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MODELLING OF PHASE EQUILIBRIA IN TI-ALLOYS

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Abstract

Ti-based alloys were one of the first material types to which thermodynamic phase diagram calculations were applied. However, the early limitations in modelling, particularly with respect to the uptake of elements such as oxygen and nitrogen restricted their use. Since then improvements in modelling and the increase in computing power has enabled very accurate predictions to be made for phase equilibria in real multicomponent alloys. For conventional Ti-alloys comparison between predicted and experimental values for β-transus, V_f of α and β as a function of temperature, elemental partitioning between α and β will be shown for a variety of commercial alloys. The α_2-Ti3Al and γ-TiAl based alloys present their own complexities and the present status of modelling for these alloys will be presented. The addition of O will be discussed and calculations will be presented to show its effect on phase equilibria.

1. Introduction

It is 23 years since a detailed presentation on thermodynamic phase diagram calculations for Titanium alloys was made by Kaufman and Nesor[1] at the 2nd World Conference on Titanium. They presented a series of computer calculated phase diagrams for Ti-based alloys and even included an early calculation for the Ti-Al system. Since then substantial advances have been made in terms of theoretical models, computer software and hardware and it is now possible to deal with extremely complex materials on a routine basis. This paper will present a series of up-to-date examples of how the CALPHAD method (Computer **CAL**culation of **PHA**se **D**iagrams) can be applied to both conventional Ti-alloys and the more complex α_2-Ti_3Al and γ-TiAl based intermetallic alloys.

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[2]. 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 phase equilibria can be calculated using software packages such as Thermo-Calc[3] 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[4] provides a fairly comprehensive coverage of these.

2. Conventional Ti-alloys

Due to their relatively low density and high strength conventional Ti-alloys offer the user a material with excellent specific properties. They are also particularly versatile in that pure Ti undergoes an allotropic transformation from the high temperature β phase which is body centred cubic to the low temperature α phase which is hexagonal close packed. This transformation occurs in all but a few Ti-alloys and allows a variety of microstructures to be 'designed', ranging from various forms of α/β duplex structures to martensitic.

Because of the potential for strengthening by control of microstructure, knowledge of fundamental properties such as the T^{β} and volume fraction of α or β as a function of temperature are critical factors in alloy design. There are empirical relationships which relate alloy content to T^{β} but these are not always generally applicable to all Ti-alloy types and can suffer from a lack of accuracy. Significantly there are no such relationships which can be generally used for predicting the amount of α and β in alloys as a function of temperature and composition and little work has been undertaken to understand the partitioning of elements between the α and β phases.

Kaufman and Nesor[1] showed that some binary and ternary phase diagrams of Ti-alloys, in particular the beta isomorphous systems such as Ti-V and Ti-Nb, could be reasonably represented by simple regular and sub-regular models. However, the combination of the chemical affinity of Ti for light elements such as O, C and N and their respectively powerful influence on phase equilibria means that even a simple alloy such as Ti-6Al-4V should be considered as a six component system. Although Kaufman and Clougherty[5] produced a calculated diagram for Ti-O this work was not generally extended to produce a database which could handle multi-component alloys with the requisite O, C and N additions. Recent studies by Gros *et al*[6] and Lee *et al*[7] have used CALPHAD methods for predicting phase equilibria in Ti-alloys. However, the models used in both papers lack the necessary light elements uptake which can easily lead to differences between experimental and observed T^{β} of up to 60-80°C.

In a recent paper Saunders and Chandrasekaran[8] showed that in a Ti-6Al-4V alloy with O,C and N included, the effect of O on the T^{β} could be very accurately predicted. This work has now been extended and a database exists[9] for the calculation of phase equilibria in Ti-based alloys from the following system

Ti-Al-Cr-Fe-Mo-Nb-Si-Sn-Ta-V-Zr-C-O-N-B

As well as α/β equilibria it is also possible to predict the appearance of minor phases such as carbides, Laves phases etc and α_2-Ti_3Al. Although Ti-alloys can become compositionally quite complex it is possible to predict T^{β}, the amount of α and β and the partitioning of elements between the α and β phases with a high degree of accuracy,.

