratio of primary γ to lamellar $\alpha_2 + \gamma$ is a critical factor in controlling mechanical properties and therefore phase diagram calculations have a potentially important part to play in the design of alloys, particularly with regard to thermo-mechanical processing schedules.

One of the major difficulties of the modelling is the Ti–Al binary system itself. In a recent Japanese report 42 versions of this diagram had been reported previous to 1990. With recent work this number is now well over 50. Phase diagram modelling for Ti–Al has been undertaken by the present author (Saunders 1990) and this forms the basis for Ti–Al–X systems now being modelled as part of a current COST 507 project (figure 2). Broadly speaking, the form of the diagram is quite well established now. The existence of the Ti$_3$Al and TiAl compounds is not disputed and their range of solubility reasonably well understood. The main outstanding problems lie in the determination of the exact position of the $\alpha + \gamma$ boundaries and whether the $\alpha + \beta$ phase boundary touches the α_2 phase field. The former problem relates to processing and microstructure formation and is therefore very important.

The extension to ternaries has been attempted by Kattner & Boettinger (1992) who used a two-sublattice model for the α_2-Ti$_3$Al and γ-TiAl phases in their description of the Ti–Al–Nb system. They were able to produce a diagram which substantially agreed with that observed in the published literature up to that point. However, although the form of the diagram appears reasonable they did not take into account the ordering of the β phase to the B2 CsCl structure which is observed in almost all Ti–Al–X systems where X is one of the refractory metals such as Nb and V. Work by the present author on both Ti–Al–Nb and Ti–Al–V has shown the importance of including this ordering in the accurate representa-
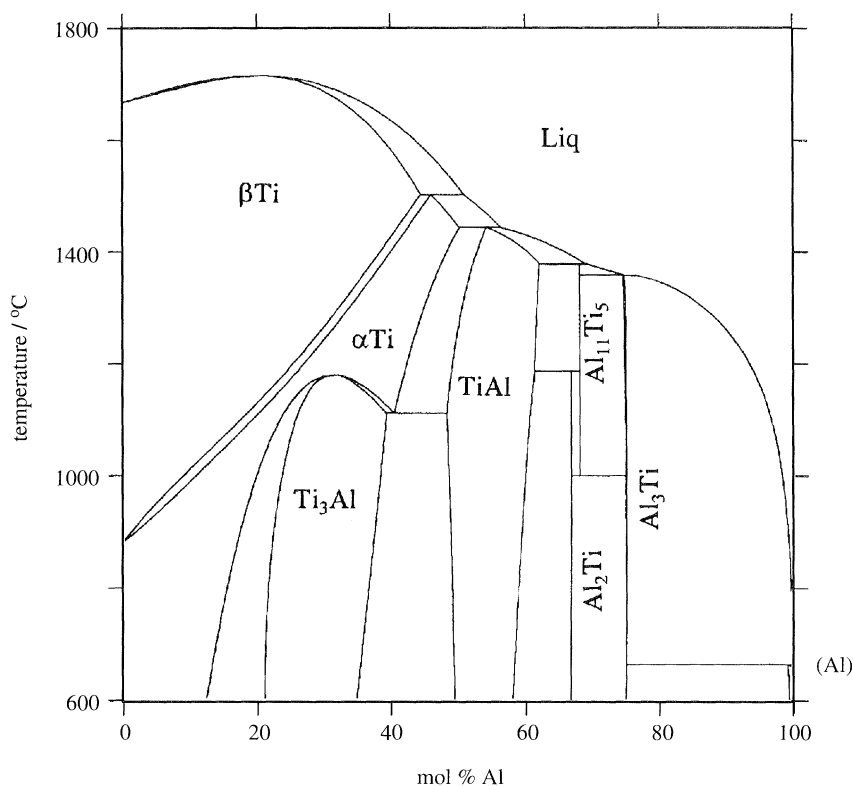
Figure 2. Calculated Ti–Al phase diagram (Saunders 1990).

tion of phase equilibria and it is of particular interest to be able to differentiate between the ordered and disordered form when considering mechanical properties.

Figures 3 and 4 show calculated isothermal sections at 1000 and 1200 °C for Ti–Al–Nb. They show the extension of the various intermetallic compounds, both Nb–Al based and Ti–Al based, into the ternary. The $\beta \rightarrow$ B2 transformation is second order and its loci of composition at each temperature are shown by dashed lines. Of particular interest is the reappearance of the B2 phase as an isolated region close to γ-TiAl which is in excellent agreement with the detailed work of Hellwig (1992).

The B2 phase has been modelled using a two-sublattice ordering model first proposed by Ansara *et al.* (1988). The present author (Saunders 1989) then showed how this model could be made equivalent to a Bragg–Williams–Gorsky model which enables the correct model parameters to be used to produce the required second-order transformation. Further work on Ti–Al–V (Saunders *et al.* 1994) has confirmed the importance of taking into account the B2 ordering and initial work on Ti–Al–Mn–Nb has shown that the modelling is extendable to multicomponent alloys.

