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An advanced method to manufacture hierarchically structured carbide-derived carbon monoliths

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ABSTRACT

The preparation of carbide-derived carbon (CDC) monoliths with a hierarchically structure in the nm and μm range is presented. Basis is the manufacturing of porous cellular SiC ceramics based on a biomorphous approach with μm porosity and subsequent conformal conversion to CDC by reactive extraction with chlorine. The SiC ceramics can be sintered at low temperatures and short times (1500 °C, 2 h) compared to classical preparation methods. The SiC ceramics show a macro pore volume (1–10 μm channel size) of 0.56 ml g^{-1}, which corresponds to 1.5 ml g^{-1} in the resulting CDC. The final carbon material exhibits an additional nano pore volume of 0.525 ml g^{-1} with a mean slit pore size of 0.86 nm. Mechanical stabilities of the highly porous CDC are excellent (bending strength 2.1 ± 0.2 MPa, corrected Weibull modulus 8.7, characteristic strength 2.2 MPa and Youngs modulus 10.0 ± 0.5 GPa). The reactive extraction of the carbide monoliths shows very high reaction rates, approx. two dimensions faster (95×) compared to non-porous samples. Thus the manufacturing of the structured carbide and CDC can be performed at lower costs.

1. Introduction

Carbide-derived carbons (CDCs) attract the attention as porous carbons. Their high purity, pore size control and reproducible material properties from batch to batch is interesting for several applications like e.g. gas storage and separation [1–3], electrical energy storage [4–7] or as catalyst support [8–12]. CDCs are prepared by the reactive extraction of the non-carbon components from carbides [13]. Mainly chlorine is used as reactant. In a conformal process the overall texture does not change, but inner porosity is created [14,15]. The resulting pore structure can be varied by the precursor carbide and extraction temperature from ultramicroporous to mesoporous. While controlling the micro- or mesoporosity is well established, methods to add a secondary porosity are less reported [16–23]. This could be necessary for porous monolithic structures, which can be advantageous in several applications as solely microporous material would suffer pore diffusion limitations for most applications. CDC with micro- and mesoporosity results from using binary metal carbides [24,25]. Kaskel et al. presented a hard- and soft-templating method to produce monolithic and mesoporous SiC from preceramic polymers and subsequently monolithic and mesoporous CDC [16,18,20,26,27]. They introduced not only random mesoporosity, but the templating results in well-ordered structure.

We reported recently that for carbides containing a free metal phase like commercial SiSiC, the reactive extraction results in the nm porosity know for CDC and an additional porosity in the micrometer ranger originating from the extraction of the free metal phase [26]. Extraction rates were shown to be approx. 20 times higher compared to compact SiC. Nevertheless, the common SiSiC material is cost-intensive due to liquid silicon infiltration (wick/capillary) operating at high temperatures ($T > 1550$ °C), long sintering times [29] and high postprocessing (grinding/polishing) costs. Also for

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the reactive extraction of the free metal phase e.g. Si in SiSiC, additional chlorine is needed. Thus, alternatives to introduce micrometer porosity are of interest. Due to the conformal conversion the secondary porosity can also be present in the carbide, like already demonstrated for the mesopore templating approaches described above. Hence, a precursor carbide monolith showing already a secondary porosity could be an option. The established common way for manufacturing SiC-parts from SiC powder either uses (a) reactive sintering processes with liquid silicon and additional carbon or (b) liquid phase sintering processes using additives like Y_2O_3 or Al_2O_3 [29–32]. Sintering temperatures have to be usually higher than 1550 °C and lead to dense microstructures (porosity < 5%), thus this processes are not suitable for porous CDC templates. Pore structure can be either generated by pore templating using sacrificial pore templates during debinding or pyrolysis of either carbon structures and ceramics [7–10]. Porous SiC ceramic foams are prepared by slurry impregnation [33–35] and feature a high porosity (P > 80%). Nevertheless, these materials show channels in the millimetre and not micrometer range. Also they exhibit poor mechanical properties due to the very high porosity and hollow struts [36]. A novel technique using a biomorphous approach producing SiC from a powder mixture of silicon, phenolic resin and natural pyrolyzed cellulose fibers, hence abundant comparably cheap raw materials have been reported by Fey et al. [37]. This route offers the possibility for porous SiC ceramics with good mechanical properties, porosity > 60%, good permeability and micrometer porosity.

The aim of this work is to study this novel method of producing SiC ceramics with micrometer porosity and their applicability as CDC precursor.

