

# Si-B-C-N PRECURSOR: SYNTHESIS AND THERMAL STABILITY

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## ABSTRACT

The synthesis and thermal behavior of boron-modified polysilazanes and polysilylcarbodiimides is discussed. The title compounds were obtained by different methods *e.g.* metathesis reactions of tris(chlorosilylethyl)boranes with ammonia or bis(trimethylsilyl)-carbodiimide, hydroboration of vinylated polysilazanes and polysilylcarbodiimides or base-catalyzed dehydrogenative coupling of ammonia and tris(hydridosilylethyl)boranes. Besides synthetic procedures, the ceramization of the Si-B-C-N polymers, monitored by thermogravimetric analysis (TGA), is reported. High temperature thermogravimetric analysis (HT-TGA) of the as-obtained amorphous ceramics carried out in inert gas atmosphere up to 2200°C, occasionally reflect their stability towards decomposition up to 2000°C. HT-TGA in air reveal resistance of the Si-B-C-N ceramics towards oxidation, due to the formation of protective Si-C-O surface layers. XRD and NMR analyses of annealed samples indicate microstructure evolution in the 1550 - 1750°C range, where the as-obtained amorphous ceramics transform into  $\alpha$ -SiC and  $\beta$ -Si<sub>3</sub>N<sub>4</sub> crystalline phases.

