PRECURSOR DERIVED Si-B-C-N CERAMICS - PROCESS AND PHASE STUDIES

Hans Jürgen Seifert and Fritz Aldinger

Max-Planck-Institut für Metallforschung
and
Institut für Nichtmetallische Anorganische Materialien
Pulvermetallurgisches Laboratorium, Heisenbergstrasse 5, D-70569 Stuttgart, Germany

ABSTRACT

Precursor-derived Si-B-C-N ceramics are produced by thermolysis of specific element-organic polymers. The structure of the resulting amorphous ceramics is characterised by strong covalent bonds and closely related to the structural units of the polymers. To simulate the phase reactions during the materials crystallisation and thermal degradation CALPHAD-type calculations were carried out. Various types of phase diagrams and phase fraction diagrams were calculated and used to explain the high-temperature behaviour.

1. INTRODUCTION

Ceramics on the basis of elements such as silicon, boron, carbon and nitrogen are of special interest due to the strong covalent bonding in their structure. A special feature of such structures is their low atomic mobility, providing an outstanding microstructure stability even at very high temperatures. These materials are conventionally prepared by powder technology with sintering additives for densification. In most cases these additives form oxidic-type secondary phases with increased atomic mobility which substantially degrade the thermal, chemical and mechanical high temperature stability.

In order to make use of the real high temperature properties of covalent ceramics alternative synthesis routes are of interest. In this context the process of thermolysis of element-organic polymers has attracted great interest in recent years because it is both scientifically and technically unique. Scientifically, because the atomic structure and microstructure of materials produced by this process can be designed to some extent by the molecular composition of the starting materials and technically, because novel materials with attractive properties can be processed in a comparatively uncomplicated manner at relatively low temperatures.

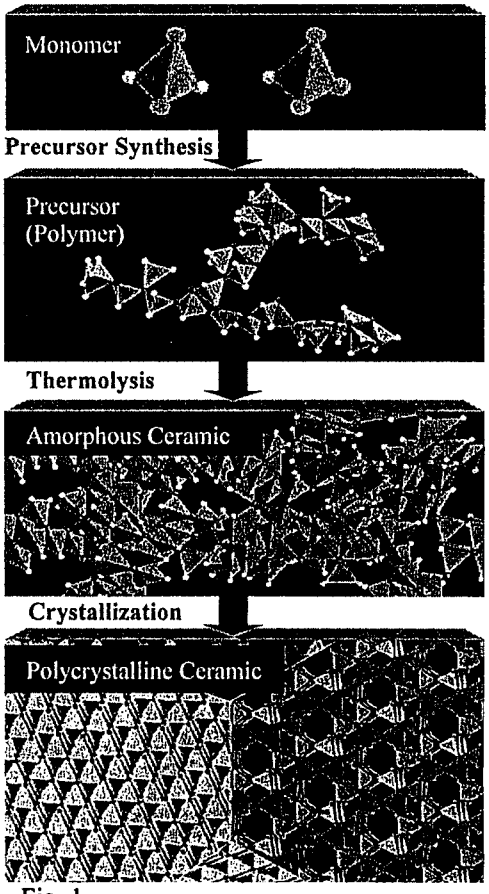


Fig. 1
Process of precursor-derived Si-B-C-N ceramics.

2. THERMOLYSIS OF PRECERAMIC POLYMERS

The process of the production of ceramic materials from element-organic polymers was first proposed by Chantrell and Popper [1], followed by others [2-5] and reviewed recently [6-10]. The process is described schematically in Fig. 1. The innovative idea of this procedure is that the atomic structure of the inorganic materials is closely related to the structural units of the starting polymers (Fig. 2). In the first step, by means of standard or ingenious new methods, polymer precursors with tailored molecular structure, varying compositions and homogeneous elemental distributions on atomic scale are produced which are transformed in a second step by thermolysis, a well-defined heat treatment into purely inorganic materials.

After thermolysis these materials are normally amorphous and atomically homogeneous. Such materials were found to have a near range-ordered atomic structure originating from the polymer structure and being similar to those in silica glass [11-14]. Therefore, on one hand they can be considered as covalent glasses representing a novel type of materials with very attractive high temperature properties. On the other hand, since they are metastable, they represent an ideal starting material to be crystallised during further heat treatments at elevated temperatures into phases thermodynamically stable at a given chemical composition. Well-defined microstructures with even nanocrystalline features can be developed by controlling nucleation and grain growth by this transfomation. In view of this the phase equilibria of the quaternary system Si-B-C-N are of great interest.

