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THE CALPHAD METHOD AND ITS ROLE IN MATERIAL AND PROCESS DEVELOPMENT

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Abstract

Successful design of materials and manufacturing processes requires the availability of reliable materials data. Commercial alloys usually contain a large number of elements, and the needed data for the design of new materials and processes are rarely available. The CALPHAD (CALculation of PHAse Diagrams) method enables the development of thermodynamic and property databases, that in conjunction with extrapolation methods of the descriptions of binary and ternary systems to higher-order systems, allow the calculation of data for higher-order systems. The results obtained from CALPHAD calculations have been shown to be invaluable in the design of new materials. This review presents an overview of the CALPHAD method, software tools and databases and gives examples of its application.

Abstract

Projeto bem sucedido de materiais e processos de fabricação exige a disponibilidade de dados fiáveis materiais. Ligas comerciais geralmente contêm um grande número de elementos, e os dados necessários para a concepção de novos materiais e processos raramente estão disponíveis. O CALPHAD (cálculo da fase Diagramas) método permite o desenvolvimento de bases de dados termodinâmicos e de propriedade, que em conjunto com métodos de extrapolação das descrições de sistemas binários e ternários aos sistemas de ordem superior, permitir o cálculo de dados para sistemas de ordem superior. Os resultados obtidos a partir de cálculos CALPHAD foram mostrados para ser valiosa para a concepção de novos materiais. Esta revisão apresenta uma visão geral do método CALPHAD, ferramentas de software e bancos de dados e dá exemplos de sua aplicação.

Keywords

CALPHAD; databases; diffusion; phase equilibria; phase-based properties; thermodynamics

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1 INTRODUCTION

Understanding of phase equilibria and the underlying thermodynamics is crucial for the understanding of materials and the transformations that may occur. For this reason phase diagrams are frequently described as roadmaps for materials development. Most materials consist of more than two or three components making the graphical representation of these systems challenging and thereby limiting their usefulness. Furthermore, for many multicomponent systems (this term will be used in this article for system with four or more components) the phase diagrams are frequently only partially known at best. Computational thermodynamics methods can help to fill these gaps.

Although the general idea of calculating phase equilibria from the thermodynamics is more than a century old [1], it took almost 50 years before it was applied to the calculation of a real alloy system, Ni-Cr-Cu [2]. Roughly at the same time, Kaufman and Cohen [3] used thermodynamic calculations to analyze the martensitic transformation in the Fe-Ni system. The foundation for what today is known at the CALPHAD (CALculation of PHAse Diagrams) method was laid by Kaufman and Bernstein [4] in 1970 providing the general features of the method including the listings of computer programs for the calculation of binary and ternary systems with the publication of their book.

The models used by Kaufman and Bernstein were regular solution type and stoichiometric models. Although these models permitted the calculation of phase equilibria within a reasonable time frame, they did not accurately reflect the physical properties of many phases, such as phases with short or long range order. Since then the models to describe phases have undergone significant development [5] and today's thermodynamic descriptions can reproduce phase diagram and thermochemical data within the accuracy given by the experimental determinations.

In addition to the computer programs listed by Kaufman and Bernstein, an increasing number of programs for the thermodynamic calculations of phase equilibria have been developed in the 1970s and 1980s [6]. With the development of the computer programs also came the development of thermodynamic databases for commercial materials.

High quality, reliable thermodynamic descriptions are the foundation for combining the description of binary and ternary system into databases for multicomponent systems. Activities in Europe in the development of a common database eventually resulted in the formation of SGTE (Scientific Group Thermodata Europe) [5]. Dinsdale [7] compiled for this group the reference data for the pure elements which are the foundation of today's multicomponent databases.

Traditional materials design and process development is time consuming and costly. The CALPHAD method was recognized early as a valuable tool for alloy development as knowledge of the phases that are present in a material and their compositions is essential for modeling the behavior and properties. It is the strength of the CALPHAD method that it currently is the only method available for efficient calculations in multicomponent, multiphase systems that has the accuracy needed for practical applications. Furthermore, CALPHAD calculations can also be used to obtain information about metastable equilibria and the driving forces for the formation of the stable phases. This has made the CALPHAD method an important tool for many industries and part of what is now known as ICME (Integrated Computational Materials Engineering) [8]. The Materials Genome Initiative (MGI) [9], announced in 2011, embraces computational tools as essential for faster, more cost efficient development, manufacture and deployment of advanced materials. In this context CALPHAD databases and software can be viewed as fulfilling the criteria of an early materials genome [10-12].

Olson [12] calls the origin of the term CALPHAD a misnomer because the method is actually not limited to the calculation of phase diagrams. Already in the 1980s Ågren [13] proposed an analog method for treating diffusional reactions in multi component alloys where the diffusional fluxes needed for the simulations were calculated from the diffusion mobility and thermodynamic factor [14]. The thermodynamic factor was obtained from thermodynamic equilibrium calculations while the diffusion mobilities were obtained from another database similar to that for the thermodynamics. Efforts have been made in recent years to apply the same methodology to the description of molar volume, bulk modulus and other properties.

