NEW PROCESSING TECHNIQUES FOR THE PRODUCTION OF PRESSURELESS SINTERED SiC PARTS

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ABSTRACT

For the preparation of SiC parts by casting techniques two different processes for the precipitation of sintering aids onto the surface of sub-micron SiC powder have been developed. In the first case, SiC particles were electrostatically coated with nano scaled carbon. In the second case, SiC has been surface modified to provide coupling groups for the subsequent chemical bonding of carbon. The results show that aqueous slips could be prepared which show no segregation for carbon during slip casting. Green parts ($\rho > 58$ %) with a homogeneous distribution of carbon additive have been obtained. As a consequence, samples could be pressureless sintered to high densities (> 98.5 %), exhibiting a high fracture strength (> 450 MPa) and a high Weibull modulus (> 10).

INTRODUCTION

Pressureless sintered silicon carbide (SSiC) has been of interest for high temperature applications for many years because this material combines excellent oxidation resistance and corrosion behavior with low thermal expansion and high strength at elevated temperatures. Since SiC is a mainly covalently bonded solid, sintering is difficult, and additives are necessary to obtain acceptable densities and strength. Small quantities of B or B_4C in combination with C have been found to enhance densification drastically [1]. While B or B_4C are used as fine grained powders, carbon has to be produced during sintering by thermal decomposition of organic polymers as a nano-scale material on the surface of SiC particles. Only under these conditions, a complete reduction of the SiO_2 layer covering each particle [2-4] is possible, which is an essential prerequirement for pressureless sintering of SiC. However, the pyrolysis process is hindered by long decomposition times and gas evolution, which can deteriorate the green bodies. These drawbacks can be overcome if a particulate carbon is used. However, wet processing of SiC powders and nano scaled carbon (n-C) is generally associated with segregation of carbon, especially if forming techniques like slip or pressure casting are used. Segregation results in concentration gradients of carbon in the green compact and consequently leads to density gradients, high residual stresses and cracking during sintering. From this point of view, it is desirable to develop processing techniques for an immobilization of carbon and providing a homogeneous distribution of carbon in SiC slurries. As reported in [5, 6], carbon can be immobilized by direct precipitation of nano-scale carbon onto the SiC particles. This approach has been used in this work, and first results about the preparation of green compacts, sintering and microstructure development will be reported.

EXPERIMENTAL PROCEDURES

The starting powder for the experiments were α-SiC (mean particle size 290 nm, BET-surface 14 m^2/g, supplied by ESK, FRG), B_4C (mean particle size 245 nmn, BET-surface 18 m^2/g, supplied by ESK, FRG) and carbon black (particle size 15-20 nm, BET-surface 300 m^2/g, supplied by BASF, FRG). The surface modification of the SiC with the carbon black was carried out as described in [5, 6]. Aqueous slips with a solid content of 63 wt.% were prepared by using of 2 wt.% of a non-ionic surfactant. Slip casting was used for the preparation of discs shaped green bodies (diameter 50 mm, height 5 to 25 mm). Carbon analysis was performed by the carrier gas hot extraction method (RC412, Leco). Sintering was carried out in a graphite lined high temperature furnace (Thermal Technology). For microstructural observations the sintered samples were ground, polished and etched in boiling Murakami's solution.

RESULTS AND DISCUSSION

Immobilization of nano-scale carbon black can be achieved by two different processes, as shown in Fig. 1 [5, 6].

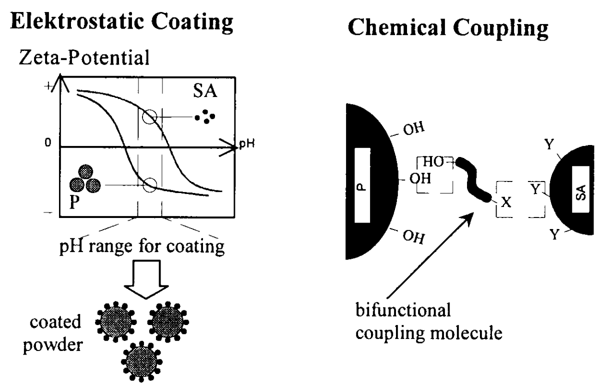

Fig.1: Basic principles for coating of SiC particles (P) with sintering additives (SA).

