

AN INTRODUCTION TO THE CALPHAD METHOD AND THE COMPOUND ENERGY FORMALISM (CEF)

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Abstract

The CALPHAD (Calculation of phase diagrams) method and the Compound Energy Formalism (CEF) are briefly introduced and a few selected examples of their application are reported.

Keywords: CALPHAD; Thermodynamics; Compound energy formalism; Alloys; Intermetallics.

UMA INTRODUÇÃO AO MÉTODO CALPHAD E AO FORMALISMO DA ENERGIA DOS COMPOSTOS (CEF)

Resumo

O método CALPHAD (*Calculation of Phase Diagrams*) e o Formalismo da Energia dos Compostos (CEF) são apresentados e alguns exemplos de suas aplicações são discutidos.

Palavras-chave: CALPHAD; Termodinâmica; Formalismo da energia dos compostos; Ligas metálicas; Compostos intermetálicos.

I INTRODUCTION

Design and preparation, use, and eventually, recycling and disposal of materials require a detailed knowledge of their constitutional properties among which, in particular, phase stabilities and equilibria as a function of the conditions the materials are subjected.

Such kind of information is provided, in a complete and concise way, by phase diagrams, which are widely used, especially in the case of non-stoichiometric materials such as alloys, ceramics, salt mixtures, etc.

Traditionally, phase diagrams have been determined by means of experimental investigations which become more and more difficult and time consuming with the increasing number of components. Moreover, phase equilibria and thermodynamic properties, unless strictly correlated, are generally determined by independent experiments and may result inconsistent with each other.

The CALPHAD approach helps to overcome these difficulties because it reduces the number of experiments needed to investigate a system, assures the self-consistency between phase equilibria and thermodynamics, makes easy to calculate any kind of sections in multi-component phase diagrams, and provides the thermodynamic basis for the

subsequent modeling of kinetic processes which determine behavior and properties of real materials.

The CALPHAD approach was introduced in the early 70s of the past century by L. Kaufman and H. Bernstein [1] and later developed by several authors: see for instance P.J. Spencer [2] for a brief history of CALPHAD. Moreover, the CALPHAD method and its theoretical as well as practical aspects have been comprehensively treated in a number of books: we may mention N. Saunders and A.P. Miodownik [3], M. Hillert [4], H.L. Lukas et al. [5].

Nowadays CALPHAD is a very complex process where not only experiments but also quantum mechanical and statistical thermodynamic calculations contribute to the determination of the parametrised expressions of the thermodynamic functions of the phases. Then, any calculation or further modelling based on these parametrised functions (e.g. phase field modelling of crystal growth, simulation of diffusion-controlled transformations, etc.) is considered part (or an extension) of the CALPHAD approach. Nevertheless, the core of the method is still represented by the block diagram shown in Figure 1.

It consists in the determination of the Gibbs energy function of all the phases involved in the system under

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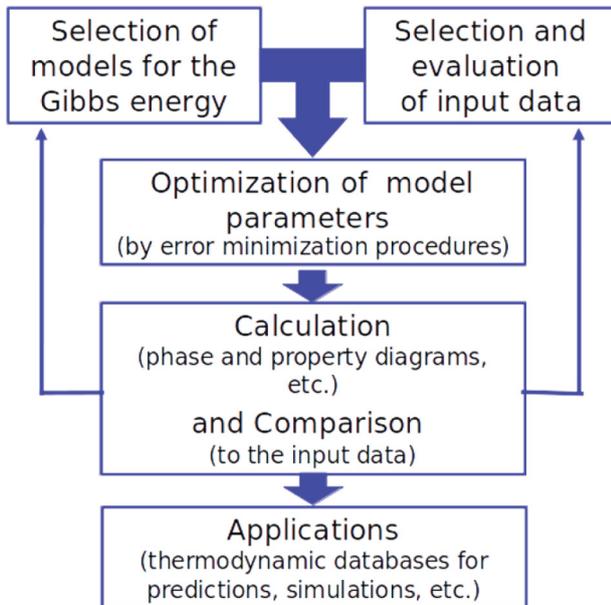


Figure 1. Flowchart representing the core of the CALPHAD method.

consideration. They are parametrized functions in that they depend on the state variables (pressure, temperature, composition, etc.) and on a series of empirical parameters characteristics of a specific phase in a specific system. Once $G^\varphi(P, T, x)$ functions have been determined for each phase φ , they are collected in a thermodynamic database which can be used to calculate phase equilibria, phase diagram and thermodynamic properties of complex multi-component systems.

More in detail, the steps of the optimization process include:

1.1 Selection of Models for the Gibbs Energy Functions

The Gibbs energy of each phase competing for equilibrium in a given system is expressed as a function of the state variables (x_i) and a number of empirical parameters (a_k) (Equation 1):

$$G^\varphi = G^\varphi(x_1, \dots, x_i, a_1, \dots, a_k) \quad (1)$$

The G functions assume different forms depending on the nature of the phase φ : this can be a stoichiometric compound, a metallic liquid, a disordered solid solution, an ordered metallic solution, an ionic liquid, etc.

The composition dependence of G is usually expressed according to the Compound Energy Formalism (CEF), a general formalism applicable to different kind of phases.

Notice that G^φ must be defined and evaluated in a wide range of conditions, generally much wider than the stability range of φ in the system under consideration.

