SPECIFIC SURFACE, CRYSTALITE SIZE OF AlB$_{12}$-NANO OF PRODUCTS OF INTERACTION "BN-Al" IN VACUUM

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Boron carbide (BC, B$_{15-x}$C$_x$ B$_4$C) has a unique combination of properties. This makes it a material for priority applications for a wide range of engineering solutions. The high melting point and heat resistance of the compound contribute to its use in refractory conditions. Due to its extreme abrasion resistance, B$_4$C is used as an abrasive powder and coating. Due to its high hardness and low density, B$_{15-x}$C$_x$ has ballistic characteristics. It is usually used in nuclear programs as an absorbent of neutron radiation Boron carbide ceramics (B$_{15-x}$C$_x$ or BC) may lose strength and toughness due to the amorphization effect under high shear stresses. Aluminum dodecaboride AlB$_{12}$ or B$_{12}$Al, as well as boron carbide B$_{12}$ [(CCC) $_x$ (CBC) $_{1-x}$] have common structural units B$_{12}$ family of boron-icosahedral structures. The bond between icosahedrons is mainly due to atoms (Al, Si, O) or chains (CMC), where M is Al, Si, B, C. Doping BC powder with a small amount of AlB$_{12}$, in cases of shock-shear stress, triggers the mechanism of "micro-cracking". Micro cracks and pores are formed in ceramics. The breakdown voltage decreases. AlB$_{12}$ synthesis is associated with known difficulties. On the other hand. The production of metal-ceramic materials for several decades is associated with the interaction of liquid aluminum and boron nitride. The calculation of this reaction shows that it is exothermic. Avoiding oxidation in vacuum, the reaction occurs through the formation of aluminum nitride and aluminum dodeca-boride. In contrast to the liquid state, the process continues until the end, at conditional temperatures of evaporation of aluminum with slight changes in vacuum. The reaction product is a mixture of nanosized AlN/AlB$_{12}$ powders with a weight ratio of 3/1 ready for baking without grinding. The acid-base properties of the nanosized powder mixture AlN + AlB$_{12}$, the products of the interaction BN + Al in vacuum, which are used optionally, emit separate in pure phases of aluminum nitride and aluminum dodeca-boride. The yield of AlB$_{12}$ is ~ 25%, boron reaches ~ 100%. The average particle size of the AlB$_{12}$ powders according to TEM and ACS $_{X-rays}$ (area of coherent $_{X-rays}$ scattering), L (nm) is L_{TEM}=110-150nm, L_{ACS}=51-70nm. The average specific surface area of the powder according to BET, TEM and ACS, $S_{BET.m2/g}$=21,0-15,0; $S_{TEM.m2/g}$=21,4-15,4; $S_{ACS.m2/g}$=46,1-33,6; (at 1460 and 1640K, respectively)[1].

Keywords: *specific surface area, crystallite size, AlB$_{12}$-nano powders, BN-Al aluminothermy, vacuum*

Introduction

Modern scientific and technological research of impact-resistant materials for over twenty years remains a priority in the use of reaction components and products of interaction in the systems: "Al - BN or $B_{15-x} C_x$ [1]" [2 - 8]. The method of vacuum aluminothermy of boron nitride brings the reaction to an end. A constant mass ratio of reaction products $AlN/AlB_{12}=1/3$ will not meet production needs. Therefore, the removal of individual compounds from the reaction mixture is relevant. In this work, we propose acid-base processing of reaction products prior to the extraction of AlB_{12} [9]. In the IPM of the NAS of Ukraine, the technology of obtaining a kilogram amount of a mixture of submicron powder $AlN/AlB_{12}=1/3$ was first developed. The practical use of this powder for the above-mentioned needs makes it possible to partially replace both expensive free boron, modify the charge of refractory carbide $B_{12}[(C\text{-}B\text{-}C)_x(C\text{-}C\text{-}C)_{1-x}]$ and to prevent of amorphous decomposition of ceramics. It is essential to facilitate up to hundreds of degrees of sintering regulations and prolong the operation of graphite equipment for hot pressing of dense ceramics without compromising the performance of products.