(*b*) Ni-*based superalloys*

Ni-based superalloys form one of the oldest class of high-temperature structural materials. They can be used at a higher value of T/T_{m} than almost any
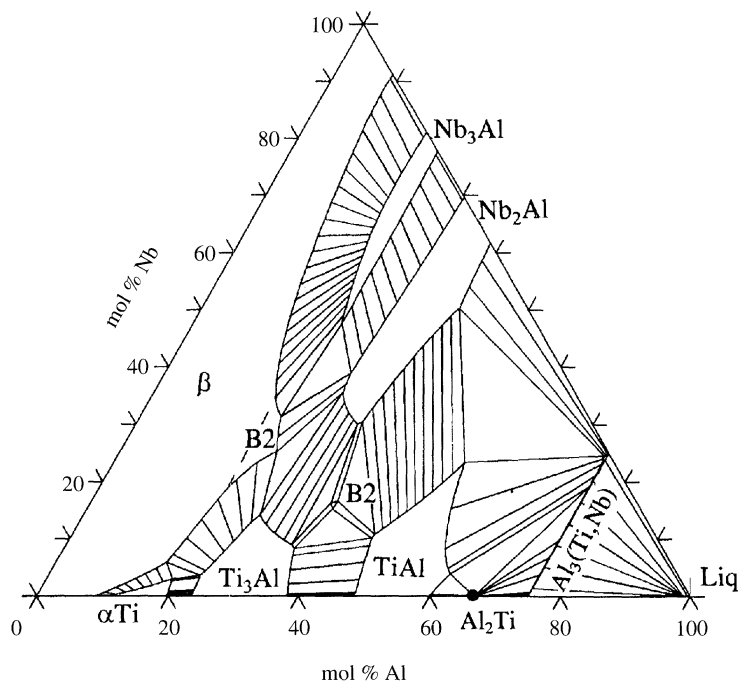
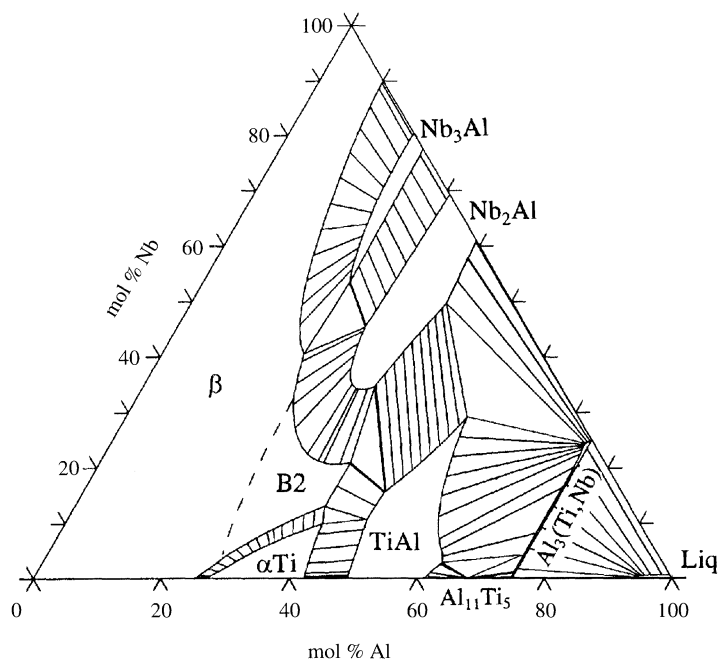Figure 3. Calculated isothermal section for Ti–Al–Nb at 1000 °C.

Figure 4. Calculated isothermal section for Ti–Al–Nb at 1200 °C.

other metallic material which allied to a high strength and excellent oxidation and corrosion resistance make them one the most widely used material types in aerospace and land-based gas turbine engines.

The strength of Ni-based superalloys comes from the precipitation of the ordered L1$_2$ compound (γ'), based on Ni$_3$Al, in a ductile FCC, Ni-based matrix (γ) and control of γ/γ' microstructure is one of the governing factors in choice of thermo-mechanical processing cycles. It is therefore of great interest to be able to predict γ/γ' equilibria accurately. Superalloys are also one of the most highly alloyed of all material types and with additions of elements such as Co, Cr, Mo and W the matrix becomes unstable with respect to embrittling TCP phases such as σ, μ and Laves phases, and the addition of C leads to the formation of a variety of carbide phases which can act as sites for TCP phases formation.

Both of the above factors are critical in the design and usage of Ni-based superalloys. Much work has been done via mathematical techniques such as regression analysis on γ/γ' equilibria (see, for example, Dreshfield & Wallace 1974) and (Harada *et al.* 1988), while the use of PHACOMP methods in predicting σ-phase formation is extensive. The limitations of regression analysis are straightforward. Firstly, the method relies on substantial previous experimentation which must be accurate. Secondly it is an interpolative technique and extrapolation outside the composition and temperature regime of the experiments used to provide the results for analysis can be quite unreliable.

PHACOMP relies on the simple concept of an average electron hole number, $\bar{N}_v$, which is made up of a weighted average of N_v values for the various elements. In itself the concept behind PHACOMP is theoretically simple and easy to use. However, there are a number of questions concerning its use and theoretical justification. For example the values of N_v used to calculate $\bar{N}_v$ are usually empirically adjusted to fit experience and the model fails to explain why σ is not observed in the binary Ni–Cr or Ni–Mo systems but appears only in the Ni–Cr–Mo ternary. Furthermore, although it pertains to describe a line for the phase boundary of γ and σ it gives no information on the temperature range where σ may be stable, nor is there information on the interaction of this boundary with the γ/μ or $\gamma/$Laves boundaries.

