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STUDY OF REACTION-BONDED BORON CARBIDE PROPERTIES

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Results are given for a study by scanning electron microscopy of the effect of original powder composition on physicomechanical properties of reaction-bonded boron carbide and during new material structure formation in the B–Si–C system.

Keywords: boron carbide, silicon carbide, grain size, fraction, pyrolysis, siliciding, microstructure, physicomechanical properties.

INTRODUCTION

Ceramics based on boron carbide and composites based on it are distinguished by high hardness,

chemical inertness, strength at high temperature, semiconductor properties, and a capacity to absorb thermal neutrons. This has given rise to extensive use in machining, radioelectronic, atomic, and other branches of industry. Dense materials based on boron carbide B_4C are prepared mainly by high-temperature hot pressing and sintering at 2000 – 2200°C. This is connected with presence within this compound of strong covalent bonds. Processes have been studied to a lesser extent for preparing materials based on boron carbide by siliciding, for example such promising systems as B_4C–SiC–C and B_4C–C.

The main problem in developing structural and other materials based on these compounds is a requirement for considering a variety of complex physicochemical processes occurring during heat treatment and siliciding workpieces in the range 1400 – 2200°C. In the opinion of the authors in [1 – 3] the main ones are as follows:

– chemical reaction of B_4C with molten silicon with formation of silicon carbide SiC and also other compounds in the B–Si–C system;

– direct formation of SiC with presence of carbon in a starting composition;

– solid solution formation in the B_4C–SiC system;

– eutectic formation in the B_4C–SiC system;

– eutectic melting at above 2070°C;

– additional phase formation during cooling of heating equipment after completion of the siliciding thermal regime.

Formation of many phases occurs with an increase in molar volume of final reaction products compared with indices of the starting components, and this leads to occurrence of internal stresses in silicided workpieces up to breakdown of their integrity.

In the course of studies it was detected that cooling during reaction bonding of B_4C and Si gives shrinkage at a different rate. The linear thermal expansion coefficient (LTEC) of B_4C is 5.6×10^{-6} K^{-1}, and for Si it is 4×10^{-6} K^{-1}, and therefore Si experiences greatest stresses, which is due to the high dislocation density [1]. Consequently, in order to develop structural materials in the B_4C–SiC–C and B_4C–C systems by reaction bonding technology it is necessary to slow down or remove the processes indicated above.

A special method has been proposed in a patent [4] for suppressing or slowing down reaction of B_4C with molten Si: preliminary of metallic silicon with boron compounds. Partial equilibrium between molten Si, B_4C, and SiC is achieved by saturating a silicon melt with boron in an amount of 8 at.%.

Analysis of contemporary information, presented in various international scientific conferences and on internet sites, shows that currently within Russia development of reaction sintered materials based on B_4C is performed by several Russian firms. Among them it is possible to distinguish OAO TsNIIM (St Petersburg) [5], OOO VIRIAL (St Petersburg) [6], OOO NPP ARMOKOM-TsENTR (Khot'kovo, Moscow region) [7], whose materials exhibit good physicomechanical

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TABLE 1. **Physicomechanical Properties of Domestic ceramic materials Based on Reaction-Bonded B_4C**

Properties	Material		
	RSBC (OAO TsNIIM)	reaction-sintered boron carbide* (OOO VIRIAL)	mixed carbide ceramic (OAO NPP ARMOKOM-TsENTR)
Density, g/cm^3	2.70 – 2.75	2.63	2.70
Porosity, %	>0.5	—	—
Ultimate strength in bending, MPa	320 – 380	250 – 300	280 – 380
Young's modulus, GPa	350 – 400	400 – 410	380 – 400
Vickers hardness, GPa	27 – 28	30 – 35	25 – 28
Fracture toughness, MPa·m$^{1/2}$	3.5 – 4.0	2.1 – 2.5	2.5

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properties and have been successfully approved for various protective structures (Table 1).

Ceramic materials have been studied quite widely overseas, and used extensively by the majority of firms (Ceradyne, Inc., MCT, Saint-Gobain, ETEC, Advanced Ceramics, etc. [8]) as an alternative to using silicon carbide ceramic for manufacturing lighter and more effective means of personal protection and transport technology.

Earlier attempts by the authors to develop reliable protective material based on B_4C by reaction sintering have not provided favorable results. This work was carried out with the aim pf preparing ceramic with a fine-grained structure in the B–Si–C system with better physicomechanical properties.

EXPERIMENTAL PROCEDURE

In this work boron carbide and silicon carbide were used of different grain size composition developed by OAO UNIKhIM with Test Plant (Ekaterinburg) and commercial-grade carbon black with a specific surface S_{sp} = 30,000 cm^2/g. Powder grain size composition is given in Table 2.

