Pressureless fabrication of dense monolithic SiC ceramics from a polycarbosilane

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Abstract

This paper presents 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 cycles. The composition and the porosity of the samples strongly depend on the processing temperature. Thus, at 1050–1100 °C, the SiC monoliths are X-ray amorphous and exhibit low amounts of oxygen and excess carbon; their porosity was rather high (>10%). Higher processing temperatures induced the crystallization of β-SiC. The removal of oxygen and excess carbon due to CO release allowed for obtaining near-stoichiometric compositions at 1700 °C. However, the residual porosity of the samples increased. The use of the PIP technique led already after six cycles to dense monoliths (residual porosity ca. 0.5%).

The present study emphasizes the potential of the polymer processing technique for the fabrication of near stoichiometric and dense SiC monoliths, which might be used for structural applications in harsh conditions.

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1. Introduction

Silicon carbide is an important non-oxide ceramic which has 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.1

Silicon carbide has been synthesized since 1892 by using the Acheson process, which involves a solid-state reaction between silica sand and petroleum coke at very high temperatures.2,3 Despite the obtained coarse ceramic is contaminated with oxygen, nitrogen and aluminum, this method is still in use for the production of silicon carbide powders useful for grinding and cutting application. There are numerous methods found in the literature for the production of high quality micro to nano-sized silicon carbide powders.4–7 Also, various processing techniques to fabricate SiC monolithic parts have been developed and reported.8,9 However, due to the highly covalent nature of the Si–C bond, silicon carbide exhibits very low self-diffusion, which restricts its densification even at high temperatures. Consequently, the production of dense silicon carbide parts is rather challenging.

Different methods have been used to produce dense silicon carbide: (i) pressureless solid-state sintering using sintering aids like boron and carbon, which delivers SiC parts with good high-temperature creep and oxidation resistance, but at the same time with poor fracture toughness,10,11 (ii) infiltration of reaction bonded (porous) silicon carbide by molten silicon, which leads to ceramic parts having limited thermal stability due to the relatively low melting point of excess silicon, and (iii) hot-pressing, which however requires also additives as well as large pressures (>2000 MPa without additives12 and 25–70 MPa with additives13,14) and very high temperatures (i.e., beyond 2000 °C15).

Liquid phase sintering (LPS) has been also used to prepare dense silicon carbide using additives such as Al2O3 or

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Al₂O₃ + Y₂O₃, The strength of the obtained ceramics is however affected and limited by the presence of additives, which in turn restrict its use at high temperatures. Thus, there is an obvious and urgent need to find new processing techniques, which allow for producing dense silicon carbide parts without using additives. Within this context, polymer-processing of ceramics has been shown to be a highly promising alternative toward dense ceramic parts, also ceramic films, fibers as well as miniaturized, complex-shaped parts can be obtained via polymer-processing and have been shown to be applicable also for SiC-based materials.

Within this paper, the feasibility of the polymer-processing route for preparing dense, crack-free and stoichiometric silicon carbide monoliths upon using an allyl hydrido polycarbosilane as liquid polymeric precursor was assessed. Thus, the overall process for the fabrication of dense silicon carbide-based ceramic parts involved four major steps:

(i) curing/pre-crosslinking of the liquid preceramic polymer at moderate temperatures to obtain a polycarbosilane-based powder;
(ii) shaping using warm-pressing techniques;
(iii) ceramicization process (pyrolysis) of the shaped green-bodies, which are converted into SiC-based monoliths by heat treatment at temperatures ranging from 1100 to 1700°C and
(iv) liquid precursor infiltration and pyrolysis (PIP).

The prepared green bodies and the ceramic monoliths were investigated with respect to their phase and chemical composition as well as concerning their evolution at high temperatures.

2. Experimental procedure

2.1. Materials processing

A commercially available allyl hydrido polycarbosilane was used as suitable polymer for the preparation of SiC monoliths (SMP-10, Star Fire Systems). SMP-10 is a clear, amber-colored, viscous liquid which requires no solvents for processing. The molecular structure of SMP-10 (Fig. 1) indicates that two main mechanisms can contribute to its thermal cross-linking process, i.e., hydrosilylation and dehydrocoupling reactions (Fig. 2).

