

PHASE EQUILIBRIA IN MULTI-COMPONENT γ -TiAl BASED ALLOYS

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Abstract

A reasonable experimental literature has now been built up on Ti-Al-X ternary phase diagrams. However, although these basic systems give insight to phase equilibria in certain commonly used γ -TiAl based alloys it is difficult to interpret phase relationships in multi-component alloys using just this information. Thermodynamic calculations via the CALPHAD route¹ offer a means by which phase equilibria in multi-component alloys can be predicted and the present paper presents typical results which can now be achieved using this methodology. As well as basic relationships between the γ -TiAl, α_2 -Ti₃Al, β and α phases, the ordering of the β phase to B2 and the effect of O will be analysed and discussed.

Introduction

The computer calculation of phase equilibria in multi-component alloys via the CALPHAD route¹ is becoming increasingly popular and is now being used in practical applications for predicting phase equilibria in a number of the more commonly used metallic and intermetallic alloys. These range from Ni-based superalloys² to Al-alloys³. Further, they can be used to predict phase formation under conditions well away from equilibrium. This paper will present results that can now be obtained in γ -TiAl based intermetallic alloys.

The CALPHAD method first requires that sound mathematical models exist for describing the thermodynamic properties of the various phases that can appear in an alloy. The coefficients used

by the models are then held in databases that are accessed by software packages such as Thermo-Calc⁴ 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 that can deviate substantially from equilibrium^{1,5,6,7}.

Attempts at modelling of γ -TiAl based alloys have mainly concentrated on the binary phase diagram^{8,9,10} or ternary sub-systems^{11,12}. However, although these basic systems give insight to phase equilibria in certain commonly used γ -TiAl based alloys it is difficult to interpret phase relationships in multi-component alloys using just this information.

The present paper provides a brief introduction to the CALPHAD method and then presents a series of calculations for phase equilibria in a variety of γ -TiAl based alloys.

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. Details of modelling procedures can be found in the reviews of Ansara¹³ and Saunders and Miodownik¹. All types of models require input of coefficients that uniquely describe the properties of the various phases and these coefficients are held in databases that are either in the open literature or proprietary.

The main models used in the present work are the substitutional type model and the multiple sublattice model, details of which can be found in refs.1&14. Both of these models can broadly be represented by the general equation for a phase

$$\Delta G = \Delta G^{\circ} + \Delta G_{\text{mix}}^{\text{ideal}} + \Delta G_{\text{mix}}^{\text{xs}} \quad (1)$$

where ΔG° is the Gibbs energy of the phase in its pure form, $\Delta G_{\text{mix}}^{\text{ideal}}$ is the ideal mixing term and $\Delta G_{\text{mix}}^{\text{xs}}$ is the excess Gibbs energy of mixing of the components. While it is not within the scope of the present paper to describe these models in detail it is useful to briefly discuss some of their aspects.

For a substitutional phase the Gibbs energy of mixing of for a many component system can be represented by the equation

$$\Delta G_{\text{m}} = \sum_i x_i \Delta G_i^{\circ} + RT \sum_i x_i \log_e x_i + \sum_i \sum_{j>i} x_i x_j \sum_v \Omega_v (x_i - x_j)^v \quad (2)$$

where $x_{i,j}$ are the mole fractions of components i and j , ΔG_i° defines the Gibbs energy of the phase in the pure component i , T is the temperature and R 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 arising 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. The multi-sublattice model¹⁴ is substantially more complex and considers the phase to be 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 -TiAl phase the sublattice occupancy would be described as $(\text{Ti},\text{Al})_{0.5}(\text{Ti},\text{Al})_{0.5}$ and ΔG° would be written as

$$\begin{aligned} \Delta G^{\circ} = & y_{\text{Ti}}^1 y_{\text{Ti}}^2 \Delta G_{\text{Ti:Ti}} + y_{\text{Ti}}^1 y_{\text{Al}}^2 \Delta G_{\text{Ti:Al}} \\ & + y_{\text{Al}}^1 y_{\text{Ti}}^2 \Delta G_{\text{Al:Ti}} + y_{\text{Al}}^1 y_{\text{Al}}^2 \Delta G_{\text{Al:Al}} \end{aligned} \quad (3)$$

where $y_i^s = n_i^s / \sum_i n_i^s$ and $\sum_i y_i^s = 1$. y_i^s is the site fraction of component i , in this case Ti 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

$$\begin{aligned} \Delta G_{\text{mix}}^{\text{ideal}} = & RT [0.5(y_{\text{Ti}}^1 \log_e y_{\text{Ti}}^1 + y_{\text{Al}}^1 \log_e y_{\text{Al}}^1) \\ & + 0.5(y_{\text{Ti}}^2 \log_e y_{\text{Ti}}^2 + y_{\text{Al}}^2 \log_e y_{\text{Al}}^2)] \end{aligned} \quad (4)$$

