

SiC/BN Composites by Spark Plasma Sintering (SPS) of Precursor-Derived SiBNC Powders

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Abstract

Preceramic polyborocarbosilazane was pyrolysed at 900 °C and 1400 °C, respectively, yielding amorphous SiBNC. The as-obtained powders were subsequently spark plasma sintered (SPS) at temperatures in a range between 1400 °C and 1800 °C for 10 minutes under uniaxial pressure of 50 MPa. The samples have been characterized by SEM, TEM, XRD, helium pycnometry and Vickers hardness measurements. Independent of the pyrolysis temperature of the starting materials, the most compact samples were obtained by SPS at 1800 °C. In SPS conditions the onset of crystallization and phase separation of the amorphous SiBNC ceramic is substantially reduced as compared to conventional heating. A composite microstructure is obtained, which consists of SiC crystallites with diameters smaller than 500 nm, embedded in a matrix of turbostratic BN. Hardness values increase to 3 GPa when the SPS temperature is raised. TGA in O₂ shows a high resistance against oxidation of the SPS compacts.

Keywords: Precursor-derived ceramics, composites, microstructure analysis, SiC, Spark plasma sintering

I. Introduction

Challenging established high-temperature structural materials like SiC and Si₃N₄, ceramics based on amorphous networks containing the elements Si-B-N-C¹⁻⁴ were introduced in the 1990s. These materials are produced by pyrolysis of preceramic polymers, a method which ensures a homogeneous distribution of the constituting elements at an atomic level.

The obtained amorphous materials show a high resistance against oxidation, due to the formation of a protective passivation double-layer, and an extraordinary stability against crystallization up to temperatures of around 1700 °C, or even higher, depending on the precursor system used⁵⁻⁸. This exceptional resistance to crystallization results from the 3-dimensional network of strong covalent bonds and from low self-diffusion of the constituting elements. Typical building blocks are SiN₄ and BN₃ units, carbon is either bonded to nitrogen or other carbon atoms, but not to silicon or boron^{9,10}.

Up to now, processing of SiBNC ceramics has mainly focussed on the production of fibers for reinforcement in ceramic composites (CMCs). By spinning the viscous melt, a thin thread of polymer is obtained, which is subsequently cured until it becomes unmeltable, and finally pyrolysed. Typical diameters of the resulting ceramic fibers are 8–14 μm. The pyrolysis gases can be carried out of the body of the fiber easily. After the heat treatment, the fibers show a tensile strength of 2-4 GPa and a density of 1.8 g/cm^{32,11}.

In this work, amorphous SiBNC powders were used as starting materials for producing compact SiC/BN composites by spark plasma sintering (SPS).

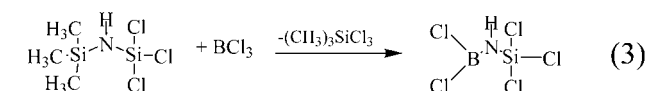
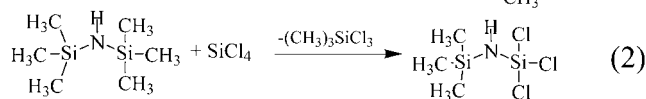
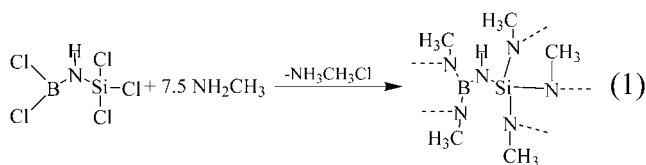
Similar composites have occasionally been studied before. For example, composites of hard ceramics containing boron nitride have been shown to have high thermal shock resistance¹², and h-BN was introduced in Si₃N₄ ceramics to improve the machinability by the formation of weak boundaries^{13,14}. SiC-BN composites were produced using SiC and BN starting powders¹⁵ or by the chemical reaction of Si₃N₄ + B₄C + 2C¹⁶.

In SPS treatment, a pulsed current is applied to a powder mixture, which facilitates the use of lower sintering temperatures and shorter dwell times. At short dwell times, this procedure generally reduces grain coarsening, yields a finer microstructure and a good compaction even of refractory materials. For example, with this approach, nanostructured cobalt ferrites were prepared¹⁷, Si₃N₄ with smaller grain sizes as compared to hot pressing¹⁸, and SPS-processed SiC shows higher strength and toughness than a conventionally hot-pressed reference^{19, 20}.

