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Diamond composites with nanoceramic boride bonding phases

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ABSTRACT

Purpose: Basic mechanical properties of the studied tool composites and microstructure of diamond- titanium diboride composite, and diamond-titanium diboride-titanium nitride composite with participation of nanopowders have been presented.

Design/methodology/approach: Composites were prepared on the basis diamond powders of 3-6 μm (MDA36, Element Six) and the TiB_2/TiN nanopowders of below 45 nm (Neomat Co. Lithuania firm) and nanopowder of TiB_2 with size of crystallite below of 100 nm (American Elements firm). Different amount of a bonding phase changing in range from 10 to 30 wt% was used. Compacts in the shape of disc with dimension Ø15x5 mm were sintered at pressure 8.0±0.2 GPa and temperature of 2235 K using the Bridgman type apparatus. Microstructure studies using scanning microscope, X-ray and electron diffraction phase analysis were used.

Findings: The influence of the bonding phase amount on the tested properties was observed. Vicker's hardness HV1 was changed in the range from 20.0 to 50.0 GPa, Young's modulus (E) from 360 to 600 GPa and density (ρ) from 3.30 to 3.63 g/cm^3. The highest values of Vickers hardness and Young's modulus were obtained for diamond composites sintered with 10 wt% TiB_2 of bonding phase.

Practical implications: : In this work the effect of reduction powder size from submicron scale to nano scale of two ceramic bonding phases: titanium diboride and titanium diboride-nitride in diamond composites on selected mechanical properties has been reported. The results show that using of the TiB_2 powders in nano scale size increase the Vicker's hardness about 30 wt% in comparison to using of the TiB_2/TiN phase.

Originality/value: These investigations allow enhance possibility of using this materials as burnishing tools and rational use of existing ceramic tools.

Keywords: Diamond-titanium diboride composite; Diamond-titanium diboride-titanium nitride composite; Nanopowder; Vicker's hardness;Young's modulus; SEM image; Wear resistance

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MATERIALS

1. Introduction

Trends in the metal cutting industry are driven by the manufacturers' need to continually improve performance, reduce costs and, increasingly, comply with environmental legislation. These trends are also influenced by workpiece material development and for this reason the use of polycrystalline diamond PCD and polycrystalline cubic boron nitride PCBN in machining technology practice have been preferred. Wear resistance and toughness are the most important properties of cutting tool material (Fig. 1) [1].

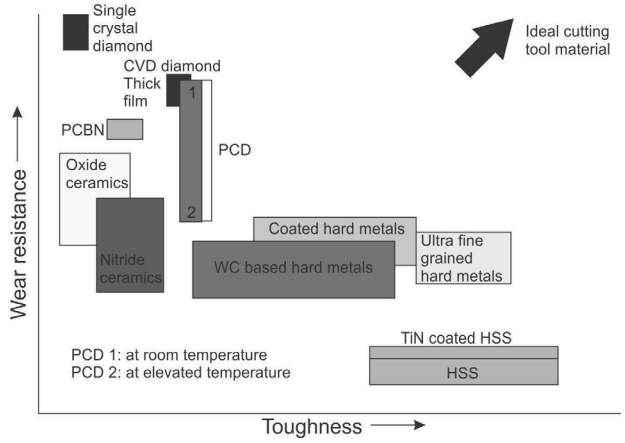


Fig. 1. Properties of cutting tool materials [1]