A $\Delta G_{\text{mix}}^{\text{xs}}$ term can also be considered which accounts for interactions between the components on the sublattice and can be quite complex^{1,14}. As the level of complexity of the structure becomes more complex, more sublattices are needed to consider its Gibbs energy, for example the σ phase may be described using a three sublattice model.

The B2 phase is described using a modification of the two-sublattice model¹⁵ whereby the Bragg-Williams-Gorsky model of Inden^{16,17,18,19} can be replicated. This model allows the second order transformation of $A_2 \rightarrow B_2$ to be reproduced and simple estimates for ordering energy can be based on knowledge of the excess energy of mixing of the BCC phase. More details of the method can be found in refs.1&15.

Incorporation of interstitial elements

Interstitial elements are incorporated into the modelling by considering the interstitial sites as a separate sublattice where interstitial atoms and vacancies exist^{1,14}. For an FCC, A2 phase with C as the interstitial element and Va the interstitial vacancy sublattice occupation is described $(A,B)_i(C,\text{Va})_j$. For the γ -TiAl phase sublattice occupancy would be given as $(\text{Al},\text{Ti})_{0.5}(\text{Al},\text{Ti})_{0.5}(\text{C},\text{Va})$ with ordering occurring on the substitutional sites as Ti preferentially occupies one type of site and Al the other.

Once the thermodynamics of the various phases are defined phase equilibria can be calculated using a variety of software packages. For more information the review by Bale and Eriksson²⁰ provides a fairly comprehensive coverage of these. The method used by such programmes is a Gibbs free energy minimisation process and there are now a variety of such software packages that can perform complex multi-component calculations. Thermo-Calc⁴ is the programme used in this work.

Calculated Ti-Al phase diagram

The current modelling incorporates an assessment of the Ti-Al binary system produced as part of a recent European COST 507 project²¹. Much discussion on the form of the Ti-Al system exists in the literature and it would be reasonable to say that, while the overall features are now well established, discrepancies still exist as to the detailed positioning of certain phase boundaries. The present diagram (Fig.1) provides a good match with the now accepted form of the diagram and provides calculations for key alloys that are consistent with observed behaviour.

