

## Effect of HPHT Sintering on Crystal Structure of NbC and TaC Carbides in PcBN Composites of cBN-NbC-Al and cBN-TaC-Al Systems

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(Received 15 April 2023; revised manuscript received 25 June 2023; published online 30 June 2023)

Ceramic-matrix composites based on cubic boron nitride (cBN) with binders, containing refractory compounds of transition metals and aluminum, are widely used for high-speed (300 – 500 m/min) and finishing metal processing of hardened alloy steels and heat resistant alloys. PcBN composite materials of the BL group obtained in the cBN–NbC–Al and cBN–TaC–Al systems (60:35:5 vol. % charge content) have good application prospects. The purpose of this work was to study the effect of high pressure – high temperature (HPHT) sintering conditions (7.7 GPa, 1600 – 2450 °C) on the crystal structure of NbC and TaC carbides, which form together with aluminum the binder of the charge. As a result of a detailed X-ray diffraction study, it was shown that the original NaCl type crystal structure of these carbides is modified under barothermal exposure. Namely, an additional position for the placement of small atoms (nitrogen and/or carbon) is formed. During HPHT sintering, the interaction of NbC and TaC with Al atoms in the charge, as well as with the nitrogen flow formed during partial decomposition of cBN, results in the formation of solid solutions. At the same time, the dissolution of aluminum takes place in accordance with the type of Nb or Ta atoms substitution by it (up to 2.5 at.% Al). Accumulation of nitrogen atoms in the TaC structure occurs by filling vacancies in the carbon sublattice (dissolves up to 1 at.% N). In the NbC structure this process goes through interstitial of nitrogen atoms with their placement on the additional position of a modified NaCl-type structure (dissolves up to 5 at.% N). Besides, the carbon atom also partially moves from its basic positions. This accumulation of defects leads to a significant increase in the lattice parameter of NbC carbide (a relative increase of 0.28% for NbC versus 0.11% for TaC). It is shown that the carbide compositions can be described as Nb<sub>0.96</sub>Al<sub>0.04</sub>(C, N)<sub>1.17</sub> and Ta<sub>0.95</sub>Al<sub>0.05</sub>(C, N)<sub>1</sub>. for composites of the cBN–NbC–Al and cBN–TaC–Al systems with the best operational characteristics (HPHT sintering at 7.7 GPa and 2150 °C).

**Keywords:** High Pressures, cBN Superhard Materials, Monocarbides, X-ray Diffraction Method, Crystal Structure.

DOI: [10.21272/jnep.15\(3\).03030](https://doi.org/10.21272/jnep.15(3).03030)

PACS numbers: 72.80.Tm, 81.05.Je

### 1. INTRODUCTION

The industrial need to increase the processing productivity of modern metal alloys permanently requires the use of new ceramo-matrix materials. Among them the cBN-based ceramic materials (PcBN), having extreme hardness and chemical inertness, are the most promising for high-speed and finishing metalworking of hardened steels and heat-resistant alloys [1,2]. One way to improve performance of PcBN materials could be made by varying the composition of the binder material, containing refractory carbides, nitrides, borides, etc.

For this purpose the composite materials of the BL group in the cBN–NbC–Al and cBN–TaC–Al systems have been synthesized by HPHT sintering at pressure of 7.7 GPa in the temperature range of 1600 – 2450 °C. Previously, for these materials the features of components' solid state interaction have been studied only by methods of X–ray diffraction phase analysis and electron microscopy [3–5]. Besides, despite the fact that an anomalous sintering temperature dependence of the lattice parameters of NbC and TaC phases was revealed, their crystal structures were not studied in details.

