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Mechanical Properties of Injection Molded B_4C–C Ceramics

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Various mechanical properties of carbon-doped boron carbide ceramics, prepared by the fabrication route, injection molding/pressureless sintering/post-hot isostatic pressing (HIP) were investigated as a function of the sintering temperature and the carbon additive level used. An optimum combination of mechanical properties (flexural stregth, fracture toughness, Young's modulus, Knoop's hardness) is thus obtained with 100% dense and very fine grained materials (mean grain size 1–4 μm) which were sintered at temperatures from 2150 to 2175°C and post-HIPed at 2050°/200 MPa Ar, having an approximate final composition of 96 B_4C–4C (wt%). © 1997 Academic Press

1. INTRODUCTION

Components made of dense boron carbide are widely used in wear resistant applications, e.g., as blast nozzles, wheel dressing tools, and light weight armor plates. Since boron has a large cross section for the absorption of thermal neutrons, boron carbide articles are also used in nuclear industry as neutron absorber pellets and shieldings (1).

Geometric simple shapes and pellets can be easily fabricated by a press-and-sinter process, developed in the late 1970s, which uses boron carbide powders of submicrometer particle size (specific surface area, 10–20 m^2/g) and firing of dry pressed compacts in inert atmospheres to temperatures near 2150°C (2).

However, for "near net shape" mass production of nozzle shapes without the need for expensive diamond machining, injection molding as the most suitable forming process has been developed for boron carbide at Elektroschmelzwerk Kempten (ESK). For pressureless sintering of the moldings, the boron carbide must contain small additions of amorphous carbon, which acts as a sintering aid. Up to now, the carbon has been added almost exclusively as phenolic resin, e.g., Novolac, introduced in organic solution or as an emulsion in water (3–5). During drying of the boron carbide particle suspension a thin resin film is deposited on the boron carbon surface. Later the resin film is coked to amorphous carbon coatings, while the shapes are heated to the sintering temperature.

This was for many years a well-established technique for die-pressed, isopressed, and injection molded shapes. Nevertheless, the resin route showed two major drawbacks, (i) the fairly complex handling of the resin-doped powders and (ii) environmental problems during pyrolysis in a seperate coking step carried out at temperatures up to 1000°C. The direct blending of carbon black with B_4C has been suggested as an alternative, but until recently incomplete densification was achieved with this additive, namely because of the inhomogeneity of the initial B_4C–C particulate dispersions (6).

After an improved method of dispersing carbon black in B_4C powders was developed, the resin route was substituted by the carbon black route and was used successfully for the injection molding process of nozzle shapes (7).

The aim of this work is to

(i) show the potential of carbon black as a sintering aid for B_4C and

(ii) to investigate microstructure and mechanical properties of injection molded B_4C–C ceramics.

2. EXPERIMENTAL PROCEDURE

2.1. *Sample Preparation*

The boron carbide powder, selected as starting material, had a purity of $B + C = 98.5\%$ (total carbon, 20.86 wt%), a specific surface area of 15.0 m^2/g (BET), and a maximum particle size of 3 μm. The impurities are (ppm): oxygen (9800), nitrogen (3200), free carbon (6400), and metals (1500).

Carbon black (Printex 60, Degussa AG., Frankfurt a.M.), showing a particle size of 20 nm and a specific surface of 120 m^2/g, was used as a carbon source. Carbon additions were employed at levels up to 5 wt%. Early sintering experiments with varying carbon additions have shown that an essential drop of sinterability is obtained with addition levels below 2 wt% carbon black (relative densities < 90–95% TD). Consequently 2 wt% carbon black was selected as the safe lower limit of carbon additions in the

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present work. To prepare homogeneous B_4C–C batches, 100 parts of the B_4C powder were mixed with 2/3/4 and 5 parts of carbon black, this being achieved by wet-dispersing of the powders in deionized water (8). After spray drying of the wet-sieved (20 μm mesh size) slurries, the granulated powders were further processed to shaped components via injection molding. A flow chart, showing steps of the molding/sintering process, is presented in Fig. 1. In the first step, the B_4C–C powder mixtures were compounded in heated kneaders with 18 wt% of an organic binder system (melting point range between 50 and max. 150°C) to produce the injection molding granulates, which are fed into conventional injection molding machines. In the second step, optimum molding conditions (injection temperature, 120°C; die temperature, 32°C; die pressure, ~ 45 MPa; viscosity, ~ 100 Pa s for the shear velocity range 1000–3000 s^{-1}) were elaborated for prismatic test bars which were molded together with B_4C nozzles (7), under real production conditions. A test bar tool providing two side-gated cavities was used. For their dimensions a linear shrinkage of 18% was considered to obtain a 3.5 × 4.5 × 45.0 mm test bar. In the third step, dewaxing was accomplished by heating the molded test bars (molded density, 1.90–1.93 g/cm^3) in gas pressure controlled (100 mbar) ovens. Thereby the binders were removed by evaporation and/or thermal decomposition (cycle length, 4 days) at temperatures up to 450°C.

In the fourth step, the dewaxed parts with a green density of 1.56–1.58 g/cm^3 ($>60\%$ TD) were placed into a graphite resistance furnace and sintered pressureless by heating to sintering temperature (90 min heat up) under an atmosphere of 10 mbar argon. Sintering temperatures were at 25°C intervals in the range 2125 to 2225°C with 120 min hold at maximum temperature. Temperature measurement accuracy was ± 5°C (optical pyrometer).