High speed and dry machining technology are two examples where the adoption of these practices can substantially increase the cost viability of using PCD and PCBN tools [2,3,4]. Polycrystalline diamond PCD tools featuring excellent wear resistance and long tool life are made by sintering diamond powders. They are being used in the automotive and electronics industries as the tools that realize high speed, high efficiency and high precision machining of non-ferrous metals and nonmetals [5,6]. The microstructure and mechanical properties of synthesized at high pressure and high temperature polycrystalline diamond (PCD) are strongly influenced by a type of applied bonding phase. The first methods of diamond compacts manufacturing, namely solid state and liquid phase sintering have been developed in the early 1960s and 1970s. Hall has reported solid state sintering of diamond powder without additives under high pressure [7,8]. The most popular PCD are those with cobalt due to good wetting of diamond crystallites by this metal. Katzman and Libby have used sintering of diamond crystallites with cobalt liquid phase [9]. The above property allows producing compacts characterized by low amount (below 10 wt%) of bonding phase resulting in their high hardness. However, high brittleness of this bonding material results in poor toughness of such PCD is undermining their practical applications. Additionally, the cobalt containing PCD are chemically stable only up to 900°C, while working temperatures might rise even higher. Therefore, a new material characterized by at least as good wetting of diamond but producing synthesis reaction products both less brittle and chemically stable at even higher temperatures - then those containing cobalt would be of interest [10]. A titanium silicon carbide Ti_3SiC_2 was reported to have interesting properties in between ceramics and metals, explained by its laminar structure with two octahedron (Ti_6C) layers separated by single silicon layer. Mechanical properties and wear tests of diamond- Ti_3SiC_2 showed very good wear resistance of these compacts with 20 wt% of Ti_3SiC_2 as the bonding phase [11]. Recently a greater attention is paid on boride ceramic phase used as a addition to the different matrix materials [12,13,14]. To make the most of unique properties of diamond and to diminish an influence its disadvantageous properties new diamond tool composites with ceramic bonding phase (TiB_2) has been proposed [15]. TiB_2 is a new ceramic material with the dual purposes of structural ceramics and functional ceramics as well as the following superior physical and chemical properties: high melting point (T=3253 K), high hardness (34 GPa), good electrical conductivity (p=14.4 μΩ·cm), excellent chemical stability, outstanding thermal conductivity (25 $Wm^{-1}K^{-1}$), low coefficient of thermal expansion (8.1×10^{-6} K^{-1}), erosion resistance against molten metal and exceptional mechanical property at high temperature [16]. The existence of the covalent bonding is the reason for low ductility, high hardness and high melting point of TiB_2. Due to their high electrical conductivity they can be easily machined using the technique of electrical discharge machining (EDM). This advantage is used during shaping tools from the diamond-TiB_2 composite. Matthews [17] in 1992 year patented results of his work concerning with obtaining composites based on diamond with different ceramic (including TiB_2). There are a great many industrially useful materials that can be fabricated from a combination of a dielectric or semiconductor phase and a conductive phase. Examples of semiconductor refractory materials are: aluminum oxide, zirconium oxide, silicon carbide, silicon nitride, diamond and boron carbide. Examples of refractory materials serving as conductors are: titanium nitride, titanium carbide, titanium diboride, tungstem carbide. Due to the refractory nature of starting materials, composites are usually produced by preparing powder compacts that are subjected to a given sequence of pressures and temperatures to achieve densification. The main interest of the author were produced dense body from mixtures of materials with significant different electrical resistivity under pressure and with an intense electric current pulse of sufficiently short duration such that the heating is largely confined to the material of superior electrical conductivity. Diamond-titanium diboride composite are typical of the process. Preparation of composites between diamond and refractory ceramics is difficult because of the tendency of diamond to graphitize at high temperatures and low pressure, thus moderate pressure and extremely fast heating was used. The composite diamond-60wt% and TiB_2-40wt% with size of grains in the range 40-60 μm were obtain under pressure of 73 MPa. This composite wasn't being used as the tool materials. The main goal of the presented work is reported the effect of reduction powder size from submicron scale to nano scale of phase components in titanium diboride and titanium diboride-nitride on selected mechanical properties. These investigations allow enhance possibility of using this materials as burnishing tools. The advantages of such tools is possibility of obtaining of the surface with very low roughness and possibility of ecological working without application of cooling lubricants.

2. Experimental procedure

Starting materials used in this study were commercially available synthetic diamond powders (Element Six MDA 36, 3-6 μm grade), titanium diboride nanopowder (American Elements firm) with size of crystallites about 100 nm and TiB_2/TiN nanopowder of below 45 nm grade (Neomat Co. Lithuania firm). The nanopowders of TiB_2/TiN and TiB_2 ranging 10, 20 and 30 wt% were mixed with diamond powder and pressed at 90 MPa into cylindrical shapes of 15 mm diameter. The green discs were placed into the internal graphite heater in a special gasket assembly for sintering. The experiment was carried out using high pressure and high temperature (HP-HT) of the Bridgman type toroidal apparatus at temperature 2230 ±50 K, pressure 8±0.5 GPa (Figs. 2, 3). Duration of the sintering process was 25 s. The sintering temperature were established experimentally for each composite to obtain crack-free samples with highest values of density and mechanical properties.