As a result of series of industrial testing of these materials it was revealed that maximum values of the Young's and shear modulus (635 GPa and 270 GPa, respectively) are detected for cBN–NbC–Al ceramic obtained at 1950 °C, while a further increase in the

sintering temperature leads to reduced stress-strain properties [3, 4]; the microhardness of the cBN–TaC–Al composite reaches its maximum value (34 GPa) at 2150 °C, while the Young's modulus is maximum (590 GPa) at 1600 °C [5]. Set of the properties of cBN–NbC–Al and cBN–TaC–Al composites of BL group obtained by HPHT sintering at 2150 °C made it possible to recommend them for high-speed turning of tempered high-alloyed steel (up to 60 HRC) as well as for nickel-based alloy (Inconel 718) at high temperatures in the cutting area [3-5].

### 2. STATEMENT OF THE PROBLEM AND EXPERIMENTAL TECHNIQUE

In this work, taking into account the above-mentioned prospects for the industrial application of cBN–NbC–Al and cBN–TaC–Al composites, we carried out a detailed X-ray diffraction (XRD) study of changes in the crystal structures of NbC and TaC carbides, which they in presence of cBN and Al undergo at high pressure and temperatures. Particular attention was paid to the role of aluminum in this process, which was added to the charge in order to facilitate sintering process and contribute to the absorption of residual oxygen, because it is known that at high pressure the decomposition of cBN starts at about 2200 °C, while aluminum reacts much earlier.

In our opinion the information obtained from these studies could be contributed to the understanding of the processes occurring during the solid-state interaction of NbC and TaC carbides with both aluminum and boron nitride.

The study of structural features of NbC and TaC carbides affected by high pressure and temperature was carried out for samples obtained by the Authors of Refs. [3–5]. Namely, two powder blends of cBN–NbC/TaC–Al (60:35:5, vol.%) were mechanically alloyed (MA) with further HPHT sintering in a high pressure apparatus of toroid type (pressure 7.7 GPa) at temperatures range 1600 – 2450 °C.

X–ray diffraction patterns were obtained in discrete mode on STOE STADI MP X–ray diffractometer (CuK $\alpha$  radiation, observation range was  $2\theta = (20 - 100)^\circ$ , step scan of  $0.015^\circ$  and counting time per step at 3 s). The original software package [6], including full complex of standard Rietveld procedures, has been used for analysis and interpretation of the XRD patterns obtained, namely, determination of both peak positions and integral intensities of the Bragg reflections by means of full profile analysis; carrying out qualitative and quantitative phase analysis using PDF data for phase identification and the least square method for lattice parameters refinement; testing of the structure models proposed and refining crystal structure parameters (including coordinates of atoms, atomic position filling, texture, etc.); calculation of the parameters of the real structure of the individual phases (coherent block sizes and lattice strain values).

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

The results of qualitative and quantitative XRD phase analyzes of diffraction patterns obtained for cBN–NbC–Al and cBN–TaC–Al composites, sintered at a set of temperatures, have confirmed our previous data [3–5]. Namely, it was shown that barothermal processing of the initial charge leads to formation of a small amount (less than 2 wt.%) of NbB<sub>2</sub> or TaB<sub>2</sub> as well as possibly a very small amount of AlN nitride (Table 1).

However, despite the minor change in the phase composition for both systems with sintering temperature, the lattice parameters of NbC and TaC carbides change remarkably (Fig. 1, 2).

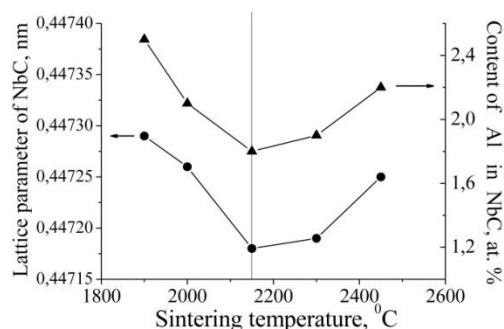
The above mentioned variation in the lattice parameters of NbC and TaC carbides with sintering temperature (Fig. 1, 2) probably indicates a modification of their crystal structures. According to available data, under normal conditions the non-stoichiometric NbC<sub>0.95</sub> and TaC<sub>0.95</sub> carbides are characterized by following lattice parameters: 0,4469 nm and 0,4456 nm, respectively, while in our case after barothermal action on the initial mixture, the lattice parameters of carbides increase significantly (Table 1). The observed increase in the lattice parameters of NbC and TaC can only be due to the embedding of additional atoms into the interstices of carbides' crystal structures.