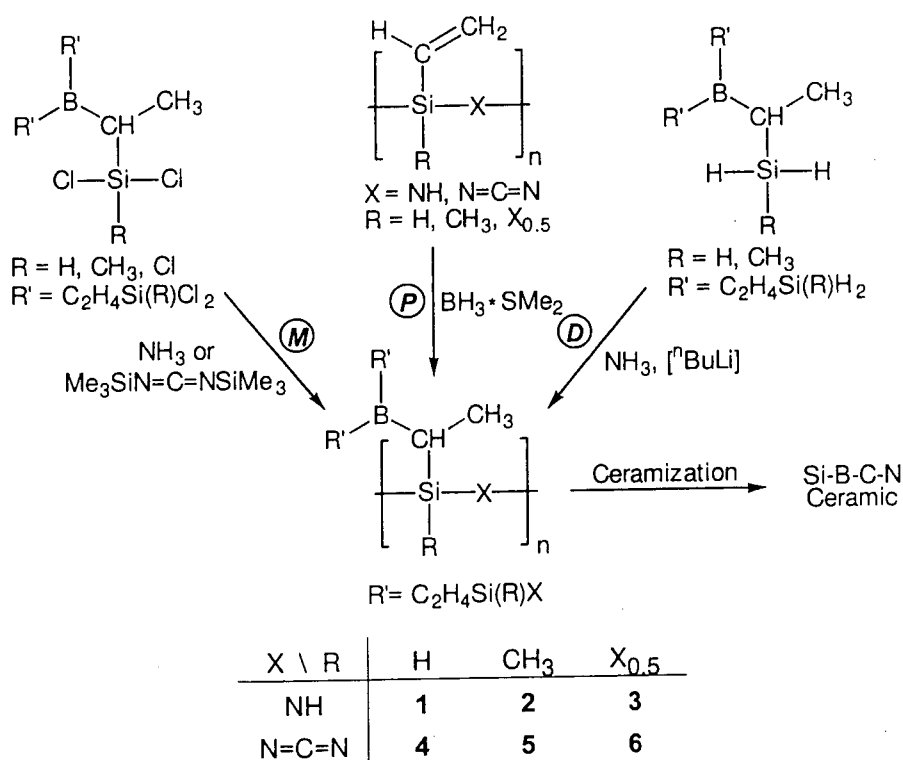
## 1. INTRODUCTION

Thermolysis of polymeric organosilicon networks such as polysilanes, polycarbosilanes, and polysilazanes is a suitable method for the synthesis of a wide variety of high performance ceramics, *e.g.* Si<sub>3</sub>N<sub>4</sub> and SiC. <sup>[1-4]</sup> Within this decade, boron-modified silicon-based ceramics became of substantial interest because of their exceptional high temperature stability even up to 2000°C. <sup>[5]</sup> First orienting results were described by Seyferth et al. in 1990 who reacted oligosilazanes with borane dimethylsulfide to obtain silazane-substituted borazine derivatives. <sup>[6]</sup> Structurally comparable borazine-based Si-B-C-N polymers were also obtained by Sneddon et al. from borazine via thermal dehydrocoupling with oligo- or polysilazanes <sup>[7]</sup> and from Paine et al. who published a method for the synthesis of borazine-based Si-B-C-N polymers from B-chloroborazines, LiSi[TMS]<sub>3</sub> and HMDS. <sup>[8]</sup> Polyborosilazanes as Si-B-C-N precursor were described by Baldus and Jansen, who published aminolysis of TADB <sup>[9]</sup> and by Riedel et al. who obtained Si-B-C-N preceramics by ammonolysis of B[C<sub>2</sub>H<sub>4</sub>Si(CH<sub>3</sub>)Cl<sub>2</sub>]<sub>3</sub>. <sup>[5,10]</sup> Both systems have proven to be especially promising precursors for high-temperature stable fibers and bulk parts.

In addition to demonstrating outstanding thermal stability, other important issues in Si-B-C-N polymeric precursor design include: low mass loss during thermolysis, good processability, controlled reactivity and low cost. In our recent investigations, the focus was on development of novel precursors by simple reactions, delivering high temperature-stable Si-B-C-N ceramics with high ceramic yields.

## 2. SYNTHESIS

The basic structural elements of the polymeric Si-B-C-N precursors in this study are vinyl-substituted Si-N (polysilazanes) or Si-N=C=N units (polysilylcarbodiimides). Their modification by hydroboration yields Si-B-C-N polymers. Initial studies on polymers of the general type  $\{B[C_2H_4Si(R)NH]_3\}_n$  were published in 1994 by Riedel et al. <sup>[10]</sup> who synthesized  $\{B[C_2H_4Si(CH_3)NH]_3\}_n$  (**2M**, also T21, see Scheme 1) by ammonolysis of  $B[C_2H_4Si(CH_3)Cl_2]_3$ . Even though ceramics obtained from this precursor possess outstanding thermal stability, there are remarkable disadvantages, *i.e.* a time-intensive processing and low ceramic yields due to thermally induced depolymerization. To increase the ceramic yields and to simplify the work-up, both the molecular structure and the reaction pathways were modified (Scheme 1).



**Scheme 1** Synthesis of polymers  $\{B[C_2H_4Si(R)X]_3\}_n$  (1-6) using different reaction pathways. *M* = monomer route, *P* = polymer route, *D* = dehydrogenative coupling.

Replacing the methyl group in **2M** (Monomer route, Scheme 1) with a hydrogen atom or a NH-unit by using  $B[C_2H_4Si(R)Cl_2]_3$  ( $R = H, Cl$ ) as starting compounds, delivers the expected polymers  $\{B[C_2H_4Si(R)NH]_3\}_n$  (**1M**:  $R = H$ , **3M**:  $R = (NH)_{0.5}$ ) as colorless solids. <sup>[11,12]</sup> However, due to the decreased solubility of **1M** as compared to the methyl-substituted derivative **2M**, the yield is only 70% whereas the high crosslinking in **3M** causes it to be insoluble in all common solvents, resulting in only 5% yield.

A modified procedure for the synthesis of compounds 1-3 is the hydroboration of vinyl-substituted polysilazanes with borane dimethylsulfide (Polymer route, Scheme 1). <sup>[12,13]</sup> Both

reactants are soluble in organic solvents and are drop-wise mixed. In contrast to the synthesis by ammonolysis of the respective tris(chlorosilylethyl)boranes, no solid by-products form in the final reaction step; the only by-product is dimethylsulfide which can be easily removed, together with the solvent by vacuum distillation. Moreover, **1-3P** are obtained in quantitative yield using this reaction pathway.

