0272-8842(95)00097-6

Ceramics International 22 (1996) 233–239

0272-8842/96/$15.00

Chemical Formation of Ceramics

Ralf Riedel & Wolfgang Dressler

Technische Hochschule Darmstadt, Fachbereich Materialwissenschaft, Fachgebiet Disperse Feststoffe,
Hilpertstr. 31/D, D-64295, Darmstadt, Germany

(Received 5 July 1995; accepted 3 August 1995)

Abstract: Technical non-oxide ceramic materials are fabricated according to conventional powder processing methods, which involves heat-treatment at temperatures up to 1700–2100°C and addition of metal oxides for the purpose of enhanced densification. Since the investigations of Verbeek *et al.* and Yajima *et al.* in the mid-1970s, a new method has been available to produce advanced ceramics at significantly lower temperatures (800–1500°C) by the polymer pyrolysis of appropriate organometallic precursors. The work presented in this paper focuses on the synthesis and characterization of advanced ceramic fibres, bulk materials and powders based on the binary, ternary and quaternary systems Si–N, Si–C–N and Si–*E*–C–N. Herein *E* refers to B, Al, Ti, P or Zr. In particular, the cross-linking and pyrolysis behaviour of polysilazanes, polysilanes and polysilylcarbodiimides has been analysed by chemical analysis, FTIR, TGA, XRD, analytical TEM and mass spectrometry. Additionally, the crystallization behaviour of the pyrolysed amorphous intermediates into multiphase ceramic materials has been characterized. Since the partitioning of boron containing ternary and quaternary systems has been shifted to extraordinarily high temperatures (1700°C), a novel class of metastable, amorphous high-temperature materials could be generated, which is not available using conventional techniques. The study of the oxidation behaviour of dense polysilazane derived Si–C–N bulk materials revealed corrosion resistance in pure oxygen up to 1600°C.

1 INTRODUCTION

For thousands of years[1] ceramics derived from clay have been well known as materials for products of daily use, e.g. plates, pitchers and vases. During the last decades the development of *advanced ceramics* resulted in numerous technical applications, such as turbocharger rotors, glow plugs, cutting tools, substrates for electronic devices, sensors and bioceramics. The most presently applied technical ceramics are carbides, nitrides and oxides of elements of the third and fourth main groups (B, Al, Si), as well as of the transition metals Ti, Zr, Mo and W. Owing to the different chemical and physical properties of the constituents, the ceramic materials derived exhibit partially metallic, ionic or covalent bonding. Thus, outstanding chemical and physical material properties can be adjusted.

On the contrary, the brittleness and, thus, the low reliability of structural ceramics as well as the insufficient reproducability of the excellent properties of functional ceramics prevent technical application in many cases. In recent years, these serious handicaps could be obviously reduced by microstructural design and by pronounced improvements in the course of single manufacturing steps. In particular, tailor-made Si_3N_4 ceramics with optimized mechanical properties have been developed, which has led to the use of silicon nitride in engine components.[2]

The synthesis of new ceramic materials and the development of novel fabrication techniques are expected to be key factors for further optimization of properties, especially at high temperatures. Besides the conventional powder processing route, the chemical formation of high-purity advanced ceramics has been utilized by chemical vapour deposition (CVD), sol–gel technology and polymer pyrolysis. In the case of CVD, high-volatile compounds are decomposed in the gas phase and precipitated as oxide or non-oxide ceramics, as well as metals or semi-conductors, depending on the starting material. In contrast, the sol–gel and the polymer pyrolysis process employs non-volatile inorganic–organic polymers to generate both oxide and non-oxide ceramics, preferentially via the liquid or solid state.

This paper is concerned with the synthesis of Si-based ceramics by the polymer pyrolysis process, as well as with the resulting material properties. In particular, novel amorphous materials and micro/nano-sized composites in the systems Si–N, Si–C–N, and Si–*E*–C–N (*E* = B, Al, Ti, P) are presented. Their processing into fibres, powders and bulk materials is explained briefly. Additionally, the crystallization behaviour, microstructural development and oxidation resistance of polymer-derived ceramics is discussed.

