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Silicon carbide fiber-shaped microtools by extrusion and sintering SiC with and without carbon powder sintering additive

F.J. Clemens [*], V. Wallquist, W. Buchser, M. Wegmann, T. Graule

Laboratory for High Performance Ceramics, Swiss Federal Laboratories for Materials Testing and Research (EMPA),
CH-8600 Dübendorf, Switzerland

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Abstract

Silicon carbide powder was mixed with a thermoplastic polymer binder system consisting of a wax and a polyethylene. Thermal gravimetric analysis under argon showed that a carbon residue remains in the powder after binder decomposition. Because of the possibility of utilizing this residue as a sintering aid, two different feedstock series were tested: one series with and one without an additional carbon black sintering additive. Strength measurements on sintered fibers showed that the residue from the binder cannot be used as a sintering additive. Fibers made from the feedstock series without additional carbon black powder were characterized by a lower sinterability and a bigger grain size in the sintered fiber microstructure. Bigger grain size is caused by the absence of free carbon during the heating ramp up to the sintering temperature. To achieve dense silicon carbide fibers, a SiC content above 52 vol% in the feedstock is a prerequisite.

Keywords: A. Extrusion; B. Fibers; D. SiC

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1. Introduction

Silicon carbide parts are well-established in the marketplace in a variety of applications [1]. Because of their inherent very high hardness, SiC components possess superior wear resistance [2]. The material has a low thermal expansion coefficient compared to metals, an unusually high thermal conductivity for a ceramic, and excellent resistance to corrosion in its pure form. Thanks to these properties, SiC is used in a wide range of applications including high temperature capacitors, seals and pump parts, valves, bearings in magnetic drives, cyclone liners, radial burners, heat exchanger tubes, refractory tools, thermocouple protection tubes and electric heating elements [3–7]. Since the mid 1990s, microfabrication of silicon carbide parts such as chemical reactors, heat exchanger tubes, thermocouple protection tubes, heating elements or substrates for semiconductors has been of great interest to a number of industries. For producing such "microtools", two different methods are described in literature: microinjection molding and microextrusion [8–11].

Knitter et al. [8] combined microstereolithography and a low-pressure injection molding process for the fabrication of ceramic microcomponents. With this method, single prototypes up to small-lot series can be tested. Wien et al. [9] described a method with which three-dimensional ceramic turbine and compressor blades with feature sizes down to 200 μm can be fabricated.

Techniques to produce silicon carbide fibers are well known from the refs. [10–15]. One of the oldest methods is the deposition of SiC onto a tungsten or carbon core [10,11]. The disadvantage of the process is its limited geometrical flexibility, with only the fabrication of round fibers being possible. In the mid-1970s Yajima et al. [12] described the production of fine silicon carbide fibers by spinning a polycarbosilane precursor. Yong-Gang et al. [13] showed, that it is also possible to produce fibers with non-circular cross-sections when using ceramic precursors for silicon carbide fiber production. Other techniques like converting carbon into silicon carbide fibers are discussed in refs. [14,15]. The disadvantage of the precursor route is the high shrinkage and the resulting large statistical fluctuations of the fiber diameter. Such fluctuations are too big

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[*] Corresponding author. Present address: Überlandstr. 129, 8600 Dübendorf, Switzerland. Tel.: +41 43 823 4821; fax: +41 43 823 4150.
E-mail address: frank.clemens@empa.ch (F.J. Clemens).

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for microtool applications where dimensional variations of only a few micrometers are acceptable.

Wegmann et al. [16] described a method for producing ceramic fibers, hollow fibers and microtools by using a microextrusion technique. With this extrusion method, circular as well as non-circular (e.g. triangular and rectangular) cross sections can be produced [17,18]. Furthermore, the process can yield near-net-shaped microtools with low dimensional variations.

In the current case, a microextrusion method was used to fabricate microtools with a large aspect ratio. With this method, it is possible to produce SiC microheating elements, flat planar face fiber substrates for the semiconductor industry, or micro-heat exchanger tubes. Because of the polyethylene/wax binder system used, the focus of this investigation was the influence on the sintering behavior of the carbon residue which results from pyrolyzing the binder components during the debinding process under vacuum.

