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LOCATION OF Al AND Si ATOMS IN SUBSTITUTED BORON CARBIDE

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Boron carbide is a material of interest for personal body armor, but its low fracture toughness and amorphization limits its widespread use. Al and Si atoms in doped boron carbide reduce this problem. Passage of the substitution reaction in boron carbide powders with Al and Si vapors in vacuum was found. Certification methods: chemical analysis, full-profile XPA (Powder Cell for Windows. Version 2.4 FREE, W. Kraus & G. Nolze) and modeling in format of the 15-atomic unit cell $B_{12}(C-C-C)$ of trigonal syngony, spatial group $R\bar{3}m$, $Z = 3$. A mixture of powders of boron carbide, aluminum or silicon is heat treated in vacuum at conventional evaporation temperatures of Al (1520 K) or Si (1640 K) for 1–5 h. The samples were purified with alkali and analyzed by arbitration chemical analysis for boron, carbon, aluminum and silicon. The formula composition of the input powders of boron carbide was determined as $B_{12}[(C-B-C)_x(C-C-C)_{1-x}]$, where $x = 0.4-0.6$. The aluminum substitution reaction takes place in both types of boron carbide chains and corresponds to the formula $B_{12}(C-Al-C)$ or $AlB_{12}C_2$. In the presence of silicon, the reaction took place exclusively at the positions of the tri-carbon chains. The composition of the obtained solid solution corresponds to $B_{12}[(C-B-C)_{0.4}(C-Si-C)_{0.6}]$, starting powder $B_{12}[(C-B-C)_{0.4}(C-C-C)_{0.6}]$. The absence of boron phases of silicide, such as SiB_3 ($SiB_{2.89}$), SiB_6 , SiB_n ($n \approx 23$) indicated greater resistance of C–B–C chains to interaction with vaporous Si. The content of Al and Si in the substituted phases is equal to 13.3 and 4.0 (% at.). Equivalent molar amounts of $Al_8B_4C_7$ and SiC of gas-nano-phase origin were measured in the reaction products with vapor-like Al and Si. The area of tolerance chains of the boron carbide structure in the format of the average specific electronegativity ($\chi_{N-Si/r_{ai}}$) was found. It is in the range of values: $2.79 \geq CCC \geq CBC \geq CSiC \geq BBC \geq 2.18$.

Keywords: Al, Si, atoms, location, substituted, powders, boron carbide, area of tolerance, structure

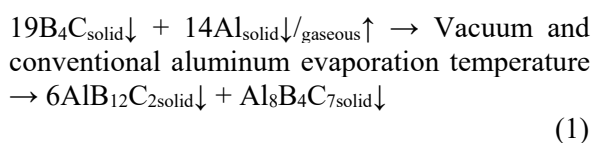
INTRODUCTION

The interaction of boron carbide powder with liquid aluminum and silicon mainly with a diffusion mechanism of interaction has a wide array of information [1–9]. From a chemical viewpoint, the study of the reactivity of boron carbide powders to the topological reactive substitution of some atoms of the composition by vapors of other chemical elements in a vacuum remains relevant. Modern achievements of materials science in the format: composition, structure and properties of boron carbide, BC, $B_{15-x}C_x$ are systematically reflected in the review [10]. Boron carbide (BC, $B_{15-x}C_x$, B_4C) has a unique combination of properties. The material is a priority for applications for a wide range of engineering solutions. The high melting point and heat resistance of the compound contributes to the creation of fire-resistant devices. Due to its extraordinary tribomechanical resistance to abrasion, B_4C is used as abrasive powders and coatings. Due to its high hardness and low

