Netsu Sokutei **24** (4) 188-193

論 文

Thermodynamic Databases of Ceramic Materials

Hans Jürgen Seifert and Fritz Aldinger

(Received May 10, 1997)

Assembling of thermodynamic databases requires the development of consistent analytical descriptions of the functions of states for all phases of the treated system. To provide high-quality data sets the Gibbs energy functions are assessed by computer supported optimisation of phase diagrams using all experimental data available in the literature as well as own experiments. The unary, binary and ternary system descriptions are combined in order to extrapolate to higher-component systems. The CALPHAD method (CALculation of PHAse Diagrams) and the phase modelling is described with special emphasis on ceramic solution phases. The method is illustrated by the thermodynamic assessment of the B-C-N-Si-O system. The results are compared with experimental data.

1. Introduction

Reliable, high-quality thermodynamic computer databases are an important basis to make best use of thermodynamic calculations in order to support materials development and processing.[1] The modern way to handle thermodynamic information is the storage of all functions of state in a computer data base and calculate phase equilibria, heat evolution or- consumption etc. for the conditions and processes relevant in application. This so-called CALPHAD method (CALculation of PHAse Diagrams) is a part of the interdisciplinary field of "Computation Thermodynamics" and couples thermodynamic and phase diagram data.[2] Reliable databases are developed by the thermodynamic optimisation.[3] Based on consistent analytical descriptions for the functions of state for all unary, binary and ternary phases extrapolations to experimentally not investigated multi-component systems are possible. Using well established thermodynamic relationships enables these descriptions to be used to calculate all of the related thermodynamic functions as well as the phase diagram for the specific system. Criteria for the development of databases to calculate ceramic systems are described in the following chapters and illustrated by the B-C-N-Si-O system.

2. The CALPHAD Method

The CALPHAD method requires self-consistent high-quality thermodynamic descriptions of the Gibbs energy functions for all phases (and gas species) relevant for the system investigated. **Figure 1** illustrates the CALPHAD method. To develop data sets the thermodynamic optimisation is used.[3, 4] The best way to construct thermodynamic databases would be the ab-initio calculation from first principles using quantum mechanics and statistical mechanics, because no experiments are necessary. However, presently this method was successfully used only for comparatively simple systems. The main problem here is, that the interesting differences of energies between competing states are very small percentages of the total energies. Therefore, the total energies must be calculated to an accuracy of four to six digits to show up these differences to get the interesting part of the result to an accuracy of two or three digits. The semi-empirical way uses the first principles only to construct models, which

Max-Planck-Institut für Metallforschung and Institut für Nichtmetallische Anorganische Materialien, Universität Stuttgart, PML, D-70569 Stuttgart Germany

may be simplified and result in analytical descriptions of the functions of state, which contain adjustable parameters. The numerical values of these parameters can be found by a systematic trial and error approach with parameter variation until satisfying correspondence with the experimental data is obtained. If specific experimental data are missing then estimates using rules derived from comparison with similar phases or results of quantum mechanical calculations can be used. Very often a large amount of parameters has to be adjusted, which may be impossible by using trial error. If there are a lot of experimental data available and several coefficients have to be adjusted the thermodynamic optimisation using the Gauß method is recommended. A software (BINGSS, BINFKT, TERGSS, TERFKT and PMLFKT) was developed at our laboratory[3, 4] using the Gaussian least squares method for the determination of adjustable model parameters.

All kind of experimental values can be used quantitatively connected with thermodynamic information: Calorimetric heat measurements, electromotive force (emf) measurements of vapor pressure data and all kinds of quantitative phase equilibrium data. All measured values have to be input in the programs and are collected in a specific file. In case of using the programs BINGSS and TERGSS there is number of standard formulations for measured values, covering almost all types of thermodynamic and phase diagram measurements.[4]