1.2 Selection and Evaluation of Input Data

All the data which may be related to the Gibbs energy of the phases must be used to evaluate the empirical parameters a_k . To this end, several input data may be considered:

- Experimental results (e.g. from DTA, DSC, calorimetry, EMF, vapor pressure, LOM, SEM, X-ray diffraction, etc.);
- Calculation results (e.g. from ab initio and first principles calculations, from semi-empirical models, etc.);
- Estimated data (e.g. by extrapolation / interpolation procedures, or by applying chemical criteria based on the similarity between elements, etc.);

A preliminary critical evaluation of the available literature is mandatory to select the most reliable data to be used.

1.3 Optimization of Model Parameters

Empirical parameters a_k are evaluated by an error minimization procedure such as non-linear least squares (different software packages use different algorithms). An appropriate weight factor must be associated to each input datum. Correlation between input data and model parameters must be checked. When necessary, constraints and approximations may be introduced to reduce the number of independent parameters to be evaluated.

1.4 Calculations and Comparisons

The Gibbs energy functions containing the newly optimized a_k parameters are used to calculate phase and property diagrams which may be compared to known equilibria or data.

Metastable equilibria and thermodynamic functions in metastable conditions must also be checked.

Extrapolation to higher order systems and comparison with known data is also recommended.

Unsatisfactory comparisons may lead to the adoption of more appropriate thermodynamic models for selected phases or to the selection of new or different input data.

1.5 Applications

The optimized interaction parameters are generally used for the implementation of new databases or the improvement of existing ones. Then, databases for specific materials may be used to predict phase equilibria and thermodynamic properties in higher order systems, or, in combination with other data, to predict various materials properties such as microstructure and kinetic-related

properties, mechanical properties, corrosion resistance, etc. or to simulate materials behavior during processing.

One of the most attractive aspects of the CALPHAD approach is its increasing predictive ability. For instance, as the number of system components increases, the number of new empirical parameters needed to obtain a satisfactory description of the Gibbs energy of the phases tend to decrease. In other words, if the optimization of binary systems may require the evaluation of a relatively high number of parameters (and, consequently, the need of a large number of experimental data), the optimization of a ternary system may require the introduction of a limited number of new parameters (in addition to those already evaluated for the binary sub-systems), and consequently a relatively limited number of new experimental data. In practice, once the binary and ternary interaction parameters have been evaluated, quaternary and higher order systems may be reliably calculated without need of new empirical parameters. Thanks to this behavior it can be said that the Calphad approach is essentially an optimization method for 2-3 component systems, while, for multi-component systems it assumes, more and more, the characteristics of a prediction method. This makes Calphad particularly useful for the development of technologically relevant materials which are typically multi-component.

On the contrary, the main limitation of the Calphad approach is the impossibility to predict the stability of a multi-component phase not already present in lower-order systems. In the more recent years, this limitation has partially been overcome by coupling thermodynamic modelling and ab initio calculations. In fact, the stability of phases which may be expected to compete for equilibrium in a specific systems can be calculated (typically by DFT method) and included in the Calphad equilibrium calculations.

2 COMPOUND ENERGY FORMALISM

The thermodynamic modeling of the phases, i.e. the way we use to express their thermodynamic properties as a function of the state variables, is certainly one of the crucial points in the CALPHAD approach. The importance of the modeling was well expressed by Mats Hillert (p. 400)[4]:

The purpose of modeling is two-fold. From a scientific point of view one likes to learn how nature functions. One way to gain knowledge is to define some hypothesis resulting in a model and test it by comparing the predictions from the model with experimental information. [...]

From a more technological point of view one likes to predict the properties of a particular system in order to put it to efficient use in some practical construction or operation. Then it is often most convenient to have a model which yields an analytical expression.

In the simplest case modeling is just the selection of a mathematical form which has proved useful, whether it is based on some physical model or not. However experience shows that a model is usually more powerful if it is based upon physically sound principles. With such a model one can hope to make predictions outside the tested range with some confidence.

If the Gibbs energy dependence on temperature and pressure, though complicated, may be represented by a general expression, applicable to all kind of phases, the dependence on composition is strongly affected by nature and strength of the atomic interactions. In this case it is not possible to adopt a single model for all phases.

The best solution proposed until now is the "Compound Energy Formalism" (CEF) [6], a general formalism which allows to select the most appropriate model for each phase in the framework of the same formalism. According to the CEF, the different constituents of a phase (neutral atoms, ions, vacancies, etc.) are distributed in one or more thermodynamic sublattices where they mix according to the classical solution theory (adopting ideal, regular, subregular, etc. behavior) with different interaction parameters in different sublattices. The Gibbs energy of the phase will then depend on the site fractions (i.e. the mole fractions relative to each sublattice) instead of the overall composition.

Thermodynamic sublattices can have different physical meanings in different phases: in ionic compounds, for example, they can be used to separate anions and cations; in alloys they can be identified with crystallographic sublattices. In this case, for instance, it is clear that atoms in the same crystallographic site have the same interaction with their surroundings, while atoms in different sites generally have different coordination and, then, different interaction with the rest of the structure.

