

Structural and Mechanical Properties of Activated Sintered Boron Carbide-Based Materials

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Boron carbide based materials ($B_4C-Me_x^{IV-VI}B_y$) were obtained by pressureless sintering at 2150–2250°C in the presence of some transition metal (IV–VI group) carbides ($Me_x^{IV-VI}C_y$, where Me is Ti, V, Cr, and W). The structural and mechanical (micro hardness, abrasive wear resistance) properties of these materials were studied. Changes of the boron carbide lattice parameters were observed after sintering. EDS analysis showed the presence of a transition metal phase in the boron carbide structure. A considerable increase in microhardness (76 GPa) and abrasive wear resistance values of the sintered materials (1.8 times as compared to “pure” hot-pressed B_4C) was registered. A new class of superhard boron carbide-based materials was obtained by pressureless sintering. The materials processed by this method are promising for high performance applications.

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I. INTRODUCTION

Boron carbide possesses a combination of properties which give it a leading role among materials suitable for high performance applications (1–3). The prevailing covalent character of the bonds in the crystal lattice of boron carbide determines both its valuable properties and its low sinterability. This is why the method of hot pressing is the most used method for obtaining high-density boron carbide bodies under industrial conditions (4, 5). Activated sintering methods for boron carbide powders have been reviewed in Refs. (6, 7). The activating effect of some transition metal (group IV–VI) carbide additives on the densification process during sintering of boron carbide powders has been established in (8, 9). Dense materials based on boron carbide have been obtained by a combination of physical and chemical methods of activated sintering (10, 11). The mechanical properties and the chemical stability of the products are similar to or better than those of hot-pressed boron carbide (12–14). The subject of this work is the influence of some transition metal

carbides on the properties of sintered boron carbide based materials.

The changes in phase composition of the sintering additives $Me_x^{IV-VI}C_y$ to $Me_x^{IV-VI}B_y$ (Me is Ti, V, Cr, W) after high-temperature interaction have been registered. The alteration of the lattice parameter values of boron carbide powders during sintering in the presence of TiC, VC, and WC have also been registered. The structure peculiarities and metal-containing phase distribution of pressureless sintered boron carbide when Cr_3C_2 and VC are used as sintering additives have been studied. The dependence of the microhardness values of the sintered boron carbide-based composite materials $B_4C-Me_x^{IV-VI}B_y$ (where Me is V, W, Cr) as well as of hot pressed “pure” boron carbide on the composition and the indenter loadings have also been studied. The abrasion wear resistances of sintered W_2B_5 - and CrB_2 -doped boron carbide and of hot pressed boron carbide materials have been compared.

II. EXPERIMENTAL

II.1. Sample Preparation

A boron carbide^{2*} powder containing 77.54 wt.% combined boron and 21.70 wt.% total carbon was used to produce dense samples. Transition metal (group IV–VI) carbides^{2**} (TiC, VC, Cr_3C_2 , and WC), were utilized as sintering aids. Submicrometer size powders were obtained by intensive mechanical treatment in a centrifugal planetary mill.^{2***} Stainless steel milling bowls and balls were used. Because of the highly abrasive ability of boron carbide and metal carbide powders, a large quantity of Fe-containing contaminants were introduced into the milled powders from the milling accessories. The impurities were removed by a chlorine acid solution (1:1). Powdery $B_4C-Me_x^{IV-VI}C_y$ mixtures were obtained by homogenization in a planetary mill. Polyamide bowls and Teflon balls with steel cores were used to prevent contamination during the treatment. Cylindrical dense bodies suitable for structural and mechanical examinations were densified by pressureless sintering and

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² Produced by *Ventron Alfa Products, **Merck, ***Fritsch GmbH.

by hot pressing. The sintering process was carried out at temperatures ranging from 2150 to 2250°C in a furnace³ equipped with a graphite resistant heater. Protective medium of flowing pure Ar was used. The hot pressing process was performed at 2200°C and 20 MPa in a graphite die under Ar.