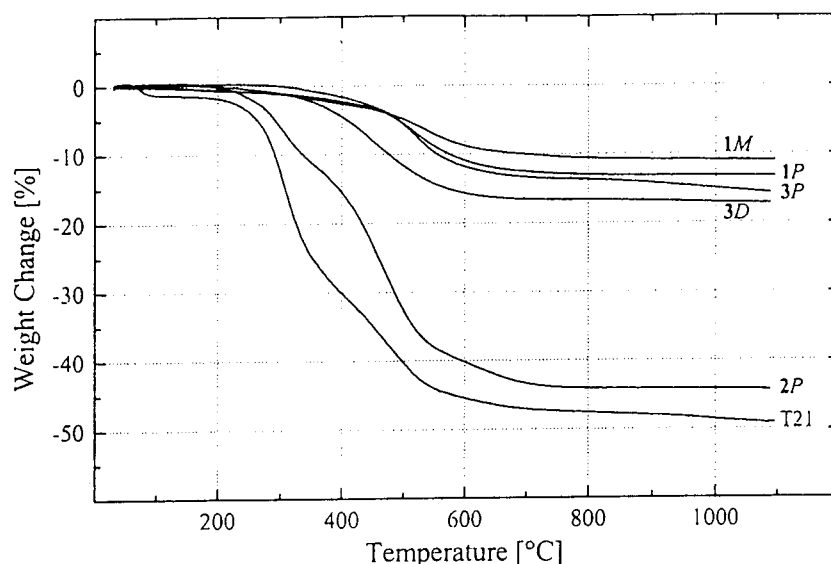
A novel method for the synthesis of boron-modified polysilazanes with only hydrogen as by-product is the base-catalyzed dehydrogenative coupling (index *D*, Scheme 1) of ammonia and tris(hydridosilylethyl)boranes,  $B[C_2H_4Si(R)H_2]_3$  ( $R = H, CH_3$ ).<sup>[14,15]</sup> Initially, the strong base, *e.g.* *n*-butyl lithium, deprotonates ammonia. The highly nucleophilic amide replaces a silicon-bonded hydride to form a silylamine and lithium hydride, which then deprotonates ammonia, resuming the catalytic cycle. Under the conditions used, silylamines are not stable and by the elimination of ammonia, polysilazane frameworks form. In addition, the compounds  $B[C_2H_4Si(R)H_2]_3$  are best obtained from vinylsilanes,  $H_2C=CHSi(R)H_2$  ( $R = H, CH_3$ ), and borane dimethylsulfide.<sup>[15,16]</sup>

The synthesis of boron-containing polysilylcarbodiimides **4-6**, shown in Scheme 1 was also performed using different reaction sequences.<sup>[17,18]</sup> One possible approach is to synthesize polymeric vinyl-substituted polysilylcarbodiimides which are in a second reaction step hydroborated at the olefin unit with *e.g.* borane dimethylsulfide,  $BH_3 \cdot S(CH_3)_2$  in synthesis of compounds **4-6P**. Alternatively, the reaction of bis(trimethylsilyl)carbodiimide with boron-substituted chlorosilanes of type  $B[C_2H_4(R)SiCl_2]_3$  ( $R = H, CH_3, Cl$ ) produces the boron-containing polysilylcarbodiimides **4-6M**. Remarkably, this synthetic pathway does not require solvents. The starting compounds are mixed at room temperature either stoichiometrically or with excess bis(trimethylsilyl)carbodiimide. In a *trans*-silylation reaction the polymer forms under evolution of methyltrichlorosilane.