2 MODELS AND GIBBS ENERGY MINIMIZATION

The thermodynamic equilibrium of a system at constant pressure is given by the minimum of the Gibbs energy, G. For multiphase equilibria this means that the sum of the molar Gibbs energies for the stable phases is at a minimum:

$$G=\sum_{\varphi} n^{\varphi} G_m^{\varphi} = minimum, \qquad (1)$$

where n^{ϕ} is the number of moles and G_m^{φ} is the molar Gibb energy of phase ϕ. The Gibbs energy of a phase can be written as the composition of different contributions:

$$G_m^{\varphi} = {}^{ref}G_m^{\varphi} + {}^{cfg}G_m^{\varphi} + {}^{phy}G_m^{\varphi} + {}^{exs}G_m^{\varphi}, \qquad (2)$$

where ${}^{ref}G_m^{\varphi}$ represents the frame of reference, such as the weighted molar Gibbs energies of the phase constituents or so-called endmember compounds, ${}^{cnf}G_m^{\varphi}$ is the configurational term, ${}^{phy}G_m^{\varphi}$ describes the contributions from other physical phenomena, such as magnetism, and the term ${}^{exs}G_m^{\varphi}$ is used to describe deviations of the Gibbs energy relative to the first three terms. Except for ${}^{cnf}G_m^{\varphi}$ these terms are functions of temperature, T, pressure, P, and molar fractions of the constituents, y_i^{φ}, of the individual phases. The constituents can be the elements, vacancies or molecules in a disordered solution phase or so-called species in phases with an ordering tendency, and can be elements, molecules, ions or vacancies. Ordering tendencies are accounted for by describing a phase consisting of sublattices which generally correspond to the different sites in the crystal structure of the phase. For liquids that reveal short range order, “sublattices” can be used to distinguish different tendencies of ionization of the constituents. For the configurational term it is assumed that all constituents occupying the same sublattice, s, are mixing ideally:

$$^{cnf}G_m^{\varphi}=RT\sum_i y_{is}^{\varphi}\,ln\left(y_{is}^{\varphi}\right), \qquad (3)$$

where R is the molar gas constant.

2.1 Models for temperature and pressure dependence

The temperature dependence of $^{ref}G_m^{\varphi}(T)$ and $^{exs}G_m^{\varphi}(T)$ are usually expressed as a series of temperature terms:

$$^{ref,exs}G_m^{\varphi}(T)=a+bT+cT\,ln(T)+\sum_n d_n T^n, \qquad (4)$$

where a, b, c and d_n are coefficients and n are integers. For representing $^{ref}G_m^{\varphi}(T)$, the n are typically 2, 3, −1 and 7 or −9 [7] and several functions may be used to represent the Gibbs energy for different ranges. The coefficients of the third and higher n-terms describe the heat capacity, $C_P=-T\left(\frac{\partial^2 G}{\partial T^2}\right)$. The heat capacity is frequently not known for solution phases or intermediate compounds. In this case it is assumed that the Neumann-Kopp rule [15], where the heat capacity is treated as the weighted sum of the heat capacity of the components, applies and $^{exs}G_m^{\varphi}(T)$ is then described using only the first two terms of Eq. 4.

Various models have been proposed to describe the pressure dependence of the terms [16-18]. These models use a description of the temperature and pressure dependence of the compressibility, which is the reciprocal of the bulk modulus, and the molar volume. Although these functions may result in physically unrealistic behavior at extremely high pressures [19] such as those found in in geological systems, they are sufficient for the description of most materials under commercial processing conditions. Indeed, the pressure dependence of the Gibbs energy of condensed phases at normal and moderate pressures is usually ignored.

Even at moderate pressures, the contribution from the pressure on the gas phase cannot be ignored. The pressure dependence of the Gibbs energy of an ideal gas is described by adding the term $RT\,ln\left(P/^{\circ}P\right)$ to the Gibbs energy with the reference pressure $^{\circ}P$. Non-ideal gases can be modeled by adding a power series in p to the ideal gas formalism or by replacing the pressure with the fugacity, f in the ideal gas formalism [20]. Unland et al. [21] developed a function, applying an approach similar to that used in equation of state descriptions, but also found that it may be necessary to use a different function at very high pressures to avoid artifacts that may be produced by these functions.

These formalisms for the description of temperature and pressure dependence of the Gibbs energy are used in practically all currently available thermodynamic databases for multicomponent systems. Although the introduction of the SGTE unary database [7] laid the foundation for the development of these databases, these formalisms had built-in artifacts [22] and the description of the temperature dependence was limited to temperatures above 298.15 K. Workshops were organized in 1995 and 2013 to develop improved new formalisms [21, 23]. One of the major recommendations of these workshops was to use different formalisms for the description of the solid and liquid phases that better reflect the underlying physics.

