Phase Diagrams—Understanding the Basics F.C. Campbell, editor

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CHAPTER **13**

Computer Simulation of Phase Diagrams

PHASE DIAGRAMS have traditionally been determined purely by experimentation, which is costly and time consuming. While the experimental approach is feasible for the determination of binary and simple ternary phase diagrams, it is less efficient for the complicated ternaries and becomes practically impossible for higher-order systems over a wide range of compositions and temperatures. Commercial alloys are multicomponent in nature, and a more efficient approach is needed in the determination of multicomponent phase diagrams. In recent years, a phenomenological approach, the CALPHAD approach—after the acronym <u>CAL</u>culation of <u>PHAse D</u>iagrams—has been widely used for the study of phase equilibria of multicomponent systems.

While thermodynamic models that represent nonstoichiometric solution phases have existed for many decades, it was not until the advent of computer technology that it became possible to calculate thermodynamic equilibria between such phases. The seminal works of Kaufman and coworkers in the development of computer-based methods marked the beginning of what has become known as the CALPHAD approach. As computing power increased, it became possible to use more complex descriptions of thermodynamic properties and move from binary and ternary alloys to actual multicomponent alloys used in industrial practice. Although the scientific methodology had been available to do this for some time, practical applications required a minimum of computing capability before they became useful. In the past few decades, groups have been established worldwide that specialize in both the development of software for the calculation of complex multicomponent phase equilibria and the development of thermodynamic databases that describe the properties of the relevant phases in the alloy of interest. It is the linking of software to thermodynamic databases, especially developed and validated for multicomponent alloys, that has held the key to the practical and everyday use of CALPHAD methods in industry. As computational speeds further increased, it has become possible to use CALPHAD methods as a general tool that could be linked to material models for phase transformations and subsequently to the modeling of more general material properties, such as physical and mechanical properties.

There are two main requirements for the calculation of phase equilibria:

- The thermodynamic properties of the phases in an alloy must be represented.
- A Gibbs energy minimization must be performed so that the phase equilibria between the requisite phases can be calculated.

13.1 Thermodynamic Models

Thermodynamic modeling of solution phases lies at the very core of the CALPHAD method. In metallic alloys, it is only rarely that calculations involve purely stoichiometric compounds. Solution phases are defined here as any phase in which there is solubility of more than one component.

Random substitutional models are used for phases such as the gas phase or a simple metallic liquid and solid solutions, where components can mix on any spatial position that is available to the phase. For example, in a simple body-centered cubic phase, any of the components could occupy any of the atomic sites that define the cubic structure, as shown in Fig. 13.1. In a gas or liquid phase, the crystallographic nature of structure is lost, but otherwise, positional occupation of the various components relies on random substitution rather than the occupation of any preferred site by a particular component.



Fig. 13.1 Simple body-centered cubic structure with random occupation of atoms and all sites consisting of eight-unit cells. Source: Ref 13.1

Dilute Solution Models. There are a number of areas in materials processing where low levels of alloying are important, for example, in refining and some age-hardening processes. In such cases, it is possible to deal with solution phases by dilute solution models. These have the advantage that there is substantial experimental literature that deals with the thermodynamics of impurity additions, particularly for established materials such as ferrous- and copper-base alloys. However, there are fundamental limitations in handling concentrated solutions.

General solution models include the ideal and nonideal models.

Ideal Solution Model. The simplest solution model is an ideal substitutional solution, which is characterized by the random distribution of components on a lattice with an interchange energy equal to zero.

Nonideal Solutions—Regular and Subregular Solution Models. The regular solution model is the simplest of the nonideal models and basically considers that the magnitude and sign of interactions between the components in a phase are independent of composition. However, it has been realized for a long time that the assumption of composition-independent interactions is too simplistic. This led to the development of the subregular solution model, where interaction energies are considered to change linearly with composition.

Most methods of extrapolating the thermodynamic properties of alloys into multicomponent systems are based on the summation of the binary excess parameters. The relevant formulae are based on various geometrical weightings of the mole fractions.

One of the assumptions of this approach is that the ternary interactions are small in comparison to those that arise from the binary terms. This may not always be the case, and where the need for higher-order interactions is evident, these can be taken into account with an excess ternary interaction parameter. There is little evidence of the need for any higherorder interaction terms, and prediction of the thermodynamic properties of substitutional solution phases in multicomponent alloys is usually based on an assessment of binary and ternary values. Various other polynomial expressions for the excess term in multicomponent systems have been considered. However, these are based on predicting the properties of the higher-order system from the properties of the lower-component systems.

More complex representations of the thermodynamic properties of solution phases exist, for example, the sublattice model, where the phase can be envisioned as composed of interlocking sublattices (Fig. 13.2) on which the various components can mix. It is usually applied to crystalline phases, but the model can also be extended to consider ionic liquids, where mixing on ionic sublattices is considered. The model is phenomenological in nature and does not define any crystal structure within its general mathematical



Fig. 13.2 Simple body-centered cubic structure sites consisting of eight-unit cells with preferential occupation of atoms in the body center and corner positions. Source: Ref 13.1

formulation. It is possible to define internal parameter relationships that reflect structure with respect to different crystal types, but such conditions must be externally formulated and imposed on the model. Equally, special relationships apply if the model is to be used to simulate order-disorder transformations.