Thus, the trial models of the crystal structures of NbC and TaC carbides existing in HPHT sintered cBN–NbC–Al and cBN–TaC–Al composites were created on the basis of the following assumptions:

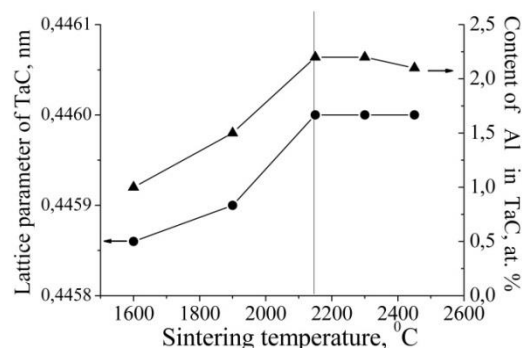
**Table 1** – Results of X-ray diffraction phase analysis for cBN–NbC–Al and cBN–TaC–Al composites sintered at HPHT method

Sintering temperature, °C	Phase composition	Lattice parameter, <i>a</i> , nm
cBN–NbC–Al composite		
Initial blend after MA	cBN+NbC <sup>1)</sup>	0.44605(8)
1900	cBN+NbC+NbB <sub>2</sub> +AlN <sup>2)</sup>	0.44729(5)
2000	cBN+NbC+NbB <sub>2</sub> +AlN ?	0.44726(2)
2150	cBN+NbC+NbB <sub>2</sub> +AlN	0.44718(3)
2300	cBN+NbC+NbB <sub>2</sub> +AlN ?	0.44719(3)
2450	cBN+NbC+NbB <sub>2</sub> +AlN ?	0.44725(1)
cBN–TaC–Al composite		
Initial blend after MA	cBN+TaC	0.44550(3)
1600	cBN+TaC	0.44586(3)
1900	cBN+TaC	0.44592(4)
2150	cBN+TaC+TaB <sub>2</sub> <sup>3)</sup>	0.44601(2)
2300	cBN+TaC+TaB <sub>2</sub>	0.44600(3)
2450	cBN+TaC+TaB <sub>2</sub>	0.44600(2)

- 1) Aluminum is amorphized under MA action
- 2) Phase content (wt.%): 50:47:2: <1
- 3) Phase content (wt.%): 26:72:2



**Fig. 1** – Temperature dependences of lattice parameter of NbC in HPHT sintered cBN–NbC–Al blend (marked as circles) as well as of aluminum content in NbC (marked as triangles).



**Fig. 2** – Temperature dependences of lattice parameter of TaC in HPHT sintered cBN–TaC–Al blend (marked as circles) as well as of aluminum content in TaC carbide (marked as triangles).

1. Formation of NbB<sub>2</sub> and TaB<sub>2</sub> borides (Table 1) should be accompanied by the formation of vacancies in the metal sublattice of NbC and TaC carbides.

2. Vacancies in the metal sublattice of NbC and TaC carbides can be occupied by atoms of aluminum, which was amorphized under MA.

3. The nitrogen, generated as a result of partial decomposition of cBN, migrates through HPHT sintered composites and locates in the interstices of the NbC or TaC carbide lattice as well as in the vacancies of the carbon sublattice.

As a result of the structural calculations of some trial models proposed the model with the best agreement between the experimental and calculated values of the intensities of diffraction reflections observed (RB factors did not exceed 0.01) has been developed. Namely, Fm3m space group, (q1Me+(1-q1Al) in 4(a) 0,0,0; q2(C+N) in 4(b) 0.5, 0.5, 0.5; q3(N+C) in 24(e) 0.320, 0, 0. Finally, for the structures of NbC and TaC carbides, existing in each sample of the cBN-NbC-Al and cBN-TaC-Al composites studied, the values of atomic position fillings (q1, q2, q3 parameters), as well as the values of isotropic temperature factor B have been refined using 7 reflections available on diffraction patterns.