2 SYNTHESIS OF CERAMICS BY POLYMER PYROLYSIS

Since the work of Verbeek and Winter[3] in Germany, as well as of Yajima *et al.*[4] in Japan, both published in the 1970s, the polymer pyrolysis of appropriate organosilicon preceramic polymers has been known as a practicable method to produce Si-based non-oxide ceramics at noticeably low temperatures (800–1500°C). This chemical route of ceramic fabrication is composed of:

- The synthesis of oligomers or polymers from low molecular compounds (precursors), which consist of structural elements as desired in the final product.
- Chemical or thermal cross-linking of the as-synthesized precursors in order to obtain high molecular compounds convertible into ceramics with high yields.
- Pyrolysis of the cross-linked polymer providing the desired ceramic material, accompanied by the formation of gaseous reaction products.

The main advantages of this production route are the easy purification of starting materials and thus the extraordinarily effective reduction of impurities in the final product, the adjustment of the viscosity of the polymers in a wide range and the generation of novel, metastable, amorphous materials that cannot be produced by conventional methods, as well as the low fabrication temperatures. This enables not only the manufacture of extremly creep- and oxidation-resistant ceramic materials for high-temperature applications, but also the processing of the polymers by well-established industrial methods such as coating of substrates and spinning of fibres.

2.1 History

The development of the polymer pyrolysis process for the synthesis of advanced ceramic materials can be originally attributed to the chemistry of molecular non-oxide organosilicon polymers. In 1921, Kipping[5] first synthesized polydiphenylsilanes by the Wurtz–Fittig analogous reaction of dichlorodiphenylsilane with molten sodium in an inert solvent, xylene:

$$\mathrm{n\,ph_2SiCl_2 \xrightarrow{Na} [ph_2Si]_n + 2n\,NaCl} \qquad (1)$$

Polydimethylsilanes, synthesized by a similar dechlorination reaction in benzene, were reported in 1949 by Burkhardt:[6]

$$\mathrm{n(CH_3)_2SiCl_2 \xrightarrow{Na} [(CH_3)_2Si]_n + 2nNaCl} \qquad (2)$$

Unfortunately, the received organosilicon polymers could be characterized only in terms of the chemical composition. The determination of the molecular weight distribution and the molecular structure was difficult or even impossible at that time and remains a basic problem in the characterization of organoelement polymers.* Additionally, no subsequent transformation of the synthesized compounds into ceramic materials has been performed. Therefore, the field of polysilane synthesis was not further pursued until Yajima *et al.*[7] reported on the thermal conversion of polysilanes into SiC-based ceramics in 1975. Since then, a broad variety of new organosilicon polymers in particular and organoelement polymers in general have been developed as precursors for the synthesis not only of Si-based but also of Al-, B- or Ti-based non-oxide ceramics. A review of relevant precursors and their pyrolytic products are given in Table 1. The Si-based inorganic polymers can be subdivided into five groups: (1) silicones (polysiloxanes), (2) polysilsesquioxanes,

Table 1. Preceramic molecular compounds for the synthesis of non-oxide ceramics.

Ceramic Product	Organoelement Polymer
AlN	$[RAlNH]_n$ and $[Cl_2Al-N(H)Si(CH_3)_3]_n$
BN	$[HNBCl]_3 + ((CH_3)_3Si)_2NH$
BC_4N	$C_5H_5N \cdot BH_3$
BC_2N	$HNC_4H_8NH \cdot BH_3$
B_4C/BN	$[B_{10}H_{12} \cdot H_2N-CH_2-CH_2-NH_2]_2$
SiC	$H-[CH_3SiH]_n-H$
SiC/C-composite	$[CH_3SiH]-CH_2]_n$ and $[((CH_3)_2Si)_x(CH_3SiC_6H_5)_y]_n$
$Si_xC_yN_z$	$[CH_3SiHNH]_m \cdot [CH_3SiN]_n$
$Si_xC_yO_z$	$[(CH_3)_2SiO]_m \cdot [CH_3SiO_{1.5}]_n$
TiN	$[(C_4H_9N)_2Ti]_n$
ZrB_2	$Zr[BH_4]_4$

---

*Organoelement polymers are compounds containing direct, polar $E^{\delta+}-C^{\delta+}$ bonds between the involved heteroatoms (metal, semi-metal or non-metal) and carbon.

(3) polysilanes, (4) polycarbosilanes and (5) polysilazanes:

1) $[-R^1R^2Si-O-]_n$ 2) $[RSiO_{1.5}]_n$ 3) $[-R^1R^2Si-]_n$
4) $[-R^1R^2Si-CH_2-]_n$ 5) $[-R^1R^2Si-NH-]_n$

where R, R^1, $R^2 = H$, CH_3, C_6H_5 (phenyl) or $CH{=}CH_2$ (vinyl).

