



Modelling of phase diagrams and thermodynamic properties using *Calphad* method – Development of thermodynamic databases

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ABSTRACT

The *Calphad* method is very important method for the modelling of thermodynamic properties and phase diagrams of multicomponent systems. The method is based on a semi-empirical approach and sequential modelling from simpler to more complicated systems. Therefore reliable experimental data are necessary for the description of the thermodynamic and phase properties of unary and binary systems. Basic principles of the method will be described in this paper, especially from the point of view of preparing the reliable theoretical thermodynamic description of simpler systems, which allow reliable prediction and assessment of higher order systems.

The thermodynamic data, describing assessed binary and ternary systems are collected in the form of the thermodynamic databases, which allow (together with proper software) the prediction of properties for multicomponent systems corresponding to real materials. The software packages, based on *Calphad* method, are currently the only theoretical tools, applicable for complex materials as steels, superalloys, etc.

The thermodynamic databases and outputs of the theoretical calculations are also important for many other applications and multi-scale simulations. They serve as input for phase field simulations, diffusion processes modelling, phase transformations, material properties and structure morphology development, including the processes on interface.

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1. Introduction

The understanding of phase diagrams and phase equilibria is crucial for the understanding of processes governing the materials properties and development. Basically, the material and physical properties of alloys are very much governed by the microstructure, which is mainly governed by the phase composition and morphology. This can be deduced for the phase diagrams and therefore the phase diagrams offer very useful tool for prediction which phases should be expected for given conditions (temperature, pressure, overall composition of the alloy). Even if the material in question is not in the equilibrium state, the metastable phase diagram can be established in some cases and the knowledge of equilibrium phase diagram can offer the insight into the processes, which can be expected during the exploitation of the material.

The phase diagrams are based on the knowledge of thermodynamic properties of the materials, and as soon as they are established for simpler systems, there is a possibility to calculate phase diagrams even for complex systems. Nevertheless, such possibility requires powerful computers and development of suitable

theoretical methods; therefore, until recently, the experimental studies of phase diagrams prevailed.

The results of the phase diagram experimental studies have been published in various phase diagram compendia both in the form of collected phase diagrams, e.g. [1] or in the form of critically assessed evaluations of existing results (e.g. [2,3]). The experimental approach, despite being still necessary, is generally time consuming and expensive, and the complexity of real materials makes practical application of experimental studies for the establishment of complex phase diagrams very difficult. Therefore this subject was mainly of interest in the field of basic science and small understanding of predictive possibilities of phase diagrams existed among researchers working in the field of applied research.

First attempts to apply a theoretical approach to the problem of the phase diagrams and thermodynamic properties modelling can be traced deep into beginning of 20th century [4], nevertheless more intensive development started after WWII and first practical outcomes appeared in seventies and eighties. The background of the *Calphad* method, which will be briefly described in this paper, was laid by Kaufman as well as Hillert and their coworkers [5–8] and the practical use of the theoretical modelling started by the development of several software packages [9–12], using the basic principles laid by in above mentioned works and developed into the more general form by Sundman and Ågren [13].

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Currently, the modelling of phase diagrams and thermodynamic properties offers not only valuable information in the field of equilibrium thermodynamics, but it can be used as useful source of data for multiscale modelling, as modelling of diffusion processes in multicomponent systems [9], prediction of physical, mechanical and chemical properties of alloy, modelling of grain growth and processes on the interface, and using phase field method [14]. Many industrial laboratories are now discovering the power of this theoretical approach.

Nevertheless, despite the fast development of the commercial software for the phase diagram modelling, the crucial condition for the calculation of plausible and applicable phase diagrams for materials of industrial interest is the existence of reliable and consistent thermodynamic databases, containing crucial data for the calculation of Gibbs energies of all phases and for all constituents existing in studied system. Without such database, even the most sophisticated software is just an empty shell with no relevance to the nature. Therefore, the main part of this paper will deal with basic rules for the development of general thermodynamic database, which will be accompanied by presenting several examples of such databases and their application.

2. Calphad method for the modelling of phase diagrams

The detailed and very comprehensive description of the *Calphad* method was published by Saunders and Miodownik [15] and by Lukas et al. [16]. Only basic principles of the method will be given here and interested reader should study above mentioned books. The book [16] is more oriented towards the practical application of the *Calphad* method.

The *Calphad* approach is semi-empirical method based on the sequential modelling of the thermodynamic properties of multicomponent systems, which needs basic amount of experimental data for creation of robust, consistent and reliable set of thermodynamic parameters describing simple systems. Such data allows extrapolation of phase diagrams and thermodynamic properties modelling to regions not studied experimentally and/or to more complex systems (Fig. 1).

We start the modelling from the simplest case – a selection of well established and reliable descriptions of the Gibbs energy of the pure elements. The temperature dependences of the Gibbs energy of the element in various crystallographic structures (either

stable or metastable) are expressed in the form of polynomial, and are fundamental for the calculations of phase diagrams. The coefficients of those polynomials are stored as parameters in the unary thermodynamic databases [17,18].

This is followed by the careful and experimentally well supported assessment of the binary systems. For such modelling we need to know the Gibbs energies of both pure elements in all phases existing in the concrete binary system (even if only one of the elements exists in some crystallographic structure in the reality). These data are usually taken from the above mentioned unary thermodynamic databases. During the assessment we also need to model the Gibbs energies of intermediate phases and include the mutual interactions between both elements in all phases in the system, which define e.g. the solubility of elements in various phases. Having available reliable and sufficient set of experimental data, it is possible to model such a system with high precision. It is important to have experimental measurements of both the thermodynamic properties of the individual phases (e.g. heat capacity, enthalpies of formation or mixing, activities) and the phase equilibria (e.g. temperatures of phase transformations, compositions and amounts of phases).

As the next step, using the thermodynamic parameters obtained from such robust description of binary systems it is possible to predict the phase diagrams of ternary systems. The differences from the experimental observations can be reflected by adding parameters describing mutual interaction between all three elements of the system. Such parameters must not influence the Gibbs energies of the relevant lower order systems. The so called “binary prediction” of ternary system (the calculation of ternary phase diagram using binary parameters only) can offer the researcher valuable insight into the possible relations between the phases and allows him to propose experimental program which can be aimed on the most promising compositions and temperatures. The time and money can be saved using this prediction. Nevertheless, the *Calphad* method does not allow the prediction of e.g. the solubility of third element in a phase existing in the complementary binary system, or the presence of ternary phases, i.e. the phases which exist only in the studied ternary system and not in any of the relevant binaries. Those solubilities or the Gibbs energy of the ternary phase has to be assessed using results of experimental observations (see Section 3.1).

The thermodynamic data collected in this way allows us finally to predict the properties of complex systems, corresponding to the real materials, with surprising success. This exploitation of theoretical methods lead to a significant decrease of the experimental work necessary to verify the presumptions used during the material design and also enables to broaden significantly the number of proposed compositions with favourable materials properties.

The phase diagram modelling based on *Calphad* method is currently the most advanced with respect to its applicability in practical applications. Existing software and thermodynamic databases allows working with wide variety of industrial materials (steels, superalloys, solders, ...) and are more and more used also in applied research and industrial labs.

