PHASE DIAGRAM CALCULATIONS FOR NI-BASED SUPERALLOYS

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Abstract

At high temperatures, and when subjected to mid-range temperatures for long times, superalloys can reach states which approach equilibrium. Knowledge of stable phase structure at fabrication and working temperatures can, therefore, be very important and experimental determination of Ni-based binary and ternary systems has been reasonably extensive. However, when working with such highly alloyed multi-component materials as superalloys information based purely on experimental determination of lower order systems cannot always be directly applied to 'real' alloys. The field of computer aided thermodynamic phase diagram calculations holds substantial promise in this respect as it possible to make predictions for the phase behaviour of multi-component alloys based on models for the binary and ternary phase diagrams.

This paper will present a review of results which can now be obtained in alloys from the following multi-component system

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

Current work involving the extension of the database to include Fe and Re will also be presented. A further advantage of the CALPHAD route is that it is possible to predict properties other than those associated with equilibrium diagrams and the application to non-equilibrium solidification and the prediction of APB energies in γ' will be presented.

Introduction

The computer calculation of phase equilibria in multi-component alloys is becoming increasingly commonplace and it is now possible to make very accurate predictions for phase equilibria in a number of the more commonly used metallic and intermetallic alloys. These range from steels[1] to Ti-aluminides[2]. This paper will present results which can now be obtained in Ni-based superalloys giving a number of examples of where this methodology has been applied.

The CALPHAD method first requires that sound mathematical models exist for describing the thermodynamic properties of the various phases which can appear in an alloy. The coefficients used by the models are then held in databases which are accessed by software packages such as Thermo-Calc[3] which then perform a series of calculations, usually via Gibbs energy minimisation, to provide the user with detailed information on phase equilibria. These calculations can be augmented with kinetic modelling to provide answers for phase formation under conditions which can deviate substantially from equilibrium[4,5].

Early attempts at modelling of superalloys mainly concentrated on ternary sub-systems[6,7,8]. They provided some guidance in the search for high temperature eutectic reactions but the simple model types used in this early work inherently limited their more general usage. For example γ' was treated as a stoichiometric or line compound whereas it is substantially non-stoichiometric in practice. New models have been developed which now allow the full solubility range and thermodynamic properties of intermetallic compounds such as γ' to be modelled very accurately[9,10].

Some four years ago a development programme between Thermotech Ltd and Rolls-Royce plc was started to develop a database which could be used for CALPHAD and related calculations in Ni-based superalloys. Results[11,12] have demonstrated that the accuracy of calculated phase equilibria lies close to that obtained experimentally for commercial superalloys. Some examples of superalloys for which calculations have been made and validated are shown in Table 1. As can be seen they include all types of superalloys ranging from Nimonic types through to single crystal blade alloys. This paper will provide a brief background to the CALPHAD modelling and demonstrate the accuracy of results which are now obtained. Some applications of the database will then be shown including application to non-equilibrium solidification, σ phase formation and prediction of APB energies in γ'.

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

Background to the Calculation Method

The roots of the CALPHAD approach lie in the mathematical description of the thermodynamic properties of the phases of interest. If they are stoichiometric compounds 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. Details of modelling procedures can be found in the review of Ansara[13]. 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 proprietary.

The main models used in the present work are the substitutional type model[13] and the multiple sublattice model[10]. Both of these models can broadly be represented by the general equation for a phase

$$\Delta G = \Delta G^o + \Delta G_{mix}^{ideal} + \Delta G_{mix}^{xs} \qquad (1)$$

where $\Delta G°$ is the free energy of the phase in its pure form, ΔG_{mix}^{ideal} is the ideal mixing term and ΔG_{mix}^{xs} is the excess free energy of mixing of the components. It is not within the scope of the present paper to describe in detail these models, particularly the multiple-sublattice model, but it is useful to briefly discuss some of their aspects.

The free energy of the substitutional model (ΔG_m) for a many component system can be represented by the equation

$$\Delta G_m = \sum_i x_i \Delta G_i^o + RT \sum_i x_i \log_e x_i + \sum_i \sum_{j>i} x_i x_j \sum_v \Omega_v (x_i - x_j)^v$$

$$(2)$$

where x_i is the mole fraction of component i, ΔG_i^o defines the free energy of the phase in the pure component i, T is the temperature and R is the gas constant. Ω_v is an interaction coefficient dependent on the value of v. When v=0, this corresponds to the regular solution model and when v=0 and 1 this corresponds to the sub-regular model. In practice the value for v does not usually rise above 2.

Eq.2 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 other polynomial expressions for the excess term have been considered, see for example the reviews by Ansara[13] and Hillert[14], however all are based on predicting the properties of the higher-order system from the lower-component systems.