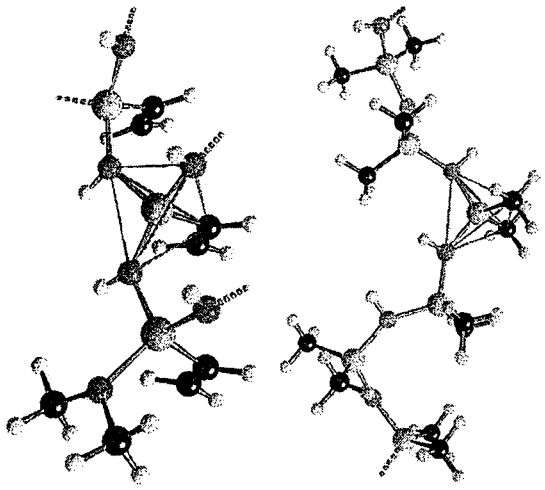


Fig. 2
Structural units of precursor polymers.

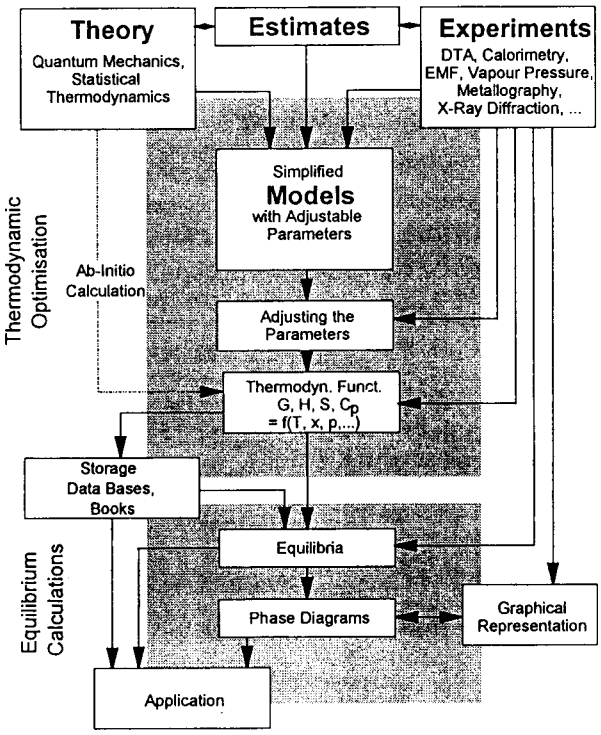


Fig. 3
Scheme of the CALPHAD method [15].

3. THE SYSTEM Si-B-C-N

Phase equilibria and phase reactions can be simulated by thermodynamic calculations. The high temperature behaviour of crystalline materials can be explained by this method.

3.1 Computational phase studies

To facilitate calculation of phase equilibria, phase reactions and thermodynamic functions of multicomponent systems under physico-chemical conditions not previously subjected to experimental investigation the CALPHAD method (CALculation of PHAse Diagrams) is used. A scheme of the method is shown in Fig. 3 [15]. Receiving reliable results from extrapolating calculations requires self-consistent high quality analytical descriptions of all thermodynamic functions of state.

Therefore, analytical formulae have to be provided describing the Gibbs energies for all stable phases and gas species of the particular system. In the course of the so-called ``thermodynamic optimisation'' model parameters are adjusted to various types of experimental data (phase diagram and thermodynamics), using the least squares method after Gauss. In case of incomplete experimental data, estimates and ab initio data can be taken into account. The thermodynamic data are stored in a computer database and binary and ternary system descriptions can then be combined to extrapolate to multicomponent phase diagrams. Well–established CALPHAD software packages are available and used in this work such as BINGSS/BINFKT [16], THERMO-CALC/PARROT [17,18] and CHEM-SAGE [19]. For the success of the CALPHAD method when applied to a practical problem it is crucial that the most appropriate diagrams for the particular case being considered be calculated, e.g. reaction schemes, isothermal sections, isopleths and phase fraction diagrams, respectively.

3.2 Phase modelling and development of a consistent set of thermodynamic data

Analytical descriptions for all unary and binary phases of the Si-B-C-N system were developed. The homogeneity ranges of these phases were taken fully into account. The ternary phase SiC_2N_4 [20] is not stable under conditions treated here (p = 1 bar, T>1000 °C). The unary phase data for the pure elements Si, B, C and N and the descriptions for the gaseous species were taken from the SGTE substance database (Scientific Group Thermodata Europe) [21].