2.1. Gibbs energy modelling

To calculate the thermodynamic equilibrium of the system, we need to find a state with minimum total Gibbs energy for a given set of independent variables (e.g. pressure, temperature, overall concentration). This total Gibbs energy may be expressed as the weighted sum of Gibbs energies of the individual phases. The individual Gibbs energy of any phase ϕ (G_m^ϕ) is in the *Calphad* approach expressed by additive principle as a sum of different contributions:

$$G_m^\phi = G_{ref}^\phi + G_{id}^\phi + G_E^\phi + G_{mag}^\phi + G_P^\phi + G_{surf}^\phi + \dots \quad (1)$$

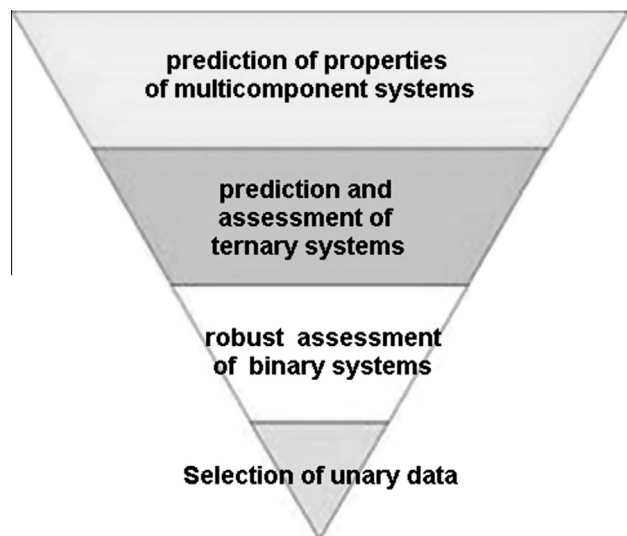


Fig. 1. Sequential modelling of thermodynamic properties of systems, exploited by *Calphad* method.

First term in the equation G_{ref}^ϕ (reference) is the weighted sum of the molar Gibbs energies of all elements or compounds (called the constituents) in the crystallographic structure corresponding to the structure of the phase in question, relative to their chosen reference states (usually the value of the actual thermodynamic property of the element in the stable structure at 25 °C and normal pressure, so called Standard element reference – SER – state, is used).

The particular terms of Eq. (1) can have different forms depending on the character of modelled phase. For substitutional solid solutions or liquids, where random mixing exists among all constituents, the contributions G_{ref}^ϕ (corresponding generally to mechanical mixing of constituents) can be expressed as:

$$G_{ref}^\phi = \sum_{i=1}^n x_i \cdot {}^0G_i^\phi \quad (2)$$

and its temperature dependence is given by

$${}^0G_i^\phi(T) = a + bT + cT \ln(T) + \sum_i d_i T^n \quad (3)$$

where a – d_i are adjustable coefficients.

Second term, G_{id}^ϕ , describes the contribution to the Gibbs energy from ideal random mixing of the constituents on the crystal lattice, and is expressed in the form

$$G_{id}^\phi = R \cdot T \cdot \sum_{i=1}^n x_i \cdot \ln(x_i), \quad i = 1, \dots, n \quad (4)$$

for an n -constituents system.

G_E^ϕ is the excess Gibbs energy, describing the real behaviour of the phase – generally covering all other contributions to the Gibbs energy not covered by the terms in (Eq. (1)) (the influence of non-ideal mixing behaviour on the thermodynamic properties of a solution phase and mutual interactions and reactions between constituents) and mostly the Muggianu extension of the Redlich–Kister formalism [19,20] is used to mathematically describe the contribution:

$$G_E^\phi = \sum_{\substack{i,j=1 \\ i \neq j}}^n x_i x_j \sum_{z=0}^m {}^zL(x_i - x_j)^z + \sum_{\substack{i,j,k=1 \\ i \neq j \neq k}}^n x_i x_j x_k L_{ijk} \quad z = 0, \dots, m \quad (5)$$

where zL are the temperature dependent interaction parameters, describing the influence of the mutual interaction between constituents i and j on the overall Gibbs energy of the phase ϕ .

In the case where the phase in question is a stoichiometric compound $A_a B_b$, its molar Gibbs energy G_m^ϕ is usually expressed in the form of the hypothetical Gibbs energy of formation G_{form}^ϕ of the phase from pure constituents in the same crystallographic structure, relative to the chosen reference state:

$$G_m^\phi = \frac{a}{a+b} \cdot G_A^\phi + \frac{b}{a+b} \cdot G_B^\phi + G_{form}^\phi \quad (6)$$

Complex phases, such as nonstoichiometric intermetallic compounds, are usually modelled using the compound energy formalism (CEF) [13,16,21] where the crystal structure can be considered as comprising a number of sublattices l , which exhibits preferential occupancy by one or more constituents. For such a phase, G_{ref}^ϕ is now given by

$$G_{ref}^\phi = \sum y_i^s \cdot y_j^t \cdots y_k^u \cdot G_{(ij:\dots:k)}^\phi, \quad i, j, k = 1, \dots, n, \quad s, t, u = 1, \dots, m \quad (7)$$

where y variables are called “site fractions” and define the composition of each constituent in the sublattice s ($s = 1, \dots, m$). The term $G_{(ij:\dots:k)}^\phi$ represents the Gibbs energy of formation (Eq. (6)) of ‘virtual compound’ or Gibbs energy of pure constituent, if each

sublattice is occupied by the same constituent. Typically, only few of these virtual compounds can exist in the reality, but all relevant so-called end members are needed for the modelling and several ways of establishing these Gibbs energies will be mentioned later.

The ideal mixing term is in the CEF given by

$$G_{id}^\phi = \sum_{p=1}^l f_p \cdot \sum_{i=1}^m y_i^p \cdot \ln(y_i^p) \quad (8)$$

where f_p is the stoichiometric coefficient for a sublattice p and the second sum describes the effect of the ideal mixing within the sublattice p . The expression of the excess Gibbs energy contribution can be very complicated in the case of several sublattices model, but for simpler case of two sublattices and mutual interaction between two constituents in one sublattice only (often used e.g. for modelling of interstitial solid solution and many simpler intermetallic compounds) is given as:

$$G_E^\phi = \sum_{k=1}^n y_k^2 \sum_{i,j=1}^n y_i^1 \cdot y_j^1 \cdot L_{(ij:k)} + \sum_{k=1}^n y_k^1 \sum_{i,j=1}^n y_i^2 \cdot y_j^2 \cdot L_{(ki,j)}, \quad (9)$$

where $L_{(ij:k)} = \sum_z {}^zL_{(ij:k)} \cdot (y_i^p - y_j^p)^z$.

The parameter $L_{(ij:k)}$ describes the mutual interaction of constituents i and j in the first sublattice, when the second sublattice is fully occupied by constituent k . This description can be extended in the same way to any number of sublattices and the most general expression for the Gibbs energy evaluation is shown e.g. in the original paper from Sundman and Ågren [13] or in [16].

