LASERINDUCED SYNTHESIS AND CHARACTERIZATION OF BORON DOPED NANOSIZED SILICON CARBIDE POWDERS

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Ultrafine boron doped SiC powders, both stoichiometric and with carbon excess, were produced by a CO_2 laser induced reaction using $SiH_4/C_2H_2/B_2H_6$ mixtures as gasphase precursors. Characterization of the obtained powders by chemical analysis, transmission electron microscopy (TEM), X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) showed a decrease of mean particulate size and the mean size of β-SiC crystallites for the boron containing powders compared to the boron-free powders. Consistently the amorphous powder fraction increased. During powder production temperature profiles were measured in the reaction flame with high spatial resolution by the BoxCARS (Coherent Anti-Stokes Raman Scattering) technique.

INTRODUCTION

Boron is a common additive for compacting SiC powders by sintering and hot isostatic pressing (HIPing). The production of in-situ boron doped SiC-powders is thus of special interest, because it leads to homogenous composites on a microscopic scale. It has been suggested that non-stoichiometric carbon rich SiC powders may improve the compaction properties of the powders by lowering the necessary temperatures during compaction. Exact knowledge about the temperature distribution in the reaction flame gives reference to possible reaction routes leading to SiC and SiC/B powders. The non-invasive BoxCARS technique is applied to determine the temperature.

EXPERIMENTAL

Experiments resulting in the production of nanosized SiC, SiC/B, CSiC and CSiC/B powders were performed using a laser chemical flow reactor which is described in detail elsewhere [1,2]. Powders were produced at a rate of approx. 35 g/h and collected, stored and handled under inert gas. The laser induced synthesis experiments discussed here were carried out at a gas pressure of 50 kPa using the

10P20 line emitted by a cw CO_2 laser. This line is strongly absorbed by the ν_4 fundamental vibration of SiH_4. The precursor mixture consisted of silane (SiH_4), acetylene (C_2H_2) and diborane (B_2H_6). The quantity of diborane was chosen to obtain a boron content of 2.5-4 wt.% in the resulting powders, which is sufficient for densification of the powders without further addition of boron. A flow of 13 slm argon was used as protective gas. The experimental conditions are listed in Table 1.

Run		reaction gas flow rate			laser intensity
		Φ_{SiH_4} (sccm)	$\Phi_{B_2H_6}$ (sccm)	$\Phi_{C_2H_2}$ (sccm)	I_L (W/m^2)
SiC	P1	333	---	167	$5 \cdot 10^7$
SiC/B	P2	323	15	162	$5 \cdot 10^7$
CSiC	P3	333	---	397	$2.5 \cdot 10^7$
CSiC/B	P4	323	15	392	$2.5 \cdot 10^7$

Table 1: Experimental conditions for SiC powder production

RESULTS AND DISCUSSION

Powder characterization

Chemical analysis of the obtained powders show an increase in oxygene content for the boron doped powders compared to the boron-free powders as well as for the carbon-rich powders compared to the stoichiometric powders. Assuming that oxygene is bound completely to SiO_2 and a maximum amount of SiC is formed, the carbon excess for the powders P3 and P4 leads to a content of free carbon of more than 30 wt.%. Table 2 shows the results of chemical analysis in detail.

Run		powder composition			
		Si (wt.%)	C (wt.%)	B (wt.%)	O (wt.%)
SiC	P1	67.4	30.6	---	0.93
SiC/B	P2	64.7	28.0	4.0	1.49
CSiC	P3	62.9	35.3	---	1.76
CSiC/B	P4	54.3	38.6	2.7	4.26

Table 2: Results of chemical analysis

Transmission electron microscope (TEM) recordings like figure 1 (micrograph of sample P1) show chainlike powder agglomerations. The size distributions of the individual particulates evaluated from the recording are narrow (figure 2).