Four years ago a development programme involving Thermotech and Rolls-Royce plc, Derby was begun to produce a multicomponent database for the prediction of phase equilibria in Ni-based superalloys. This work has now reached the stage where a database exists containing the following elements:

<div align="center">

Ni Al Co Cr Hf Mo Nb Ta Ti W Zr B C

</div>

It is therefore at a point where real industrial superalloys can be routinely handled. As well as simple predictions concerning freezing ranges, γ' solvus temperatures, etc., the database allows the user to predict the composition and temperature conditions under which the various secondary phases such as σ, μ, Laves and η can form (successfully differentiating between them) and takes into account the various types of carbides found in superalloys.

Part of the project has involved a validation procedure for the accuracy of the database which, particularly with respect to γ/γ' equilibria, can be statistically quantified. Figure 5 shows the comparison between predicted and experimentally observed critical temperatures such as γ' solvus (γ'_s), liquidus and solidus where the average difference between predicted values and those observed experimentally is of the order of 10 °C. Extensive work has been done on measurements concerning γ/γ' equilibria and it is possible to compare in detail predicted values with those observed experimentally.
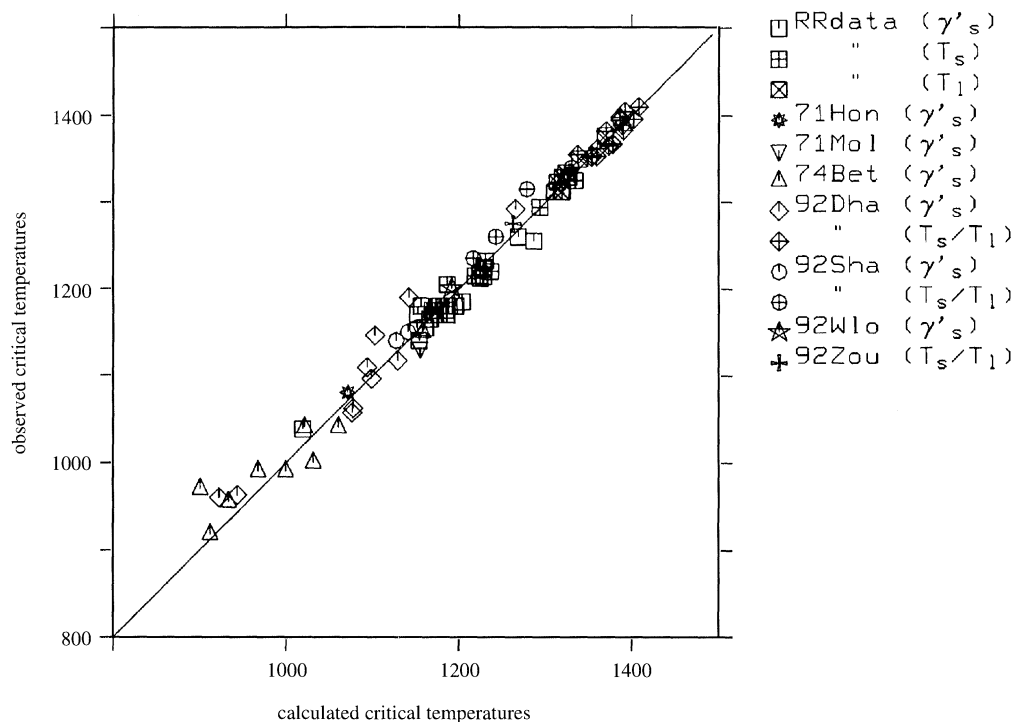
Figure 5. Comparison between calculated and experimentally observed critical temperatures in Ni-based superalloys.

Figure 6 shows a comparison between predicted and observed amounts of γ' in a variety of superalloys where the average difference between predicted values and those observed experimentally is of the order of 4%. In the comparison, results can be in either weight% or volume%. For the latter case, as lattice mismatches are so small, mole% values will give almost identical values to volume%. Figure 7*a–g* shows comparisons of the chemical compositions of γ and γ'. Where experimental results are given in weight% they have been converted to atomic% to provide a consistent basis for comparison. The average difference between predicted values and those observed experimentally is of the order of 1 at.% for Al, Co, Cr and 0.5 at.% for Mo, Ta, Ti and W. Table 1 gives some examples of superalloys used in the validation procedure.

Apart from its success in predicting liquid phase relationships and γ/γ' equilibria the database has been able to successfully predict transitions between the σ and μ phases and to differentiate between the different types of carbide that can be form in Ni-base superalloys. It has also been strikingly successful at predicting the susceptibility to η phase formation, for example in alloys such as Nimonic 263 (Betteridge & Heslop 1974) and IN939 (Shaw 1992, personal communication).