Materials and research methods

The production of submicron aluminum dodecaboride powders [9, 10] and carbon bonding products [11] has led to the adaptation of known methods of analysis of borides to a specific substance, such as AlB_{12}, $AlB_{40}C_4$, $AlB_{12}C_2$, $Al_8B_4C_7$, or $Al_4B_{48}C_4$. These methods include the determination of the main elements - boron and aluminum, as well as gas-forming and technological impurities, such as hydrogen, nitrogen, oxygen, carbon, water hardness elements, the amount of magnesium and calcium, as well as the presence of iron. If necessary, procedures for determining impurity phases of free boron, B_2O_3 and free carbon were tested [12 - 22]. Investigation of the porous structure of the samples was carried out using an ASAP 2000M (Accelerated Surface Area and Porosimeters System),]. Calculated specific surface by the method of BET (S_{BET}, m^2/g). The method of roentgenography and transmission microscopy (PEM) in this work was used to determine the phase and size composition of AlB_{12} crystallites with using HZG-4A diffractometer, Cu-Kα radiation with a Ni-filter and JEM 100 CX instruments.

Results and discussions

The interaction products of boron nitride and aluminum are a mixture of powders of aluminum nitride and aluminum dodecaboride in the mass ratio $AlN / AlB_{12} = 1/3$. The chemical properties of the formed compounds differ slightly in acid-base terms. It was found that the nano-dimensional state of AlN and AlB_{12} enhances this difference, which made it possible to develop regulations for chemical treatment for the selective extraction of individual components of powders. Complex processing of intermediate technological solutions made it possible to obtain other useful materials. This applies to powders: AlB_{12}; AlN, as well as γ - Al_2O_3 and aqueous ammonia solution as by-products. Analysis of the interaction of synthesis products with mineral solvents, acids and alkalis are presented in Table 1. The interaction reaction is exothermic. Vacuum filtration of the precipitate using a Bunsen funnel and a Buchner flask. Washing with water to pH ~ 5 (universal indicator). Washing with ethanol. Drying at 130ºC. Screening. Packing in dense container.

Extraction of AlB_{12} was performed by alkaline decomposition of AlN according to the equation of chemical reaction (1):

$$AlN+AlB_{12}+NaOH+2H_2O \rightarrow Na[Al(OH)_4]_{solution}+AlB_{12}\downarrow_{solid} +NH_3\uparrow_{vapor} \quad (1)$$
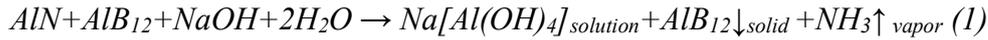
Certification of AlB₁₂. The synthesis of four batches of AlB_{12} powder in the field of external heating temperatures of the charge "BN+13Al" was carried out in order to determine the effect of temperature on the average particle size of the powder and the composition of the obtained aluminum dodecaboride. The results of the analysis of AlB_{12} powders are presented in Table 2. The atomic ratio of the main components and the content of gas-forming impurities are within acceptable limits regarding the quality of the obtained products. The average particle size (L_{AlB12}) and the specific surface area (S_{BET}, m²/g) of powders were determined and calculated. The obtained results are presented in the Table 3. The values of L_{TEM} and L_{ACS} differ almost twice. Calculation of the specific surface area ($S_{spesific}$, m²/g) of the powder surface and comparison with S_{BET} values showed that S_{TEM} is closer to the experimental values. Moreover, obviously, the powders are somewhat agglomerated. The conglomerates of which are twice the minimum size of the average elementary particles of the studied samples (Table 3.)