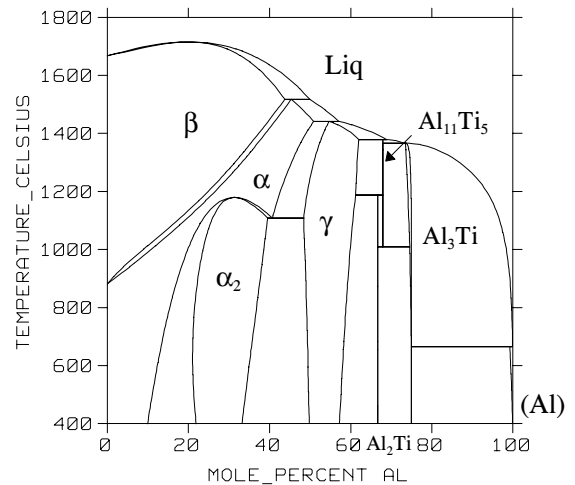


Fig.1 Calculated Ti-Al phase diagram²¹

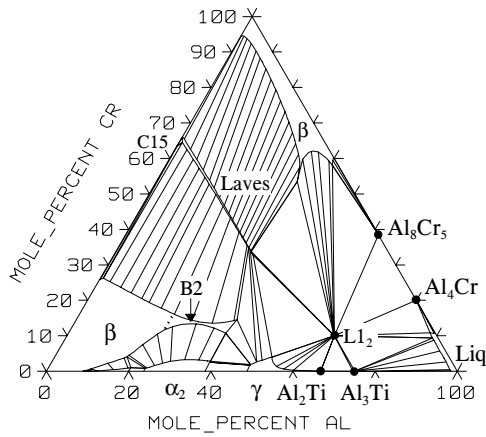


Fig.2 Calculated isothermal section for Ti-Al-Cr at 1000°C

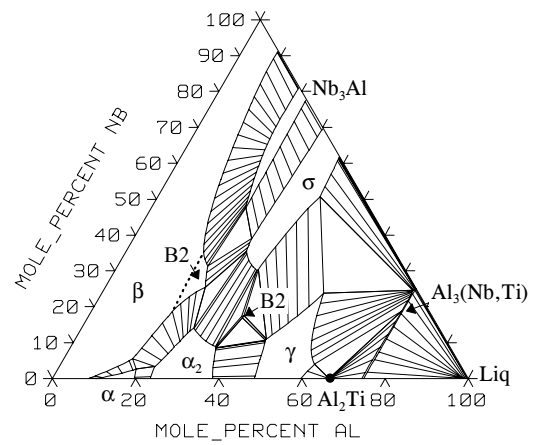


Fig.3 Calculated isothermal section for Ti-Al-Nb at 1000°C

Calculated Ti-Al-X systems

Multi-component calculations are based on extrapolations of binary and ternary thermodynamic parameters and, as such, it is useful to view some of the critical ternary diagrams. Figs.2&3 show the Ti-Al-Cr and Ti-Al-Nb systems. They are quite different in general form but both are characterised by the formation of a ternary B2 phase.

Although only observed in ternary systems, the B2 phase is basically an extension of the B2 phase in Ti-Al that is only just metastable. (There is a recent report²² that it may actually be just stable at high temperature in the binary system). As both Cr and Nb stabilise the β phase the ordering becomes apparent in the ternary. By normal chemical ordering theory the B2 phase is stabilised by maximising the number of attractive bonds in the BCC structure. In the case of Ti-Al-X systems (where X is a transition metal) the strongest pair interactions are between Al and Ti or X which leads to one of the substitutional sublattices becoming predominantly filled with Al and the other predominantly filled with Ti and X.

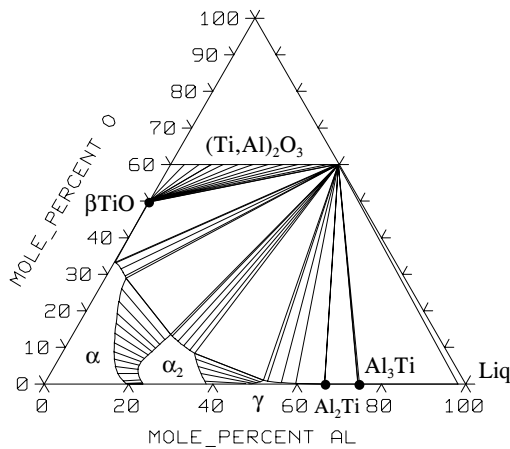


Fig.4 Calculated isothermal section for Ti-Al-O at 1000°C

It is well known in conventional Ti-alloys that interstitial elements such as C, N and O stabilise the α phase. In the case of O addition the α₂-Ti₃Al is also particularly stabilised. A thermodynamic assessment for this system has been previously reported²³ and Fig.4 shows the calculated diagram. The strong partitioning of O to the α₂-Ti₃Al phase means that it acts as a “getter” for O in dual-phase structures containing γ-TiAl and α₂-Ti₃Al. This prediction is in very good agreement with experimentally observed behaviour in both binary Ti-Al alloys²⁴ and that measured in a Ti-48Al-2Cr-2Nb alloy using an atom probe technique²⁵. The consequences are that the O level of the γ-TiAl phase is much reduced in comparison to the bulk level. The ductility of TiAl can be substantially lowered by high levels of O^{26,27} and it has been suggested that “gettering” of O by α₂-Ti₃Al may improve the ductility of γ-TiAl based alloys²⁸.

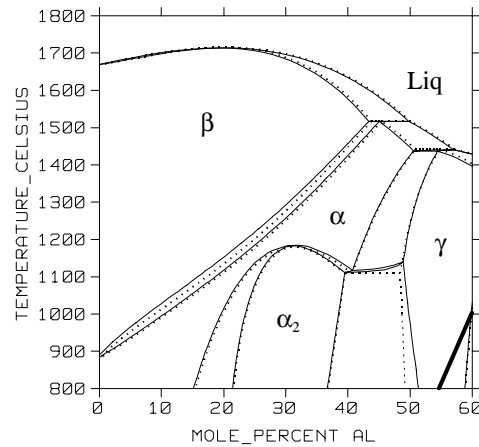


Fig.5 Vertical section through Ti-Al-O at 500ppm (wt%) of O. Dotted line indicates Ti-Al binary diagram. Thick line denotes appearance of Al₂O₃.