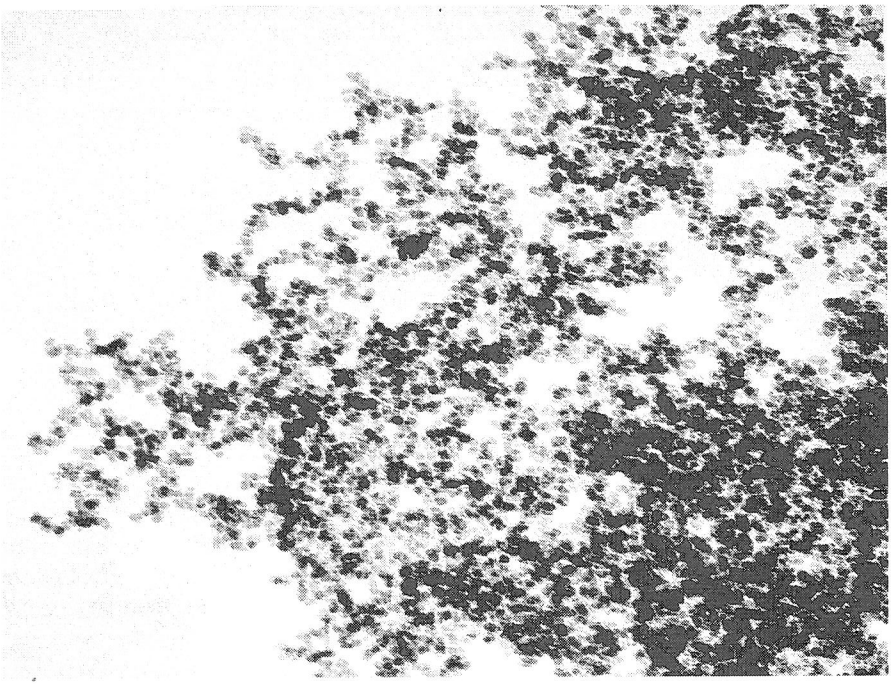

Figure 1: TEM recording of powder SiC P1 with d_{Part}= 14.6 nm ± 1.4 nm (↔: 60 nm)

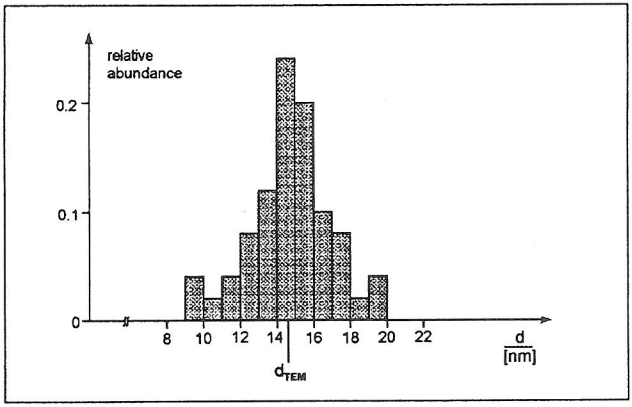

Figure 2: TEM particulate diameter size distribution for powder SiC P1

X-ray powder diffraction (XRD) spectra of the powders were used to calculate the crystallite size via the peak width of the (220)- bragg reflection. The intensity ratio between peak and background was used to estimate the amount of amorphous powder for the samples P1 and P2. Table 3 shows a significant decrease in mean particulate size, crystallite size and degree of crystallization for the boron doped powders. In addition there is a decrease in crystallite size and mean particulate diameter for the carbon rich powders. For the density of the amorphous state 80% of the bulk density of SiC (3.21 g/cm^3) was assumed.

Run		powder characteristics		
		d_{Part} (nm)	d_{Cryst} (nm)	amorphous fraction
SiC	P1	14.6	5.1	65 vol.%
SiC/B	P2	13.1	3.2	74 vol.%
CSiC	P3	12.6	3.9	n.c.
CSiC/B	P4	10.1	2.3	n.c.

Table 3: Mean particulate diameter, crystallite size and crystallization degree

High resolution TEM recordings show crystal imperfections like grain boundaries and stacking faults in the individual particulates which are the origin of broad XRD-peaks resulting in small calculated crystallite sizes. Furthermore, single particulates are either crystalline or amorphous, i.e. the idea of particulates consisting of small crystallites embedded in an amorphous mass is not adequate.

X-ray photo electron spectroscopy (XPS) of the produced powders indicates that boron addition results mainly in free amorphous boron and boron oxide (B_2O_3), no evidence for the formation of boron carbide or boron silicide was found. For the carbon rich powders strong peaks corresponding to carbon-carbon bonds were found in good agreement with the results of chemical analysis.