In the last step, the sintered test bars (sintered density $>95\%$ TD) were subjected to a post-densification to a densitiy of $>99.5\%$ TD, by hot isostatic pressing (HIP) at 2050°C without encapsulating in a high-pressure autoclave furnace under a gas pressure of 200 MPa argon. Since HIP was essentially below sintering temperature, post-HIPed parts underwent no additional grain growth, which actually would have lead to strength degradation of the components.

2.2. *Testing Procedure*

The total carbon content of the sintered materials was analyzed by combustion in oxygen and determination of CO_2. To infer the composition B_4C–$C_{(\text{free})}$, the free carbon was calculated approximately from the total carbon according to the relation

$$\text{wt\% } C_{\text{free}} = 1.256 \text{ wt\% } C_{\text{total}} - 25.6,$$

taking the composition of C-saturated boron carbide as $B_{4.33}C$ (9). The percentage of B_4C by weight was computed according to $(\text{wt\% } C_{\text{total}} - \text{wt\% } C_{\text{free}}) \cdot 4.9001 = \text{wt\% } B_4C$.

The densities were determined either by the water immersion technique or by calculation from mass and dimensions of the prismatic test bars. The relative density, in % theoretical density (TD), is based on the theoretical density of the B_4C–C composite material. The theoretical density was calculated from the final phase composition B_4C–C (% by weight) of the composite materials according to the law of mixtures

$$\text{TD}(\text{g/cm}^3) = \frac{100}{\left(\frac{\text{wt\% } B_4C}{2.52}\right) + \left(\frac{\text{wt\% } C_{\text{free}}}{2.27}\right)},$$

$$\% \text{ TD} = \frac{\text{Bulk Density}}{\text{TD}} \times 100.$$

All flexural tests were conducted on 3.5 × 4.5 × 45.0 mm test bars with surfaces ground and lapped to R_a values <0.1 μm using a 10–20 μm diamond lapping disk. Strengths were measured by four-point flexure test using an inner span of 20 mm, an outer span of 40 mm, and a stressing rate of 750 N/min on a 100 kN universal testing machine (Zwick 1474). Flexural strength values (σ_B, 4pt) were mean values of 10 measurements, the relative standard deviation, $(s/\bar{\sigma}) \times 100$, was in the range of 8 to 15%. To determine the fracture toughness of the B_4C–C materials, the Bridge Indentation Method with a controlled flaw in the region of maximum tensile stress was used. Sets of five specimens were used for the toughness measurements. The test bars were precracked on the center of the tensile surface (3.5 × 5.0 mm) with a Knoop diamond indentation (150 N load) and the crack was then driven across the surface and halfway down into the sample with a hard metal bridge. Then the test bar was dipped for 5 min into a penetrant dye (fluorescent ink), dried, and finally broken in analogy to flexural stength determination. After fracture, the crack depth, a, was measured to ± 0.01 mm at 25-fold magnification in a stereo microscope under ultraviolet light. K_{IC} was finally computed according to the equations

$$K_{IC} = \frac{F_{\max}}{B\sqrt{W}} \times Y$$

$$Y = \frac{S_1 - S_2}{W} \times \frac{3\sqrt{\alpha}}{2(1-\alpha)^{3/2}} \times \left[1.9878 - 1.326\alpha - \frac{(3.49 - 0.68\alpha + 1.53\alpha^2)\alpha \times (1-\alpha)}{(1+\alpha)^2}\right],$$

where $\alpha = a/W$ is the ratio crack depth/sample height, $B = 3.5$ mm, $W = 4.5$ mm, $S_1 = 40$ mm, $S_2 = 20$ mm, and $F_{\max}$ = fracture stress in N.