To view the effect of O on phase equilibria in Ti-Al alloys a vertical section through Ti-Al-O at 500 wt.ppm was calculated and shown in Fig.5. The effect of O on phase equilibria is not marked at high temperatures, but at lower temperatures the γ/γ+α₂ phase is shifted to higher Al concentrations because of the preferential partitioning of O to α₂. It is also noticeable that Al₂O₃ encroaches into the γ-TiAl single phase field.

Calculations for Multi-component Alloys

Multi-component alloy phase diagrams become difficult to represent and interpret. In these circumstances it is more usual to show phase equilibria in specific alloys using phase % vs. temperature plots and a calculated diagram is shown for an early 1st generation alloy Ti-48Al-1V.

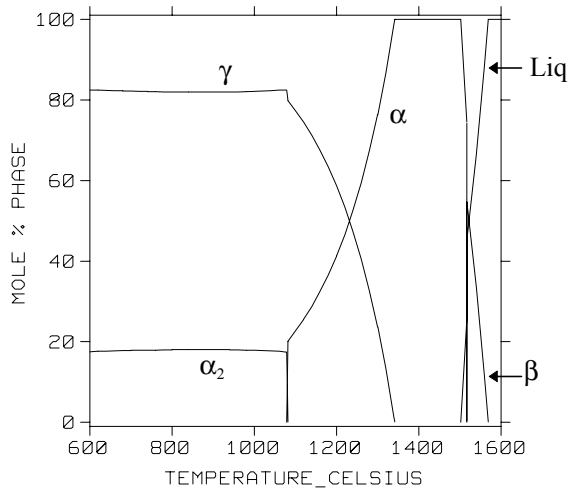


Fig. 6 Calculated mole % vs. temperature plot for a Ti-48Al-1V alloy

The alloy exhibits quite classical behaviour, as would be expected with such a small alloy addition, and critical features such as the α -transus and α_2 + γ eutectoid temperature are close to binary values. The β phase is the primary phase to form from the liquid and is involved in much of the solidification. This is because V is a β stabiliser. In other alloys where this stabilisation is not strong the α phase may predominate.

One of the main features that is measured quantitatively is the α -transus (α_T) and Table 1 shows a comparison between calculated and experimental observation for a series of multi-component alloys. Where information is provided the O concentration has also been input. Agreement is rather good.

Table 1. Comparison between experimental and calculated α -transus temperatures for multi-component γ -TiAl based alloys

Alloy	α_T (exp.)	α_T (calc.)	ref.
Ti-48Al-2Cr-2Nb	1364	1357	29
Ti-49.5Al-1.1Mn-2.5Nb	1436	1425	30
Ti-46.7Al-3Nb-1W	1350	1353	31
Ti-46Al-2.5Nb-2.1Cr-0.2B	1330	1327	"
Ti-46.48Al-2.07Nb-2.03Cr	1343	1337	32
Ti-47.73Al-1.77Nb-1.99Cr	1366	1369	"
Ti-47.54Al-1.83Nb-1.86Cr-0.45W	1361	1363	"
Ti-46.57Al-2.02Nb-2.15Cr-0.54W	1359	1336	"
Ti-47.82Al-1.87Nb-1.98Cr-0.91W	1358	1371	"
Ti-46.37Al-2.06Nb-2.19Cr-1.04W	1344	1342	"
Ti-47Al-2.6Nb-1Cr-0.9V	1355	1356	33
Ti-47Al-2.3Nb-1.5Cr-0.5V	1362	1353	"
Ti-46.5Al-2.1Cr-3Nb-0.2W	1325	1342	"
Ti-47Al-1.5Cr-0.5Mn-2.6Nb-0.15B	1365	1367	"

Using the CALPHAD method it is now interesting to track alloy development on an historical basis. Figs. 7&8 show phase % plots for two early types of alloy; Ti-48Al-2Mn-2Nb and Ti-48Al-2Nb-2Cr with 750 wt.ppm. Although nominally called 48-2-2 alloys the level of Al can often vary between 45-48Al and a base level of 47Al has been taken here.