A description of the solid phase, based on the Einstein or Debye model for the heat capacity, describes the thermodynamic function below room temperature satisfactorily but requires additional terms for better description of the heat capacity at higher temperatures. The model proposed by Chen and Sundman [24] is based on the Einstein model:

$$ {}^{ref}G_m^{\alpha}(T) = E_0 + \frac{3}{2}R\theta_E + 3RT\,ln\left[1 - exp\left(\frac{\theta_E}{T}\right)\right] - \frac{a}{2}T^2 - \frac{b}{20}T^5, \quad (5) $$

where E_0 is the total energy at 0 K and θ_E is the Einstein temperature. A slightly modified equation is used for temperatures above the melting point to avoid undesired artifacts at high temperatures. For the description of the liquid and amorphous phase Chen and Sundman adopted the so-called two-state model proposed by Ågren [25] where the liquid is assumed to consist of solid-like (amorphous-like, *al*) and liquid-like (*ll*) atoms:

$$ {}^{ref}G_m^{Liq} = {}^{ref}G_m^{al} - RT\,ln\left[1 + exp\left(-\frac{\Delta G_d}{RT}\right)\right], \quad (6) $$

where $\Delta G_d = {}^{ref}G_m^{ll} - {}^{ref}G_m^{al} = a + bt + cT\,ln(T)$ and ${}^{ref}G_m^{ll}$ and ${}^{ref}G_m^{al}$ are the Gibbs energies of the liquid-like and amorphous-like states, respectively. These models have been applied to develop new descriptions of Fe [24] and Mn [26] and have been combined with conventional descriptions in the thermodynamic assessment of the Cr-Fe [27] system.

The currently used description of the magnetic contribution to the Gibbs energy is based on an approximation that was proposed by Inden [28] for the heat capacity which was expanded by Hillert and Jarl [29] into a formalism for the Gibbs energy. Although this formalism was originally developed for treating the ferromagnetic transition, Hertzman and Sundman [30] showed that it also can be applied to the antiferromagnetic transition. Chen and Sundman [24] proposed a slight modification of this formalism to obtain better agreement with experimental heat capacities of bcc-iron. Gheribi et al. [31] proposed an expansion of Hillert and Jarl formalism to include the pressure dependence.

2.2 Models for the composition dependence

The model descriptions most frequently used to describe the composition dependence of the Gibbs energy are variants of the Compound Energy Formalism (CEF) [32]. These formalisms can be used to describe the gas phase, regular solid and liquid solutions, intermetallics, ordered phases and liquids that reveal short range order. To illustrate the formalism, the Gibbs energy function of a phase with two sublattices and two constituents on each, i.e. $(A,C)_a(B,D)_b$, will be described. For the indices of the model parameters customary CALPHAD notation is used in which the constituents are separated by ':' if they are on different sublattices and by ',' if they are on the same sublattice. If polynomials, which are usually Redlich-Kister polynomials [33], are used the symbol L is used for the parameter and their exponents are indicated after a ";" following the constituent list. For this model the terms in Eq. (2) are:

$$\begin{aligned} {}^{ref}G_m^{\varphi}= & \; y_A^{'}y_B^{''}{}^{\circ}G_{A:B}+y_A^{'}y_D^{''}{}^{\circ}G_{A:D}+y_C^{'}y_B^{''}{}^{\circ}G_{C:B}+y_C^{'}y_D^{''}{}^{\circ}G_{C:D} \\ {}^{cfg}G_m^{\varphi}= & \; RT\left\{a\left(y_A^{'}\,ln\,y_A^{'}+y_C^{'}\,ln\,y_C^{'}\right)+b\left(y_B^{''}\,ln\,y_B^{''}+y_D^{''}\,ln\,y_D^{''}\right)\right\} \\ {}^{exs}G_m^{\varphi}= & \; y_A^{'}y_C^{'}\left(y_B^{''}\sum_{i=0}^{n_1}L_{A,C:B;i}\left(y_A^{'}-y_C^{'}\right)^i+y_D^{''}\sum_{i=0}^{n_1}L_{A,C:D;i}\left(y_A^{'}-y_C^{'}\right)^i\right), \\ + & \; y_C^{''}y_D^{''}\left(y_A^{'}\sum_{i=0}^{n_3}L_{A:C,D;i}\left(y_C^{''}-y_D^{''}\right)^i+y_B^{'}\sum_{i=0}^{n_3}L_{B:C,D;i}\left(y_C^{''}-y_D^{''}\right)^i\right) \\ + & \; y_A^{'}y_C^{'}y_B^{''}y_D^{''}L_{A,C:B,D} \end{aligned} \tag{7}$$