Sublattice modeling is now one of the most predominant methods used to describe solution and compound phases. It is very flexible and can account for a variety of different phase types ranging from interstitial phases, such as austenite and ferrite in steels, to intermetallic phases, such as sigma and Laves, which have wide homogeneity ranges.

13.2 Computational Methods

The previous section dealt with thermodynamic models, because these are the basis of the CALPHAD method. However, it is the computational methods and software that allow these models to be applied in practice. In essence, the issues involved in computational methods are less diverse and mainly revolve around Gibbs energy minimization.

It is also worthwhile to make some distinctions between methods of calculating phase equilibrium. For many years, equilibrium constants have been used to express the abundance of certain species in terms of the amounts of other arbitrarily chosen species. Such calculations have significant disadvantages in that some prior knowledge of potential reactions is often necessary, and it is difficult to analyze the effect of very complex reactions involving many species on a particular equilibrium reaction. Furthermore, unless equilibrium constants are defined for all possible chemical reactions, a true equilibrium calculation cannot be made, and, in the case of a reaction with 50 or 60 substances present, the number of possible reactions is massive.

CALPHAD methods attempt to provide a true equilibrium calculation by considering the Gibbs energy of all phases and minimizing the total Gibbs energy of the system (G). The CALPHAD methodology has the significant advantage that, because the total Gibbs energy is calculated, it is possible to derive all of the associated functions and characteristics of phase equilibria, that is, phase diagrams, chemical potential diagrams, and so on.

13.3 Calculation of Phase Equilibria

The actual calculation of phase equilibria in a multicomponent, multiphase system is a complex process involving a high level of computer programming. Details of programming aspects are too lengthy to go into detail, but most of the principles by which Gibbs energy minimization is achieved are conceptually quite simple. This section therefore concentrates on the general principles rather than going into detail concerning the currently available software programs, which, in any case, often contain proprietary code.

Essentially, the calculation must be defined so that the number of degrees of freedom is reduced, the Gibbs energy of the system can be calculated, and some iterative technique can be used to minimize the Gibbs energy. The number of degrees of freedom is reduced by defining a series of constraints, such as the mass balance, electroneutrality in ionic systems, composition range in which each phase exists, and so on.

Most thermodynamic software uses local minimization methods. As such, preliminary estimates for equilibrium must be given so that the process can begin and subsequently proceed smoothly to completion. Such estimates are usually set automatically by the software and do not need to accurately reflect the final equilibrium. However, the possibility that phases may have multiple minima in their Gibbs energy formulations should be recognized and start points automatically set so that the most stable minima are taken into account. Local minimization tools have the advantage of being rapid in comparison to global minimization methods, which automatically search for multiple Gibbs energy minima. As such, local minimization methods were invariably favored in the early days of CALPHAD. However, with the advent of faster computers, such an advantage becomes less tangible when dealing with relatively simple calculations, and the user will notice little effective difference in speed. Codes such as Thermo-Calc and PANDAT now offer global minimization methods as part of their calculation capability. However, if the problem to be solved involves multicomponent alloys with numerous multiple sublattice phases containing a potentially large number of local minima, speed issues will still arise.

Whether to use local or more global methods is a pertinent question if reliability of the final calculation is an issue. For the case of calculation of multicomponent alloys, such as those used by industry and where the composition space is reasonably prescribed, local minimization methods have been used successfully for many years and have proved highly reliable.

One of the earliest examples of Gibbs energy minimization applied to a multicomponent system was by White et al., who considered the chemical equilibrium in an ideal gas mixture of oxygen, hydrogen, and nitrogen with the species H, H₂, H₂O, N, N₂, NH, NO, O, O₂, and OH being present. The problem here is to find the most stable mixture of species. These authors presented two methods of Gibbs energy minimization, one of which used a linear programming method, and the other is based on the method of steepest descent using Lagrange's method of undetermined multipliers. The method of steepest descent provides a rapid solution to the minimization problem and was later used in the software codes SOLGAS and SOL-GASMIX. SOLGAS, the earlier code, treated a mixture of stoichiometric condensed substances and an ideal gas mixture, while SOLGASMIX was further able to include nonideal solution phases.

The minimization methods used by later programs such as ChemSage, the successor to SOLGASMIX; F*A*C*T; FactSage, the recent combining of ChemSage and F*A*C*T; Thermo-Calc; and MTDATA are, in the broadest sense, similar in principle to that described previously, although there are clear differences in their actual operation. Thermodynamic models are now more complex, which may make it necessary to consider further degrees of freedom. However, constraints are still made to the system such that the Gibbs energy may be calculated as a function of extensive variables, such as the amount of each phase present in the system. Initial estimates are made for the Gibbs energy as a function of phases present, their amounts and composition, and so on. The Gibbs energy is then calculated and some numerical method is used, whether it be through Lagrangian multipliers or a Newton-Raphson method, by which new values can be estimated and which will cause the Gibbs energy to be decreased. When the difference in calculated Gibbs energy between the iterative steps reaches some smallenough value, the calculation is taken to have converged.