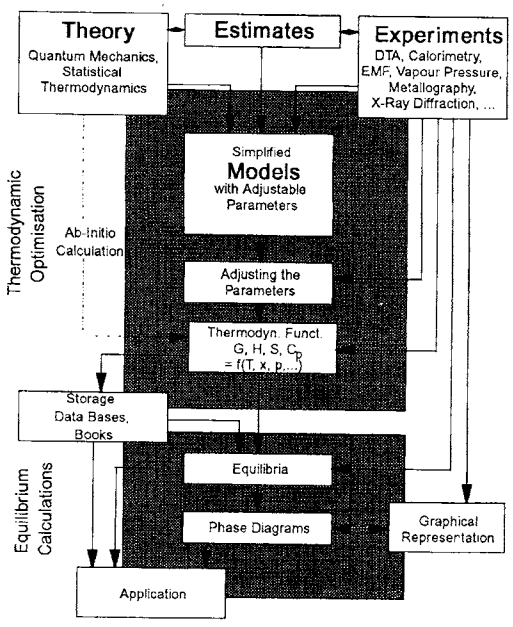

Fig.1 The CALPHAD method.

Two main points have to be considered in the application of the least squares method. The statistical theory requires the "Gaussian normal distribution" of the errors around the "true" values. Contradicting series of measurements indicate systematic errors not fulfilling the condition of the "Gaussian normal distribution." Contradictions of that type have to be critically assessed and less reliable data must not be used in the least squares calculation. Currently, an increasing number of experimentally working groups use CALPHAD to control consistency of their results and ruling out of systematic errors during experimental work. Another crucial point is the question, which model maybe best sufficient to describe the thermodynamic functions of a specific system phase. One has to determine carefully which type of parameters can be adjusted to the experimental data. If more coefficients are adjusted than defined by experimental data the minimum of the squares of error does not necessarily correspond to the optimum set of data. Extrapolating calculations in areas not covered by experimental values can result in physically impossible course of the functions. The results of the optimisation procedure always have to be controlled in order to find out the relationship between analytical descriptions and diagram curves (graphical representations). For example the Gibbs energy of a stoichiometric phase maybe determined in a narrow range of temperature only. The temperature dependence of G, $G = H - T \cdot S$ is described by two coefficients H and S. As only G is determined at virtually one temperature, T_0, only, an attempt to adjust H and S independently, may create unphysically large values giving just the correct value of the expression $H - T \cdot S$, but unrealistic G values at other temperatures. If however, also measurements of the enthalpy H exist, the independent adjustment of the two coefficients H and S is possible and necessary. Therefore, the selection of the models and the selection, which and how many coefficients shall be adjusted, has to be carefully discussed.

To compare different type of experimental data and to apply the least squares method all errors have to have the same dimension. This is achieved by dividing the differences between calculated values and measured

values by the estimated mean error of the specific measurement. All errors become dimensionless and can be summed up and comparison of errors is possible. To find the mean error the measurement includes to treat the different measured values in a similar way and not to accept without criticism the mean errors given by the publications, if they are not determined according to the same criterion in the different publications. These questions cannot be answered completely by the computer calculation and have to be discussed for each system and the programs have to support each decision.

The models have to be derived from physical models in close orientation to their (crystal) structure and physico-chemical properties. It is also possible to use pure curve fitting formulas which should reproduce an empirical found shape of the Gibbs energy function. However, this method can result in not reliable results when combining these functions for extrapolating calculations of high component systems. Therefore, most important are formulas based on sufficient physical models, describing the deviations from the ideal model by additional terms with the character of curve fitting formulas. For pure elements and for stoichiometric phases (Phases without homogeneity region) the Gibbs energy has to be expressed as function of temperature only. To describe the homogeneity range of solution phases the Gibbs energy description according to the Wagner-Schottky model is frequently used.[5] This model assumes a concentration independent enthalpy of formation of the defects. Antistructure atoms, interstitial atoms and vacancies are considered as defects. The Compound Energy Formalism[6] treats instead the enthalpy of formation of a phase with full occupation of a sublattice with defects. Wagner-Schottky model and Compound Energy Formalism are equivalent as long as the assumption of concentration independent enthalpy of formation of defects is valid. Using modern computer software the sublattice site occupancies can be calculated. Phases with complete occupation of the sublattice with defects are quite fictitious and far away from states that can be realized. However, to achieve consistency and compatibility between different thermodynamic data sets including the same types of phase an international agreement on reference states has to be reached. Presently, this is a crucial point in CALPHAD discussion.[7]

In most cases metallic liquid phases can be described by the Redlich-Kister model,[8] however ceramic oxide, silicate and oxynitride systems have to be modelled by sublattice formulas for (partial) ionic liquids containing charged and neutral species simultaneously.[9] Other models frequently used are the associate model[10] and the modified quasichemical model.[11] These approaches have proved to give satisfying results even for high-component systems using the formulas according to Muggianu[12] or Kohler[13] for extrapolation.

