JOURNAL OF MATERIALS SCIENCE 28 (1993) 3931–3938

Hydroboration of polymethylvinylsilane – a novel route to silicon boron carbide ceramics

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Polymethylvinylsilanes (PMVS) of the general composition $[R_2Si]_m$ $[RR'Si]_n$ with $R = CH_3$ and $R' = CH = CH_2$ (vinyl) have been synthesized by the dechlorination of dichlordimethylsilane $(CH_3)_2SiCl_2$ and dichlormethylvinylsilane $CH_3(CH_2 = CH)$ $SiCl_2$ with sodium in toluene. Subsequently, the vinyl groups have been hydroborated by the reaction of the as-synthesized polysilane with various borane adduct compounds such as dimethylsulphide borane $(CH_3)_2S{\cdot}BH_3$. The hydroborated polymer was characterized by infrared and ^{13}C-, ^{1}H-, and ^{11}B-NMR spectroscopy as well as by the measurement of the molecular weight distribution. The pyrolysis of the boron-containing polysilane at 1100 °C in argon results in the formation of X-ray amorphous silicon boron carbide, $Si_xC_{x+y}B_z$ in 63% yield. The crystallization behaviour of the polymer-derived covalent ceramic product at temperatures up to 2200 °C is discussed. The microstructure was characterized by transmission electron microscopy. Analytical results were obtained with the novel electron spectroscopic imaging (ESI) technique.

1. Introduction

The pyrolysis of polydiorganosilanes $[-R_2Si-]_n$ and polycarbosilanes $[-R(H)\ Si-CH_2-]_n$ with R = alkyl and/or aryl under inert gas conditions is of great interest with respect to the preparation of SiC-based ceramics [1, 2]. SiC fibres as well as SiC-containing powders can be prepared by the thermal decomposition of appropriate precursors [2]. Furthermore, it has been shown that the direct transformation of polymeric shapes into silicon-based ceramic parts comprised of SiC_{1+x} and $Si_xC_yN_z$ (silicon carbonitride) without the addition of sintering aids, can be performed at unusually low temperatures (800–1200 °C) [3, 4].

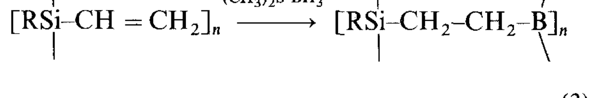
In the course of our work, we have investigated the preparation and application of boron-containing polysilanes for the formation of ceramics in the ternary system Si–C–B. Recently, polyborosilanes were synthesized via the simultaneous dechlorination of mixtures comprised of BCl_3 and dialkyldichlorosilanes R_2SiCl_2 with a Na/K alloy according to Equation 1 [5].

$$BCl_3 + Cl\text{-}SiR_2\text{-}Cl \xrightarrow{Na/K} [-R_2Si-B<]_n \quad (1)$$

Alternatively, Riccitiello *et al.* [6] succeeded in preparing polyborosilanes by the reaction of BH_3-adduct compounds with monomeric ethinyl- and vinylalkylsilanes (Equation 2).

$$(CH_2 = CH)_2Si(CH_3)_2 \xrightarrow{BH_3\cdot THF} [>B-CH_2-CH_2Si(CH_3)_2-CH_2-CH_2-]_n \quad (2)$$

In the present work we describe the synthesis of polyborosilanes by the hydroboration of polydiorganosilanes substituted with reactive vinyl $(CH_2=CH)$ groups such as $[RSi(CH = CH_2)]_n$ with R = alkyl.



$$[RSi-CH = CH_2]_n \xrightarrow{(CH_3)_2S\cdot BH_3} [RSi-CH_2-CH_2-B]_n$$

(3)

The hydroboration of the vinyl groups results in an enhanced cross-linking of the polymer. As a consequence, the viscosity of the polyorganosilane is increased depending on the amount of vinyl groups present in the starting material and on the applied molar ratio $(CH_2 = CH)/BH_3$. The viscosity can be varied and controlled over a wide range by this chemical reaction. The control over the viscosity is of great importance for the synthesis of preceramic polymers suitable for the production of SiC-based ceramics such as fibres, coatings, powders and monolithic materials. In the case of fibres and coatings, soluble or fusible

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polysilanes are required, whereas infusible precursors have to be applied for the preparation of powders as well as for the ceramization of polymeric shapes [3]. Generally, melt-spun polycarbosilane fibres have subsequently to be cross-linked in order to prevent melting during the pyrolysis leading to the SiC-fibre. In the case of the Nicalon fibre, cross-linking is achieved by curing the polymer fibre in air at 200 °C [2]. The main disadvantage of this procedure is the high oxygen concentration in the pyrolyzed fibres with the result of decreased high-temperature stability [7]. In contrast, fibres made of polyorganosilane substituted with reactive vinyl groups could be cross-linked via the hydroboration reaction which makes the synthesis of Si–B–C fibres with low oxygen content possible. Furthermore, the higher the cross-linking of the polymer, the higher is the ceramic residue after thermolysis. In addition, the thermal decomposition of hydroborated polyorganovinylsilanes with a boron content lower 2 wt % may yield sinteractive SiC powders. At higher amounts of boron, the formation of ultrafine composites containing SiC, B_4C, and carbon can be expected. In the present paper, we will report on the synthesis, characterization, and pyrolysis of polyborosilanes as well as on the crystallization of the resulting amorphous silicon boron carbide material.