Formally, the Gibbs energy of a phase ϕ can be expressed as the sum of three main terms as shown in Equation 2: the reference term, one ideal mixing term and an excess term. They can be followed by further terms in case further interactions (such as magnetic, electrical, etc.) occur:

$$G^\phi = {}^{\text{ref}}G^\phi + {}^{\text{id}}G^\phi + {}^{\text{ex}}G^\phi + {}^{\text{mag}}G^\phi \quad (2)$$

In case of a pure element, second and third terms are missing and any dependence on composition of course disappears. Equation 2 becomes Equation 3:

$$G^\phi = {}^{\text{ref}}G^\phi + {}^{\text{mag}}G^\phi \quad (3)$$

Where the terms in Equation 3 are given by Equations 4 and 5:

$${}^{\text{ref}}G^\phi(T) = A^\phi + B^\phi T + C^\phi T \ln T + D^\phi T^2 + \dots \quad (4)$$

$${}^{\text{mag}}G^\phi = RT \cdot f(\tau) \cdot \ln(\beta(x) + I) \quad (5)$$

where A, B, C, D, \dots are the empirical parameters which must be evaluated for any specific element, on the basis of the experimental information. In the magnetic term (Equation 5), based on the model introduced by Inden [7] and subsequently adapted by Hillert and Jarl [8], β is the average magnetic moment per mole of atoms in Bohr magnetons, τ is the ratio T/T_C (T_C = critical temperature for magnetic ordering), and $f(\tau)$ is a polynomial expression obtained by expanding Inden's description of the magnetic heat capacity into a power series of τ . Temperature and magnetic parameters for pure elements are available in the PURE database by SGTE [9].

If two or more components are present, mixing can occur and all terms of Equation 2 are significant. Depending on the mixing (or non mixing) mechanism a few typical situations may be distinguished:

2.1 Substitutional Random Solutions

In the simplest case of random mixing, as in the liquid or in the terminal solid solutions, only one sublattice is needed and the three main terms of Equation 2 are given in Equation 6:

$$\begin{aligned} \text{ref } G^\phi &= \sum_i x_i G_i^\phi(T) \\ \text{id } G^\phi &= RT \sum_i x_i \ln x_i \\ \text{ex } G^\phi &= \text{ex}^2 G^\phi + \text{ex}^3 G^\phi + \dots \end{aligned} \quad (6)$$

where: x_i is, at the same time, the site fraction in the unique sublattice and the overall mole fraction of component i . $G_i^\phi(T)$ is the Gibbs energy of the pure component i in the ϕ phase (Equation 3), $\text{ex}^2 G^\phi$ and $\text{ex}^3 G^\phi$ are the binary and ternary excess terms, respectively. They are expressed according to Equations 7 and 8:

$$\text{ex}^2 G^\phi = \sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i x_j \sum_v L_{i,j}^\phi(T) (x_i - x_j)^v \quad (7)$$

$$\text{ex}^3 G^\phi = \sum_{i=1}^{n-2} \sum_{j=i+1}^{n-1} \sum_{k=j+1}^n x_i x_j x_k (u_i L_i^\phi(T) + u_j L_j^\phi(T) + u_k L_k^\phi(T)) \quad (8)$$

respectively, with the coefficients given by Equation 9:

$$\begin{aligned} u_i &= x_i + \frac{l - x_i - x_j - x_k}{3}, \quad u_j = x_j + \frac{l - x_i - x_j - x_k}{3}, \\ u_k &= x_k + \frac{l - x_i - x_j - x_k}{3} \end{aligned} \quad (9)$$

$L^\phi(T)$ in Equations 7 and 8 are empirical parameters whose temperature dependence is similar to that of $G^\phi(T)$ given in Equation 4, as presented in Equation 10:

$$L^\phi(T) = A^\phi + B^\phi T + C^\phi T \ln T + D^\phi T^2 + \dots \quad (10)$$

For a binary phase with magnetic ordering the composition dependence of ${}^{\text{mag}}G^\phi$ (Equation 5) results from the composition dependence of T_C and β , which are expressed by a Redlich–Kister series expansion (Equation 11):

$$\begin{aligned} T_C^\phi(x) &= x_A T_C^\phi(A) + x_B T_C^\phi(B) + x_A x_B \sum_{i=0..n} {}^i T_C^\phi \cdot (x_A - x_B)^i \\ \beta^\phi(x) &= x_A \beta^\phi(A) + x_B \beta^\phi(B) + x_A x_B \sum_{i=0..n} {}^i \beta^\phi \cdot (x_A - x_B)^i \end{aligned} \quad (11)$$

where ${}^i T_C^\phi$ and ${}^i \beta^\phi$ in Equation 11 are expansion parameters to be evaluated on the basis of the experimental information available.

2.2 Stoichiometric Phases (or Compounds)

Stoichiometric phases or compounds are modelled by an n -sublattice model with each sublattice occupied by only one element. As in the case of pure elements, mixing terms of the Gibbs energy are null. In this case, Equation 6 reduces to Equation 12:

$$\text{ref } G^\phi = \sum_i x_i G_i^{\text{SER}}(T) + \text{form } G^\phi(T) \quad (12)$$

where $G_i^{\text{SER}}(T)$ is the Gibbs energy of the pure component i in its standard element reference state (SER) and $\text{form } G^\phi(T)$ is the Gibbs energy of formation of the compound expressed, as a function of temperature, according to Equation 4.