Additional terms are often necessary for the proper description of the Gibbs energy from Eq (1). G_{mag}^ϕ in Eq (1) is the magnetic contribution after [22] and G_p^ϕ is the pressure term. The excess Gibbs energy term G_E^ϕ and the magnetic contribution G_{mag}^ϕ , if the material exhibits magnetic behaviour, are the most important terms for the modelling of the thermodynamic properties of the phase. Other terms may describe contributions e.g. from the interface energy, energy of plastic deformation, etc. The size of these contributions is usually significantly lower in metallic systems than the terms for the excess Gibbs energy and the magnetic contribution, nevertheless as great attention is given now to nanomaterials, the contribution of surface energy G_{surf} to the overall Gibbs energy is very significant in the case of nanomaterials. This is important now as great attention is paid to modelling of properties of this class of materials.

These general principles for Gibbs energy modelling apply to all phases, but for successful evaluation of the Gibbs energy contribution, the character of the phase should be taken into the account. More specific models have been developed for variety of phases with different crystallography and/or physical properties, e.g. for simple solid solutions, for phases with complex crystallography, such as gamma brass, or for phases which show a tendency to short range ordering (e.g. associate-solution model, when the attractive forces are not strong enough to form molecule constituents). This approach also allows modelling of particularly complicated phases such as those with order-disorder transformations. More detailed descriptions of such special cases and their typical treatment can be found in [15,16,23].

After evaluation of the total Gibbs energy of the whole system, the thermodynamic equilibrium of the system is calculated through its constrained minimisation for a given temperature, pressure and overall composition. This technique is used in all available software packages for the modelling of thermodynamic properties and calculation of phase diagrams for multicomponent systems. The concrete technique used for the minimisation differs significantly in all software packages currently in practical use [9–12]. Both the concrete methods for the minimisation and the mapping algorithm for tracing the phase boundaries are different and

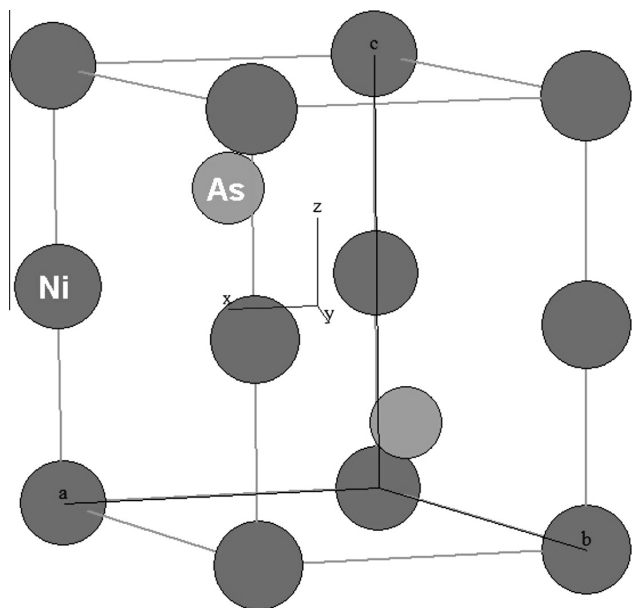


Fig. 2. Crystallographic structure of NiAs phase, Pearson symbol hP4.

lead to different reliability of results. One of the crucial problems to be solved is the existence of multiple minima on the Gibbs energy surface, which can result in metastable phase equilibria being calculated by the software. The existence of such solution can create confusion for the user of the software and implicitly requires some preliminary knowledge of the studied system by the researcher to be able to identify such equilibrium. This danger was more eminent in older versions of the software packages and the solutions accepted are briefly described especially in [10,11]. E.g. in the case of Thermocalc software, the so called Gibbs energy minimisation technique is used, which is one of the most efficient minimisation method. It ensures the consistency of the thermodynamic data in solved system; nevertheless it does not assure that the minimum found is the global one. The global minimisation technique is employed to assure that the calculated minimum is the stable one and also the other composition sets are created to test the presence of miscibility gaps. Therefore the preliminary knowledge of the system is not necessary as in the case of older versions of the software packages. The stability of the calculations is traded off for the speed; the minimisation procedure is many times faster when the global minimisation technique is switched off.

3. Thermodynamic databases – crucial condition for successful modelling of phase diagrams and thermodynamic properties of multicomponent systems

The results of theoretical modelling of phase diagrams and thermodynamic properties are strongly dependent on the quality of thermodynamic data available for studied system and even the most advanced software is useless without the reliable and consistent data in the form of the thermodynamic database.

3.1. Theoretical assessment of the system

The correct thermodynamic datasets for the Gibbs energy evaluation are crucial for successful calculation. The parameters, describing properly Gibbs energy polynomials for all relevant phases in the system are obtained using the process called the theoretical assessment. This part of the whole process starts with summarising all the relevant experimental thermodynamic and

phase equilibrium data for the system of interest. Consequently the researcher has to carry out a critical evaluation of all data, checking their consistency, accuracy and precision. The selection of the best possible set of experimental data from all of the data available is the most important step in the assessment procedure. For most systems, the literature contains many experimental studies dealing with the same measured entities and it must be decided which is the best. The author of the assessment has to be able to make a critical consideration of experimental techniques, their suitability for measuring given entity, inherited precision of the measurements, quality of the work, etc.

The final result of such evaluation is the creation an experimental dataset, which contains all relevant and mutually consistent experimental data. Currently, with the fast development of methods, allowing calculation of thermodynamic entities (e.g. the energies at 0 K) by theoretical methods based on quantum mechanics principles (ab initio), such data can be also included into the dataset. The data are consequently used for the optimisation of the Gibbs energy model parameters using a least-square minimisation process. These optimised parameters should offer the best possible agreement between calculated and experimental information. This part of the whole process needs a lot of understanding of the system behaviour, and understanding of basic thermodynamic principles and phase transformation processes. Detailed description of assessment technique is described e.g. in [24].

The accuracy and correctness of the theoretical assessment, carried out using the above mentioned experimental dataset will be influenced not only by errors of the experimental data but also by their miscellany.

To obtain reliable theoretical assessment, the existence of any set of good quality experimental thermodynamic measurements (e.g. enthalpies of mixing, enthalpies of formation, heat capacities) is very advantageous. If no such data are available and only phase equilibrium and phase boundaries data exist, it is possible to create several theoretical datasets of thermodynamic parameters which will reproduce the phase diagram correctly, but the thermodynamic properties of the particular phases will differ significantly. The reasonability of such dataset can be tested e.g. by calculating some of the thermodynamic properties – e.g. the absolute entropies of all solid phases at room temperature [24]. Sometimes the problems may appear later when the dataset is used for phase diagram assessment of higher system.

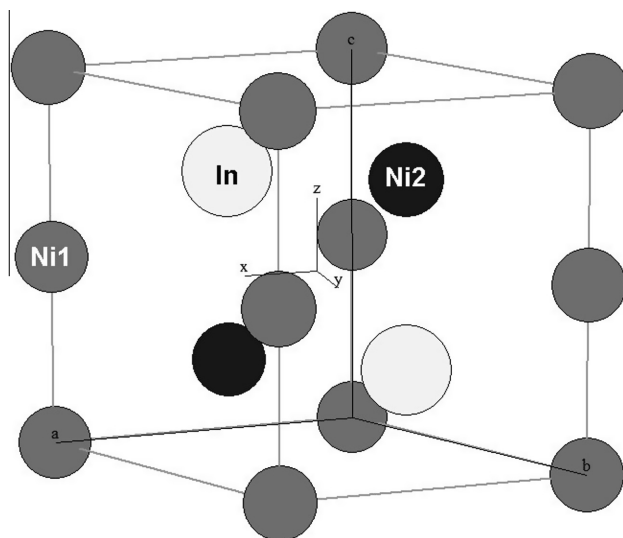


Fig. 3. Crystallographic structure of Ni₂In phase, Pearson symbol hP6.