Fig.1 shows a comparison between observed[10,11,12,13,14,15,16,17,18,19,20] and calculated β-transus temperatures for a wide variety of alloys, some of which are given in Table 1. The advantage of using the CALPHAD route is that it is now possible using the same database to make predictions for the amount of α and β in any alloy of interest and Figs.2-4 show calculated 'β-approach curves' in comparison with experiment[17,19,21,22,23] for (i) a near-α alloy, Ti-6Al-4V, (ii) an α/β alloy, SP700 and (iii) a near-β alloy, Ti-10V-2Fe-3Al. The comparison is between predicted mole% and observed volume% results. This gives a very good correlation as the molar volumes of the α and β are quite similar and any inaccuracy incurred by this approximation is small.

The partitioning of elements to α and β is also predicted and the comparison between experiment and prediction in Ti-6Al-4V is shown in Fig.5. Following the example of Lasalmonie and Loubradou[24], one of the V results from the β phase has an arrow indicating that the true experimental result is likely to be higher than shown in the figure. This is because the β grains were so small some overlap with the α matrix occurred during measurement by EPMA, resulting in a V reading that is almost certainly too low.

It is clear that the use of CALPHAD methods is a powerful tool in the prediction and understanding of fundamental features of conventional Ti-alloys and it can be further extended into areas associated not usually with 'equilibrium' calculations, e.g. martensitic transformations[1], the formation of omega[25] and the modelling of microstructure formation using a software package such as DICTRA[26].

3. Ti-Al based intermetallic alloys

The α_2-Ti_3Al 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. Similarly to conventional Ti-alloys, the properties of γ-TiAl based alloys are strongly controlled by their microstructure and the various microstructure types and their effect on mechanical properties are now well documented[27].

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 (Fig.6) has been undertaken by the present author[28] and this forms the basis for Ti-Al-X systems now being modelled as part of a current COST 507 project. Although there was early controversy concerning the existence of Ti_3Al phase and whether the α/β phase boundary came into equilibrium with the liquid, the form of the diagram is quite well established now with the solubility and temperature range of the α_2-Ti_3Al and γ-TiAl phases reasonably well established. 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.

One of the first extensions to ternaries was attempted by Kattner and Boettinger[29] for the Ti-Al-Nb system. However, although the form of their diagram is 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[30] on a series of Ti-Al-X ternaries, where X=Cr,Mn,Mo,Nb,V has shown the importance of including this ordering in the accurate representation of phase equilibria and it is of particular interest to be able to differentiate between the ordered and disordered form when considering mechanical properties.

Figs.7(a-d) show calculated isothermal sections at 1000° for four of the ternary alloys mentioned above and they also serve to demonstrate the different topologies which can exist for Ti-Al-X diagrams. The $\beta \rightarrow B2$ transformation is second order and its loci of composition 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 experimental work of Hellwig[31]. At a temperature just below 1000°C the same effect occurs in the Ti-Al-Cr system. The B2 phase has been modelled using a two-sublattice ordering model first proposed by Ansara et al[32]. The present author[33] 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. However, although a good basis now exists for predicting phase equilibria in multi-component Ti-aluminide based alloys, there is still a need for further experimental work to be done, particularly with respect to solubility limits of elements such as C and Si, and on the effect of alloying additions to Ti-Al-B alloys.

Similarly to conventional alloys, it is of interest to understand the likely effects of light elements on phase equilibria in Ti-Al based alloys. Calculations were presented by Lee *et al*[34] or the Ti-Al-O system based on the calculated Ti-Al diagram of Saunders[13]. The modelling methodology was subsequently re-examined by Saunders and Lee[35] and a new calculated diagram produced (Fig.8). Of particular interest is the effect of O at the levels normally found in γ-TiAl alloys on the Ti-Al diagram and Fig.9 shows a vertical section through the Ti-Al-O system at 500ppm (wt%) and compares this with a calculation for zero O. In the area of main interest to γ-TiAl alloys the diagram is essentially unaltered with the exception of γ boundary in equilibrium with α_2 where it is significantly shifted to more Al-rich levels. This is due to the substantial partitioning of O to α_2 which is quite consistent with known affinity for O of the α_2 phase in α_2/γ alloys. As Al levels increase above those show in Fig.9 Al_2O_3 is predicted to appear at most temperatures

The modelling of the light elements in the α_2 and γ phases has raised a number of quite complex modelling issues. However, the methodology adopted by Saunders and Lee[20] is quite readily extrapolated to higher order systems and a sample calculation of a Ti-45Al-2Mn-2Nb alloy with 500ppm of O (wt%) is shown in Fig10. This can be compared with results for the same alloy with zero O (Fig.11). The results are rather similar but it is interesting to examine the partitioning of O between the various phases. At the start of the $\alpha \rightarrow \alpha_2 + \gamma$ eutectoid the predicted concentrations of O in the α_2, α and γ phases are respectively (in wt%) 0.46, 0.134 and 0.033 clearly demonstrating the strong gettering effect of the α_2 phase in any α_2/γ based microstructure.