2. Experimental procedures

For the experiments, a submicron silicon carbide powder (UF-15, Saint-Gobain Ceramic Materials, AS, Norway), carbon black (Printex U, Degussa, Germany) and boron carbide (Grade HS, HC Starck, Germany) sintering additives and a binder system consisting of wax (Licomont EK 583, Clariant GmbH, Germany) and polyethylene (1700MN18C Lacqtene PEBD, elf atochem S.A., Switzerland) were used. The SiC powder has a mean particle size of 0.6 μm and a specific surface area of 15 m^2/g. Licomont EK 583 is a polyolefin wax and has a softening point of 115 °C. The polyethylene has a melting temperature of 108 °C and a MFI (melt flow index) of 70 g/10 min (ISO 1133). The decomposition behavior up to 800 °C under argon was investigated by thermal gravimetric analysis (TGA; Netzsch STA 409, Netzsch Gerätebau GmbH, Germany).

Extrusion feedstocks with 44, 50 and 52 percentage by volume of silicon carbide powder were prepared with a high-shear mixer fitted with roller blades (Rheomix 3000 Torque Rheometer, Thermo Electron Corporation, Germany). The torque was recorded as a function of time during mixing.

The rheological behavior of the feedstocks was analyzed by using a twin-bore capillary rheometer (RH7-2, Rosand Precision Limited, Germany). For these measurements, a capillary of 1 mm diameter and 16 mm length was fixed in the left bore. To be able to calculate the real viscosity according to the Cogswell theory, a short (zero-length) die of the same diameter in the right bore was used to determine the die inlet pressure drop.

The ceramic-thermoplastic feedstocks were extruded with a single screw extruder (Rheomex 202, Thermo Electron Corporation) at temperatures between 110 and 140 °C.

The green fibers were prepared for sintering by placing them on horizontal carbon substrates featuring parallel v-shaped slots. Each substrate could accommodate 80 fibers. Green fibers with a diameter of 500 μm were thermally debound under vacuum up to 500 °C and sintered under argon at 2180 °C/30 min (KCE, Spezialmaschinenbau). Because of the low fiber mass, the sintered density of the fibers could not be directly measured. The sintered density was therefore calculated from the shrinkage of the fibers and the theoretical density of silicon carbide (3.18 g/cm^3).

The sintered fibers were prepared for tensile strength measurements by first gluing them onto square paper frames with a free clamping length of 50 mm. In earlier internal studies, the optimal glue for this purpose was found to be Pattex Universal-Sekundenkleber (Henkel & Cie AG) which contains cyano acrylate and gives a good non-slip bond. Using this sample mounting technique generally results in the fibers breaking in the free clamped length. After clamping the ends of a given paper frame in a Zwick Z005 universal testing machine (Zwick GmbH), the sides of the frame were cut such that the tensile load would be born by the mounted fiber and the test was performed. The test settings were: pre-load 0.5 N, pre-load speed 0.15 mm/min, and test speed 0.3 mm/min. The load cell was a 500 N HBM U1. After fracture, the fibers were investigated under a light microscope to determine the presence of defects on the fracture surface.

Three fibers from a given batch were analyzed by scanning electron microscopy (SEM; JEOL JSM-6300F, Germany); one with a high tensile strength, one with a tensile strength close to the average and one with a low value. The fibers were mounted on specially-designed wheel-shaped aluminum sample holders designed in-house that could fit 72 fibers placed in vertical v-shaped slots. With this type of sample holder, fibers can be quickly prepared for analysis and the fracture surface of the fibers is protected from damage. Each fiber was imaged at a magnification of 150×, allowing the whole fracture surface to be seen, and at a magnification of 4000× to analyze the microstructure.

3. Results and discussion

3.1. TG/DTA

The decomposition of Licomont takes place between 300 and 500 °C, and the PE similarly exhibits its major mass loss between 380 and 480 °C. Thus, during debinding, and especially between 380 and 480 °C the heating rate must be kept low to prevent cracks from forming in the green bodies.