where $Y_A^{'}$ is the constituent fraction of A in sublattice 1; ${}^{\circ}G_{A:B}$ is the Gibbs energy or lattice stability of 'compound' AaBb, usually called an 'endmember' of the phase; and $L_{A,C:B;i}$ is the interaction parameter between A and C on the first sublattice when the second sublattice is filled with B. The endmember and interaction parameters may depend on the temperature and pressure. In most cases the constituents will be atoms, vacancies or ions, but the formalism also permits the consideration of molecular species. If the number of sublattices is reduced to one the formalism then describes a regular solution phase:

$$G_m^{\varphi}=x_A{}^{\circ}G_A+x_B{}^{\circ}G_B+RT\left\{x_A\,ln\,x_A+x_B\,ln\,x_B\right\}+x_Ax_B\sum_{i=0}^{n_{AB}}L_{A,B;i}(x_A-x_B)^i, \tag{8}$$

where x_A and x_B are the mole fractions of elements A and B, ${}^{\circ}G_A$ and ${}^{\circ}G_B$ are the lattice stabilities of the elements and $L_{A,B;i}$ are the excess parameters. If only one sublattice exists and no interactions are allowed, the CEF describes an ideal solution or the gas phase and if only one species is allowed on each sublattice the formalism describes a stoichiometric compound.

The CEF also describes phases that show chemical order-disorder transformations and requires that constraints between the different model parameters be introduced. Ansara et al. [34] introduced a modified formalism that permits independent evaluation of the properties of the ordered and disordered states by separating the contributions from the ordered and disordered states.

A two-sublattice variant of the CEF is used to describe short range order in the liquid phase [35]. One of these sublattices is the cation sublattice that is solely occupied by cations, $C_i^{\nu_i}$, with the charge v_i while the other sublattice, the anion sublattice, is occupied by anions, $A_j^{\nu_j}$, neutral species, B_k^0, and hypothetical charged vacancies, Va^{-Q}. This results in the formula $(C_i^{\nu_i})_P\left(A_j^{\nu_j},Va^{-Q},B_k^0\right)_Q$. The hypothetical charged vacancies ensure electroneutrality. For the same reason the stoichiometric numbers, P and Q, of the two sublattices, vary with composition and are equal to the average charge of the other sublattice.

These models are the most commonly used models and can be used with all CALPHAD software. Other frequently used models, although specific to certain software, are the modified quasi-chemical model for the liquid phase [36] and the cluster site approximation for order-disorder transformation in the fcc and hcp phases [37].

2.3 Determination of the model parameters

The model parameters of the Gibbs energy functions have traditionally been determined from experimental data for the system. Phase diagram and thermochemical data are taken into account for obtaining an optimized model parameter set to fit all types of data. In recent years experimental data have been supplemented by computational data from atomistic methods [37, 39]. Data from these computational methods, especially if the structure of the phase is considered, are very valuable, especially if it is not possible to determine quantities experimentally, as for the case of the Gibbs energy of formation of a hypothetical endmember phase needed for a CEF model description. The model parameters can be adjusted to fit the available critically evaluated data using a trial-and-error method or mathematical methods. The trial-and-error method is only feasible if few different types of data are available and the system is relatively simple. For complex systems and/or systems for which a multitude of data are available, mathematical methods, such as the least-squares method of Gauss [40], the Levenberg-Marquardt method [41] or Bayesian estimation method [42], are more efficient and have been implemented in various CALPHAD software.

Determination of the coefficients is frequently called “assessment” or “optimization” of a system. Lukas et al. [32] provide detailed guidance for the assessment procedure. The first step in the assessment of the thermodynamic description of a system is the critical evaluation of the available data since an equally weighted use of all available data in most cases will result in a rather arbitrary description of the system. During the assessment the validity of the thermodynamic descriptions of the individual phases must be verified. The description must be able to reproduce the phase diagram and thermochemical properties without artifacts over wide temperature and composition ranges, as well as produce reasonable metastable phase diagrams where one or more phases are absent [43]. Since both, thermochemical and phase equilibria data, from CALPHAD calculations are obtained for one set of functions describing the system the data are self-consistent.