A clear graphical representation designed for the solution of specific problems, scientific as well as application oriented is crucial to make best use of the thermodynamic data sets. Depending on the special demand the most appropriate diagram has to be selected. Tabulated numerical results offer exact quantitative data. However, large amounts of numbers may be involved and too abstract for immediate understanding of the specific problem. The general types of phase diagrams have been discussed by Pelton and Schmalzried.[14] Any two-dimensional section through multi component systems and property diagrams can be calculated easily by available computer software. Notations for the different types of graphical representations are not standardized and similar types of graphical representations are often labeled with different names.[15] The thermodynamic data set development using CALPHAD will be illustrated in the following part with the B-C-N-O-Si system as example.

3. The B-C-N-Si-O System

The system provides some most important ceramic materials such as Si_3N_4, SiC, BN and $B_{4+8}C$. A group of promising high technology materials are formed from organoelemental polymers in the B-C-N-Si system.[16] These materials have in common a high fraction of covalent bonds with good high temperature resistance and high hardness. For further development of these materials the knowledge of the constitution of the quinary B-C-N-O-Si system is essential. The data for the 10 binary and 10 ternary subsystems had to be established to enable extrapolations to each of the 5 quaternary systems. No stable ternary phases are reported in literature. Some analytical system descriptions were available from literature and the SGTE database

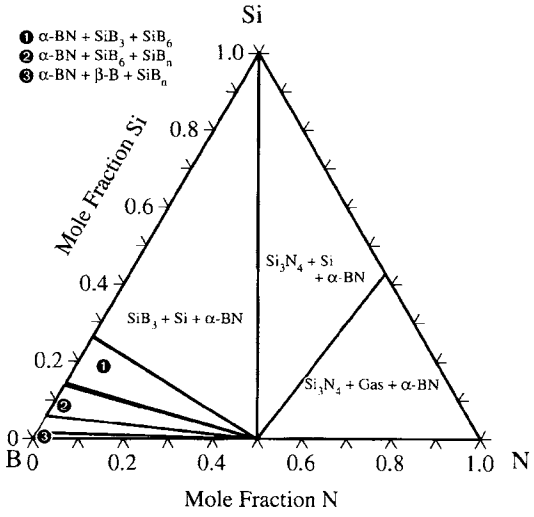

Fig.2 Caluculated isothermal section in the B-N-Si system ($T = 1273$ K, $p_{N2} = 1$ bar).

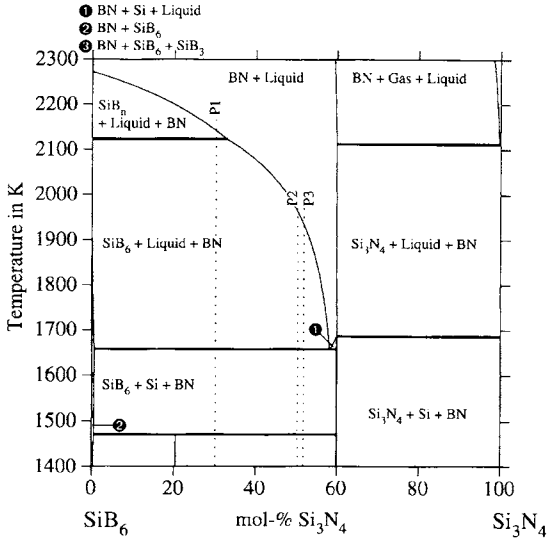

Fig.3 Caluculated SiB_6-Si_3N_4 isopleth with some experimental compositions (P1-P3).