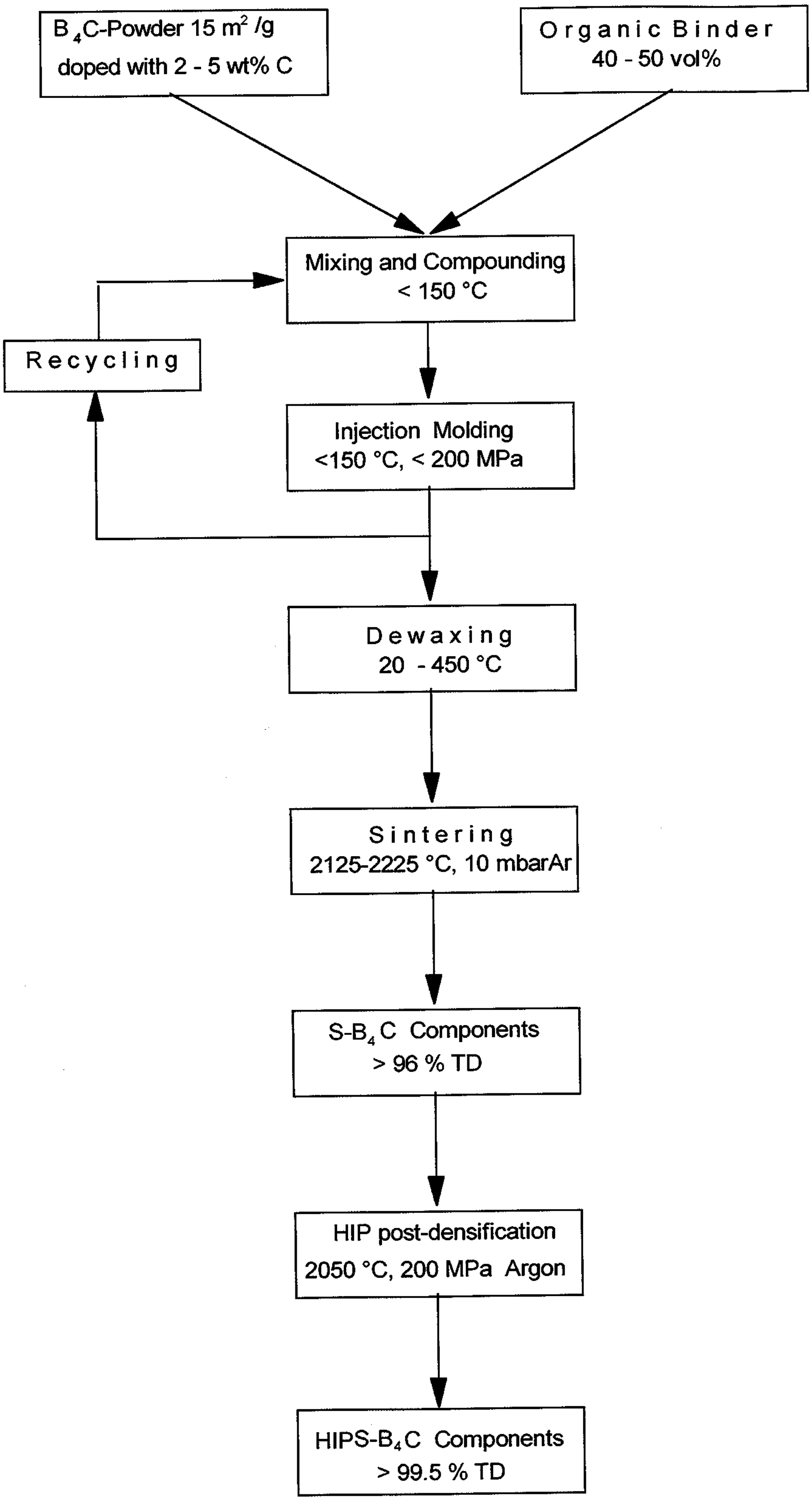

FIG. 1. Flow chart for dense carbon-doped B_4C components via injection molding.

TABLE 1
Compositions and Theoretical Densities of Sintered B_4C–C Moldings

Moldings	Sintered bodies			
Carbon black addition (wt% C)	Total carbon (wt% C)	Free carbon (wt% C)	Composition[a] B_4C–C (wt% C)	Theoretical density (g/cm^3)
2	23.25	3.60	96.3–3.6	2.51
3	24.00	4.54	95.3–4.5	2.51
4	24.81	5.56	94.3–5.5	2.51
5	25.50	6.43	93.4–6.4	2.50

Note. Sintering conditions: 2175°C, 120 min, 10 mbar argon.

[a] Metal impurities: 0.15 wt% (total), oxygen + nitrogen was below 0.05 wt%.

The mean variation of K_{IC} about the average was 0.2 MPa m$^{1/2}$. Young's modulus was calculated from vibration resonance spectra using five test bars per composition and the Förster Elastomat 1024. The Knoop microhardness number, HK-0.1, was measured by indentation (10 values per sample) with a Knoop diamond at a load of 0.1 kp ($\sim$ 0.98 N) on a Leitz Miniload Tester.

For microstructural characterization, samples were polished to 1 μm diamond finish and etched electrolytically with diluted sulfuric acid. The linear intercept method was employed to measure the mean grain size on a semiquantitative image analyzer (Videoplan/Kontron Comp., Munich).

3. RESULTS AND DISCUSSION

3.1. *Sintering and HIP Treatment*

Table 1 shows the effect of the addition of carbon black on the chemical composition of resulting B_4C–C composite materials. The data illustrate that, with carbon additions in the range 2–5 wt%, B_4C–C composites with free carbon contents of between 3.6 and 6.4 wt% are obtained. The free carbon in the sintered bodies is present as particulate graphite ($<$ 2 μm size) homogeneously dispersed and can be easily distinguished from pores on the polished surface using light microscopy with crossed polarizers. As given in Table 1 the B_4C–C composite materials had from $\sim$ 1.4 to 1.6 wt% excess carbon beyond the wt% carbon black additions. This can be explained by the free carbon content (0.6 wt% C) in the starting B_4C powder and additional free carbon ($\sim$ 1 wt%) resulting from coking of the organic binders used for injection molding.

In Fig. 2 the responses of the B_4C–C powder batches to the applied sintering conditions are summarized. In general, the final density increases with increasing sintering temperature and is hardly affected by the amount of free carbon. This observation agrees well with the results of Dole and Prochazka (10, 11) who found that the density of B_4C becomes independent of the carbon addition above $\sim$ 4 wt% C. As shown in Fig. 3, post-densification by HIP to 100% of the theoretical density was possible with 2150 and 2175°C sintered materials having a sintered density $\geqslant$ 96% TD. Since the 2125°C predensified materials with a sintered density of about 95% TD revealed small amounts of open porosity, they could only be post-HIP to a relative density of 96–99%. The drop of HIP densities for the 2200 and 2225°C sintered materials (see Fig. 3) can be entirely accounted for by their coarse grained microstructure revealing intragranular porosity, which could not be closed during HIP.