density, $B_{15-x}C_x$ excels in ballistic performance. BC is used in nuclear projects as an absorber of neutron radiation [10]. $B_{15-x}C_x$ has a berthollide character. These are solid solutions of mutual substitution of boron and carbon (mainly in the composition of chains). Their carbon content usually can range from 9.88 to 23.40 % wt. The composition of the unit cell varies from $B_{12}[(BBC)_{0.66}(CBC)_{0.34}]$ to $[(B_{12})_{0.8}(B_{11}C)_{0.2}](CCC)_{1.0}$. The basis of the BC structure is the structural units of boron B_{12} or $B_{11}C$ (icosahedral sublattice) within the framework of trigonal syngony, spatial gr. $R\bar{3}m$, $Z = 3$ (with average unit cell parameters $a = 0.5598$ nm, $c = 1.2120$ nm). The connection between the icosahedra occurs mainly due to linear or angular, tri-carbon C–C–C, carbon-boron-carbon C–B–C or less often boron-boron-carbon B–B–C chains in polar or equatorial settings, respectively. The chemical formula of the unit cell of stoichiometric $3(B_4C)$ can be written as $B_{12}(C-C-C)$ or $B_{11}C(C-B-C)$. The B/C ratio ≤ 4

encourages the atomic fate of $B_{11}C$ dodecahedra in the composition of B_{12} icosahedra to increase. In the area of ratios $5 \geq B/C \geq 4$, the formula of the unit cell will mainly have the form $B_{12}[(CBC)_n(CCC)_{1-n}]$. This means that the operational characteristics of finished products within the specified structure of berthollides depend on the composition of the raw materials. When using each batch of boron carbide powder, it is necessary to pay attention not only to the quality certificate from the manufacturer, but also to the absolute atomic ratio of the elements of the main phase or the individual chemical formula of the sample. Naturally, the chemical formula of boron carbide determines the individual nature and depth of transformations of the material during the technological process.

Boron carbide, when used as an impact-resistant ceramic, can lose strength because of amorphization. It was shown that a small amount of Si (up to 1.0 % at.) when alloying of hot-pressed $B_{15-x}C_x$ leads to a significant reduction of this effect [8–10]. The formation of micro cracks and pores in single-phase polycrystalline granular anisotropic ceramics reduces the fracture stress [11]. The above BC composition of the formula is suitable for consideration of possible interaction with Al and Si in positions: $B_{12}; (C-B-C)_n$ or $C-C-C)_{1-n}$, where $1 \geq n \geq 0$. The formation of stable double and triple crystalline phases in the system: $B_4C-SiC-Si$ (Al) was analyzed in the review [12]. Boron carbide interacts with aluminum according to the found topological exchange reaction [13]:



Contrary to the expected $AlB_{40}C_4$ according to data [12], an icosahedral phase derived from the BC structure was obtained: $AlB_{12}C_2$ or $B_{12}(C-Al-C)$ – dodeca-boron-aluminum-di-carbon. For the last time, a reactive link was found in the structure of BC in the form of central atoms of tri-carbon C-C-C or carbon-boron-carbon C-B-C chains (NATO ESCD, SPS Program N°5070, «New shock-resisting boron-based ceramics: computer modeling, production, testing»).

Stable crystalline ternary phases are known in the system: B-Si-C [12]. Solid solutions of substitution by silicon (space group $R\bar{3}m$; $a > 0.5617$; $c > 1.2137$ nm) in chains

$B_{12}[(CBC)_n(CCC)_{1-n}]$, have a variable (indeterminate according to data [12]) composition of type $B_{12}(C;B;Si)_3$. Substitution solutions $B_{12}(B,C,Si)_3$ have four times lower hardness and can play the role of a “soft stabilizing component” in the composition of composite ceramics in relation to boron carbide [12]. The reduction of amorphous destruction has become an urgent goal in the format of changing the link of boron (carbon)-carbon chains in the BC structure due to topochemical gas-phase reactions of replacing carbon and/or boron with basic elements of the natural aluminosilicate series (Al, Si) with a similar external electronic structure.

Theoretical calculations of several configurations with $B_{12}C_3$ and $B_{12}C_2Si$ stoichiometries calculated using density functional theory show that $B_{12}C_2Si$ can have two ground states [14]. The first is $B_{11}Si(C-B-C)$ with silicon in the icosahedral polar position, the second is $B_{12}(CSiC)$ in the equatorial, where silicon is in the middle of the corner chain. If the $B_{12}(C-C-C)$ configuration is present in the initial sample, the formation of the $B_{11}C(C-B-C)$ equilibrium configuration is inhibited by the high activation energy of carbon removal from the icosahedral polar site. Comparison of X-ray patterns of synthesis products and simulated structural configurations confirmed the $B_{12}(CSiC)$ configuration [14].