II. Experimental procedures

The preceramic polymer was obtained by the reaction (eq. 1) of trichlorosilyl-amino-dichloro-borane (TADB) with methylamine as described by Baldus et al¹. TADB is synthesized in a two-step reaction of hexamethyldisilazane with SiCl₄ (eq. 2) and subsequently BCl₃ (eq. 3).

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All reactions were performed using the standard Schlenk technique under argon for protection against air and moisture. Liquid polyborosilazane was pyrolysed in BN crucibles placed in a quartz tube by heating up in a flow of argon to 900 °C (100 °C/h, dwell time 3 h at 300 °C and 900 °C). According to literature, this material still contains reactive sites and volatile components, which are removed by further heating up to 1400 °C (corundum tube, argon flow, 300 °C/h, dwell 3 h)¹⁰. The starting materials used in the SPS experiments were subjected to two different heat treatments, either at 900 °C or at 1400 °C. The former batches are still sensitive to air and moisture, and were handled in a glove box.

The powders were ground under inert atmosphere in a WC ball mill for 60 min and then filled in a graphite die with a diameter of 8 mm, which was placed into the SPS setup (Dr.Sinter-Lab, 515S, Sumitomo Coal Mining Co.). The die was lined with a carbon foil for an easier removal of the product after treatment. A pressure of 50 MPa was applied, while the chamber was evacuated to $1 \cdot 10^{-3}$ mbar. SPS was performed with a dwell time of 10 min at varying temperatures between 1400 °C and 1800 °C, and a heating rate of 200 °C/min. The temperature was recorded with a pyrometer, which was focused on a drilled cavity in the die. The true temperature within the powder mixture exceeds the temperature measured at the graphite container²¹. The temperatures given throughout this paper are the values measured by the sensor.

The samples are labelled as follows: C[pyrolysis temperature]-[SPS temperature], e.g. sample C900-1400 was made from a powder pyrolysed at 900 °C and subsequently spark plasma treated at 1400 °C.

Crystalline portions of the samples were identified with X-ray diffraction (XRD) (Bruker D8, Cu K α radiation). The respective microstructures were examined using scanning electron microscopy (SEM) (Philips XL30 ESEM) on samples polished down to 1 μm diamond suspension, and transmission electron microscopy (TEM) (Zeiss 912 Omega). This TEM is equipped with an in-column energy filter for taking elemental maps by acquiring energy-filtered TEM (EFTEM) images. For the TEM investigations a wedge of the compact sample was prepared by the tripod polishing technique (Allied Multiprep). A slice of the sample was polished with diamond foils down to a diamond grit size of 0.5 μm from one side, followed by polishing with colloidal silica. The reverse side was polished in the same manner, but inclined by an angle of 2° with respect to the first side. The surface was cleaned by ion thin-

ning (Gatan Pips) at an angle of 8°. After this treatment, one edge of the sample was electron transparent and could be used for TEM investigations.

Chemical compositions were determined with a Leco TC-438 hot-gas extraction analyzer for nitrogen and oxygen, simultaneously. Carbon was quantified with a Leco C-200 hot-gas extraction analyzer, boron and silicon with a Vista Prosimultanes ICP-OES spectrometer, after digestion of the samples in 48% HF in a Teflon-lined autoclave²².

The hardness was determined by Vickers indentation (Buehler Micromet 1 Micro Hardness Tester) with 20 s loading time and a load of 1 kg. For statistics, 20 indentations were made per sample, and the diagonals were measured using SEM. Density was measured by helium pycnometry (micromeritics AccuPyc 1330 GB). The high-temperature stability was recorded with TGA (Netzsch STA 409), applying a heating rate of 10 K/min to 1300 °C in constant oxygen flow.

III. Results and discussion

All SPS experiments resulted in compact samples. The polished cross-sections in fig. 1 show the significant decrease of the porosity in compacted C900 powders with an increase in sintering temperature. At the lower SPS temperature of 1400 °C the cohesion of the grains is still so poor, that during polishing whole flakes are torn out (fig. 1a). The surface of such bodies is rough, and the shapes of the original grains from the powder are still discernible. After treatment at 1600 °C, the samples have sufficient stability for cutting and polishing (fig. 1b). But even these samples still show a high amount of porosity, which is reduced considerably, when the SPS temperature is increased to 1800 °C (fig. 1c).