2. Experimental procedure

2.1. Synthesis and characterization of the materials

Polymethylvinysilane (PMVS) is synthesized by the reaction of 50 ml (0.41 mol) $(CH_3)_2SiCl_2$, 100 ml (0.77 mol) $CH_3(CH_2=CH)SiCl_2$, and 50 ml (0.39 mol) $(CH_3)_3SiCl$ with 63.2 g Na (2.8 mol) in a mixture of 500 ml toluene and 50 ml tetrahydrofurane under nitrogen or argon at 100 °C. In order to minimize the oxygen content in the polymeric product, the standard aqueous work-up of the reaction mixture is replaced by filtration of the soluble polysilanes from solid NaCl and from insoluble polymers. Evaporation of the solvent results in PMVS with a yield between 60% and 70%.

From the amount of starting silane, $CH_3(CH_2=CH)\,SiCl_2$, the vinyl-content of 20 ml synthesized PMVS is estimated to be approximately 0.25 mol, because 1 mol BH_3 can react with 3 mol vinyl groups. Therefore, in a typical experiment 8.2 ml (82 mmol) 10 M solution of dimethylsulphideborane ($BH_3{\cdot}S(CH_3)_2$) in dimethylsulphide are carefully dropped at room temperature into a solution consisting of 19.25 g (20 ml) PMVS in 50 ml toluene. The reaction is conducted under argon in a glass vessel equipped with a magnetic stirrer. The hydroboration reaction is started by adding the first drops of $BH_3{\cdot}S(CH_3)_2$. During the addition of the borane-adduct the reaction mixture warms up and gels. The gel is then resolved by increasing the temperature up to 110 °C for 1 h. Subsequently, the reaction mixture is cooled down to room temperature. After evaporation of the solvent, the hydroborated PMVS can be isolated in the form of a dark yellow resin in nearly quantitative yield (95%). Final heat treatment of the as-synthesized polymer at 200 °C for 1 h yields a yellow-coloured polymer powder. Similarly, PMVS can be hydroborated with the $BH_3{\cdot}THF$ adduct compound. The hydroboration can be achieved without solvent if $BH_3{\cdot}N(C_2H_5)_3$ as the hydroborating agent is used. In this case, however, higher reaction temperatures of 80–90 °C have to be used. The soluble polymers have been characterized by infrared (continuous wave IR-spectrometer, Perkin-Elmer 883), and ^{13}C-, ^{1}H-, and ^{11}B-NMR spectroscopy (NMR-spectrometer, Bruker AC 250 and AM 200, Karlsruhe, Germany). The molecular weight distributions of the synthesized polymers are investigated by gel permeation chromatography (GPC) with polystyrol as the standard.

The pyrolysis behaviour and the yield of the polyborosilane derived ceramic material was determined by thermo-gravimetric analysis (TGA) (TGA-STA 429, Netzsch Gerätebau, Selb, Germany, coupled with MS QMG 511, Balzers, Liechtenstein) in the temperature range between room temperature and 1500 °C in flowing argon. For the elucidation of the crystallization behaviour, the samples were isothermally annealed in argon for 1 h in a graphite furnace at temperatures of up to 2200 °C. After cooling to room temperature, the heat-treated samples were characterized by X-ray powder diffraction using monochromated CuK_α radiation (wavelength 154.178 pm). Elemental analysis was performed to investigate the quantitative composition of the pyrolytically formed Si–C–B-ceramic. Silicon and boron have been determined by optical emission spectroscopy in an inductively coupled plasma (OES–ICP) (ICP Model 5500, Perkin-Elmer, Konstanz, Germany). Carbon, nitrogen, and oxygen contents were measured by the method of hot gas extraction. (C,S-Analyser, Model 244 and N,O-Determinator Model TC 436, LECO Corp., St. Joseph, MI, USA).

2.2. Transmission electron microscopy and electron spectroscopic imaging

For the analytical TEM characterization, a prototype energy filtering electron microscope has been used. By means of an imaging energy filter, two-dimensional elemental distribution images can be produced via the novel electron spectroscopic imaging technique (ESI). The ESI method [8] is based on the inelastic scattering processes between the fast incident electrons and atomic electrons of the sample. In the energy loss spectrum, the inelastic scattering leads to characteristic edges with onset energies, ΔE (the characteristic edges for each element correspond to the ionization energies of the atom) which are used for the elemental mapping.

For an elemental distribution image, three energy-filtered images at different energy losses have to be acquired: two images at two energy losses below the characteristic edge (ΔE_1 and ΔE_2) and one image above the energy loss edge (ΔE_3). The images taken at the energy losses ΔE_1 and ΔE_2 are used for a background extrapolation. The signal of the specific element is the difference of the total signal intensity at the energy loss, ΔE_3, minus the intensity of the extrapolated background.

The instrument employed for the ESI investigation is a prototype of the Zeiss EM 912 Omega(C. Zeiss Inc., 7082 Oberkochen, Germany), which incorporates a new integrated imaging electron energy loss spectrometer [9, 10]. The microscope is equipped with a SIT 66 TV rate camera (Dage-MTI Inc., Michigan city, IN 46360, USA) and an image processing system (Kontron Elektronic Inc., 8057 Eching, Germany). The maximum accelerating voltage is 120 kV.