2.3 Ordered Solutions

Ordered solutions are intermetallics with a reference stoichiometry, but characterised by more or less extended solubility ranges. The solubility mechanism is generally due to the reciprocal substitution between components in their crystallographic sites. In this case each component can occupy two or more (possibly all) sublattices. A typical example may be an ordered binary solution represented by a two-sublattice model where each sublattice is mainly occupied by one component but its substitution by the other element is allowed. Then both elements can occupy both sublattices. When a new component is added, it will preferentially occupy one of the sublattices, but it will also be allowed to occupy the other one.

Whenever more components are allowed to mix in two or more sublattices the Gibbs energy is expressed as a function of the site fractions $y_i^{(s)}$, the mole fractions of each component i in the sublattice s . Site fractions obey the conditions given by Equation 13:

$$\begin{aligned} \sum_i y_i^{(s)} &= 1 \\ \frac{\sum_s n^{(s)} y_i^{(s)}}{\sum_s n^{(s)} (1 - y_{VA}^{(s)})} &= x_i \end{aligned} \quad (13)$$

where $n^{(s)}$ are the stoichiometric coefficients relating the sublattices. Notice that Equation 13 has been formulated assuming that vacancies (VA) can also be included in one or more sublattices. This accounts for a second solubility mechanism, namely vacancy formation in one or more sublattices.

Equation 6 becomes Equation 14:

$$\begin{aligned} \text{ref } G^\phi &= \sum_i \sum_j \dots \sum_k y_i^{(1)} y_j^{(2)} \dots y_k^{(s)} G_{i,j,\dots,k}^\phi \\ \text{id } G^\phi &= \frac{I}{s} RT \sum_s \sum_i n^{(s)} y_i^{(s)} \ln y_i^{(s)} \\ \text{ex } G^\phi &= \text{ex}^2 G^\phi + \text{ex}^3 G^\phi + \dots = \\ &= \sum_s \sum_i \sum_j y_i^{(s)} y_j^{(s)} \sum_{r \neq s} \sum_k y_k^{(r)} L_{i,j,\dots,k}^\phi(T) + \dots + \text{ex}^3 G^\phi + \dots \end{aligned} \quad (14)$$

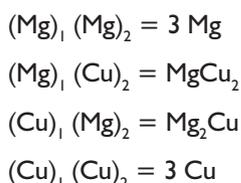
where $G_{i,j,\dots,k}^\phi$ in $\text{ref } G^\phi$ are the Gibbs energies of all the so-called “end members”, the stoichiometric compounds (either stable, metastable or unstable) formed when only one constituent is present in each sublattice. $L_{i,j,\dots,k}^\phi(T)$ in $\text{ex}^2 G^\phi$ are binary interaction parameters corresponding to the mixing of components i and j on the sublattice s while the other sublattices are singly occupied. More terms can be added to $\text{ex}^2 G^\phi$, corresponding to simultaneous mixing on two sublattices while the remaining sublattices are singly occupied. $\text{ex}^3 G^\phi$ accounts for the possible interactions of three elements in a given sublattice.

A simple case is represented by the Laves phase MgCu_2 type (Pearson symbol cF24, strukturbericht designation C15). It is described in the space Group $Fd-3m$ (num. 227). Mg occupies the 8a Wickoff position, while Cu is in 16d, but both elements are allowed to occupy the other position, at least partially. Then the phase may be modelled by a 2-sublattice model:



where each sublattice corresponds to a crystallographic site and the 1:2 stoichiometry correspond to the ratio 8:16 between the site multiplicities. Each sublattice is typically occupied by the element reported in bold, but all the elements are allowed to enter all sublattices to reflect the substitution mechanism responsible for the homogeneity range of the phase.

It is important to notice that the model adopted generates four so called end-members, i.e. four stoichiometric compounds which correspond to all the possible combinations with each sublattice occupied by a single element:



Among them, only the second one corresponds to a stable phase and can be evaluated on the basis of experimental information. However the Gibbs energies of formation of all of them, $G_{\text{Mg:Mg}}^\phi$, $G_{\text{Mg:Cu}}^\phi$, $G_{\text{Cu:Mg}}^\phi$, $G_{\text{Cu:Cu}}^\phi$, appear in Equation 14. The three values which correspond to metastable or even unstable compounds cannot be derived from experimental data, but, in many cases, can be directly calculated by ab initio methods, or indirectly evaluated on the basis of experimental phase equilibria.

2.4 Ordered Phases Related to Random Solutions

A special case, relatively frequent in intermetallic systems, are the ordered phases which may be related to disordered ones, as in the case of the AuCu_3 type phase (Pearson symbol tP2, strukturbericht designation L1₂) related to the disordered fcc structure (Cu type, Pearson symbol cF4, strukturbericht designation A1), or the CsCl type phase (Pearson symbol cP2, strukturbericht designation B2) related to the disordered bcc structure (W type, Pearson symbol cI2, strukturbericht designation A2). In some cases ordered and disordered structures are stable in the same system and can transform to each other by a first order as well as a second order transformation. A typical example of this behaviour can be found in the Al-Fe system. In this system, when the transformation is second order, A2 and B2 are in equilibrium at the same composition (no two-phase field between them can exist) and this implies that there is no discontinuity between the Gibbs energy of the two phases (or between their composition derivatives) at the equilibrium composition. Such a behaviour may be modelled by introducing one single Gibbs energy expression for both ordered and disordered phases. The ordering state will depend on the occupation of the different sublattices. This means that, in the case of A2/B2 ordering in Al-Fe, we can assume a two-sublattice model, $(\text{Al,Fe})_{0.5} (\text{Al,Fe})_{0.5}$, which become equivalent to $(\text{Al,Fe})_1$ when the two sublattices have identical occupation and, consequently, become indistinguishable. This is realised by introducing the expression for the Gibbs energy given by Equation 15:

$$G^{A2/B2} = G^{A2}(x) + G^{B2}(y_1, y_2) - G^{B2}(x, x) \quad (15)$$

where $G^{A2}(x)$ is the Gibbs energy of the disordered phase calculated at the concentration x according to the one sublattice model (Equation 6), while $G^{B2}(y_1, y_2)$ and $G^{B2}(x, x)$ are the Gibbs energies of the ordered phase (Equation 14) calculated first at the site fractions y_1, y_2 (ordered state) and then at the site fractions x, x (disordered state). So, the difference $G^{B2}(y_1, y_2) - G^{B2}(x, x)$ is the Gibbs energy of ordering.

If a 4 sublattice model is introduced, a larger number of ordered phases related to the same bcc lattice can be described. This is illustrated in Figure 2.

The correspondence between site occupancies and structures is the following:

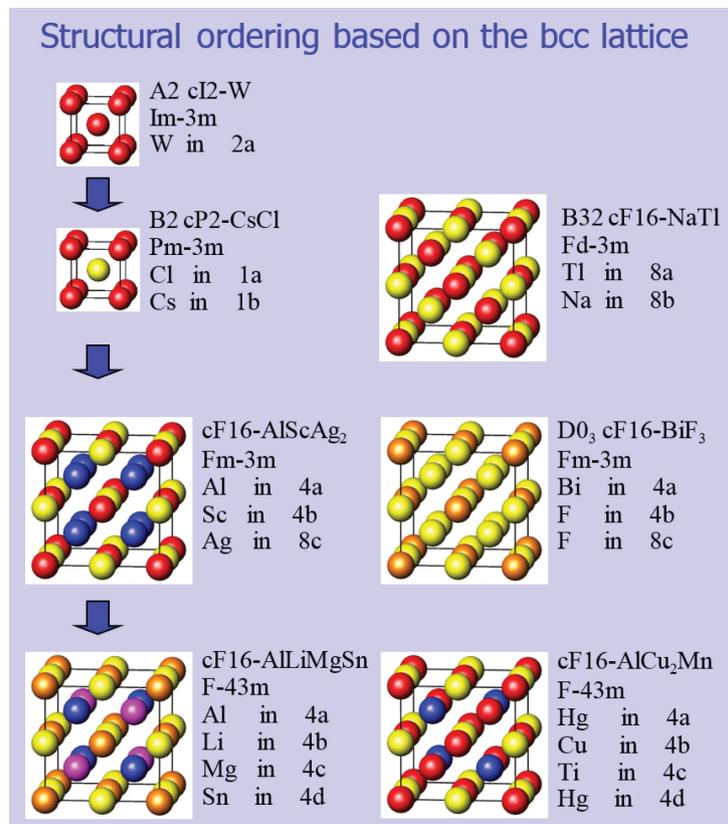


Figure 2. Ordered structures based on the bcc lattice which may be represented by a four sublattice model.

Sublattice occupation	Corresponding structure
$(A)_{1/4}(A)_{1/4}(A)_{1/4}(A)_{1/4}$	A2 cI2-W
$(A)_{1/4}(A)_{1/4}(B)_{1/4}(B)_{1/4}$	B2 cP2-CsCl
$(A)_{1/4}(B)_{1/4}(A)_{1/4}(B)_{1/4}$	B32 cF16-NaTi
$(A)_{1/4}(B)_{1/4}(C)_{1/4}(C)_{1/4}$	cF16-AlScAg ₂
$(A)_{1/4}(B)_{1/4}(B)_{1/4}(B)_{1/4}$	D0 ₃ cF16-BiF ₃
$(A)_{1/4}(B)_{1/4}(C)_{1/4}(D)_{1/4}$	cF16-ALiMgSn
$(A)_{1/4}(B)_{1/4}(C)_{1/4}(A)_{1/4}$	L2 ₁ cF16-ALCu ₂ Mn

All of them are special cases of the general model:

$$(A,B,C,D)_{1/4}(A,B,C,D)_{1/4}(A,B,C,D)_{1/4}(A,B,C,D)_{1/4}$$

Which is used to express thermodynamic functions

of this group of phases.

Similar 4-sublattice models may be used to describe the ordered structures related to the fcc or hcp lattices.

To summarise, a selection of examples of CEF modelling of different kind of phases is reported in the Table I below:

3 SELECTED EXAMPLES

In the following a few examples of CALPHAD applications are reported, taken from recent results obtained in the author's lab. These examples show how CALPHAD