Also the surface of the C1400 samples, spark plasma treated up to 1600 °C, retain a granular structure which originates from the grains of the starting powder (fig. 2a and b). At a sintering temperature of 1800 °C, again a dense structure is obtained (fig. 2c). As the only difference between the differently pretreated starting materials, the C900 powder shows a lower onset temperature for coalescence of the powder than the C1400 powder. This higher sintering ability of C900 is related to the incomplete pyrolysis of the preceramic polymer at 900 °C. The pyrolysis is, de facto, finished during SPS treatment, resulting in a more active surface of the grains.

The Vickers hardness of the samples increased with increasing SPS temperature (fig. 3). After the treatment at 1800 °C, a hardness of 3.3 GPa is attained by the C900 samples, while the C1400 samples show a maximum hardness of 3.0 GPa at 1800 °C. These hardness values are in the same order of magnitude as those for the Si₃N₄/BN system (4-9 GPa)¹⁴.

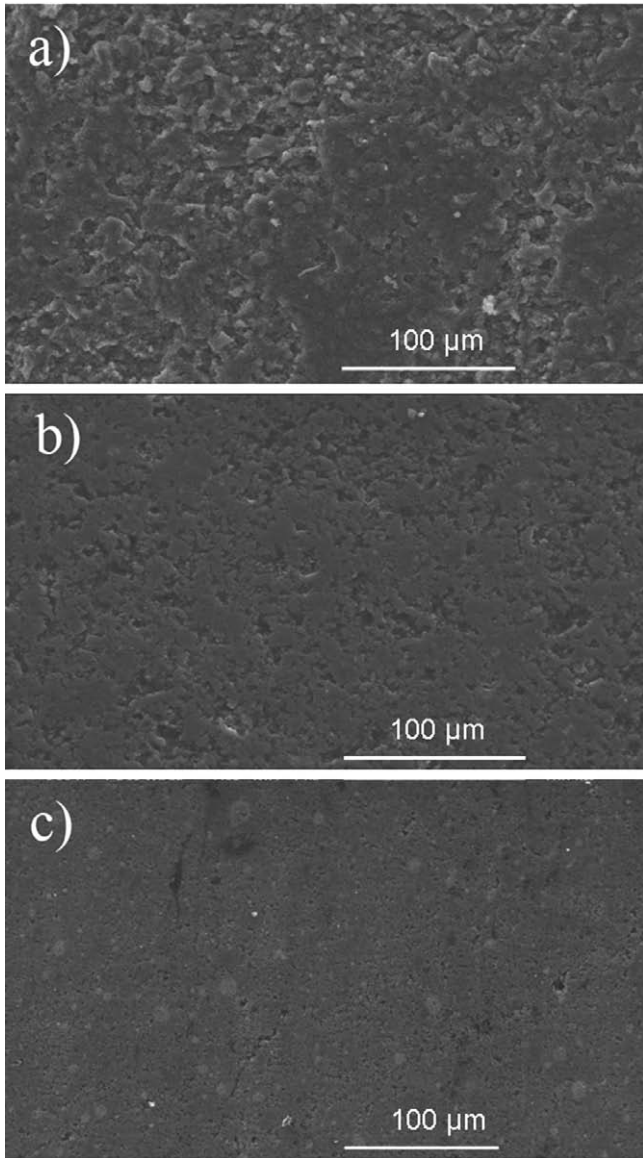


Fig. 1: Polished surfaces of the C900 samples, SPS at a) 1400 °C, b) 1600 °C and c) 1800 °C.