Datasets for the binary systems Si-B, Si-C, B-C and B-N were thermodynamically optimised in the scope of our work on the quaternary system [22-24]. Descriptions for the binary systems C-N and Si-N were used from literature [21,25]. The liquid phases and the solid phases β-boron, graphite, β-Si_3N_4, α-/β-SiC, α-BN, $B_{4+\delta}C$, B_3Si, B_6Si and B_nSi were taken into account. The only solid phase with significant homogeneity range within Si-B-C-N is $B_{4+\delta}C$ which was modelled in close orientation to the crystal structure with the compound energy formalism [26] using the sublattices $(B_{11}C,B_{12})(CBC,CBB,BVaB)$. The boron-rich part of the B-C phase diagram with experimental data (symbols) in comparison with calculation (solid lines) is shown in Fig. 4. Experimental data at temperatures higher than 2300 K deviate

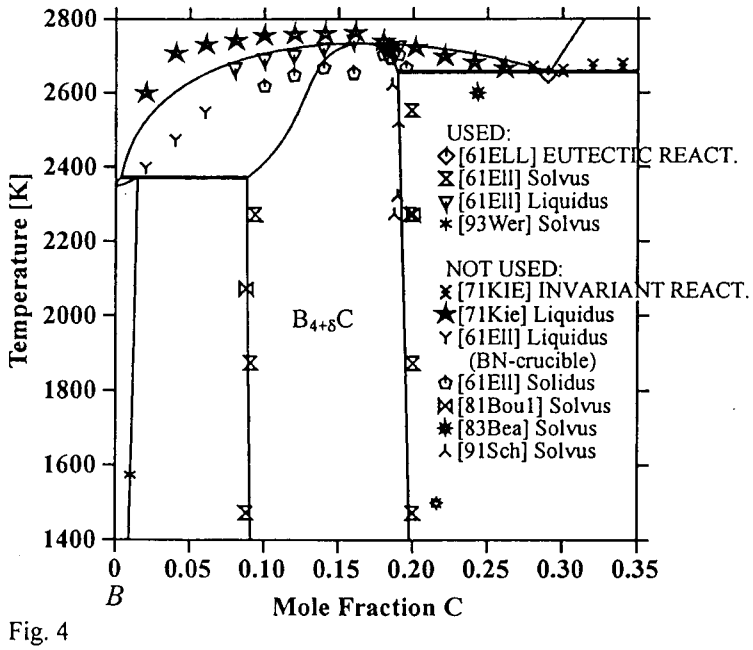


Fig. 4
Boron-rich part of the B-C system [24].

significantly from each other and only data not influenced by systematic errors were used for the thermodynamic optimisation.
The ternary system Si-B-C was thermodynamically optimised in the scope of this work [22,24]. The other three ternary systems (Si-B-N, Si-C-N, B-C-N) could be calculated comprehensively by thermodynamic extrapolation. The comparison with experimental data

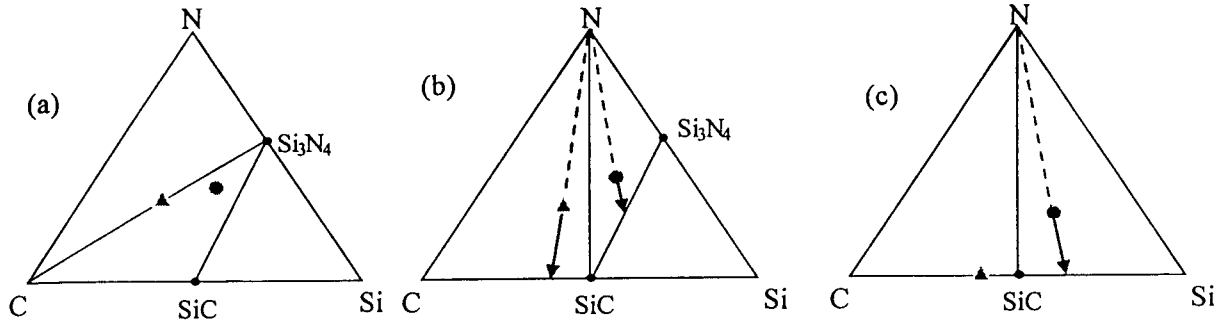


Fig. 5
Isothermal sections in the Si-C-N system (arrows indicate reaction paths).
(a) T<1484 °C (b) 1484 °C <T < 1841 °C (c) T>1841 °C

shows that adjustment of ternary parameters is not necessary. Of special interest for the precursor-derived ceramics and the understanding of the phase reactions and thermal