II.2. Sample Examinations

The specific surface area of the milled powders was established by the BET method. The phase compositions of the samples were determined by X-ray diffraction (XRD) using a Philips diffractometer equipped with a Cu target X-ray tube. The changes of the lattice parameters after sintering of boron carbide in the presence of TiC, VC, and WC were registered. Microhardness studies on sintered $B_4C-Me_x^{IV-VI}B_y$ materials and on “pure” hot pressed boron carbide were carried out. Microhardness (H) was measured at room temperature using an optical microscope equipped with a Vickers diamond pyramidal indenter. The H values were determined according to the expression $H = kP/d^2$ (MPa), where k is a factor equal to 1.854, P denotes the load applied (N), and d , the length of the impressed diagonal (m). The H values were taken as the average of 10 indentations. The microhardness values were measured on samples whose densities after sintering were 95.5–96.4% of the theoretical value for every composition. The density of the hot pressed samples was 2.52 g cm^{-3} (100% t.d.). The samples for microhardness investigations were prepared by grinding and polishing with diamond disks and pastes. The microhardness was measured on boron carbide areas free of pores and metal boride phases. The latter were clearly visible on the smooth polished $B_4C-Me_x^{IV-VI}B_y$ surface because of their higher reflective ability. The microstructures of the sintered materials were characterized by scanning electron spectroscopy (SEM) (JSM 840 equipped with a Link QK 200 dispersive X-ray analyzer). The bulk chemical composition of the metal-containing phases was determined by energy dispersive X-ray spectroscopy (EDS). The abrasion wear resistances of activated sintered and hot pressed boron carbide materials were determined by the weight loss after grinding of the samples in a water medium (Fig. 1). A grinding disk⁴ with a diamond layer was used. The average size of the diamond particles was $60 \mu\text{m}$. The compressive stress was $4.9 \times 10^{-2} \text{ MPa}$ and the velocity of the grinding disk 150 rpm.

III. RESULTS AND DISCUSSION

After intensive mechanical treatment in a planetary mill, the powders acquired ultrafine sizes. The specific surface

³ Produced by Degussa, Germany.

⁴ Produced by Struers, Denmark.

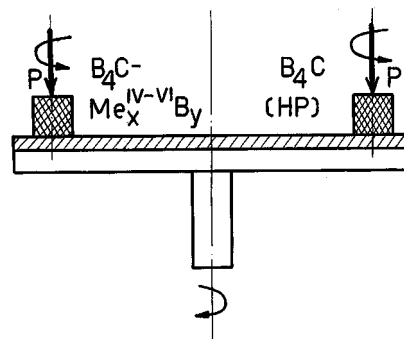
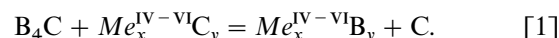


FIG. 1. Abrasive wear resistance of dense boron carbide materials.

areas of the boron carbide and metal carbide powders were 8.5 and $2.1\text{--}2.8 \text{ m}^2 \text{ g}^{-1}$, respectively. The large contact area of the powders, as well as the effects of mechanochemical activation, determined their activity during sintering (10). The transition metal carbides used as sintering additives reacted completely during sintering at temperatures of $2150\text{--}2250^\circ\text{C}$ according to



Interaction between B_4C and transition metal carbides is a widely used method for synthesis of transition metal borides (15). Complete proceeding of Reaction [1] during sintering of B_4C in the presence of WC and transformation of sintering additives into W_2B_5 were shown in a previous work (16). XRD patterns of boron carbide sintered in the presence of Cr_3C_2 are presented in Fig. 2. The amounts of the sintering aids were chosen to obtain, after interaction according to reaction [1], sintered materials with the compositions $B_4C\text{--}10 \text{ wt.}\% \text{ CrB}_2$ and $B_4C\text{--}20 \text{ wt.}\% \text{ CrB}_2$. After introduction of a larger amount of Cr_3C_2 , the carbon obtained was registered as a graphite phase (Fig. 2b). The relative density of the sintered material in that case was lower (94.2%) as compared to the material $B_4C\text{--}10 \text{ wt.}\% \text{ CrB}_2$ (96.4%). The results obtained were in accordance with the phase equilibria $B\text{--}C\text{--}Me^{IV-VI}$ (17).

It was shown that the absolute change in value of lattice parameter C was larger than that of the parameter a (18). The elongation of the boron carbide crystal lattice, particularly in the direction of the hexagonal C axis, after high-temperature interaction between B_4C and Al has been established by Lipp and Roder (19). It is this alteration of the boron carbide lattice parameter C after sintering in the presence of TiC, VC, and WC additives that is shown in Fig. 3. The lattice parameter a change during sintering is less pronounced. When B_4C is sintered in the presence of 10 wt% and 20 wt% WC, the parameter a changes as followed: from $0.5601 \pm 0.0002 \text{ nm}$ for “pure” sintered B_4C to $0.5596 \pm 0.0002 \text{ nm}$ and $0.5606 \pm 0.0002 \text{ nm}$ for the two