4. Summary

Phase diagram modelling of Ti-alloys is at a stage where excellent results can now be obtained for conventional Ti-alloys with the critical inclusion of the light elements C,O and N taken into account. An advantage of using the CALPHAD route is that not only are critical features such as the β-transus predicted successfully but further information such as the amount of α and β as a function of temperature, elemental partitioning, activity of all elements etc. are all readily obtained. The extension of the modelling to intermetallic alloys is at an advanced stage with a large number of critical ternary Ti-Al-X systems already characterised. The addition of O to the modelling of the α_2-Ti_3Al and γ-TiAl phases has been successfully accomplished and a database for general use in Ti-aluminide alloys is nearing completion.

Acknowledgements

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Table 1 Some alloys used in comparison of experimental and calculated T^{β}

IMI 834	6-2-1-1	IMI 679	Beta C
8-1-1	Ti1100	Corona-5	UNS R58010
UNS R5421	IMI 318	IMI 325	Beta III
IMI 367	6-2-4-2Si	SP-700	Transage 175
IMI 685	IMI 550	Ti-17	15-3-3-3
6-2-4-6	IMI 829	10-2-3	Transage 129

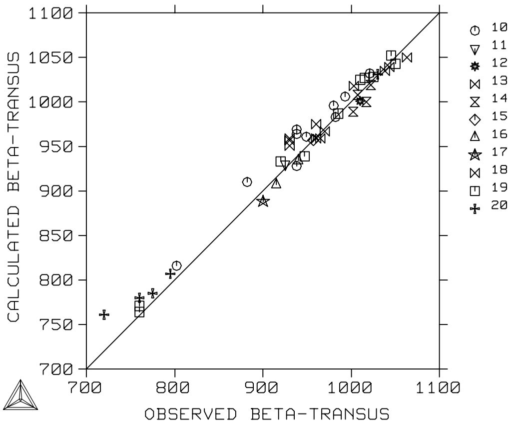

Fig.1 Comparison between experimentally observed and calculated β-transus temperatures for Ti-alloys.

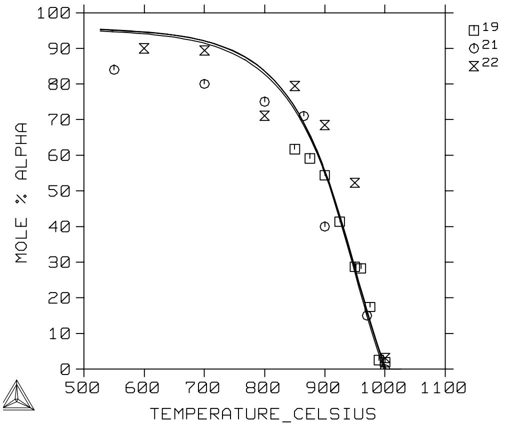

Fig.2 Comparison between experimentally observed vol% α and calculated mole % α for Ti-6Al-4V alloys.

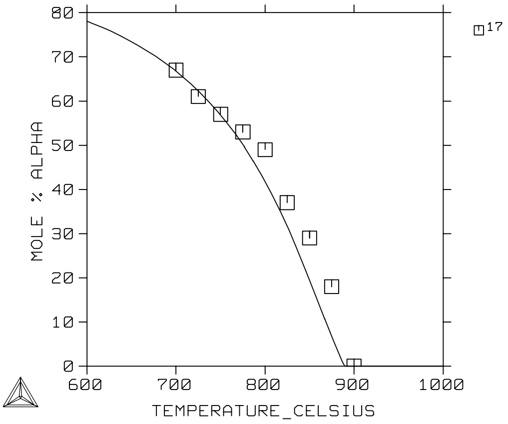

Fig.3 Comparison between experimentally observed vol% α and calculated mole % α for a SP 700 alloy.