Elemental distribution images have been acquired for boron, carbon, nitrogen, oxygen and silicon. The *K*-edges have been used for all elements. The selected width of the energy windows (slit width) was 10–20 eV for the light elements and 50 eV for silicon. For the latter, the background was removed by simply subtracting one background image which was acquired immediately before the edge.

For the ESI investigations thin particles were produced by grinding the annealed powder with an agate mortar and pestle. Subsequently, a diluted suspension in ethanol was produced, dripped on a thin carbon film supported by a copper grid, and dried in air.

For a general characterization of the microstructure a high-voltage electron microscope (EM 7, AEI Scientific Apparatus Ltd, UK) with an accelerating voltage of 1000 kV, was used. Owing to the high accelerating voltage, powder particles with thickness up to several micrometres could be investigated.

3. Results and discussion

3.1. Hydroboration and pyrolysis of PMVS

The reaction of dichlor (organo) vinylsilanes with potassium or potassium/sodium alloy yields polycarbosilanes and is accompanied by the loss of the reactive vinyl function. In contrast, dechlorination with sodium results in the formation of polyorganovinylsilanes [11]. Accordingly, PMVS is obtained by the reaction of dichlordimethyl- and dichlormethylvinylsilane with sodium in toluene (Equation 4).

$$m\,\mathrm{CH_3(CH_2=CH)SiCl_2} + n\mathrm{(CH_3)_2SiCl_2} \xrightarrow{\mathrm{(CH_3)_3SiCl/Na}} \mathrm{(CH_3)_3Si}\,[\text{–}\mathrm{(CH_2=CH)SiCH_3}\text{–}]_m[\text{–}\mathrm{CH_3SiCH_3}\text{–}]_n\mathrm{Si(CH_3)_3} \quad (4)$$

The vinyl groups present in PMVS react with $(CH_3)_2S \cdot BH_3$ resulting in the addition of BH_3 to the C=C double bond. Further intermolecular reaction of the hydroborated product enhances the crosslinking of the polymer which is confirmed by a significant increase of the molecular weight (Table I). The average of the molecular weight of the as-synthesized polymethylvinysilane is determined to be 831 g mol^{-1} with a polydispersity $M_w/M_n = 3.7$ and is raised to $M_n = 1224$ g mol^{-1} with $M_w/M_n = 17.6$ in the hydroborated product.

Fig. 1 shows the infrared spectra of PMVS before and after hydroboration. It is obvious that the typical vinylic C–H vibrations of PMVS located at 3050, 1005, and 936 cm^{-1} are completely eliminated in the hydroborated PMVS. The appearance of a broad band at 2530 cm^{-1} implies that not all B–H bonds have reacted during hydroboration. The strong Si–H stretching band at 2100 cm^{-1} in the polyborosilane is due to a reduction of residual Si–Cl bonds present in the synthesized PMVS $\nu_{Si-Cl} = 530$ cm^{-1}) by the reaction with BH_3. The vinylic carbon atoms in PMVS show chemical shift values of $\delta = 131.5$ p.p.m. ($=CH_2$ and 137 p.p.m. ($=CH$) in the ^{13}C-NMR spectrum. In the ^{1}H-NMR spectrum, the vinylic H-atoms lead to a multiplet centred at 5.9 p.p.m. The ratio of the amount of vinyl to methyl groups is determined to be 1:6.5 by estimation from an integration of the peak areas. In contrast, vinylic absorption frequencies cannot be found by NMR spectroscopy in

TABLE I Molecular weight distributions (GPC) of PMVS and of hydroborated PMVS. The elemental compositions of the polymeric and ceramic materials are also listed. The pyrolysis of the hydroborated PMVS and the isothermal heat treatments of the ceramic products were conducted in an argon atmosphere.

Product	M_n (g mol^{-1})	M_w/M_n	Composition (wt %)						
			Si	C	B	H	O	S	Cl[a]
PMVS	831	3.7	n.d.	47.8	–	9.6	n.d.	–	1.7
Polyborosilane[b] as-synthesized	1224	17.6	37.3	46.0	4.1	9.9	1.3	0.4	1.2
Polyborosilane[c] as-synthesized	1464	16.1	n.d.	n.d.	n.d.	n.d.	n.d.	–	n.d.
$Si_xC_{x+y}B_z^d$, 1000° C	–	–	48.8	38.7	6.7	–	2.5	0.2	1.0
$Si_xC_{x+y}B_z$, 1700° C	–	–	49.4	39.4	6.9	n.d.	n.d.	n.d.	n.d.
$Si_xC_{x+y}B_z$, 2000° C	–	–	49.5	39.9	6.3	n.d.	n.d.	n.d.	n.d.
$Si_xC_{x+y}B_z$, 2200° C	–	–	50.3	40.4	5.4	n.d.	n.d.	n.d.	n.d.

[a] Owing to the non-aqueous work-up, the as-synthesized polymers contain residual chlorine.
[b] Hydroborated with $BH_3 \cdot S(CH_3)_2$.
[c] Hydroborated with $BH_3 \cdot THF$.
[d] Analytical data were derived from PMVS hydroborated with $BH_3 \cdot S(CH_3)_2$.