Table 1. Products of system interaction: "$AlB_{12solid} \downarrow$ + 12AlN $_{solid} \downarrow$" with water, solutions of mineral acids and alkali

H_2O hot↓	HNO_3 solution↓	H_2SO_4 solution↓	HCl solution↓	NaOH solution↓
$AlB_{12}\downarrow$ + $AlN\downarrow$				
AlB_{12} hot↓	dissolved	dissolved	AlB_{12} hot↓	AlB_{12} hot↓
$NH_3\uparrow_{gas}$, $Al(OH)_3\downarrow$	NH_4NO_3, $Al(NO_3)_3$ dissolved	$NH_4)_2SO_4$, $Al_2(SO_4)_3$, dissolved	NH_4Cl, $AlCl_3$ dissolved	$NH_3 \uparrow_{gas}$, $Na[Al(OH)_4]$ dissolved

Table 2. Chemical (component) composition of AlB_{12} powders synthesized at temperatures of 1460-1600K

№№	W_B%	W_{Al}%	Al%$_{at.}$/B%$_{at.}$	W_C%	W_O%	ΣW_{Ei}%	T K
1	81.7	16.5	1/12.4	0.23	0.68	99.1	1463
2	81.9	17.1	1/12.0	0.19	0.72	99.9	1533
3	82.3	16.7	1/12.3	0.18	0.60	99.8	1593
4	81.9	17.2	1/11.9	0.13	0.50	99.7	1643

Table 3. Characteristics of the average particle size and specific area of the synthesized AlB_{12} powders at temperatures of 1460 - 1640K

№ sample AlB_{12}, T K synthesis	The average particle size of the powder according to TEM and ACS_{X-ray}, L (nm)		The average specific surface area of the powder according to BET and calculated according to TEM and ACS_{X-ray} (Area of Coherent X-ray Scattering), $S_{specific.}$(m^2/g)		
	L_{TEM}	L $_{ACS, X-ray}$	S_{BET} experiment	S_{BET} experiment	$S_{ACS, X-ray}$ calculated
1 (1460)	110	51	21,0	21,4	46,1
4 (1640)	150	70	15,0	15,7	33,6

ACS - Area of coherent scattering X-ray of a single radiographic reflection hkl, the half-width of which is calculated by the average particle size of the powder L_{AlB12};

($S_{BET,}$ (m^2/g)), BET - specific surface area determined by the method of Brunauer S., Emmett P. H., Teller E. - BET [23 - 25];

S_{TEM}, $S_{ACS, X-ray}$ - calculated according to L_{TEM} and $L_{ACS, X-ray}$ in a cubic orthogonal assumption;

Where: $S_{part} = 6 L^2$ - the average area of the particle;

$V_{part.} = L^3$ - average particle volume;

$N_{part} = 1 \cdot 10^{-6}/cV_{part}$, where c = 2.55 g/$cm^3$ - the average number of particles in a volume occupying 1 g of AlB_{12} powder cm^3/c;

where S_{TEM}, $SACS = S_{part} \cdot n_{part}$ (m^2/g).

X-ray phase analysis is a single-phase product.

Syngony is tetragonal. Spatial group: $P4_12_12$; $P4_32_12$; a = 1,016; c = 1,428 (nm), according to ICDD file No. 12 - 640 [26].

Morphology, according to TEM: transparent tetragonal planar crystals;

- average size: 60 - 40 nm;

- maximum - 100 - 150 nm.

The visual color of the powder is light brown.

The chemical composition and atomic ratio of the mass fractions of aluminum and boron is W_{Al}/A_{Al} : W_B/A_B = 1/11,9, where A_{Al} and A_B are the atomic masses of aluminum and boron;

W_O impurities - 0.3 - 0.5%; W_N <10-2%; W_H <10-2%; W_C - 0.2-0.5%; $W_{Ca; Mg; Fe; Si}$ <10^{-2}% (wt.).

The experimentally established hardness (according to Vickers) of the sintered sample - 0.75 AlB_{12} - 0.25 AlN is 26 ± 2 GPa at kilogram loads [9].