For further processing of the liquid SMP-10, it was necessary to convert it thermally into powder. Thus, the thermal curing of the liquid SMP-10 was done at moderate temperatures \( T \leq 250°C \); annealing time of 0.5, 1 or 3 h, see Table 1) via hydrosilylation reaction and provided yellowish polycarbosilane-based powders, which were subsequently ball-milled in inert gas atmosphere (zirconia balls, 180 rpm, 2 h) and further processed into monoliths by using uniaxial warm-pressing at significant higher temperatures \( T > 250°C \). Thus, while uniaxial pressing, further cross-linking of the polymer (by means of dehydrocoupling reactions) occurred and led to infusible polycarbosilane-based monoliths.

The obtained powder from the thermal curing process of SMP10 \( (250°C, 3 \text{ h}) \) was uniaxially warm-pressed in a steel dye (diameter 10 mm) at temperatures between 180 and 300°C under different applied pressures (Table 2). At low temperatures \( (180–250°C) \), no compaction of the powders was observed. This is due to the fact that obviously the hydrosilylation process is already completed during curing/pre-cross-linking of the liquid SMP-10 polymer and the dehydrocoupling processes need higher temperatures. Thus, the compaction of the powder occurred at temperatures as high as 300°C. However, crack formation within the green bodies occurred and was related to the high uniaxial pressures applied. Further optimization of the process (see Table 2) eventually led to the fabrication of crack-free SMP-10 based green bodies. Thus, the optimized green-body fabrication process involved a pre-compaction step at room temperature (ca. 127 MPa), followed by pressure release and pressureless cross-linking.

The optimized green-bodies were converted into ceramic pellets upon pyrolysis at 1050°C under argon environment. The obtained SiC-based samples were annealed subsequently at 1300°C, 1500°C, and 1700°C for 3 h in argon atmosphere in a high-temperature graphite furnace (Fig. 3).

In order to reduce the residual porosity of the obtained SiC ceramic parts, the polymer-infiltration-pyrolysis (PIP) technique was applied. Thus, the ceramic monoliths prepared upon pyrolysis of the green-bodies at 1100°C and subsequently annealing at 1700°C were immersed in SMP-10 in argon atmosphere for >24 h (PIPSiC). The infiltrated monoliths were removed from the liquid polymer, placed in quartz crucibles and pyrolyzed at 1050°C under argon. The same process was repeated for several cycles.

2.2. Characterization

The polymer-to-ceramic transformation of SMP-10 was investigated by means of thermogravimetric analysis (TGA, Table 1: Mass losses of SMP-10 upon thermal treatment at 250°C for different dwelling times.

<table>
<thead>
<tr>
<th>Curing temperature [°C]</th>
<th>Dwelling time [h]</th>
<th>Mass loss [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>0.5</td>
<td>3.20</td>
</tr>
<tr>
<td>250</td>
<td>1.0</td>
<td>4.84</td>
</tr>
<tr>
<td>250</td>
<td>3.0</td>
<td>7.60</td>
</tr>
</tbody>
</table>

Fig. 1: Structure of allyl hydrido polycarbosilane (SMP-10) used for this study.
a) \[
\text{SiH}_2\text{CCH}_2 + \text{SiH} \rightarrow \text{SiH}_2\text{CCH}_2\text{SiH} + \text{Si} + \text{H}_2
\]

Fig. 2. Hydrosilylation (a) and dehydrocoupling (b) reactions occurring upon thermal cross-linking of SMP-10.

Table 2
Green-body fabrication from the cured SMP-10 powder.

<table>
<thead>
<tr>
<th>No.</th>
<th>Temperature [°C]</th>
<th>Pressure [MPa]</th>
<th>Holding time [min.]</th>
<th>Mass loss [wt%]</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>180</td>
<td>80–160</td>
<td>30</td>
<td>–</td>
<td>No compaction</td>
</tr>
<tr>
<td>2</td>
<td>250</td>
<td>80–160</td>
<td>90</td>
<td>–</td>
<td>No compaction</td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>51–63.7</td>
<td>30</td>
<td>–</td>
<td>Compaction; however, crack formation</td>
</tr>
<tr>
<td>4*</td>
<td>300</td>
<td>127.4*</td>
<td>60</td>
<td>4–6</td>
<td>Crack-free green body</td>
</tr>
</tbody>
</table>

* In these experiments the force was applied prior to the thermal loading; i.e., cold pressing + pressure release + pressureless cross-linking.