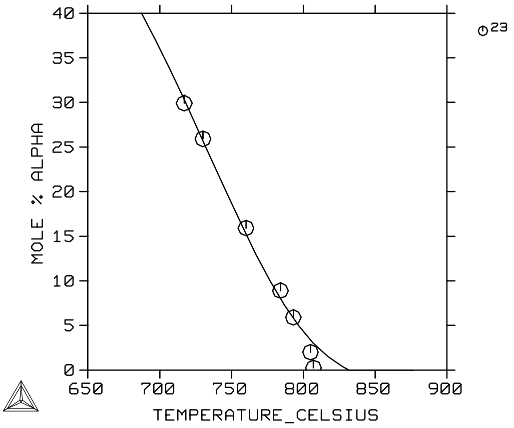

Fig.4 Comparison between experimentally observed vol% α and calculated mole % α for a Ti-10V-2Fe-3Al alloy.

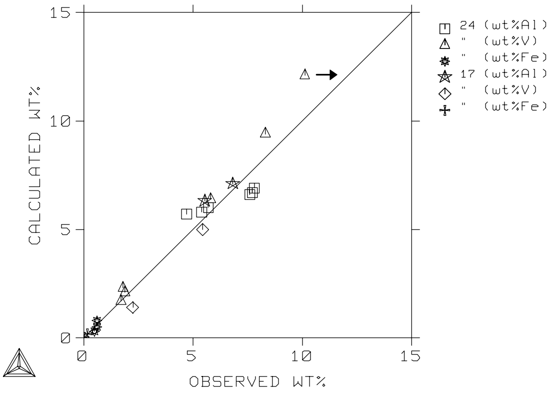

Fig.5 Comparison between experimentally observed compositions of α and β in Ti-6Al-4V alloys at various temperatures.

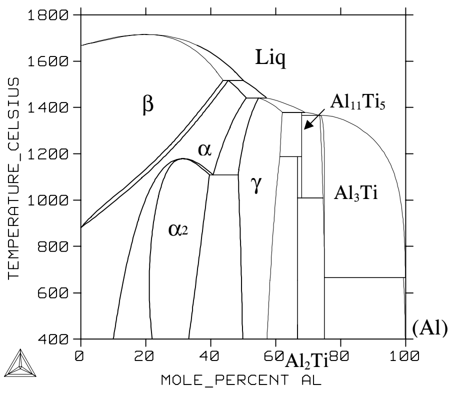

Fig.6 Calculated Ti-Al Phase Diagram[28]