2.4 Systems with more than two components

One strength of the CALPHAD method is that it can use the extrapolation of the descriptions of the lower component subsystems for calculation of a higher component system. Different extrapolation formalisms can be used for weighing the contributions of the constituent subsystems. Several of these formalisms were evaluated by Hillert [44] who recommended the Muggiano formalism [45] because it can be easily generalized. For example, the Gibbs energy of a ternary solution, where the binaries are described by Redlich-Kister polynomials (Eq. 8) and the Muggianu formalism is applied, is:

$$\begin{aligned} G_m^{\varphi} = &\; x_A {}^{\circ}G_A + x_B {}^{\circ}G_B + x_C {}^{\circ}G_C + RT\left\{x_A\, ln\, x_A + x_B\, ln\, x_B + x_C\, ln\, x_C\right\} \\ + &\; x_A x_B \sum_{i=0}^{n_{AB}} L_{A,B;i}(x_A - x_B)^i + x_A x_C \sum_{i=0}^{n_{AC}} L_{A,C;i}(x_A - x_C)^i + x_B x_C \sum_{i=0}^{n_{BC}} L_{B,C;i}(x_B - x_C)^i, \end{aligned} \quad (9)$$

where the parameters are the same as in Eq. 8 for each of the binary systems. In case it is necessary to describe interactions between all three elements, a ternary excess term, $x_A x_B x_C L_{A,B,C}(T, x_i)$ can be added. The results of such an extrapolation are then compared to the selected experimental and theoretical data and, if necessary, excess terms are added for the description of the phases in the higher-order system. This strategy is followed for all 3, ... n constituent systems of an n-component system. True quaternary phases are rare in metallic systems and assessment of the ternary systems is generally sufficient to describe an n-component system. However, this strategy creates a strong dependency of the description of an n-component system on the descriptions of the constituent susbsystems. For example, if the description of one of the unaries in a six-component is changed, this will affect the descriptions of five binaries and ten ternaries containing this unary. As a result, the CALPHAD community has become increasingly reluctant to adopt changes in models and endmember phase properties, even when it is known that updates need to be applied. Efforts are underway to overcome this issue by development of an automated procedure for re-assessments of binary and ternary systems [46].

2.5 Gibbs energy minimization

A commonly used algorithm for minimizing the Gibbs energy of a system, implemented in most CALPHAD software, is based on a method for determining the unknowns that was proposed by Hillert [47]. In a general case the unknowns will be the fractions of the species on the sublattices and the phase amounts. These unknowns cannot vary freely as they are subject to side conditions or constraints, such as that mass balance is fulfilled and the sum of the species fraction on each sublattice is unity. The side conditions are taken into account by multiplying them with Lagrange multipliers and adding them and adding them to the total Gibbs energy:

$$L = \sum_{\varphi} n^{\varphi} * G_m^{\varphi} + \sum_{A} \mu_A \left[N_A - \sum_{\varphi} n^{\varphi} x_A^{\varphi}\right] + \sum_{\varphi}\sum_{s} \lambda^{\varphi,s}\left[\sum_{i} y_i^{\varphi,s} - 1\right], \quad (10)$$

where n^{ϕ} is the amount of phase ϕ, N_A is the total amount of component A, x_A^{φ} is the amount of A in ϕ, $y_i^{\varphi,s}$ is the fraction of species i on sublattice s in ϕ and μ_A and $\lambda^{\phi,s}$ are Lagrange multipliers. The second term in Eq. 10 describes the mass balance and the third term describes the condition for the sum of species fractions on a sublattice. Other conditions, for example, electroneutrality, can be added after being multiplied by Lagrange multipliers. Hillert [47] showed that the Lagrange multiplier, μ_A, is identical to the equilibrium chemical potential of the system. With this approach other equilibrium conditions, for example prescribed chemical potentials or phase fractions, can also be considered.

Different approaches have been employed to solve Eq. 10. Hillert [47] suggested a two-step technique. In the first step equations for the correction of the species fractions are determined and in the second step new values for the chemical potentials and phase amounts are obtained. These two steps are repeated until convergence criteria and external conditions are fulfilled. The approach taken by Lukas et al. [48] uses one step to find a solution for Eq. 10 when all derivatives of the Lagrange function with respect to the unknowns and the Lagrange multipliers are zero. The Newton-Raphson technique is usually used for the iterations.

The solution obtained for the above described methods strongly depends on the values used at the beginning of the iteration and is susceptible to finding a local minimum, resulting in a metastable equilibrium, rather than the global minimum of the Gibbs energy (true equilibrium) for the given conditions. Different approaches have been introduced [49-51] to address this problem. The basic method is to create a grid and calculate the Gibbs energy of all phases at each of the grid points. The phases and gridpoints that represent minimum for the given conditions are then used as initial values for Gibbs energy minimization using the Lagrange function.

The use of the Lagrange function instead of using only a grid minimizer has a number of advantages. Most obviously is that the solution obtained by the Lagrange method does not depend on the meshing size selected for the grid. Another advantage of the Lagrange method is that many partial derivatives are directly calculated from the functions rather than numerical differences between two separate calculations.

It should be emphasized that other approaches for the minimization of the Gibbs energy can and have been used [52-56].