The used methodological approach was updated. The paper presents the sequence of determining the composition of structural units of powders $B_{12}(C-M-C)$, where $M = B, C, Al, Si$, using the methods of chemical analysis and X-ray diffraction (Powder Cell for Windows 2.4 FREE, W. Kraus & G. Nolze). (This work is supported by the NATO Science for Peace and Security Program, Project G5773 and National Academy of Sciences of Ukraine).

MATERIALS AND RESEARCH METHODS

Industrial boron carbide powder is ground in a layer mill with an excess of aluminum or metallurgical silicon powder of 99.9 % purity. The samples were placed in carbon crucibles with lids, degassed and annealed. Substitution products obtained as a result of vacuum heat treatment up to 1670 K for 1–5 h. The powders were purified by the alkaline method [15], washed and dried. The structure of the powders and the content of the phases were investigated

using X-ray phase analysis (Powder Cell for Windows 2.4 FREE, W. Kraus & G. Nolze) using a DRON-4.0-07 diffractometric apparatus and computing complex in CuK_α radiation with a graphite monochromator. The composition is found according to the data of chemical analysis and modeling of the atomic ratio of the components with normalization to the 15-atom unit cell $\text{B}_{15-x}\text{C}_x$ in accordance with the laws of general and inorganic chemistry. Input control of the composition of used boron carbide (BC) and reaction products was carried out in accordance with GOST 5744-85, GOST 26327-84 and works [16–19]. The authors have some experience in the reliable calculation of the composition of multiphase systems using phase chemical analysis data [20-23]. The combination of the results of X-ray diffraction and chemical analysis turned out to be sufficient to found the full composition of the initial powder BC, $\text{B}_{12}(\text{C-Al-C})$, of the solid solution of $\text{B}_{12}(\text{B, C, Si})_3$ and the degree of chain substitution $(\text{B, C, Si})_3$.

RESULTS AND DISCUSSION

The composition of the initial boron carbide powders from different manufacturers and lots has a certain difference, and therefore must pass the incoming control. Different batches of BC powder have non-critical deviations in the composition and content of impurities. The main phases of BC are non-stoichiometric, carbon deficient. Not all chains are three-carbon. The content of boron-di-carbon chains is: $\text{B}_{12}[(\text{CBC})_x(\text{CCC})_{1-x}]$ $0.68 \geq x \geq 0.48$ part of the total. From the point of view of absolute atomic ratios, the formulas of the main phase of BC differ significantly. During heat treatment, sintering, substitution reactions, applied coatings and created neutron protection systems, it is

important to know the real atomic ratio or formula of a given powder of the BC phase. The information is necessary for planning the tactics of using raw materials, technological methods of forming the structure while achieving the standard properties of finished products.

In the case of BC and Al substitution products, despite the chemical alkaline treatment, two phases remain, reaction (1). The molar phase ratio was determined by X-ray analysis. The available information base identified the first phase as $\text{AlB}_{40}\text{C}_4$ [24], labeled with an index of 0.87 or 87.0 mass. % The second is the known phase $\text{Al}_8\text{B}_4\text{C}_7$ 0.13 or 13.0 mass. %. The calculated partial content of the compound $\text{Al}_8\text{B}_4\text{C}_7$ 0.13 was used as a denominator for finding the partial difference in the content of the identified substance. The further procedure is like establishing the absolute atomic ratio within the elementary cell of BC. It consists of the following steps. Bringing the content of elements from 87 % up to 100 mass. % or 1 mole of the $\text{Al}_x\text{B}_y\text{C}_z$ substance. Relative atomic ratios of elements and their sum. The absolute atomic ratios of elements and the formula of the compound in the format of the unit cell $\text{B}_{15-x}\text{C}_x$ were found. Obtained: $0.98_{\text{Al}}+12.02_{\text{B}}+1.98_{\text{C}} = \Sigma 14.98_{(\text{Al}+\text{B}+\text{C})}$. Compound formula: $\text{B}_{12}(\text{C-Al-C})$ or $\text{AlB}_{12}\text{C}_2$ [24]. The results of X-rays studies of the washed (according to the results of the procedure for dissolving metallic Si and impurities in the alkali) samples are shown in Table 1.