(Scientific Group Thermodata Europe,[17] and others had to be thermo-dynamically optimised. Special care had to be taken to establish a consistent and compatible data set using appropriate reference states. New descriptions were established for the binary systems B-C, B-O, B-Si, C-N.[18] The systems B-N, C-N, C-O and N-O were accepted from the SGTE database.[17] The systems C-Si, N-Si and O-Si were taken from publications provided by Grobner,[19] Dumitrescu and Sundman[20] and Hallstedt,[21] respectively. All input parameters for calculations shown in this publication were taken from references (17-21). These consistent data were combined in order to calculate the higher-component systems. Most of the ternary systems could be calculated by extrapolation. The system B-C-Si was optimised[18] and the data for C-N-Si and C-O-Si systems were accepted from Gröbner.[19] In case of missing literature information the results were controlled by own experiments. There are no experimental data on the B-N-Si system available which could be used for a thermodynamic optimisation. Therefore, the B-N-Si system was calculated combining the optimised binary systems B-N, B-Si and N-Si and using the Muggianu formalism[12] to extrapolate. **Figure 2** shows the calculated isothermals section at 1273 K. **Figure 3** presents the SiB_6-Si_3N_4 isopleth. The caluculated isothermal sections and isopleths of technical relevance were confirmed by subsequent experimental investigations.[18] The samples were prepared by powder mixtures of SiB_6 and Si_3N_4 and were sintered in BN-crucibles under Ar-of N_2-atmosphere ($p = 1$ bar). The produced materials were investigated by X-ray diffraction, chemical analysis and metallographic methods such as light optical microscopy and scanning electron microscopy.

4. Phase Fraction Diagrams in the B-C-N-Si System

Schaible *et al.*[22] carried out investigation on the crystallisation of new materials in the B-C-N-Si system. These ceramic composites were formed from polymers. Schaible *et al.* found a relation between the boron content and the temperature of the beginning of the crystallisation. With increasing boron content, the crystallisation starts at higher temperatures. The B-C-N-Si-O dataset was used to simulate the high temperature stability of these precursor-derived materials. Calculations of the phase equilibria for two compositions were carried out (X1: 5.93 B, 25.93 C, 26.66 N, 41.48 Si and X2: 12.12 B, 27.27 C, 24.24 N, 36.37 Si, in mol%). The results were plotted as phase fraction diagrams (property type diagrams) and are shown in **Figs.4**(a) and (b).[18] From these diagrams the phase reactions can be directly derived, *e.g.* the decomposition of Si_3N_4 at $T = 2113$ K

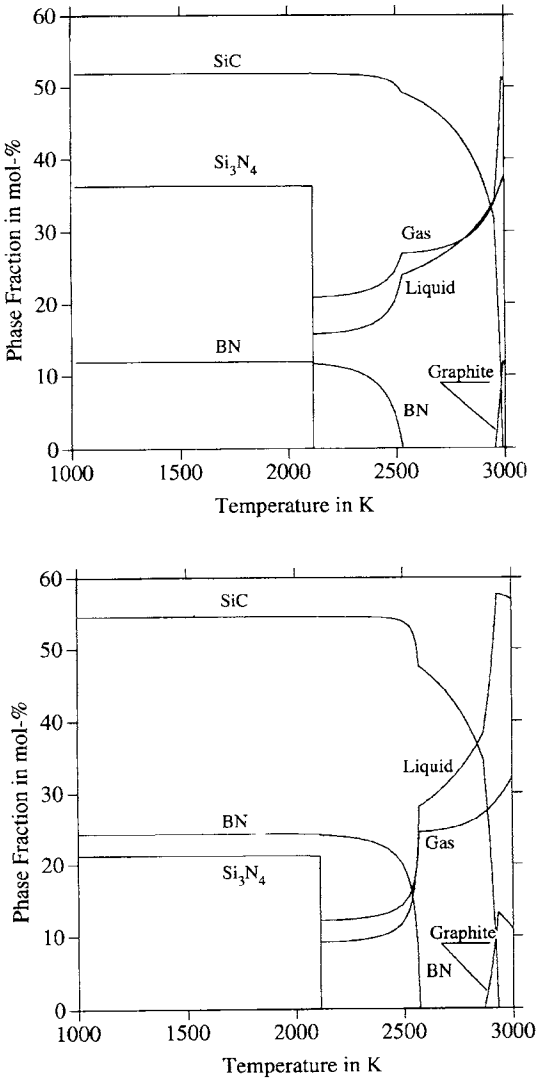

Fig.4 Phase fraction diagram in the B-C-N-Si system for composition (a) X1 and (b) X2.