Table 1
NiAs and Ni₂In type phases in selected binary systems and their original models.

System	Phase	Original model	Solubility of element B (at.%)
<i>NiAs prototype</i>			
Au–Sn	δ	(Au) ₁ (Sn) ₁	50.0–50.5
Bi–Ni	NiBi	(Bi) _{0.5} (Ni,Va) _{0.5}	45–49
Bi–Pd	γ	(Bi,Pd)	63–75
Cu–In	η′	(Cu) _{0.545} (Cu,In) _{0.122} (In) _{0.333}	35.2–37.8
Pb–Pd	β-Pd ₅ Pb ₃	(Pd) ₁ (Pb) ₁ (Pd,Va) ₁	62–63
Cu–Sn	η	(Cu) _{0.545} (Cu,Sn) _{0.122} (Sn) _{0.333}	43.5–44.5
<i>Ni₂In prototype</i>			
Ni–In	Ni ₂ In	(Ni) ₂ (In) ₁	33.3
Cu–In	η	(Cu) _{0.64} (In) _{0.36}	35–38
Ni–Sn	Ni ₃ Sn ₂ -HT	(Ni,Sn) ₁ (Ni) ₁ (Ni) ₁	37.5–40.5

The experimental errors of the measured quantities or the estimated uncertainties of quantities calculated by ab initio approach will also influence the accuracy of the assessment. There will be always disagreement between the calculation and experiment, and the degree of the disagreement can be evaluated by comparison of the calculated phase diagram and existed experimental and ab initio data. It is usually enough to compare the figure showing the experimental information and corresponding calculated values. The deviations should exhibit Gaussian distribution over the whole range of existence. The accuracy of the theoretical dataset is directly related to the mutual consistency of the related experimental data published by different authors. This again underlines the importance of the precise analysis of available experiments. More detailed analysis of the accuracy and precision of the theoretical datasets were done by Schmid-Fetzer et al. in his review [24].

The Gibbs energy parameters created by above mentioned theoretical assessments are assembled in the form of thermodynamic database; nevertheless the thermodynamic database is not just a collection of such datasets. Even if all the included individual datasets are correctly assessed and internally consistent, the careful check of the consistency of the complete database has to be done, as the authors of various assessments, included in the database, can use different polynomials, models, assumptions, etc. in their works.

3.2. Creation of consistent thermodynamic database

The Gibbs energy descriptions of all phases and constituents included in the database must be unique, based on the same assumptions, conditions and models [25].

It means that the polynomials and series used to represent the temperature, pressure and composition dependence of the Gibbs energy of any constituent have to be mutually compatible, including any additional contributions to it (e.g. related to magnetic properties, surface energy contribution).

Similarly we have to use the same models for the description of the Gibbs energy of the phases with the same or similar crystallographic structure, existing in different systems (binary, ternary, etc.) in the scope of the database, and also the names assigned to these phases have to be identical.

The last condition for reaching consistency of the database is related to the identical sets of parameters used for the description of the Gibbs energy of the pure constituent in given crystallographic structure, either stable or metastable, in all systems in the database.

More detailed discussion of the above mentioned conditions will be shown in following part of the paper.

3.3. Consistency of polynomials and models

The Redlich–Kister series [20] for the concentration dependence of excess Gibbs energy, extended by Muggianu [19] to ternary systems, shown in Section 2.1 (Eq. (5)) is the most frequent expression used in the assessments published today, especially for the metal based systems. Alternative methods have also been developed for the extrapolation of the Redlich–Kister series, e.g. by Kohler [26], Colinet [27] or Toop [28], their approaches are overviewed in more details in [15,16]. The differences are not significant, first two methods are also symmetrical as Muggianu's, but they cannot be

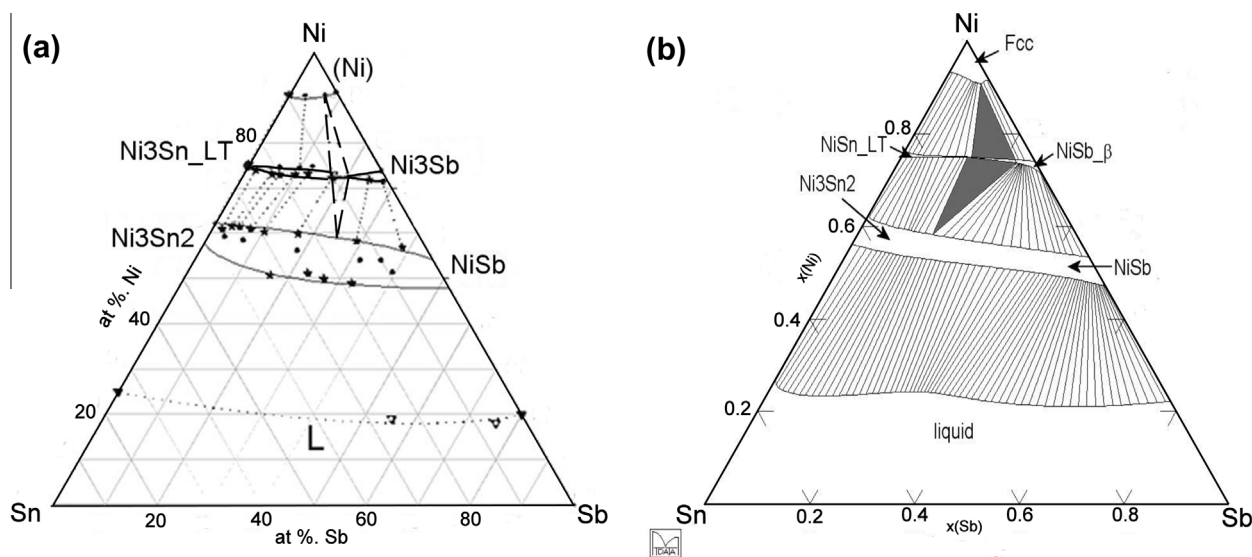


Fig. 4. Experimental (a) and calculated (by MTDATA™) (b) isothermal section of Ni–Sb–Sn system at 900 °C with unified model for the NiAs/Ni₂In prototype structure [30].