The first route is based on the electrostatic coating of SiC with nano-scale carbon black and requires well dispersed slurries of both compounds with opposite charged particles in a certain pH range. Heterocoagulation can be carried out then by mixing both slurries, and a n-C coated SiC powder is obtained.

In the second route a sintering additive is directly linked to the surface of an SiC particle by means of a chemical bond. For this purpose the surface of SiC has to be modified with compounds which can provide stable bonds to the additive, [5]. As shown in [7], suitable compounds are organoalkoxy silanes of the type $X\text{-}(CH_2)_n\text{-}Si(OR)_3$ ($n > 2$, X: NH_2, COOH, CH_3, SH, ...), which can be bonded to the SiC surface by a condensation reaction of the alkoxy groups with the Si-OH groups of the silica layer. Moreover, an additional functional group is provided for a coupling reaction with carbon. In Fig. 2 a reaction scheme for the linkage of an acidic carbon black with an amino silane modified SiC is shown.

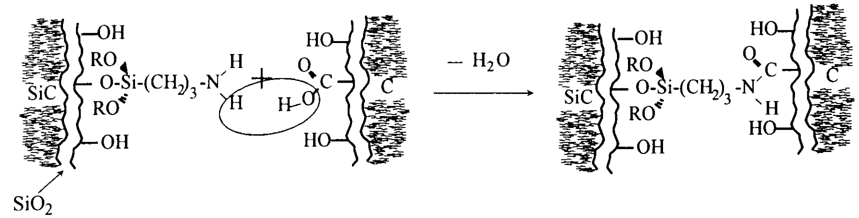

Fig.2: Reaction scheme for the chemical coupling of acidic carbon black with amino silane modified SiC.

The electrostatical coating is stable under certain pH conditions, and for redispersing and slip preparation non-ionic surfactants have to be used. In contrast, the chemical route leads to a coated powder more stable in a wide pH range and, therefore, can be redispersed either under acidic or basic conditions as well as with non-ionic surfactants. However, both techniques gave carbon coated SiC powders, and in Fig. 3 a representative SEM picture of a SiC grain with a chemically bonded nano-scale carbon black is shown.

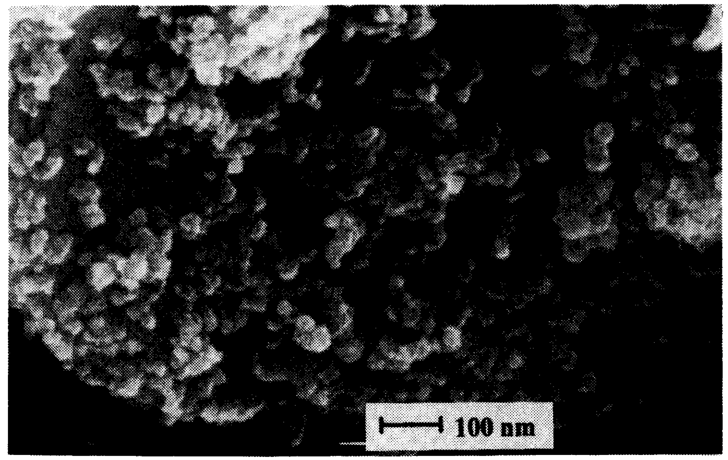

Fig. 3: SEM picture of a SiC grain with a chemically bonded carbon.

Carbon is homogeneously distributed on the SiC particle surface, and good processing and sintering properties can be expected for such a powder. Both coating techniques have been tested in casting processes. Aqueous slurries with an overall composition of 63 wt.-% SiC, 2.5 wt.-% C and 0.65 wt.-% B_4C were prepared which exhibited a low viscosity of 10-15 mPa.s and a particle size distribution between 100 and 500 nm. Slip casting as well as pressure slip casting experiments gave green compacts with green densities in the range of 58 to 63 %. These specimens are further characterized by an excellent carbon distribution, as demonstrated in Fig. 4. No significant concentration gradient in carbon distribution could be detected, and thus,