Apart from the commercial fabrication of ceramic fibers according to a method suggested by Yajima,[4] organoelement polymer-derived advanced ceramics are promising candidates for the following potential applications:

- synthesis of multicomponent ceramic powders and bulk materials,
- formation of ceramic protective coatings against corrosion, abrasion, etc., by dip- or spin-on coating of the polymer followed by pyrolysis of the polymer film,
- formation of ceramic matrices in porous structures such as fiber prepregs by polymer infiltration, and subsequent pyrolysis of the infiltrated part,
- ceramic binder,
- formation of porous materials such as ceramic filtration membranes.

2.2 Ceramics in the ternary system Si–C–N

2.2.1 Polysilazane-derived materials

SiC, Si_3N_4 and SiC/Si_3N_4-composites are the most promising ceramic materials for future applications in gas turbines and automotive or engine devices. The best method to generate Si–C–(N) ceramics by the polymer pyrolysis process is the thermal decomposition of organo-substituted polysilazanes. Contrary to the expensive dechlorination reaction of chlorodiorganosilanes with Na or K used to synthesize the polysilanes, the polysilazanes are much more easily accessible in high amounts by the simple ammonolysis of R_2SiCl_2 and subsequent base-catalysed cross-linking of the received oligosilazane, according to the method described by Seyferth:[8]

$$n\,CH_3SiHCl_2 + 3n\,NH_3 \xrightarrow[-2n\,NH_4Cl]{} [CH_3SiH-NH]_n \quad /n = 3 \text{ or } 4 \qquad (3)$$

$$n\,[CH_3SiH-NH]_4 \xrightarrow{KH/-mH_2} \underset{\mathbf{1}}{[CH_3SiH-NH]_{4n-m}[CH_3SiN]_m} \qquad (4)$$

The molecular composition of the synthesized polysilazanes can be varied either by the substitution of the methyl groups by alkyl, aryl or vinyl groups or by the coammonolysis of, for example, CH_3SiHCl_2 and $(CH_3)_2SiCl_2$. The coammonolysis is already used for the synthesis of commercially availabe polysilazanes.* Low-carbon and carbon-free polysilazanes are obtained by the reaction of $[(CH_3)_3Si]_2NH$ with $HSiCl_3$ and by the ammonolysis of $SiH_2Cl_2 \cdot 2$ pyridine, respectively, and are also produced commercially.[10,11]

The final step in manufacturing of ceramics by the thermal decomposition of organoelement polymers is the pyrolysis of the cross-linked polysilazanes. During this process the composition of the final material can be varied by the applied reaction atmosphere, Ar or NH_3, according to the following simplified reaction equations:

$$[CH_3SiH-NH]_{4n-m}[CH_3SiN]_m \xrightarrow{1000°C/Ar} Si_xC_yN_z + H_2 + CH_4 + \ldots \qquad (5)$$

$$[CH_3SiH-NH]_{4n-m}[CH_3SiN]_m \xrightarrow{1000°C/NH_3} Si_xN_y + H_2 + CH_4 + \ldots \qquad (6)$$

In the case of polysilazanes the decomposition starts in the temperature range between 400 and 500°C and is completed at temperatures exceeding 800°C. According to thermal gravimetric analysis (TGA) in combination with mass spectrometric analysis, the main gaseous by-products evolved during pyrolysis are hydrogen and methane (Figs 1 and 2). The solid reaction products obtained at 1000°C with high ceramic yields (Table 2) are completely single phase and amorphous as could be

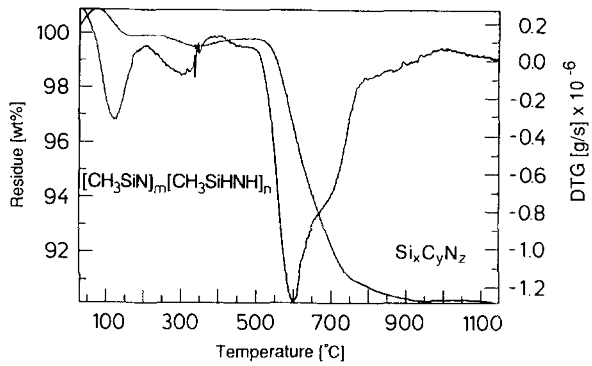


Fig. 1. Thermogravimetric analysis of polysilazane polymer in N_2, providing amorphous $Si_{2.0}C_{1.0}N_{1.8}$.