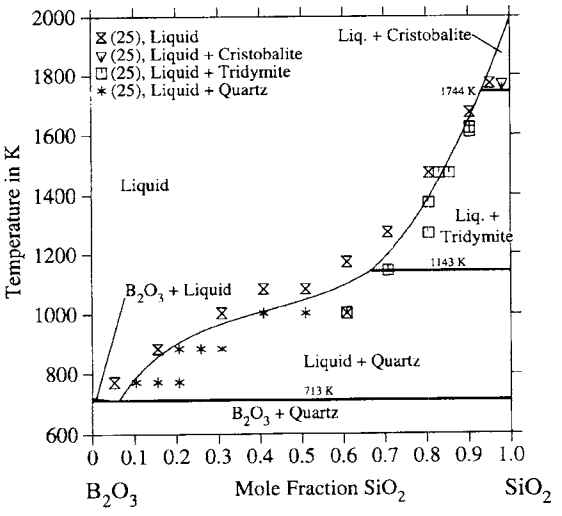

Fig.5 The optimised phase diagram of the B_2O_3-SiO_2 system with experimental data accordimg to Rockett and Foster.[25]

to form a liquid phase (silicon) and gas (N_2). Other reactions at higher temperatures are more complex and include more phases. The equilibrium phases are calculated as function of temperature for the given total composition of the system. The BN fraction is higher in material of composition X2 than in X1. According to Jalowiecki *et al.*[23] the BN content significantly influences the materials crystallisation behavior. Nanocrystalline BN layers occuring between Si_3N_4 and SiC grains were investigated by transmission electron microscopy.[23] Due to the BN layers the diffusion controlled exchange of Si, C and N between Si_3N_4 and SiC grains is lowered and the grain growth will be slower. As the composition X2 has a higher BN content, thicker layers may be considered, resulting in higher crystallisation temperatures.

5. Optimisation of the B_2O_3-SiO_2 System

The oxidation resistance of precursor-derived materials is also very interesting.[24] Therefore, the B-C-N-Si dataset was extended by oxygen and the quasibinary section B_2O_3-SiO_2 in the ternary B-Si-O system was optimised[18] using experimental values of (25) . The analytical description of B_2O_3 was taken from the SGTE-database,[17] the analytical descriptions of the SiO_2-modifications quartz, cristobalite and tridymite were accepted from Hallstedt *et al.*[21] . No mutual solubilities of SiO_2 and B_2O_3 are known and these phases were treated as stoichiometric. The liquid phase was analytically described using the partial ionic liquid model[9] introducing two sublattices, one of them occupied with cations the other with anions and neutral species.

The following species sublattice occupancy was used: $(B^{+3}, Si^{+4})_P(O^{-2}, SiO_4^{-4}, Va^{-Q}, B_2O_3, SiO_2)_Q$, with Va = vacancies. P and Q are the number of sites on the sublattices and are calculated to fulfil the condition of

electroneutrality. The optimised system in comparison with the experimental data is shown in **Fig.5**. The formation of liquid phase was derived from appearance of glass phase in quenched samples.[25]

In order to develop a consistent analytical description of the quinary liquid phase, the Redlich-Kister description used for the B-C-N-Si liquid phase[17-21] was formally transferred to a two-sublattice description.[18] The resulting quinary liquid description is: $(B^{+3}, Sr^{+4})_P(O^{-2}, SiO_4^{-4}, Va^{Q}, C, N, B_2O_3, SiO_2)_Q$.