Waxes and plastics tend to form a carbon residue during decomposition (i.e. during feedstock debinding) in vacuum or under inert gases like argon or nitrogen. The TG results show, that only 83 wt% of the Licomont wax is removed under argon and that the polyethylene also leaves behind a carbon residue of 4 wt%. Based on these results when using a wax/PE ratio of 9, the overall amount of carbon residue after debinding process will be 15.7% by weight. Mizrah et al. [19] and Lenk et al. [20,21] have shown that carbon residue from a resin can be used as a sintering additive for silicon carbide materials. To investigate the suitability of the carbon residue from the polyethylene/wax binder system as a sintering additive, the silicon carbide/boron carbide powder mixture in

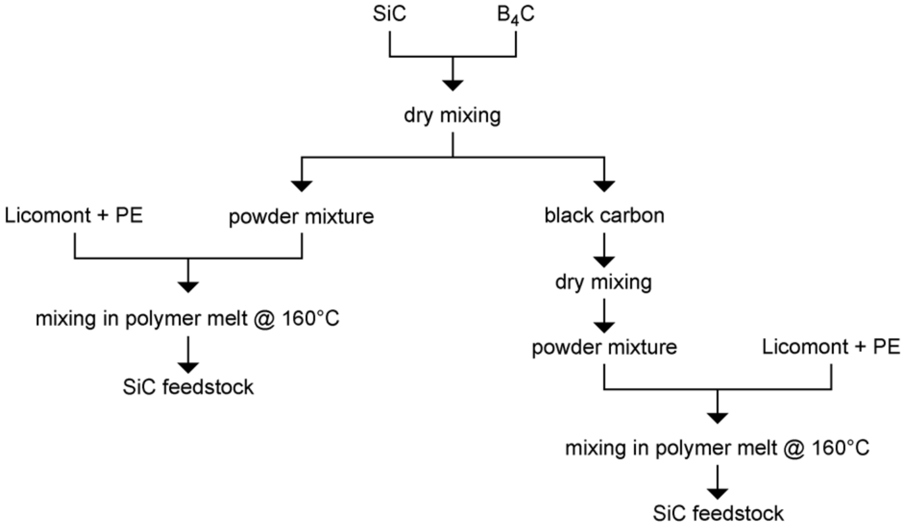

Fig. 1. Mixing procedure of the SiC feedstocks.

this study was processed both with and without addition of carbon black powder.

3.2. Mixing procedure

Silicon carbide and 0.6 wt% boron carbide were dry mixed before mixing with the polymer binder. In accordance with the work of Mitzrah et al. [19], 3 wt% carbon black powder was added into one of the silicon carbide/boron carbide powder mixtures. Fig. 1 shows a flow chart of the mixing procedures for mixtures with and without carbon black.

3.3. Torque rheometer

At the end of the homogenization process with the torque rheometer, the equilibrium torque was recorded for each feedstock composition. Fig. 2 shows this data summarized as a plot of the reciprocal torque versus the ratio between the binder and the inorganic powder. We assume that by extrapolating the data to zero reciprocal torque (i.e. when the torque for such a composition will be of infinite magnitude) the maximum powder loading for the different SiC batches can be determined.

With this method, a maximum powder loading of 62% by volume was calculated for the SiC feedstock prepared with carbon black sintering additive. For the SiC feedstocks without carbon black, the maximum loading is only 57 vol%. This result corresponds with the fact that it was not possible to produce an extrudable carbon black-free SiC feedstock with a powder loading higher than 52 vol%. The feedstocks prepared at 53 and 54 vol% were powdery, very brittle and did not exhibit any plastic behavior. In contrast, with carbon black added it was easy to reach a loading level higher than 52 vol%, but these feedstocks showed slip-sick behavior at low shear rates.

3.4. Rheological test

For calculating the real shear viscosity of the different feedstocks, the Cogswell theory was used [22]. According to this method, the inlet pressure drop is directly measured with a short die instead of using an extrapolation to zero length as is described by Bagley et al. [23]. In Figs. 3 and 4, the real shear viscosity as a function of the real shear rate is shown for the experimental series without and with carbon black sintering additive, respectively.