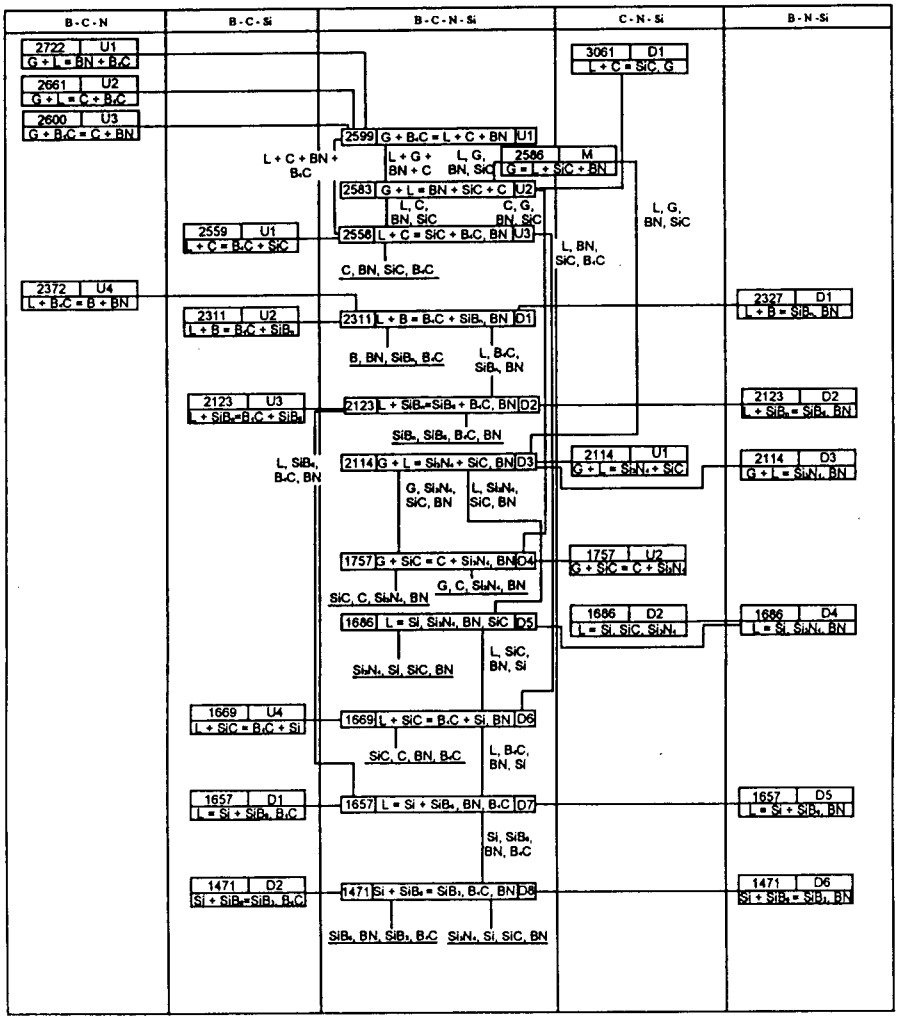


Fig. 6
The Scheil reaction scheme of the Si-B-C-N system.

degradation is the System Si-C-N. Two important invariant reactions accomponied by nitrogen loss (i.e. precursor ceramic sample mass loss) appear, $Si_3N_4 + 3C = 3SiC + 2N_2$ (1) at a temperature of 1484 °C and $Si_3N_4 = 3Si + N_2$ (2) at 1841 °C. Figs. 5 a-c show isothermal sections at temperatures lower, in between and higher than these reaction temperatures with typical compositions of ceramics derived from VT50 and NCP200 respectively and their reaction paths during thermal degradation, i. e. N_2 degassing at temperatures greater than 1484 °C. A quantitative explanation of the thermal degradation could be based on the calculated phase fraction diagrams [27]. The ternary subsystems were combined in a computer database and extrapolating calculations into the quaternary system were carried out.