The multi-sublattice model is substantially more complex and considers the phase to made up of multiple interlocking sublattices. There are then interaction terms to be considered (i) between the sublattices and (ii) on the sublattices themselves. For a 2-sublattice model as used to describe the γ′ phase in Ni-Al the sublattice occupancy would be shown schematically as below:

$$(Ni,Al)_3(Ni,Al)$$
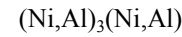
$\Delta G°$ would be written as

$$\Delta G^o = y_{Ni}^1 y_{Ni}^2 \Delta G_{Ni:Ni} + y_{Ni}^1 y_{Al}^2 \Delta G_{Ni:Al}$$
$$+ y_{Al}^1 y_{Ni}^2 \Delta G_{Al:Ni} + y_{Al}^1 y_{Al}^2 \Delta G_{Al:Al} \qquad (3)$$

where $$y_i^s = \frac{n_i^s}{\sum_i n_i^s}$$

and $$\sum_i y_i^s = 1$$

y_i^s is the site fraction of component i, in this case Ni or Al, on sublattice s, n_i^s is the number of moles of constituent i on sublattice s. The ideal entropy of mixing is written as

$$\Delta G_{mix}^{ideal} = RT[3(y_{Ni}^1 \ln y_{Ni}^1 + y_{Al}^1 \ln y_{Al}^1) + (y_{Ni}^2 \ln y_{Ni}^2 + y_{Al}^2 \ln y_{Al}^2)] \qquad (4$$

The ΔG_{mix}^{xs} term considers the interactions between the components on the sublattice and can be quite complex, see for example Saunders[15]. As the level of complexity of the structure becomes more complex, more sublattices are needed to consider it Gibbs energy, for example the σ and μ phase may described using a three sublattice model.

Once the thermodynamics of the various phases are defined phase equilibria can be calculated using software packages such as Thermo-Calc[16] which is the programme used in this work. The main method of such programmes is usually a Gibbs free energy minimisation process and there are now a variety of such software packages which can perform complex multi-component calculations. For more information the recent review by Bale and Eriksson[17] provides a fairly comprehensive coverage of these.

Results

Binary and ternary systems

It is instructive to demonstrate how the current database has been built up by showing some of the lower order binary and ternary systems. This will also enable some aspects of γ/γ' elemental partitioning to be discussed. Fig.1 shows the calculated phase diagram for Ni-Al with data points for phase boundaries included. For references to the original studies the review of Nash et al[18] contains most these.
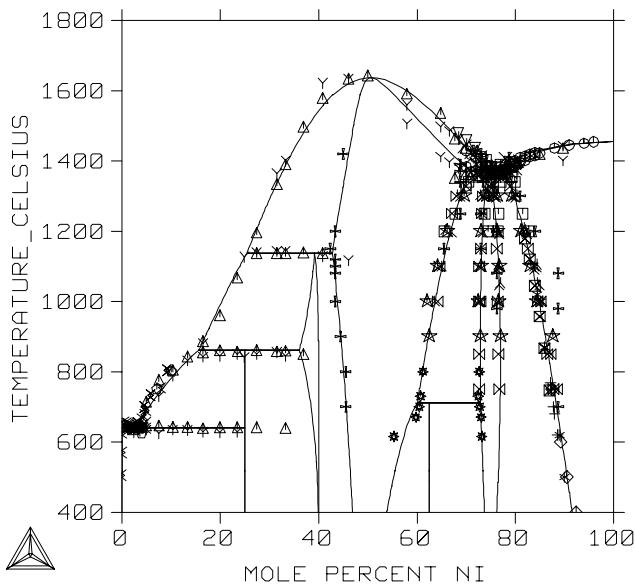

Fig.1. Calculated Ni-Al phase diagram with experimental phase boundaries superimposed

It is noted that the calculated diagram gives a eutectic reaction between γ and γ' rather than a peritectic as proposed in some recent work[19]. This is a consequence of matching all of the available data and it is noted that liquidus points from the Vorhoeven et al[19] are actually in very good agreement with the calculated boundaries. In practice whether the reaction is eutectic or peritectic is not important as the change in free energy to get either reaction is very small and its consequence on calculated equilibria in higher order systems is almost negligible.