A novel procedure which was also developed recently for the synthesis of Si-B-C-N polymers by a polyaddition type reaction of oligovinylsilazane,  $[H_2C=CH)SiHNH]_n$  and tris(hydridosilylethyl)boranes and is described in detail elsewhere.<sup>[19,20]</sup> This process contrasts with other known procedures for the formation of highly cross-linked Si-B-C-N polymers. It delivers the precursors in excellent yields by a thermally induced hydrosilylation reaction, which requires neither solvents or catalysts and which doesn't produce by-products.

### 3. THERMOLYSIS

The thermally induced polymer-to-ceramic conversion is accompanied by formation of gaseous by-products. A suitable method for determining the amount of species that form and the corresponding temperature range, is given by thermogravimetric analysis (TGA). Figure 1 shows a comparison of the thermogravimetric behavior of compounds **1-3** during thermolysis. The replacement of the methyl-group in T21 with cross-linking  $(NH)_{0.5}$  units results in increased ceramic yields of 83% (**3D**) and 84% (**3P**) compared to 51% (T21). The substitution of the methyl group in T21 with hydrogen results in precursors with even higher ceramic yields of 86.5% (**1P**) and 88% (**1M**).<sup>[13]</sup>



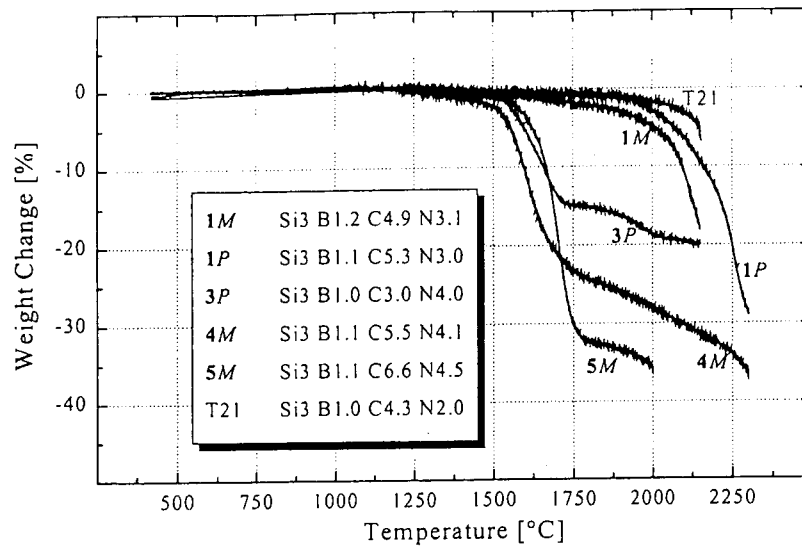
**Figure 1** Thermogravimetric analysis of compounds *1-3* in argon; heating rate 2°C/min.

These TGA findings indicate that the ceramic yield of preceramics of type  $\{B[C_2H_4Si(R)NH]_3\}_n$  is mainly a function of the silicon-bonded unit R, whereas the reaction pathway applied does not significantly influence the polymer-to-ceramic conversion.

The single reaction steps that occur during thermolysis were investigated in detail by solid state NMR spectroscopy.<sup>[21-23]</sup> In the  $^1H$  NMR spectra it is observed that in between 300 and 500°C the hydrogen resonance signals disappear. Likewise, in the  $^{13}C$  NMR spectra aliphatic CH resonance signals also disappear in this temperature range. At 1050°C carbon is observed in the  $sp^2$  and  $sp^3$  hybridized state. The  $^{29}Si$  NMR spectra are more complex. Depending on the chemical composition of the polymers either  $SiN_4$ ,  $SiCN_3$ , or  $SiC_2N_2$  sites are seen. Interestingly, boron is four-fold coordinated in the polymers, possibly due to  $N \rightarrow BC_3$  interactions in the solid state. Usually, at  $\sim 400^\circ C$  the boron sites change dramatically because of B-C bond cleavage and simultaneous B-N bond formation whereby trigonal planar  $BN_3$ -sites form.