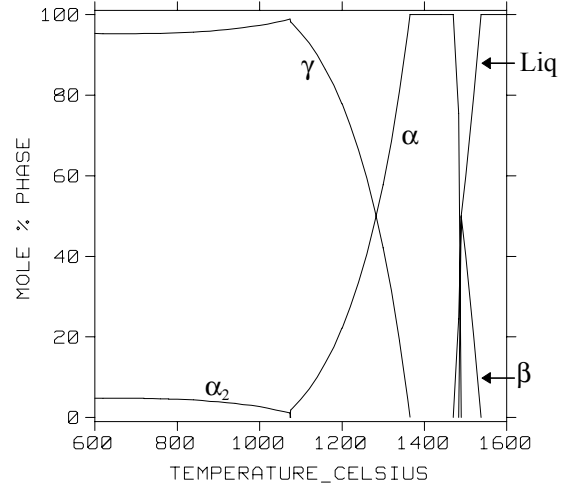


Fig. 7 Calculated mole % vs. temperature plot for a Ti-47Al-2Mn-2Nb alloy

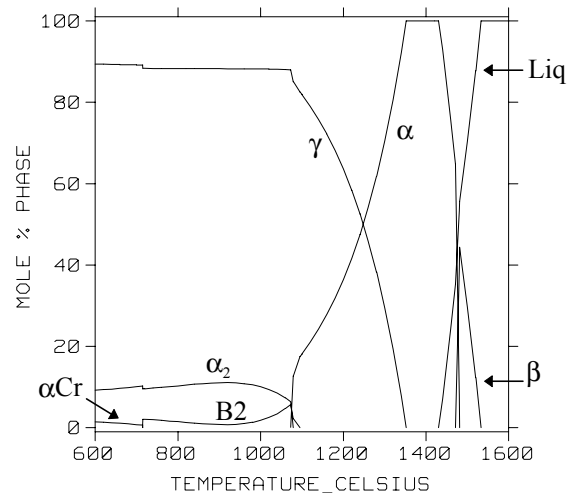


Fig. 8 Calculated mole % vs. temperature plot for a Ti-47Al-2Cr-2Nb alloy

While both alloys have a base of 47Al and 2Nb the effect of Mn and Cr is quite different. The Mn reduces the α_2 -Ti₃Al level, but otherwise its behaviour is similar to a standard Ti-48Al type alloy. On the other hand the effect of Cr is more dramatic with the appearance of the B2 phase predicted to appear at lower temperatures which is in good accord with experimental observation^{32,34}. It is also predicted that at low temperatures there is a possibility of formation of a Cr-rich BCC phase. The addition of B to 48-2-2 type alloys was tried and Fig. 9 shows a calculated phase % plot for a Ti-46Al-2Mn-2Nb-0.2B alloy. In this case it is shown that the TiB₂ is dissolved in the liquid phase just above the solidus.

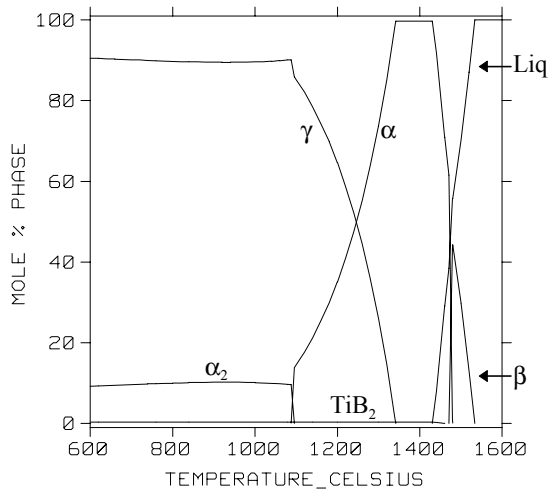


Fig.9 Calculated mole % vs. temperature plot for a Ti-46Al-2Mn-2Nb-0.2B alloy

As newer generation alloys were developed elements such as W and Ta were added and the number of components increased. The work of Fuchs³² looked at the straightforward addition of W to a Ti-48Al-2Nb-2Cr alloy. The effect of W is quite striking stabilising the BCC based phases and also causing the additional formation of a W-rich BCC phase at low temperatures (Fig.10). If such a precipitation was to occur it would be interesting in terms of its effect on creep properties.