Also it should be noted that the following assumptions were made at crystal structure modeling and at its calculations:

1. It was assumed that aluminum completely fills the vacancies formed in the metal sublattice of carbides at HPHT;

2. Additional nitrogen atoms were placed according with the model proposed by us in Ref. [7] for TiN nitride (modified NaCl type structure model);

3. Total content of nitrogen and carbon atoms, located in additional 24(e) position, was determined from the close values of their scattering functions.

The composition of NbC and TaC carbides existing in each sample of cBN-NbC-Al and cBN-TaC-Al composites was determined using refined values of q1, q2, q3 parameters.

Content of aluminum, dissolved in NbC and TaC carbides at different temperatures, was calculated using q1 value. Correlation between temperature dependences of aluminum content in NbC and TaC carbides and their lattice parameter values is clearly seen (Figs. 1 and 2).

Content of carbon and nitrogen in carbides was determined using refined q2 and q3 parameters. It was found that nitrogen atoms in TaC are located exclusively in the vacancies of its carbon sublattice (4(b)). However, nitrogen atoms in NbC are located in 24(e) position, where a significant part of the carbon atoms migrates from 4(b) position also. The total content of carbon and nitrogen atoms is shown in Fig. 3 for each carbide.

Thus, it is shown that the barothermal effect for NbC and TaC carbides is different, namely, the smaller lattice of TaC ( $a = 0,44550 \text{ nm}$ ) accumulates a small amount of nitrogen atoms, which have occupied the vacancies of the carbon sublattice. While in the larger lattice of NbC ( $a = 0,44605 \text{ nm}$ ), nitrogen atoms placed in the interstices, where a significant amount of carbon atoms moves also. The total fraction of nitrogen and carbon atoms located in the interstices of NbC lattice is significant and increases with increasing of HPHT sintering temperature (Fig. 4).

The effect of nitrogen atoms penetrating into the crystal structures of carbides during sintering leads to

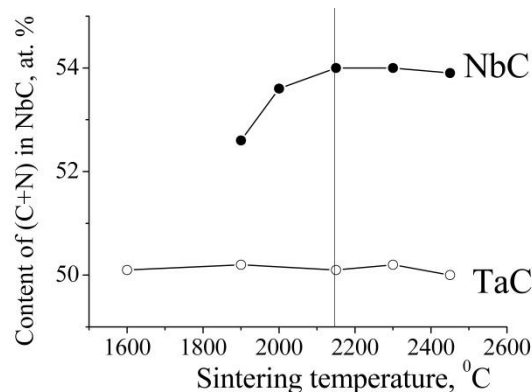


Fig. 3 – Temperature dependences of total content of carbon and nitrogen in NbC and TaC carbides.

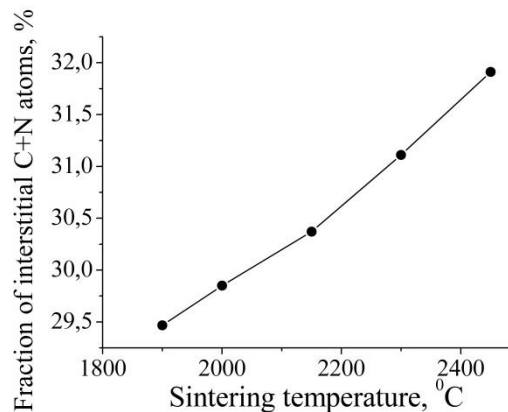


Fig. 4 – Temperature dependences of total fraction of nitrogen and carbon atoms located in the interstices of NbC lattice.

an increase in their lattice parameters. Moreover, for TaC this increase is about 0.11%, while for NbC it is more than 0.28%.