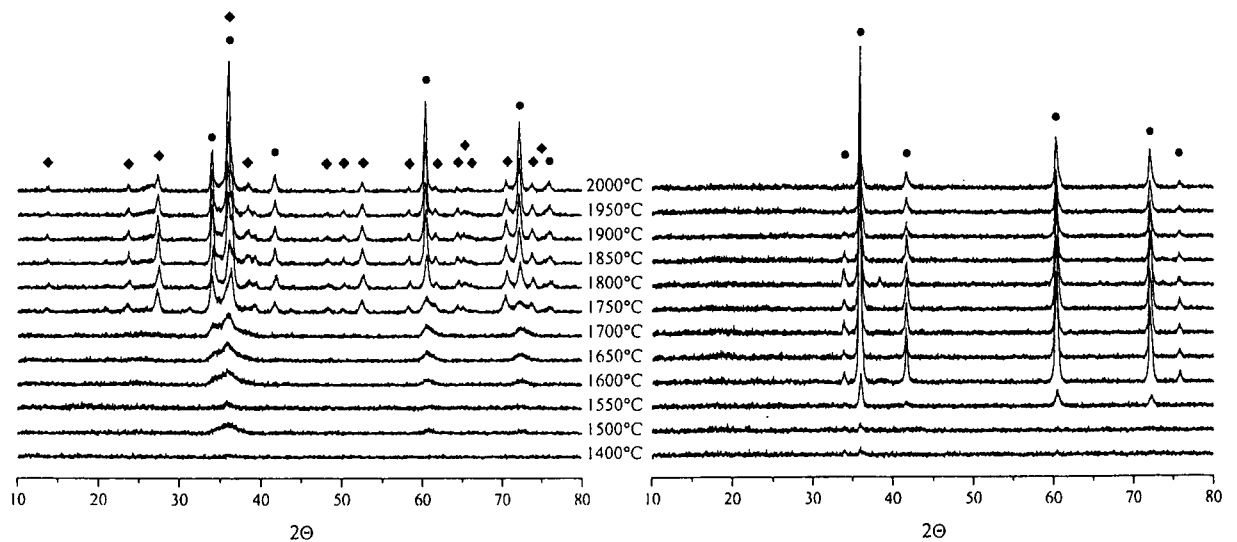
#### 4. HIGH TEMPERATURE INVESTIGATIONS

High temperature investigations of the ceramic materials were performed using TGA up to 2300°C (Figure 2) as well as XRD (Figure 3) and solid state  $^{29}Si$  CP-MAS NMR (Figure 4) up to 2000°C. A comparison of the TGA of selected ceramics demonstrates a significant difference in their thermal stability. While the *1M*, *1P*, and T21 ceramics decompose around 2000°C, the more nitrogen-rich *3P*, *4M*, and *5M*-derived materials decompose at approx. 1500 - 1550°C.<sup>[13,18]</sup>



**Figure 2** High temperature TGA of selected ceramic samples with different composition. Heating rate  $T < 1400^{\circ}\text{C}$ :  $5^{\circ}\text{C}/\text{min}$ ,  $T > 1400^{\circ}\text{C}$ :  $2^{\circ}\text{C}/\text{min}$ ; argon atmosphere.

The findings of the HT-TGA investigations reflect the observations in the XRD experiments (Figure 3) which were carried out with samples annealed at  $1400 - 2000^{\circ}\text{C}$  under 1 bar nitrogen for 3h in carbon crucibles. While  $\alpha$ -SiC crystallizes from the 3P ceramic between  $1500^{\circ}$  and  $1550^{\circ}\text{C}$ , the 1P material does not crystallize until  $1700^{\circ}\text{C}$ . Above  $1750^{\circ}\text{C}$ ,  $\alpha$ -SiC and  $\beta$ -Si<sub>3</sub>N<sub>4</sub> reflections are observed in the 1P material which are stable up to  $2000^{\circ}\text{C}$ .