The calculations for Ni-Al can then be combined with those of Ni-Ti and Al-Ti as part of the calculation for the Ni-Al-Ti ternary system. A calculated isothermal section at 1000°C is shown in Fig.2 below.
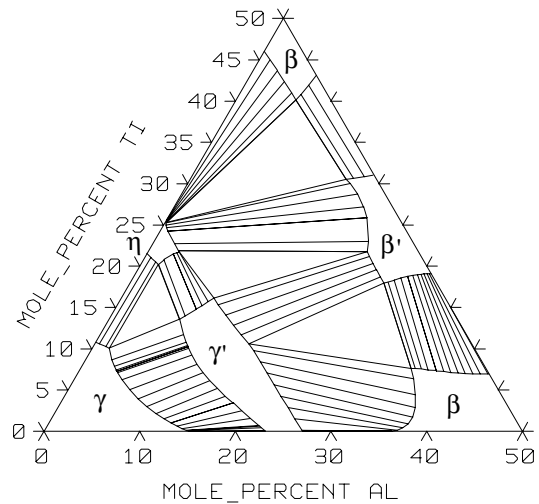

Fig.2. Calculated isothermal section for Ni-Al-Ti at 1000°C.

The diagram is in excellent agreement with that observed in practice. As is known in superalloys, Ti partitions preferentially to γ' but its value for $k^{\gamma/\gamma'}$ is about 0.5 with additions of 3-5at%Ti. This is substantially higher than observed in normal superalloys where the value is closer to 0.1[20].
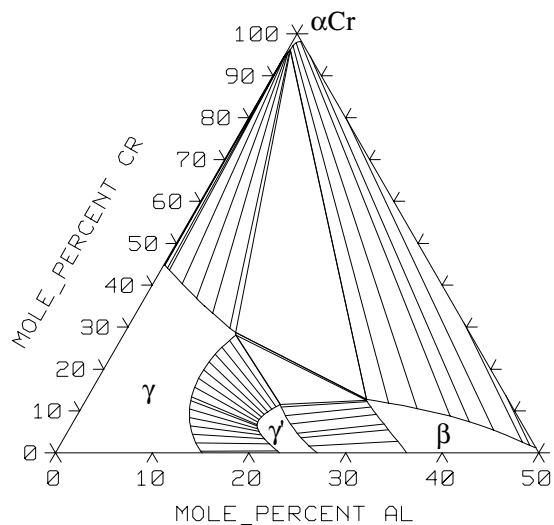

Fig.3. Calculated isothermal section for Ni-Al-Cr at 1000°C.

The behaviour of Cr in γ/γ′ equilibria is interesting as the γ′ intrusion into Ni-Al-Cr as well as pointing to Ni-Cr exhibits a tendency to go towards Cr as well (Fig.3). Cr partitions towards γ and k$^{γ/γ′}$ is slightly less than 2 in the range 10-20at%Cr. This is substantially lower than observed in superalloys[20] where the value lies closer to 7.

In both Ni-Al-Cr and Ni-Al-Ti the calculated tie-lines are in excellent agreement with those observed in practice and it is therefore clear that on alloying the respective Cr and Ti partition coefficients are substantially altered. This is something that cannot be predicted from the experimental determination of the ternary sections alone. The ability to predict the correct partitioning behaviour in both the ternary as well as higher order system is one of the strengths of the CALPHAD route and is something that automatically follows from a sound description of the underlying thermodynamics.

Before proceeding to look at superalloys themselves it is also instructive to look at the ternary system Ni-Cr-Mo. This with other elements such as Co, Mo and W forms the basis for σ and μ formation in superalloys. Due to its simple nature the use of PHACOMP does not allow for the true complexity of topologically close-packed (TCP) phase formation to be taken into account. This is a factor to consider even before questions concerning accuracy are discussed. There are three TCP phases which can form in Ni-Cr-Mo, σ, μ and P and Fig.4 shows a calculated isothermal section at 850°C which is in good agreement with the detailed study of Raghavan et al[21]. The P phase is not often seen in superalloys as Co tends to stabilise μ over P in the quaternary Ni-Co-Cr-Mo. The clear strength of the CALPHAD method is that as well as giving good levels of accuracy for TCP phase formation and its temperature dependence it can also consider the interplay between them.
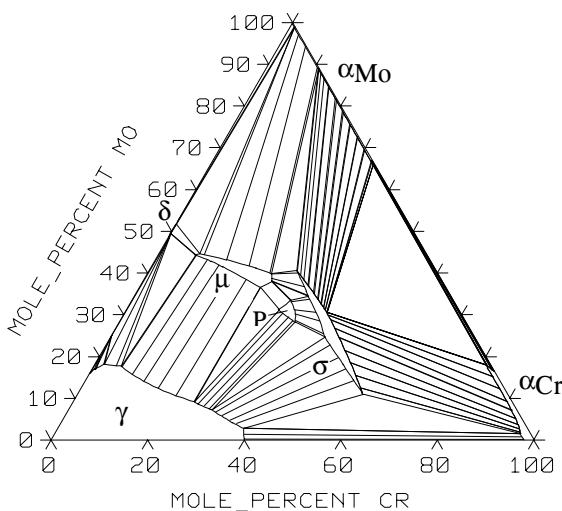
Multi-component alloys