Fig. 3. Scheme of the processing of SMP-10-based ceramic monoliths.

449C Jupiter, Netzsch, Gerätebau GmbH, Selb, Germany) coupled with evolved gas analysis, EGA (in situ mass spectrometry, QMS, 403C Aëolos, Netzsch, Germany)

The green-bodies and the prepared SiC ceramics were investigated by means of attenuated-total-reflectance FT-IR spectroscopy (ATR-FTIR, Bruker Vertex 70, USA), elemental analysis (carbon analyzer, CS 800, Eltra GmbH, Neuss and N/O analyzer, Leco TC-436, Leco Corporation, Michigan) and powder X-ray diffraction (XRD, STOE & Cie GmBH Germany). The skeletal density of the obtained SiC ceramics was measured by the Archimedes method, using water as the infiltration medium. Scanning electron microscopy (SEM) studies were performed on a Philips XL30 FEG, Netherlands with an acceleration voltage of 10–15 kV.

3. Results and discussion

The SMP-10-based powders obtained via thermal curing of the liquid polycarbosilane using different conditions were investigated by means of ATR–FTIR spectroscopy (Fig. 4). The band at ca. 2121 cm\(^{-1}\) in the FTIR spectrum of the liquid SMP-10 was assigned to Si–H groups, whereas the bands at 1631 and 3070 cm\(^{-1}\) were assigned to the allyl groups (low intensity, due to the low amount, i.e., 4.8 mol%). As the polycarbosilane is thermally treated at high temperatures, the disappearance of the allyl bands indicates that hydrosilylation occurred under these conditions.

As obvious from the FTIR spectra, there is a large excess of Si–H groups (if related to the amount of allyl groups). Accordingly, after the complete hydrosilylation process, subsequent cross-linking is expected to rely only on dehydrocoupling reactions.\(^{31}\)

Fig. 4. ATR-FTIR spectra of liquid SMP10 as well as of two pre cross-linked samples.
The polymer-to-ceramic conversion of SMP-10 was studied by means of TGA/EGA. As the TGA curve shows (Fig. 5), the decomposition of SMP-10 occurs mainly in two major steps. Major mass loss has been observed in the temperature range of 300–650 °C, due to dehydrocoupling reactions, as discussed below. At temperatures beyond 800–850 °C, no significant mass change is recorded, thus it is concluded that the polymer-to-ceramic transformation is completed at temperatures up to 800–850 °C. The ceramic yield amounts ca. 77 wt%.

In situ EGA study indicates that in the first main decomposition step (T < 250 °C) hydrogen (m/z = 2) and small polymer fragments evolve. These processes occur in the same time as the hydrosilylation process (zero mass change process). In the second major decomposition step (400–850 °C), which represents the conversion of the preceramic polymer into an inorganic materials, the release of H₂ (m/z = 2), SiH₄ (m/z = 32), and CH₃SiH₃ (m/z = 46) has been analyzed (Fig. 6).