Some of the ways in which the database can be used are shown by taking the specific example of Udimet 720 (U720). Figure 8 shows a calculated phase percent plot for this alloy which shows the various phases which exist in the alloy as a function of temperature; the alloy composition is given in table 2. The alloy was originally developed for land-based gas turbine applications and for long-term service at temperatures up to 900 °C. However, its excellent forging character-
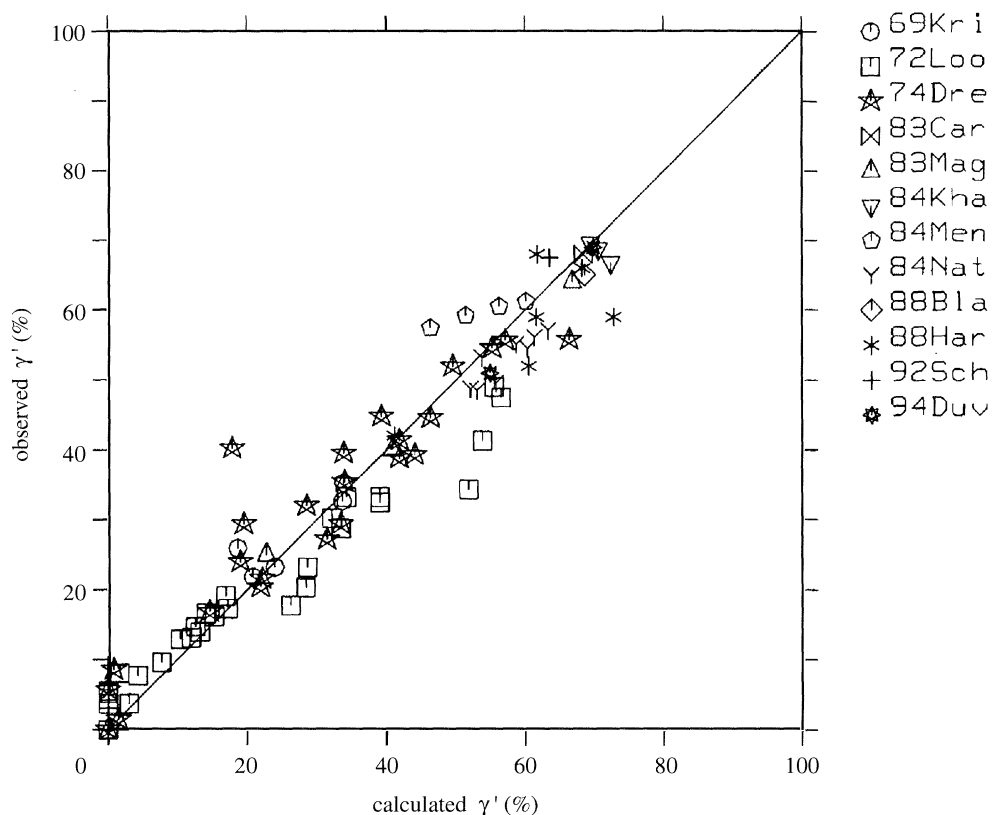
Figure 6. Comparison between calculated and experimentally observed amounts of γ' in Ni-based superalloys.

Table 1. *Some alloys used in the validation of the* Ni-*based superalloy database*

Inconel 700	Nimonic 263	MAR-M247
Nimonic 115	EPK 55	PWA 1480
René 41	EPK 57	IN738LC
Udimet 500	Udimet 520	SRR 99
Udimet 700	CMSX-2	AF2 1DA
Waspaloy	IN939	AP1
Nimonic 80A	IN 100	APK6
Nimonic 81	Udimet 710	CH88-A
Nimonic 90	MXON	Udimet 720
Nimonic 105	B1900	MC2

