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MECHANICAL PROPERTIES OF DIAMOND–TiB₂ COMPOSITES

The presented paper characterizes the basic mechanical and physical properties of sintered diamond-titanium diboride (submicro) and diamond-titanium diboride (nano) composites. The effect of reduction of powder size from the submicron scale to the nano scale of the ceramic bonding phase (TiB₂) in diamond composites on selected mechanical properties (Young's modulus, Vickers hardness, fracture toughness, coefficient of friction) has been reported. Composites were prepared from initial powders of diamond (MDA36, Element Six) with addition of 10 mass % submicron TiB₂ (H.C. Starck F) and 10 mass % nanopowder TiB₂ (American Elements). Compacts were sintered at pressure 8±0,5 GPa and 2233±50 K using the high pressure-high temperature Bridgman type apparatus. These investigations allow the possibility of using this materials to be enhanced as ceramic tool materials, in particular as burnishing tools.

Key words: diamond composite, TiB₂ bonding phase, HP-HT sintering, fracture toughness, Vickers hardness.

Introduction

Diamond composites have a wide range of compositions and applications. They have been often referred to as PCD (polycrystalline diamond), PDC (polycrystalline diamond compact/cutter) and TSP (thermally stable polycrystalline diamond composite, sometimes represented as TSDC) [1]. Polycrystalline superhard cutting materials are obtained by sintering together graded diamond or cubic boron nitride powders with a metallic binder or catalyst, at temperatures and pressures similar to those used in their original synthesis. The resultant compact is circular, with diameter and thickness depending on the chamber size and load, and can be cut into a large variety of shapes for cutting tools, and special wear-resistant parts [2]. The type of the bonding phase has a significant influence on the microstructure and mechanical properties of diamond compacts. The most popular PCD are those with cobalt, due to good wetting of diamond crystallites by this metal.

PCD with cobalt is a subject thermally stable only up to 1173 K because cobalt is a metal catalyst for the graphite – diamond and diamond – graphite conversion process [3, 4]. Due to high toxicity of cobalt, the exposure to metal powders or to metal dust during the cutting processes is particularly hazardous. Also in the sintered diamond with a metal binding phase, which forms internal lattice carbides, usually non-stoichiometric compounds are formed. As a result of the non-stoichiometric chemical composition there is a significant damage of structure which affects the deterioration of mechanical properties of the material, especially reducing its hardness. Studies of the sintering of diamond powders with the non-metallic binding phase were carried out earlier by L. Jaworska [5].

Attractive properties of TiB_2 made it the subject of research for manufacturing tool components for several years. Titanium diboride with high melting point (3498 K), low density (4.5 g/cm^3), high hardness (25 GPa), good thermal conductivity ($96 \text{ W/m}\cdot\text{K}$), high electrical conductivity ($22 \cdot 10^6 \text{ }\Omega\cdot\text{cm}$) and considerable chemical stability is one of the candidates for high temperature structural and wear applications. This unique combination of properties of TiB_2 -based materials makes them suitable for a wide range of technological applications, such as armour materials, wear components, conductive coatings, cathode materials for the Hall-Herroult cell, aluminium evaporation boats and electro discharge machining (EDM) electrodes [6–9]. Boride materials of MeB_2 type have a high value of critical stress intensity factor K_{IC} , approximately from 5 to $7 \text{ MPa}\cdot\text{m}^{1/2}$ [5]. Titanium diboride, due to its high hardness and poor sinterability was sintered with metallic additions. The presence of metals increases toughness and sinterability of the TiB_2 ceramics, but the metal addition affects binder corrosion at elevated temperatures [10]. The existence of the covalent bonding is the reason of low ductility, high hardness and high melting point of TiB_2 . Due to its high electrical conductivity TiB_2 can be easily machined using the technique of electrical discharge machining. This advantage is used during shaping the cutting edge of tools made of the diamond- TiB_2 composite. The use of hard phase binder such as TiB_2 in the sintering process for diamond powders is a kind of innovation because for commercial diamond materials ductile binding phases are used for example Co or Ni. These materials provide pseudoisostatic pressure distribution during the HP-HT process of diamond. During the HP-HT sintering in the pressure range corresponding to the thermodynamic stability of diamond, the allotropic transformation process occurs from diamond to graphite on the surface bordering with pores. A removal of voids is crucial, as otherwise the diamond particle is only locally bound with the binder or finer diamond, keeping the diamond in a compressive force state, i.e. preserving diamond stability. The application of nanometer binding phase particles that can fill the voids between grains of diamond may be very important in the sintering process.