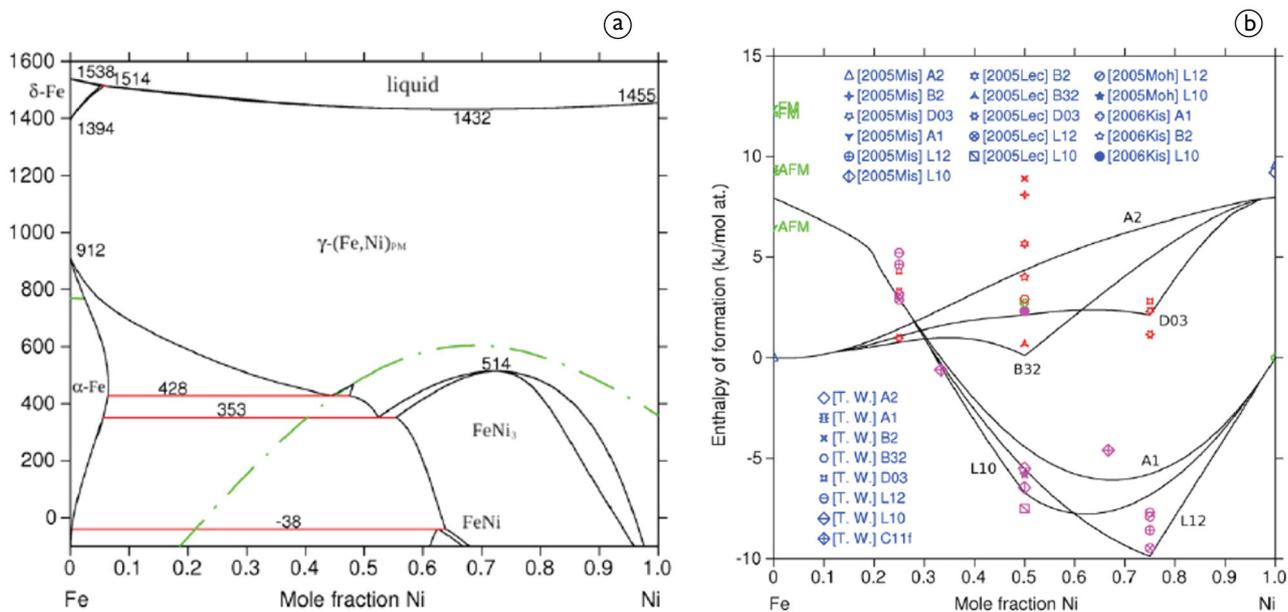
can be used to understand and/or predict the behaviour of real systems and how it can be used to solve application problems.

3.1 CALPHAD assessment supported by quantum DFT calculations: the Fe-Ni system

Fe-Ni is a key system for a large number of technological alloys. From a scientific point of view it shows an interesting combination of structural and magnetic ordering in conjunction with very experimental difficulties due to the very slow kinetics at temperatures lower than about 500 °C. For all these reasons it is a very interesting playground for CALPHAD modelling. Recently [10] we assessed the system by using four sublattice models for the fcc- and bcc-based ordered phases and used DFT atomistic calculation to evaluate the enthalpy of formation of all ordered end-members. As a result we were able: 1) to confirm the presence of the tricritical point ("Nishizawa horn") related to the magnetic ordering of the fcc solid solution (Figure 3a); 2) to confirm the low temperature stability of the L1₀ fcc ordered phase (experimentally supported by the analysis of meteoric samples), as well as the metastable, low temperature miscibility gap in the fcc solid solution, 3) to underline the role of the magnetic interactions in the establishment of the Fe-Ni phase equilibria; 4) to calculate the thermodynamic stability of the stable and/or metastable

Table I. Examples of CEF modelling

Phase type	Typical sublattice model	Example phase	Example sublattice model
Substitutional disordered solutions	(A,B)	liquid-(Cu,Ni) fcc-(Co,Ni)	(Cu,Ni) (Co,Ni)
Stoichiometric compounds	(A) _u (B) _v	Al ₃ Ni	(Al) ₃ (Ni) ₁
Substitutional solutions with interstitials	(A) _u (B,Va) _v	bcc-(Fe-N)	(Fe) ₁ (N,Va) ₃
Substitutional ordered solutions	(A,B) _u (A,B) _v	C15-Cu ₂ Mg	(Cu,Mg) ₂ (Cu,Mg) ₁
Ionic solids	(Cations) _u (Anions) _v	NaCl+CaCl ₂ spinel	(Ca ²⁺ ,Na ⁺) ₁ (Cl ⁻ ,Va) ₂ (Mg ²⁺ ,Al ³⁺) ₁ (Mg ²⁺ ,Al ³⁺) ₂ (O ²⁻) ₄
Semiconductors with point defects	(A,B,B ⁺) (A,A ⁻ ,B) (Va,e ⁻) (Va,h ⁺)	GaAs	(As,Ga,Ga ⁺) (As,As ⁻ ,Ga) (Va,e ⁻) (Va,h ⁺)
Order/disorder relations	(A,B) and (A,B) _u (A,B) _v	fcc-(Au,Cu) and (AuCu ₃)	(Au,Cu) and (Au,Cu) _{1/4} (Au,Cu) _{3/4}

**Figure 3.** (a) the calculated Fe-Ni phase diagram; (b) the calculated enthalpy of mixing of the ordered and disordered fcc and bcc Fe-Ni phases compared with results of ab-initio calculations.

ordered and disordered phases (Figure 3b). This is especially important for the modelling of higher order systems.