2.6 Other phase-based properties

The CALPHAD method was originally developed for modeling the thermochemical properties and phase diagrams of metallic systems. It was shortly thereafter adopted for modeling inorganic systems in general. The approach taken by the CALPHAD method that descriptions of subsystems can be used for the extrapolation of multicomponent systems makes the CALPHAD method attractive to the modeling of other phase properties. It has been successfully used for the description of diffusion mobilities [13, 14], molar volumes [57], and elastic properties [58]. New property specific models are being developed for the description of temperature and pressure dependence of these properties. Basically the same models as for the thermodynamics are used to describe the composition dependence of these properties.

It should be noted that many properties exhibit anisotropy for non-cubic crystals. The CALPHAD method is, by its basic concept, a method that is concerned with modeling the properties of a bulk system. Therefore, anisotropy is generally ignored and averaged values of the quantities are modeled.

Diffusion—Ågren [13] used the phenomenological theory of diffusion, introduced by Onsager [59], to model diffusion using the CALPHAD method. In this theory the diffusional flux of an element is assumed to depend on diffusivities and the concentration gradients. The diffusivities are functions of the atomic mobilities and the thermodynamic driving forces. For example, the intrinsic diffusivity in the lattice fixed frame of reference, ${}^{L}D_{kj}$, can be expressed as:

$$ {}^{L}D_{kj}=x_kM_k\frac{\partial\mu_k}{\partial x_j}, \quad (11)$$

where j is the diffusing component and k is the gradient component, M_k is the atomic mobility of k and $\frac{\partial\mu_k}{\partial x_j}$ is the thermodynamic factor which is partial derivative of the chemical potential of k, μ_k, with respect to the mole fraction of j, x_j. For diffusion simulations using the CALPHAD method, the thermodynamic factor can be easily obtained from thermodynamic calculations.

Andersson and Ågren [14] developed a formalism based on the CALPHAD method to describe diffusion mobilities in multicomponent systems. Assuming a vacancy exchange diffusion mechanism in a crystalline phase, the mobility matrix, M_i, which is both composition and temperature dependent, can be written as

$$M_i={}^{\circ}M_i\frac{1}{RT}exp\left(\frac{-Q_i}{RT}\right), \quad (12)$$

where ${}^{\circ}M_i$ is the frequency factor representing the atomic jumps of i and Q_i is the diffusion activation energy of i in a given phase. The atomic mobilities are modeled using CALPHAD models for the composition and temperature dependence. ${}^{\circ}M_i$ is usually included in the activation energy term $\left(Q_i^{'}=Q_i-RT\,ln\left({}^{\circ}M_i\right)\right)$.

Similar to the Gibbs energy function parameters, the diffusion mobility parameters are determined from experimental or theoretical data for each system and can be evaluated using trial-and-error methods or mathematical methods that minimize the error between the calculated and experimental diffusion coefficients. The CALPHAD modeling of diffusion was reviewed in detail by Kattner and Campbell [60].

Volume—Molar volume is not only a thermodynamic quantity that is needed for the modeling of the pressure dependence of the Gibbs energy, but it is also an important quantity for process simulations. However, efforts have been made only in recent years to model the molar volume and include it into CALPHAD databases. A database assuming pressure independent molar volume can be developed for pressure up to 1 GPa [61].

The temperature dependence of the molar volume is defined as function of the linear thermal expansion, α, is:

$$V_m = {}^{\circ}V_m \, exp\left(\int_{{}^{\circ}T}^{T} 3\alpha dT\right), \quad (13)$$

where ${}^{\circ}V_m$ is the molar volume at the reference temperature, ${}^{\circ}T$. For magnetic phases a magnetic contribution, $\Delta^{mag}V_m(T)$, needs to be added. The temperature dependence of linear thermal expansion above the reference temperature can be expressed by a polynomial in T [62]. Alternatively, Hallstedt et al. [61] proposed to describe the temperature dependence of the molar volume directly by a polynomial in T. Both models describe the molar volume above the reference temperature which is usually room temperature. Zhang et al. [63] derived a Debye-Griineisen equation to describe the thermal expansion between 0 K and the melting temperature and evaluated the thermal expansion for 42 metallic elements.

Only few assessments of the molar volume and thermal expansion of unaries, binaries or intermetallics have so far been published using the formalisms of Lu at al. and Hallstedt et al. However, descriptions are already included in some commercial databases, e.g. TCFE8, TCNI8, TCAL4, TCSLD3 [64].