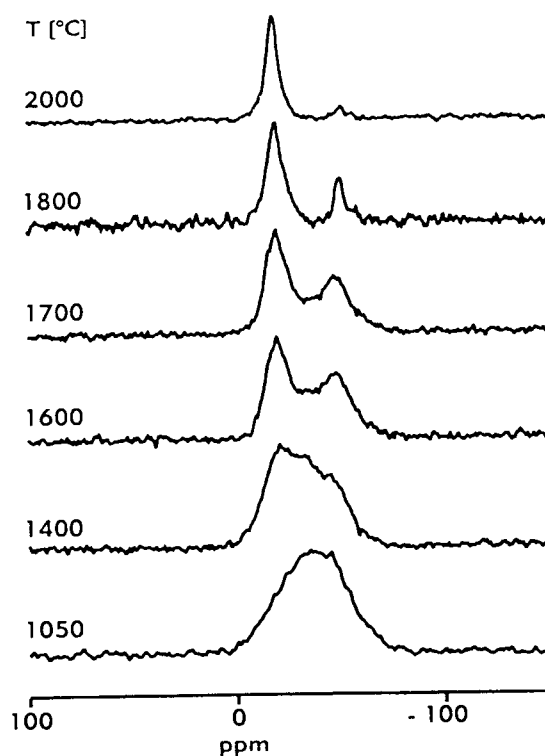


**Figure 3** X-ray diffraction patterns of the ceramics obtained from 1P (left), and 3P (right) annealed at various temperatures each for 3h. ● =  $\alpha/\beta$ -SiC, ◆ =  $\beta$ -Si<sub>3</sub>N<sub>4</sub> reflexes

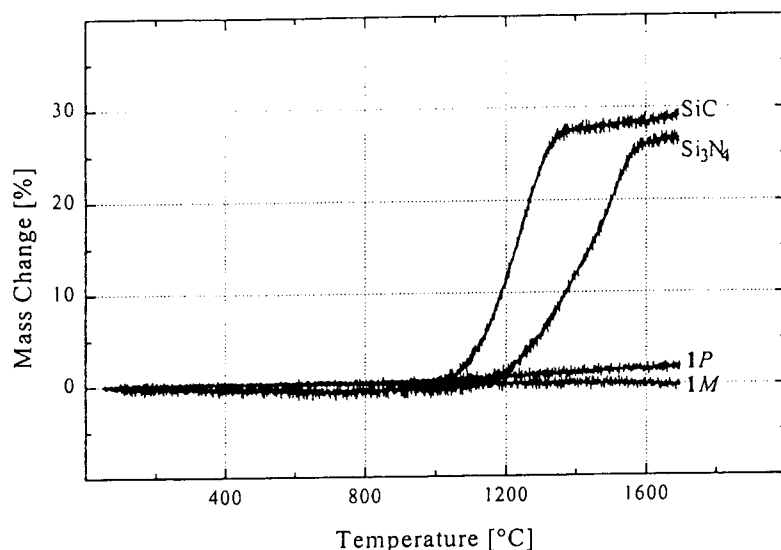
Silicon carbide and silicon nitride phase formation in the 1P-material at around 1800°C is also observed in the  $^{29}\text{Si}$  CP-MAS NMR spectrum (Figure 4).<sup>[23]</sup> The broad resonance signals of the 1050 and 1400°C samples at around -35 ppm suggest the presence of  $\text{N}_3\text{SiC}$  sites in the amorphous state. At 1600°C initial signal splitting is observed, further maintained at 1700°C and finally results in two distinct resonance signals at -19 and -48 ppm. These chemical shift values can be assigned to  $\text{SiC}_4$  and  $\text{SiN}_4$  sites which are typical for SiC and  $\text{Si}_3\text{N}_4$  ceramics. The significantly decreased intensity of the latter resonance at 2000°C is likely due to beginning decomposition of  $\text{Si}_3\text{N}_4$  at this temperature.