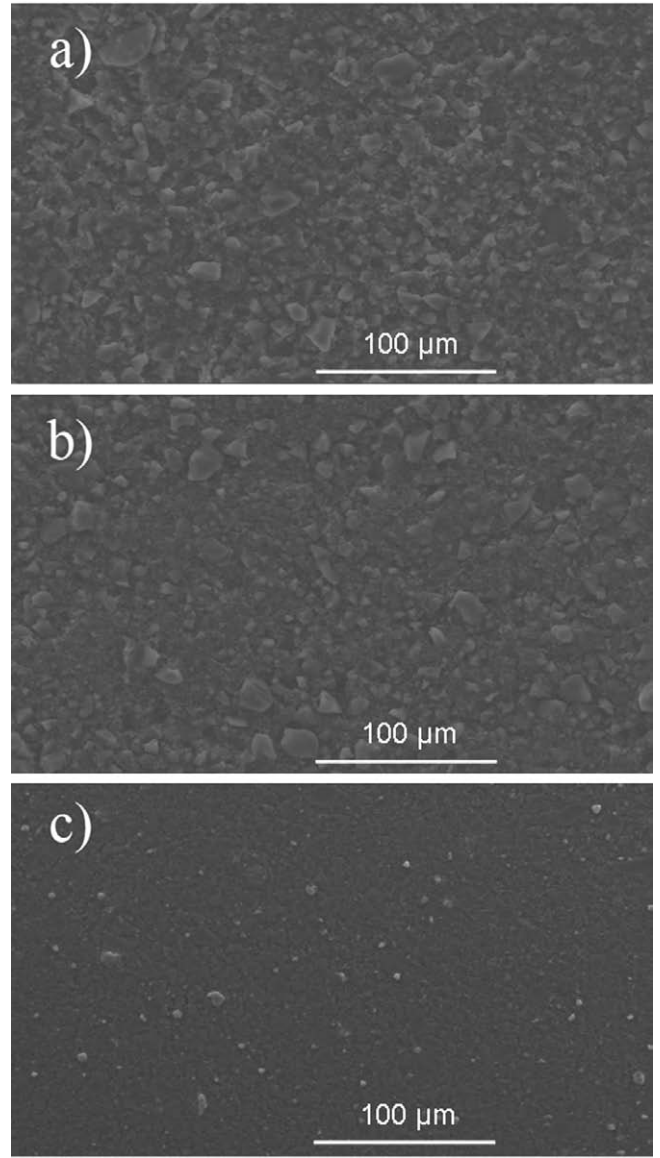


Fig. 2: Polished surfaces of the C1400 samples, SPS at a) 1400 °C, b) 1600 °C and c) 1800 °C.

The density of the compact samples as a function of the sintering temperature is shown in fig. 4. Up to C900-1600 the measured density increases with temperature from 1.95 g/cm³ (at 1400 °C) to 2.35 g/cm³ (at 1600 °C), and more slowly above 1600 °C. The density of the C900-1800 sample is 2.50 g/cm³. The C1400 samples show a rather similar behavior, with the density rising to 2.44 g/cm³ at 1600 °C, and reaching 2.55 g/cm³ at 1800 °C.

The evolving crystalline phases were determined using XRD (fig. 5 and 6). Only C1400-1400 retained a fully amorphous structure. In all other measured XRD patterns the presence of β-SiC with reflections at 35.6°, 41.3°, 60.0°, 71.8° and 75.5° is evident. Additional peaks appear around 33.7° and 38.0°, which originate from stacking faults of SiC. With increasing sintering temperatures a higher ratio of SiC crystallites is formed by both C900 and C1400, which is expressed by more distinct intensities. The reflection at 26° is assigned to boron nitride. It evolves from the amorphous background at a SPS temperature of 1800 °C. Peak broadening indicates a turbostratic disorder of that phase²³.

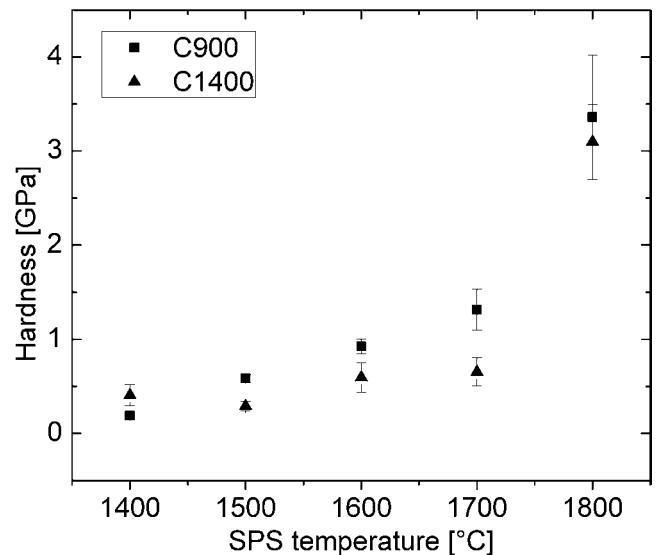


Fig. 3: Vickers hardness of SPS processed C900 and C1400 samples plotted against sintering temperature.

