COLLOIDAL PROCESSING OF TEMPERATURE SHOCK RESISTANT SiC WITH TAILORED POROSITY

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ABSTRACT

From aqueous slurries containing SiC powder coated with nano-scaled carbon black, green bodies were prepared by slip casting. On slip cast green bodies the densification, microstructural development and mechanical properties were investigated. Depending on the sintering temperature and boron carbide content samples with different relative densities between 0.90 and 0.988 were obtained after pressureless sintering. In all samples a homogeneous microstructure (distribution of the residual pores and grain morphology) was observed. Due to this homogeneity the sintered samples showed high amount of fracture strength of about 500 MPa, even at large residual porosities of 10 %. The thermal shock resistance of samples with different porosities measured by water quenching revealed the critical temperature difference to be around 700 K.

INTRODUCTION

Silicon carbide (SiC) combines a variety of properties like high strength, high hardness, high oxidation and corrosion resistance and high thermal conductivity which make it an interesting material for high temperature applications. But these intrinsic properties are strongly influenced by the microstructure, like defect size and defect size distribution, grain size and grain boundary seggregations. Since SiC can be sintered only by using sintering additives like carbon and boron the distribution of sintering additives, especially carbon, is an important parameter with respect to microstructural development. According to [1] an excellent carbon distribution in SiC green bodies can be obtained by chemical bonding of carbon on SiC or electrostatically coating of SiC by nano dispersed carbon black. It has been shown that green bodies with homogeneous carbon black distribution can be densificated to nearly theoretical density, even by pressureless sintering [1,2]. The mechanical properties such as fracture strength and hardness of the sintered SiC parts are comparable to the properties of SiC parts densificated by pressure assisted sintering techniques as reported in [2].

The aim of the present work is to investigate the microstructural development of SiC samples prepared using this technique both in the range of open and closed porosity and to determine the influence of microstructure on mechanical properties.

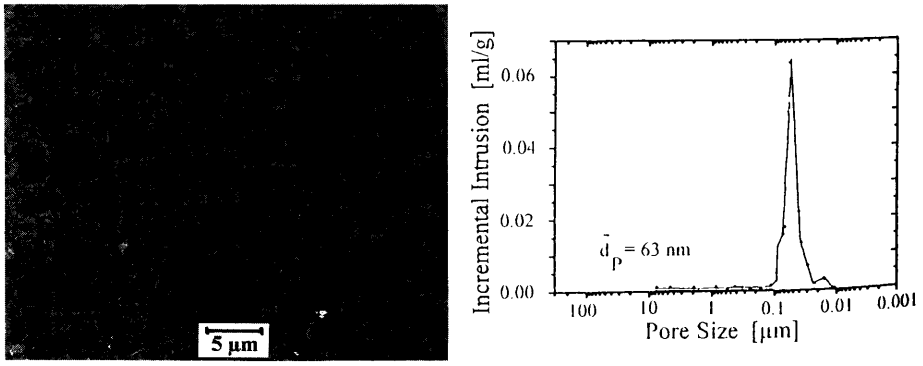
EXPERIMENTAL

Powders used for experiments were α-SiC (mean particle size 290 nm, BET-surface 14 m^2/g). B_4C (mean particle size 245 nm, BET-surface 18 m^2/g) and carbon black (mean particle size 20 nm, BET-surface 300 m^2/g). Aqueous SiC slips containing 2 wt.-% carbon black and 0- 0.65 wt.-% B_4C as sintering aids with an overall solid content of 35 vol.-% were prepared from SiC

powder electrostatically coated with nano-scaled carbon black. For the electrostatical coating the pH-value was kept between 5 and 6 during the slip preparation. In this pH range SiC and carbon black are charged oppositely (SiC negatively, carbon black positively). The coated SiC/B_4C was stabilized by using of a non-ionic surfactant in a concentration of 2 wt.-%, as described in [1]. Green bodies (55 x 55 x 5 mm^3) were prepared by slip casting. Sintering was carried out in a graphite lined high temperature furnace under flowing argon in the temperature range of 2150 °C to 2180 °C. From sintered plates test bars of dimensions 3 x 4 x 25 mm^3 were prepared and used for the determination of fracture strength by 3-point bending with a span width of 20 mm. For the determination of thermal shock resistance the bending bars were heated to elevated temperatures (700°C) for 10 min and then quenched in water (20 °C). Their remaining strength was measured by 3-point bending tests. For microstructural characterization sintered samples were embedded in epoxy resin. After grinding and polishing, samples were etched with boiling Murakami's solution. Samples in open porosity range (D < 0.95) were evaluated without etching. The pore size distribution in sintered samples was measured by a computer assisted image processing system, the microstructure of sintered samples was investigated by light microscope, SEM and TEM.