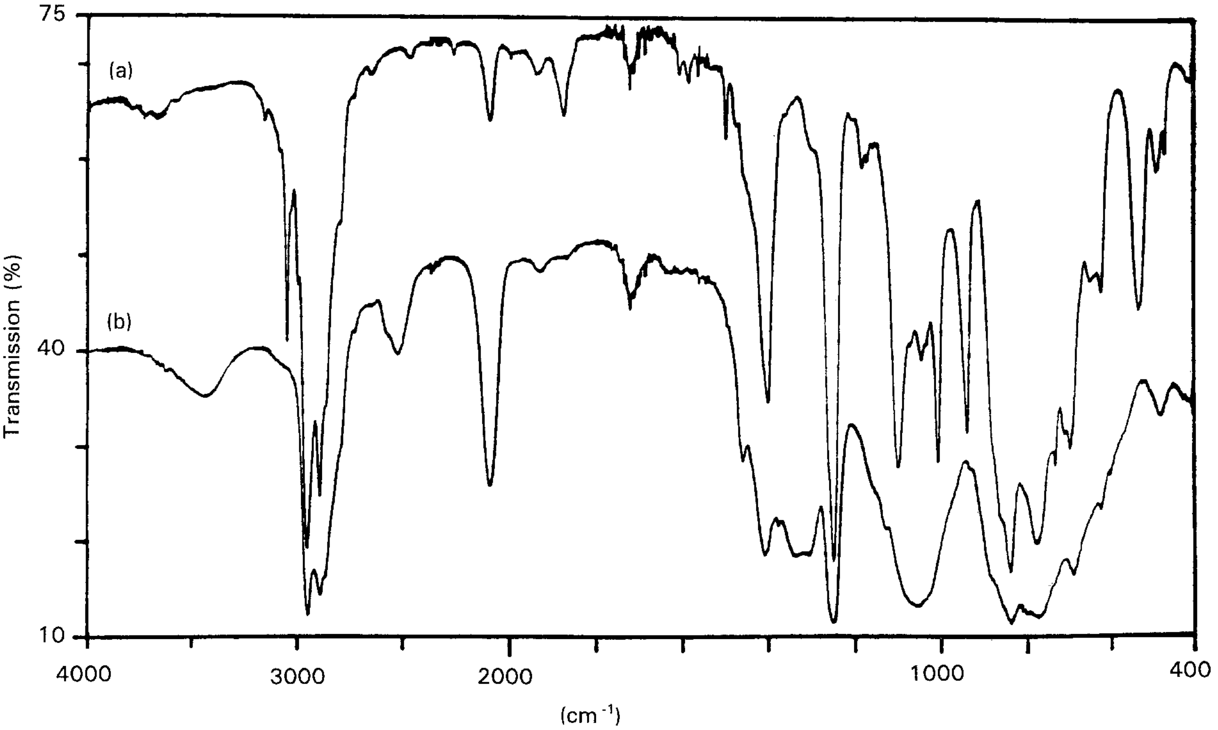

Figure 1 Infrared spectra of polymethylvinylsilane (PMVS); (a) as-synthesized, (b) after hydroboration with $BH_3{\cdot}S(CH_3)_2$ in toluene.

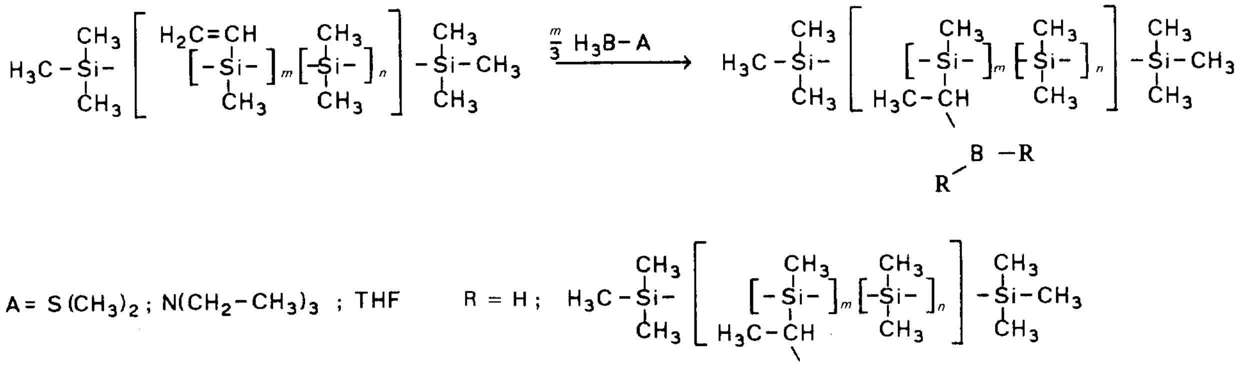

Figure 2 Reaction scheme representing the hydroboration of PMVS with $BH_3{\cdot}S(CH_3)_2$ in toluene.

the hydroborated PMVS. ^{11}B-NMR investigations of the polyborosilane reveal a broad single peak located at 80 p.p.m indicating the presence of trigonal boron atoms surrounded by carbon atoms. Additionally, higher boranes are found as by-products in the reaction mixture. B_5H_9 can clearly be identified by the chemical shift values of $\delta = -12.85$ and -51.99 p.p.m [12] in the proton decoupled $\{^1H\} - {}^{11}B$-NMR spectrum. The formation of higher boranes is due to the applied excess $BH_3{\cdot}S(CH_3)_2$. According to the spectroscopic findings, the hydroboration reaction of PMVS can be represented by the reaction scheme given in Fig. 2. The elemental composition of PMVS and the hydroborated product are listed in Table I.