The elemental analysis of the ceramics obtained via pyrolysis of the liquid SMP-10 polymer handled completely under argon shows a carbon content of 34–35 wt% and 3–4 wt% of oxygen present in the ceramic. This is thought to be related to a specific amount of oxygen present in the SMP-10 polymer. The presence of minor amounts of the oxygen has been reported in the literature to range from 3 to 6.7 wt% and might be related to polymer synthesis and handling issues. The elemental analysis of the ceramic monoliths prepared within this study (i.e., obtained via warm-pressing of cured SMP-10 followed by pyrolysis at 1100–1300 °C) shows the incorporation of 5–6 wt% of oxygen within the ceramic network (Table 3, Fig. 7). The slightly higher amount of oxygen (if compared to that of the sample prepared upon pyrolysis from liquid SMP-10, Fig. 6. Quasi multiple ion detection (QMID) current curves during the polymer-to-ceramic transformation of SMP-10.
Table 3
Elemental composition of SMP10-derived SiC monoliths (the number in the sample codes, e.g. 11 in 11SiC, indicate the preparation temperature of the samples, i.e. 1100 °C for 11SiC, 1300 °C for 13SiC etc.).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental content [wt%]</th>
<th>Empirical formula</th>
<th>Calculated content [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>11SiC</td>
<td>62.45</td>
<td>31.88</td>
<td>5.67</td>
</tr>
<tr>
<td>13SiC</td>
<td>64.12</td>
<td>29.65</td>
<td>6.23</td>
</tr>
<tr>
<td>15SiC</td>
<td>64.95</td>
<td>32.22</td>
<td>2.83</td>
</tr>
<tr>
<td>17SiC</td>
<td>69.65</td>
<td>30.24</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Table 4
Mass loss, volume shrinkage, density and porosity of SiC-based ceramic samples annealed at different temperatures (the sample at 1050 °C was set as reference sample).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature. [°C]</th>
<th>Annealing time [h]</th>
<th>Mass loss [wt%]</th>
<th>Volume shrinkage [vol%]</th>
<th>Skeletal density [g/cm$^3$]</th>
<th>Open porosity [vol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>11SiC</td>
<td>1050</td>
<td>2</td>
<td>–</td>
<td>–</td>
<td>2.67</td>
<td>12.37</td>
</tr>
<tr>
<td>13SiC</td>
<td>1300</td>
<td>3</td>
<td>0.64</td>
<td>11.07</td>
<td>2.63</td>
<td>13.59</td>
</tr>
<tr>
<td>15SiC</td>
<td>1500</td>
<td>3</td>
<td>4.52</td>
<td>13.17</td>
<td>2.69</td>
<td>15.57</td>
</tr>
<tr>
<td>17SiC</td>
<td>1700</td>
<td>3</td>
<td>12.29</td>
<td>18.99</td>
<td>2.67</td>
<td>22.42</td>
</tr>
</tbody>
</table>

which was not warm-pressed) can be explained as a consequence of the warm-pressing step, during which the materials comes in contact with air for a short period of time. The incorporation of oxygen within the ceramic in turn produces amorphous silica in the ceramic upon annealing at high temperatures. The results of the elemental analysis of ceramic obtained at different temperatures show that the content of carbon as well as oxygen decreases with increasing the annealing temperature (Table 3, Fig. 7). This consequently leads at higher temperatures (i.e., 1700 °C) to near stoichiometric silicon carbide composition, due to the carbothermal conversion of silica to silicon carbide.

$\text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO}$

Mass loss, volume shrinkage, density and porosity of SiC-based ceramic pellets at higher temperature are indicated in Table 4. The results show that the mass loss and the porosity of the ceramic monoliths increase with the temperature.

From the results obtained here we can conclude that the SiC ceramic monoliths obtained upon pyrolysis at 1050°C contains some excess carbon (ca. 7 wt%) and oxygen; however, annealing at high temperatures leads to stoichiometric SiC compositions (as for the monolith prepared upon annealing at 1700°C). At the same time, the release of oxygen and of excess carbon (in form of CO) increases the porosity of the monoliths. The bulk density of the obtained SiC ceramics was 2.63–2.69 g/cm$^3$, thus indicating that probably closed porosity is present within the samples, as it will be discussed later.

Fig. 8 shows the XRD pattern of the samples annealed at different temperature under argon. The ceramic obtained by heat treatment at 1300°C for 3 h was X-ray amorphous. The XRD data of the ceramic materials annealed at higher temperatures indicate the crystallization of β-SiC. Additionally, small amounts of α-SiC were identified (Fig. 8). Interestingly, despite the high temperature, the samples were not fully crystalline. Differences in thermal stability against crystallization between the prepared monolithic materials and SiC-based powders...
Table 5
The porosity of SiC monoliths after PIP processing (pyrolysis was performed at 1050 °C) and subsequent annealing at 1700 °C (ND: not determined).