As the database contains many of the elements seen in superalloys it is possible to validate calculated results against a substantial literature, particularly with respect to γ/γ′ and liquid phase equilibria. Fig.5 shows a comparison for nearly 150 values of critical temperatures such as γ′$_s$, liquidus and solidus. The level of accuracy is excellent with the average difference ($\overline{d}$) between the calculations and experiment lying close to 10°C. The liquidus in particular is very well predicted with a $\overline{d}$ of 6-7°C. It is noted that the results come from all types of superalloys ranging from low γ′ types such as Waspaloy through very highly alloyed types such as IN939 to single crystal alloys such as CMSX2 and SRR99.
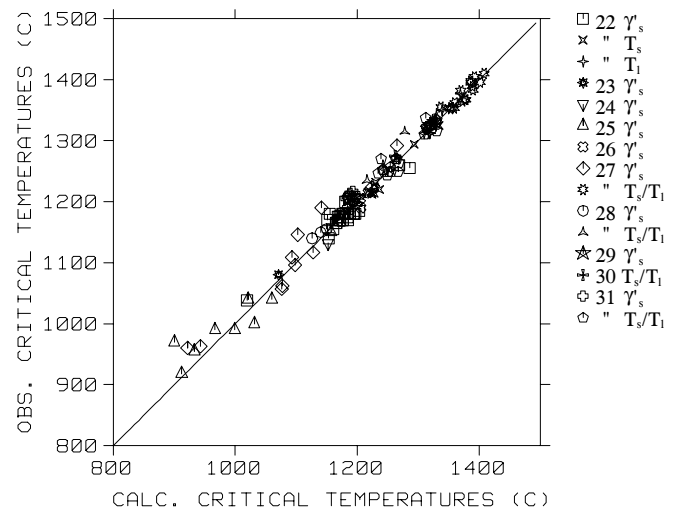
Fig.5. Comparison between observed and calculated critical temperatures for Ni-based superalloys.

There is a similarly large literature concerning amounts of γ′ and compositions of both γ and γ′. Fig.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 wt% or volume%. For the latter case, as lattice mismatches are so small, mole% values give almost identical values to volume%.

Figs.7-11 show some of the comparisons for the composition of γ and γ′ where the high standards of results is maintained. Where experimental results have been quoted in wt% they have been converted to at% to allow for consistency of comparison. The average difference for elements such as Al,Co and Cr is close to 1at% while for Mo,Ta,Ti and W this value is close to 0.5at%. Too few experimental values for Hf and Nb were found to be statistically meaningful but where possible these were compared and results for average differences were found to be slightly better than obtained for Mo,Ta etc.

Fig.4. Calculated isothermal section for Ni-Cr-Mo at 850°C.

One important thing to come from the results of calculated γ/γ′ equilibria is that partition coefficients for elements such as Cr and Ti are well matched so the calculations have given the correct answer for both lower and higher order systems. The exaggeration of the lower order partitioning for Cr and Ti is due to the fact that they have repulsive thermodynamic interactions. Ti is very tightly bound to γ′ which consequently causes Cr to be rejected from γ′. This increases levels of Cr in γ which in turn causes a rejection of Ti to γ′.

Apart from its success in predicting liquid phase and γ/γ′ phase equilibrium the new database allows excellent predictions to be made for TCP phase formation. In a recent study at Rolls-Royce the database correctly predicted switches between $M_{23}C_6$ and M_6C formation and between σ and μ. The accuracy which can be obtained now allows for alloy design to be made with very specific targets. For example most superalloys are designed to be σ safe. Within a PHACOMP scenario this would mean the average electron hole number $\overline{N}_v$ of the alloy would be below a critical value. However, this critical value is not necessarily a fixed number and may often found by experience for each alloy.

Using the CALPHAD route a σ-solvus temperature can now be calculated below which σ will form and this value can be used to help define 'σ-safety'. A good example of this concept is in U720. This alloy was used in land based gas turbine engines and for long term use up to 900°C[46], but its excellent all round properties suggested that it could be used as a disc alloy. However, while long-term exposure at high temperatures produced only minor susceptibility to σ formation its use at 750°C led quickly to σ formation and in large amounts[46]. Clearly the alloy was either close to or above its σ-solvus at the higher temperature and it was found necessary to reduce Cr levels to destabilise σ at lower

temperatures. This led to the development of U720LI with levels of Cr 2wt% less than for U720. Levels of C and B were also lowered to reduce the formation of borides and carbides which acted as nucleation sites for σ formation.

