

Physico-mechanical and physicochemical interaction at sintering of cBN–TiB₂ composites under ultrahigh pressure

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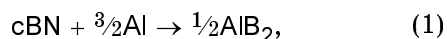
It has been shown in experiment that at the reactive sintering of cubic boron nitride with aluminum under high pressures and temperatures, addition of TiB₂ results in shifting of the reaction towards crystallization of aluminum diboride instead of higher diborides and provides the absence of residual aluminum in the reaction products. The calculated values of residual thermal stresses in cBN and TiB₂ phases sintered under 8 GPa at 2300 K are considerably lower than the phase flexural strength.

Экспериментально показано, что при реакционном спекании в условиях высоких давлений и температур кубического нитрида бора с алюминием добавки TiB₂ смещают реакционное взаимодействие в сторону кристаллизации из расплава диборида вместо высших боридов алюминия и обеспечивают отсутствие в продуктах реакции остаточного алюминия. Расчетные значения остаточных термических напряжений после спекания при 8 ГПа и 2300 К в фазах cBN и TiB₂ значительно ниже прочности фаз на изгиб.

Polycrystalline materials based on cubic boron nitride (PCBN) are used mainly in cutting of hard materials [1, 2]. The cBN content in commercial PCBN is 45 to 90 %, other phases include titanium carbide or nitride (up to 50 %) and minor amounts of high-melting aluminum compounds being the hard alloy components.

This work is aimed at development of novel cBN composites bound with titanium diboride that is introduced in the raw mixture, similar to titanium carbide at the sintering of KIBORIT-3 composite. The purpose of the work is to study physicochemical and physico-mechanical interaction of TiB₂ with the mixture components (cBN, Al) at the high-temperature sintering under superhigh pressure in the thermodynamic stability region of sphalerite BN modification [3].

Interaction of cBN with Al at reactive sintering results in formation of aluminum nitride and borite phases. The main reactions are:



The specific feature of the reactive interaction under high pressure consists in that the AlB₂ stability region becomes shifted towards high temperatures and overlaps the stability region of AlB₁₂. Therefore, either the reaction (1) can be completed or the reaction (2) does not run to completion and residual Al(B) solid solution is formed [4]. The idea of this work is as follows. First, in the presence of TiB₂ phase (being a structural analogue of AlB₂ having very close crystal lattice periods), the interaction between cBN and Al (the reaction products crystallization from Al melt) should be shifted towards the reaction (1), so the products should not contain Al metal. Second, the thermal expansion coefficients of cBN and TiB₂ are close to one another, thus would provide a low level of residual interphase stresses in the composite. Finally, TiB₂ exceeds somewhat TiC not only in hardness but also in elasticity constants. Thus, substitution (partial or complete) TiB₂ for

Table 1. Mixture composition and calculated phase composition of sintered composite basing on the mass balance in reactions (1)–(2) type.

No.	Mixture, p.c. mass			Calculated (1), p.c. mass				Calculated (2), p.c. mass			
	cBN	Al	TiB ₂	cBN	AlN	AlB ₂	TiB ₂	cBN	AlN	AlB ₁₂	TiB ₂
1	90	10	–	83.87	10.13	6.0	–	81.5	14.0	4.5	–
2	85	10	5	78.87	10.13	6.0	5	76.5	14.0	4.5	5
3	80	10	10	73.87	10.13	6.0	10	71.5	14.0	4.5	10
4	75	10	15	68.87	10.13	6.0	15	66.5	14.0	4.5	15

Table 2. Phase composition (p.c. mass) and properties of samples sintered under 8 GPa at 2300 K.

No.	cBN	AlN	AlB ₂	TiB ₂	Al	HKN, GPa	ρ/ρ_0
1	85.5	11.9	3.7	–	2.6	27±2	0.976±0.003
2	82.0	8.4	–	9.6	–	27±3	0.973±0.002
3	73.1	11.5	–	15.4	–	29±3	0.98±0.01
4	67.0	10.6	–	22.4	–	27±3	0.968±0.001

Table 3. Crystal lattice periods of AlB₂ structure type phases.