6. Conclusion

Reliable thermodynamic databases can be developed using the CALPHAD method. Analytical descriptions of all functions of state can be derived from thermodynamic optimisation or the trial and error approach. Suitable model thermodynamic descriptions are required for ceramic solution phases. Based on these data technically relevant systems for the development of ceramic materials and composites can be calculated. Depending on the scientific or technical problem, a large variety of graphical representations of the results is possible such as isothermal sections, isopleths, and phase fraction diagrams (as shown for the B-C-N-Si-O system) and potential phase diagrams.

References

1) K. Hack (ed.) The SGTE Casebook, The Institute of Materials, London, UK (1996).
2) L. Kaufman and H. Bernstein, *Computer Calculation of Phase Diagrams*, Acad. Press, New York (1970).
3) H. L. Lukas, E.-T. Henig and B. Zimmermam, *CALPHAD* **1**, 225-236 (1977).
4) H. L. Lukas and S. G. Fries, *J. Phase Equilibria* **13**, 532-541 (1992).
5) C. Wagner and W. Schottky, *Z. Phys. Chem.* **11**, 163-210 (1930).
6) J.-O. Andersson, A. Fernandez Guillermet, M. Hillert, B. Jansson and B. Sundan, *Acta Metall.* **34**, 437-445 (1986).
7) B. Sundman and F. Aldinger, *CALPHAD* **19**, 433-571 (1995).
8) O. Redlich and A. T. Kister, *Indust. and Eng. Chem.* **40**, 345-348 (1948).
9) M. Hillert, B. Jansson, B. Sundman and J. Ågren, *Met. Trans. A* **16A**, 261-266 (1985).
10) F. Sommer, *Z. Metallikd.* **73**, 72-76 and 77-86 (1982).
11) A. D. Pelton and M. Blander, *Metall. Trans.* **17B**, 805-815 (1986).
12) Y.-M. Muggianu, M. Gambino and J. P. Bros, *J. Chiem. Phys.* **72**, 83-88 (1975).
13) F. Kohler, *Monatsh. Chemie.* **91**, 738-740 (1960).
14) A. D. Pelton and H. Schmalzried, *Met. Trans.* **4**, 1395-1404 (1973).
15) H. J. Seifert, H. L. Lukas and G. Petzow, in: Design Fundamentals og High Temperature Composites, Intermetallics and Metal-Ceramic Systems (R. Y. Lin, Y. A. Chang, R. G. Reddy and C. T. Liu, eds.) pp.297-308, The Minerals, Metals and Materials Society, Warrendale, PA (1996).
16) J. Bill and F. Aldinger, *Adv. Mater.* **7**, 775-787 (1995).
17) SGTE Substance Database, Version 1992, Domaine Universitare, B.P.66, 1992 F-38402 St. Matin d'Heres, Cedex, France.
18) B. Kasper, *Phasengleichgewichte im System B-C-N-Si*, Dissertation, Max-Plank-Institut für Metallforschung and Universität Stuttgart (1996).
19) J. Gröbner, *PKonstitutionsberechnungen im System Y-Al-Si-C-O*, Dissertation, Max-Plank-Institut für Metallforschung and Universität Stuttgart (1994).
20) L. Dumitrescu and B. Sundman, *J. Europ.Ceram. Soc.* **15**, 239-247 (1995).
21) B. Hallstedt, *CALPHAD* **16**, 53-61 (1992).
22) S. Schaible, R. Riedel, U. Klingbiel, J. Bill and F. Aldinger, Proc. Annual Meeting Deutsche Gesellschaft für Materialkunde (DGM), 24.-27.05. 1994, Göttingen 327 (1994).
23) A. Jalowiecki, J. Bill, M. Frieß, J.Mayer, F. Aldinger and R. Riedel, *Nanostruct. Mat.* **6**, 279-282 (1995).
24) D. Heimamm, *Oxidationsschutzschichten für kohlefaser verstarkte Verbundwerkstoffe durch Polymer-Pyrolyse*, Dissertation, Max-Plank-Institut für Metallforschung and Universität Stuttgart (1996).
25) T. J. Rockett and W. R. Foster, *J. Am. Ceram. Soc.* **48**, 75-80 (1965).