Analysis of starting boron carbide powder showed a high content of the main B_4C phase (96 – 96.8%) and presence of admixtures of Fe in an amount 0.3% and B_2O_3 in an amount of 0.26%, and this corresponds to GOST 26327.

In order to slow down or remove the processes indicated above the siliciding temperature was reduced to 1550°C, and cooling rate in the range from 1550 to 1350°C to 20°C/h.

Boron carbide, silicon carbide, and carbon black powders were mixed by a liquid-phase method. The binder used was phenolformaldehyde polymer oligomer by semidry compaction under a pressure of 700 – 750 MPa for preparation of plates with a size of 70 × 70 × 10 mm. Siliciding was performed in a graphite assembly in a vacuum at 1550°C using semiconductor purity silicon. Excess silicon in the reaction system provided a possibility of occurrence of chemical reactions and filling of residual porosity in specimens of metallic silicon. Specimens were cut from plates that were used in determining density, porosity, studying microstructure and phase composition, measurement of ultimate strength in bending, microhardness, ultrasound propagation rate, and other indices.

Density and porosity were determined by hydrostatic weighing, and standard specimens with a size of 7 × 7 × 70 mm were used in order to determine ultimate strength with three-point bending. Critical stress intensity factor K_{1c} and microhardness of the main phase according to the Vickers scale were measured by indentation with a load of 200 g in a DuraScan 50 instrument. Microstructure was studied in specimen polished surfaces by means of an Axio Observer MAT optical inversion microscope. Phase compo-

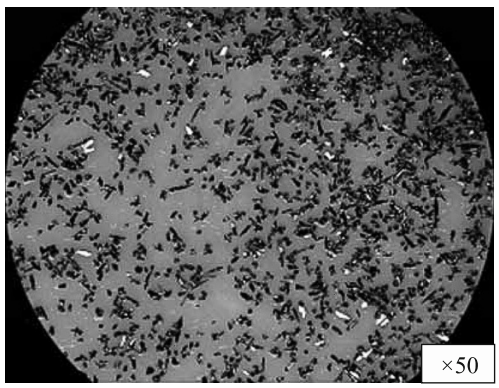

Fig. 1. Macrostructure of B_4C powder fraction F 220.

TABLE 2. **Properties of Boron and Silicon Carbides Powders Produced by OAO UNIKhIM with OZ**

Powder	Fraction	Specific surface, m^2/g	Main fraction (>50%), μm
B_4C	6U-13	11500	2 – 5
	F 220	1200	60 – 80
	F 240	1400	50 – 60
	F 320	1500	40 – 50
SiC	F 1200	7200	3 – 5

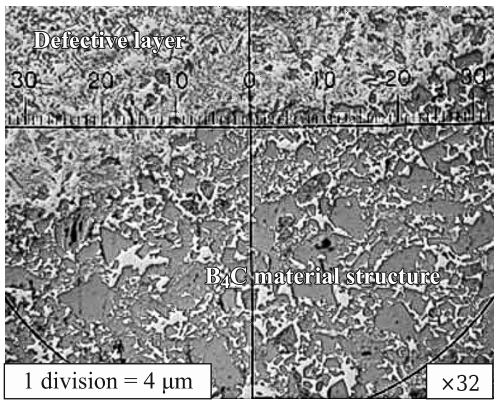

Fig. 2. Boundary of defective region of reaction-bonded B_4C specimen.

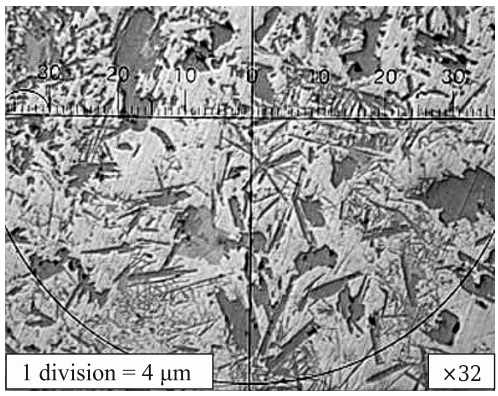

Fig. 3. Microstructure of defective layer of reaction-bonded B_4C specimen.

sition was determined by x-ray phase analysis (XPA) in a DRON-6 unit (CuK_α-radiation, Ni filter).

EXPERIMENTAL SECTION

Microscope studies of boron carbide powder showed that B_4C has an extended acicular shape (Fig. 1).

Nine compositions were prepared from test powder batches, containing in order to obtain maximum packing density 70% of coarse (F 220, F 240, and F 320) and 20 – 30% fine (6U-13) B_4C fractions and 10% SiC or C addition. Specimens were separated into three groups (Table 3). For specimens of group 2 (compositions 4 – 6) there was typically good particle packing density (1.59 – 1.68 g/cm^3) and the maximum value was achieved on introducing 10% SiC (specimen 6). It should be noted that in groups 1 and 3 the maximum density values were also achieved with addition of 10% SiC.