Diagnostic of the reaction flame

The narrow-band scanning spatially resolving CARS diagnostic set-up was developed in our institute and is similar to a CARS set-up published previously [3,4]. Spectra of H_2 (Q-branch, cold band) were taken at different locations in the reaction zone. Rotational temperatures were evaluated using a numerical fitting procedure. Figure 3 compares the axial temperature distributions of SiC (P1) and SiC/B (P2) powders.

The measured temperature gradients for the SiH_4/C_2H_2 flames with and without diborane are almost identical ($3.1 \cdot 10^6$ K/m). Assuming a mean precursor flow velocity of 2.3 m/s the measured heating rates are $7.1 \cdot 10^6$ K/s. For the B_2H_6 containing flame, a

high temperature plateau (≈900-1000 K) of the reactant gas volume is found already several millimeters before the gas flow reaches the CO_2 laser focus line.

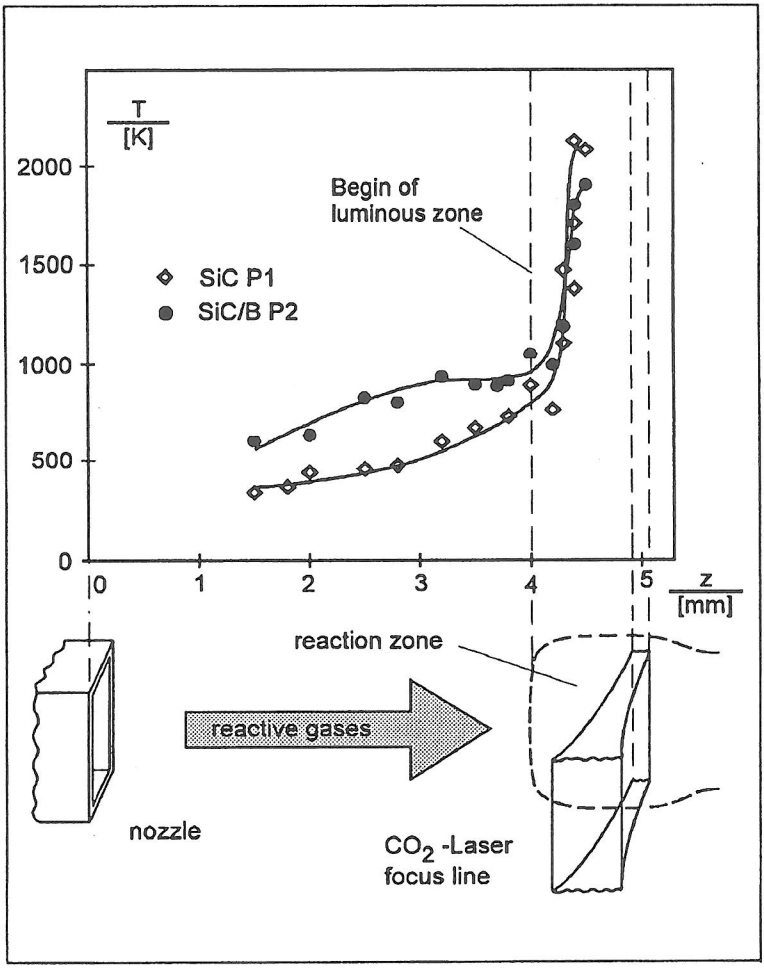

Figure 3: Axial temperature profile for the pyrolysis flames SiC and SiC/B

Due to high Peclet numbers of the gas flow this temperature increase cannot be explained by thermal diffusion. A reason for the observed behaviour might be either the catalytic property of B_2H_6 or alternatively a boron containing intermediate species in the flame.

CONCLUSION

Ultrafine SiC powders with variable boron and carbon content were produced by CO_2 laser pyrolysis with narrow size distribution. Diborane addition resulted in particulates of reduced size, reduction of crystallite size and a growth of the amount of amorphous particulates. The boron containing powders show an enhanced affinity to oxygene. The formation of boron oxide and free amorphous boron in the powders is shown by XPS. CARS measurements inside the reaction flames indicate an increase in temperature upstream the CO_2 laser focus for the boron containing flame. This effect might by caused by diborane induced pre-reactions.

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