Fig.12 shows a calculated phase % vs temperature plot for U720 and it can be seen that its σ-solvus is indeed very close to 900°C and at 750°C the alloy would contain substantial levels of σ in excellent accord with experimental observation. Keefe et al[46] further determined TTT diagrams for both U720 and U720LI and these are shown in Fig.13.
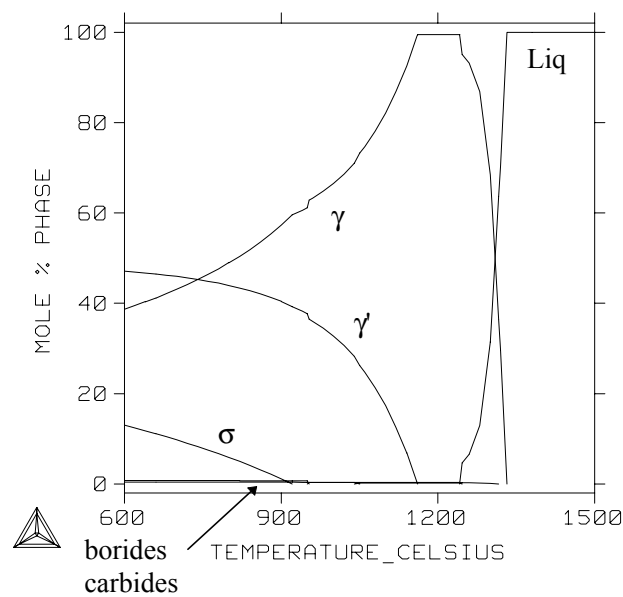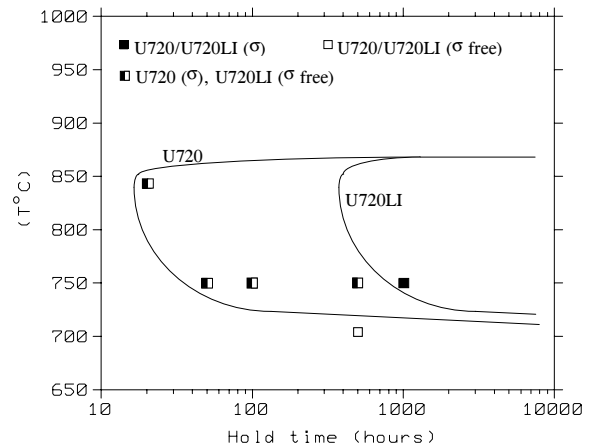

Fig.13   TTT diagrams for U720 and U720LI after Keefe et al[46].

As has been previously pointed out[12] decreasing the Cr levels must decrease the σ-solvus and, as the high temperature part of the TTT diagram asymptotes to the σ-solvus temperature, the two TTT diagrams should have distinct and separate curves. Taking the σ-solvus calculated for U720 and U720LI it was proposed[12] that the TTT diagrams should have the form as shown in Fig.14.
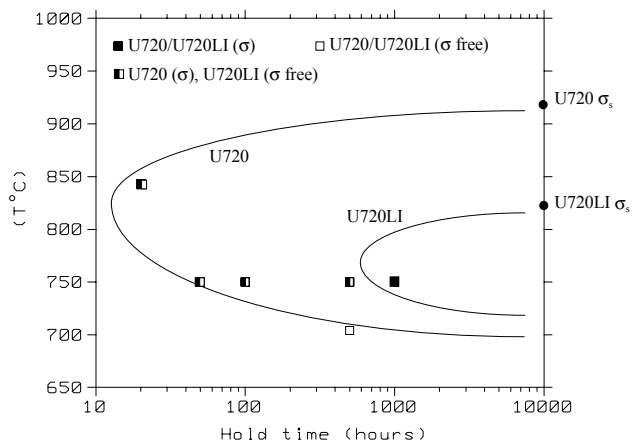

Fig.14   TTT diagrams for U720 and U720LI based on calculated σ-solvus temperatures