istics and mechanical properties suggested it could be used as a disc alloy. Unfortunately, although long-term exposure of the alloy at these high temperatures showed only a minor susceptibility to formation, tests done at 750 °C showed that σ formed very readily and in large amounts (Keefe *et al.* 1992). To overcome
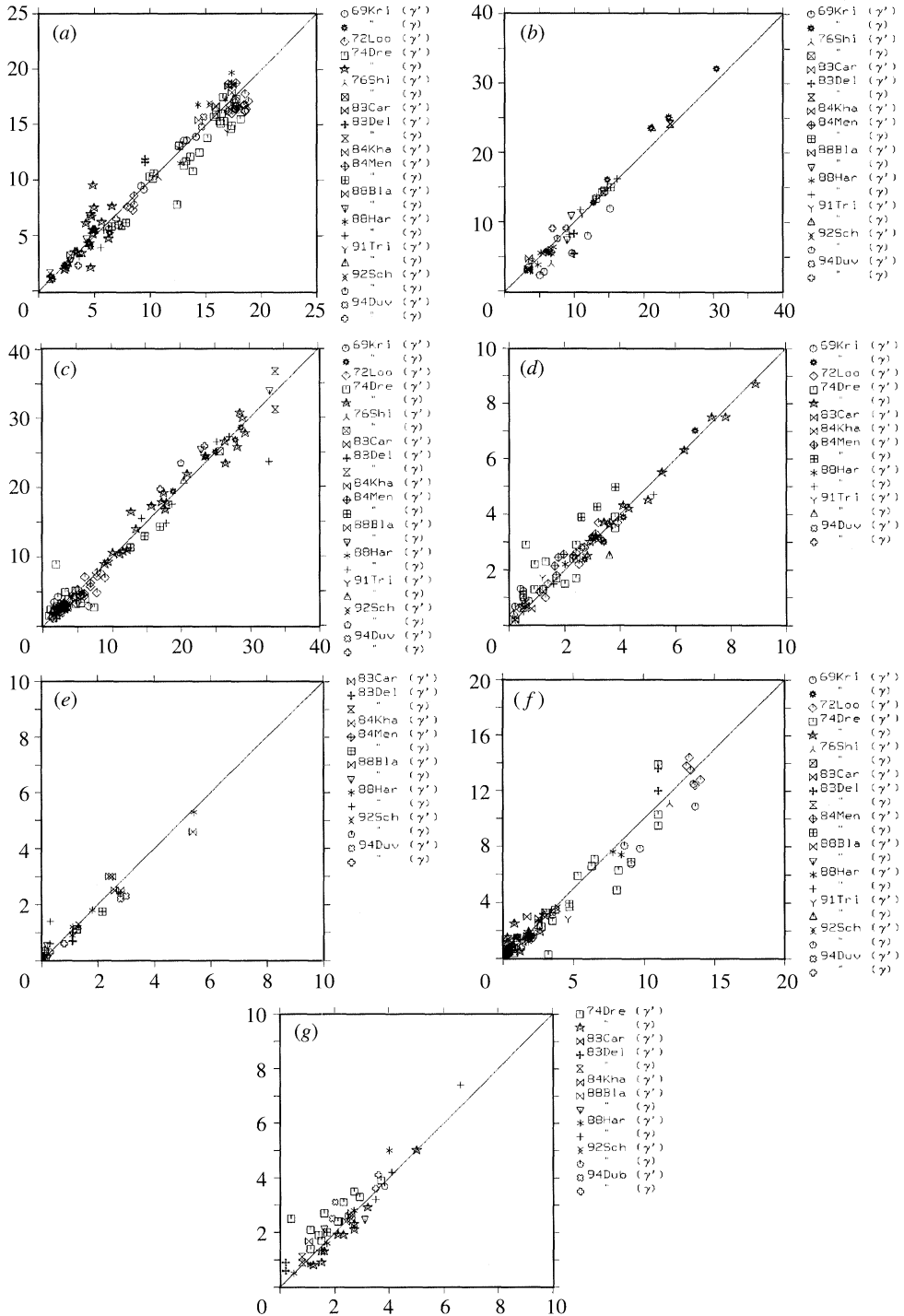
Figure 7. Comparison between calculated and experimentally observed compositions of γ' in Ni-based superalloys. (*a*) Al, (*b*) Co, (*c*) Cr, (*d*) Mo, (*e*) Ta, (*f*) Ti and (*g*) W.
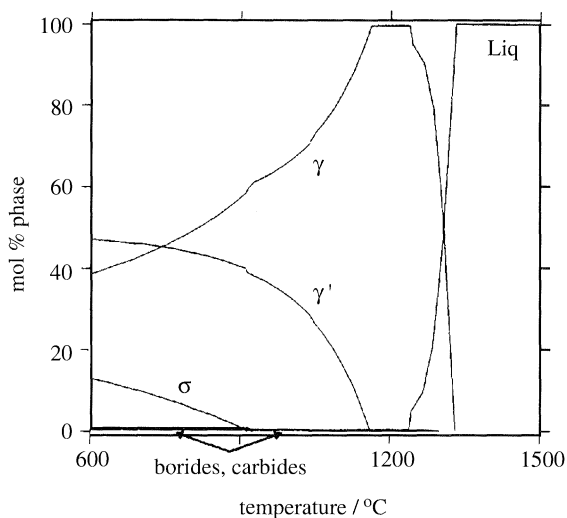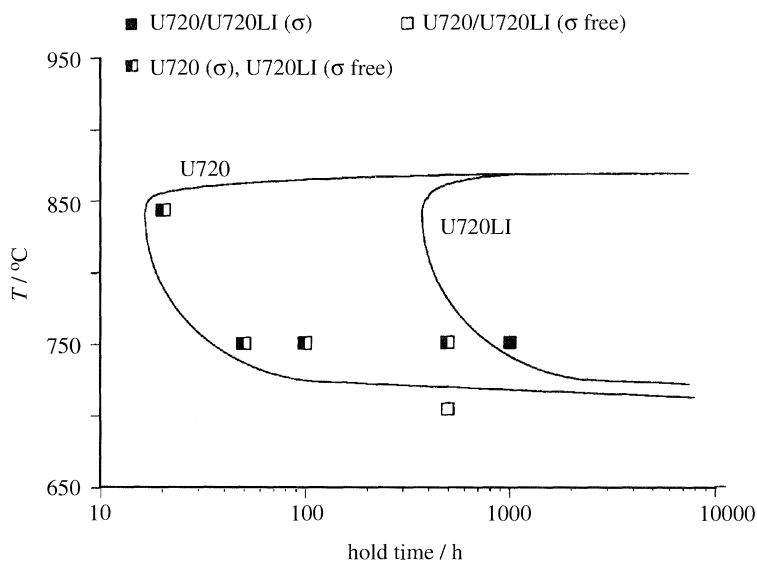
Figure 8. Calculated phase percent plot for U720.