For reaching 100% TD and elimination of all residual porosity in post densification, the predensified materials must fullfill mainly three requirements:

(i) securing a reasonable high sintered density ($\geqslant$ 96% TD),

(ii) ensuring absolutely 100% closed porosity, i.e., no residual intercommunicating pores, which are open to the surface,

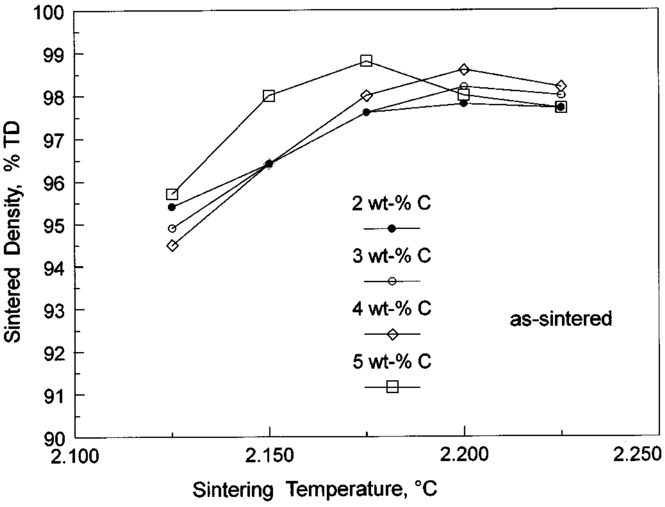

FIG. 2. Sintered density of C-doped B_4C as a function of the sintering temperature (120 min hold/10 mbar Ar).

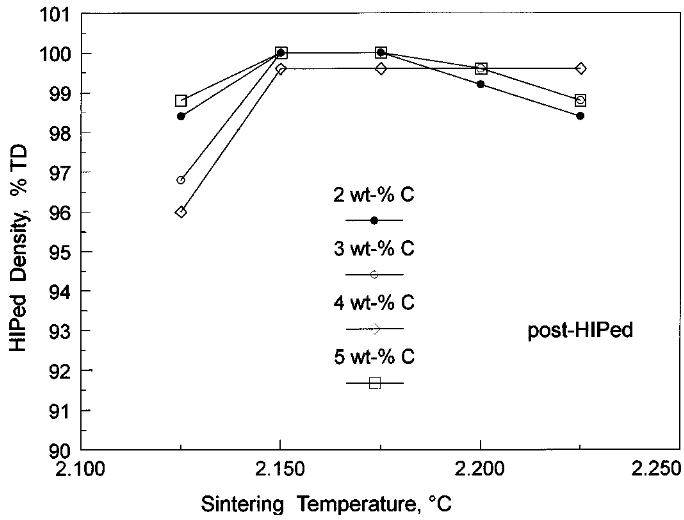

FIG. 3. HIP density of C-doped B_4C as a function of the sintering temperature (HIP conditions: 2050°C, 200 MPa Ar).

(iii) guaranteeing absence of intragranular porosity by providing a fine grained microstructure (mean grain size 1–4 μm).

3.2. Microstructure

The typical microstructure development of injection molded boron carbide over the sintering temperature range of 2125–2200°C is shown in Figs. 4A–4D, for HIP treated sintered B_4C doped with 2 wt% carbon black (final composition, 96 B_4C–4C wt%). In agreement with an earlier work (12), beyond a certain sintering temperature limit, which seemed to be specific for the individual B_4C powder used, discontinuous grain growth has been observed. In the sample sintered at 2125°C (Fig. 4A), the microstructure is composed of fine equiaxed grains with a mean grain size of 1.3 μm. In the samples sintered at 2150 and 2175°C, the mean grain size increases to 1.6 and 3.9 μm, respectively, and bimodal grain distributions are observable. As shown in Fig. 4B at 2150°C a small amount of larger grains (5–10 μm) is embedded in a fine grained matrix (0.3–5.0 μm).

However, at 2175°C (Fig. 4C), only small amounts of finer grains remain in a matrix of larger grains (max. grain size 20 μm). The microstructure of the samples sintered at 2200°C (Fig. 4D) is almost entirely large grained (mean grain size of 9.9 μm, max. grain size ~ 50 μm). It is interesting to note, that distribution of the second phase graphite particles (0.3–2.0 μm size) also depends significantly on sintering temperature. At ≤ 2150°C the graphite phase is distributed only on the grain boundaries and at grain corners. In the coarser grained samples sintered at ≥ 2175°C an increasing amount of carbon, dispersed within the boron carbide grains ("intragranular graphite"), together with extensive twinning of the B_4C grains, is observed.

In view of the sintering mechanism hitherto known for C-doped B_4C, it seems obvious that the very fine grained microstructure (mean size, 1–4 μm) obtained in the present

TABLE 2
Sintering Response and Mechanical Properties of Injection Molded Boron Carbide Ceramics

Carbon black addition (wt%)	Sintering temperature[a] (°C)	Sintering condition	Final density (g/cm^3)	Relative density (%TD)	Mean gain size (μm)	Flexural strength (MPa)	Young's modulus (GPa)	Knoop's hardness (HK-0.1)	Fracture toughness (MPa m$^{1/2}$)
2C	2150	S	2.42	96.4		475 ± 69	406		2.8
		HIPS[b]	2.51	100.0	1.6	579 ± 47	440		2.4
(23.25)[c]	2175	S	2.45	97.6		484 ± 41	421		2.9
		HIPS	2.51	100.0	3.9	564 ± 46	444	2950 ± 167	3.2
3C	2150	S	2.42	96.4		410 ± 37	401		2.6
		HIPS	2.51	100.0	1.5	490 ± 70	436		2.6
(24.00)[c]	2175	S	2.45	97.6		399 ± 34	408		2.8
		HIPS	2.51	100.0	2.8	474 ± 58	434	2862 ± 205	3.2
4C	2150	S	2.42	96.4		462 ± 62	393		2.4
		HIPS	2.50	99.6	1.4	464 ± 66	430		2.6
(24.81)[c]	2175	S	2.46	98.0		484 ± 40	402		2.7
		HIPS	2.50	99.6	1.6	576 ± 51	430	2786 ± 197	2.5
5C	2150	S	2.45	98.0		454 ± 44	394		2.7
		HIPS	2.50	100.0	1.3	565 ± 58	410		2.8
(25.50)[c]	2175	S	2.47	98.8		405 ± 40	402		3.3
		HIPS	2.50	100.0	1.5	439 ± 68	412	2737 ± 144	3.1

[a] Hold time, 120 min (10 mbar Ar).
[b] HIP: 2050°C, 200 MPa Ar, 30 min.
[c] Content of C total (wt%) after sintering.