The aim of this study is to obtain the diamond- TiB_2 ceramic composite with submicrometer and nanometer powders of TiB_2 , using the High Pressure-High Temperature (HP-HT) process. Mechanical and physical properties of composites with nano TiB_2 will be compared to the composites with submicrometer powders.

Experimental procedure

The following commercially available powders were used to prepare the mixtures:

- synthetic diamond powders (Element Six): MDA 36; 3–6 μm grain size;

- titanium diboride submicrometer powder (H.C. Starck F): 2.5–3.5 μm grain size;
- titanium diboride nanopowder (American Elements): about 100 nm grain size.

The above powders of TiB_2 in the amount of 10 mass % with diamond powder were mixed in acetone using Turbula mixer and then the powders were dried. After drying the mixtures, were preliminarily consolidated into pellets of 15 mm diameter and 5 mm height under the pressure of about 200 MPa. The green compacts were placed into the internal graphite heater in a special ceramic gasket assembly for sintering. The samples were sintered using the HP-HT method at the pressure of 8 ± 0.5 GPa and temperature of 2233 ± 50 K using the Bridgman type toroidal apparatus (fig. 1). The sintering process lasted 25 seconds. After sintering, the materials were subjected to a study of physical and mechanical properties.



Fig. 1. View of the HP–HT Bridgman type apparatus

Metallographic specimens were prepared using the Struers apparatus with polishing agents. Apparent density ρ and porosity were measured using the hydrostatic method. Young's modulus E measurements of the sintered samples were also taken, using the ultrasonic method measurements of the transition speed of transverse and longitudinal waves, by the Panametrics Epoch III flaw detector. Elasticity modulus (Young's modulus) values are the characteristic parameters for many technical materials. In the case of ceramics the elasticity modulus can be considered as the main parameter, which determines their properties as well as suitability for the given applications. The calculations are carried out according to formula

$$E = \rho V_T^2 \frac{3V_L^2 - 4V_T^2}{V_L^2 - V_T^2}, \quad (1)$$

where V_L – velocity of the longitudinal wave; V_T – velocity of the transversal wave.

Hardness was determined by the Vickers method at a load of 9.8 N using a digital hardness tester (future Tech. Corp. FM-7).

Fracture toughness K_{IC} was measured by the conventional method based on the single-edge notched bending (SENB) specimens. Relationship of $K_{IC} = f(c)$ is given by equations

$$K_{IC} = 1.5 \frac{P_c S}{W^2 B} Y c^{1/2} \quad (2)$$

$$Y = \frac{\sqrt{\Pi}}{(1-\beta)^{3/2}} \left[0,3738\beta + (1-\beta) \sum_{i,j=0}^4 A_{ij} \beta^i \left(\frac{W}{S}\right)^j \right] \quad (3)$$

where P_c – critical load; S – support span; W – width; B – specimen thickness; Y – geometric function; c – crack length; β – c/W , A_{ij} coefficients [11].

Coefficients of friction for the diamond–TiB_{2sub} and diamond–TiB_{2nano} composites in sliding contact Si₃N₄ ceramic were measured in ball-on-disc tests, using CETR UMT-MT universal mechanical tester. In the ball-on-disc method, sliding contact is conducted by pushing a ball specimen onto a rotating disc specimen under a constant load. For measurements of values of friction coefficient the non-ferrous pair of friction materials was used which corresponds to the assumption that diamond tool material cannot be used for machining of alloys containing iron (and other materials from the iron group), due to the solubility of carbon in iron.

Friction coefficient was calculated from equation

$$\mu = \frac{F_t}{F_n} \quad (4)$$

where F_t – measured friction force; F_n – applied normal force.

For the materials after grinding and ionic precision etching the surface (equipment model 682 PECS Gatan) of the sintering compacts was analyzed using the JEOL JSM-6460LV scanning electron microscope.