Fig. 3 shows the thermal behaviour of polyborosilane between room temperature and 1500 °C. The weight loss starts at 125 °C and is completed at 850 °C. In the low-temperature range up to 300 °C, evaporation of volatile oligomers occurs, whereas at temperatures above 300 °C, decomposition of the polymer with loss of hydrogen and hydrocarbons (CH_4) and with the simultaneous formation of an inorganic network takes place [13]. The ceramic residue is determined to be 63%. At $T \geq 1350$ °C an additional mass loss is observed, indicating the evolution of residual hydrogen as well as CO and SiO due to oxygen contamination of the as-synthesized polyborosilane [13].

Generally, hydroboration is reversible, as can be found in low molecular organoboron compounds [14]; hydroborated PMVS, however, can be thermally decomposed without losing boron. The measured silicon, carbon and boron contents of the polyborosilane-derived Si–C–B ceramic obtained at 1100 °C are also listed in Table I. It is evident that the molar Si/B ratio decreases from 3.53 in the hydroborated polymer to 2.74 in the ceramic. Thus, it can be concluded that the relative amount of silicon-containing decomposition products released during pyrolysis is higher than that of boron-containing pyrolysis gases.

The Si–C–B material obtained at a reaction temperature of 1000 °C is completely X-ray amorphous

(Fig. 4) and can be considered to be a silicon boron carbide. In combination with the results of the elemental analysis, the amorphous solid has a molar composition $\mathrm{Si}_{1.7}\mathrm{C}_{3.2}\mathrm{B}_{0.6}$. The boron content in the polymer and hence in the $\mathrm{Si}_x\mathrm{C}_{x+y}\mathrm{B}_z$ ceramic can be increased by the hydroboration of PMVS containing a higher amount of vinyl groups. As a consequence, the carbon content will also be increased.

3.2. Crystallization of silicon boron carbide at higher temperatures

According to the ternary Si–C–B phase diagram [15] the formation of the thermodynamically stable phases β-SiC, $\mathrm{B}_4\mathrm{C}$, and carbon is expected at higher temperatures (≫ 1000 °C)

$$\mathrm{Si}_x\mathrm{C}_{x+y}\mathrm{B}_z \xrightarrow{\Delta} x\beta\text{–SiC} + \frac{z}{4}\mathrm{B}_4\mathrm{C} + \left(y-\frac{z}{4}\right)\mathrm{C} \quad (5)$$

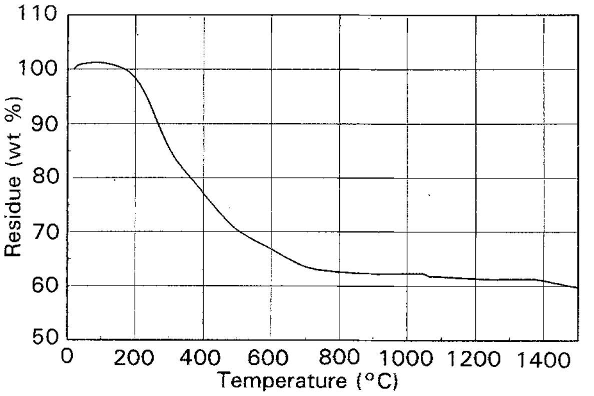

Figure 3 Thermal gravimetric analysis of hydroborated PMVS in the temperature range between room temperature and 1500 °C in flowing argon.

In our case, the values for x, y, and z are calculated to be 1.7, 1.5, and 0.6. X-ray powder diffractometry reveals that annealing of $\mathrm{Si}_{1.7}\mathrm{C}_{3.2}\mathrm{B}_{0.6}$ at 1500 °C in an argon atmosphere for 1 h gives rise to crystallization of β-SiC. The generation of $\mathrm{C}_{\mathrm{graphite}}$ and $\mathrm{B}_4\mathrm{C}$ can be observed in the silicon boron carbide heat treated at $T \geq 1700$ °C as is shown by Fig. 4. In addition to the typical diffraction pattern of β-SiC, the (0 2 1) reflection stemming from $\mathrm{B}_4\mathrm{C}$ (5R-phase) located at $2\Theta = 37.79$ (literature value $2\Theta = 37.79$ [16]) is visible with low relative intensity (~2%) in the material annealed at 2000 °C. Additionally, the (0 0 2) reflection of graphite is clearly assigned at $2\Theta = 26.4$ [17]. The analytical data given in Table I show that the boron content decreases at temperatures exceeding 2000 °C.