As mentioned earlier, recent progress has been made in developing more global minimization codes, for example, Thermo-Calc and PANDAT. Such codes use mathematical methods to search out all possible minima and compare Gibbs energies of the local minima so that the most stable equilibrium is automatically calculated.

13.4 Application of CALPHAD Calculations to Industrial Alloys

From the beginning, one of the aims of CALPHAD methods has been to calculate phase equilibria in the complex multicomponent alloys that are used regularly by industry. Certainly the necessary mathematical formulations to handle multicomponent systems have existed for some time, and they have been programmed into the various software packages for calculation of phase equilibria since the middle of the last century. However, it is interesting to note that, until the 1990s (with the exception of steels), there had been very little actual application to the complex systems that exist in technological or industrial practice, other than through calculations using simple stoichiometric substances, ideal gas reactions, and dilute solution models. Dilute solution modeling has been used for some time because it is not very intensive in computational terms, and some industrially important materials, although containing many elements, are actually quite low in total alloy or impurity content (e.g., high-strength low-alloy steels). Although useful for certain limited applications, they could not with any accuracy begin to handle highly alloyed materials such as stainless steels or nickel-base superalloys. Substance calculations, while containing large numbers of species and condensed phases, are in many ways even more limited in their application to alloys, because they do not consider interactions in phases involving substantial mixing of the components.

The main areas of application for more generalized models were, until the 1990s, mainly restricted to binary and ternary systems or limited to "ideal industrial materials," where only major elements were included. The key to the general application of CALPHAD methods in multicomponent systems was the development of sound, validated thermodynamic databases for use in the available computing software. Until then, there had been a dearth of such databases. Steels were a notable exception to this trend and, in particular, stainless and high-speed steels, where alloy contents can rise to well above 20 wt%. For such alloys, a concentrated solution database (Fe-Base) has existed since 1978. However, although far more generalized than dilute solution databases, its range of applicability is limited in temperature to between 700 and 1200 °C (1290 and 2190 °F). The lack of similar databases for other material types presented severe problems for CALPHAD calculations with any of the other commonly used materials and led to a concentration of application to steels. However, during the 1990s, further multicomponent databases were developed for use with aluminum alloys, steels, nickel-base superalloys, and titaniumand TiAl-base alloys. These databases were created mainly for use with industrial, complex alloys, and the accuracy of computed results was validated to an extent not previously attempted. Simple, statistical analysis of average deviation of calculated result from experimental measurement in "real," highly alloyed, multicomponent alloys has demonstrated that CALPHAD methods can provide predictions for phase equilibria whose accuracy lies close to that of experimental measurements.

The importance of validation of computed results cannot be stressed too highly. Computer models, such as those used to simulate materials processing, rely on input data that can be time consuming to measure but readily predicted via CALPHAD and related methods. For example, it is possible to model the processing of a steel at all stages of manufacture, starting from the initial stages in a blast furnace, through the refinement stages to a casting shop, followed by heat treatment and thermomechanical processing to the final product form. Such a total modeling capability requires that confidence can be placed in the predictions of each of the building blocks, and, in the case of CALPHAD methods, the key to success is the availability of high-quality, validated databases.

13.5 Databases

Substance Databases. From a simple point of view, substance databases have little complexity because they are assemblages of assessed data for stoichiometric condensed phases and gaseous species. They have none of the difficulties associated with nonideal mixing of substances, which is the case for a "solution" database. However, internal self consistency still must be maintained. For example, thermodynamic data for $C_{(s)}$, $O_{2<g>}$, and $CO_{2<g>}$ are held as individual entries, which provide their requisite properties as a function of temperature and pressure. However, when put together in a calculation, they must combine to give the correct Gibbs energy change for the reaction $C_{(s)} + O_{2<g>} \leftrightarrow CO_{2<g>}$. This is a simple example, but substance databases can contain more than 10,000 different substances; therefore, it is a major task to ensure internal self-consistency so that all experimentally known Gibbs energies of reaction are well represented.

Solution databases, unlike substance databases, contain thermodynamic descriptions for phases that have potentially very wide ranges of existence, both in terms of temperature and composition. For example, the liquid phase usually extends across the whole of the compositional space encompassed by complete mixing of all of the elements. Unlike an ideal solution, the shape of the Gibbs energy space arising from nonideal interactions can become extremely complex, especially if nonregular terms are used.

Although it may seem an obvious statement, it is important to remember that thermodynamic calculations for multicomponent systems are multidimensional in nature. This means that it becomes impossible to envision the types of Gibbs energy curves that are illustrated in many teaching texts on thermodynamics and which lead to the easy conceptualization of miscibility gaps, invariant reactions, and so on. In multicomponent space, such things are often very difficult to understand, let alone conceptualize.