Figure 9. Observation of σ in U720 and U720LI with TTT diagrams proposed by Keefe *et al.* (1992).

this, Udimet 720LI (U720LI), a low Cr version, was developed (table 2) which substantially reduced σ susceptibility at 750 °C. Keefe *et al.* (1992) suggested that a TTT diagram of the type shown in figure 9 could explain the difference in behaviour of the two variants. It is interesting to note that in their diagram the TTT curves for the two variants join at about 870 °C, but show substantially different behaviour below this temperature. Their diagram consequently suggests that the σ solvus temperature (σ_s) for both alloys is identical, which is unlikely as a change in composition must change this value.

It was therefore instructive to calculate the σ_s temperature for both alloys.

Table 2. *Nominal compositions of Udimet 720 and Udimet 720LI*

(After Keefe *et al.* 1992.)

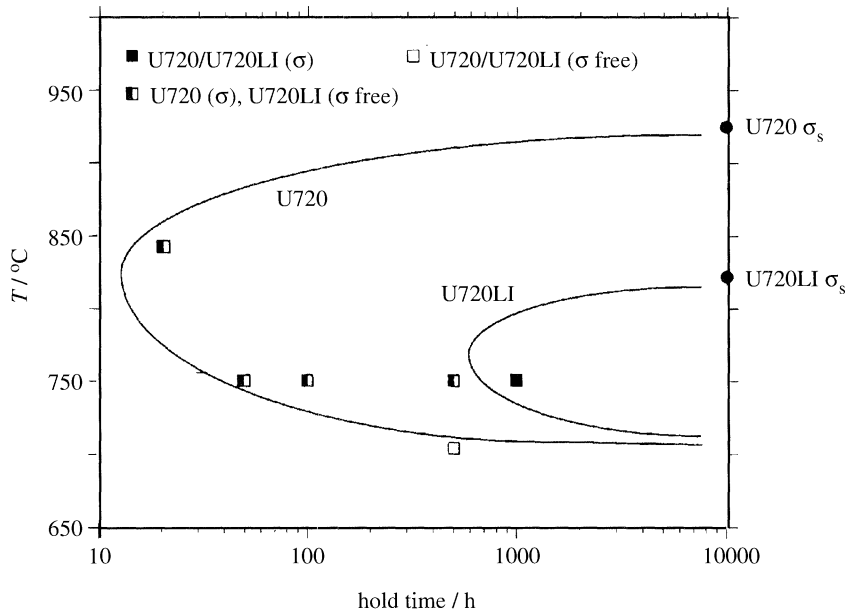|	Cr	Co	Mo	W	Ti	Al	C	B	Zr
U720	18.0	14.7	3.0	1.25	5.0	2.5	0.035	0.033	0.03
U720LI	16.0	14.7	3.0	1.25	5.0	2.5	0.010	0.015	0.03

Figure 10. TTT diagrams proposed here for U720 and U720LI based on calculated σ_s values.

These are plotted on a similar diagram and also included are suggested TTT curves based on these results (figure 10). It can be seen that the difference in σ susceptibility can be almost completely explained by the 100 °C drop in σ_s when the Cr concentration is lowered.

It is now also possible to begin quantifying TTT diagrams such as this using a combined kinetic and thermodynamic approach. In recent years a European project has led to the creation of a software package, DICTRA, which links the simulation of diffusion-controlled processes in multicomponent systems with thermodynamic properties obtained directly and interactively from the phase diagram calculation package THERMO-CALC (Andersson *et al.* 1991; Inden *et al.* 1993). Work with DICTRA has mainly concentrated on ferrous-based alloys, for example the growth of ferrite from austenite, but preliminary work has shown that it is capable of simulating the growth of σ in a multicomponent Ni-based, γ matrix (Jönsson & Ågren 1993, personal communication).

It is also useful to know how variations in chemistry within proposed commercial specification limits affect σ_s and figure 11 shows the variation predicted as each element is changed between its maximum and minimum specification. What was at first surprising was the prediction that the greatest effect on σ_s was due to
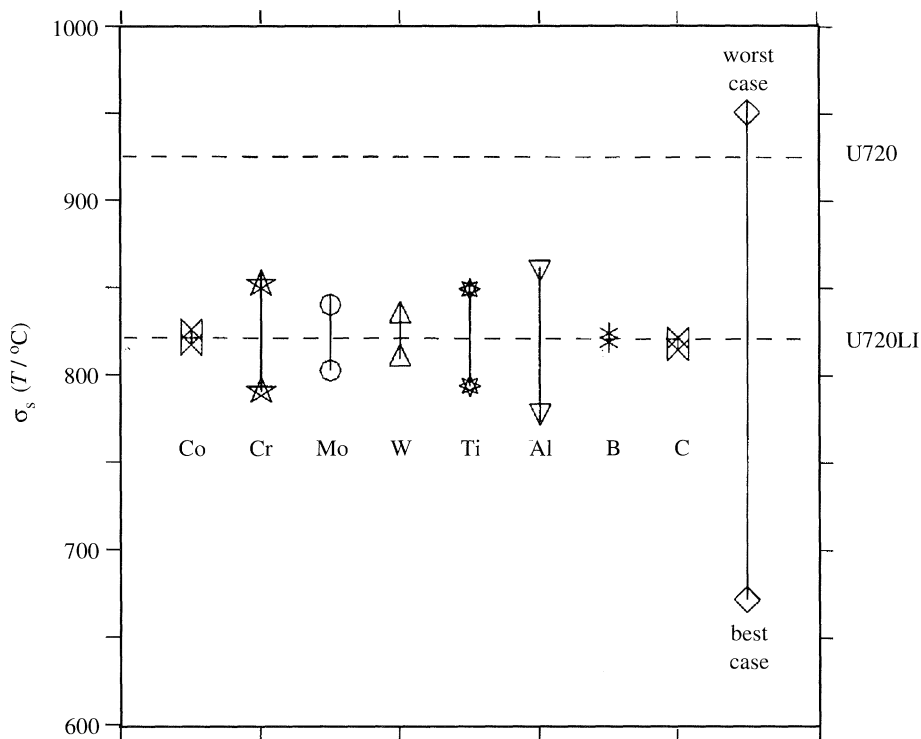
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Figure 11. Variation in calculated σ_s as each element in U720LI is changed between its maximum and minimum specification.