Elastic properties—For thermodynamic calculations at pressures above 1 GPa, the pressure dependence of the Gibbs energy needs to be considered:

$$G(T,P) = G(T) + \int_{{}^{\circ}P}^{P} V(T,P)\, dP, \quad (14)$$

A proper equation of state (EOS, a mathematical relation between P, T and V) that can be integrated needs to be formulated in the form of $V = V(T,P)$. This formalism requires that the isothermal compressibility, κ, (or the bulk modulus, $B = 1/k$) is known [61]. Lu et al. [17] proposed an EOS suitable for CALPHAD modeling:

$$V(T,P) = {}^{\circ}V(T) - c(T)\, ln\left(\frac{{}^{\circ}\kappa(T)}{\kappa(T,P)}\right), \quad (15)$$

where ${}^{\circ}V(T)$ and ${}^{\circ}\kappa(T)$ are molar volume and isothermal compressibility at reference pressure, ${}^{\circ}P$, and $c(T)$ is an adjustable function to fit the pressure data. The extrapolation behavior of an EOS to high pressures and temperatures provides a criterion for its quality. It has been found that the EOS from Eq. 15 gives reasonable extrapolations up to 200 GPa and 6000 K [61]. Although the bulk moduli of the elements and many compounds are known, these quantities are also needed for the hypothetical endmember phases in the CEF and can be derived from the elastic constants obtained from first principles calculations [58].

Non-thermodynamic properties—The basic concept of the CALPHAD method can also be applied to describe other phase-based properties, such as electrical resistivity, thermal conductivity, thermoelectric, optical or acoustic properties. Gheribi and Chartrand [65] proposed a CALPHAD method to predict the thermal conductivity for dielectric and semiconductor phases. Campbell et al. [66] presented an extensive review of the modeling of these and other phase-based properties, and showed that the CALPHAD method can even be applied to interphase properties, such as interfacial energies, surface tension of the liquid phase, nucleation, grain boundary diffusion or thermal migration.

3 SOFTWARE AND DATABASES

3.1 Software

A variety of software packages are available for the calculation of phase diagrams. In the early days of CALPHAD, available software was dominated by free source codes, such as SOLGASMIX [67] or the Lukas programs [40]. First commercial software began to appear [68] shortly thereafter. Today a number of fully integrated, commercial software packages are available. There are too many to list them in entirety, but a few of the more well-known are CaTCalc [69], FactSage [70], MatCalc [71], MTDATA [72], Pandat [73] and Thermo-Calc [74].

Some of these software integrate thermodynamic equilibrium calculations with the simulation of kinetic processes. MatCalc [71] has the simulation of precipitation kinetics, diffusion, phase transformations/moving phase boundaries, lattice Metropolis and kinetic Monte Carlo integrated. The simulation of precipitations kinetics is also integrated in Pandat [73]. Another group of software uses thermodynamic calculations as input for diffusion simulations (DICTRA [74]), precipitation kinetics simulations (TC-PRISMA [74], phase field simulation of microstructure evolution (MICRESS [75]), and calculation of various mechanical, thermo-physical and physical properties and phase transformation diagrams (JMatPro [76]).

Most of the model descriptions used for metallic and ceramic systems are common to all of these programs. However, not every package has specific model descriptions, such as the quasi-chemical model or models for aqueous and polymer solutions. Although the features offered by the individual software packages differ, some modules, such as for the calculation of binary and ternary phase diagrams, are common to all software packages. The software packages allow a choice of thermodynamic databases, including user-specified databases. Most of the software packages also include an assessment module for the refinement of the thermodynamic functions of the phases with respect to experimental and theoretical data. The majority of the software also has programming interfaces for coupling with other software implementations.

In recent years the development of free CALPHAD software, such as Gibbs [77], OpenCalphad [78] and pycalphad [79], has gained momentum. These programs have all of the main features that can be expected from CALPHAD software with the exception that Gibbs is limited to calculations of systems with simple regular-solution and stoichiometric models.

3.2 Databases

CALPHAD-type databases are constructed from the assessments of binary, ternary and quaternary systems. For the description of commercial alloys, however, it is quite likely that at least a dozen elements need to be considered. The number of constituent subsystems of a

n-component system is determined by the binomial coefficient $\begin{pmatrix} n \\ k \end{pmatrix}$, where k is the number of components in the subsystem. A 12-component system consists accordingly of 66 binary, 220 ternary and 495 quaternary subsystems. These numbers suggest that it will be impossible to obtain descriptions of all the subsystems in a reasonable time frame. However, as previously mentioned, quaternary excess parameters are only rarely needed. For example, to develop a database for Ni-base superalloys, it is sufficient to consider only the ternary systems with Ni, considerably reducing the number of needed assessments. Also, if an element occurs only in fairly small quantities then assessments of the binary systems are usually sufficient. Based on this, a number of databases have been developed for various commercial alloy systems and inorganic systems.

Thermodynamic and diffusion mobility databases have been developed for the major alloy families, oxide and salt systems and work continues to refine these systems, to improve accuracy, and to develop improved models. Simultaneously databases for new material classes, such as high entropy alloys are being developed. Most databases for commercial materials are developed by the same companies that develop commercial CALPHAD software and it should be noted that commercial databases are only compatible with the software for which they were developed. However, there are a few free multicomponent databases available, e.g. COST 507 for light-weight alloys [80], NIST-Sn for solder alloys [81] and NIST-Ni for phase equilibria between the liquid, γ and γ' [82] and NIST-Ni-mob for diffusion in the γ phase in Ni-base superalloys [83]. Descriptions of many binary and higher order systems can be also found at the websites of the National Institute of Materials Science (NIMS [84]) and the National Institute of Standards and Technology (NIST [85]). Most of these openly available databases and descriptions are in the TDB (thermodynamic database) format which can be read by the majority of CALPHAD software. This data format was originally developed for Thermo-Calc [86] but has evolved into a de facto standard.