Miscibility gaps can appear in ternary and higher-order systems, even though no miscibility gap exists in the lower-order systems, and the Gibbs phase rule becomes vitally important in understanding reaction sequences. Partition coefficients that apply in binary systems are usually altered in a multicomponent alloy and may change sign. Also, computer predictions can be surprising at times, with phases appearing in temperature/composition regimes where an inexperienced user may well not expect. In practice, many scientists and engineers who require results from thermodynamic calculations are not experts in CALPHAD. As such, it is necessary to validate the database for multicomponent systems so that the user can have confidence in the calculated result.

13.6 Industrial Applications

Although industrial processes rarely reach an equilibrium state, knowledge of phase stabilities, phase transformation temperatures, phase amounts, and phase compositions in an equilibrium state is critical in the determination of processing parameters. In this section, four examples are presented to show how multicomponent phase diagram calculation can be readily useful for industrial applications.

In Example 1, phase diagram calculation is used to predict bulk metallic glass formability.

In Example 2, calculations are made for nickel alloys, focusing on the major concerns in the development of nickel-base superalloys, such as γ' solvus temperature, matrix (γ)/precipitate (γ') misfit, and the formation of deleterious topologically close-packed (tcp) phases.

In Example 3, phase diagram calculation is applied to commercial titanium alloys. The β transus (temperature at which a starts to precipitate from β) and β approach curve (fraction of β phase as a function of temperature) are calculated for a variety of titanium alloys and compared with experimental data. The effect of interstitial elements, such as oxygen, carbon, nitrogen, and hydrogen, on the β transus temperatures is also discussed.

In Example 4, phase diagram calculation is used to predict dilation of iron alloys during phase transformations from austenite to ferrite and from austenite to martensite.

Example 1: Prediction of Bulk Metallic Glass Formability. Bulk metallic glass (BMG) materials exhibit unique properties, such as high strength, wear and corrosion resistance, castability, and fracture toughness. These properties make them extremely attractive as materials having great potential for practical applications in the areas of sports and luxury goods, electronics, medical, defense, and aerospace. Regardless of their importance, BMGs are mainly developed by experimental trial-and-error approaches involving, in many cases, the production of hundreds to thousands of different alloy compositions. Therefore, there is a need to either formulate a theoretical model or develop a computational approach for predicting families of alloy compositions with a greater tendency for glass formation. In recent years, Chang and his colleagues (Ref 13.2) have used multicomponent phase diagram calculation to identify the alloy compositions that have high BMG formability. The theoretical basis of their approach is that the reduced glass transition temperature (T_r) , which is defined as the ratio of the glass formation temperature and the liquidus temperature, should be on the order of 0.6 or higher. According to this argument, BMGs are often found to form near deep eutectic invariant reactions where high T_r can be achieved. In addition, due to the low liquidus temperature at a deep eutectic region, the liquid has an exceptionally high viscosity, further suppressing nucleation by inhibiting mass transport. It has been found that the formation of BMG usually requires three or more elements, even though they do form in some binary systems. This implies that, in principle, if phase diagrams of multicomponent systems are known as functions of temperature and composition, potential alloy compositions that favor BMG formation can readily be identified. Unfortunately, accurate liquidus projections and phase diagrams of multicomponent systems, which are required to guide the exploration of BMGs, are rarely available, and this is true even for many ternary systems. Multicomponent phase diagram calculation thus becomes a desirable approach for efficiently scanning the vast number of possible compositions that may yield BMGs. The methodology is to develop a thermodynamic database for the system to be studied, from which the lowering liquidus valley can be calculated. Key experiments will then be arranged to validate the BMG formability for alloy compositions being identified by the calculation.

To demonstrate the capability of this approach, two examples are given here. The first one is for the identification of BMG formers in the Zr-Ti-Cu-Ni system, and the second is for the effect of titanium on the glass formability of the Zr-Cu-Ni-Al alloys. In the first example, a thermodynamic database for the Zr-Ti-Cu-Ni system was developed. The liquidus projection was then calculated for this quaternary using Pandat software, and 18 five-phase invariant equilibria were identified that show low-lying liquidus temperatures. The compositions of the liquid phase at these invariant temperatures, shown as solid circles in Fig. 13.3, are found to be located in two areas in the composition diagram, which is in excellent agreement with those identified experimentally. Doing the calculations first would save a tremendous amount of experimental work.

In the second example, the effect of titanium on the glass-forming ability (GFA) of Zr-Cu-Ni-Al quaternary alloys was studied first by thermodynamic calculation and then validated by experimental approach. The quaternary $Zr_{56.28}Cu_{31.3}Ni_{4.0}Al_{8.5}$ alloy was first found to be a BMG-forming alloy based on the calculated low-lying liquidus surface of the quaternary Zr-Cu-Ni-Al system. By calculating the liquidus projection of the Zr-Cu-Ni-Al-Ti system, the liquidus temperature was found to decrease rapidly from the quaternary alloy $Zr_{56.28}Cu_{31.3}Ni_{4.0}Al_{8.5}$ (at.%) due to the addition of titanium. Further calculation of several isopleths revealed that the liquidus temperature decreased the fastest when zirconium was replaced by titanium and reached a minimum at 4.9 at.% Ti, as shown in Fig. 13.4. Alloy ingots of nominal compositions $Zr_{56.28-c}Ti_cCu_{31.3}Ni_{4.0}Al_{8.5}$ (c = 0 ~ 10.0 at.%) with different amounts of titanium were then prepared for experimental study of the GFA of these alloys.