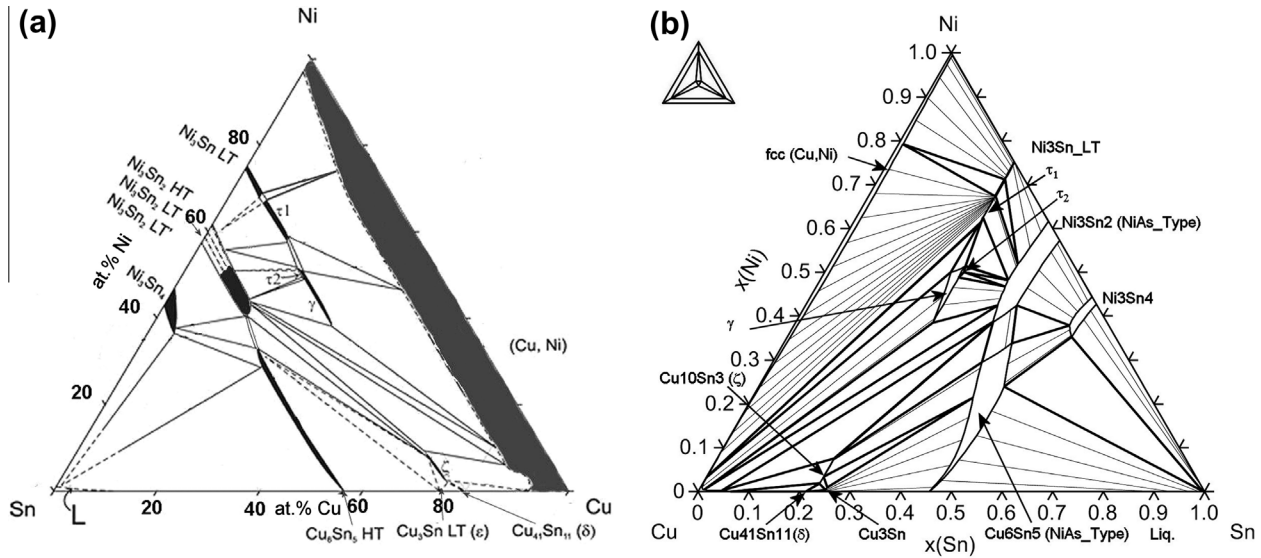


Fig. 5. Experimental (a) and calculated (by Thermo-Calc™) (b) isothermal section of Cu–Ni–Sn system at 400 °C with unified model for the NiAs/Ni₂In prototype structure [31].

combined in one database. The Muggianu extrapolation is preferred as it is easier to formulate. One of the elements is treated differently in the Toop method and therefore it can offer an advantage when one element has different properties in comparison with others (e.g. gas element in the system with two metals). Nevertheless it is very difficult to incorporate such approach to large databases and therefore other modelling tools are used to describe properly the properties in the case of such systems [16].

Some models can use different approach for the expression of entropy term, especially when the assumption about random mixing is not acceptable. One of them is e.g. the modified quasichemical model [29] which is incompatible with above mentioned formalism. Other formalisms can sometimes be used for ternary systems with specific properties. Therefore, the type of the polynomials used for the expression of Gibbs energy (and especially the excess Gibbs energy) has to be checked and the same models applied throughout the database.

This type of consistency has to be also checked in connection with the modelling of order/disorder transition, where several approaches can be used (e.g. [23]). The sets of parameters for such phases are not compatible when different approaches are used to model the order/disorder transformation in different assessments with the same phase.

The above mentioned problems are not very frequent now, as the advantages of some approaches are significant and the unification of polynomials and series used for the Gibbs energy modelling is now also supported by formats used by main software and database producers.

Very difficult situation exists in the case of second condition of consistency – the selection of proper model for description of

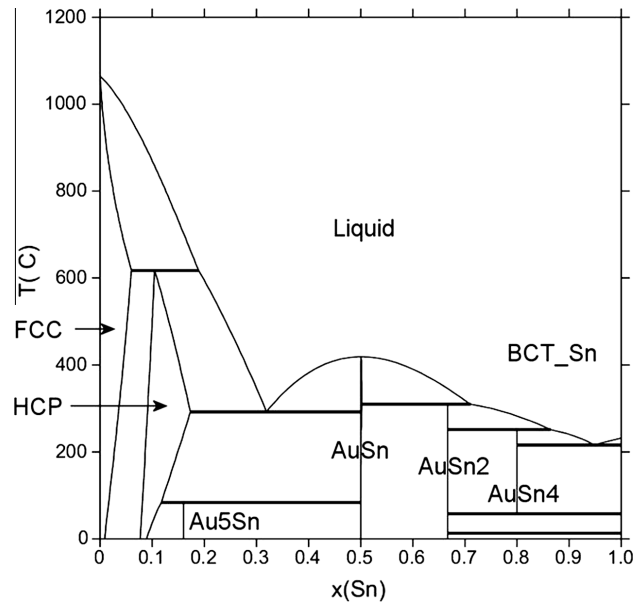


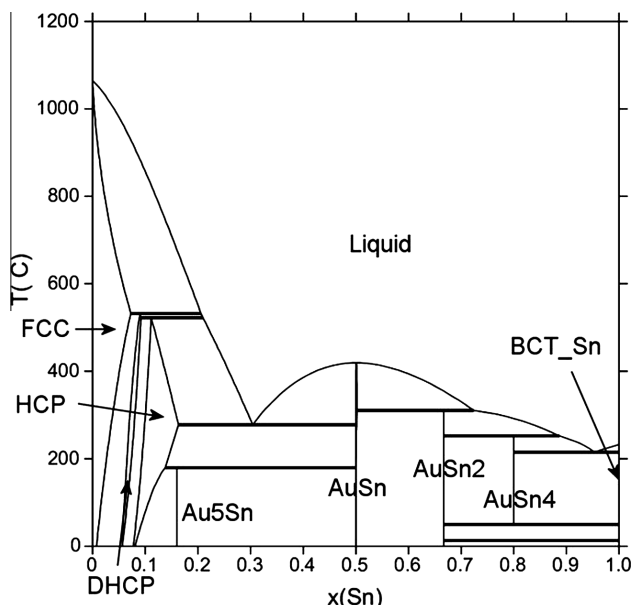
Fig. 6. Incorrect binary diagram of Au–Sn system, when the assessment using originally unary data from SGTE database ver. 1.0 [17] was combined with ver. 4.4 of the SGTE database [18]. The AuSn phase is modelled using the stoichiometric model for AuSn phase (calculated by Thermo-Calc™).

Table 2
Example of different lattice stabilities for metastable crystallographic structures of Sn and Sb in different versions of SGTE database [17,18].

Lattice stability value	SGTE ver. 1.0	SGTE ver 4.4
$G_{\text{Sb}}^{\text{BCT-A5}}$	$1000 + G_{\text{Sb}}^{\text{SER}}$	$13,000 - 8 * T + G_{\text{Sb}}^{\text{SER}}$ (SER = Rho.A7)
$G_{\text{Sn}}^{\text{FCC-A1}}$	$4150 - 5.2 * T + G_{\text{Sn}}^{\text{SER}}$	$5510 - 8.46 * T + G_{\text{Sn}}^{\text{SER}}$ (SER = BCT.A5)
$G_{\text{Sn}}^{\text{HCP-A3}}$	$2400 - 3.1 * T + G_{\text{Sn}}^{\text{SER}}$	$3900 - 7.464 * T + G_{\text{Sn}}^{\text{SER}}$ (SER = BCT.A5)
$G_{\text{Sn}}^{\text{TET-A6}}$	$5015.5 - 7.5 * T + G_{\text{Sn}}^{\text{SER}}$	$5387 - 8.26212 * T + G_{\text{Sn}}^{\text{SER}}$ (SER = BCT.A5)

concrete phase. Only minor discrepancies can be expected in the case of substitutional and interstitial solid solutions and liquids, as there is general agreement about the model used for the expression of the Gibbs energy for this type of phases. Nevertheless, even here we have to check the details of the models, as in some cases e.g. the associate model can be used for liquid. In the case of interstitial solid solution, two-sublattice model is generally used, one sublattice containing the substitutional constituents, e.g. metals, the other sublattice containing the interstitials. Here some elements as boron can occupy the positions either in substitutional or interstitial sublattice and careful check is necessary when accepting datasets from different authors.