Initial explanations of the extraordinary high-temperature stability of precursor-derived Si-B-C-N ceramics were presented previously by Jalowiecki et al.<sup>[24]</sup> The authors investigated the microstructure of boron-doped silicon carbonitride composites by HR-TEM and found turbostratic BN(C) segregation occurring along grain boundaries of nano-sized silicon carbide and silicon nitride crystals. We propose that the BN(C) phase binds free carbon, thus decreasing the carbon activity. As a consequence, the thermodynamically expected reaction of free carbon, which has been present in all investigated materials with silicon nitride according to  $\text{Si}_3\text{N}_4 + 3\text{C} \rightarrow 3\text{SiC} + 2\text{N}_2$  is shifted to higher temperatures. At 1 bar  $\text{N}_2$ , this reaction would take place at 1484°C.<sup>[25]</sup> In addition, the BN(C) grain boundary may serve as a diffusion barrier and retards grain growth. As a result of encapsulation of the silicon nitride grains by the turbostratic BN(C) phase, the nitrogen pressure within the “shell” is sustained to some extent. The decomposition temperature for the reaction of silicon nitride into silicon and nitrogen is thus raised to higher values.<sup>[13]</sup>

The resistance of 1M- and 1P-derived ceramics towards oxidation and hydrolysis at elevated temperature was investigated by TGA in air up to 1700°C and compared with SiC and  $\text{Si}_3\text{N}_4$  (Figure 5).<sup>[13]</sup>

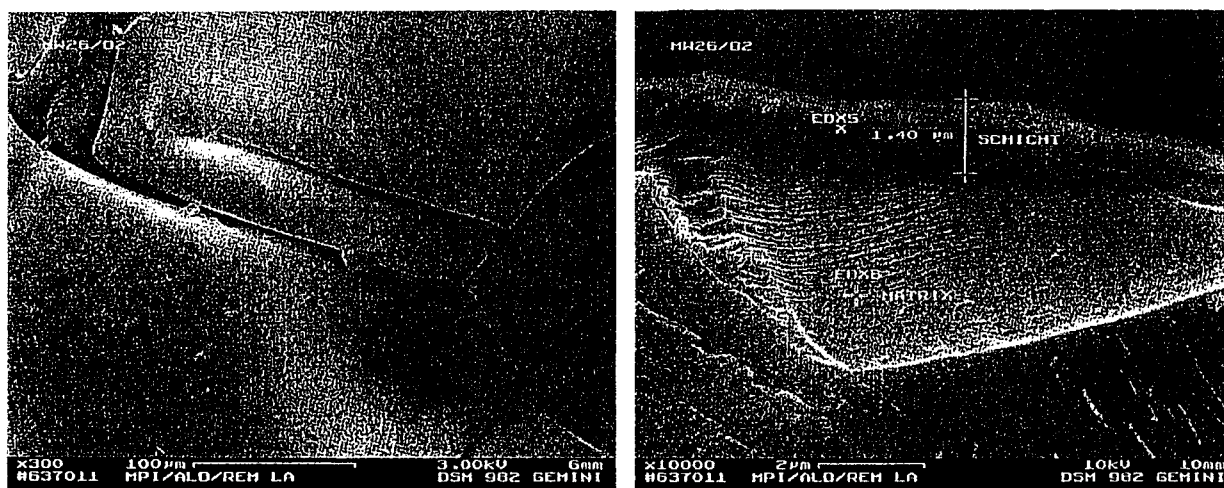


**Figure 4**  $^{29}\text{Si}$  NMR spectra of 1P ceramic annealed at various temperatures (3h).



**Figure 5** Oxidation behavior (TGA) of SiC, Si<sub>3</sub>N<sub>4</sub>, and  $\{B[C_2H_4SiH_2NH]_3\}_n$  (1M, 1P) ceramics. Heating rate: 5°C/min, flowing air.