Fig.12 Phase % vs temperature plot for U720

The corollary to such calculations is to calculate the how the σ-solvus varies as the composition of the different elements are altered. Fig.15 shows such variations in σ-solvus temperature for U720LI as each element is changed within its nominal composition specification.
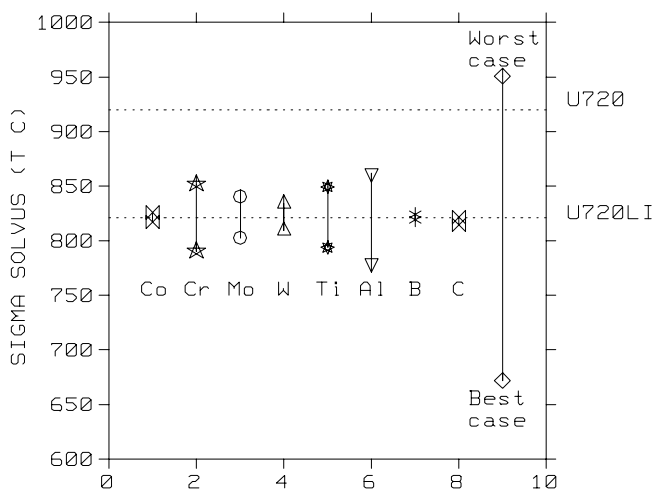

Fig.15 Variation in calculated σ-solvus temperature as elements in U720LI change between maximum and minimum specified limits

It is interesting to note that the greatest sensitivity is to Al, with Ti similar to Cr. This is because increases in Al and Ti increase the levels of γ' in the alloy and reject σ forming elements such as Cr, Mo and W into γ whose amount has decreased. This gives rise to very significant concentration increases of these elements in γ and leads to higher susceptibility to σ formation. Taking the information in Fig.15 it is now possible to define σ-sensitivity factors for each of the elements with a very simple mathematical formula. This can then be used to monitor σ-susceptibility of different heats during alloy production, replacing PHACOMP methods. Such sensitivity factors can be defined for all types of production features where phase equilibria can be important, for example γ' heat treatment windows, levels of γ' at heat treatment or forging temperatures, solidus and liquidus temperatures etc.

The results discussed so far have addressed issues mainly concerned with equilibrium behaviour, and in practice such issues are of importance to materials behaviour. However, one of the great strengths of a CALPHAD approach is that it can be combined with kinetic modelling to model features not usually associated with equilibrium calculations. For example growth rates[4], which can allow TTT diagrams to be produced, and modelling of non-equilibrium solidification[47]. Further the underlying thermodynamics controls some basic features which control mechanical properties such as stacking fault energies (SFEs)[48], APB energies in γ'[49] and even coefficients of thermal expansion[50]. The last part of this paper will discuss

how such calculations can be tackled and give some examples of applications.

For some time it has been possible to use packages such as Thermo-Calc to model non-equilibrium solidification under 'Scheil' conditions, i.e. solidification assuming no back diffusion takes place in the solid phase(s) during growth of the solid phase(s)[3,51]. For Al-alloys in particular[52] it can be shown to give exceptionally good predictions for features such as fraction solid transformed/latent heat evolution as a function of temperature as well as the non-equilibrium phases which can appear. The technique has already been successful[12] in predicting the unexpected formation[22] of η in the interdendritic regions of a 'single crystal' U720 alloy in which the B and C had been removed.

As part of a progressive upgrading of the present database there is now sufficient data included for Fe to consider preliminary modelling of the solidification behaviour of IN718. Fig.16 shows plots of fraction solid transformed vs. temperature for an alloy with a standard composition specification[53] under both equilibrium and 'Scheil' conditions
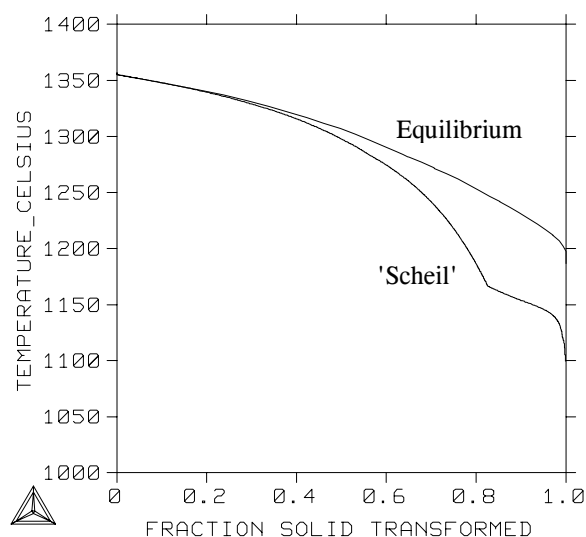

Fig.16 Fraction solid vs temp. plots for IN718 calculated for equilibrium and 'Scheil' conditions.

The final part of the 'Scheil' plot corresponds to the formation of the Laves phase as is commonly observed in this alloy, see for example Cao et al[54] and Murata et al[55]. The formation of the Nb-rich MC carbide is correctly predicted and some small amounts of Ni_3Nb and M_3B_2 (if B is present) may also form in the very last liquid to solidify. It is further noted that the Laves formed during solidification is metastable and will be dissolved on high temperature annealing as observed in practice. It is accepted that some back diffusion will occur and solidification will usually proceed somewhere between the two curves shown in Fig.16.