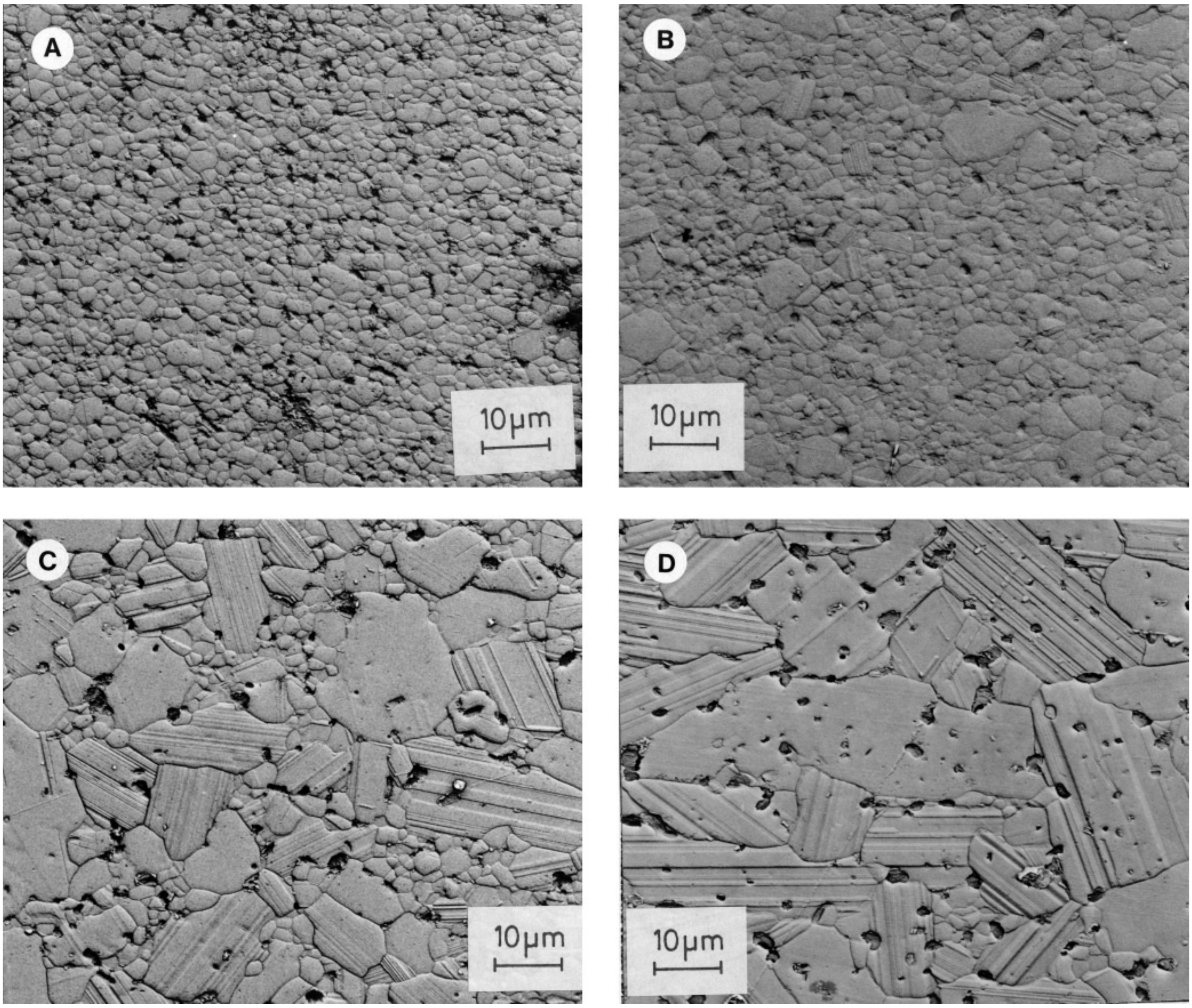

FIG. 4. Microstructures of dense, injection molded B_4C (2 wt% carbon black doped) sintered at different temperatures (120 min, 10 mbar Ar) and HIP-postdensified (2050°C, 200 MPa Ar, 30 min). (A) Sintered at 2125°C; mean grain size, 1.3 µm; max. grain size, 5 µm. (B) Sintered at 2150°C; mean grain size, 1.6 µm; max. grain size, 10 µm. (C) Sintered at 2175°C; mean grain size, 3.9 µm; max. grain size, 20 µm. (D) Sintered at 2200°C; mean grain size, 9.9 µm; max. grain size, 50 µm.

work results from the homogeneous distribution of nanosized carbon black particles (diameter, 20 nm) (i) on the surface of the B_4C grains and (ii) at B_4C/B_4C grain boundaries. The role of carbon as a sintering aid in solid state sintering of B_4C is therefore twofold. First, during the early sintering stage, amorphous carbon inhibits coarsening, brought about by surface-to-surface matter transport (2), e.g., by suppressing vapor-phase transport via deoxidation (11).