No such agreement exists for more complex, mainly intermetallic phases, where the CEF is mostly used. Usually there is a



tendency of the authors of the assessment to respect the crystallography of the phase as much as possible, as this can incorporate the physical background into the calculations and assures the conservation of some properties of the phase, but selecting the number of sublattices, their occupancy and their stoichiometric coefficients is very much influenced by his own decision.

There is general tendency to create as simple model as possible to decrease possible number of parameters, and therefore, if there is not enough experimental information about the phase, there is a tendency to respect the composition of the phase for the definition of the number of the sublattices and their properties (occupying elements, stoichiometric coefficients, etc.). If new information appears later, and related binary systems with the same type of phase are assessed, new author of the assessment can easily select different model for the same phase and consequently, the two binary assessments are not compatible for the prediction of ternary system behaviour, especially when the complete solubility between those two binary phases can be envisaged.

Even if the crystallography of the phase is respected, the amount of sublattices not always corresponds to the number of independent crystallographic positions in the lattice. There is a tendency to join the positions, which have similar crystallographic properties (e.g. coordination number, or crystal symmetry of the position itself, etc.) to decrease the number of sublattices and possible parameters. Therefore careful check of models is necessary when combining two binary assessments from different authors into one general database.

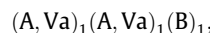
Even more difficult situation can appear when systems with crystallographically different albeit related structures are modelled independently and no information about the ternary system exist at the time of the assessments. Group of phases with the crystallographic structures of NiAs/Ni₂In prototypes is a characteristic example. These phases appear in many important systems, where it plays important role from the point of view of possible influence on alloy material properties.

3.3.1. NiAs And Ni₂In type phases

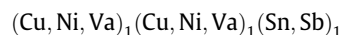
The structures corresponding to NiAs and Ni₂In prototypes are closely related (Figs. 2 and 3). The NiAs structure has the Pearson

symbol hP4, two independent crystallographic positions and its structure can be seen in Fig. 2. The Ni_2In prototype (Fig. 3) has Pearson symbol hP6 and three independent crystallographic positions. It can be seen from the figures, that in both phases two positions are identical, the Ni_2In structure contains additional position, which can be occupied by the Ni-equivalent element. This structure gives a great degree of versatility to various intermetallic phases with these structures and they exist in many binary systems, with different compositions and degree of nonstoichiometry (Table 1). They very often influence significantly the phase relations in the ternary systems, exhibiting either complete solubility both between identical and related structures or two phase fields region exists between them. Ni-Sb-Sn and In-Ni-Sn systems are examples of the former case. Cu-Ni-Sn system of the latter.

In the case of Ni-Sb-Sn system, there is complete solubility between the Ni_3Sn_2 phase and NiSb phase (NiAs prototype) [30] as shown in Fig. 4. In the case of Cu-Ni-Sn system, there is no complete solubility between the phases, but the solubility of Cu is very high in Ni_3Sn_2 (Ni_2In prototype) in the temperature region, where also the Cu_6Sn_5 -HT phase (NiAs prototype) exists [31]. The necessity to unify the models for above mentioned prototypes appeared in the scope of the development of the SOLDERS and MP0602 databases [32,33], where above mentioned ternary systems has being assessed. Taking into account the crystallography and also the information about the possible presence of vacancies in concrete crystallographic positions (which allows the intermetallic phases to cover different compositions and solubilities), three sublattice model was proposed in the form:



Which means for the Ni-Sb-Sn and Cu-Ni-Sn systems:



The results of the model unification are shown in Figs. 4 and 5.

3.4. Unary data consistency

Another important feature of consistent thermodynamic database is the consistency with respect to the Gibbs energy of pure constituent in given crystallographic structure used in various binary or ternary assessments. As mentioned above, one of important features of *Calphad* method is the need to establish the Gibbs energy of the “end members” – the elements or compounds (real or

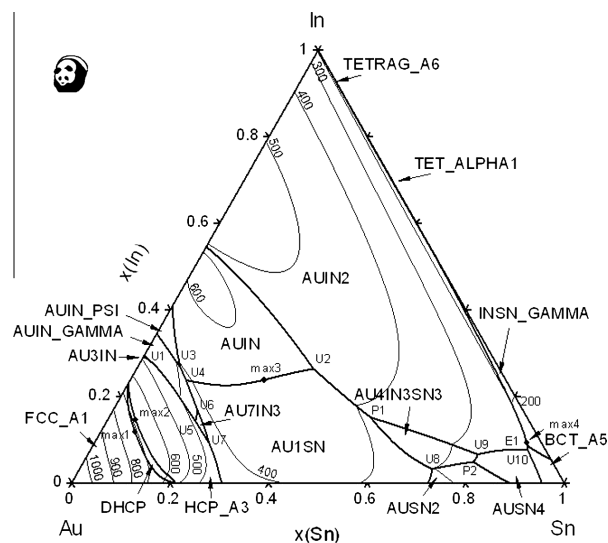


Fig. 8. Liquidus projection of the Au-In-Sn system (calculated by PANDATTM) [35].

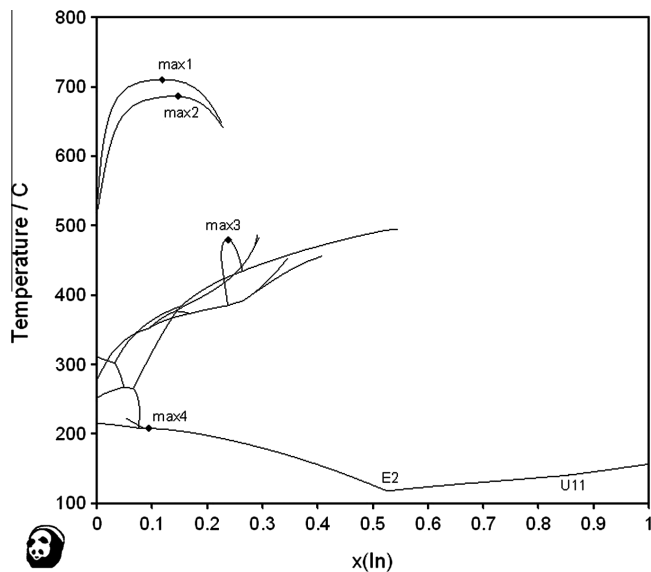


Fig. 9. Liquidus lines in the Au-In-Sn system projected onto the $T-x(\text{In})$ plane (calculated by PANDAT™) [35].

