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New superhard $B_{12-n}C_3Me_n$ boride♣

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The aim of this paper is to study the microhardness of boride composite materials $B_{l2}C_3$+Mex^{IV-VI} B_y sintered without pressing, and to elucidate the reasons for the drastic increase of the hardness of $B_{12}C_3$ (50 - 77 GPa). This increase, as compared with HP-high pressure- $B_{12}C_3$ (29-34 GPa) was established. XRD data show that the lattice parameter *c* of $B_{12}C_3$ decreases significantly from 12.12 to 12.02 Å after sintering of the composite materials $B_{12}C_3+Me_xB_y$. The dissolution of the transition metal into the crystal lattice of $B_{12}C_3$ led to the formation of new superhard ternary borides with formulae $B_{12-n}C_3Me_n$. The hardness of the new ternary borides exceeded considerably that of pure $B_{12}C_3$, and was equal to the hardness of cubic-BN and some synthetic diamonds of the type "CB" or "Carbonado ACPK".

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1. Introduction

Superhard substances have a hardness of 20 GPa, i.e. higher than that of corundum [1], or a Vickers hardness Hv above 40 GPa [2]. About 10 superhard non-metal substances and refractory compounds, forming a "hardness pyramid" are known [1], diamond being at the top, followed by boron nitride and boron carbide.

The superhard substances among metal-like refractory compounds form a similar pyramid, with the transition metal borides at its top. However, the maximum hardness found for them is inferior to that of the non-metal substances. The interest in borides is due to their extraordinary hardness (up to 1873^0C) as compared to other refractory compounds.

The hardest boride ($B_{12}C_3$) is used in industry as a wear resistant polycrystalline material, armor tiles, etc. [3]. However, its application is restricted by its high brittleness due to the strong covalent bonds in its crystal lattice.

One of the ways of diminishing the brittleness of this compound is its doping with components introducing non-localized electrons. The IV-V group transition metals are suitable for this purpose [4]. The same authors have observed also a sharp increase, up to 63 – 60 GPa, of the microhardness of boron carbide in $B_{12}C_3$-Ti and $B_{12}C_3$-Zr alloys. This is attributed to partial dissolution of the metals in the boron carbide.

Ternary compounds were predicted by Lipp and Roder [5] using X-ray studies of the hot pressing of the $B_{12}C_3$+Al composite material. They established the dissolution of Al in the carbide lattice and the formation of a $B_{12}C_2Al$ compound. The authors explained this by the formation of a linear C-A1-C chain at the expense of the middle carbon atom. On this basis, they predicted the formula $B_{12}C_{3-n}Me_n$ for the "new class of compounds" expected by them.

Synthesis of new superhard ternary phases in the B-C-N system using the laser-heated diamond anvil cell is investigated in the review [6]. A novel superhard phase c-BC_2N was synthesized at a pressure of 18 GPa and temperatures above 1930^oC, with a hardness Hv=76 GPa [6].

The boron carbide microhardness was found to increase with increasing amount of the metal boride [7]. However, no detailed explanation of the results was given.

The aim of this paper is to study the microhardness of the boron carbide in the composite material $B_{12}C_3$ + Me $\underline{x}^{IV-VI}B_y$ obtained by sintering, and to show the place of the new boride ternary phases among the superhard compounds.

2. Experimental

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The $B_{12}C_3$ and $Me^{IV\text{-}VI}C$ carbides (produced by "Ventron Alfa Products" and "Merck") were homogenized in Frisch planetary mill, pressed at 200 MPa and then sintered at 2100 - 2250°C in a Degussa furnace with a graphite heater in an Ar atmosphere. The hardness was determined using a "Leitz" hardness tester with loads of Hv0.5 to Hv1. The structure was investigated using an Automated DRON-3 diffractometer, with CuK_α radiation.

The morphology was characterized by scanning electron spectroscopy (SEM) (JSM 840 equipped with a Link QK 200 dispersive X-ray analyzer).

3. Results and discussion

An exchange reaction takes place during the interaction of transition metal carbides with boron carbide above 2000°C, because the thermodynamically more stable boride is formed. If well known substances participate in the high temperature reaction (as in the present case), it is recommended to use the approximate method for calculating the equilibrium, i.e. the Gibbs energy change, depending on temperature:

$$\Delta G_T = \Delta H_{298} - T\Delta S_{298} \qquad (1)$$

where ΔG_T, ΔH_{298}, T and ΔS_{298} are the change in the Gibbs free energy, the change in the enthalpy at 298K, the absolute temperature and the change in the entropy at 298K.