Second, during the later sintering period, the carbon particles migrate with the boundary, thereby controlling grain growth, until they are agglomerated as graphite aggregates at boron carbide grain corners (2).

The microstructures of the 3–5 wt% carbon-doped B_4C ceramics where not much different from those of the 2 wt% composition exept that mean and maximum grain sizes were somewhat smaller, dependent on the free carbon content used (see Table 2). At sintering temperatures of 2225–2250°C grain growth was very fast ("abnormal grain growth") and led to elongated grains with lengths up to 100–200 µm. Thus, free carbon once present mainly as micrometer-sized intragranular graphite cannot inhibit further coarsening of the B_4C microstructure. All microstructures containing large B_4C grains (100–200 µm size) showed transgranular microcracking (crack lengths, 80–200 µm) which could be revealed after etching of ceramographic

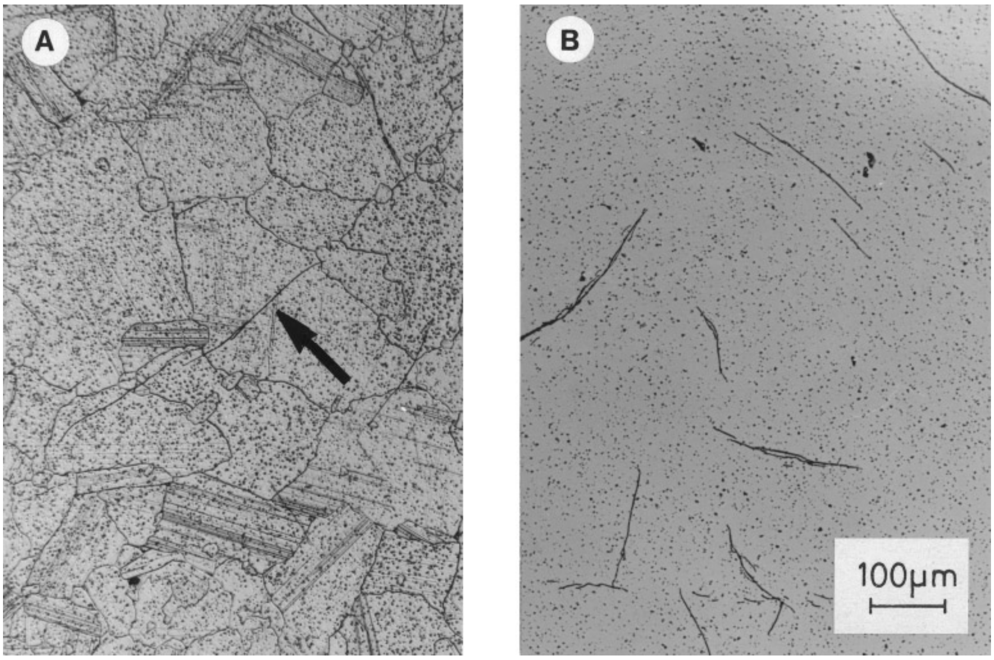

FIG. 5. Transgranular microcracks in coarse grained boron carbide. (A) Polished and etched section of a HIPS–B_4C (3%C doped), annealed at 2225°C/180 min, mean grain size, 120 µm; notice twinning and transgranular cracking. (B) Same material as (A) but after repolish to exhibit microcracks.

sections especially by repolishing (Fig. 5). This microcracking occurred during cooling of coarse grained boron carbide and is linked to its thermal expansion anisotropy, as already was found by Prochazka *et al.* (13).

3.3. Mechanical Properties

In Table 2 the final density, mean grain size, flexural strength, Young's modulus, Knoop's hardness, and fracture toughness of sintered (S) and post-HIPed boron carbide (HIPS), doped with 2–5 wt% carbon black are summarized. The data of Table 2 cover the sintering temperature range 2150–2175°C, where post-densification by HIP led to substantially pore-free ceramics (100% TD) with optimized properties. Data corresponding to other sintering temperatures are displayed only graphically in Figs. 6, 7, 9, and 10.

3.3.1. Flexural strength. As can be seen from Figs. 6 and 7, the strength increases up to sintering temperatures of 2150–2175°C, where it begins to drop significantly. This behaviour was typical for all B_4C–C compositions and did not depend on the free carbon content or on HIP treatment. Since transgranular cracks were formed in large grained samples at temperatures $> 2200°C$, it is concluded that the decreasing strength is linked with residual stresses and especially with observed microcracking. As expected, the average strength of fine grained materials is substantially increased by the applied HIP post-densification (see Fig. 7). By comparison of the maximum strength achievable with identical B_4C–C compositions ($C_{total} = 24.8$ wt%, 94 B_4C–6C wt%), but using different sample fabrication routes, it is clearly seen that the injection molded, carbon-black-doped composition is superior to the isopressed resin-doped material (Fig. 8). Is is believed that the extraordinarily high strength obtained for injection molded HIPSB_4C (average, 576 MPa; maximum value, 650 MPa) reflects not only the smaller grain size but also smaller flaw size, the latter being

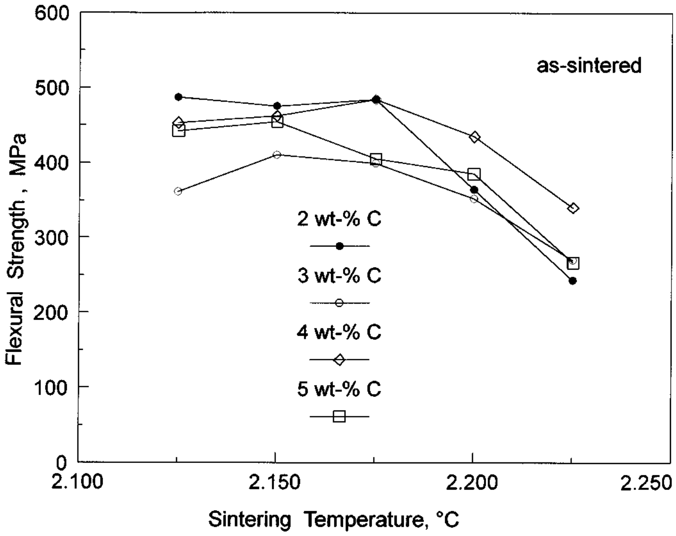

FIG. 6. Flexural strength of as-sintered B_4C doped with carbon black as a function of sintering temperature.