Al and that variations within the Ti specification limit were nearly as potent as for Cr. This can be explained fairly readily. Al and Ti are powerful γ' formers and any increase in their levels increases the amount of γ' and reduces the amount of γ. As Cr and Mo strongly partition to γ, any increase in γ' levels markedly increases their concentration in γ hence making the alloy more susceptible to σ formation. It should be stressed that σ-sensitivity factors as shown in figure 11 are compositionally dependent and as such their values can significantly change depending on the alloy studied. However, the relative effect of the elements does seem to be maintained.

There is interest in understanding the solidification behaviour of Udimet 720 and to this end a 'single crystal' alloy was prepared at Rolls-Royce without B and C additions (Small 1993, personal communication). Initial examination appeared to show a familiar structure of Ni-rich γ dendrites with some γ' in the interdendritic regions. However, microprobe analysis across the interdendritic region showed many of the precipitates to have very high Ti and low Al levels and these were associated with a more needle-like morphology. It is possible to make predictions for non-equilibrium solidification assuming no back-diffusion in the solid using a standard Scheil–Gulliver simulation within the Thermo-Calc software package. The results from this clearly indicated that as well as γ' there would be a susceptibility for η formation in the interdendritic regions explaining the high Ti and low Al levels which were observed in needle-like precipitates.
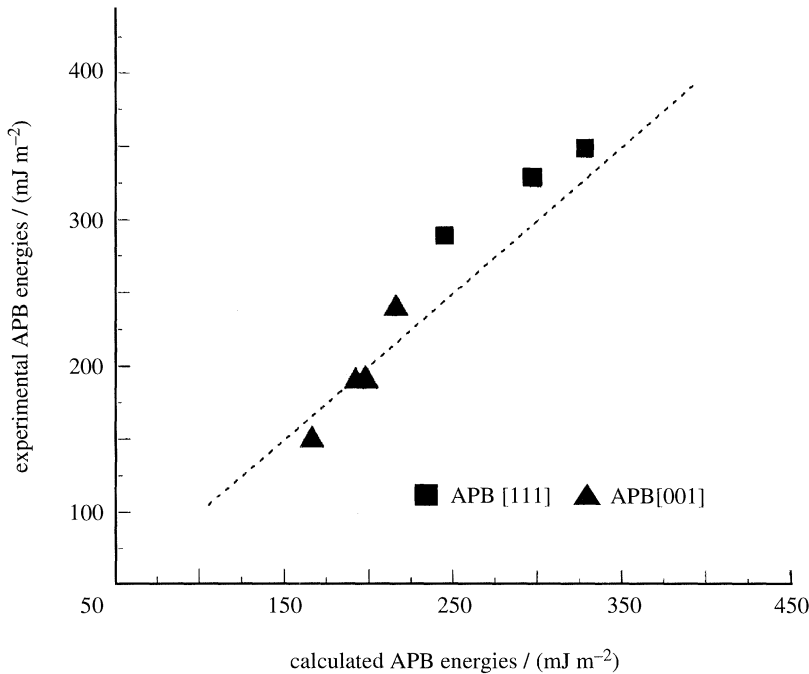
Figure 12. Comparison between calculated and experimentally observed APB energies for several Ni-based superalloys including U720.

There is also interest in being able to predict the mechanical behaviour of Ni-based superalloys. Several models exist but these rely on input data for properties such as stacking fault energies (SFE) in γ and antiphase domain boundary (APB) energies in the γ'. Although not readily associated with the CALPHAD method, such properties can be predicted, for example SFEs in Fe–Ni–Cr alloys were predicted by Miodownik (1978) based on $\Delta G^{\mathrm{FCC} \rightarrow \mathrm{CPH}}$ for alloys in this system. Clearly if similar data were available for Ni-based systems such a method could be applied for Ni-based superalloys.