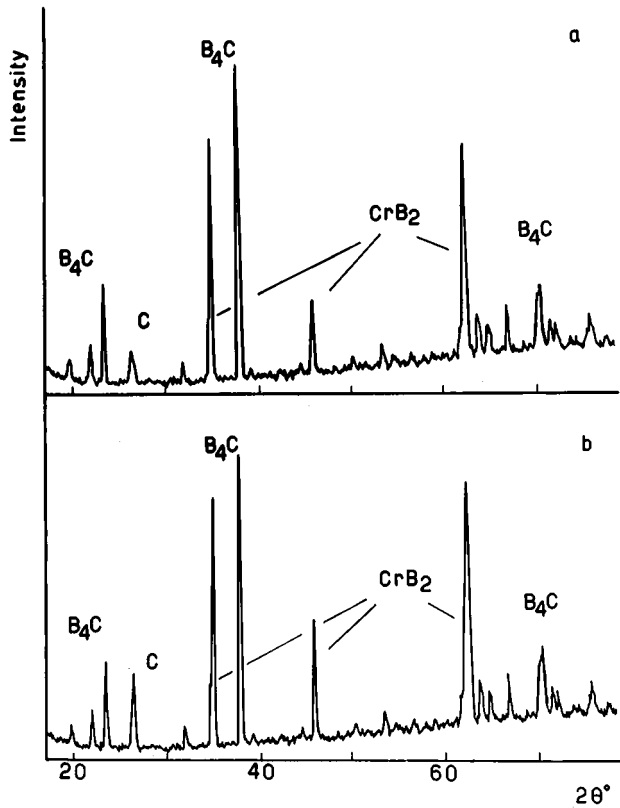


FIG. 2. XRD of activated sintered: (a) B_4C -10 wt% CrB_2 ; (b) B_4C -20 wt% CrB_2 .

doped boron carbide samples. The syntheses of $Me_x^{IV-VI}B_y$ borides are, according to Reaction [1], connected with a decrease in boron content of the boron carbide lattice. The amounts of TiB_2 , VB_2 , and W_2B_5 , presented in the sintered boron carbide-based materials are 1.16, 1.15, and 1.08 times higher, respectively, than the corresponding amounts of the metal carbides in the green compacts $B_4C-Me_x^{IV-VI}C_y$. After introduction of equal amounts of $Me_x^{IV-VI}C_y$, sintering additives, the boron carbide loses different amounts of boron to form the borides $Me_x^{IV-VI}B_y$. The boron amount needed to synthesize TiB_2 is 1.2 times larger than that needed for VB_2 and 3 times larger than that for W_2B_5 . The lowering of the boron carbide lattice parameter C values is due to the reduced boron content after interactions during the sintering process, according to Reaction [1]. The tendency to an increase in the C values with the transition metal carbide ($Me_x^{IV-VI}C_y$) content (over 20 wt.%) is probably due to some solubility of the metal-containing phases in the boron carbide lattice during the sintering process. High-temperature interaction between part of the boron carbide and the sintering additives $Me_x^{IV-VI}C_y$ according to Reaction [1] leads to formation of secondary $Me_x^{IV-VI}B_y$ phases. Figure 4 shows a scanning electron micrograph of the fracture surface of B_4C -10 wt% CrB_2 composite material sintered at

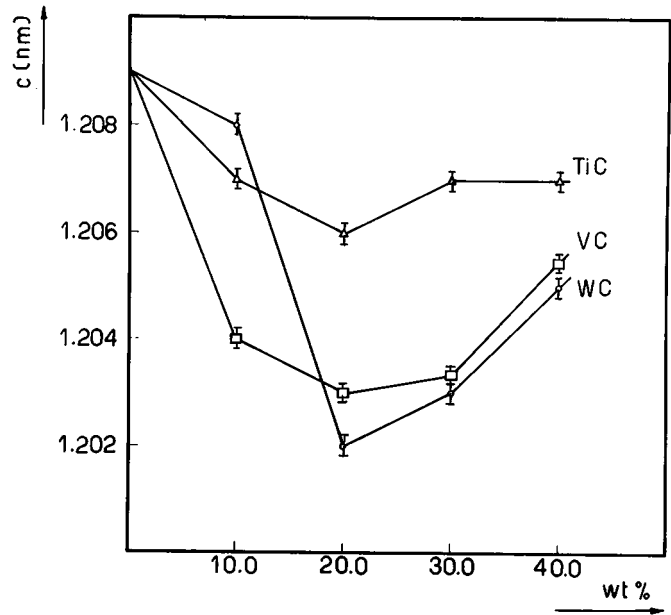


FIG. 3. Changes of boron carbide lattice parameter C after sintering of $B_4C-Me_x^{IV-VI}C_y$ materials.