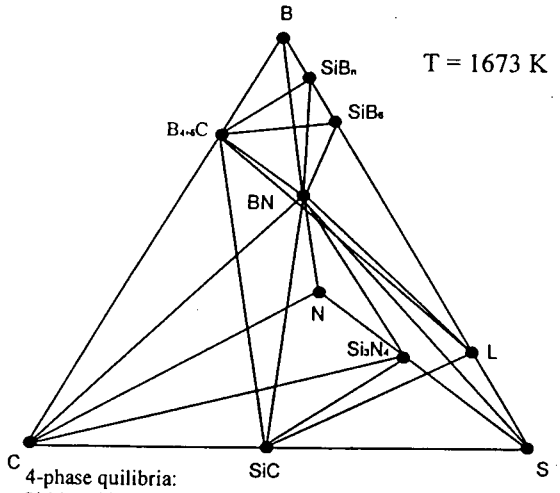
3.3 Scheil reaction scheme

The nonvariant reactions occuring in the quaternary system could be derived from these calculations and the Scheil reaction scheme was constructed (Fig. 6). It shows the connection of univariant and nonvariant reactions and the high potential to develop a large variety of multiphase composites.

The reactions (1) and (2), introduced for the ternary Si-C-N system, appear in the quaternary Si-B-C-N system as well. Note that BN does not influence these degenerated reactions.

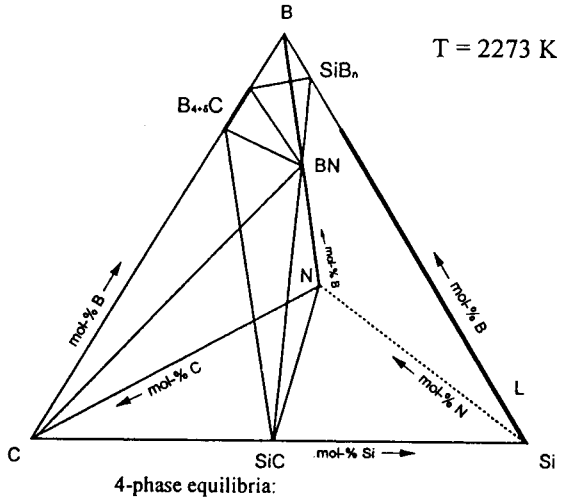
3.4 Isothermal sections

Information on phase equilibria at constant temperatures were calculated from quaternary



4-phase quilibria:

$Si_3N_4 + SiC + Si + BN$
$C + SiC + Si_3N_4 + BN$
$C + Si_3N_4 + Gas + BN$
$B_4C + SiC + BN + C$
$B_4C + L + BN + SiC$
$B_4C + L + BN + SiB_6$
$B_4C + BN + SiB_6 + SiB_n$
$B_4C + B + SiB_n + BN$
$L + Si + BN + SiC$



4-phase equilibria:

C, BN, SiC, B_4C (L, BN, SiC, B_4C)
B, BN, SiB_n, B_4C (G, L, SiC, BN)
C, G, BN, SiC (L, B_4C, SiB_n, BN)

Fig. 7
Isothermal sections in the Si-B-C-N system.
(a) T=1400 °C
(b) T=2000 °C For reasons of clarity liquid containing equilibria are not indicated.

isothermal sections. The isothermal sections at 1400 °C and 2000 °C respectively, are shown in Figs. 7a and b. In both cases the regular concentration tetrahedron is separated by different irregular tetrahedra indicating the 4-phase equilibria at the specific temperature. Concentration sections through the 1400 °C and 2000 °C tetrahedra (Fig. 7) respectively, at a constant boron content were calculated and are shown in Figs. 8a and b. The compositions of some high temperature stable precursor derived Si-B-C-N ceramics are indicated. They are located in the

phase field Si_3N_4+SiC+BN+C. This phase field is formed by reaction D4 (Fig. 6) at 1484 °C (1757 K) and remains stable as low as room temperature.