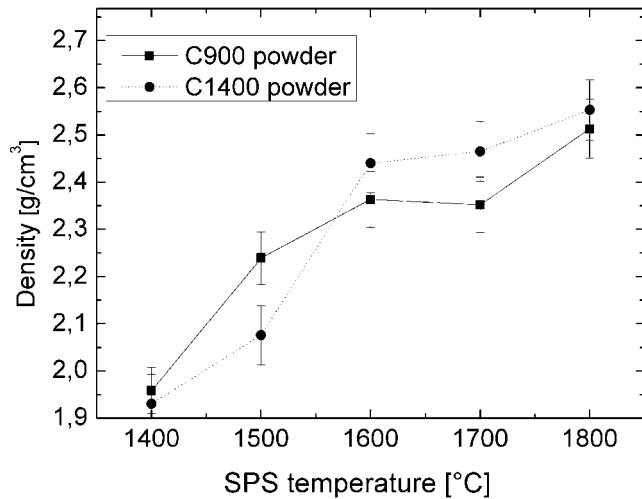


Fig. 4: Density of SPS samples of Si-B-N-C with increasing sintering temperature.

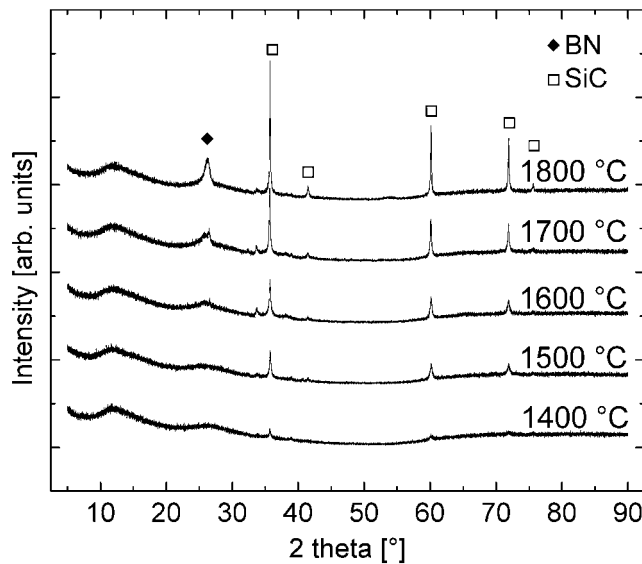


Fig. 5: Powder-XRD pattern for C900 after SPS at temperatures between 1400°C and 1800°C.

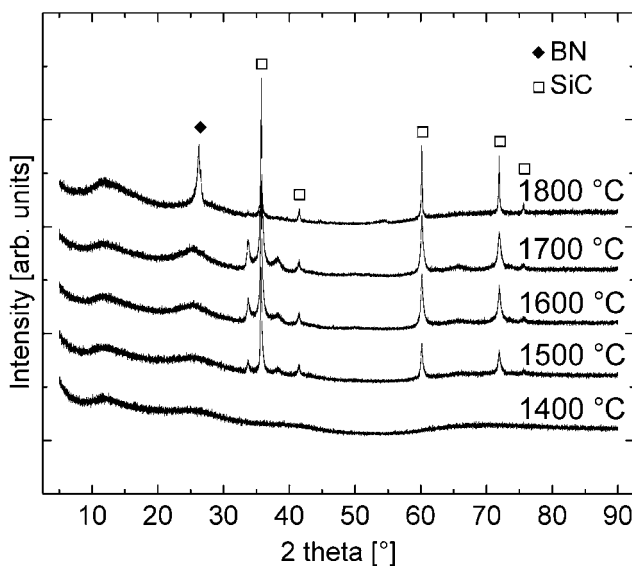


Fig. 6: Powder-XRD pattern for C1400 after SPS at temperatures between 1400°C and 1800°C.

It was reported, that TADB-derived SiBNC is stable against crystallization up to a temperature of 1900 °C⁵. The low self diffusion of those ceramics at high temperatures hinders crystallization as well as sintering. The lower offset of crystallization observed at SPS is obviously related to the temperature difference between the sensor and the powder mixture²¹. Consequently, in SPS processing we observe the formation of SiC at a significantly lower temperature.