The thermodynamic probability for the model reaction:

$$5B_4C+8WC=4W_2B_5+13C \qquad (2)$$

was calculated from literature data which is shown in Fig. 1.

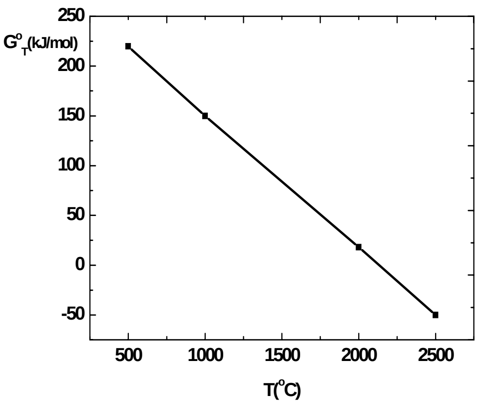

Fig. 1. Thermodynamic probability for the reaction $5B_4C+8WC=4W_2B_5+13C$

It is obvious that the reaction is only possible at temperatures above 2200^0C, i.e. at temperatures close to the melting point of boron carbide (2447°C). SEM of a fracture surface of $B_{12}C_3$ - 50 wt % W_2B_5 material (sintered at 2250^0C) with a grain size of 2-7 μm is shown in Fig.2.

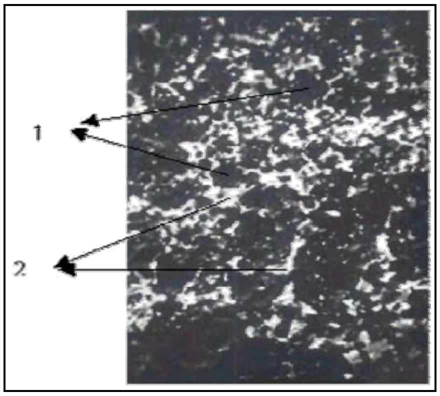

Fig.2 Structure of $B_{12}C_3$ *(1) + 50%*W_2B_5 *(2)sintered at 2250°C (x530)*

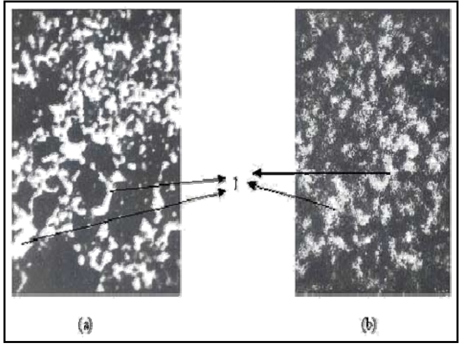

Fig. 3 Distibution of the W-phase (1) and C-phase in $B_{12}C_3$*+50%*W_2B_5 *material (x530)*

Fig. 3 shows uniform distributions of composite phases, and clearly formed grains of boron carbide.

At larger magnifications (2000x), a thin eutectic binder is visible at the grain boundaries. The appearance of an eutectic as a result of interaction between the two carbides is not unexpected, taking into account the eutectic character of the ternary diagrams of B-C-$Me^{IV\text{-}VI}$ [8] and the quasi-binary systems B_4C-MeB_2 [9]. The appearance of the eutectic leads to the brittle boron carbide becoming stronger, due to the Me_xB_y particles. This results in a significant decrease in brittleness of the recrystallized composite, and an increase in its crack-resistance. The critical coefficient of the stress intensity (KIc), measured by the indenting method in differently oriented eutectics ($B_{12}C_3$-MeB_2), ranges from 6-12 MPa to 2.5-3.5 MPa for the different components. This result indicates that the use of eutectics as a new class of composite materials resistant under extreme conditions is promising.

The microhardness values of boron carbide in composite $B_{12}C_3$ + Me_xB_y, as compared to hot-pressed pure boron carbide, and the values obtained by other authors are presented in Table 1. The data show that the boron carbide hardness in the composite materials is much higher than that of pure boron carbide and other composites based on $B_{12}C_3$.