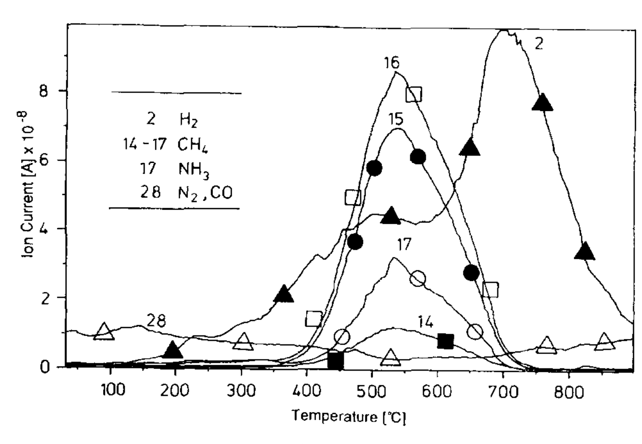


Fig. 2. Mass spectrometry of polysilazane polymer in vacuum.

---

*Polysilazanes NCP 100 and NCP 200, Chisso Corp., Tokyo, Japan, and VT 50 and ET 70, Hoechst AG, Frankfurt, Germany.[9]

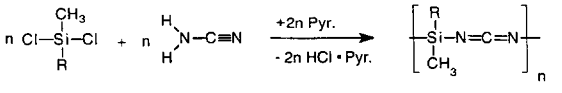
Table 2. Ceramic yields and chemical compositions of amorphous polymer derived ceramics (1000°C/Ar)

Starting Polymer		Composition	Ceramic Yield [wt%]
$[\text{-CH}_3\text{SiH - NH}]_{4n-m}[\text{CH}_3\text{SiN -}]_m$ pyrolysis in NH_3	**(1)**	$Si_3N_{3.4}$	72
$[\text{-CH}_3\text{SiH - NH}]_{4n-m}[\text{CH}_3\text{SiN -}]_m$	**(1)**	$Si_{1.8}C_{1.0}N_{1.5}$	75
$[\text{-H(CH}_3\text{)Si-N=C=N-}]_n$	**(2a)**	$Si_{1.0}C_{1.1}N_{1.4}$	65
$[\text{-(CH}_3)_2\text{Si-N=C=N-}]_n$	**(2b)**	$Si_{1.0}C_{1.8}N_{1.3}$	30
$[\text{-CH=CH}_2\text{(CH}_3\text{)Si-N=C=N-}]_n$	**(2c)**	$Si_{1.0}C_{2.0}N_{1.2}$	63
$[\text{-(CH}_3)_2\text{Si-NH-}]_{n\text{-}4m}$ $[\text{-Ti(N(Si(CH}_3)_2\text{-)}_3]_m$	**(3)**	$Si_{2.1}Ti_{0.1}C_{1.0}N_{1.8}$	65
$\left[\text{B}\left(\text{-CH(CH}_3\text{)-Si(CH}_3\text{)NH-}\right)_3\right]_n$	**(4)**	$Si_{3.0}B_{1.0}C_{4.3}N_{2.0}$	58

determined by comprehensive X-ray and analytical transmission electron microscopic investigations. Hence, the as-synthesized silicon carbonitride, $Si_{1.8}C_{1.0}N_{1.5}$, and silicon nitride, $Si_3N_{3.4}$, can be considered as metastable solid solutions.

2.2.2 Polysilylcarbodiimide derived materials

In 1993 Kienzle *et al.*[11] developed the synthesis of $Si_xC_yN_z$ ceramics derived from a new class of polymeric precursors, the polysilylcarbodiimides $[–R_2Si–NCN–]_n$. This organosilicon compound can be synthesized by the reaction of organochlorosilanes with cyanamide:


(7)

2

R = H (**2a**), CH_3 (**2b**), $CH=CH_2$ (**2c**)