The results of measurements of the composition of the initial $\text{B}_{12}[(\text{C-B-C})_n(\text{C-C-C})_{1-n}]$ and the purified mixture of phases after a 5-hour heat treatment of $\text{B}_{12}(\text{B, Si, C})_3+\text{SiC}+\text{Si}$ are presented in the Table 2.

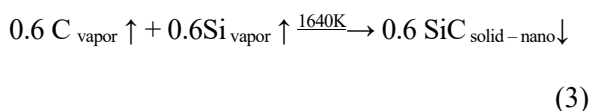
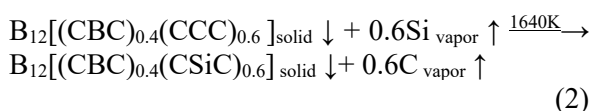
Table 1. Calculated results of X-ray phase analysis of heating treatment products for 5 h at 1640 K in the system: $\text{B}_{12}[(\text{C-B-C})_n(\text{C-C-C})_{1-n}] - \text{Si}$, after purification in 20 mass. % NaOH solution

Phases	Lattice parameters, nm		5 hours exposure at 1670 K
	<i>a</i>	<i>c</i>	Relative phase composition, mole fractions q_i
B_{12}C_3 initial $\text{R}\bar{3}\text{m}$	0.5602	1.2088	-
B_{12}C_3 heat treated $\text{R}\bar{3}\text{m}$	0.5609	1.2102	≤ 0.0001
$\text{B}_{12}(\text{B, Si, C})_3$ $\text{R}\bar{3}\text{m}$	0.5655	1.2348	0.8388
SiC-2H $\text{P6}_3/\text{mc}$	0.3021	0.5055	0.1541
SiC- β $\text{R4}\bar{3}\text{m}$	0.4362	-	≤ 0.0001
Si \downarrow undissolved	0.417	-	0.0071 $\Sigma q_i \approx 1.0002$

Table 2. The composition of the initial BC of the products of the 5-hour heat treatment $B_{12}(B, Si, C)_3+SiC+Si$, washed in alkali and the $B_{12}(B, Si, C)_3$ phase

Materials	The mass fraction of the element W_E , wt. %			
	W_B	W_C	W_{Si}	ΣW_i
$B_{12}[(C-B-C)_n(C-C-C)_{1-n}]$	81.15	18.80	-	99.95
$\Sigma [B_{12}(B, Si, C)_3+SiC+Si]$	63.90	15.80	19.95	99.65
$B_{12}(B, Si, C)_3$	76.18	13.33	10.07	99.58

The absolute atomic ratio for 15 atoms of the elementary cell of the initial BC is: $12.41_B + 2.59_C = \Sigma 15(B + C)$ atom. abs. or 12_B atoms – icosahedra, $0.41_B + 2.59_C = 3$ atoms – chains. Formula BC is $B_{12}[(CBC)_{0.4}(CCC)_{0.6}]$. Boron carbide was used in the experiment, in which 40 % of the chains were (C-B-C), and 60 mass. % were purely carbonic – (C-C-C). The composition of $B_{12}(B, Si, C)_3$ is made considering the mole fractions of the phases calculated using the X-ray method and chemical analysis data (Tables 1, 2). Absolute atomic ratio for 15 atoms of the unit cell $B_{12}(B, Si, C)_3$ is: $12.41_B + 1.95_C + 0.63_{Si} = \Sigma 14.99(B + C + Si)$ ads. atoms or 12_B atoms – icosahedra, $0.41_B + 1.95_C + 0.63_{Si} = 2.99$ atoms – chains. Formula $B_{12}(B, Si, C)_3$ is $B_{12}[(CBC)_{0.4}(CSiC)_{0.6}]$. Thus, boron carbide was used in the experiment, in which 40% of the chains were (C-B-C), and 60%_{mass} were purely carbonic - (C-C-C). Only the central carbon atoms in the (C-C-C) chains were replaced by Si, as (C-Si-C). Therefore, the entire process can be written in the form of the following chemical substitution reactions:



Micron boron carbide powder interacts with silicon vapor at the site of three-carbon chains (reaction 2). The central carbon atom is replaced by Si. A solid solution of BC-Si, where Si - 10.07 mass. %, of the specified composition and parameters of the crystal lattice is formed (Table 2). An equivalent amount of vaporous carbon (4.4 mass. % of $C_{gas} \uparrow$) is released into the gas phase, reacts with Si gaseous \downarrow , (reaction 3), with the formation of SiC solid nano \downarrow . The absence of boron phases of silicide, such as SiB_3 ($SiB_{2.89}$), SiB_6 , SiB_n ($n \approx 23$) indicates greater

resistance of C-B-C chains to interaction with vaporous Si.

CONCLUSIONS

It was of certain interest to assess how much the substitutions in BC chains strengthen or loosen the structure. Table 3 shows the known strength and geometric characteristics of the atoms of the chains that connect the B_{12} dodecahedra to each other. The specific electronegativity (modern data χ_{n-sh} according to Nourizadeh-Shakerzadeh [25]) was calculated, which considers the electrophilicity of atoms in the classical Allred-Rokhov system [26], which has a physical meaning as $\chi_A = Z_{eff} \cdot e^2 / r_{kov}^2$ relative to the size of the atomic-ionic radii of the elements (r_{ai} according to Slater [27]). The average specific electronegativity of real and possible BC chains was estimated. As can be seen from Table 3, the average value of the specific electronegativity (χ_{n-sh}/r_{ai}) of existing chains in berthollides BK are in the region of $2.79 \geq CCC \geq CBC \geq BBC \geq 2.18$. According to the work [28], carbon-enriched BC micro crystals have a higher melting point of up to 100 K compared to boron-enriched samples, which corresponds to a decrease in the average specific electronegativity of CCC to CBC and BBC chains from 2.79 to 2.18 units (χ_{n-sh}/r_{ai}). Chains of $BBB = CAIC = 1.93$ are typical limit for the BC structure. The values of the specified values for CSiC chains = 2.14 will experimentally prove to enter the region of tolerant stability of the BC structure in the case of complete replacement of the chains or $CCC(2.79) \geq CBC(2.50) \geq BBC(2.18) \geq CSiC(2.14)$.

The actual composition of powders with the boron carbide structure, according to [10], namely: from $[(B_{12})_{0.8}(B_{11}C)_{0.2}](CCC)_{1.0}$ to $B_{12}[(BBC)_{0.66}(CBC)_{0.34}]$, has a decrease in the specific electronegativity of the chains of the specified compounds $2.79 \rightarrow 2.29$. In our case, when carbon is replaced by silicon in the

composition of $B_{12}[(CBC)_{0.4}(CCC)_{0.6}]$ with $B_{12}[(CBC)_{0.4}(CSiC)_{0.6}]$, the specific electronegativity (SE) of the chains, while preserving the BC structure, decreased by $2.67 \rightarrow 2.28$, or by $\approx 15\%$. That is, the area of tolerance of the BC structure expanded downwards by only 0.01 units χ_{n-s}/r_{ai} or $2.79 \rightarrow 2.28$. A decrease in the specific electronegativity of silicon in substituted BC solid solutions correlates with their lower hardness. Si-solid solutions of BC can play a role

as a “soft stabilizing component” in the composition of complex ceramics in relation to the boron carbide base [12]. When replacing carbon and boron with aluminum in the composition of $B_{12}[(CBC)_{0.4}(CCC)_{0.6}]$ compounds with $B_{12}(CAIC)$, the SE of the chains decreased by $2.67 \rightarrow 1.93$, or by $\approx 28\%$, which reaches to limit tolerances structure of boron carbide for CAIC. The specific electronegativity of BBB chains is also equal to 1.93, but it's no longer belongs to the structure of boron carbide.