Experimental results and their discussion

The results of measurements of ρ , E , Poisson's number ν , Vickers hardness HVI , K_{IC} and μ of the diamond–TiB₂ and diamond–TiB_{2nano} samples obtained by HP-HT sintering are given in Table.

Selected results of the mechanical and physical properties of the diamond–TiB₂ and diamond–TiB_{2nano} composites obtained by HP-HT sintering

Sample	Density, g/cm ³	Young's modulus, GPa	Poisson's number	Vickers hardness, GPa	Fracture toughness, MPa·m ^{1/2}	Coefficient of friction
10 mass % submicrometer titanium diboride						
DTiB _{2sub}	3,35	569	0,10	49,7	6,72	0,26 ± 0,04
10 mass % nanometer titanium diboride						
DTiB _{2nano}	3,32	561	0,08	46,3	10,4	0,11 ± 0,04

In the case of diamond composites with submicrometer TiB₂ as a binding phase, apparent density obtained after sintering is about 3.40 g/cm³, while the highest value of apparent density for the sample with nanometer TiB₂ as a binding phase is 3.40 g/cm³. The highest value of Young's modulus is equal to 569 GPa for the diamond–TiB₂ samples and 561 GPa for the diamond–TiB_{2nano} samples. The average value of Vickers hardness for diamond composites with submicrometer TiB₂ is equal to 49.7 GPa. A lower (about 7 %) value of the Vickers hardness for the diamond–TiB_{2nano} samples was obtained. In the case of fracture toughness, the higher value was obtained for the diamond–TiB_{2nano} samples (10.4 MPa·m^{1/2}) in comparison to the diamond–TiB₂ (6.72 MPa·m^{1/2}).

The curves (fig. 2) presented the results of measurements of friction coefficients for the diamond–TiB₂ and diamond–TiB_{2nano} samples for the Si₃N₄ ceramic ball contact. The values of friction coefficient μ of the tested composites at the contact with the Si₃N₄ ceramic ball exhibit lower values ($\mu = 0.11–0.15$) for the diamond–TiB_{2nano} samples in comparison to the diamond–TiB₂ samples.