3.2 CALPHAD simulation of a non-equilibrium process: diamond synthesis by micro-plasma CVD

It is well known that the equilibrium synthesis of diamond crystals requires very high pressures and temperatures. By a non-equilibrium process, however, small diamond crystals can be obtained at low pressure and relatively low temperature. When a high temperature plasma jet formed by a mixture of hydrogen and methane impinges on a metal substrate at a temperature of about 500-1000 °C various carbon structures (graphite, diamond, graphene, nanotubes...) may grow on the metal surface, depending on the process parameters, namely total pressure, metal substrate temperature, plasma temperature, gas composition. A possible explanation of the diamond formation is that the highly energetic atomic hydrogen present in the plasma is adsorbed on the carbon

surface and promotes the transition of carbon from the sp^2 to the sp^3 hybridisation states. Once the hydrogen is released as H_2 molecules, the sp^3 hybridisation is maintained and a new layer of diamond structure has grown.

This non-equilibrium non-dissipative process may be modelled according to the CALPHAD approach by introducing a hypothetical new phase, called “activated graphite” (G^*), which represents graphite excited by the interaction with atomic hydrogen. Its thermodynamic properties then depend on a combination of the properties of regular graphite at the temperature of the substrate and the properties of atomic hydrogen at the temperature of the plasma. According to this model, first introduced by Wang et al. [11], diamond can grow when it is more stable than the activated graphite. In a recent paper [12] we calculated, in a pressure vs. temperature diagram, the diamond growth region and verified the good agreement of the model calculations with the experimental results, as shown in Figure 4. Notice that exotic carbon forms are obtained in the region where activated graphite is

more stable than diamond, while, on the opposite side of the diamond region, regular graphite is obtained, as expected.

3.3 CALPHAD simulation of wetting experiments: Ni alloys in contact with UHTC

UHTCs (Ultra High Temperature Ceramics) are materials characterised by melting temperatures in excess of 3000°C. Among them diborides of the group 4 metals (Ti, Zr, Hf) are candidate materials for application in extreme conditions such as leading edges of vehicles for hypersonic flight, atmospheric re-entry vehicles, rocket propellers, refractory linings, electrodes, cutting tools, etc.

Wetting and joining properties of these materials with metals and alloys are scarcely known. So they have been recently investigated, especially by means of wetting experiments carried out using the sessile drop technique and assisted by CALPHAD calculations [13-17].

In one of the mentioned works [16], for example, phase diagram calculations easily explained the observed sequence of unusual isothermal transformations occurring during a wetting experiment of a Ni-B alloy in contact with a ZrB_2 substrate.

As shown in Figure 5, the Ni-17at%B alloy in contact with ZrB_2 at 1130°C melts and reacts with the ceramic substrate. During the isothermal reaction the composition of the liquid drop moves along the line shown in the Figure 5a

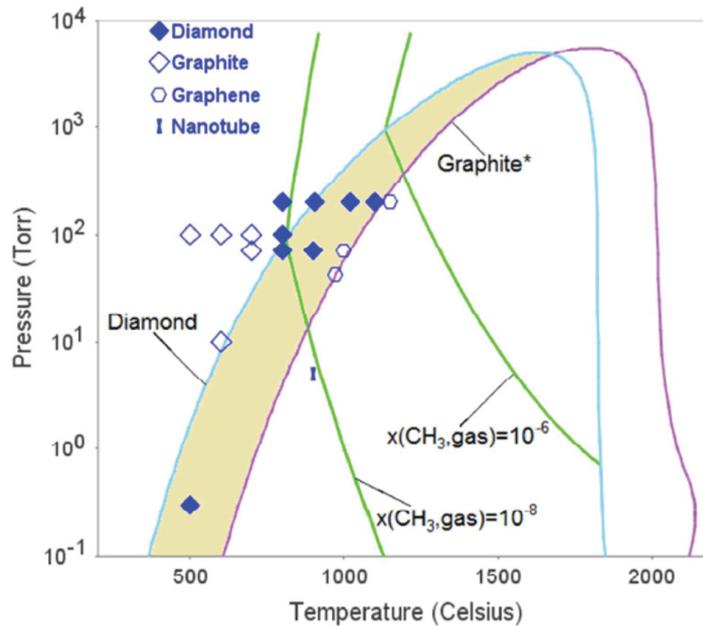


Figure 4. The pressure vs. temperature phase diagram of carbon where the stability areas of diamond and activated graphite are superimposed and compared with experimental results. The coloured area represent the range where diamond can be obtained by micro-plasma CVD process.