4 APPLICATIONS

In recent years the application of thermodynamic and kinetic information to practical processes obtained from calculations has increased significantly. A variety of examples of applications are presented summarized in a number of publications [87-92]. Extensive collections of detailed examples can be found in a number of books, such as “User Applications of Alloy Phase Diagrams” [93], “User Aspects of Phase Diagrams” [94] or the two editions of “The SGTE Casebook, Thermodynamics at Work” [95].

The coupling of CALPHAD calculations with phase field methods in recent years has become increasingly popular [96-98]. The phase field method allows non-equilibrium situations considering local interactions, interfaces and diffusion. Although the CALPHAD method provides information on a global equilibrium, this information can be utilized in phase field simulations using the concept of local equilibrium. Coupling CALPHAD calculations with phase field simulations enables realistic predictions of the microstructure evolution in multicomponent alloys. Kitashima [98] has reviewed the different coupling methods being used. Phase field simulations utilizing CALPHAD data have been carried out for dendritic growth, peritectic reactions, eutectic solidification, recrystallization and grain growth and solid state transformations. Examples of such simulations can be found in the papers resulting from the “Second symposium on phase-field modelling in materials science” [99] and “Third international conference on phase-field method” [100]. Liu et al. [101] give an example how different computational tools can be integrated for the simulation of materials over several length scales.

A major application of the CALPHAD method is materials design and process development. Olson [102] pioneered the numerical implementation of materials science principles utilizing a hierarchy of computational approaches. Using this approach, Olson and co-workers succeeded in reaching the qualified design-allowable for two landing-gear steels in 8.5 years and 5 years, respectively [103]. The latter time matches the acceleration goal set by the US Materials Genome Initiative [9]. Reed et al. [104] employed design rules to reduce a large compositional space, about 100 000 alloy compositions, to a few promising compositions for Ni-based single crystal superalloys using the results from CALPHAD calculations together with estimates of creep resistance, density, cost and castability. The alloy compositions were evaluated using histograms, trade-off diagrams and scatter diagrams of the alloy properties. More systematic approaches employ genetic algorithms [105] and mesh adaptive direct search algorithms [106] for finding new promising alloy compositions.

Although there are many success stories regarding the use of the CALPHAD method in materials design and process development, there is still room for improvement. Zhao and Henry [107] found that CALPHAD calculations are still useful for superalloy design despite the fact the prediction of the TCP (topologically close-packed) phase was not very reliable. Seiser et al. [108] compared predictions from CALPHAD calculations of superalloys with structure maps for the occurrence of the TCP phases and found that, although the formation of one of these phases was predicted correctly, the CALPHAD calculations did not correctly predict other TCP phases. The problem of incorrectly predicting the formation of certain intermetallic phases in multicomponent alloys is a result of lack of sufficient experimental data for many of the constituent ternary systems. The use of data from first principles calculations in the CALPHAD descriptions of these phases is imperative to overcome this shortcoming.

Currently the reliability of CALPHAD results from multicomponent databases is expressed by plotting experimental data versus calculated results under the same conditions. The usefulness of the CALPHAD method for materials design and process development would be increased if methods for uncertainty quantification for results from CALPHAD calculations were available. Currently no such methods exist.

5 FURTHER READING

Many references are given in the present article and several books on the CALPHAD method have been published. The book by Saunders and Miodownik [6] gives a comprehensive overview of the CALPHAD method and its applications while the book by Lukas et al. [32] provides insight in the details of modeling using the CALPHAD method.

The two editions of the SGTE casebooks [94] provide an excellent collection of examples of the application of the CALPHAD method.

6 SUMMARY

The Gibbs energy and other properties of phases are described with the CALPHAD method as functions of temperature, pressure and composition. The formalism used for representing the composition dependence of the functions gives the CALPHAD method the ability to extrapolate the properties to higher-order systems after accurately defining the needed binary, ternary, and when necessary quaternary systems. This makes the CALPHAD method a powerful tool for alloy development and process design. A variety of experimental data and first principles results are used as inputs by the CALPHAD method to fit the Gibbs energy, diffusion mobility and other property functions of lower order system which are then combined into databases for multicomponent systems. The currently available thermodynamic and diffusion mobility databases are used in a wide range of applications to predict material properties and microstructure evolution. The development of auxiliary property databases will increase the range of applications.

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