Table 3. Power (χ_A), dimensional (r_{ai}) and specific (χ_{N-S}/r_{ai}) characteristics of atoms of constituent chains in powders of type B_{12} (C-M-C), where M = B, C, Al, Si. Determination of the area of tolerance of the BC structure

The name of the element	Degree of oxidation	Electro-negativity (χ_{n-m})	Atomic-ionic radius r_{ai} (angstrom)	χ_{N-S}/r_{ai}	(χ_{N-S}/r_{ai}) average chain
C	IV±	1.954	0.70	2.79	CCC – 2.79 CBC – 2.50
B	III+	1.637	0.85	1.93	BBC – 2.18 BBB – 1.93
Si	IV±	1.430	1.10	1.30	CSiC – 2.14
Al	III+	1.200	1.25	0.96	CAIC – 1.93

In view of the above, one can hope that in the presence of a stoichiometric sample or a carbon-enriched BC, it will be possible to replace all CCC chains with CSiC up to Si –

6.67 at. %. And to expand the tolerance area of the BC structure to the value of SE – 2.14 and to obtain a softer component of composite ceramics based on BC, free from shock amorphization.

Розташування атомів Al та Si у заміщеному карбіді бору

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Карбід бору є цікавим матеріалом для індивідуальних бронезилетів, але його низька в'язкість призводить до руйнування та аморфізації, що обмежують його широке використання. Атоми Al і Si в дифузійно легovanому карбіді бору зменшують цю проблему. Встановлено проходження реакції заміщення в порошках карбиду бору парами Al і Si у вакуумі. Методи сертифікації: хімічний аналіз, повно-профільний РФА (Powder Cell for Windows 2.4 FREE, W. Kraus & G. Nolze) та розрахунок формули у форматі 15-атомної елементарної комірки $B_{12}(C-C-C)$ тригональної сингонії, просторової групи $R3m$, $Z = 3$. Суміш порошків бору карбиду, алюмінію або силіцію термічно обробляли у вакуумі при умовних температурах випаровування Al (1520 K) або Si (1640 K) протягом 1–5 год. Зразки очищали лугом і аналізували арбітражним хімічним аналізом на бор, карбон, алюміній та силіцій. Формульний склад вхідних порошків карбиду бору визначено як $B_{12}[(C-B-C)_n (C-C-C)_{1-n}]$, де $n = 0.4-0.6$. Реакція заміщення алюмінію відбувається в обох типах ланцюгів

карбіду бору і відповідає формулі $B_{12}(C-Al-C)$ або $AlB_{12}C_2$. В присутності силіцію реакція відбувалася виключно в положеннях три-карбонових ланцюгів. Формула отриманого твердого розчину з порошку складу $B_{12}[(C-B-C)_{0.4}(C-C-C)_{0.6}]$ відповідає - $B_{12}[(C-B-C)_{0.4}(C-Si-C)_{0.6}]$. Відсутність фаз силіцидів бору, таких як SiB_3 ($SiB_{2.89}$), SiB_6 , SiB_n ($n \approx 23$), свідчить про більшу стійкість ланцюгів C-B-C до взаємодії з паро-подібним Si. Вміст Al і Si в заміщених фазах дорівнює 13.3 і 4 (% ат.), відповідно. Виміряно еквівалентні молярні кількості $Al_3B_4C_7$ і SiC газо-нано-фазного походження в продуктах реакції з пароподібними Al і Si. Встановлено область толерантності структури карбіду бору у форматі середньої питомої електро-негативності ланцюжків (χ_{N-Si}/r_{ai}) , що знаходиться в діапазоні значень: $2.79 \geq CCC \geq CVC \geq CSiC \geq BBC \geq 2.18$ одиниць (χ_{N-Si}/r_{ai}) .

Ключові слова: Al, Si, атоми, розташування, заміщені, порошки, бору карбід, область толерантності, структура

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