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Fig. 13.3 Comparison of thermodynamically calculated compositions of liquid alloys at the five-phase invariant equilibria with those identified experimentally as bulk metallic glass formers for the Zr-Cu-Ni-Ti system. Source: Ref 13.3 as published in Ref 13.2



Fig. 13.4 Calculated isopleth of the quinary Al-Cu-Ni-Ti-Zr system expressed in terms of temperature as a function of titanium concentration (at.%). The composition of titanium at the origin is 0; corresponding to $Zr_{56.2}Cu_{31.3}Ni_{4.0}Al_{8.5}$, the compositions of copper, nickel, and aluminum are fixed at 31.3, 4.0, and 8.5 at.%, respectively. The shaded area denotes the experimentally observed bulk glass-forming range. Source: Ref 13.2

As shown in Fig. 13.5, the critical diameters of the amorphous rods formed increased from 6 mm (0.24 in.) for the base quaternary alloy to 14 mm (0.55 in.) for the quinary alloy with 4.9 at.% Ti and then decreased again. It is worth pointing out that 14 mm (0.55 in.) was the diameter limit of the casting mold used in the experiment. An amorphous rod with larger diameter could have been obtained if a larger casting mold had been used. It is not difficult to imagine how many alloys must be studied in a five-component system to identify the alloys with high GFA if a purely trial-and-error experimental method is used. These two examples thus demonstrate the great power of thermodynamic calculation in quickly locating the alloy chemistries with a high potential of GFA and guiding the experimental study.

Example 2: Design and Development of Nickel-Base Superalloys. Nickel-base superalloys are a unique class of metallic materials that possess an exceptional combination of high-temperature strength, toughness, and resistance to degradation under harsh operating environment. These materials are widely used in aircraft and power-generation turbines, rocket engines, and other challenging environments, including nuclear power and chemical processing plants. To improve the performance of nickel-base superalloys, alloy composition and processing conditions must be carefully optimized to promote the formation of desired phases and microstructure and to avoid the formation of deleterious phases.

Multicomponent phase diagram calculation therefore plays an important role in nickel-base superalloy design. With this approach, not only equilibrium phases but also phase amounts and phase transformation temperatures can be predicted, given alloy chemistry. As an example, the liquidus, solidus, and γ' solvus for a number of Rene' N6 alloys in the specification range are calculated and compared with those determined by experiments. As shown in Fig. 13.6, the liquidus varies in the temperature range of 1660



Fig. 13.5 Critical diameters of the cast glassy rods as a function of the titanium concentration in atomic percent. Source: Ref 13.2



Fig. 13.6 Comparison of calculated liquidus, solidus, and γ' solvus temperatures with those determined by experiment. Source: Ref 13.4 as published in Ref 13.2

to 1700 K (1385 to 1425 °C), the solidus of 1615 to 1675 K (1340 to 1400 °C), and the γ' solvus of 1525 to 1585 K (1250 to 1310 °C). Obviously, even for the same group of alloys whose compositions are all within the specification range of Rene' N6, their phase transformation temperatures can differ significantly, depending strongly on the alloy chemistry. It is important that these temperatures can be calculated, because they are critical parameters needed for the determination of processing conditions.

Another example is shown in Fig. 13.7, which compares the calculated and experimentally determined volume percent of γ' phase for a number of nickel-base superalloys containing aluminum, chromium, molybdenum, titanium, and tungsten. The two major phases of nickel-base superalloys are γ and γ' , and the presence of a high volume fraction of γ' is the key to strengthening. This figure clearly shows that a high volume fraction of γ' can be obtained through the optimization of alloy composition. Calculations were carried out using the PanNi thermodynamic database (Ref 13.6) and experimental data. Good agreement was obtained.

Because the matrix phase (γ) and the precipitate phase (γ') of nickel-base superalloys are crystallographically coherent, the precipitate-matrix misfit results in internal stresses that influence the shape of the precipitates and thus the final mechanical properties. The precipitate-matrix misfit (δ) can be calculated as:



Fig. 13.7 Comparison of the calculated and experimentally determined percent of γ' in the $\gamma + \gamma'$ two-phase mixture for a number of Ni-Al-Cr-Mo-Ti-W alloys. Source: Ref 13.5 as published in Ref 13.2

$$\delta = \frac{a_{\gamma'} - a_{\gamma}}{0.5(a_{\gamma'} + a_{\gamma})}$$

where $a_{\gamma'}$ and a_{γ} are the lattice parameters of the γ' and γ phases, respectively. Obviously, the precipitate-matrix misfit is determined by the lattice parameters of the γ' and γ phases, which depend on the compositions of these two phases. Elemental partitioning is therefore an important alloy design consideration, because the compositions of the constituent phases will directly impact both the mechanical and environmental characteristics of the alloy. With the computational tool for multicomponent phase diagram calculation, the phase composition and elemental partitioning can be readily calculated if a reliable thermodynamic database is available for the alloy system. Figure 13.8(a) compares the calculated and experimentally determined aluminum contents in the γ and γ' phases for a number of nickel-base superalloys, while Fig. 13.8(b to e) are for those of cobalt, chromium, molybdenum, and titanium. All calculations are carried out using the PanNi database, and experimental data from the literature are used for comparison. In all cases, there is good agreement between the calculated and experimental data.