The extension of the database to model lower temperature solid state equilibria still requires some additional work.

However, this should be completed very shortly and already very reasonable predictions for the solvus temperatures of δNi₃Nb, γ′ and σ are obtained.

Apart from information concerning formation of phases it is also possible to calculate the heat evolution during solidification. This is of considerable importance in the modelling of heat flow during solidification and subsequent modelling of casting processes. By taking the latent heat evolved at each step of the calculation the latent C_P of solidification vs temperature plot of the 'Scheil calculation for IN718 was calculated and is shown in Fig.17. The C_P plot has been calculated by averaging the C_P over 2° steps and can be readily incorporated into casting simulation packages in this way.

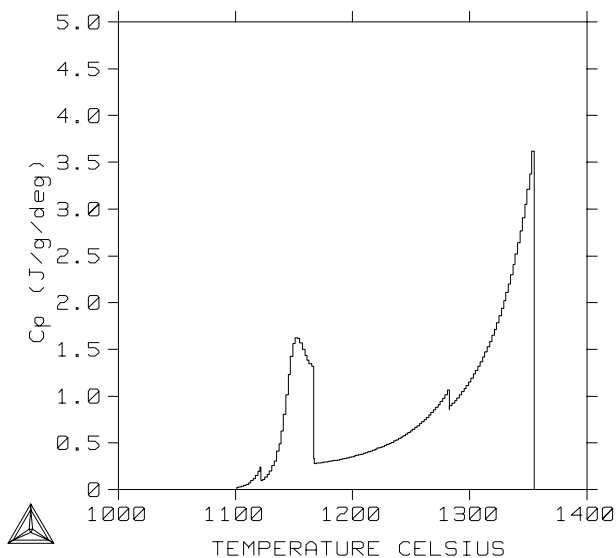Recent attempts at solidification modelling using data based on the early Kaufman work have been made for René N4[56]

Fig.17   Plot of Latent Cp of solidification vs temp. for
IN718 during 'Scheil' solidification.

and IN718[57] and it is interesting to briefly discuss these results. The work on IN718 by Boettinger et al[57] is in quite reasonable agreement with the known behaviour of this alloy and the form of their 'Scheil' plot is very similar to the current work except that the liquidus is slightly lower and slightly less eutectic Laves is predicted to occur. The higher liquidus of the present calculations is more consistent with experimental observation[54] and the present work also considers C and B. But otherwise conclusions from both studies remain essentially similar.

The results for René N4, however, are quite different than obtained from the present work. The liquidus temperature from Chen et al[56] is some 45°C lower than would be calculated here which, considering the high level of accuracy for liquidus predictions from the present database, does raise some questions. Further their 'Scheil' simulation for this alloy produced a freezing range far greater than observed in

practice. To account for this apparent discrepancy a new type of solidification mechanism was proposed and a modified 'Scheil' plot was produced[56]. However, it is noted that a straightforward 'Scheil' plot using the current database gives a very similar freezing range to the modified plot of Chen et al[56]. Clearly there is little need to resort to new and complex solidification mechanisms in this particular case.

From the above it is unclear within which composition range the Kaufman-base data can be used with confidence for input into solidification models. The composition of IN718 is based predominantly on the Ni-Cr-Fe ternary system with addition of other elements, notably Nb and Mo. The total of other elements is less than 2-3wt%. René N4, on the other hand is much more complex with high levels, greater than 4wt% each, of Al,Co,Cr,Ta,Ti and W. It is clear that a detailed validation exercise is necessary before this issue of confidence can be resolved.

It is sometimes forgotten that underlying thermodynamics of materials is inherently important in defining a number of basic materials properties. For example in a review of models concerned with fundamentals of strengthening in superalloys[58] two of the most important contributions were the stacking fault and APB energies. Calculations of SFEs in austenitic stainless steels have been performed very successfully[48] where the main input parameter has been the free energy difference between the austenitic FCC structure and the underlying CPH phase. Information can be extrapolated quite straightforwardly for the CPH phase in superalloys from the constituent lower order systems and therefore such techniques can now be applied to superalloys.