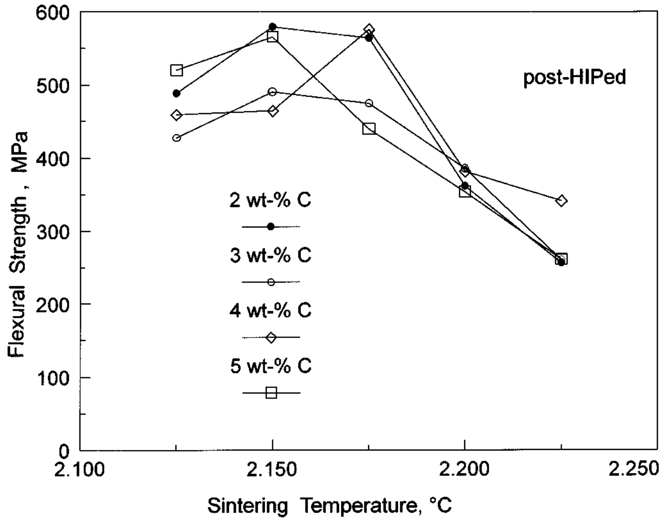

FIG. 7. Flexural strength of HIP-treated sintered B_4C doped with carbon black as a function of the sintering temperature.

a consequence of almost defect free and very homogeneous green moldings.

3.3.2. Fracture toughness. In Fig. 9 the fracture toughness data of HIP-treated sintered B_4C–C materials are compiled as a function of the sintering temperature. As can be seen, the toughness starts with values around 2 MPa $m^{1/2}$ (comparable to B/C-doped sintered SiC) for 2125°C, increases up to $\sim$4 MPa $m^{1/2}$ for sintering temperatures $>$ 2200°C, and is not much affected by the carbon addition level used. The corresponding curves of K_{IC} versus temperature for sintered materials without HIP post-densification were almost identical. The rising toughness with rising sintering temperature is primarily attributed to an increase in grain size (Fig. 10). The reason for the grain size effect on fracture toughness is not clear. There is probably a dependence on residual stress and microcracking induced by larger B_4C grains. It should be noted that maximum strength achieved for C-doped HIPSB_4C materials correlate to a median fracture toughness of between 2.6–3.2 MPa $m^{1/2}$.

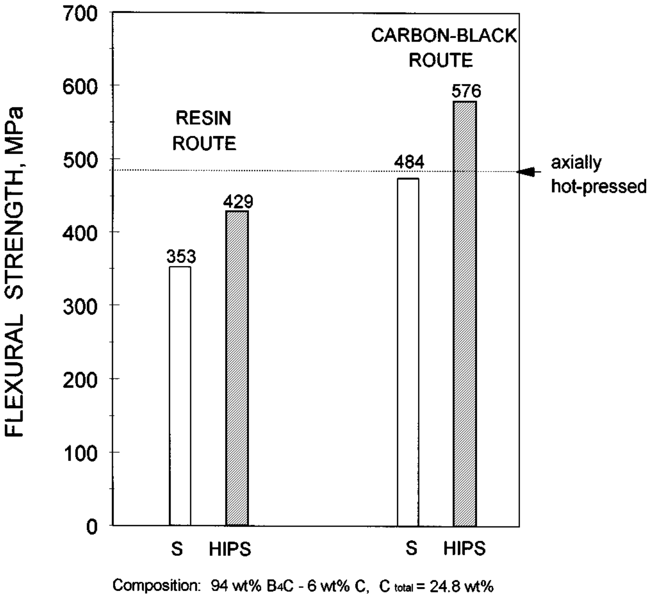

FIG. 8. Flexural strength of sintered (unhatched) and post-HIPed (hatched) 94 B_4C–6C test bars (total C, 24.8 wt%) produced by different fabrication routes. (Left) isopressed, resin doped. (Right) injection molded, carbon black doped.

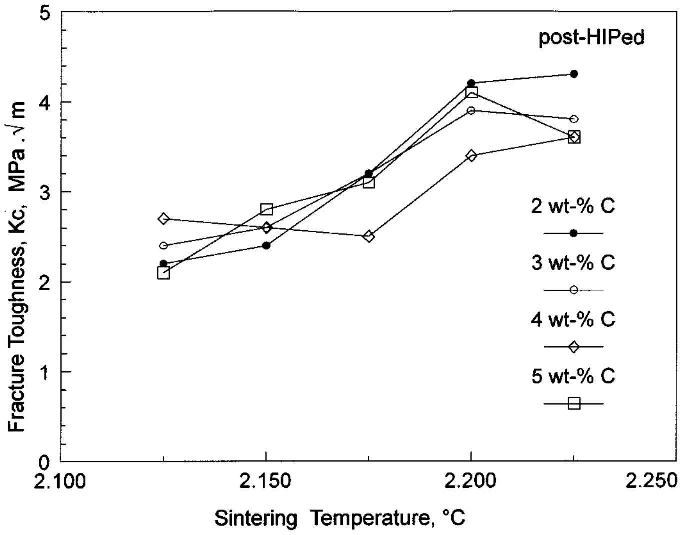

FIG. 9. Fracture toughness of HIP-treated sintered B_4C doped with carbon black as a function of the sintering temperature.