The obtained results indicate a certain stability and relative purity of the component composition of AlB_{12} powders in the range of synthesis temperatures 1463 - 1643K. The average particle size and specific surface area of the powder increases by ~ 22%. AlB_{12} particles are somewhat agglomerated. The average size of conglomerates does not exceed 150 nm and is twice as large as that of elementary particles of aluminum dodecaboride powder. The characteristics of the certification of aluminum dodecaboride powders are given below.

Conclusions

Pure powders of AlB_{12}-nano (40-60nm), AlN-nano (40nm) and г-Al2O3-nano (4.0-10nm) were synthesized in significant quantities by chemical treatment of boron nitride vacuum aluminothermy products.

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ПИТОМА ПОВЕРХНЯ, РОЗМІРИ КРИСТАЛІТІВ AlB₁₂-NANO ПРОДУКТІВ ВЗАЄМОДІЇ "BN-Al" У ВАКУУМІ

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Бору карбід (БК, B₁₅₋ₓCₓ B₄C) має унікальні поєднання властивостей. Це обумовлює його, як матеріал, щодо пріоритетних застосувань для широкого кола інженерних рішень. Висока температура плавлення та термостійкість сполуки сприяє до застосування у вогнетривких умовах. Завдяки надзвичайній стійкості до стирання B₄C використовують, як абразивні порошки та покриття. Завдяки високій твердості та низькій щільності, B₁₅₋ₓCₓ відрізняється балістичними характеристиками. Зазвичай, він використовується в ядерних програмах, як абсорбент нейтронного випромінювання Кераміка бору карбіду (B₁₅₋ₓCₓ або БК) при дії високих зсувних напружень може втрачати

міцність та в'язкість внаслідок ефекту аморфізації. Додекаборид алюмінію AlB_{12} або $B_{12}Al$, як і бору карбід $B_{12}[(CCC)_x(CBC)_{1-x}]$ мають спільні структурні одиниці B_{12} сімейства бор-ікосаедричних структур. Зв'язок між ними відбувається здебільше за рахунок атомів (Al, Si, O) або ланцюжків, (CMC), де M – Al, Si, B, C. Легування порошку БК невеликою кількістю AlB_{12}, у випадках ударно-зсувного напруження, запускає механізм «мікро-крекінгу». Утворюються мікро тріщини та пори (cracks and pores) в кераміці. Напруга руйнування зменшується. Синтез AlB_{12} пов'язано з відомими труднощами. З іншого боку. Виробництво металокерамічних матеріалів протягом декількох десятиліть пов'язане з взаємодією рідкого алюмінію та нітриду бору. Розрахунок теплоти реакції, показує, що вона екзотермічна. Уникаючи окислення у вакуумі, реакція відбувається шляхом утворення нітриду алюмінію та додекабориду алюмінію. На відміну від рідкого стану, процес триває до кінця, при умовних температурах випаровування алюмінію з незначними змінами вакууму. Продукт реакції являє собою суміш нанорозмірних порошків AlN/AlB_{12} із ваговим співвідношенням 3/1, готових до спікання без подрібнення. Кислотно-основні властивості нанорозмірної порошкової суміші $AlN+AlB_{12}$, продуктів взаємодії $BN+Al$ у вакуумі в чистих фазах нітриду алюмінію та додекабориду алюмінію виділяють окремо. Вихід AlB_{12} становить ~ 25%, по бору досягає ~ 100%. Середній розмір частинок порошків AlB_{12} за даними ТЕМ та ОКР (рентгенівська область когерентного розсіювання), L (нм) становить L_{TEM} = 110-150 нм, L_{OKP} = 51-70 нм. Середня питома поверхня порошку за ВЕТ, ТЕМ та ОКР, $S_{BET.}$ $м^2/г$ = 21,0-15,0; $S_{TEM.}$ $м^2/г$ = 21,4-15,4; S_{OKP} $м^2/г$ = 46,1-33,6; (при 1460 та 1640К відповідно).

Ключові слова: питома поверхня, розміри кристалітів, порошки AlB_{12}-нано, алюмотермія "BN-Al", вакуум