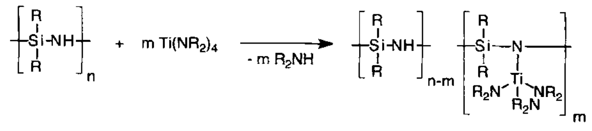
The transformation of this polysilylcarbodiimide into Si–C–N ceramics can be performed by direct pyrolysis of the as-synthesized polymer. On this occasion the character of the sidegroup R determines the chemical composition of the amorphous, single-phase pyrolysis product (Table 2). Only in the case of H and $CH=CH_2$ are high ceramic yields up to 65% obtained. Owing to the different structure of polysilazanes ([–Si–N–] chain) and polysilylcarbodiimides ([–Si–NCN–] chain), different properties of the pyrolysed intermediates were expected. This connection between the structural features of the polymers and the properties of the pyrolysis products is a current field of research. Additionally, the reactive carbodiimide group of polysilylcarbodiimides can be utilized either to increase the cross-linking of the polymer by hydrosilylation or to add new elements by a similar reaction. The former process adjusts the polymer viscosity important for the fabrication of fibres. The latter treatment enables the synthesis of ceramic materials in the quaternary systems Si–*E*–C–N (*E* = B, Al, Ti, P).

2.3 Ceramics in the quaternary system Si–E–C–N

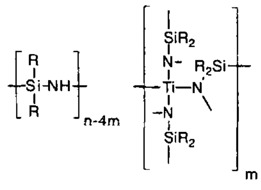
In the field of multicomponent materials two aspects are particularly important. First, the fabrication of multicomponent amorphous ceramic powders is suitable to produce composite materials comprised of two or more binary compounds. For that purpose multicomponent amorphous powders containing the desired elements were subjected to heat-treatment wherein both densification and phase partitioning takes place. Second, some multicomponent amorphous materials crystallize at extraordinarily high tempreratures and thus can be used for high-temperature applications.

However, the synthesis of multicomponent ceramic materials by conventional powder-processing is difficult, owing to the thermodynamic instability of their solid solutions. By way of contrast, metastable solid solutions are producable by the polymer pyrolysis of appropriate organoelement precursors. The manufacture of multiphase ceramic materials by the pyrolysis process can be realized by three different methods:

- Mixing polycarbosilanes or polysilazanes with metal powders (Al, Ti, Zr, V, Nb, Ta, W) to form a homogeneous polymer/metal powder composite, and subsequent pyrolysis under Ar or NH_3, according to Seyferth *et al.*[12] This method provides multiphase composite ceramics consisting of silicides, nitrides and carbides of the applied metal, as well as of silicon carbide in different volume fractions depending on the pyrolysis atmosphere and the polymer/metal ratio.
- Reaction of non-oxide Si-polymers with monomers containing the desired elements as the main component. Recently, Bill *et al.*[13] suggested the transamination of polysilazanes with $Ti[N(CH_3)_2]_4$, resulting in polytitaniumsilazanes.

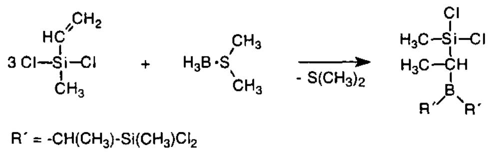

(8)

Further proceeding of the reaction leads to complete elimination of dimethylamine and results in a highly cross-linked polytitanosilazane (**3**):


3

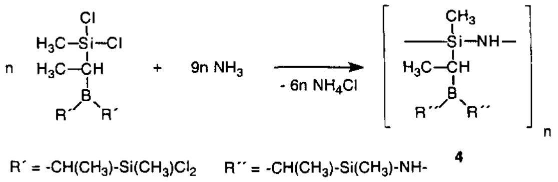
By using analogous Al, B, P or Zr amides to perform the transamination reaction the corresponding polymetalsilazanes can be received.

- Hydroboration of dichloromethylvinylsilane provides a molecular compound containing boron and silicon.



(9)

Subsequent polycondensation of this heteroelement reaction product in the presence of ammonia results in the formation of polyborosilazanes (**4**) as reported by Kienzle.[14]



(10)

The molar ratio B:Si in the as-synthesized polymer amounts to 1:3. Pyrolysis of the obtained heteroelement polymers (**3** and **4**) at 1000°C in Ar provides amorphous intermediates in the quaternary systems Si–B–C–N and Si–Ti–C–N with ceramic yields up to 65% (Table 2). During the thermolysis of (**4**) the B:Si ratio remains constant. Additionally, the boron-containing monomer can be converted into new polyborosiloxanes (silicones) and polyborosilanes by cross-linking in the presence of water, glycol, or Na/K instead of ammonia.