2240°C and kept at this temperature for 10 min. The microstructure shows a uniform distribution of the CrB_2 phase (lighter in color) mainly around the boron carbide grains. This is due to the uniform green composition of compacts

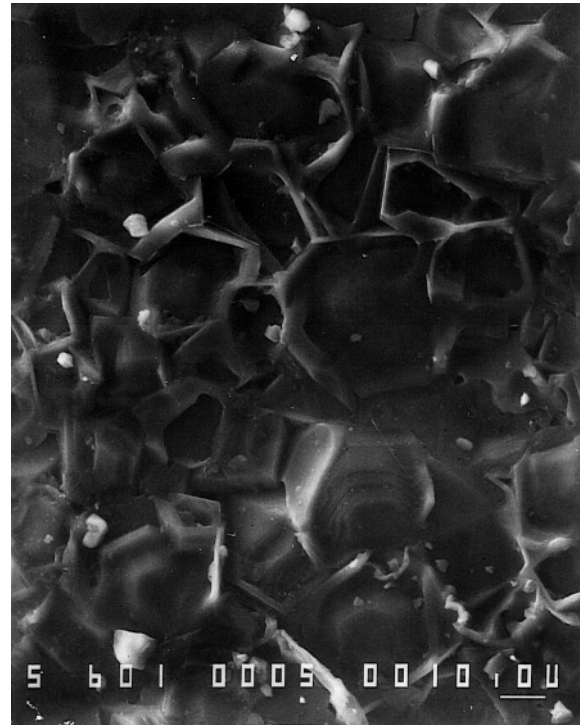


FIG. 4. SEM of activated sintered B_4C -10 wt% CrB_2 , $\times 600$, bar = 10 μm .

$B_4C-Cr_3C_2$. The structure of the material is dense, the main size of the B_4C particles being about $20\ \mu m$. The density is 96.4% of the theoretical density for that composition. Several pores of about $1\ \mu m$ are visible. The coarsening of boron carbide particles, their rearrangement, and their roundness are due to the peculiarities of the liquid phase sintering (20).

SEM of a fracture surface of sintered $B_4C-10\ wt\% VB_2$ material is shown in Fig. 5. The vanadium diboride phase (lighter in color) consists of particles measuring $3-7\ \mu m$. It is situated among boron carbide grains. An energy dispersive X-ray spectrometer has been used for analysis of the sintered samples by SEM, in order to determine the distribution of the secondary metal boride phase. The beam has been focused on grains containing boron carbide (points T_1, T_2) and vanadium boride (points T_3, T_4) phases. The corresponding EDS spectra are shown in Fig. 6a-d. The presence of a V-containing phase (point T_1) in the boron carbide matrix is registered. The intensity of the metal phase peak increases when a boron carbide particle (point T_2) is situated just next to the VB_2 phase (point T_3). The presence of vanadium and carbon in point T_4 and the structure of the phases indicate the appearance of the triple eutectic $B-C-V$ during the sintering process.

The dependencies of the microhardness of boron carbide phases in some $B_4C-Me_x^{IV-VI}B_y$ materials on the indenter loadings are shown in Fig. 7. The amounts of the sintering aids VC, WC, Cr_3C_2 are chosen so that after complete interaction according to Reaction [1] dense bodies with the compositions $B_4C-5\ wt\% VB_2$, $B_4C-10\ wt\% VB_2$, $B_4C-10\ wt\% W_2B_5$, and $B_4C-10\ wt\% CrB_2$ are obtained. The microhardness values of activated sintered boron carbide materials exceed those of "pure" boron carbide (B_4C-HP)

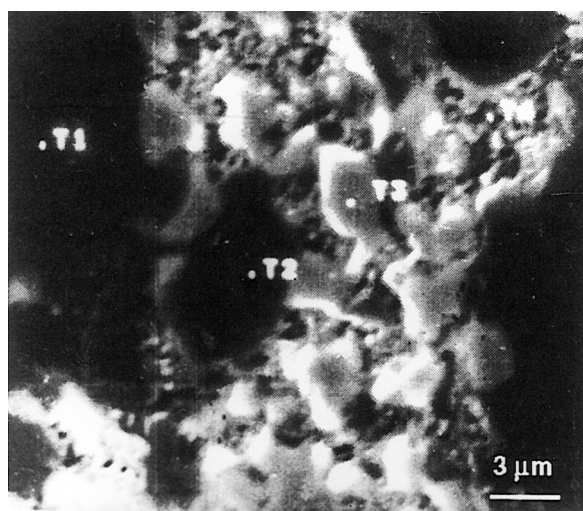


FIG. 5. SEM of activated sintered $B_4C-10\ wt\% VB_2$, $\times 3000$.

