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Effect of boron incorporation on the phase composition and high-temperature behavior of polymer-derived silicon carbide

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ABSTRACT

Within the present work, boron-containing silicon carbide (SiBC) powders and monoliths were prepared from a polyborocarbosilane. The main aspect addressed here relates to the fate of boron in the prepared SiBC ceramics, which has not been clarified unambiguously so far. X-ray diffraction data, corroborated with XPS, FTIR and Raman spectroscopic results indicate that boron preferably gets incorporated within the segregated carbon phase present in polycarbosilane-derived SiC; thus, the prepared SiBC samples show dispersed boron-containing carbon phases with boron contents from ca. 9 to 18 at%. Interestingly, the B-containing carbon phase does not convert into crystalline boron carbide, even upon annealing at very high temperatures and despite the high boron content. Moreover, processing details concerning the pressureless preparation of dense Si(B)C monoliths are considered in the present paper and their high temperature evolution is analyzed.

1. Introduction

Silicon carbide is an important non-oxide ceramic for diverse industrial applications due to its outstanding properties, such as very high hardness and strength, chemical and thermal stability, high melting point, oxidation resistance, high erosion resistance, excellent thermal shock resistance, *etc.*, [1,2].

Due to the highly covalent nature of the silicon-carbon bond, silicon carbide exhibits very low self-diffusion, which restricts its densification upon sintering processes even at high temperatures. Initially, the densification of SiC ceramics was achieved *via* solid-state sintering upon hot-pressing using small amounts of B and C as additives at about 2100 °C. Lange and Gupta suggest that a liquid boron silicon carbon phase activates the densification process and thus silicon carbide can be densified upon liquid-phase sintering processes by using small amounts of ca. 3 wt% carbon and 0.5 wt% of boron [3,4]. However, the required sintering temperatures and pressures are rather high and make these sintering routes costly. Moreover, an inhomogeneous distribution of the additives within silicon carbide might be also considered as being critical [5].

Allylhydrido polycarbosilane (AH-PCS) is considered as a very prominent polymeric source for the production of near stoichiometric silicon carbide [7]. Recently, single-source polymeric precursors for boron-containing SiC have attracted attention due to the improved homogeneity of the resulting ceramics. The allyl and hydrido substituents at silicon in the AH-PCS help to adjust its chemistry and network architecture. The incorporation of boron within the network of AH-PCS was achieved upon hydroboration reactions of the allyl groups [8–10]. Thus, borane complexes (such as borane dimethyl sulfide complex, BMS) and 9-borabicyclo-[3.3.1]nonane (9-BBN) were used for hydroboration purposes. In the available studies, it was reported that SiC prepared from BMS-modified AH-PCS is difficult to process due to its high crosslinking degree [8]. Thus, processing of BMS-modified AH-PCS in monolithic form using warm pressing is not well investigated, due to the poor thermoplastic behavior of the modified precursor.

We have recently reported on the pressureless preparation of dense and crack-free near stoichiometric SiC monoliths *via* cross-linking and pyrolysis of a polycarbosilane, followed by polymer-infiltration-pyrolysis (PIP) cycles [7]. In the present paper we compare the results obtained from AH-PCS with those achieved with the BMS-modified precursor. We report on the thermoplastic processing of BMS-modified AH-PCS and its pressureless conversion into B-containing SiC monoliths with minimum residual porosity. Thus, the overall process for the fabrication of dense boron-containing silicon carbide-based ceramic parts involved

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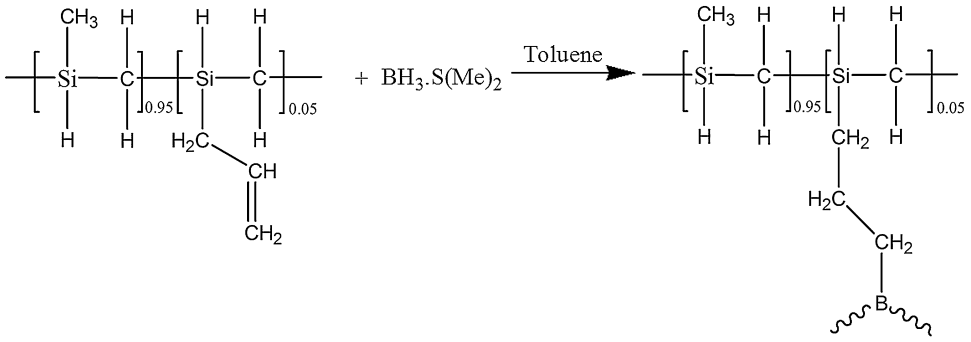

Fig. 1. Hydroboration reaction of SMP-10 by using BMS.

three major steps: (i) synthesis of the single-source-precursor from AH-PCS and BMS; (ii) shaping using warm-pressing and (iii) ceramization process (pyrolysis) of the shaped green-bodies upon heat treatment at temperatures ranging from 1100 to 1900 °C.