3 TRANSFORMATION OF THE DERIVED POLYMERS INTO CERAMIC MATERIALS

The amorphous intermediate polymers can be processed into both monophased and multiphased crystalline ceramics by an additional heat treatment. During this reaction the metastable intermediate is partitioned into the thermodynamically stable phases. Since some multicomponent intermediates crystallize at elevated temperatures (> 1700°C), they can be directly used as amorphous high-temperature materials.

The technical utilization of the derived pyrolysis products strongly depends on their rheological behaviour and volatility.

- Polymers with high volatility are applied for CVD processes to generate coatings and spherical powders.
- Polymers with appropriate viscosities are processed to ceramic fibres by melt spinning or dry spinning, as well as to films by dip coating or slip casting.
- Highly cross-linked polymers revealing low volatilities as well as high viscosities and ceramic yields are used for fabrication of ceramic powders and bulk materials.

4 MATERIAL PROPERTIES OF MULTICOMPONENT POLYMER-DERIVED CERAMICS

The as-synthesized amorphous intermediates are promising candidates for high temperature applications. Thus, the high-temperature behaviour has to be characterized in terms of crystallization and oxidation resistance.

4.1 Crystallization behaviour

As mentioned previously, the pyrolysed multicomponent materials are completely amorphous and single-phase. Since the pyrolysis products can be used as both amorphous and crystalline materials, the onset temperature of crystallization and the microstructural development during the phase transformation are of great importance with respect to the maximum application temperature of the amorphous species and to the physical, chemical and mechanical properties of the polycrystalline ceramics.

As shown in Fig. 3 the onset temperature of crystallization of the polymer-derived intermediates providing the thermodynamically stable phases increases with increasing number of components. Thus, the binary compound $Si_3N_{3.4}$ crystallizes at 1000°C, forming α-Si_3N_4, whereas the ternary Si–C–N and the quaternary Si–B–C–N systems partition at 1450 and 1700°C, respectively,

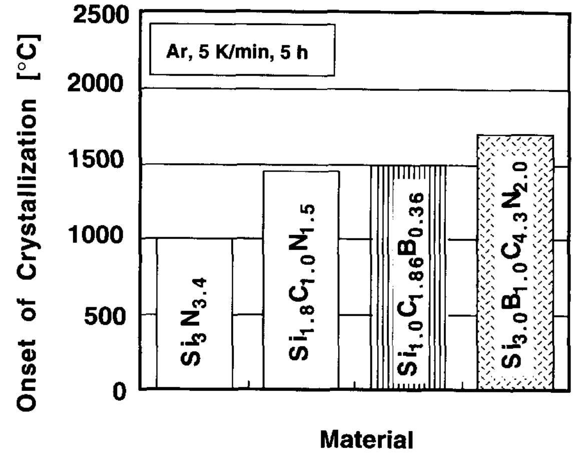


Fig. 3. Onset temperature of crystallization of different polymer-derived amorphous ceramic materials.

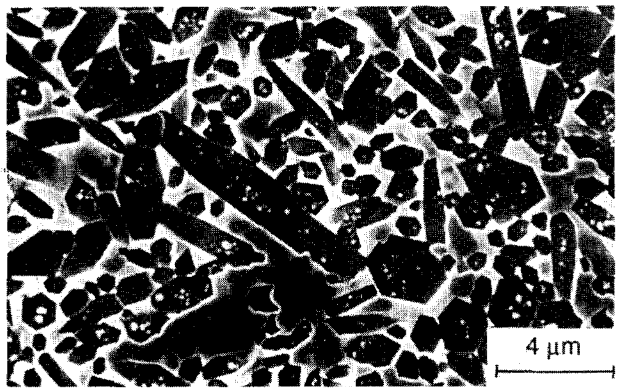


Fig. 4. Microstructure of polyvinylsilane/Si_3N_4 powder blend derived Si_3N_4/SiC micro/nano-composite, gas pressure sintered at 1850°C applying 10 MPa N_2.

generating composite materials consisting of the thermodynamically stable phases SiC and Si_3N_4 (Si–C–N), as well as β-SiC, β-Si_3N_4, α-BN and C (Si–B–C–N). Additionally, Fig. 3 reveals that the substitution of N by B leads to a higher crystallization temperature. Moreover, Baldus *et al.*[15] have reported a $Si_{1.6}B_{1.0}C_{1.0}N_{3.3}$ intermediate that resists crystallization up to 1900°C. This points out that an additional relevant parameter is the composition of the metastable product, which can be varied in a wide range by the adjustment of the chemical composition of the used starting polymer.