APB energies have been predicted for a number of Ni-based superalloys including Udimet 720, using a model based on the calculation of bond energies across the APB (Miodownik & Saunders 1994). The method relies on calculating nearest neighbour interaction energies for the γ' phase, up to the third nearest neighbour. These can be estimated using the ordering energy of the γ' phase from the disordered FCC γ phase and the heat of formation of the FCC phase of the same composition. The treatment was applied to several selected alloys, including Udimet 720, and these were compared with subsequently determined experimental values (Small 1994, personal communication) for the APB[111] and APB[001]. The results are shown in figure 12 and the comparison is extremely satisfactory.

4. General comments and summary

It has not been possible within the scope of this paper to go into detail concerning many of the applications which are possible using the CALPHAD method, nor to describe recent work on conventional Ti-alloys (Saunders 1994). However, it should be stressed that complex alloys can now be routinely handled, and

with high degrees of accuracy. This leads to an ability to quantify and under-stand many issues of interest concerning materials for use in high-temperature applications.

For too long, materials such as superalloys have been considered too complex for modelling of this type. This has led to a reliance on approaches such as PHACOMP which are at best semi-quantitative and at worst inaccurate and has further led to a mystique surrounding the phase behaviour of such materials. It is to be hoped, now basic phase behaviour can be predicted with a high degree of confidence, that more quantitative modelling approaches can be applied for a variety of materials design and process issues, thus leading to a greater under-standing of material behaviour, the optimization of properties and some quality control aspects in production.

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Discussion

R. W. CAHN (*University of Cambridge, UK*). My compliments on a most convincing demonstration of the power of the CALPHAD method as applied to 'real' industrial alloys! To complete this exposition, could Dr Saunders tell us something about the kind of experimental data that are needed as input for the sort of CALPHAD calculations he has exemplified.

N. SAUNDERS. The calculations for the multicomponent systems presented in

the paper are based on predicting the thermodynamic properties of higher-order systems from the thermodynamic modelling of the lower-component systems. In the present calculations these lower-component systems are binaries and ternaries. It is therefore necessary to have data such as the experimental determination of binary and ternary phase diagrams and experimental measurements of thermodynamic properties such as enthalpies of formation, activities, etc. Preferably such information should be of good quality.

R. W. CAHN. Dr Saunders hinted at a rather remarkable claim. When there are several distinct measurements of a phase equilibrium feature, you suggest you can pick out a faulty measurement by comparison with a CALPHAD calculation. But surely, the precision of such a calculation is linked to the precision of the thermochemical measurements which contribute your input. Shouldn't a curve calculated by CALPHAD actually show upper and lower confidence limits depending on your judgement of the reliability of the input measurements?

N. SAUNDERS. The answer to Professor Cahn's question is yes and no. In an ideal world, where all experimentation is reliable and of good quality, I would agree that the curve calculated by a CALPHAD calculation could have such confidence limits imposed. Unfortunately, this is not often the case and, for example, sets of measured datapoints for a liquidus in a simple binary system can vary considerably. In some high melting point systems it is not unusual for these differences to be of the order of 100 °C or higher. Sometimes a simple comparison of the original datapoints can show that one particular set of results is obviously inconsistent with other reported values and this forms the basis of experimental phase diagram assessment work by people such as Hansen. Unfortunately in others cases the position is not so clear cut. The CALPHAD calculation does impose a self-consistency between the underlying thermodynamics and the phase diagram and therefore can be used as an arbiter between conflicting values.

M. McLEAN (*Imperial College, London, UK*). To what extent is the accuracy of the phase diagram calculation dependent on (*a*) the calculation methods used in the different software systems available and (*b*) the thermodynamic databases available? In particular, have there been round robins using the same data, but different software, to calculate the same information?

N. SAUNDERS. If I may I will try and answer Professor McLean's second question first. In Europe there is an organization called SGTE (Ansara & Sundman 1987), which is a grouping of several centres which are active in the CALPHAD area. Workers from this group use at least four different software packages for doing CALPHAD calculations. The programs rely on some form of Gibbs free energy minimization and a brief background to this can be found in a paper by Hillert (1979). Such techniques do not give unique solutions and, therefore, there will be differences in the answers. However, such differences are typically very small. It may be that some software packages have thermodynamic models which are unique to that package and, therefore, it would not be possible to do a similar calculation on another package. However, it would be reasonable to say that, given the same implementation of models, identical database input and the correct starting points to begin the calculation, the various software systems within SGTE will provide effectively identical answers.

To answer his first question, the accuracy of the phase diagram calculations

presented here relies solely on the thermodynamic database and is not a function of the software package that is used.

M. RAPPAZ (*EPFL, France*). Phase diagram calculations give volume fractions of phases which are at equilibrium (lever-rule). They can be easily adapted to the case of no-diffusion in the solid during a solidification experiment (Scheil) by 'freezing' the concentration at the newly formed interface. How easy (or difficult) is it to couple phase diagram computations with back-diffusion models?

N. SAUNDERS. There have been recent publications in the literature which have attempted to do just this with a good degree of success (see, for example, Matsumiya 1992). The DICTRA program mentioned earlier (Andersson *et al.* 1991; Inden *et al.* 1993) is also capable of accounting for backdiffusion during solidification.

D. G. PETTIFOR (*University of Oxford, UK*). In the prediction of the B2 phase field in the ternary Ti–Al–Nb system, was it necessary to readjust the accepted data for the binary systems?

N. SAUNDERS. No.

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