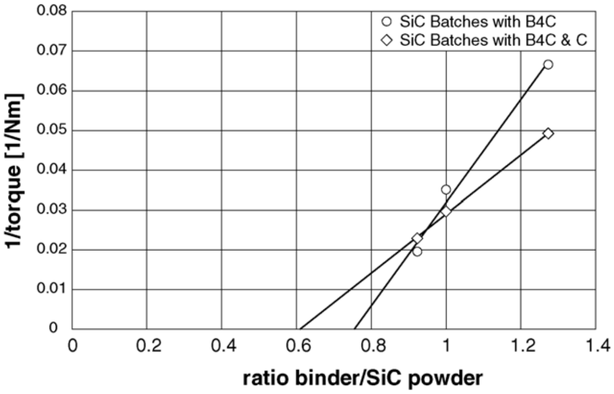

Fig. 2. The reciprocal torque as a function of the binder to SiC powder ratio to calculate the maximum loading for the feedstock.

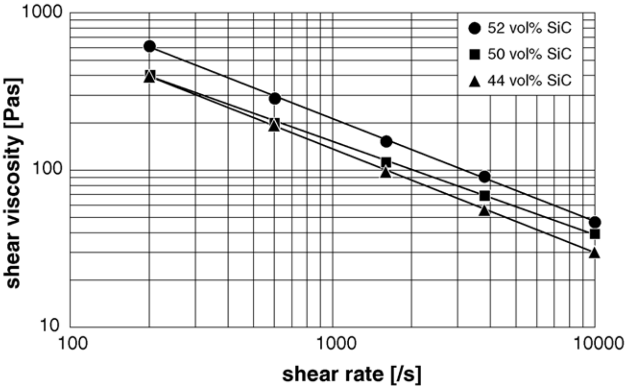

Fig. 3. Shear viscosity as a function of shear rate and powder loading without carbon black additive.

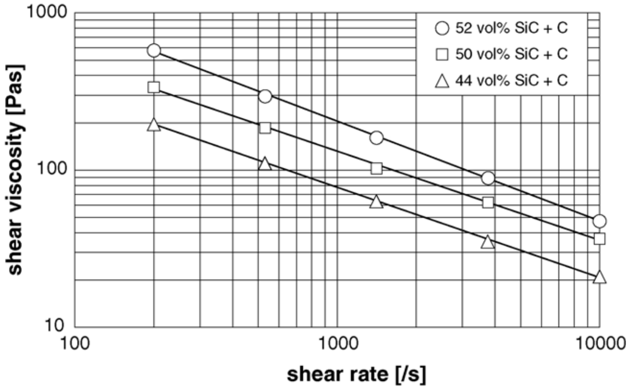

Fig. 4. Shear viscosity as a function of shear rate and powder loading with carbon black additive.

At shear rates greater than 200 s^{-1} the shear viscosities increase slightly by increasing the amount of silicon carbide powder in the feedstock. Because of the higher concentration of silicon carbide powder, the amount of wax and polymer between the particles, and consequently the interparticle separation distance, is reduced. This leads to higher internal friction in the feedstock and therefore a higher measured viscosity.

In contrast to the results for the feedstock series without carbon black (Fig. 3), the increase in viscosity for the feedstocks with additive shows much more clearly (Fig. 4). Comparing only the 44 vol% feedstocks shows, that the viscosity for the feedstock with carbon black is significantly lower than for its counterpart without additive. At 50 vol%, the same trend can be observed. This indicates the possibility that the carbon black acts as an internal lubricating agent. At 52 vol%, no difference in viscosity between the feedstocks with and without additive can be observed; nevertheless the positive influence of the carbon black is still present when one considers the silicon carbide loading in excess of 52 vol%. Using the torque rheometer, feedstocks with 54 vol% could be successfully prepared for the series with carbon black additive, while without the sintering additive the feedstock with 54 vol% was still like powder after mixing and did not show any plasticity.