TABLE 3. **Experimental Specimen Charge Composition and Raw Material Density**

Composition	Content, wt.%						Raw material density, g/cm^3
	B_4C				SiC	C	
	F 220	F 240	F 320	6U-13	F 1500	soot	
				Group I			
1	70	—	—	30			1.49
2	70	—	—	20	—	10	1.43
3	70	—	—	20	10	—	1.53
				Group II			
4	—	70	—	30	—	—	1.63
5	—	70	—	20	—	10	1.59
6	—	70	—	20	10	—	1.68
				Group III			
7	—	—	70	30	—	—	1.55
8	—	—	70	20	—	10	1.50
9	—	—	70	20	10	—	1.58

RESULTS AND DISCUSSION

Macrostructural analysis showed that in many specimens in the area of workpiece contact with molten silicon a defective layer up to 1 mm thick formed, whose microstructure consists of prismatic and irregular morphology with a size of 4 – 50 μm, and also intergranular phase (light area) (Fig. 3). According to XPA data the defective layer consists of a main phase Si_{cub}, β-SiC, and traces of $B_{12}(C,Si,B)_3$ (silicon carbide solid solution in boron carbide). During analysis of physicomechanical properties of specimens it was established that for all of the compositions values of porosity are

TABLE 4. **Test Specimen Physicomechanical Properties and USV Velocity**

Composition	Density, g/cm^3	Porosity, %	Ultimate strength in bending, MPa	Microhardness, GPa	USV velocity, m/sec	Fracture toughness, MPa·m$^{1/2}$
			Group I			
1	2.50 – 2.55	0.4	230	31	11800	4.5
2	2.65 – 2.70	0.3	220	33	12100	4.3
3	2.55 – 2.60	0.3	220	34	11700	4.0
			Group II			
4	2.55 – 2.60	0.3	330	28	12280	4.0
5	2.65 – 2.70	0.3	330	28	12400	4.1
6	2.55 – 2.60	0.3	340	27	12120	3.9
			Group III			
7	2.55 – 2.60	0.3	350	24	12230	3.7
8	2.65 – 2.70	0.3	340	21	12168	3.5
9	2.55 – 2.60	0.3	340	23	11910	3.4

at one level and do not exceed 0.4% (Table 4). Maximum density values of 2.65 – 2.70 g/cm^3 are achieved in specimens containing carbon black.

Specimens of group III are distinguished by maximum strength values. The greatest K_{1c} value is achieved in specimens of group I. It should be noted that maximum strength values of (for a specimen of composition 7 σ_{ben} is 350 MPa) and fracture toughness (for a specimen of composition 1 K_{1c} is 4.5 MPa·m$^{1/2}$) were typical for specimens containing only B_4C fractions. A reduction in grain size to 40 μm (fraction F 320) leads to an increase in strength, and an increase to 60 – 80 μm (fraction F 220) combined with fine faction 6U-13 provides an increase in fracture toughness.

The greatest microhardness is exhibited by group I specimens, manufactured from coarse-grained B_4C powder. Introduction of 10% carbon black increases HV to 33 GPa (specimen of composition 2) and introduction of 10% SiC to 34 GPa (specimen of composition 3). USV velocity for specimens of all compositions is within the limits 11,700 – 12,400 m/sec.

A study of microstructure and phase composition was performed on specimens of group II, for which high values of all test indices are typical: strength, microhardness, and fracture toughness.

According to XPA data specimens of group II consist silicon carbide β-SiC (main phase, associated compounds $B_{12}(C, Si, B)_3$ and $B_{12.97}C_{2.88}Si_{0.35}$, rhombohedral boron carbide of structure $B_{13}C$ and $B_{10}C$, and a small amount of silicon Si_{cub}.

Studies of specimen polished surfaces by optical microscopy showed that the microstructure is formed by four phases. In studies of a microsection in an optical microscope it is separated with respect to color (Fig. 4): white phase, which does not have clearly defined morphology (free silicon Si); gray phase is grains of different morphology (prismatic indefinite agglomerates) with well-formed boundaries (silicon carbide SiC); dark gray phase in the form of inclusions in grains of gray color or in the form of individual grains (B_4C boron carbide), and dark phase (tear-outs, formed during microsection preparation, and pores). In all specimens there is a volume content of phases differing with respect to color characteristics (Table 5).

As studies showed, in specimens of compositions 4 – 6 during siliciding there is no marked grain growth of the primary boron carbide, although presence is revealed of especially coarse grains (up to 100 μm) of extended shape.