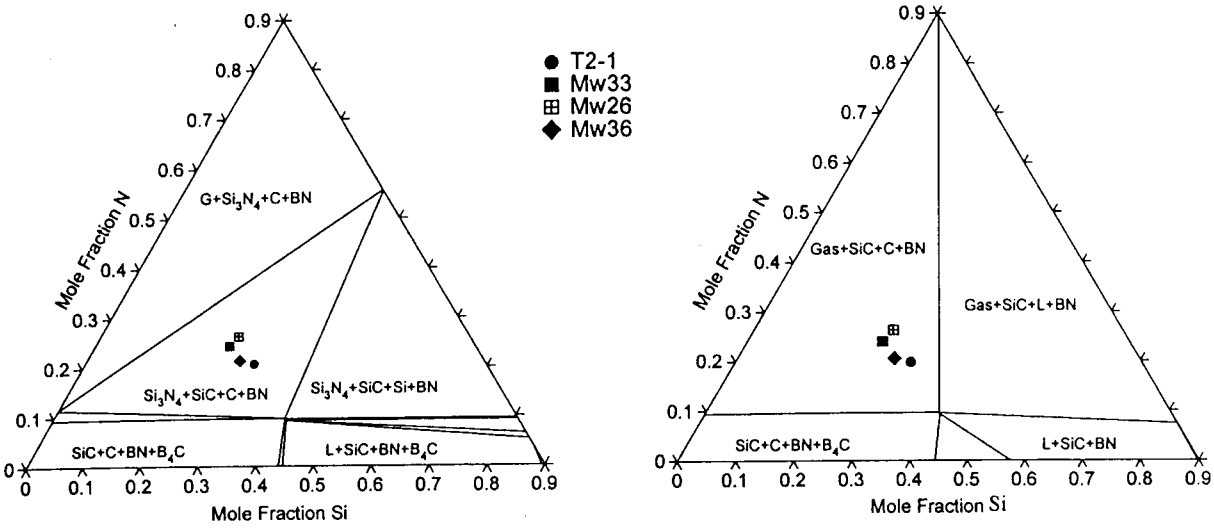


Fig. 8
Concentration sections in the Si-B-C-N system at constant boron content (9.7 at.%) and temperatures. Compositions of some high-temperature stable precursor-ceramics are indicated.
(a) 1400 °C (b) 2000 °C

3.5 Phase fraction diagrams

Quantitative information on the phase reactions in the Si-B-C-N system are obtained from phase fraction diagrams for compositions corresponding to those of the precursor-derived Si-C-N and Si-B-C-N ceramics. Figs. 9a and b show the results for ceramics derived from VT50- and NCP200-precursors respectively. The VT50 ceramic shows a one-step decomposition according to equation (1). The NCP200 ceramic decomposes in two steps according to equations (1) and (2). Both reactions are accomponied by nitrogen losses, i.e. sample mass loss. Figs. 9c and d show the phase fraction diagrams for the high-temperature stable precursor ceramics T2(1) and MW33. In both cases the reaction (1) appears. BN does not take part in this reaction.

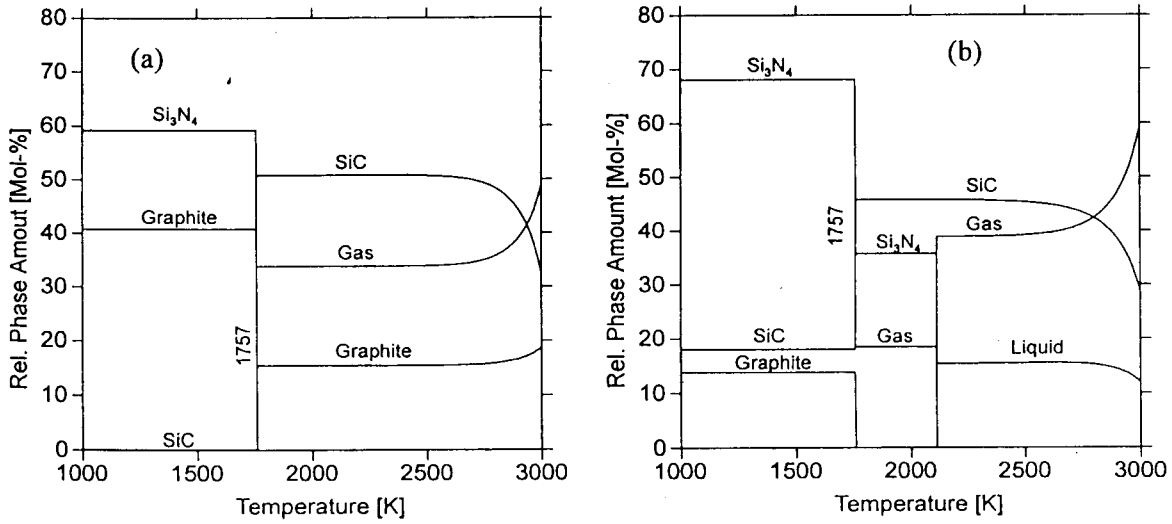


Fig. 9
Phase fraction diagrams for selected precursor derived ceramics.
(a) Si-C-N ceramics derived from VT50 precursor.
(b) Si-C-N ceramics derived from NCP200 precursor.