RESULTS AND DISCUSSION

Fig. 1 shows representatively the SEM picture of the fracture surface of a green body with a relative green density of 0.63 prepared by slip casting and the corresponding pore size distribution as measured by Hg porosimeter. The green microstructure contains no pores larger than average particle size of SiC powder used (fig.1a). Considering the measured pore size distribution between 20 and 100 nm with an average value of 63 nm (fig. 1b) in can be concluded a very homogeneous green microstructure to be presenting. Additively, no concentration gradients for carbon black within the green bodies was detected.



a b

Fig.1: Green microstructure (a) and pore size distribution (b) of slip casted SiC green bodies.

Sintering experiments were performed with these green parts and the final densities were adjusted by different boron carbide concentrations (0-0.5 wt. %) as well as different sintering temperatures (2150 - 2180 °C). Sintered parts with relative densities 0.90, 0.94, 0.96 and 0.988 were obtained.

The microstructure of the samples were examined in terms of pore size distribution, fracture surface, grain morphology and grain boundary composition. Figure 2 shows the microstructure of SiC samples with relative densities 0.90 and 0.985, respectively. The low density sample is characterized by an extremly homogeneous distribution of residual pores. The shape of the pores is nearly spherical (fig.2a). In the dense sample (D = 0.985, fig 2b) nearly equaxed grains of average size 5 µm are present. No indication for an anomalous grain growth can be seen.

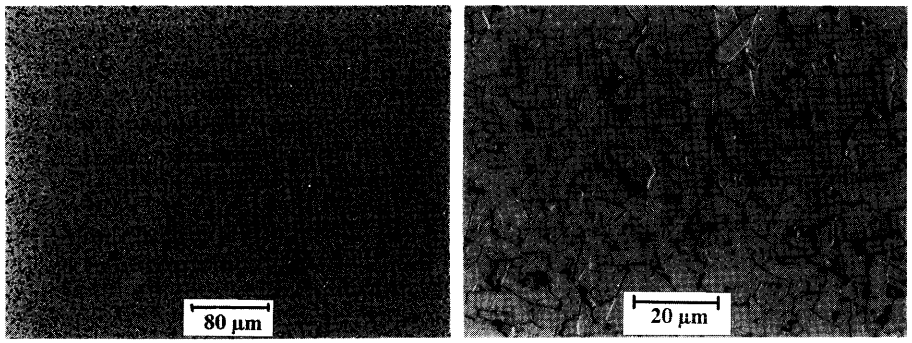


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Fig 2: Microstructure of pressureless sintered SiC with different relative density; a) D = 0.90, unetched, b) D = 0.985, etched

The observation of the fracture surface of the sintered samples with similar densities as in fig. 2 revealed the fracture mode to be transgranular (fig. 3a). The conclusion of this observation is that grain boundary strength is as high as grain strength due to the clean grain boundaries without any glassy phase. This was confirmed by TEM investigations of grain boundaries and grain junctions (fig. 3 b).

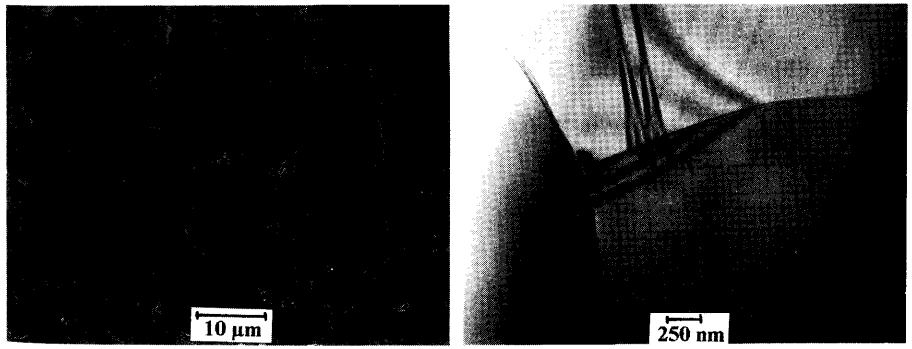

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Fig. 3: SEM picture of the fracture surface (a) and TEM picture of the grain boundaries (b) of a sintered SiC sample (D = 0.988)

In order to characterize the densification of green bodies, the pore size distribution during sintering was determined. Fig 4 shows a representative set of pore size distribution measurements on SiC samples with different densities. It is evident that the average pore size continuously decreases from 4.10 µm (D = 0.89) to 1.55 µm (D = 0.94) with increasing density and the distribution range is getting narrower. Considering the sintering theory this clearly indicates a homogeneous densification. Beside the high initial green density and uniform pore size the homogeneous densification can be traced back to the homogeneous distribution of nano scaled carbon black within the green bodies. This suggestion will be clear by considering of the role of carbon as sintering additive in SiC; 1) increasing of surface energy by removing of the SiO_2-layer, 2) increasing the grain boundary diffusion of SiC, 3) suppressing the grain growth if present in excess [3].