In a specimen of composition 4 of pure boron carbide there is weak particle adhesion and absence of fine B_4C fraction (see Fig. 4). Presence within specimens of compositions 4 – 6 of a considerable amount of β-SiC and complex compounds $B_{12}(C,Si,B)_3$ and $B_{12.97}C_{2.88}Si_{0.35}$ confirms that fine B_4C powder enters into reaction with silicon with formation of secondary SiC and complex compounds in the S–B–C system, which form at a surface coarse grains of original boron carbide (lighter shell over a grain surface), and this correlates well with previously published data [9].

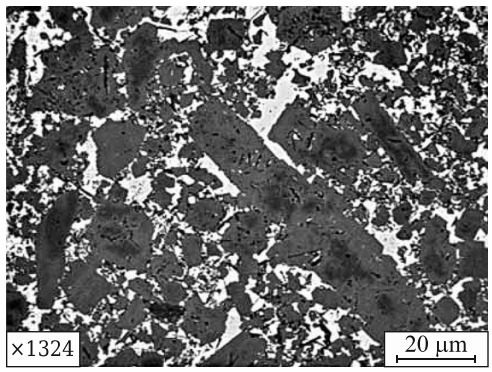

Fig. 4. Microstructure of specimen of composition 4.

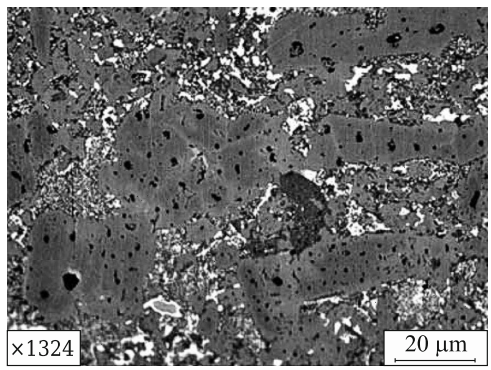

Fig. 5. Microstructure of specimen of composition 5.

It should be noted that reaction of B_4C with Si with solid solution and silicon carbide formation occurs with a reduction in volume. This leads to a situation that intergranular space is weakly filled with secondary SiC, and in some cases there is formation of intergranular and intragranular porosity.

With introduction of 10% C to an original workpiece material is prepared with a more densely reacted structure (specimen of composition 5, Fig. 5). It is well known that direct formation of silicon carbide from C and Si proceeds with an increase in volume by factor of 2.3 and leads to more complete filling of pore channels and formation of an inter-

TABLE 5. **Phase Content According to Light Characteristics in Specimens of Group 1**

Specimen composition	Phase content, %				
	white	grey	dark gray	black	fine particles in white color phase
4	17	60	22	<1	—
5	9	52	27	<1	11
6	20	50	29	<1	—

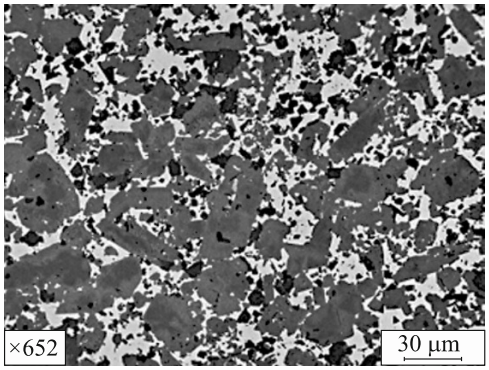

Fig. 6. Microstructure of specimen of composition 6.

connected structure [4]. A specimen of composition 5 (see Table 5) has the least volume content of free silicon (white phase).

Within a specimen of composition 6 with 10% SiC there is formation of secondary silicon carbide both on coarse B_4C grains (light rim on born carbide grains), and also on fine SiC grains (accumulation of light gray grain between coarse grains). This leads to occurrence of a volumetric structure (Fig. 6). A considerable content of free silicon (see Table 5) points to a situation that there is inadequate carbon in order to form a volumetric carcase of secondary SiC.

CONCLUSION

By varying the content of different fractions of boron carbide, carbon, and silicon carbide additions ceramic materials have been prepared by reaction bonding based on boron carbide whose density is in the range 2.55 – 2.7 g/cm^3. The optimum microstructure and mechanical properties (σ_{ben} = 330 – 340 MPa, *HV* = 27 – 28 GPa) are exhibited by compositions containing 70% F 240 fraction.

It has been established that during siliciding of boron carbide there is formation of a volumetric material structure consisting of primary boron carbide and silicon carbide, secondary silicon carbide, complex compounds in the Si–B–C system, and also free silicon admixture. Secondary silicon carbide forms on grains of both primary silicon carbide and primary boron carbide, thereby creating a strong interconnected structure.

It has been shown that presence within ceramic composition of silicon carbide, solid solution of silicon carbide in boron carbide, and metallic silicon, point to formation of a microstructure by a secondary silicon carbide formation mechanism with direct reaction of carbon with silicon and boron carbide with silicon.

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