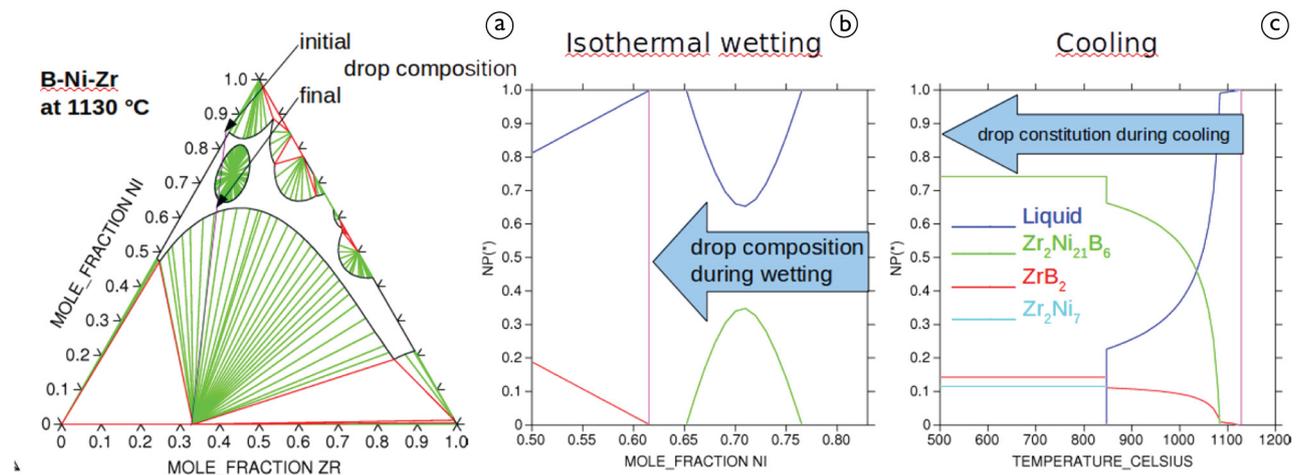


Figure 5. Evaluation of the reaction between a Ni-B alloy drop and a ZrB_2 substrate. a) and b) Equilibrium during wetting. c) Equilibrium during cooling.

until it reaches the saturation composition, in equilibrium with ZrB_2 . Doing so it crosses the two-phase field where the ternary compound $Zr_3Ni_{20}B_6$ becomes stable. Accordingly, during the isothermal wetting experiment precipitation and subsequent re-dissolution of a solid phase is observed, as evidenced in Figure 5b. Once the equilibrium between ZrB_2 and the drop is reached, the system is cooled down. In Figure 5c the solid phases formed during cooling are shown. They correspond to the phases actually identified in the solidified drop.

The same procedure has been successfully used to predict and/or interpret the results of many more wetting experiments.

4 CONCLUSION

CALPHAD is a very useful and powerful method in materials science and processing. Thank to its ability to predict phase equilibria and thermodynamic functions in multi-phase and multi-component systems it has been successfully applied to the description and simulation of very complex technological materials and processes. Thanks to the integration of CALPHAD modelling with DFT and/or molecular dynamics calculations, on one side, and kinetic simulations, on the other side, an “all scales” modelling of materials may be achieved.

REFERENCES

- 1 Kaufman L, Bernstein H. Computer calculation of phase diagrams. New York: Academic Press; 1970.
- 2 Spencer PJ. A brief history of CALPHAD. *Calphad*. 2008;32:1-8.
- 3 Saunders N, Miodownik AP. CALPHAD (calculation of phase diagrams): a comprehensive guide. Oxford: Pergamon; 1998.
- 4 Hillert M. Phase equilibria, phase diagrams and phase transformations: their thermodynamic basis. 2nd ed. Cambridge: Cambridge University Press; 2008.
- 5 Lukas HL, Fries SG, Sundman B. Computational thermodynamics: the CALPHAD method. Cambridge: Cambridge University Press; 2007.
- 6 Hillert M. The compound energy formalism. *Journal of Alloys and Compounds*. 2001;320(2):161-176.
- 7 Inden G. The role of magnetism in the calculation of phase diagrams. *Physica B+C*. 1981;103(1):82-100.
- 8 Hillert M, Jarl M. A model for alloying in ferromagnetic metals. *Calphad*. 1978;2:227-238.
- 9 Dinsdale AT. SGTE data for pure elements. *Calphad*. 1991;15:317-425. [http://dx.doi.org/10.1016/0364-5916\(91\)90030-N](http://dx.doi.org/10.1016/0364-5916(91)90030-N).
- 10 Cacciamani G, Dinsdale A, Palumbo M, Pasturel A. The Fe–Ni system: thermodynamic modelling assisted by atomistic calculations. *Intermetallics*. 2010;18:1148-1162.
- 11 Wang J-T, Wei Zhang D, Ding S-J, Wang P-F. A new field of phase diagrams of stationary nonequilibrium states. *Calphad*. 2000;24:427-434.
- 12 Ghezzi F, Cacciamani G, Caniello R, Toncu DC, Causa F, Dellasega D, et al. Carbon structures grown by direct current microplasma: diamonds, single-wall nanotubes, and graphene. *The Journal of Physical Chemistry C*. 2014;118:24714-24722.
- 13 Kaufman L, Cacciamani G, Muolo ML, Valenza F, Passerone A. Wettability of HfB_2 by molten Ni(B) alloys interpreted by CALPHAD methods, Part I: definition of the B–Hf–Ni system. *Calphad*. 2010;34:2-5.
- 14 Cacciamani G, Riani P, Valenza F. Equilibrium between MB_2 ($M=Ti, Zr, Hf$) UHTC and Ni: a thermodynamic database for the B–Hf–Ni–Ti–Zr system. *Calphad*. 2011;35:601-619.
- 15 Valenza F, Muolo ML, Passerone A, Cacciamani G, Artini C. Control of interfacial reactivity between ZrB_2 and Ni-based brazing alloys. *Journal of Materials Engineering and Performance*. 2012;21:660-666.
- 16 Artini C, Muolo ML, Passerone A, Cacciamani G, Valenza F. Isothermal solid–liquid transitions in the (Ni,B)/ ZrB_2 system as revealed by sessile drop experiments. *Journal of Materials Science*. 2013;48:5029-5035.
- 17 Artini C, Muolo ML, Passerone A, Valenza F, Manfrinetti P, Cacciamani G. Experimental investigations and thermodynamic modeling in the ZrB_2Ni section of the BNiZr system. *Journal of Alloys and Compounds*. 2014;592:115-120.

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