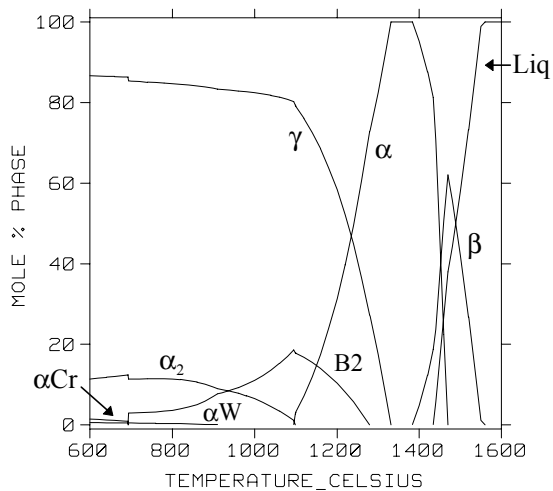


Fig.10 Calculated mole % vs. temperature plot for a Ti-47Al-2Cr-2Nb-0.5W alloy

One of the most complex alloys developed so far is Ti-47Al-2Nb-1Mn-0.5W-0.5Mo-0.2Si. However, although truly multi-component in nature, the total refractory metal addition to a basic Ti-Al alloy is still only 4at%. Fig.11 shows a phase % plot for this alloy and the microstructure would be similar to a conventional type of alloy but also containing β phase particles, enriched in Mo and W, and Ti_5Si_3 . These predictions are in quite good agreement with Seo et al.³⁵ who found precipitate types rich in W and Mo and silicides of the Ti_5Si_3 type.

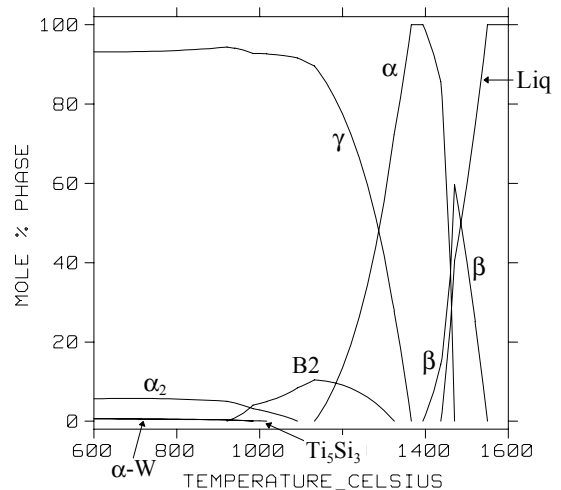


Fig.11 Calculated mole % vs. temperature plot for a Ti-47Al-2Nb-1Mn-0.5W-0.5Mo-0.2Si alloy

Site occupancy of the B2 phase

The model currently used for the B2 phase takes into account preferential partitioning of the elements between the ordered sites on the B2 sublattices. The predicted occupancy follows closely what would be expected from chemical ordering theory, with the transition elements occupying one sublattice preferentially while Al preferentially occupies the other. This occupancy maximises the strong attractive bonds that are formed between Al and transition metal pairs and minimises the repulsive bonds formed in pairs between Ti and elements such as Mo, Cr and W. The effect of O has been taken as neutral in the ordering scheme. This may not be an accurate assumption but little information exists on which to base its effect.

Conclusions and Summary

Calculations for phase equilibria in γ -TiAl based alloys have been made using the CALPHAD methodology. Good overall agreement is found with observed behaviour for these alloys. The effect of ordering of the β phase to B2 has been included in the modelling as well as the take up of interstitial elements like O in all of the major phases.

Strong partitioning of O to the α_2 phase is predicted and is in accordance with experimental observation. This supports a ductilisation model based on α_2 "gettering" γ of O.

The B2 phase is modelled using a 2-sublattice order-disorder model which produces results closely matching those expected from a modified Bragg-Williams-Gorsky model after Inden¹⁶⁻¹⁹. This model tends to maximise the attractive Al-transition metal pairs while minimising the repulsive pairs which are formed by Ti with elements such as Cr, W and Mo. The formation of the B2 in multi-component alloys seems quite well matched.

As well as phase equilibria the CALPHAD route provides thermodynamic properties such as activity and heat capacity and can be used as an information source for process modelling and understanding chemical behaviour.

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