3.5. Sintering

Green fibers were extruded with a single screw extruder using the different feedstocks from both series with and without carbon black powder. Fibers with a diameter of either 150 or 500 μm were successfully produced and subsequently sintered. In Table 1, the measured and calculated shrinkage of the sintered fibers are presented. The porosity was calculated by measuring the shrinkage on sintered fibers. It can be shown, that denser fibers are obtained by using additional carbon black as a sintering additive. To reach the same density of a fiber without carbon black additive, a feedstock with a higher volume percentage of silicon carbide must be used. Comparing fibers which were produced with 52 vol% (without carbon black) and with 44 vol% (with carbon black) solids loading, it can be estimated that the solids loading for feedstocks without additional carbon black must be 10 percentage points higher to reach the same density in the sintered state as fibers prepared with carbon black.

Table 1
Shrinkage of the different SiC fibers

SiC content (vol%)	44	50	52	44	50	52
Carbon black	No	No	No	Yes	Yes	Yes
Measured shrinkage (%)	3	3.6	4.4	9.4	10	12
Calculated shrinkage (%)	23.9	20.6	19.6	21.7	20.6	19.6
Porosity (%)	20.9	17	15.2	12.3	10.6	7.6

The densification can be controlled by the amount of inorganic powder in the feedstock. Comparing the density of the sintered fibers with additional carbon, it is obvious, that only with a high concentration of ceramic powder in the feedstock can dense fibers be achieved. Zhao and Harmer [24] showed, that a lower packing density in TiO_2 green bodies tended to lower the sintered density because the sintering activity is reduced by the lower packing density.

The shrinkage of the sintered fibers which were made from the feedstock series without carbon black is reduced compared to the fibers prepared with the sintering additive. The lower shrinkage implies a reduced sintering activity despite the presence of the carbon residue resulting from incomplete binder decomposition. From these results it can be concluded that in our case the carbon residue from the binder cannot be used as a sintering additive for silicon carbide.

3.6. Mechanical testing

After sintering the fibers were glued onto a paper frame with a free clamping length of 50 mm. Before testing the tensile strength, the sides of the supporting paper frame were cut in the middle with scissors to transfer the tensile load to the fiber. Thirty fibers from each feedstock with and without additional carbon black sintering additive were tested. The results of the tensile strength test for the sintered fibers which had a fiber diameter of 500 μm after extrusion are shown in Fig. 5.

According to Fig. 5, the tensile strength of the sintered fibers increases as the content of ceramic powder in the mixtures increases. The higher tensile strength correlates directly with the lower porosity which is achieved by increasing the amount

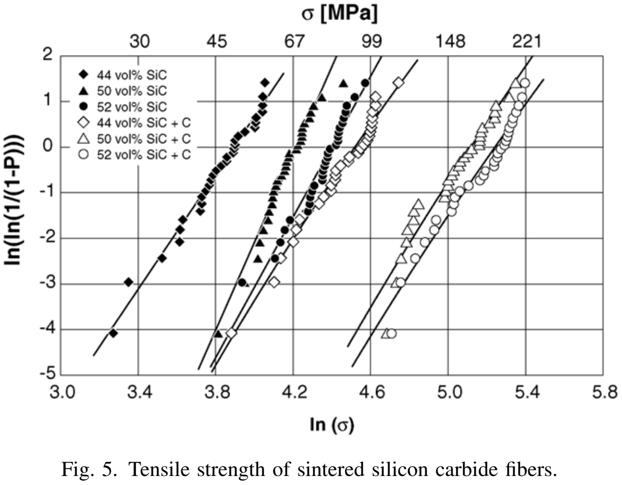

Fig. 5. Tensile strength of sintered silicon carbide fibers.

Table 2
Mechanical properties of sintered silicon carbide fibers

SiC content (vol%)	44	50	52	44	50	52
Carbon black	No	No	No	Yes	Yes	Yes
Sintered fiber diameter (μm)	485 ± 6	482 ± 4	478 ± 5	453 ± 7	450 ± 6	440 ± 7
σ_0 (MPa)	47	68	81	92	169	190
m_{corr}	8.5	7.8	8.4	6.5	6.2	6.8

of ceramic powder in the mixture (see Table 1). As described before, the higher shrinkage is due to a higher sintering activity imparted by the higher packing density of the silicon carbide powder in the green fiber state.