The phase	a , nm	c , nm	c/a	$a^2c \cdot 10^3$ nm ³	Reference
AlB ₂	0.3009±0.0001	0.3262±0.0001	1.0841	29.53±0.03	[6]
AlB ₂	0.30062±0.00001	0.32548±0.00001	1.0827	29.414	[7]
TiB ₂	0.30245	0.32326	1.069	29.57	[8]
TiB ₂	0.3028	0.3228	1.066	29.60	[9]
AlB ₂	0.30096±0.00007	0.32608±0.00024	1.0835	29.53	This article

TiC in KIBORIT-3 could be assumed to provide improved elasticity constants [5].

The experimental samples were prepared using the mixture characterized in Table 1. The sintering was carried out in an HPA high-temperature furnace with graphite heater in two stages: I, soaking with Al melt under pressure ($p = 2.5$ GPa, $T = 1300$ K); II, reactive sintering at $p = 8$ GPa, $T = 2300$ K or $p = 4.2$ GPa, $T = 1700$ K. The sample was cooled with the furnace from the sintering temperature to ambient one, then depressurized. The samples were diamond-ground to clean the surface from residual graphite. The phase composition of sintered samples was calculated basing on the mass balance in the type (1) and (2) reactions assuming no reactive interaction between TiB₂ and the mixture components (see Table 1). The experimental phase composition was determined by X-ray structure analysis basing on intensity of strongest lines of each phase in the XRD spectrum [4] using cBN–TiB₂ reference mixtures. The hardness (HKN) was measured by Knup indenter under 9.8 N indenter load; density (ρ), by hydrostatic weighing (in acetone);

the pore-free sample density (ρ_0) was calculated according to the "mixture rule" from the concentrations and density values of individual phases (Table 2).

Consideration of the calculated and experimental phase composition characteristics shows that the content of the phase identified as TiB₂ in the reaction products exceed that expected from the mass balance, that is, the titanium diboride content in the mixture. This is explained most likely by superposition of XRD spectra from TiB₂ and AlB₂ phases in the total spectrum from the sintered sample. In Table 3, presented are the lattice periods of those phases taken from the most popular data sources while in Table 4, the variations of the TiB₂ lattice periods revealed in our experiments (statistical averages at the confidence level 0.68 and the number of samples studied from 5 to 7). The data of Table 4 evidence a significant increase of the TiB₂ lattice periods and the effect of the sintering conditions (p, T) thereon. In the same experiments, the cBN lattice period shows a trend to increase after sintering at high p and T parameters;

Table 4. Evolution of TiB₂ lattice periods and unit cell volume at sintering of cBN–TiB₂–Al system.

The conditions of sintering	<i>a</i> , nm	<i>c</i> , nm	<i>c/a</i>	<i>a</i> ² <i>c</i> ·10 ³ nm ³
Mixture 5–15 % TiB ₂	0.30303±0.00005	0.32286±0.0001	1.065	29.647±0.001
4.2 GPa, 1700 K	0.3031±0.0002	0.3228(2)	1.065	29.656±0.003
8 GPa, 2300 K	0.30326±0.00009	0.32302(8)	1.065	29.707±0.003

Table 5. Evolution of cBN lattice periods and unit cell volume at sintering of cBN–TiB₂–Al system.

The conditions of sintering	<i>a</i> , nm	<i>a</i> ³ ·10 ³ nm	Vol. % TiB ₂ in the mixture
Mixture 1	0.36151±0.00003	47.25±0.01	0
Mixture 2, 3, 4	0.36153±0.00006	47.25±0.02	5–15 %
4.2 GPa, 1700 K	0.36147±0.00004	47.230±0.016	0
4.2 GPa, 1700 K	0.36152±0.00008	47.25±0.03	5–15 %
8 GPa, 2300 K	0.36158±0.00002	47.273±0.008	0
8 GPa, 2300 K	0.36158±0.00004	47.273±0.016	5–15 %

however, that increase is not associated with the TiB₂ influence (Table 5).