During this crystallization process, tailor-made microstructures with different amounts and species of thermodynamically stable phases can be derived. Owing to their outstanding physical and mechanical properties reported by Gleiter,[16] Niihara[17] and Wakai,[18] nano-sized materials are of great technological interest. Figure 4 shows the microstructure of an inter/intra-granular (classification according to Niihara[17]) Si_3N_4/SiC micro/nano-composite derived from polyvinylsilane/Si_3N_4 powder mixture.[19]

It is obvious from Fig. 4 that SiC nano-particles are embedded within the Si_3N_4 grains and that SiC micro-crystals are located within the Si_3N_4 grain boundaries.

One basic problem in the course of manufacturing of ceramics by the polymer pyrolysis process is the development of gaseous species during the crystallization step. As shown in Fig. 5 the composition of the as-synthesized amorphous Si–C–N intermediate (A) derived from polysilazane does not fit with the stoichiometry of SiC/Si_3N_4 composites (tie line between SiC and Si_3N_4). Accordingly, evaporation of N_2 occurs during partitioning and the SiC/Si_3N_4 material of composition B is formed. This results in an increase in porosity. Therefore, further investigations concerning the adjustment of chemical composition are necessary in order to shift the composition of the intermediate (A) on to the SiC–Si_3N_4 tie line.

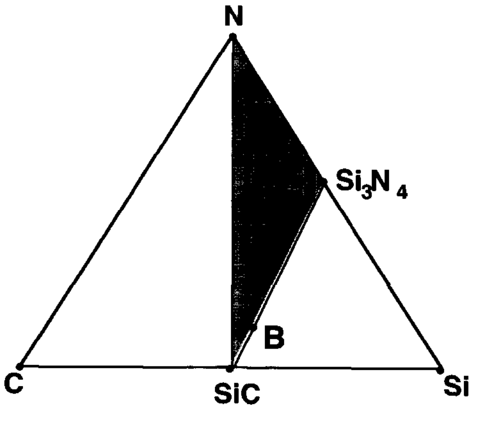


Fig. 5. Phase relations in the ternary Si–C–N system at temperatures 1440°C < T < 1850°C proposed by Lukas and Effenberg[20] in 1987. (A) Composition of polysilazane derived pyrolysis product; (B) composition of the crystallized ceramic product.

4.2 Oxidation behaviour

Since the polymer-derived materials are expected to be applied at elevated temperatures in air, oxidation resistance is one of their most important properties. Investigations by Schönfelder[21] revealed that polysilazane-derived Si–C–N ceramics resist oxidation in pure oxygen up to 1600°C for a period of 60 h. This experimental result can be explained by SiO_2 surface passivation owing to the low coefficient of oxygen diffusion in pure, solid SiO_2, which prevents further oxidation of the bulk. The mass gain during annealing has been lower than 1 wt%. The process is schematically shown in Fig. 6.

In contrast, liquid phase sintered Si_3N_4 based ceramics are oxidized completely during heating at 1600°C in air for a time period of 60 h, Fig. 7. In this case the secondary phase is liquid during oxidation. Thus oxygen can diffuse very rapidly through the liquid phase, reacting with the liquid

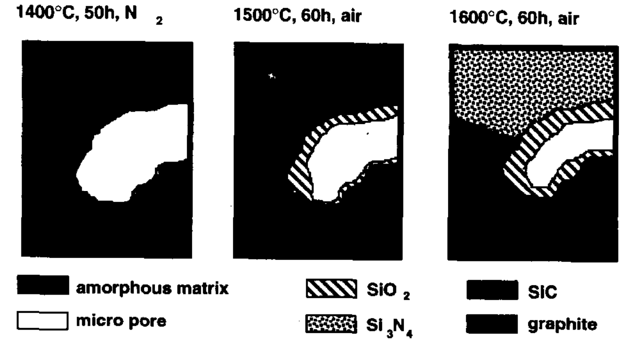


Fig. 6. Oxidation behaviour of polysilazane-derived Si–C–N ceramics at different temperatures.