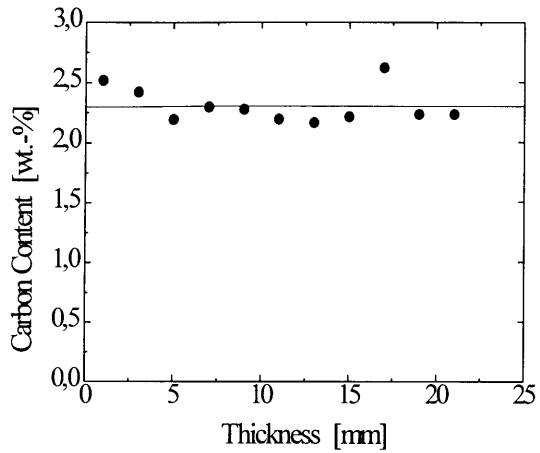

Fig.4: Carbon distribution in a pressure slip casted green body (10 bar)

it was possible to cast thick parts (< 25 mm) with a homogeneous green microstructure (Fig. 5).

Due to the homogeneous microstructure and especially the carbon black distribution throughout the SiC matrix, green specimens could be pressureless sintered to high densities (98.5 % - 99.3 %) in the temperature range between 2050 and 2160 °C. Fig. 6 shows a typical microstructure of an SiC sample sintered at 2160 °C for 30 min which is characterized by a fine grained microstructure of nearly equiaxed grains with an average grain size of 5.2 µm.

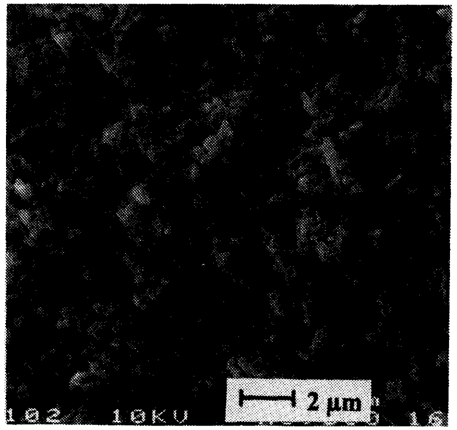

Fig. 5: Green microstructure of the sample from Fig.4.

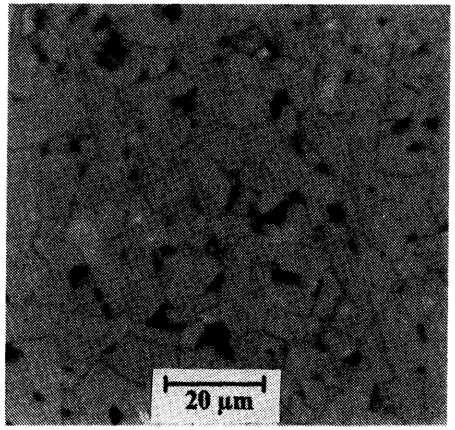

Fig. 6: Microstructure of a SiC sample sintered at 2160 °C for 30 min (D = 0.987)

In Table 1 the mechanical properties of pressureless sintered SiC parts prepared from powders electrostatically coated and chemically coated with carbon black are compared with the properties of specimens prepared by the conventional polymer technique.

	This work electrostatic	chemical	Conventional [8]
ρ [g/cm³]	3.17	3.18	3.10-3.12
E [GPa]	440	470	400-420
$HV_{0.5}$ [GPa]	29	29	25-27
K_{IC} [MPa.m$^{0.5}$]	3.0 - 3.5	3.0 - 3.5	3.0-3.5
G [µm]	4-7	3-5	5-10
σ_b [MPa] (3-point-bending)	530	560	450-530
Weibull modulus	10-11	11-12	10

Table 1: Comparison of mechanical properties of pressureless sintered parts prepared by different processing techniques.

In comparison with the conventional polymer route, the novel processing techniques lead to SiC parts with improved material properties. These results have to be attributed to the extremely homogeneous distribution of carbon black in the green compacts, which lead to a nearly complete reduction of SiO_2 (> 99 %), as found by oxygen analysis using hot gas extraction.

CONCLUSION

A coating process for sub-micron SiC powders with nano-scale carbon black particles has been developed. The modified powder has been successfully used for the preparation of very homogeneous multicomponent slips ($SiC/B_4C/C$), which are stable against segregation during storage and in casting processes. As a result, excellent additive distributions could be obtained within green compacts, and by pressureless sintering material properties could be achieved which normally require hot pressing or a post-HIP treatment. It can therefore be concluded that direct deposition of sintering additives on matrix powders leads to improved processing properties of ceramic slurries as well as material properties. This process offers new opportunities for tailoring ceramic microstructure as well as material properties.

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