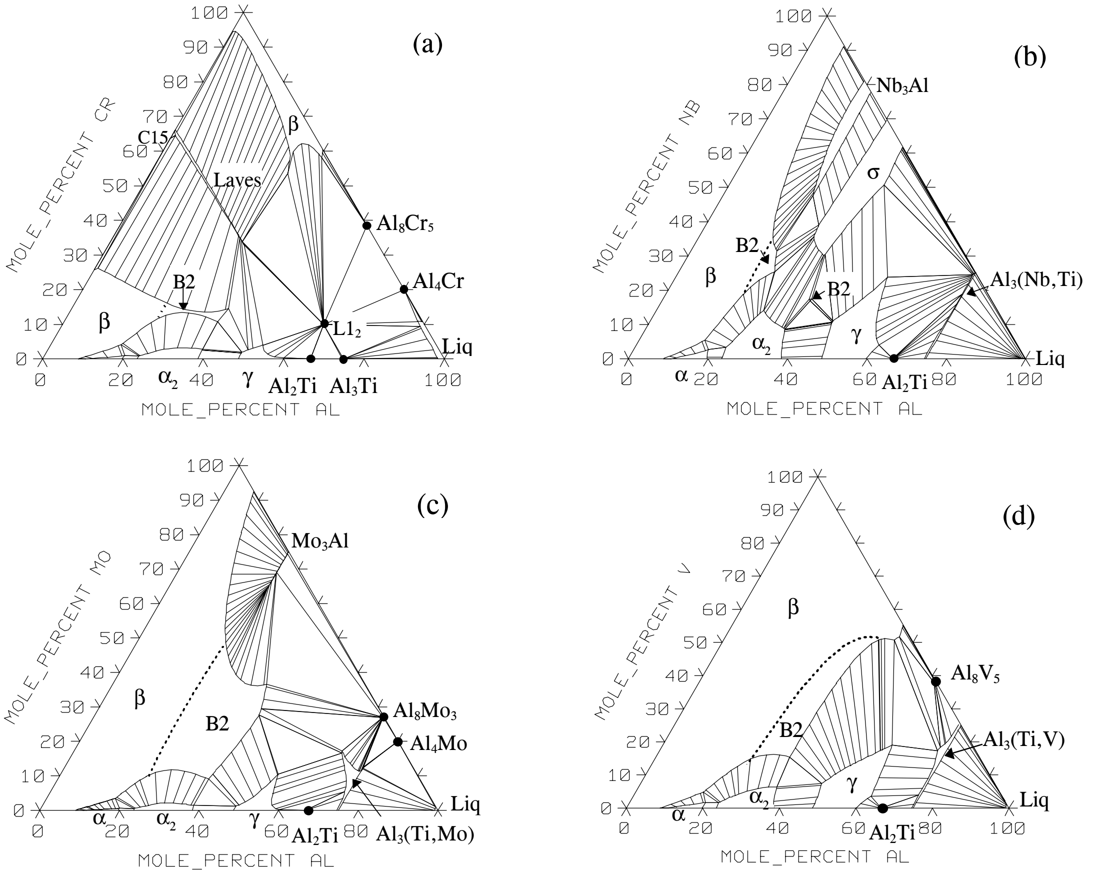

Fig.7 Calculated isothermal sections at 1000°C for (a) Ti-Al-Cr (b) Ti-Al-Nb (c) Ti-Al-Mo and (d) Ti-Al-V

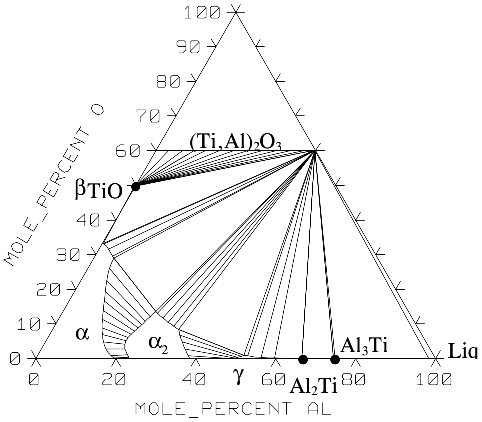

Fig.8 Calculated isothermal section for Ti-Al-O at 1000°C.

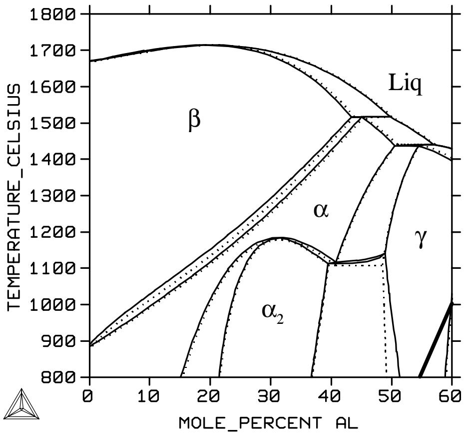

Fig.9 Vertical section through Ti-Al-O system at 500ppm (wt%) of O. Dotted line indicates position of boundaries in Ti-Al. Region to Al-rich side of thick line denotes existence of Al_2O_3.

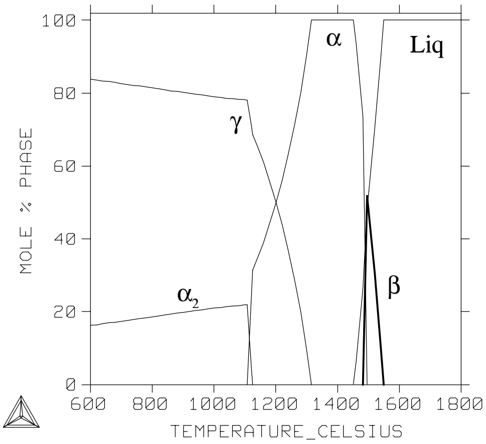

Fig.10 Calculated phase % vs. temperature plot for a Ti-45Al-2Mn-2Nb alloy with 500 ppm (wt) of O.

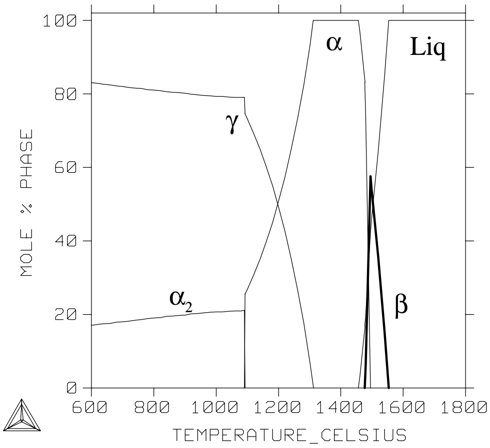

Fig.11 Calculated phase % vs. temperature plot for a Ti-45Al-2Mn-2Nb alloy (zero O)