Table 1. Microhardness (GPa) of the composite Materials $B_{12}C_3+Me_xB_y$

Material (weight %)	HV	HV_{05}	Ref.
$B_{12}C_3+W_2B_5$ (10; 50)	**50;58**	**53*; 77****	
$B_{12}C_3+CrB_2$ (10)	**56**	**77****	
$B_{12}C_3+VB_2$ (10)	**43**	**52**	
$B_{12}C_3$+Ti (7)	-	63	[4]
$B_{12}C_3$+Zr (10)	-	60	[4]
$B_{12}C_3$+Cr(10)	-	34	[4]
$B_{12}C_3$+ Al (50)	25	-	[5]
$B_{12}C_3$+SiC (30)	25	-	[12]
$B_{12}C_3+TiB_2$ (10; 20)	-	45; 55	[13]
$B_{12}C_3+TiB_2$ (10;25)	-	30; 34	[14]
$B_{12}C_3+ZrB_2$(20)	-	27; 34	[14]
$B_{12}C_3+TiB_2$(10)+ W_2B_5(5)	-	37; 42	[14]
$B_{12}C_3$-HP "pure"	**34**	**30;38**	[7,10]

* - Length of pyramid diagonal indentation [μm]: * 4.4; ** 3.15

The sharp increase in hardness is due to dissolution of transition metals in the crystal lattice of boron carbide. During the chemical interaction of the two carbides the boron needed for the reaction comes from the boron carbide lattice. Since from the investigations of Lipp et al. [10] it is known that the homogeneity region of $B_{4+x}C$ has no substantial effect on its hardness, the only reason for the sharp increase in boron carbide hardness should be the formation of new superhard ternary compounds with the formula $B_{12-n}C_3Me_n$ (Fig. 4). These compounds do not differ essentially from the ternary compounds $B_{12}C_{3-n}Me_n$ (predicted by Lipp and Roder [5]). The difference is that with the latter compounds, the replacement of c_o (at. radius 0.91 Å) by the larger element Al (at. radius 1.43 Å) leads to a considerable increase in the size of the unit cell in the direction of the hexagonal C axis and of the lattice volume (Table 2). In our case, just the opposite happens. The volume shows no substantial change, whereas the parameter c decreases (see Table 2).

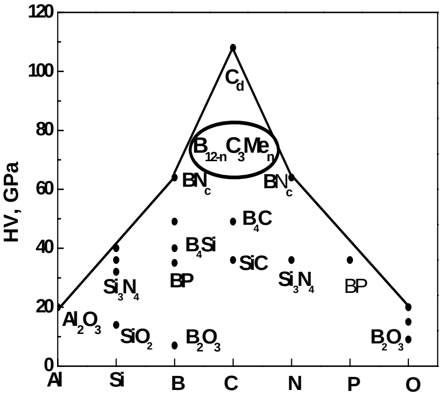

Fig. 4. Hardness pyramid with the new superhard ternary compounds $B_{12}C_{3-n}Me_n$

Table 2. Parameters of the crystal lattice of the composite materials $B_{12}C_3+Me_xB_y$

Compounds	a_o[Å]	c_o[Å]	V [nm^3]	Ref.
$B_{11}C_3W$-10%W_2B_5	**5,601**	**12,078**	**0,32757**	
$B_{11}C_3W$-20%W_2B_5	**5,604**	**12,024**	**0.32697**	
$B_{11}C_3W$-50%W_2B_5	**5,606**	**12,054**	**0,32802**	
$B_{11}C_3Ti$ - 10 –20% TiB_2	**5,607**	**12,06- 12,07**		
$B_{11}C_3V$ 10- 20% VB_2	**5,605**	**12,02- 12,05**		
$B_{12}C_2Al$	5,65	12,39	0,34252	[5]
$B_{12}(C,Si)_3$	5,60	12,1	0,3286	[1]
$B_{13}C_2$	5,67	12,19	0,33938	[11]
$B_{12}C_3$	**5,60**	**12,12**	**0,32915**	[10]

This is attributed to an increase in carbon content in the homogeneity region of the boron carbide [11], which is due to elimination of boron from the compound. The decrease in the parameter c_o, while the crystal lattice volume remains unchanged, indicates that the metal atoms are incorporated most probably in the icosahedron B2 and B1 sites.

Due to the strongly extended lattice during the incorporation of Al and Si into the C-C-C axis, the phases $B_{12}C_2A1$ and $B_{12}C_2Si$ have a microhardness (HV_1 = 25GPa) even lower that that of pure boron carbide (Table

1).

4. Conclusions

It was established that superhard ternary compounds based on boron carbide with dissolved IV-VI group metals ($B_{12-n}C_3Me_n$) can be obtained by sintering without pressure.

The hardness (50-77GPa) of the new borides is much higher than that of "pure" boron carbide sintered by hot pressing. It is equal to that of cubic boron nitride (i.e. next to diamond) and even of some polycrystalline diamonds of the type "Carbonado" and "CB". However, the price of the new boride is several orders of magnitude lower.

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