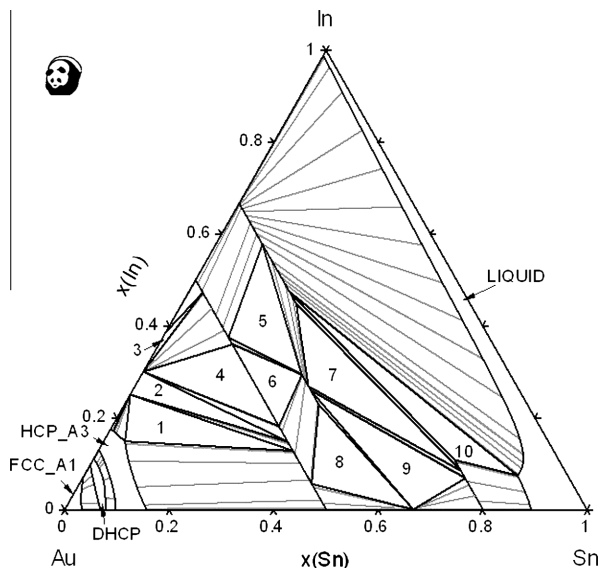


Fig. 10. Calculated isothermal section at 250 °C for the Au-In-Sn system (calculated by PANDAT™) [35].

Table 3

Selected composition of ternary alloys as possible materials for lead-free soldering, proposed on the basis of Calphad type thermodynamic modelling [38].

Alloy no.	Ternary compositions (mole-fraction)	Solidus T (°C)	Liquidus T (°C)	Range T (°C)
1.	Sn-0.25Au-0.20Sb	273	290	17
2.	Sn-0.29Au-0.08Cu	305	322	17
3.	Au-0.18Ge-0.10In	338.7	340	1.3
4.	Au-0.16Sb-0.22In	285.7	288	2.3
5.	Au-0.30Sn-0.24In	280.5	290	9.5
6.	Au-0.31Sn-0.01Cu	278	292	14
7.	Au-0.26Ge-0.02Bi	332	352	20
8.	Au-0.32Sn-0.01Ag	278	308	30
9.	Au-0.28Sn-0.01Zn	275	316	41
10.	Au-0.13Sn-0.10Si	271	334	63
11.	Au-0.24Ge-0.05Sb	285	348	63

virtual) in stable or metastable crystallographic structure. These Gibbs energies can be measured in the case of pure elements or compounds with real crystallographic structures or have to be theoretically established in the case of virtual compounds and pure component or compounds in metastable or unstable structures. If the same element or compound exists in more binary systems, we have to check carefully the value of its Gibbs energy, as it can differ in different assessments.

The example of such discrepancies is shown in Table 2, where so called lattice stabilities (the difference between the Gibbs energies of pure elements in metastable structures and Gibbs energy of the same element in standard reference state) are shown. The data are taken from two editions of SGTE unary Gibbs energy database [17,18]. The lattice stabilities of virtual end members or constituents in metastable or unstable structures are either estimated (main approach in the past), or modelled during the assessment of higher order system, where such structure is stable and we have some experimental information about the behaviour of the constituents in such structure, or the energy difference of such hypothetical phase is calculated at 0 K with respect to stable phases by ab initio methods.

The influence of such differences is shown in Figs. 6 and 7, where the calculated phase diagrams of the Au-Sn system are shown. Original assessment published by Liu et al. [34] used the unary data from SGTE ver. 1.0 database [17] and when it was combined with unary data from ver. 4.4 of this database [18], the incorrect phase diagram of the Au-Sn system was obtained (Fig. 6). With respect to the decision to use the newer version of the unary database [18] in the SOLDER database [32], the reassessment of the system was necessary. This work was carried out in the scope of the COST MP0602 Action [33]. The reassessment work included the remodelling of the Gibbs energy parameters for the HCP and FCC phase where the lattice stabilities for the pure Sn in metastable crystallographic structures are different. Also the model for the AuSn phase which has the crystallographic structure of NiAs type was changed, originally the phase was modelled as stoichiometric phase with two sublattices $(\text{Au})_1(\text{Sn})_1$. New model is the three sublattice one shown above. The result of the remodelling is in Fig. 7.

4. Practical application of thermodynamic properties and phase diagram modelling

The modelling of thermodynamic properties and phase diagrams of complex systems using the Calphad method is currently the most advanced method in the material science not only from the point of view of direct practical applications in basic and applied research but also as a source of data for other multiscale modelling approaches, e.g. for modelling of diffusion processes, development of structure morphology, nucleation and grain growth and prediction of material properties of complex materials. Several examples of such applications will be shown in following chapter.

Existence of sophisticated software packages, together with broad selection of thermodynamic databases, allows modelling of thermodynamic properties of very complex systems and makes the development of new materials more time and cost efficient. Reliable predictions of phase equilibria allow limiting the extent of experimental work to selected compositions which can verify the results of calculations.

The general mathematical approach of all software packages is similar. The main software packages (Thermo-Calc™ [9], MTDA-TA™ [10], Pandat™ [11], FactSage™ [12]) offer the possibility to predict thermodynamic properties of multicomponent systems and usually offer also modulus for the theoretical assessment of system based on experimental results (e.g. PARROT in Thermo-Calc

Table 4

Composition of two sides of the weld interface consisting of two different grades of steels.

Steel	Cr	Mo	Mn	Si	C	N	V
T24	2.45	1.03	0.62	0.31	0.053	0.018	0.26
P91	8.5	0.98	0.33	0.35	0.1	0.035	0.22

[9] or the Assessment module in MTDATA [10]). The software producers also offer for the scientific and engineering community a wide range of thermodynamic databases, both general and specialised ones, usually oriented towards specific groups of materials (steels, Ni-based alloys, solders, etc.) Unfortunately, the format of databases is not always compatible with all above mentioned software packages and therefore some products are available only for particular software.

4.1. Modelling of phase diagrams and prediction of solidification properties for lead-free solders

The use of *Calphad* approach for the development of new materials for lead free soldering in the temperature range 250–350 °C (high-temperature soldering) will be briefly demonstrated here. Various sections of ternary phase diagrams for the Au–In–Sn system using the SOLDER database [32] and published in the book [35] are shown in Figs. 8–10 to demonstrate the extent of information we can obtain from phase diagram calculations using software packages mentioned above.

The same database was used by Chidambaram et al. [36,37] in his study. He demonstrated very efficient use of theoretical phase diagram modelling for the development of candidate alloys for high-temperature lead-free soldering. Two main alloy systems were considered by authors as promising candidates. First set of alloys was based on Au–Sn–X (X = Ag,Cu) systems – they calculated a set of compositions close to eutectic Ag–Sn compositions. The results were used to predict the compositions of alloying capable of suppressing the precipitation of brittle Au₅Sn phase and at the same time not increasing significantly the melting temperatures. Calculations made on Ag–Au–Sn system also predicted the Sn-rich composition Sn–0.28Au–0.08Ag as possible candidate for high-temperature lead solder (Table 3). The advantage of this alloy is lower amount of Au, which favourable influences the price of the alloy. The second set of alloys was based on Au–Ge–X system (X = In,Sb,Sn) and the same approach as above used to predict suitable compositions (e.g. Au–0.18Ge–0.10In) (Table 3). Chidambaram et al. [38] also modelled the solidification process using Scheil scheme (ideal diffusion in liquid, no diffusion in solid) to obtain compositions with melting point in proper temperature region

and narrow two-phase solid/liquid region to ensure good materials properties of the alloys. Such prediction of course cannot pinpoint one “ideal” composition, the proposed alloys has to be tested for proper physical and material properties. The cost of materials, their abundance in the market, etc. play also very important role in the selection process; nevertheless the use of theoretical prediction in the pre-selection of alloys can significantly save research costs and time.