In general, refractory alloying elements, such as molybdenum, niobium, rhenium, and tungsten, are added for solid-solution strengthening of the γ phase and to provide high-temperature creep resistance. A major concern with these alloying elements is the formation of tcp phases. The tcp phases are typically rich in refractory alloying elements and are detrimen-

tal because they deplete strengthening elements from the matrix phase. Examples of tcp phases include the orthorhombic *P* phase, the tetragonal σ phase, the rhombohedral *R* phase, and the rhombohedral μ phase. Being able to predict the correlation between the stabilities of the tcp phases and the alloy composition, thereby avoiding the formation of deleterious phases by wisely adjusting the alloy composition, is of critical importance in the design of new alloys and the modification of specification ranges for existing alloys. The CALPHAD approach has been used for such purposes. One example is shown in Fig. 13.9. In this example, the effect of rhenium content on the stability of σ is presented for the CMSX-4 alloy. This figure shows that the σ precipitation temperature and its amount strongly depends on the content of rhenium in the alloy, and the higher the rhenium content, the more σ will form. The predicted trend is correct, while the accuracy of the phase transformation temperature and phase amount depends on the quality of the thermodynamic descriptions for the tcp phases.

Example 3: Prediction of β Transus and β Approach Curves of Commercial Titanium Alloys. Pure titanium has two allotropic forms: the high-temperature body-centered cubic (β) structure and the low-temperature hexagonal close-packed (α) structure. The β transus, defined as the temperature at which α starts to form from β during solidification, is 883 °C (1621 °F) for pure titanium. However, this temperature can vary by several hundred degrees due to the addition of alloying elements. Elements such as aluminum, gallium, germanium, oxygen, carbon, and nitrogen are referred to as α stabilizers because they increase the β transus temperature, while vanadium, iron, molybdenum, chromium, niobium, nickel,



Fig. 13.8 Comparison between the calculated and measured equilibrium compositions of a variety of elements in γ and γ' . Source: Ref 13.2



Fig. 13.8 (continued) Comparison between the calculated and measured equilibrium compositions of a variety of elements in γ and γ' . Source: Ref 13.2

copper, tantalum, and hydrogen are β stabilizers because they decrease the β transus. Technical multicomponent titanium alloys are classified as α , β , and α - β alloys, depending on the relative amounts of α and β stabilizers in the alloy. Within the last category are the subclasses near- α and near- β , referring to alloys whose compositions place them near the $\alpha/(\alpha + \beta)$ or $(\alpha + \beta)/\beta$ phase boundaries, respectively.

According to different applications, alloy chemistry and heat treatment conditions must be carefully optimized to achieve the desired microstruc-



Fig. 13.9 Effect of rhenium content on the σ phase precipitation temperature and its amount at different temperatures, as calculated by the PanNi database. Source: Ref 13.6 as published in Ref 13.2

ture and mechanical properties. The β transus temperature is an important reference parameter used by metallurgical engineers in the selection of specified heat treatment conditions for titanium alloys. Current aerospace industrial practice calls for measurement of the β transus on every heat of titanium material, which is costly and time consuming. These operations and their associate costs can be significantly reduced with the help of a thermodynamic modeling tool, from which the β transus temperature can be easily calculated, given alloy chemistry.

In the following, examples are presented that apply thermodynamic calculations to two α - β alloys: Ti-6Al-4V (Ti-64) and Ti-6Al-2Sn-4Zr-6Mo (Ti-6246). It is noteworthy to point out that the preceding chemistries are the nominal compositions (wt%). For commercial alloys, the actual composition in each alloy varies. In addition, it is inevitable that commercial alloys always contain minute amounts of impurities, such as iron, silicon, carbon, oxygen, nitrogen, and hydrogen. Ti-64 is the most widely used titanium alloy in the world, with 80% of its usage going toward the aerospace industry. The β transus temperatures of Ti-64 range from 950 to 1050 °C (1740 to 1920 °F), depending on the amounts of components and interstitial elements, such as oxygen, carbon, nitrogen, and hydrogen. This temperature can be readily calculated by the CALPHAD approach if the thermodynamic database is available for multicomponent titanium alloys. In this study, PanTi (Ref 13.7) was used to calculate the β transus for a large number of Ti-64 heats with slightly different chemistries, and Fig. 13.10 compares the calculated and experimentally measured temperatures. Good agreement between the calculation and measurement was obtained, with an average difference of 5.2 °C. To understand the difference between the predicted values and the experimental data, a sensitivity analysis was carried out for Ti-64. It was found that the calculated β transus is very sensitive to the interstitial impurities, such as oxygen, carbon, nitrogen, and hydrogen (Table 13.1). In this table, the nominal chemistry of Ti-64 is given as Ti-6Al-4V-0.12O-0.01C-0.01N-0.005H (wt%). It is seen that 10 weight parts per million (wppm) of additional interstitial impurities (oxygen, carbon, nitrogen, hydrogen) will change the β transus of Ti-64



