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COMPUTATIONAL THERMODYNAMICS AND INFORMATIONAL TECHNOLOGIES IN THE FIELD OF COMPUTER DESIGN OF MATERIALS

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Abstract

Computational thermodynamics and informational technologies in the field of computer desing of materials as well as appliance of CALPHAD method on resolution of thermodynamic problems are presented in this paper.

Keywords: computational thermodynamics, CALPHAD, phase diagrams.

1. Introduction

1.1. Two methods for investigations of phase diagrams and thermody namic properties

The phase diagrams are visual representation of the material state as function of temperature, pressure and concentrations of the constituent components. There are two approaches in phase diagramsinvestigations and thermodynamic properties of multi-component systems, studied by materials scientists as specialists in the field of chemistry and physics: by experimental and theoretical methods.

The experimental determination of phase diagrams and thermodynamic properties of binary and multicomponent systems is *time consuming* and costly task.

Theoretical calculations of phase diagrams and thermodynamic properties allow:
— coupling of the experimental information on phase equilibria and thermochemistry,
— decrease amount and time for experimental investigations for construction of new phase diagrams for ternary and more multi-component systems,
— predicting of the thermodynamic properties as function of composition and temperature, where experimental data are absent.

1.2. Basic stages of historical development of interconnection. between thermodynamics and phase diagrams

The theoretical foundation and geometrical connection between thermodynamic properties and phase diagrams was established more than a century ago by J.W. Gibbs. From theoretical point of view the *tie-line of the T-x phase diagram* for binary closed system is *the projection of common tangent line* to curves for Gibbs energy of different phases as functions of composition at constant temperature. After theoretical investigations of hypothetical phase diagrams by J.J.Van Laar, J.Bekker, B.Ja.Pines and D.S.Kamenetskaya, Larry Kaufman started with his pioneering work on lattice stability of pure elements (1959) for as computer calculation of phase diagrams, published in 1970 with Bernstein in book "Computer Calculations of Phase Diagrams". This book and International Journal CALPHAD were base launching pad for rapid development of numerical thermodynamic description and software for calculation of phase diagrams of binary and multicomponent systems. After the first issue of Journal CALPHAD, the International Journal "Bulletin of Phase Diagrams" was published in 1980, later renamed to Journal of Phase Equilibria, which in the beginning included only papers on assessment of experimental data of phase diagrams and later it included papers dealing with experimental and calculational methods in investigation of phase diagrams. In recent years, numerous international journals (J.Alloys Compounds, Metall.Trans., Journal of Nuclear Materials, Phys.Rev., Z.Metallkunde, Journal of Mining and Metallurgy and others) include papers on computations of thermodynamic properties of different phases and phase diagrams for binary and ternary systems. The Table.1 contains basic stages of historical development of interconnection. between thermodynamics and phase diagrams. In 2001 year, Dr. Ziu-Ki Liu (Penn.Univ., USA) was elected as chief-editor of CALPHAD Journal, replacing Dr. Alan T.Dinsdale from NPL, UK.

Table 1. The history

J.W.Gibbs.	1865-1871	The theoretical foundation and geometrical connection between thermodynamic properties and phase diagrams
J.J.Van Laar	1908	They have established the coupling between different types
J.Bekker	1937	hypothetical phase diagrams and thermodynamic properties
B.Ya.Pines	1941, 1943	binary systems using the regular solution model
D.S.Kamenetskaya	1949, 1956	
C. Zener	1946	He has calculated of phase boundaries for Fe-base binary systems near the $\alpha \leftrightarrow \gamma$ temperature of phase transformation of the Fe
J.J.Meijering	1950,1951, 1956, 1957	He has published calculated the results of miscibility gaps for ternary systems using the regular and sub-regular (with Hardy) solution models
I.L.Aptekar	1951	He has investigated influence size factor and ordered phenomenon on binary phase diagram
L.Kaufman	1959, 1967, 1970	He has investigated stability parameters for pure elements and with H.Bernstein have applied computers for thermodynamic calculations of binary and ternary phase diagrams, using the regular solution model, and published listing of computer programmers, based on Newton –Raphson algorithm.
L.Kaufman	1973 1977	He organized the project of first meeting of international CALPHAD –team, then Ð the international Journal CALPHAD as for chief Ð editor then as founded editor this Journal.