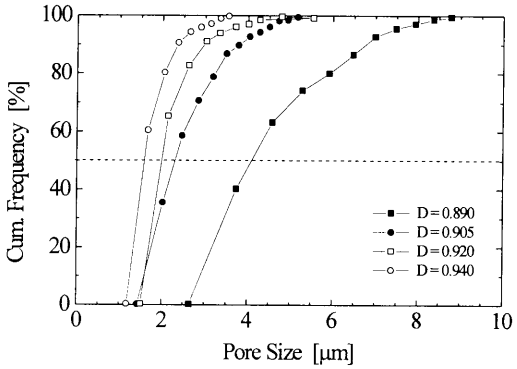

Fig. 4: Pore size distribution in sintered SiC samples with different densities

The room temperature fracture strength of SiC samples with different densities is slightly increasing with increasing density, as shown in fig. 5. But the high strength level of 500 MPa, even for samples with 10 % residual porosity, is surprising.

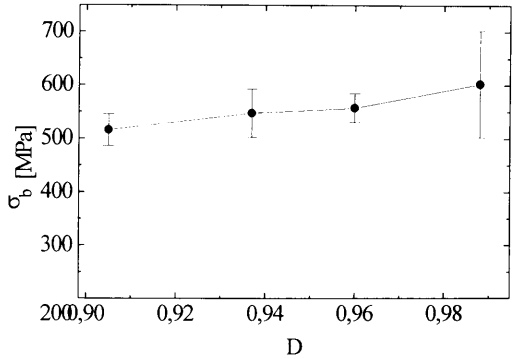

Fig. 5: Room temperatue fracture strength of sintered SiC with different densities (3-point bending, span wide 20 mm)

Thermal shock resistance of the SiC samples from fig 5 were determined by water quenching method. Fig 6 shows the fracture strength of the samples, σ_b, as a function of quenching temperature difference, ΔT. Solid lines show the best fitting for the dependency of fracture strength to the quenching temperature difference. It is evident, that the fracture strength continuously decreases with increasing temperature difference. But a significant decrease of fracture strength takes place for a ΔT between 600 and 700 K as a result of damage by thermo-mechanical stresses. The critical temperature difference, ΔT_c, is 600 K for samples with open porosity (D = 0.905 and 0.937) and 650 K for samples with closed porosity (D = 0.96 and 0.988). No relationship between porosity and critical temperature difference within the investigated ΔT and porosity range can be derived from the present data. To obtain informations about the thermal shock resistance for higher critical temperatures further experiments will be carried out.

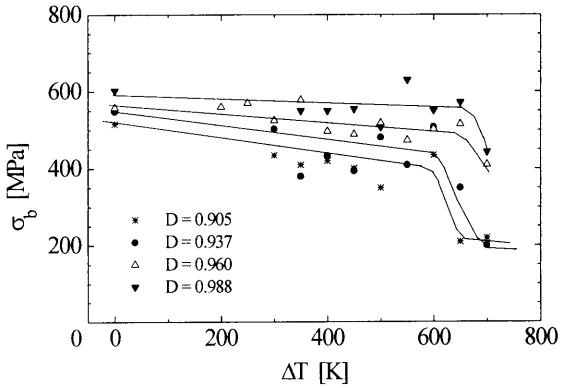

Fig 6 : Fracture strength, σ_b, as a function of quenching temperature difference, ΔT, for SiC samples with different densities.

The ΔT_c values for SiC ceramics sintered with the same sintering aids vary between 350 and 450 K as reported in the literature [4,5]. Higher ΔT_c values comparable to the results of present work are normally obtained on SiC materials containing BeO, which shows higher thermal conductivity [6]. Therefore, it can be concluded that SiC material tested should have an excellent thermal conductivity. High thermal conductivity, if it is the reason for the observed high termal shock resistance, may be explained by the pure grain boundaries present. To confirm this assumption thermal conductivity measurements will be carried out.

CONCLUSIONS

The colloidal processing of SiC, as presented in this work, allows the preparation of high dense green bodies with homogeneous distribution of sintering additives, especially of nano-scaled carbon black. As a result of this homogeneity the green bodies can be densificated to various residual porosity levels between 1 and 10 % by pressureless sintering. Sintered samples

show high fracture strength and high thermal shock resistance up to critical temperature difference of 700 K. SiC material with this properties can enlarge the use of SiC for structural thermal shock applications.

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