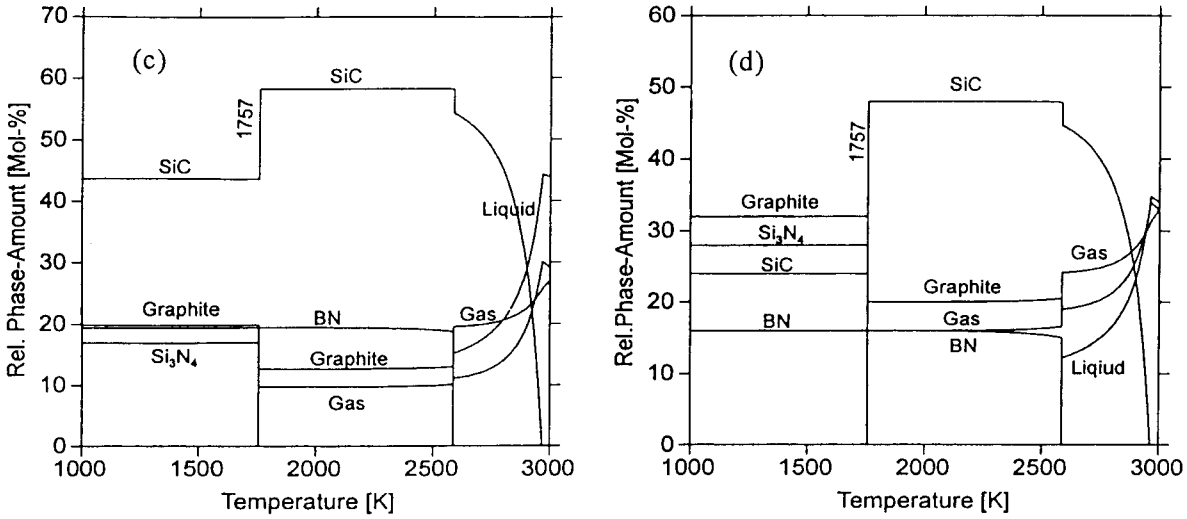


Fig. 9 (cont.)
(c) Si-B-C-N ceramics derived from T2(1) precursor.
(d) Si-B-C-N ceramics derived from MW33 precursor.

4. CONCLUSIONS

At room temperature the quaternary system Si-B-C-N is solid except in the composition range of the four-phase equilibrium G+C+SiC+Si_3N_4. Due to the reaction of free carbon with Si_3N_4 forming N_2 above 1484 °C (at 1 bar N_2) the gas phase extends to compositions of the two three-phase equilibria C+BN+SiC (stable up to 2310 °C) and BN+SiC+Si_3N_4 (stable up to 1841 °C, where Si_3N_4 starts to decompose at 1 bar N_2). Therefore, the four-phase equilibrium C+BN+SiC+Si_3N_4 most interesting for precursor-derived high temperature materials is thermodynamically stable only up to 1484 °C. In spite of this situation materials with compositions within this four-phase equilibrium and located close to the three-phase equilibrium field C+BN+SiC have shown to be thermally stable up to 2000 °C under certain conditions [7]. This surprising thermal stability was attributed to kinetic reasons, i.e. a low atomic mobility with the covalent bonded phases in combination with special morphological features of the microstructure of such materials [28,29]. Of further interest for high temperature applications might be materials with compositions of the four-phase equilibrium C+BN+SiC+B_4C which is thermally stable up to 2285 °C (2558 K, Fig. 6, U3).

ACKNOWLEDGEMENT

We thank the Deutsche Forschungsgemeinschaft and the Japan Science and Technology Corporation (JST) for financial support.

REFERENCES

1) P. G. Chantrell and E. P. Popper, "Special Ceramics", Academic Press, New York, 87-103 (1964).
2) W. Verbeek, German Patent 2 218 960, (1973).
3) S.Yajima, J. Hayashi and M. Omori, Chem. Lett., 931-934 (1975).
4) D. Seyferth and G. H. Wiseman, "Polym. Prepr.", Am. Chem. Soc. Div. Polym. Chem., **25** 10-12 (1984).
5) M. Peuckert, T. Vaahs and M. Brück, Adv. Mater., **2** 398-404 (1990).
6) M. Birot, J.-P. Pillot, J. Dunogués, Chem. Rev., **95** 1443 (1995).
7) J. Bill and F. Aldinger, Adv. Mater., **7** 775-787 (1995).
8) H.-P. Baldus and M. Jansen, Angew. Chem., **109** 338-354 (1997).