On the other hand, the increase of crystallinity explains the fact that the density of the SPS samples approaches 2.50 g/cm³ at higher SPS temperature. This corresponds to an average density value of the involved SiC (3.2 g/cm³)²⁴, the turbostratic BN (2.2 g/cm³)²⁵, and some residual closed porosity.

The total composition of the ceramic starting powder obtained by chemical analysis is SiBN_{2.5}C_{1.2}O_{0.1}. Oxygen is a negligible impurity. During SPS processing the structural rearrangement changes the total composition to SiB_{1.1}CN_{1.2}O_{0.1}, measured on C1400-1700. The ratio of the phases SiC:BN is 1:1, according to the reaction shown in eq. 4.



TEM investigations of C1400-1800 revealed a characteristic arrangement of the constituting phases (fig. 7). The size of the primary amorphous grains in the starting powder is determined by the milling conditions. During sintering the material decomposes into the crystalline fine-grained phases, with a loss of the primary grain structure.

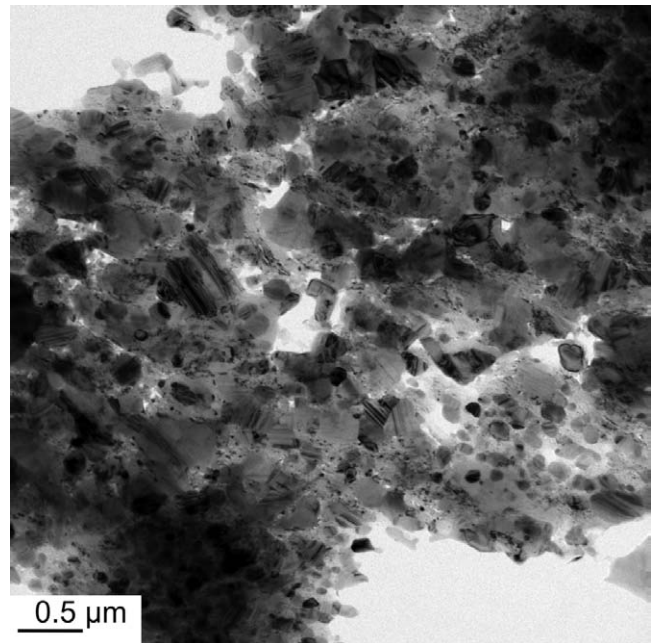


Fig. 7: Bright field TEM micrograph of C1400-1800. The average grain size is below 500 nm.

EFTEM imaging was used to generate spatially resolved elemental maps. Fig. 8a shows grains with a size of several 100 nm, which are embedded in a bright-appearing matrix. In the EFTEM maps in fig. 8b-e, bright areas correspond to high element concentration. Therefore, the grains are assigned as SiC, while the matrix consists of BN.