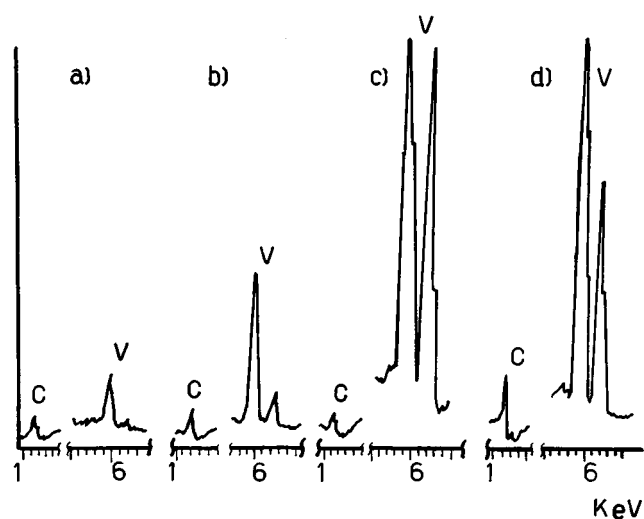


FIG. 6. EDS of activated sintered $B_4C-10\ wt\% VB_2$.

densified by hot pressing. It has been shown that the microhardness values of densified boron carbide depend on the amount and kind of metal carbide sintering aids. The highest values (58–76 GPa) are registered for activated sintered $B_4C-10\ wt\% CrB_2$.

The abrasion wear resistance of sintered boron carbide based materials has been found to correspond to their higher microhardness values as compared to hot pressed

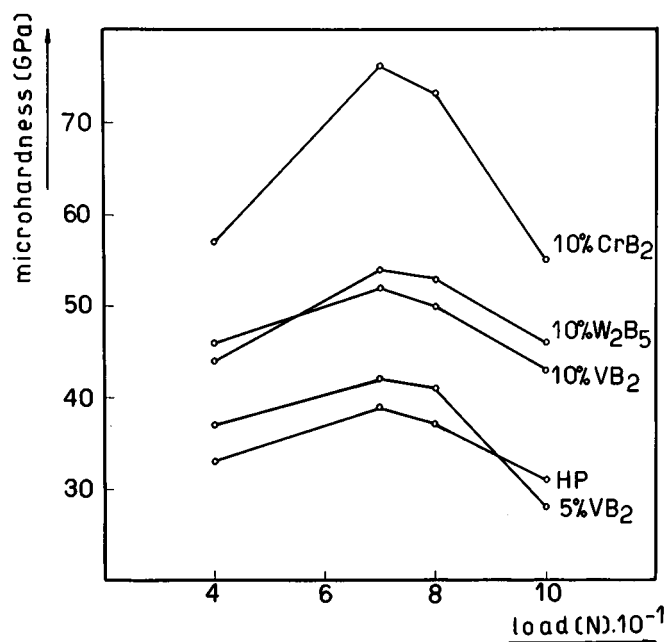


FIG. 7. Dependence of microhardness on indenter loading for dense boron carbide materials.

boron carbide. The tests have shown weight losses of hot pressed B_4C that are 1.6 and 1.8 times higher than those for B_4C-10 wt% W_2B_5 and B_4C-10 wt% CrB_2 materials densified by sintering.

The high temperature interactions of boron carbide with some transition metals and metal carbides and borides have been studied by a number of investigators. Portnoy and co-workers have attributed the higher microhardness of hot pressed boron carbide in the presence of TiB_2 and $(Ti, CrB)_2$ to some solubility of these components in the boron carbide crystal lattice (21). Makarenko has ascertained a significant increase in microhardness values of hot pressed boron carbide powders in the presence of Ti and Zr (22). The authors of (19) discuss the possibility of incorporation of Al and other elements into the boron carbide crystal lattice, leading to the appearance of a new class of $B_{12}C_{3-n}Me_n$ compounds. Nishiyama and Umekawa have registered an increase in microhardness of TiB_2 additives containing boron carbide powder sintered in the presence of WC. Tungsten carbide is present in the powdery B_4C-TiB_2 mixture due to contamination from hard metal (WC-6 wt% Co) milling accessories. In addition, the authors have registered the presence of a TiB_2 phase in the boron carbide lattice after sintering (23). Lundstroem has registered some solubility of 3d elements in the boron carbide crystal lattice (24).

The described method of activated sintering of boron carbide allows obtaining a new class of superhard materials. Their structures, compositions, and properties are a result of sintering and may be controlled by the parameters of that process.

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