Taking into account that the best performance characteristics were obtained for composites sintered at 2150 °C, here we present the refined compositions of the carbides for this particular temperature:  $\text{Nb}_{0,96}\text{Al}_{0,04}(\text{C},\text{N})_{1,17}$  and  $\text{Ta}_{0,95}\text{Al}_{0,05}(\text{C},\text{N})_1$ .

#### 4. CONCLUSIONS

Based on the results of an XRD study of the crystal structure of carbides existing in BL composites of the cBN-NbC-Al and cBN-TaC-Al systems HPHT sintered at 7.7 GPa, the following was shown:

1. The crystal structure of the NbC and TaC carbides at barothermal action can be described within the modified NaCl-type structure which we proposed earlier.

2. Interaction of aluminum with NbC and TaC carbides results in the formation of the substitutional solid solutions containing up to 2.5 at. % Al.

3. The nitrogen atoms generated during a partial decomposition of cBN boron nitride are placed in the additional position of the modified NaCl-type structure as well as in the vacancies of the carbon sublattice.

4. The lattice parameters of NbC and TaC carbides studied are dependent on the amount of aluminum and nitrogen dissolved in their crystal structures

during HPHT sintering in the temperature range of 1600-2450 °C.

5. NbC carbide accumulates a much bigger amount of nitrogen than TaC carbide and for cBN-NbC-Al and cBN-TaC-Al composites with the best performance characteristics (HPHT sintering at 7.7 GPa and 2150 °C) their compositions can be described as  $Nb_{0,96}Al_{0,04}(C,N)_{1,17}$  and  $Ta_{0,95}Al_{0,05}(C,N)_1$ .

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## Вплив НРНТ спікання на кристалічну структуру карбідів NbC і TaC у cBN композитах систем cBN-NbC-Al і cBN-TaC-Al

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Керамо-матричні композити на основі кубічного нітриду бору зі зв'язками, що містять тугоплавкі сполуки перехідних металів та алюмінію, широко використовуються для високошвидкісної (300 – 500 м/хв) та чистої металообробки загартованих легованих сталей та жароміцних сплавів. Хороші перспективи практичного застосування для цього мають cBN композиційні матеріали BL групи отримані в системах cBN-NbC-Al та cBN-TaC-Al (склад шихти в об. % 60:35:5). Метою даної роботи було вивчення впливу умов НРНТ спікання (7,7 ГПа, 1600 – 2450 °C) на кристалічну структуру карбідів NbC та TaC, які сумісно із алюмінієм формують зв'язку шихти. В результаті докладного рентгеноструктурного дослідження було показано, що притаманна цим карбідам вихідна кристалічна структура типу NaCl в умовах баротермічного впливу модифікується, набуваючи додаткову позицію для розміщення малих за розміром атомів (азоту або/та вуглецю). При НРНТ спіканні взаємодія карбідів NbC та TaC з алюмінієм шихти, а також із азотом, що утворюється при частковому розпаді cBN, веде до утворення твердих розчинів. При цьому, розчинення алюмінію відбувається за типом заміщення ним ніобію або танталу (до 2,5 ат. % Al). Акумуляція азоту в структурі TaC відбувається із дозаповненням ним вакансій в підгратці вуглецю (розчиняється до 1 ат. % N), а в структурі NbC за типом занурення з розміщенням в додатковій позиції модифікованої структури типу NaCl (розчинюється до 5 ат. % N), до якої також частково переміщується вуглець зі свого основного положення. Таке накопичення дефектів веде до суттєвого збільшення параметру ґратки карбіду NbC (відносне збільшення 0,28 % для NbC супротив 0,11 % для TaC). Показано, що для композитів систем cBN-NbC-Al та cBN-TaC-Al з найкращими експлуатаційними характеристиками (НРНТ спікання при 7,7 ГПа та 2150 °C) склади карбідів можна описати як  $Nb_{0,96}Al_{0,04}(C,N)_{1,17}$  and  $Ta_{0,95}Al_{0,05}(C,N)_1$ .

**Ключові слова:** Високі тиски, Надтверді матеріали cBN, Монокарбіди, Рентгенівська дифрактометрія, Кристалічна структура.