The fibers which were made from the feedstock series without carbon sintering additive have a poorer tensile strength compared to the fibers which were prepared from the feedstock series with carbon black powder. In Table 2, it could be shown, that the fiber diameter after sintering without additive was larger, implying lower shrinkage in this case (see Table 1), and therefore the porosity of these fibers must be higher. A higher porosity leads to a lower tensile strength, so the correlation between the results shown in Table 1, and Fig. 5 is quite good.

In Table 2, the measured properties of the different silicon carbide fibers are summarized as a function of the amount of silicon carbide in the green state and presence of the carbon black sintering additive. The tensile strength can be clearly correlated with the porosity of the sintered fibers and the content of silicon carbide in the feedstocks. It can therefore be concluded that a high content of silicon carbide and carbon black sintering additive are necessary prerequisites for successfully producing silicon carbide fibers with good mechanical properties by extrusion. In order to use such fibers for microtool applications it will be necessary to decrease the porosity and to increase the tensile strength up to 800 MPa which is typical for macroscopic silicon carbide parts.

3.7. Scanning electron microscope investigations

After mechanical testing, the fractured fibers were inspected by scanning electron microscopy. The investigation confirms the previous results, as expected: The porosity of the sintered fibers is influenced by the content of the silicon carbide in the green fiber state, with increased SiC content resulting in lower porosity.

Comparison of the SEM images shows that the microstructure is influenced by the presence of carbon black. The grain size for the sintered silicon carbide fibers which were produced from feedstocks without carbon black powder is bigger compared to the grain size for those produced from feedstocks with the sintering additive. Prochazka and Scanlan [25,26] showed that free carbon effects the sinterability of SiC. Different authors have discussed, that carbon aids sinterability by eliminating oxide impurities at grain boundaries [26–28]. The present results are in good agreement with the study by Stobierski which indicated that carbon sintering additive prevents grain growth of silicon carbide [29] by limiting SiC mass transport. When the SiC mass transport mechanism is arrested, small grains are preserved up to the temperature where boron then activates those mass transport mechanisms which eliminate pores in the microstructure.

This result is an additional indication, that for the silicon carbide fiber production, the carbon residue from the binder system Licomont wax/polyethylene 1700 MN18C is not usable as a sintering additive.

4. Conclusions

A mixture of silicon carbide powder and a thermoplastic polymer binder system consisting of a wax and a polyethylene has been investigated for the fabrication of SiC fiber-shaped microtools with a diameter between 150 and 500 μm. Because of the high amount of carbon residue which results when the binder is thermally decomposed and the fact that carbon is a recognized sintering additive for SiC, it was considered possible that the binder residue might be used as a sintering aid. To investigate this possibility, extrusion feedstocks with and without additional carbon black sintering additive were prepared and fibers extruded, sintered and characterized.

Based on the density, tensile strength and microstructural data collected for sintered fibers, it could be shown, that the carbon residue of this binder system cannot be used as a sintering additive. It is necessary that additional carbon black powder is used as a sintering aid. Without carbon black, the fibers exhibit a lower sinterability, which is manifested in larger fiber diameter and lower density, and a bigger grain size relative to fibers prepared with carbon black. The bigger grain size is caused by the absence of free carbon during the sintering process. These results are in good agreement with previous studies on sintering of silicon carbide.

In this study it could be clearly shown that in order to obtain dense silicon carbide fibers, a silicon carbide content above 52 vol% in the feedstock is a prerequisite. A clear correlation between the mechanical properties, the porosity after sintering and the content of silicon carbide in the feedstocks could be observed. In order to use such fibers for microtool applications in the future, it will be necessary to increase the density and the tensile strength up to values, which are typical for macroscopic silicon carbide parts. To achieve this, the powder loadings will have to be increased while preserving the necessary rheological properties of the feedstocks (i.e. no slip stick effect) and thus it will be necessary to tailor the organic binder system for use with the chosen inorganic powder system.

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