<table>
<thead>
<tr>
<th>No of infiltration cycles</th>
<th>Sample</th>
<th>Porosity at 1050 °C [vol%]</th>
<th>Porosity at 1700 °C [vol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PIPSiC-1</td>
<td>16.62</td>
<td>18.28</td>
</tr>
<tr>
<td>2</td>
<td>PIPSiC-2</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>3</td>
<td>PIPSiC-3</td>
<td>10.65</td>
<td>13.24</td>
</tr>
<tr>
<td>4</td>
<td>PIPSiC-4</td>
<td>3.25</td>
<td>7.87</td>
</tr>
<tr>
<td>6</td>
<td>PIPSiC-5</td>
<td>0.49</td>
<td>ND</td>
</tr>
</tbody>
</table>

synthesized upon pyrolysis and annealing of SMP-10 were significant and mostly rely on their different specific surface areas, as it was observed also for other polymer-derived ceramic materials.36

In Fig. 9, SEM micrographs of silicon carbide monolithic samples heat treated at 1050 °C and at 1700 °C are presented and clearly show the effect of the annealing temperature on the porosity. Thus, the porosity of the SiC monolith significantly increases upon annealing at 1700 °C, as it was also determined by means of water immersion technique (∼12 vol% for the sample prepared at 1050 °C vs. ∼22 vol% upon annealing at 1700 °C). In addition, the pores in the sample prepared at 1050 °C were smaller than those found in the sample annealed at 1700 °C (smaller and larger than 10 μm, respectively).

For further densification of the silicon carbide ceramic, the technique of liquid precursor infiltration and pyrolysis (PIP) has been used.37 As liquid precursor for the infiltration step, the same polymer used for the fabrication of the silicon carbide ceramic monoliths (i.e., SMP-10) has been taken, as it fulfills the requirements needed for liquid infiltration and pyrolysis, e.g. low and modifiable viscosity, high ceramic yield, phase and chemical purity upon pyrolysis, ease of use, relatively low...
volume shrinkage upon ceramization. As shown in Table 5, PIP clearly helps in decreasing the porosity of the monolith. Thus, after only 6 PIP cycles the residual porosity of the SiC monoliths was reduced to less than 1 vol%.30

As the SEM micrographs of four-times PIP-ed sample clearly shows (Fig. 10), the pores were filled by ceramic and thus a dense and crack-free surface was obtained. However, annealing of the PIP-ed samples at 1700 °C induced a slight increase of their open porosity. This relates to the fact that the infiltrated SiC(O) material exhibits some mass loss (upon CO release) while annealed at 1700 °C.

Indeed, the PIP-ed samples prepared at 1050 °C showed, similarly to the prepared SiC monoliths, some low amount of oxygen and excess carbon (Table 6). Thus, a three times PIP-ed SiC monoliths have ca. 3.8 wt% oxygen and 5.5 wt% excess carbon. However, upon annealing of the sample at 1700 °C the oxygen and the excess carbon were effectively removed and however, contributed to a slight increase of the residual porosity of the samples.

### 4. Conclusion

The present study indicates that crack-free and dense silicon carbide monoliths can be prepared pressureless upon cross-linking and pyrolysis of a polycarbosilane (SMP-10) followed by PIP treatment. The obtained monoliths were shown to be crack-free even upon annealing at high temperatures, despite of a large volume shrinkage occurring upon pyrolysis. The elemental analysis data revealed that at low annealing temperatures some excess carbon is present within the ceramic monoliths; additionally, oxygen has been found to be present (several wt%). Both the carbon and the oxygen contents decrease upon increasing the annealing temperature; thus, at temperatures beyond 1500 °C near-stoichiometric SiC can be obtained. The bulk density of the obtained SiC ceramics (2.63–2.69 g/cm3) was rather low as compared to other silicon carbide-based ceramics, due to the presence of some excess carbon and porosity in the monoliths. Thus, the obtained ceramic monoliths have been shown to exhibit residual porosities of 15–25 vol%, which however can further be reduced by using the PIP method to obtain crack-free and dense SiC-based monoliths.

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### References