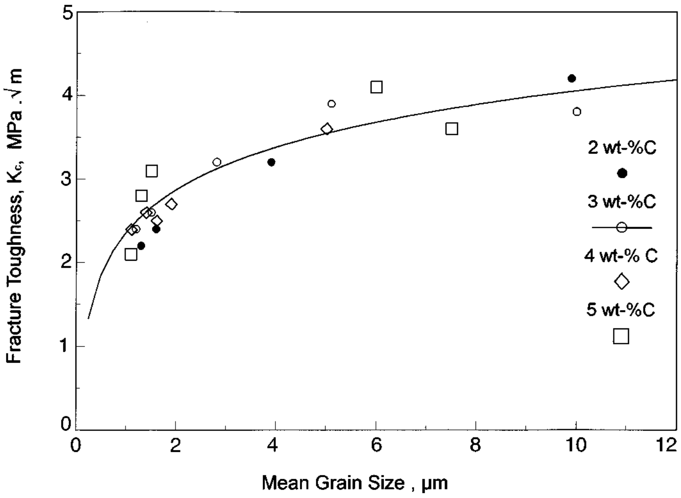

FIG. 10. Fracture toughness of HIP-treated sintered B_4C doped with carbon black as a function of the mean grain size.

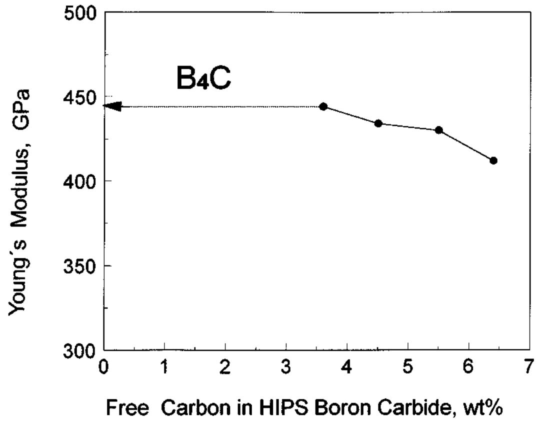

FIG. 11. Young's modulus of HIPSB_4C as a function of the free carbon content of B_4C–C compositions sintered at 2175°C.

3.3.3. Young's modulus and Knoop's hardness. For most applications in abrasive wear industry high stiffness and high hardness are required, which are best accomplished through use of pore free, 100% dense HIPSB_4C materials. Figures 11 and 12 show Young's modulus and Knoop's hardness data, respectively, as a function of the free carbon content in HIPSB_4C (sintering temperature, 2175°C). Since second phase graphite particles act like small pores, stiffness and hardness decrease with increasing free carbon content. The maximum values for Young's modulus and hardness, 444 GPa and 2950 HK-0.1, respectively, were obtained with HIP-treated B_4C doped with 2 wt% carbon black (final composition, 96 B_4C–4C wt%). Both property values are respectable and match nicely with values given in the literature for single phase, dense boron carbide (1, 14, 15).

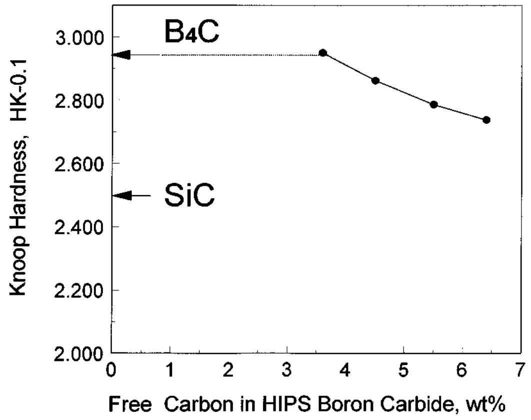

FIG. 12. Knoop's hardness of HIPSB_4C as a function of the free carbon content of B_4C–C compositions sintered at 2175°C.

4. CONCLUSIONS

A new carbon-black-doped boron carbide ceramic, prepared by the fabrication route, injection molding/ pressureless sintering/post-HIP, has been demonstrated to possess finer grain size and better strength than those of commercial HIPS–B_4C using phenolic resin as a carbon additive (5).

During solid state sintering of B_4C surface-to-surface matter transport and coarsening were effectively inhibited by the homogeneously dispersed, nanosized carbon black particles. An optimum combination of properties is thus obtained with very fine-grained materials (mean grain size, 1–4 μm) having an approximate composition of 96 B_4C–4C wt%, which corresponds to the lowest content of free carbon (~ 3.6 wt%) that still permits pressureless sintering and post-HIP to full density.

The maximum values for flexural strength, Young's modulus, and Knoop's hardness, 579 MPa, 444 GPa, and 2950 HK- 0.1, respectively, were obtained for moldings sintered at temperatures from 2150 to 2175°C. Increasing the sintering temperature to > 2200°C led to coarse grained B_4C–C ceramics with improved toughness ($K_{IC} = 4.2$ MPa $m^{1/2}$) but significantly reduced strength (200–300 MPa).

The reduction in strength is explained by the occurrence of internal stresses and/or transgranular microcracks (crack lengths, 80–200 μm) in coarse grained boron carbide (maximum grain size > 100 μm).

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