The crystallite sizes are in the range of 25 nm in the material heat treated at 1500 °C and 250 nm as the maximum size in the product obtained after tempering at 2000 °C, as determined from the transmission electron micrographs shown in Fig. 5. The β-SiC crystallites can be distinguished by their typical stacking faults (Fig. 5b). Fig. 6a shows a transmission electron micrograph of a representative particle of the material annealed at 2000 °C. The elemental distribution of boron, carbon, nitrogen and silicon analysed by ESI (Fig. 6c–f) confirms the phase separation expected

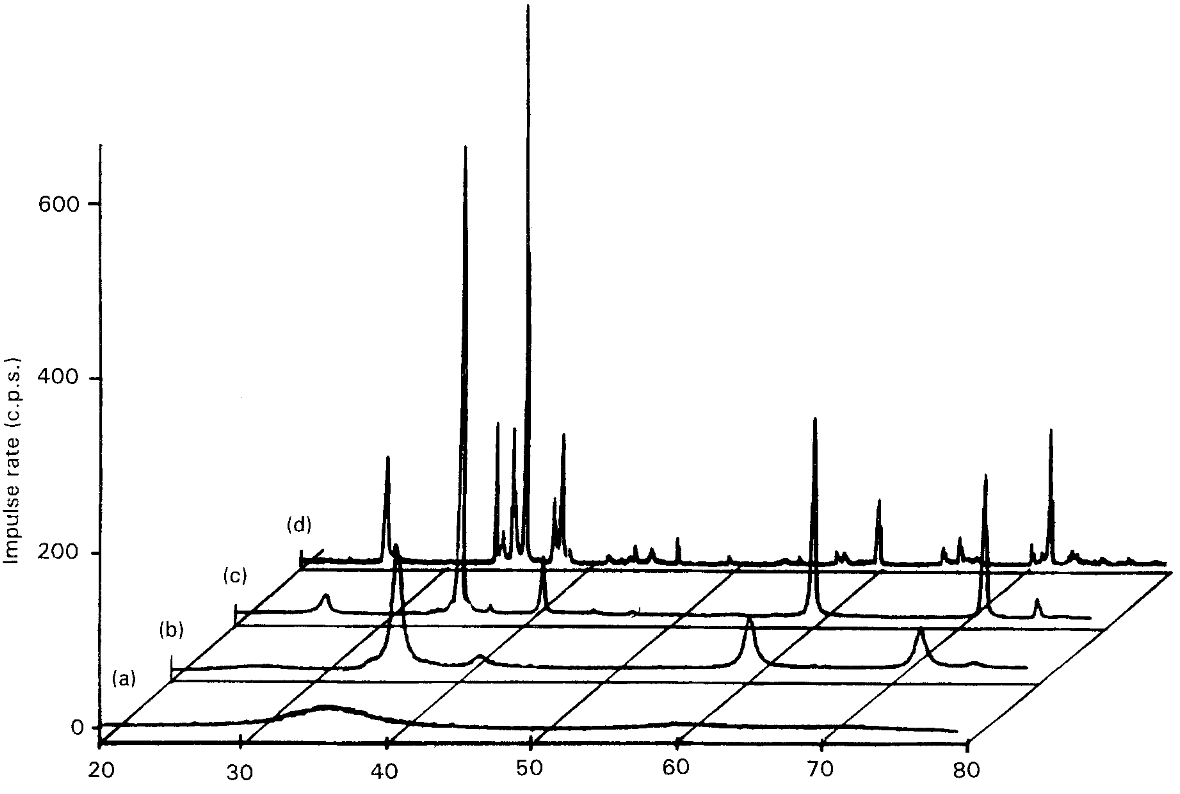

Figure 4 X-ray diffractograms of Si–C–B powder obtained after pyrolysis of hydroborated PMVS (polyborosilane) at 1000 °C in argon (1 h) and after subsequent heat-treatments of the synthesized Si–C–B material at 1500 and 2000 °C in argon with 1 h isothermal hold at the final temperature: (a) 1000 °C, (b) 1500 °C, (c) 2000 °C, (d) 2200 °C.

from Equation 5 and is in agreement with the X-ray powder diffractogram. The elemental maps clearly show the presence of B_4C and SiC particles embedded in a boron-containing carbon phase. Owing to the high mass and thickness of the SiC particles, their carbon content cannot be detected in the carbon-distribution map. Furthermore, a high background produced by the supporting carbon film has to be subtracted from the carbon-distribution image. This presumably removes the small signal produced by the carbon in B_4C as well. The carbon phase is assumed to consist of a graphite-like sheet structure with partial substitution of boron for carbon. In electron diffraction patterns the carbon phase produces Debye–Scherrer rings which could be indexed with the *d*-spacings of graphite. Taking into account the analytical results (Table I) and neglecting the formation of the few B_4C particles, the graphite-like carbon contains approximately 25 at % boron and corresponds to a composition near BC_3. Whereas the maximum amount of boron dissolved in graphite was determined by Lowell in 1967 to be 1.5 at % at 2000 °C [18], the formation of carbon materials with significantly higher contents of boron and/or nitrogen has been reported in a series of papers published in the last two decades [19–21]. For example, a compound with the stoichiometry BC_3 has been described by Kouvetakis *et al.* in 1986 and was obtained by the gas-phase reaction of boron trichloride, BCl_3, with benzene, C_6H_6 [20]. Furthermore, BN particles are also present in small amounts, indicating the dissolution and reprecipitation of boron and nitrogen by the BN crucible used. Finally, an oxygen map proved that no oxygen-containing phases have been formed. The overall microstructure resulting from the phase separation is shown schematically in Fig. 6b.