9) R. M. Laine and A. Sellinger, "Si-Containing Ceramic Precursors", in The Chemistry of Organic Silicon Compounds,Vol. 2, Z. Rappoport and Y. Apeloig, eds., J. Wiley & Sons Ltd. London, 2245-310 (1998).
10) F. Aldinger, M. Weinmann and J. Bill, Pure Appl. Chem., **70** 439-448 (1998).
11) J. Dürr, P. Lamparter, J. Bill, S. Steeb, F. Aldinger, Journal of Non-Crystalline Solids, **155** 232-234 (1998).
12) S. Schempp, J. Dürr, P. Lamparter, J. Bill, F. Aldinger, Z. Naturforsch., **53a** 127 (1998).
13) J. Bill, J. Seitz, G. Thurn, J. Dürr, J. Canel, B. Janos, A. Jalowiecki, D. Sauter, S. Schempp, H.-P. Lamparter, J. Mayer and F. Aldinger, Phys. Stat. Sol. (a) , **166** 269 (1998).
14) A. Jalowiecki, J. Bill, M. Frieß, J. Mayer, F. Aldinger and R. Riedel, Nanostr. Mat., **6** 279-282 (1994).
15) H. J. Seifert, F. Aldinger, Z. Metallkd., **87** 841-853 (1996).
16) H. L. Lukas, S.G. Fries, J. Phase Equilibria, **13** 532-54 (1992).
17) B. Sundman, B. Jansson, J.-O. Anderson, CALPHAD, **9** 153-190 (1985).
18) B. Jansson, "Evaluation of Parameters in Thermochemical Models Using Different Types of Experimental Data Simultaneously." Trita-Mac **234**, Royal Institute of Technology, Stockholm, Sweden (1984).
19) G. Eriksson, K. Hack, Met. Trans., B **21B** 1013-1024 (1990).
20) R. Riedel, A. Greiner, G. Miehe, W. Dreßler, H. Fueß, j. Bill, F. Aldinger, Angew. Chem., **109** 657-660; Angew. Chem. Int. Ed. Engl. **36** 603-606 (1997).
21) SGTE Substance Database, Version 1992, Domaine Universitaire, B.P. 66, 1992, F-38402 St. Martin d'Hères Cedex, France.
22) S.-K. Lim, H. L. Lukas, "Thermodynamische Optimierung des Systems B-C-Si und seiner Randsysteme", in: G. Petzow, J. Tobolski, R. Telle (eds.) Deutsche Forschungsgemeinschaft, Hochleistungskeramiken - Herstellung, Aufbau, Eigenschaften, Verlag Chemie, Weinheim, 606-616 (1996).
23) J. Gröbner, H. L. Lukas, F. Aldinger, Calphad, **20** 247-254 (1996).
24) B. Kasper, H. J. Seifert, A. Kußmaul, H.L. Lukas, F. Aldinger, "Entwicklung eines thermodynamischen Datensatzes für das System B-C-N-Si-O" in Werkstoffwoche '96, 28.-31.05.1996, Stuttgart, Tagungsband, 623-628 (1996).
25) M. Hillert, S. Jonsson, B. Sundman, Z. Metallkd., **83** 648-652 (1992).
26) J.-O. Andersson, A. Fernandez Guillermet, M. Hillert, B. Jansson, B. Sundman, Acta Metall., **34** 437-445 (1986).
27) J. Peng, H. J. Seifert, F. Aldinger, "Thermal Analysis of Si-C-N Ceramics derived from Polysilazanes", subm. to Proc. Euromat '99, 27.-30.09.1999, München, Germany.
28) H. J Seifert, H. L. Lukas, F. Aldinger, Ber. Bunsenges. Phys. Chem., **9** 1309-1313 (1998).
29) H. J. Seifert, F. Aldinger, "Thermodynamic Calculations in the System Si-B-C-N-O", in: J. Bill, F. Wakai, F. Aldinger, (eds.), Precursor-Derived Ceramics, Wiley-VCH, Weinheim, New York, 165-174 (1999).