While silicon carbide and silicon nitride oxidize at ~ 1000°C and ~ 1130°C, there is negligible mass change up to 1700°C for the Si-B-C-N materials. Figure 6 shows the results of scanning electron microscope investigations of oxidized 1M ceramic particles. It illustrates that the surface areas are smooth and pore-free. Sintering of the ceramic particles did not occur. Fracture surfaces point out that a 1.2 - 2.3 μm surface layer formed during oxidation. Bubble formation due to decomposition of native oxides as described by Nickel et. <sup>[26]</sup> al is not observed. EDX investigations reveal that the surface layer consists mainly of silicon and oxygen whereas the matrix is composed of silicon, carbon, nitrogen, and boron. In addition, carbon was also detected in the layer, but in a lower concentration than in the matrix.



**Figure 6** Scanning electron microscope (SEM) images of surface areas of oxidized 1M ceramic grains (left, 300x); magnification 300x and a fracture surface of oxidized 1M material (right, 10000x). EDX5 and EDX6 represent areas investigated by EDX.

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## REFERENCES

1. W. Toreki, *Polymer News*, **16** 1-14 (1991).
2. M. Birot, J.-P. Pillot and J. Dunogués, *Chem. Rev.*, **95** 1443-1477 (1995).
3. J. Bill and F. Aldinger, *Adv. Mater.*, **7** 775-787 (1995).
4. H.-P. Baldus and M. Jansen, *Angew. Chem. Int. Ed. Engl.*, **36** 328-344 (1997).
5. R. Riedel, A. Kienzle et al. *Nature*, **382** 796-798 (1996).
6. D. Seyferth and H. Plenio, *J. Am. Ceram. Soc.*, **73** 2131-2133 (1990).
7. K. Su, E. E. Remsen, G. A. Zank and L. G. Sneddon, *Chem. Mater.*, **5** 547-556 (1993).
8. D. Srivastava, E. N. Duesler and R. T. Paine, *Eur. J. Inorg. Chem.*, 855-859 (1998).
9. M. Jansen and H.-P. Baldus, DE 410 71 08 A1 (1992).
10. R. Riedel, A. Kienzle, G. Petzow, M. Brück and T. Vaahs, DE 432 07 83 A1, (1994).
11. F. Aldinger, M. Weinmann and J. Bill, *Pure Appl. Chem.*, **70** 439-448 (1998).
12. M. Weinmann, J. Bill and F. Aldinger, DE 197 41 458 A1 (1999).
13. M. Weinmann, J. Schuhmacher et al., submitted to *Chem. Mater.*
14. M. Weinmann, F. Berger, K. Müller and F. Aldinger, submitted to *Appl. Organomet. Chem.*
15. M. Weinmann, J. Bill and F. Aldinger, DE 197 41 459 A1 (1999).
16. M. Weinmann, T. Kamphowe, P. Fischer and F. Aldinger, *J. Organomet. Chem.*, in press
17. M. Weinmann, R. Haug et al., *J. Organomet. Chem.*, **541** 345-353 (1997).
18. M. Weinmann, R. Haug et al., *Appl. Organomet. Chem.*, **12** 725-734 (1998).
19. M. Weinmann, T. W. Kamphowe, J. Bill and F. Aldinger, DE 197 41 459 A1 (1999).
20. T. Kamphowe, M. Weinmann, J. Bill and F. Aldinger, *Sil. Industriels*, **63** 159-162 (1998).
21. J. Schuhmacher, M. Weinmann et al., *Chem. Mater.*, **10** 3913-3922 (1998).
22. J. Schuhmacher, K. Müller et al., *Proc. Werkstoffwoche München* (1998), in press.
23. J. Schuhmacher, M. Weinmann et al., to be submitted to *Chem. Mater.*
24. A. Jalowiecki, J. Bill, F. Aldinger and J. Mayer, *Composites*, **27A** 717-721 (1996).
25. H. J. Seifert, H.-L. Lukas and F. Aldinger, *Ber. Bunsenges. Phys. Chem.*, **102** 1309 (1998).
26. E. Butchereit and K. G. Nickel, *Key Eng. Mat.*, **132-136** 1592-1595 (1997).