Annealing the silicon boron carbide at 2200 °C results in an abnormal grain growth of the SiC crystallites which is accompanied by the phase transformation β-SiC → α-SiC. The X-ray powder diffractogram exhibits the formation of various polytypes of the SiC α-phase (Fig. 4).

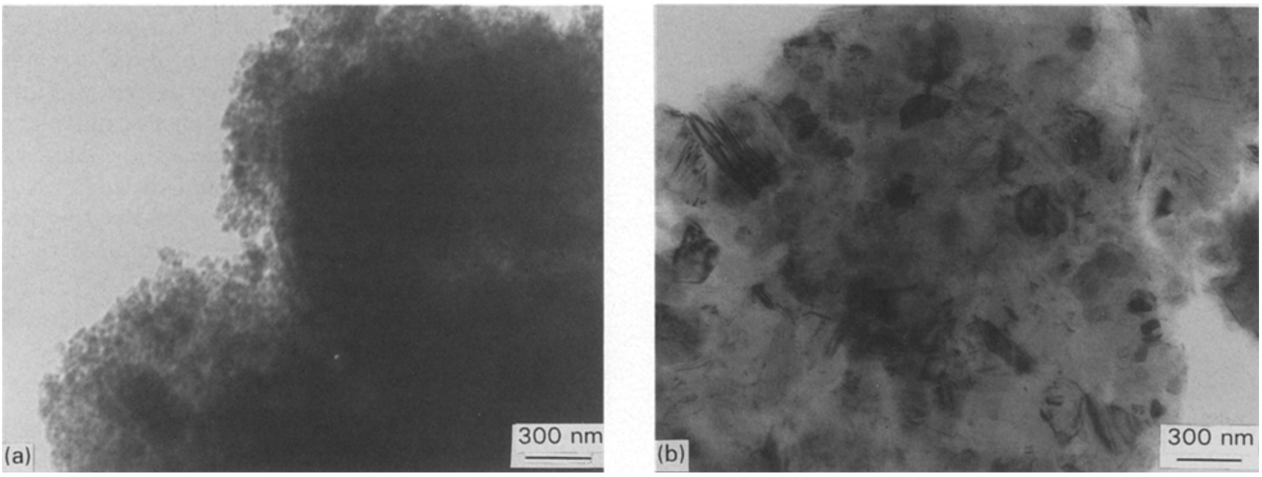

Figure 5 Transmission electron micrographs of the Si–C–B material crystallized at (a) 1500 °C and (b) 2000 °C in argon for 1 h.