4.2. Modelling of element and phase behaviour in welds of two different steels

As mentioned above, the results of the thermodynamic calculations are often important inputs for other theoretical models, e.g. modelling the diffusion processes in multicomponent alloys. The software package DICTRA [9] allows detailed simulation of diffusion controlled processes and both the thermodynamic databases and equilibrium thermodynamic calculations are important part of the software. As an example of results which can be obtained using this software, the modelling of diffusion controlled processes in weld of two different multicomponent steels (their compositions are in Table 4) are shown in Figs. 11–13. The 1-dim simulation shows the element profile in the simulated weld. The interface between a low-alloy (T24) and advanced Cr–Mo steels (P91) is shown on Fig. 11. The parameters of the modelling were

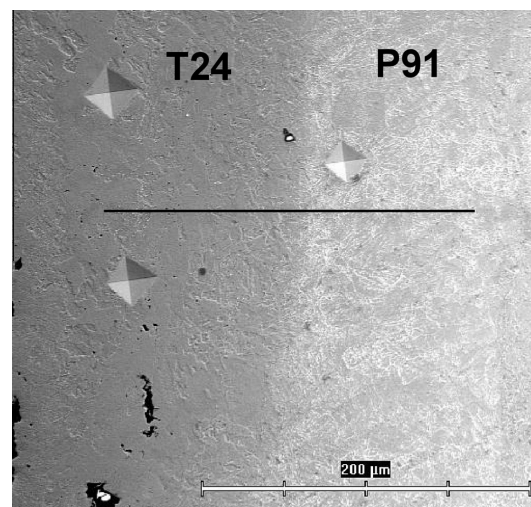


Fig. 11. Detail of the studied area of the weld, including the line, where the element distributions were experimentally measured (courtesy of Dr. Brziak from Weld Research Institute from Bratislava, Slovakia).

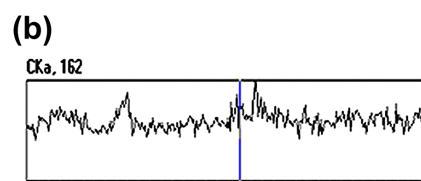
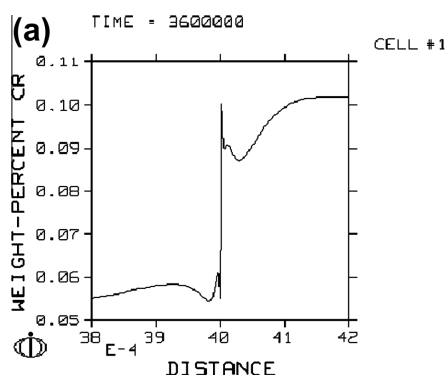


Fig. 12. The redistribution of the overall C content across the interface in the weld, theoretical (a), and experimental (b). The interface is located at the relative distance 0.004 (calculated by DICTRA™).

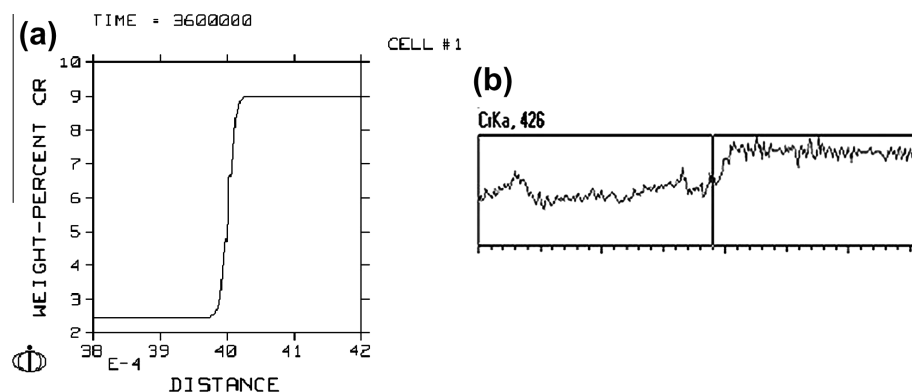


Fig. 13. The redistribution of the overall Cr content across the interface in the weld, theoretical (a), and experimental (b). The interface is located at the relative distance 0.004 (calculated by DICTRA™).

selected to correspond reasonably to the real conditions, modelling time (with respect to the experimental time of annealing) was 1000 h, temperature of annealing 600 °C, the annealing temperature was preceded by cooling (about 5 min) from the liquid region and than 5 min linear heating to the service temperature.

The predicted redistributions were reasonably confirmed by experimental measurements, including the experimental confirmation of calculated carbon depleted zone close to the interface (courtesy of Dr. Brziak from Weld Research Institute from Bratislava, Slovakia).

4.3. Use of the Calphad type thermodynamic database in other advanced simulation methods

The importance of thermodynamic modelling is not limited only to relative straightforward applications like the phase diagram modelling or prediction of phase composition, diffusion and thermodynamic properties. The thermodynamic databases and results of calculation can be used also in more distant fields of multiscale modelling both towards macro- and micro-scale.

The material properties of alloys are very much influenced by the phase composition (amount and type of coexisting phases, their stability and tendency towards further development towards thermodynamic equilibria) and morphology of structure – size of grains, their growth, nucleation and processes on the interface. In all this cases, the thermodynamic description of the system is important input for modelling of such processes.

In the field of material properties prediction, the results of thermodynamic calculations (offering stable or metastable equilibria) in the form of expected phase composition are used in other models, both empirical and theoretical, which predict the mechanical properties (e.g. hardness, tensile stress), thermo-physical and physical properties (cooling curves, etc.) and phase transformation. Example of such software package is JMatPro [39].

On the other end of the dimensional scale, the processes on the interface, including the nucleation processes can be modelled by phase-field models. As the knowledge of interface behaviour is crucial in many practical applications, the phase field method was applied for the study of precipitation sequences on solder/substrate interface [14,40]. Here the adjusted thermodynamic parameters obtained in the scope of thermodynamic assessment of the Cu–Ni–Sn system were used and the 2D and 3D simulations of the growth of the IMC layers in the presence of grain boundary diffusion in the Cu–Sn system was carried out.

5. Conclusions

The Calphad method is currently the only theoretical approach for the modelling of thermodynamic properties and phase

diagrams of multicomponent systems which can be used for complex systems, both in basic research and in the industrial applications. The method is based on semi-empirical approach, and therefore reliable experimental data are necessary for description of thermodynamic and phase properties of unary and binary systems. The thermodynamic databases are necessary for such modelling, and the thermodynamic parameters submitted into these databases have to fulfil some conditions to allow the prediction of properties for multicomponent systems corresponding to real materials. Namely:

- The polynomials and series used to represent the temperature, pressure and composition dependence of the Gibbs energy of any constituents have to be mutually compatible.
- The same models have to be used for the description of the Gibbs energy of the phases with the same or similar crystallographic structure, existing in different systems (binary, ternary, etc.) in the scope of the database, and also the names assigned to these phases have to be identical.
- The identical sets of parameters have to be used for the description of the Gibbs energy of any pure constituent in given crystallographic structure in all systems in the database.

The software packages, based on Calphad method, are currently the only theoretical tools, applicable for complex materials as steels, superalloys, etc.

The thermodynamic databases and software packages are also important for multiscale modelling. The results of calculations can serve as input for modelling diffusional processes, phase transformations, material properties and structure morphology development, including the processes on interface.

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