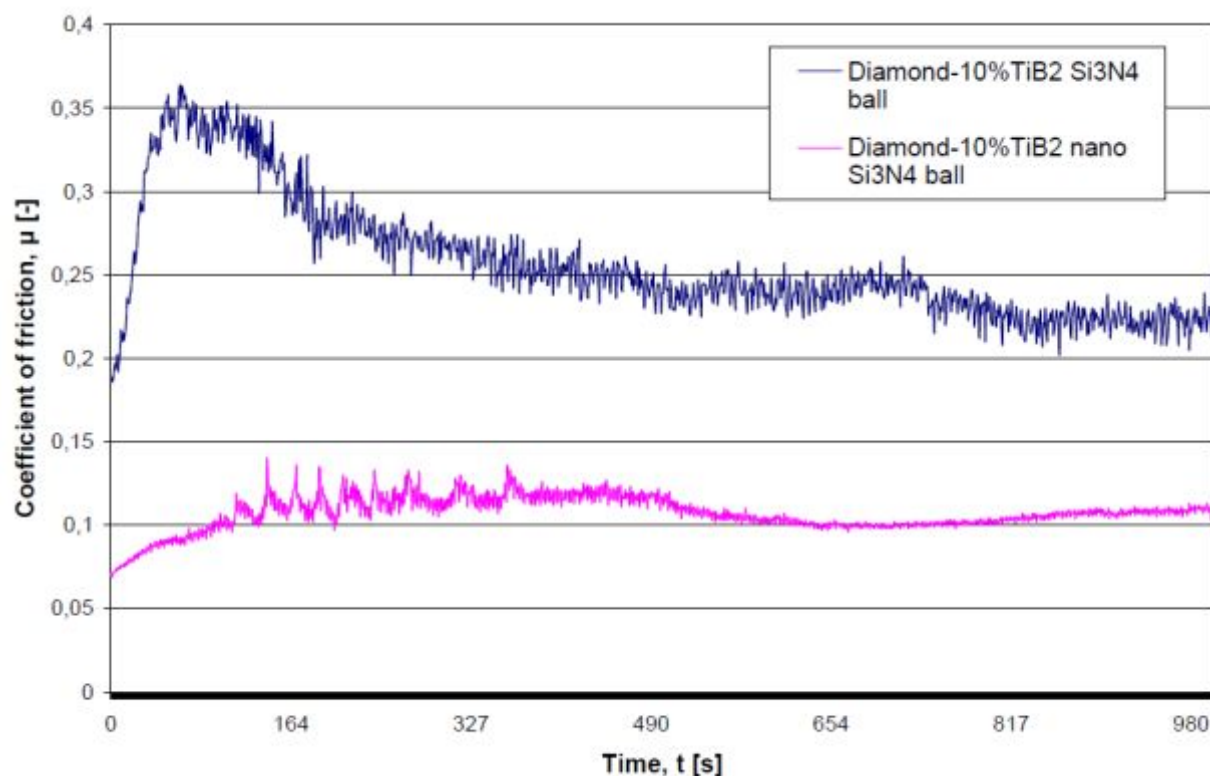


Fig. 2. Coefficient of friction of selected diamond-TiB₂ and diamond-TiB₂nano composites

Fig. 3 shows the representative microstructures of the diamond-TiB₂ and diamond-TiB₂nano composites sintered by the HP-HT process. In both microstructures the diamond-TiB₂ (fig. 3, a) and the diamond-TiB₂ (fig. 3, b) agglomerates are visible. A part from the presence of agglomerates the materials are homogeneous.

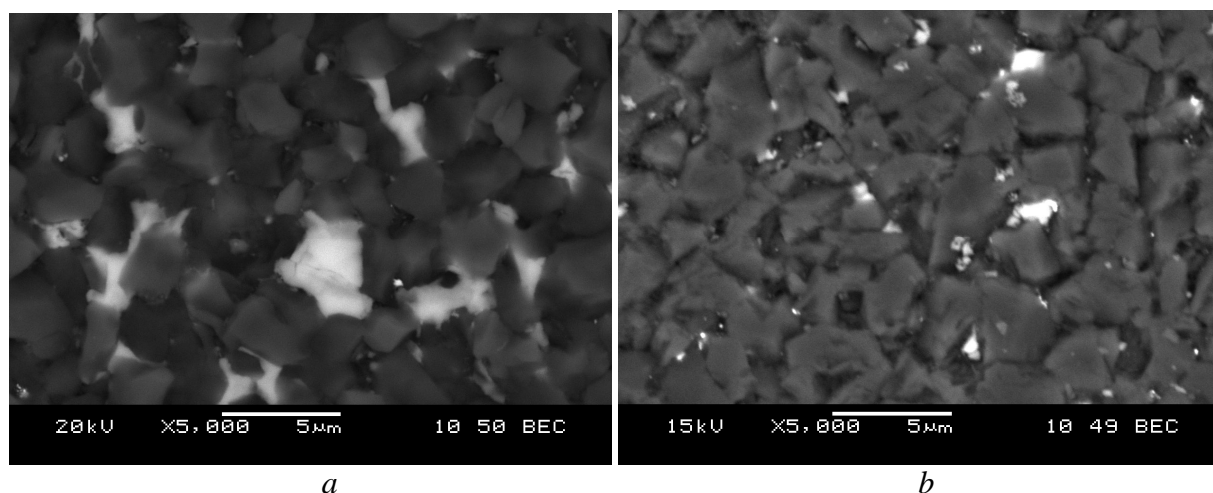


Fig. 3. SEM micrographs of diamond-TiB₂ (a) and diamond-TiB₂nano (b) samples (the titanium diboride crystallites are characterized by white colour)

Conclusions

The paper presented the method of sintering diamond with the submicrometer TiB₂ and nanometer TiB₂ powder as a bonding phase by the High Pressure-High Temperature method. The effect of powder size from the submicron scale to the nano scale of TiB₂ on selected mechanical properties was studied. The studies of mechanical and physical properties included relative density, Young's modulus, Poisson's number, Vickers hardness and fracture toughness. Also, friction

coefficients were measured and microscopic observations were carried out. Mechanical and physical properties were similar for the diamond–TiB₂ and the diamond–TiB_{2nano} composites whereas the value of Vickers hardness was slightly higher for the diamond–TiB₂ composites than for the diamond–TiB_{2nano}. For the value of fracture toughness, a higher value was obtained for the diamond–TiB_{2nano} composites. The diamond–TiB_{2nano} composite reveals higher values of friction coefficient at the contact with the Si₃N₄ ball than the diamond–TiB_{2nano} composite. Both submicrometer and nanometer TiB₂ powders have a tendency to form agglomerates which can be visible in SEM micrographs of microstructures.