In addition to the processing aspects concerning the preparation of dense Si(B)C monoliths, their high temperature behavior was carefully analyzed. The main question here related the fate of boron in the SiBC ceramics, which has not been clarified unambiguously so far in the literature. Thus, in the present paper spectroscopic and diffraction studies were performed in order to understand how and where is boron present in the SiBC monoliths prepared from polyborocarbosilanes and how their phase composition evolves at high temperatures.

2. Experimental procedure

2.1. Materials processing

A commercially available allylhydrido polycarbosilane (SMP-10, Star Fire Systems, USA) was used for the preparation of SiC monoliths. SMP-10 is a clear, amber-colored, viscous liquid and requires no solvents for processing. For the hydroboration reaction, borane dimethyl sulfide complex (BMS) and toluene (Sigma–Aldrich) were used as received (see Fig. 1).

A typical reaction was carried out using Schlenk technique. Thus, SMP-10 was dissolved in toluene in a two neck round bottom-flask. The flask was cooled to −50 °C and backfilled with argon. Subsequently, a BMS solution in toluene was added dropwise. Some gas evolution was observed. The reaction mixture was stirred under the same conditions for 2 h, allowed to reach room temperature and then stirred overnight. After the solvent removal, the obtained highly cross-linked single-source precursor was dried in vacuum (10^{-2} mbar) at 60 °C for 5 h. A number of experiments were performed using different BMS: SMP-10 weight ratios (see Table 1).

The dried solid single-source precursor was cross-linked pressureless in a steel dye (diameter 10 mm) at ca. 300 °C using a pre-compaction pressure of 127.4 MPa at 45 °C. The best behavior during the green-body preparation was found with SiBC-5, *i.e.*, only this composition leads to a crack-free green body.

The obtained B-modified polycarbosilane precursor powders and the optimized green bodies were converted into ceramic materials upon pyrolysis at 1100 °C under argon environment. Additionally, the ceramics (powders and monoliths) were annealed in argon atmosphere at 1300 °C, 1500 °C, 1700 °C and 1900 °C for 3 h using a high-temperature graphite furnace.

2.2. Materials characterization

The polymer-to-ceramic transformation of SMP-10 and the boron-modified precursor was investigated by thermogravimetric analysis (TGA, 449C Jupiter, Netzsch, Gerätebau GmbH, Selb, Germany). The SiBC-based samples were investigated by means of attenuated-total-reflectance FT-IR spectroscopy (ATR-FTIR, Bruker Vertex 70, USA). The carbon content of the samples was determined with a carbon analyzer, CS 800 (Eltra GmbH, Neuss) and the oxygen content with a N/O analyzer, Leco TC-436 (Leco Corporation, Michigan) whereas silicon and boron content were determined at Mikroanalytisches Labor Pascher (Remagen, Germany). The skeletal density and open porosity of the obtained SiC monolithic ceramics were measured by the water immersion method. Scanning electron microscopy (SEM) studies were performed on a Philips XL30 FEG, Netherlands with an acceleration voltage of 10–15 kV. The micro-Raman spectra were recorded with a Horiba HR800 micro-Raman spectrometer (Horiba Jobin Yvon, Bensheim, Germany) equipped with a green laser (irradiation wavelength 514.5 nm). The excitation line has its own interference filter (to filter out the plasma emission) and a Raman notch filter (for laser light rejection).

The specific surface area (S_{BET}) values were determined by the Brunauer, Emmett and Teller (BET) method from the linear parts of the adsorption isotherms. The pore size distribution (PSD) was calculated by the Barrett, Joyner and Halenda (BJH) method from the desorption branches of the isotherms. The total pore volume was calculated from the maximum amount of nitrogen gas adsorption at a partial pressure of $(P/P_0) = 0.999$.

X-ray photoelectron spectroscopy (XPS) measurements were done using a PHI VersaProbe 5000 spectrometer equipped with a monochromatic Al Kα source ($h\upsilon = 1486.6$ eV). The binding energies are referred to the Fermi level of Ag foil. Photoelectrons were collected with the pass energy, $E_{pass} = 23.5$ eV at $\theta = 45°$ with respect to the surface normal.

3. Results and discussion

3.1. Cross-linking of the borane-modified polycarbosilane precursor

Hydroboration and dehydrocoupling reactions are the two main mechanisms contributing to the thermal cross-linking process of the borane-modified polycarbosilane precursor. A number of experiments has been performed with different BMS to SMP-10 ratios, *e.g.*, 1 wt%, 5 wt% and 30 wt% of BMS (SiBC-1, SiBC-5 and SiBC-30), in order to investigate the effect of boron on the precursor-to-ceramic transformation as well as on the densification behavior of the resulting ceramic. The approximate boron content in the resulting ceramic samples is shown in Table 1, indicating that the amount of boron which has been incorporated within SiC upon pyrolysis of the borane-modified polycarbosilane samples containing 5 and 30 wt% borane complex does not differ significantly (0.98 and 1.27 wt%, respectively). This clearly indicates that the borane