2. Experimental

2.1. SiC ceramic fabrication

A mixture of silicon powder (d_{50} = 6.9 μm, Elkem, Meerbusch, Germany), novolac resin (SP04, Fa. Hexacom, Iserlohn, Germany) and biomorphous carbon fibres is dry mixed for 4 h in a tumbling mixer. Biomorphous fibres were prepared by pyrolysis of cellulose paper (M2992, Hahnemühle FineArt, Dassel, Germany) at 800 °C in nitrogen. Additionally the pyrolyzed paper was chaffed in a mixer (HR 2096, Philips, Hamburg, Germany) for 20 s at 10 k rpm. The ratio Si:C (biomorphous fibres) is stoichiometric, phenolic resin (amount of 20% of biomorphous fibres) is used as binder and reacts with residual non-converted Si. Novolac resin consisting of phenylic resin and hardener hexamethylentetradiamine (2 wt.-%) is cured starting at 180 °C forming a composite of fibres, silicon and cured resin. Square samples ($50 \times 50 \times 10$ mm^3) are prepared by uniaxial hotpressing at 220 °C for 30 min with 5 MPa. Machining e.g. high speed cutting can be easily done in cured state. Pyrolysis is carried out at 900 °C in nitrogen atmosphere for 2 h. Heating rate is optimized by mass controlled pyrolysis with a defined mass loss rate of 0.5 (g/s). Sintering is carried out at 1500 °C for 2 h in a vacuum kiln ($1.2 * 10^{-2}$ Pa) with a heating rate of 300 K/h. Templates for CDC cylinders are cut out with a hollow drilling tool (inner diameter 10 mm) and grinded to a thickness of 5 mm. Sample preparation for mechanical testing of SiC is carried out as bars ($4 \times 5 \times 45$ mm^3) for 4-point bending strength measurement. Thermal properties of SiC ceramic and CDC are determined on cylindrical samples with a diameter of 12 mm and a thickness of 3 mm.

2.2. Reactive extraction with chlorine

For chlorination experiments a horizontal tube reactor was used, consisting of an quartz tube (d = 34 mm, l = 1550 mm) placed in a horizontal furnace (Gero, Neuhausen, Germany) as described prior [10,12,38]. All gas flows were controlled by mass flow controllers (Bronkhorst High-Tech, Ruurlo, Netherlands). Chlorination experiments were carried out at 800–1200 °C, the chlorine gas was diluted in helium. The gas flows were always adapted for the desired superficial velocity and concentration at a certain reaction temperature. Both chlorine and helium were obtained from Linde AG, Germany with purities of 2.8 and 4.6 respectively. After chlorination, the samples were post-treated with hydrogen at extraction temperature, the degree of conversion was calculated from the mass loss assuming an ideal carbide stoichiometry and that only silicon is etched.

2.3. Characterization

Due to limitation of classification of pores size > 50 nm (according to IUPAC) we define microporosity with a pore size between 500 nm an 1 mm and macropores > 1 mm pore size.

The morphology of the SiC samples were analyzed by SEM (ESEM, Quanta 200 FEG, FEI, USA) on polished samples and fracture surfaces. Compressive strength of the SiC ceramic was measured using Instron UTM (Instron 5565, Instron GmbH, Pfungstadt, Germany) in a 4-point bending test following DIN-EN 843-1 [39]. Youngs modulus was determined by impulse excitation using Buzz-o-sonic measurement V 4.5 in longitudinal mode (BuzzMac International, Gendale, USA) [40]. Heat conductivity was measured in the range of room temperature to 1000 °C using the laser flash method (LFA 457, Netzsch Instruments, Selb, Germany) and corresponding standards. The bulk density was measured from the weight and volume. Skeletal densities were determined by helium-pycnometry (Accupyc 1330, Micromeritics, Moenchengladbach, Germany) of powdered SiC and CDC.

The porous properties were studied using gas sorption analysis with N_2 at 77 K (Quantachrome Autosorb 1P, Odelzhausen, Germany) and CO_2 at 293 K (Quantachrome Nova 4200e, Odelzhausen, Germany). Both methods probe an open porosity. Pore size distributions were calculated from sorption isotherms using the QSDFT (N_2) and NLDFT (CO_2) model for carbon slit pores. Macropores were analysed by mercury porosimetry (Thermo Electron Corporation: Pascal 140 and 440, Hofheim/Ts, Germany). Raman spectra were recorded on a Thermo Scientific Nicolet Almega XR Raman spectrometer combined with an Olympus XR 51 optical microscope with 10-fold magnification and a 532 nm laser. For each spectrum five accumulations for 40 s each were taken.

To reveal the microstructure, the samples were examined with a high resolution micro computed tomography (μ-CT)