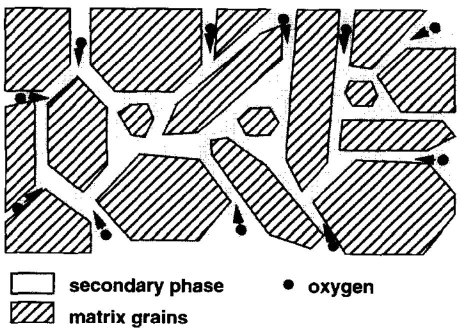


Fig. 7. Oxidation mechanism in liquid phase sintered ceramics.

phase as well as the matrix material. Subsequently the formed SiO_2 dissolves into the liquid, forming metal silicates in the presence of, for example, Al_2O_3, MgO or Y_2O_3 as sintering aids. As a consequence, no protective SiO_2 layer is formed and the oxidation proceeds even in the interior bulk material.

5 CONCLUSIONS AND OUTLOOK

The polymer pyrolysis route gives the opportunity not only to generate novel multicomponent amorphous materials, metastable up to extraordinarily high temperatures, which cannot be produced by traditional powder technology, but also to fabricate multiphase ceramic composites by crystallization of the as-pyrolysed polymers, revealing tailor-made microstructures. Additionally, additive-free ceramic materials possessing excellent oxidation- and creep-resistance up to exceptionally high temperatures can be processed by polymer pyrolysis, and manufacture of fibres, powders and bulk materials is possible using the process. Moreover, the covalently bound non-oxide Si-based ceramics can be obtained at moderate temperatures, thus requiring less energy compared to conventional densification techniques.

Future work will focus on the correlation between the molecular structure of the starting organoelement compounds and the solid state structure and microstructure of the received inorganic solid. The synthesis and characterization of novel polymers containing heteroatoms like Al, Ti, Zr, P and B are of great interest regarding the optimization of the material properties.[9]

REFERENCES

1. NOLL, W., *Alte Keramiken und ihre Pigmente*. Schweizerbartsche Verlagsbuch-handlung, Germany, 1991.
2. MITOMO, M. & TAJIMA, Y., *J. Ceram. Soc. Japan*, **99** (1991) 1014.
3. VERBEEK, W. & WINTER, G., Deutsche Offen. 2 236 078, 1974.
4. YAJIMA, S., HAJASHI, J., OMORI, M. & OKAMURA, K., *Nature*, **261** (1976) 683.
5. KIPPING, F. S. & SANDS, J. E., *J. Chem. Soc.*, **119** (1921) 830.
6. BURKHARDT, C. A., *J. Am. Chem. Soc.*, **71** (1949) 963.
7. YAJIMA, S., HAYASHI, J. & OMORI, M., *Chem. Lett.* (1975) 931.
8. SEYFERTH, D. & WISEMAN, G., *J. Am. Ceram. Soc.*, **67** (1984) C132.
9. LEGROW, G. E., LIM, T. F., LIPOWITZ, J. & REOACH, R. S., *Am. Ceram. Bull.*, **66** (1987) 363.
10. YOKOYAMA, Y., NANBA, T., YASUI, I., KAYA, H., MAESHIMA, T. & ISODA, T., *J. Am. Ceram. Soc.*, **74** (1991) 654.
11. KIENZLE, A., OBERMAYER, A., SIMON, A., RIEDEL, R. & ALDINGER, F., *Chem. Ber.*, **126** (1993) 2569.
12. SEYFERTH, D., BRYSON, N., WORKMAN, D.P. & SOBON, C.A., *J. Am. Ceram. Soc.*, **74** (1991) 2687.
13. BILL, J., FRIEß, M., ALDINGER, F. & RIEDEL, R., in *Better Ceramics Through Chemistry VI*. MRS Publications, Pittsburgh, PA, 1994.
14. KIENZLE, A., PhD Thesis, University of Stuttgart, 1994.
15. BALDUS, H. P., JANSEN, M. & WAGNER, O., In *Key Engineering Materials*, Vols 89–91. Trans-Tech Publications, Switzerland, 1994, p. 75.
16. GLEITER, H., *Phys. Bl.*, **47** (1991) 753.
17. NIIHARA, K., *J. Ceram. Soc. Japan*, **99** (1991) 974.
18. WAKAI, F., KODOMA, Y., SAKAGUCHI, S., MURAYAMA, N., IZAKI, K. & NIIHARA, K., *Nature*, **344** (1990) 421.
19. GREINER, A., Thesis, University of Stuttgart, 1993.
20. LUKAS, H. L. & EFFENBERG, G., Private communication, 1987.
21. SCHÖNFELDER, H., Thesis, University of Stuttgart, 1993.