2. CALPHAD method the modern stage of computer coupling phase diagrams and thermodynamic properties

The strategy of the CALPHAD – method include the next steps:

— the selection and assessment of experimental data on phase equilibria and ther modynamic properties of alloys for binary systems;

— the realization of computer coupling and calculation of phase diagrams and thermodynamic properties *binary systems* (calculation of optimized values of interaction parameters for describing of excess Gibbs energies as functions of concentrations and temperature for different phases of system);

— the application of thermodynamic interpolation method from calculated inter actions parameters *only* for binary subsystems to calculation of ternary phase diagram;

— the assessment or planning and receiving of experimental data on ternary alloys;

— the correction of calculations of phase diagrams and thermodynamic properties

of ternary systems or optimized values of ternary interaction parameters for different phases in three – component systems and etc.

The goal of the CALPHAD – project are:

— the construction of data base for thermodynamic properties stable and metastable phases of pure elements , for example, [1] ;
— the generation of thermodynamic data bases consistency of model description for different kind of phases (disordered solid solutions, melts, stehiometric compounds, chemical compounds with including the homogeneity fields) as well binary as ternary systems, for example, [2]
— the development general algorithms and software for calculations and opti mization phase diagrams and thermodynamic properties of multi-component systems.

3. From CALPHAD-method to Computational thermodynamics

3.1. Basic four-component of Computational Thermodynamics

But the CALPHAD – method up to day has restrictions:
— its goal is establish coupling between phase diagrams and thermochemistry only;
— it do not include coupling and predictions physical properties (parameters crystal structure solutions and chemical compounds, elastic modulus, temperatureexpansion coefficient and etc.) altogether with thermodynamic properties and phase diagrams pure elements, different phases of binary and ternary systems;
— it use very simplest phenomelogical models, which have not theoretical base;
— it use develop software packages (Lukas programs (1977), Thermo-Calc (1985),Chemsage (1990, 1995), F*A*C*T , MT-DATA.

In the last 25-30 years, the thermodynamic calculations of phase diagrams for both binary and multi-component systems received wide application. The computer programs [3-6] developed in various research centers of world are of wise use. The numerical methods involved in these programs can be divided into two classes. In studies of the first class [Counsel, 1971] , the Gibbs energy minimum is sough for heterogeneous system. In studies of the second class, the set of phase equilibrium equations (establishing the equality of chemical potentials for the components of various phases) is solved [L.Kaufman, 1970] , H.Lukas et all. [3-4], Lin et all . [6].

In this case either the Newton-Raphson iterative method or the Nelder - Mead modified simplex method is used to minimize the objective function representing the sum of residual of phase equilibrium equations. An essential constraint of the former methods is the impossibility of guaranteeing attainment of the global minimum of the Gibbs energy for heterogeneous system. This means that the calculated phase diagrams can both stable and metastable. An essential disadvantage of the latter methods is the necessity of selecting a successful initial approximation for starting the iterative process, for which there is no assurance that the iterations will converge to the desired solution. Thus , the calculating methods of the first and second class, which may refer to as first generation software, render it principally impossible to create autonomic computer programs for calculation of phase diagrams and thermodynamic properties of multiphase multicomponents alloys of systems with three or more components [7-9].

Therefore in frame computational thermodynamics were developed well-founded (with mathematical point view) method for calculations of phase diagrams and thermodynamic properties of multi-component systems [7-8, 10]. Thus the computational thermodynamics up to-date include basic four "component": 1) analytical thermodynamics of phase equilibria, 2) physical models, needed for description of thermodynamic properties of phases different types (disordered solutions, melts, chemical compounds without and with homogeneity fields and etc.), 3) mathematical – founded software and 4) experimental data on phase equilibria and thermodynamic properties of alloys.

This report will discussed of results as binary and ternary "interactions" between above – named "components".

3.2. Binary "interactions"

Analytical thermodynamics and experimental data:

Applications of some results of analytical thermodynamic to assessment of experimental data allows carry out of selection correct data in the middle of different experimental data, obtained by different scientists, for example [11]. This results allows also assessment for compositions at the temperature of non-variant equilibria for some binary systems. Another example of application of analytical thermodynamics and experimental data on phase equilibria are results of calculations of temperature FCC->L virtual phase transformation for metastable FCC – phase Cr [14].