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Наведені основні механічні та фізичні властивості спечених композитів на основі алмазу з додаванням субмікро- та нано-дидбориду титану. Вивчено вплив розміру частинок порошку від субмікронного до нано-рівня в керамічній (TiB₂) складовій алмазних композитів на їх механічні властивості (модуль Юнга, твердість за Віккерсом, в'язкість руйнування, коефіцієнт тертя). Композити були отримані з вихідних порошків алмазу (MDA36, Element Six) з додаванням 10 мас. % субмікронного TiB₂ (HC Starck F) або 10 мас. % нанопорошку TiB₂ (American Elements). Зразки спечені при тиску 8±0,5 ГПа і температурі 2233±50 К в апараті високого тиску типу торойд. Результати досліджень вказують на можливість використання одержаних композитів як інструментальних матеріалів підвищеної якості, зокрема в інструментах для вигладжування.

Ключові слова: композит алмаз–TiB₂, зв'язуюча фаза, спікання при високих тисках і температурах, в'язкість руйнування, твердість за Віккерсом.

Приведены основные механические и физические свойства спеченных композитов на основе алмаза с добавками субмикро- и нано-дидборида титана. Изучено влияние размера частиц порошка от субмикро- до нано-уровня в керамической (TiB₂) составляющей алмазных композитов на их механические свойства (модуль Юнга, твердость по Виккерсу, вязкость разрушения, коэффициент трения). Композиты были получены из исходных порошков алмаза (MDA36, Element Six) с добавлением 10 масс. % субмикро- TiB₂ (HC Starck F) или 10 масс. % нанопорошка TiB₂ (American Elements). Образцы были спечены при давлении 8±0,5 ГПа и температуре 2233±50 К в аппарате высокого давления типа торойд. Результаты исследований указывают на возможность использования полученных композитов в качестве улучшенных инструментальных материалов, в частности в выглаживающих инструментах.

Ключевые слова: композит алмаз–TiB₂, связующая фаза, спекание при высоких давлениях и температурах, вязкость разрушения, твердость по Виккерсу.

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К ВОПРОСУ МЕХАНИЗМА ОБРАЗОВАНИЯ ДЕТОНАЦИОННОГО НАНОАЛМАЗА

Предложен новый механизм образования частиц наноалмаза при детонационном синтезе. Схема процесса следующая: распад молекул тринитротолуола (ТНТ) на радикалы $\text{CH}_3\cdot$, радикалоподобный димер $\text{C}_2\cdot$ и молекул гексогена на $\text{C}_2\cdot$; одновременное образование циклогексана из $\text{C}_2\cdot$ молекулы адамантана в ионизированной форме; взаимодействие алмазоподобного ядра (иона адамантана) с метильной и другими моноуглеродными радикалами; рост частицы ДНА аналогично CVD-процессу. Ионизированная молекула адамантана зарождается в диапазоне от середины зоны химпика до плоскости Чепмена–Жуге, алмазная частица увеличивается в начальной стадии изоэнтропийного (тейлоровского) расширения газообразных продуктов детонации, захватывающих твердые частицы углерода.

Ключевые слова: *механизм образования, ударная волна, зона химпика, тринитротолуол, детонационный наноалмаз, радикалы, циклогексан, адамантан.*

Теория процесса, приводящего к образованию частиц детонационного наноалмаза (ДНА), до сих пор носит дискуссионный характер. Тем не менее, результаты анализа собственных данных и данных других авторов в основном по результатам подрыва сплава тротила с гексогеном (~50/50), позволяет постепенно подходить к пониманию механизма образования ДНА.

Детонационная волна представляет собой единый комплекс ударной волны, на фронте которой начинается разложение взрывчатого вещества (ВВ), зоны химической реакции (химпика), следующей за ударной волной и заканчивающейся в плоскости Чепмена–Жуге,