Fig. 13.10 Comparison of calculated and experimentally determined β transus for a number of Ti-64 alloys with slightly different chemistries. The calculation was carried out using the PanTi database and experimental data. Source: Ref 13.7 and 13.8 as published in Ref 13.2

Table 13.1 Effects of 10 wppm interstitial elements on the β transus of Ti-64

Alloy chemistry (wt%)	$\beta \ transus \ (^{\circ}C)$	ΔT (°C) (compare to Ti-64)	Δc (wppm) needs to change ΔT by 5 $^{\circ}C$
Ti-64: Ti-6A1-4V-0.12O- 0.01C-0.01N-0.005H	982.59		
Ti-64+10 wppm O	982.86	0.27	185.2
Ti-64+10 wppm C	983.08	0.49	102.0
Ti-64+10 wppm N	983.62	1.03	48.5
Ti-64+10 wppm H	981.51	-1.08	46.3
Source: Ref 13.2			

alloy by 0.27, 0.49, 1.03, and -1.08 °C, respectively. The small variation in the composition of these interstitial impurities (measured in wppm) that changes the β transus of Ti-64 by 5 °C is listed in the last column.

As an α - β alloy, the relative amount of α and β in the microstructure plays a key role in the determination of the mechanical properties of the final product. With multicomponent phase equilibrium calculation, the volume fractions of α and β can be calculated as a function of temperature, which provides valuable information for the selection of proper heat treatment conditions to achieve the desired microstructure. Figure 13.11 shows such an example, in which the α approach curve, that is, the fraction of a phase as a function of temperature, is calculated and compared with the experimental data for one Ti-64 alloy. In addition to Ti-64, the thermodynamic modeling tool is also applied to other titanium alloys. Figure 13.12 shows the calculated β approach curve, that is, the fraction of β phase as a function of temperature of one Ti-6242 alloy, while Fig. 13.13 calculates the distribution of aluminum and molybdenum in α and β for the same alloy. Both calculations agree very well with the experimental data. Calculations shown in Fig. 13.11 to 13.13 provide valuable guidance in the optimization of processing conditions of titanium alloys, and the good agreement between calculation and experimentation suggests that the PanTi database can be used for commercial titanium alloys beyond Ti-64.



Fig. 13.11 Plot of the phase fraction of α as a function of temperature for one Ti-64 alloy. The line was calculated by PanTi and experimental data. Source: Ref 13.7 and 13.9 as published in Ref 13.2



Fig. 13.12 Plot of the phase fraction of β as a function of temperature for one Ti-6242 alloy. The line was calculated by PanTi and experimental data. Source: Ref 13.7 and 13.10 as published in Ref 13.2



Fig. 13.13 Distribution of aluminum and molybdenum in the α and β phases for the same Ti-6242 alloy as in Fig. 13.12. The lines were calculated from PanTi and experimental data. Source: Ref 13.7 and 13.10 as published in Ref 13.2

Example 4: Calculation of Dilation during Phase Transformation of Austenite to Ferrite and Austenite to Martensite. Ferrous alloys that contain many alloy elements, such as cast iron and stainless steel, have been used worldwide as structural materials. Even though they are considered to be mature materials, there is a continuing demand to further improve their properties, with simultaneous cost reduction. Phase diagrams of this class of multicomponent materials provide the guide for processing optimization, leading ultimately to the improvement of their performance in service. For example, it is known that ferrous alloys undergo dimensional change, referred to as dilation, when subjected to heat treatment. The dilation could cause distortion and lead to cracking of a material component. The origin of this dilation is the result of phase transformation from austenite to ferrite as well as austenite to martensite during heat treatment. Experimental determination of dilation is not only tedious but also very challenging, even for an experienced experimentalist, because the accuracy of the measured data depends strongly on the cooling rate. This is particularly true when a multicomponent alloy is considered, because the phase transformation temperatures are usually unknown. On the contrary, the computational approach is more efficient and provides more consistent results. The following example demonstrates how computational thermodynamics can be used to predict the degree of dilation of a chosen ferrous alloy prior to processing this material.