Analytical thermodynamics and algorithms and computer programs:

The generalization of "equality of the areas Maxwell rule" in coordinates $\partial G/\partial x - x$, where G – molar Gibbs energy of phases as function of composition, x – composition of second chemical component in closed binary system allows create original algorithms and autonomic program for calculations of binary systems, including up to ten disordered solutions and up to ten chemical stexiometric compositions compounds [7]. Its generalization from binary to ternary systems allows create original algorithm [8] and computer program [10] for calculations of isothermal sections two-phase fields of ternary systems.

Within the framework of the vector approach to the thermodynamics of multicomponent systems the algorithm and computer program for calculations of different thermodynamic properties (chemical potentials of components, specific heat, mole fractions of phases) as function of temperature for two-phase alloys with constant composition were developed [10].

Analytical thermodynamics and physical models

Criteria of concordance for results of ab-initio calculations of difference energies between different phases at 0 K and the thermal contributions of difference specific heat for these phases of pure elements

$$\Delta H^{\alpha\to\beta}(OK) \equiv H^{\beta}(OK) - H^{\alpha}(OK) = \int_0^{T^{\alpha\to\lambda}} dT \int_0^T \frac{\left[C_P^{\beta}(T) - C_P^{\alpha}(T)\right]}{T} dT \qquad (1)$$

Physical models and experimental data:

Application of physical models for pure component allows developed method of calculation of anharmonic characteristics (Grunaisen parameters, average temperature coefficient of expansion) for FCC- and BCC- phases pure elements from harmonic properties (cohesion energy, equilibria volume and volume elastic modulus) by using of equation state of Rose et all.

The application of physical models and experimental data for description of differences of entropies elements between liquid, FCC- and BCC- phase as function of temperature [13].

Physical models and software:

Will be discussed application of different models for calculations of phase diagram of the nickel –aluminum system, obtained by different scientists in during 25 years (from simplest phenomelogical models to Gorsky - Bragg-Williams (GBW) model up to ab – initio calculations, and late results with application of CALPHAD-method).

3.3. Ternary "interactions"

Analytical thermodynamics + experimental data + physical models

Criterion of application of regular model for binary phase diagrams with aseotrop point. Criteria of appliance of regular solutions models for α– and β–phases for binary phase diagrams between A and B components with aseotrop point with coordinates (x_0, T_0) was obtained [12]:

$$\left(\frac{x_0}{1-x_0}\right)^2 = \frac{\Delta G_A^{\alpha\to\beta}(T_0)}{\Delta G_B^{\alpha\to\beta}(T_0)} \qquad (2)$$

Relationship between interaction parameters for subregular model for binary phase diagrams with aseotrop point. This result was generalized on case appliance of sub-regular solutions models for binary phase diagrams with aseotrop point for calculation difference of interaction parameters between two-phases [12].

Application of analytical thermodynamics, experimental data and autonomic programs for solution of indirect tasks. The application of autonomic computer program and experimental data of phase equilibria and thermodynamic properties of alloys for concerned system and also analytical thermodynamic allows to formulate new class of tasks, exactly, indirect tasks with using minimizing procedure with constraints.

Will be discussed the optimized results on computer coupling experimental data on thermodynamics and phase equilibria as binary systems (Al-Si, Ni-Cr, Ni-W) as ternary systems (Ni-Mo-W) and computational results of chemical potentials of components as function of temperature for (L+FCC) – phase field for alloys different constant compositions for the Ni-Al-W system.

Application of experimental data, autonomic programs and physical models for solution of indirect tasks:

The results of GBW-model calculations thermodynamic properties and distribution atoms between different sub-lattice for $Ni_{0,75\pm x}Al_{0,25\pm y}$ with $L1_2$ crystal structure and $Ni_{0,5\pm x}Al_{0,5\pm y}$ with B2 crystal structure will be discussed [15]. As another example, the results of application association regular model for calculation thermodynamic and structure properties were obtained [16].

4. Conclusion

This section will include base obtained results and new problems into fields computational thermodynamics, physical models and computer design new materials with multi-functional properties [17].

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