Successful predictions for the APB energy in γ′ from calculation of the γ→γ′ ordering energy have been made[49].
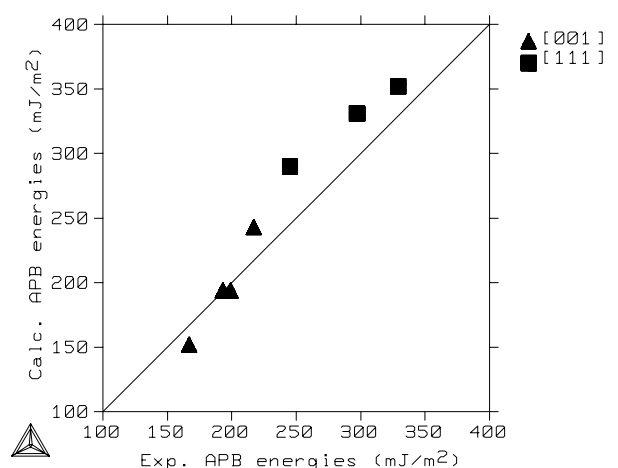

Fig.18   Comparison of calculated and experimentally
measured [111] and [001] APB energies for
some superalloys

The method directly utilises the database firstly to calculate

the composition of γ′ in the superalloy of interest. The formation energy of γ′ is then calculated followed by that of γ at the same composition. This is then used to derive the ordering energy and by using a model which relates this term to the change in number and types of bonds at the boundary very good predictions for [111] and [001] APB energies can be made. Fig.18 shows the comparison between calculated and measured[59] values for a some model superalloys including U720.

Work is currently in progress to extend the database to include Re. This work entails substantial new work as Re phase diagrams have not been, to any at great degree, experimentally studied or thermodynamically assessed by CALPHAD methods. However, initial results look very interesting and it is worth examining a calculation of an isothermal section for Ni-Al-Re at 1000°C (Fig.19). Little or no experimental work is reported for this system and the calculations for this ternary are therefore preliminary. However, it is noted that the predicted solubility of Re in γ′ at 1000°C is very limited ~1at% or 3-4wt%.

Although little experimental information exists for Ni-Al-Re there is one fairly well documented experimental feature of the ternary. There is very little solubility of Re in NiAl and a
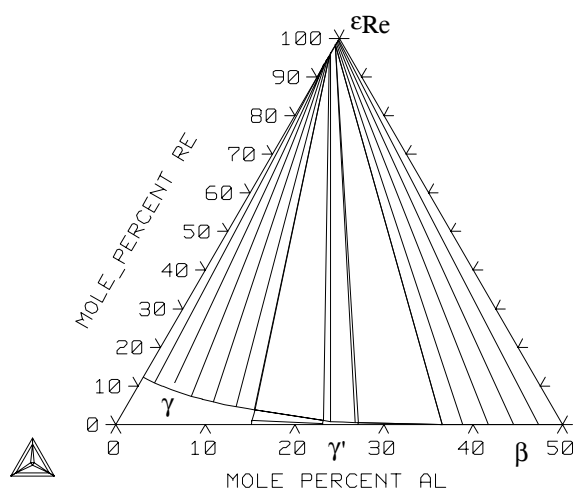

Fig.19 Calculated isothermal section for
Ni-Al-Re at 1000°C

eutectic exists between NiAl and almost pure Re with a composition of ~1.5at%Re[60,61]. This feature is very well matched by the present calculation as is the binary system Ni-Re. The predicted results for the solubility of Re in γ/γ′ alloys are therefore expected to be quite reasonable.

Interactions between Re and the other elements in an alloy such as CSMX4 will alter this solubility and perhaps enhance it, for example Ti and Re are quite tightly bound, it. However, it is clear that solubility levels will never be as high as for elements such W or Cr. Therefore, the initial conclusion is that with relatively small additions of Re one might expect Re particles to precipitate in superalloys with

high volume fractions of γ′. This appears completely consistent with observations of clustering in Re containing superalloys[39]. It would be further interesting to observe if some segregation to stacking faults in γ occurred.

Summary

Some recent applications of CALPHAD and related techniques to Ni-based superalloys have been presented using a database recently developed by Thermotech Ltd and Rolls-Royce plc. The results of the calculations show that the CALPHAD route enables high quality predictions to be made for all aspects of phase equilibria in Ni-based superalloys from the following multi-component system

Ni-Al-Co-Cr-Hf-Mo-Nb-Ta-Ti-W-Zr-B-C
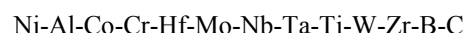
Results for calculated γ/γ′ and liquid phase equilibria can be shown to approach the levels of accuracy usually associated with experimental measurement. Some applications particularly with respect to σ formation in U720 have been discussed and the extension to areas not usually associated with phase diagrams has been presented. These include modelling of non-equilibrium solidification and calculation of APB energies.

Examples of work in progress on the inclusion of Fe and Re to the current database have shown that valuable results can already be obtained for these elements. Based on calculations for the Ni-Al-Re ternary system a possible explanation for the experimentally observed clustering of Re atoms in single crystal blade alloys is suggested.

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