The dilation can be calculated using:

$$\frac{\Delta l}{l} = \frac{V_i - V_A}{3V_A}$$

where l is the length, V_i is the instantaneous volume, and V_A is the volume of austenite at a specified temperature. The instantaneous volume (V_i) is calculated from the phase fraction and molar volume of each phase involved in the phase transformation:

$$V_i = \sum_m f_V^{\phi} \cdot V_m^{\phi}$$

where f_v^{ϕ} represents the volume fraction, and V_m^{ϕ} is the molar volume of the *j* phase. For the phase transformation from austenite to ferrite, the fractions of austenite and ferrite at a certain temperature and composition can be readily obtained by thermodynamic calculation if a reliable thermodynamic database is available for ferrous alloys. The PanFe database is suitable for such a purpose (Ref 13.11). As shown in Fig. 13.14, the calculated values of f_v for austenite are in good accordance with known experimental data for a variety of stainless alloys, an indication of the reliability of the PanFe database. These data, when combined with the molar volumes of these two phases, can then be used to calculate the dilation for



Fig. 13.14 Comparison between the calculated and measured amounts of austenite for a variety of stainless steels. Source: Ref 13.2

the phase transformation from austenite to ferrite. On the other hand, the calculation for the transformation from austenite to martensite is more challenging. Martensite, a supersaturated ferrite with the composition of the parent austenite, is a metastable phase. The total Gibbs energy change for transforming austenite to martensite is the sum of the bulk Gibbs energy difference due to the transformation from austenite to ferrite, the strain energy, the surface energy, and the interfacial work. The first part can be calculated easily because the Gibbs energies of the austenite and ferrite are well developed in the thermodynamic database, while the other three parts must be estimated by empirical equations. The martensite transformation temperature, the fraction of martensite, and the retained austenite are usually calculated from semiempirical and empirical equations. However, with the thermodynamic calculation, when the Gibbs energy for the martensite is formulated, the martensite transformation temperature for a given alloy and the fractions of martensite and austenite as a function of temperature can be calculated. These quantities, in combination with the molar volume of each phase, can be used to calculate the dilation due to the phase transformation from austenite to martensite. As an example, the dilation of the high-speed tool steel 6-6-2 is calculated and compared with experimental data (Fig. 13.15). Steel 6-6-2 is a multicomponent alloy with a composition of Fe-0.81C-0.24Mn-0.26Si-5.95W-4.10Cr-1.64V-4.69Mo (wt%). The dashed line and solid squares represent the calculated and



Fig. 13.15 Comparison between the calculated dilation versus temperature and the experimental data for high-speed steel 6-6-2. Source: Ref 13.12 as published in Ref 13.2

experimentally determined dilation for the transformation from austenite to ferrite, respectively, while the solid line and the solid circles are those for the transformation from austenite to martensite. By integrating the calculated dilation data with mechanical property prediction models, the strain, distortion, cracking, residual stress, and related properties can be predicted.

13.7 Limitations of the CALPHAD Approach

The essence of the CALPHAD method is that it provides an efficient approach to convert the experimental information of lower-order systems to self-consistent thermodynamic model parameters, on the basis of which a thermodynamic database of a multicomponent system can be established. Only a limited amount of experimental effort is needed to confirm the reliability of the database thus obtained before it can be used for industrial applications. There is no doubt of the potential power of the CALPHAD approach to save a tremendous amount of experimental work. However, like every other modeling approach, this approach has its limitations, especially when handling new phases that appear in the higher-order systems but not in the constituent lower-order systems.

Topologically closed-packed phases in the technologically important nickel-base superalloys are one example. These phases, including P, σ ,



Fig. 13.16 Isothermal section of the Ni-Cr-Mo ternary system at 1000 °C (1832 °F). Source: Ref 13.2

 μ , and R, are typically rich in refractory alloying elements and possess complex crystal structures characterized by close-packed layers of atoms. As discussed earlier, the tcp phases are detrimental because they deplete strengthening elements from the matrix phase and serve as crack-initiation sites during cyclic loading. If the stabilities of these tcp phases can be accurately predicted as a function of temperature-given alloy chemistry, formation of the deleterious tcp phases can be avoided by deliberately adjusting the alloy chemistry. Thermodynamic descriptions of the tcp phases in the current nickel database are based on the available but limited experimental information in the binaries and some ternaries where they are stable, while their Gibbs energies in other subsystems are estimated. One difficulty in the development of accurate thermodynamic descriptions for the tcp phases is that they may form in the middle of a ternary system similar to a new ternary phase while not stable in any of the three constituent binaries. One typical example is the Ni-Cr-Mo ternary system, in which σ and P are stable in the ternary but not any of the constituent binaries, as shown in Fig. 13.16. In such a situation, the experimentally well-established phase relationship in the ternary is used to optimize the model parameters in the three constituent binaries. In reality, however, the phase stabilities of these tcp phases are not known in many subsystems.

Gibbs energies thus developed for the multicomponent system should therefore be used with caution. First-principles-calculated enthalpy values may be used to improve the Gibbs energy descriptions of these phases, but it is not an easy task to obtain these values in every constituent subsystem due to the complicated structure of the tcp phases. It is also found that the stabilities of these tcp phases are comparable, which means a small difference in the Gibbs energy may lead to a totally different phase relationship. This makes the modeling of these tcp phases even more challenging. The status of the current nickel database is that it exhibits a lack of capability to accurately predict the stabilities of the tcp phases, but it does provide reasonable trends in most cases, such as the example shown in Fig. 13.9. Although more basic research is needed in this area for additional improvements of the thermodynamic descriptions of the topological phases, computational thermodynamics has been successfully used to obtain phase equilibria for practical applications.

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