In general, such changes may result from physicochemical and physico-mechanical interaction with the mixture components. The sequence of technological operations (cooling in the HPA followed by the pressure release down to standard conditions) makes it possible to evaluate the residual elastic strains (ϵ) as the sum of thermal (ϵ_{therm}) and baric (ϵ_{bar}) components [10]:

$$\epsilon = \epsilon_{therm} + \epsilon_{bar} = \alpha \cdot \Delta T + \Delta p / 3K, \quad (3)$$

where α is the linear thermal expansion coefficient; K , modulus of hydraulic compression; ΔT and Δp , the temperature and pressure drop from the sintering parameters down to 300 K and 10⁻⁴ GPa. The residual thermobaric strains were calculated using the procedure for macroisotropic biphas composite at stochastic phase distribution as proposed in [11]. The residual thermal stresses in phase 1 are

$$\langle \sigma_{ij} \rangle^{(1)} = \left[\beta_1 - \frac{K_1}{C_1 K_3} (\langle \beta \rangle - 3K_2 \alpha^*) \right] \cdot T \cdot \delta_{ij}. \quad (4)$$

For phase 2, the calculation is similar, the corresponding indices being substituted. For phases 1 and 2: C_1 and C_2 are volume concentrations; K_1 and K_2 , hydraulic compression moduli; $K_3 = K_1 - K_2$; $\beta = 3\alpha K$; α_1 and α_2 , linear thermal expansion coefficients; $\langle \beta \rangle = C_1 \beta_1 + C_2 \beta_2$; $\langle K \rangle = C_1 K_1 + C_2 K_2$; $\alpha^* = \beta^* (3K^*)^{-1}$; α^* , β^* , K^* , thermoelastic constants of the composite calculated using thermoelastic constants of individual phases, including the shear moduli (G); $T = T_{sinter} - 300$; δ_{ij} , the Kroeneker symbol (summation over repeating indices).

Tables 6 and 7 contain the initial data and calculation results for a two-phase composite (cBN/TiB₂ phase volume ratios correspond to Samples 2, 3, and 4, see Table 2). The calculations have been carried out for $T = 2300$ K. The temperature and pressure dependences of thermoelastic moduli G and K did not taken into account.

The calculated results presented in Table 7 show that in the TiB₂ phase, the residual strains $\epsilon_{therm} < 0$, therefore, the increasing volume of the crystal unit cell results most likely from the physicochemical interaction of TiB₂ with the mixture components. This is true also for the cBN phase where the increase of the lattice period is independent of the TiB₂ presence in the mixture. The residual stresses in the phases of the cBN–TiO₂ composite are much lower than the flexural strength of those phases (0.800 GPa [12] and 0.245 GPa [13]). Thus, from the standpoint of physico-mechanical compatibility of the phases in the composite, the use of TiB₂ will not cause any technological complications (cracking, failure) during the sintering, machining of the samples and functional testing of the tools.

Thus, at the reactive sintering of cBN–Al composites under ultrahigh pressure and high temperatures, addition of TiB₂ to the initial mixture shifts the interaction to-

Table 6. Thermoelastic constants of cBN [12] and TiB₂ [13].

Material	E , GPa	G , GPa	K , GPa	ν	$\alpha \cdot 10^6$, grad ⁻¹
cBN	839	378	358	0.11	5.4 (1200 K)
TiB ₂	551	214	415	0.28	5.2 (1300 K)

Table 7. Normal components of residual thermal stresses (σ) and strains (ϵ_{therm}) after sintering and cooling under pressure depending on the volume content of phases (C).

Sample	The phase					
	cBN			TiB ₂		
	C	σ , GPa	$\epsilon_{therm} \cdot 10^3$	C	σ , GPa	$\epsilon_{therm} \cdot 10^3$
2	0.954	0.012	0.034	0.046	-0.256	-0.616
3	0.905	0.025	0.070	0.095	-0.237	-0.571
4	0.857	0.037	0.103	0.143	-0.220	-0.531

wards crystallization of aluminum diboride from the melt instead of higher borides and provides the absence of residual aluminum in the reaction products, the material hardness remaining essentially unchanged. The calculated values of residual thermal stresses in cBN and TiB₂ phases after sintering at 8 GPa and 2300 K are considerably lower than the flexural strength, thus providing the absence of technological complications during the sintering and machining of the samples.

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Фізико-механічні та фізико-хімічні взаємодії при спіканні композитів cBN–TiB₂ в умовах надвисокого тиску

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Експериментально показано, що при реакційному спіканні в умовах високих тисків і температур кубічного нітриду бору з алюмінієм добавки TiB₂ зсувають реакційну взаємодію у бік кристалізації з розплаву дибориду замість вищих боридів алюмінію і забезпечують відсутність у продуктах реакції залишкового алюмінію. Розраховані значення залишкових термічних напруг після спікання при 8 ГПа і 2300 К у фазах cBN і TiB₂ значно нижчі, ніж міцність фаз на згин.