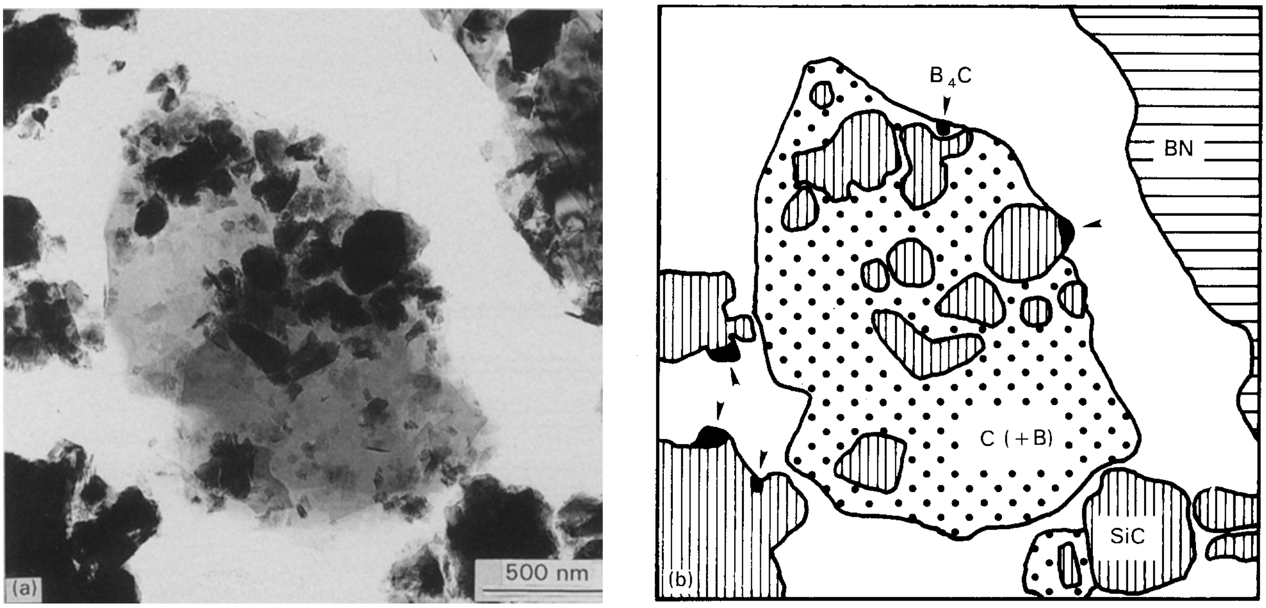

Figure 6 a, b

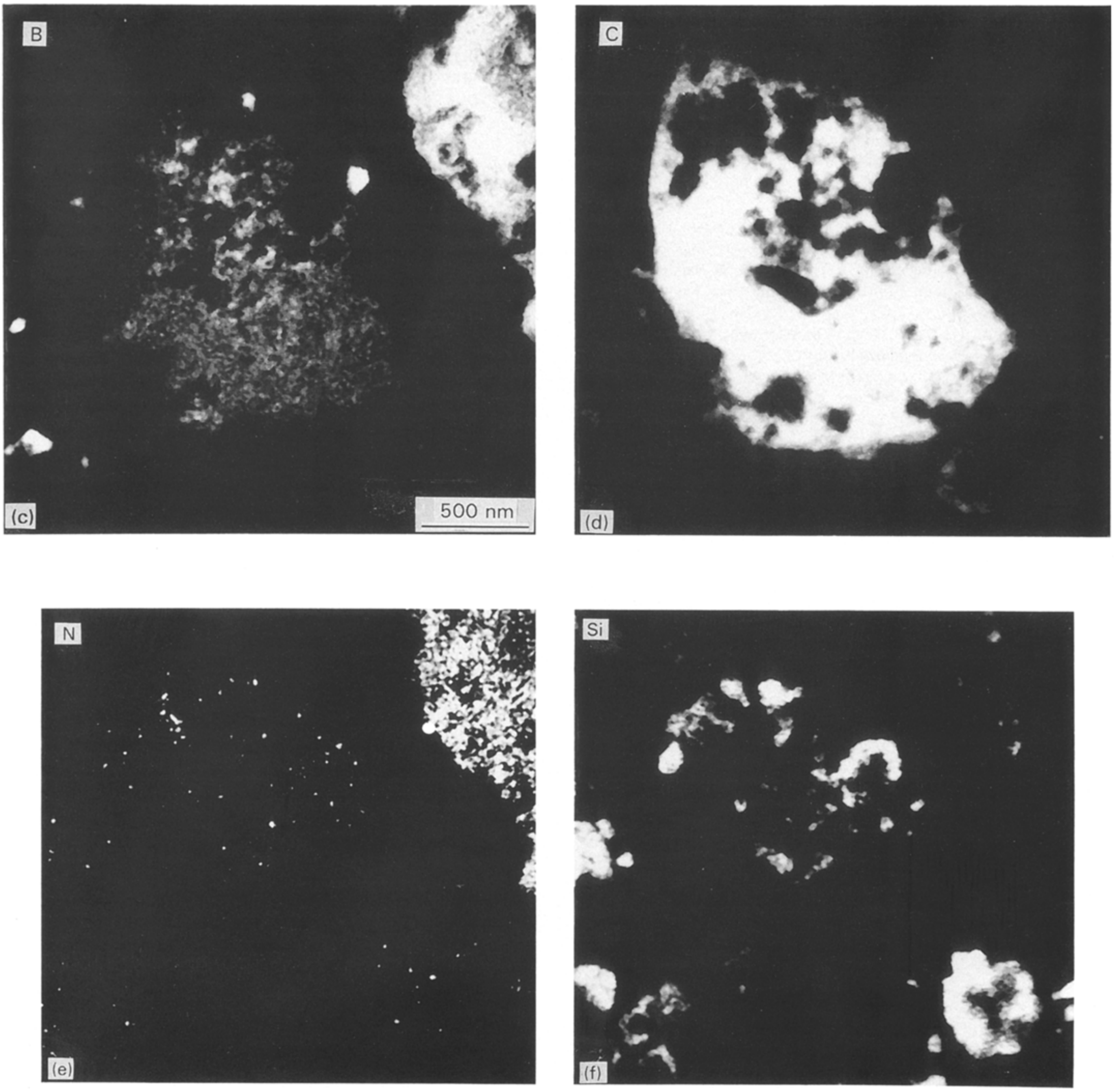

Figure 6 (a) TEM bright-field micrograph revealing the microstructure of silicon boron carbide particles heat treated at 2000 °C in argon for 1 h. The phases detected by ESI are summarized schematically in (b). Dotted areas represent the boron-containing carbon phase, vertically hatched areas the SiC, horizontally hatched regions the BN and black areas indicated by arrows the B_4C. The individual elemental distribution images of boron, carbon, nitrogen and silicon, determined by ESI are shown in (c–f), respectively, for the same specimen area.

4. Conclusions

Vinyl groups containing polyorganosilanes can be hydroborated by BH_3-adduct compounds resulting in a cross-linking of the polymer. The viscosity of the hydroborated polymers is significantly increased. This behaviour can be utilized for the adjustment of the precursor properties such as melting range, viscosity or volatility. The thermal decomposition of hydroborated polyorganosilanes results in the formation of X-ray amorphous silicon boron carbides with the general formula $Si_xC_{x+y}B_z$. At temperatures exceeding 1400 °C, the silicon boron carbide crystallizes giving ultrafine composites containing β-SiC, B_4C, and graphite-like boron containing carbon phases BC_x.

Acknowledgements

The authors gratefully acknowledge the financial support by the KSB-foundation, Stuttgart, Germany, and the Keramikverbund Karlsruhe Stuttgart (KKS), Germany. We also thank M. Knehr, Institut für Technische Chemie II, University of Stuttgart, for the measurement of the gel permeation chromatograms.

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Received 6 August 1992
and accepted 4 January 1993