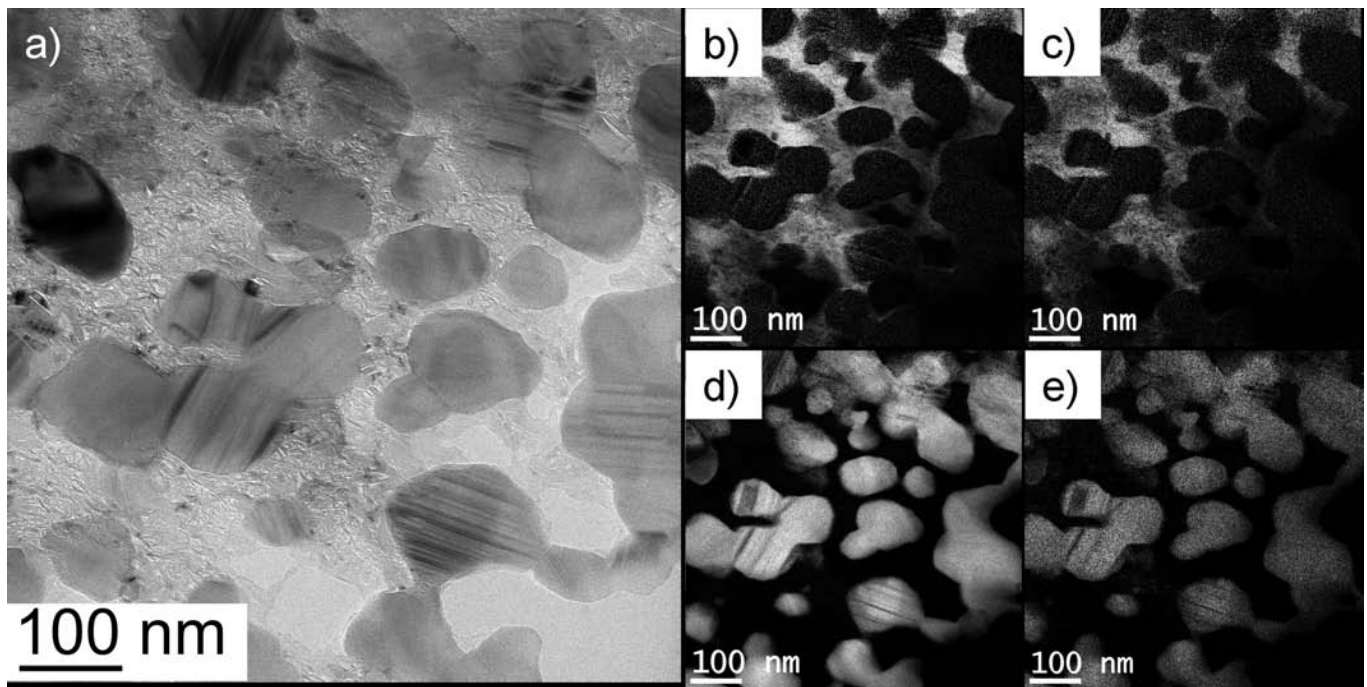


Fig. 8: a) Bright field TEM micrograph of C1400-1800; EFTEM mapping of b) boron, c) nitrogen, d) silicon and e) carbon.

This kind of microstructure is similar to crystallized polymer-derived ceramics in the system Si-B-C-N where compacts were obtained by warm pressing of polymeric powders²⁶. In our work the advantage is the rapid processing of readily pyrolysed powders without the issues of high mass loss or gas evolution during heat treatment.

The oxidation stability was determined with TGA up to 1300 °C in pure O₂ (fig. 9). A mass loss of 1.7 % occurs up to a temperature of 800 °C, and subsequently the mass increases back to 100 %. The mass loss is mainly attributed to the oxidation of residual carbon foil used for the lining of the SPS die. A subsequent uptake of mass above 800 °C arises from a surface oxidation of SiC to SiO₂, resulting in a protective layer, suppressing further oxidation.

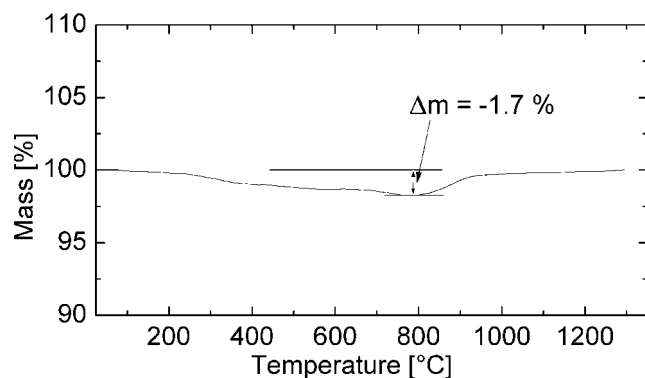


Fig. 9: TGA of C1400-1800 in O₂ atmosphere (heating rate 10 °C/min).

IV. Conclusions

The in-situ formation of a sub-micrometer SiC/BN composite structure can be successfully achieved by crystallization of SiBNC in an SPS setup. The onset temperature for crystallization is notably reduced compared to usual thermal treatment. This effect corresponds to an effective temperature difference of 300-400 °C. Good compaction was obtained with precursor-derived powders by spark

plasma sintering at 1800 °C and 50 MPa. When starting powders that were not fully pyrolysed were used, a lower onset of crystallization was observed. This can be explained by additional reactive sites in the starting material, which facilitate sintering.

During sintering a reorganization of the microstructure takes place. SiC grains are formed with a size below 500 nm, which are embedded in a matrix of BN. The fine assembly is obtained by an in-situ decomposition of the amorphous SiBNC under fast heating in SPS. The formation of the BN phase provides the coalescence of the powder. This phase also hinders the further growth of SiC crystallites by acting as a diffusion barrier. The ceramic composite shows high oxidation resistance up to 1300 °C due to formation of a protective passivation layer of SiO₂.

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