Fig. 2. Assembly for HP-HT sintering (Bridgman type apparatus)

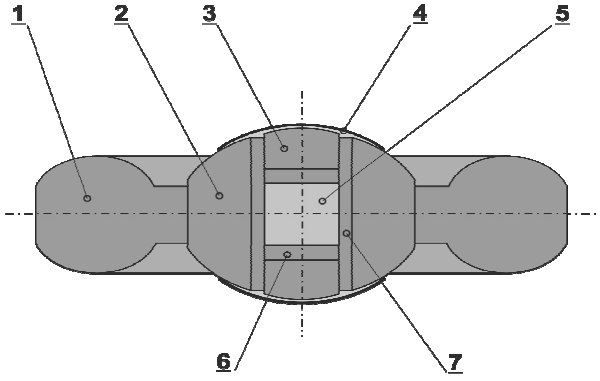


Fig. 3. Scheme of Bridgman type apparatus for HP-HT sintering: 1 - pyrophyllite external gasket; 2 - internal gasket; 3 - ceramic plate; 4 - molybdenium plate; 5 - sintered sample; 6, 7 - graphite heater

The weight percentage contents of TiB_{2nano} in the tested diamond-ceramic (DTiB_2n and DTiB_2/TiNn) compounds is presented in Table 1.

Table 1.
Contents of TiB_{2nano} in the tested compounds

Compound	Compound's composition, wt%		
DTiB_2n	10.0	-	-
DTiB_2 /TiNn	10.0	20.0	30.0

After grinding and ionic precision etching (equipment model 682 PECS Gatan firm) the surface of the sintering compacts was analyzed by X-ray diffraction method (XRD). Selected physical and mechanical properties like: Vickers hardness with 9.8 N load, Young's modulus, Poisson's ratio by means of ultrasonic method, density and porosity were determined. Modulus of elasticity (Young's modulus) of the tested composites was determined by a measuring the velocity of longitudinal and transversal ultrasonic waves transmitted through the sample. Probe sets work together with a Panametrics Epoch III ultrasonic flaw detector connected to a controlling computer. Calculations were made using the formula (1):

$$E = \rho C_T^2 \frac{3C_L^2 - 4C_T^2}{C_L^2 - C_T^2} \quad (1)$$

where: E-Young's modulus, C_L-velocity of the longitudinal wave, C_T-velocity of the transversal wave, ρ- density of the material.

The velocities of transversal and longitudinal waves were determined as a ratio of sample thickness and relevant transition time. The accuracy of calculated Young's modulus from equation (1) was estimated to be below 2%. Density and porosity P_c were determined by the hydrostatic method. The coefficients of friction for diamond-TiB_2n and diamond-TiB_2/TiNn composites in sliding contact with an 100Cr6 bearing steel and Si_3N_4 ceramic were determined in ball-on-disc tests, using a CETR UMT-2MT universal mechanical tester (USA). In the ball-on-disc method, sliding contact is realized by pushing a ball specimen onto a rotating disc specimen under a constant load (Fig. 4). Tests were carried out without lubricant. The loading mechanism applied a controlled load F_n to the ball holder and the friction force F_t was measured continuously during the test using an extensometer.

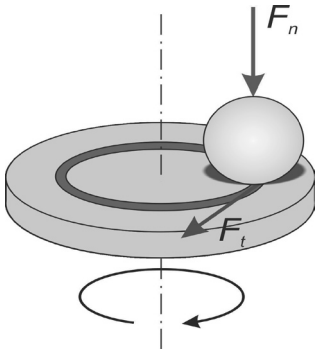


Fig. 4. Material pair for the ball-on-disc method: F_t - measured friction force, F_n - applied normal force

For each test, a new ball was used or the ball was rotated such that a new surface was in contact with the disc. After mounting of the ball and sample, materials were washed in ethyl alcohol and

dried. The size of the disc-shaped samples was ~13.5 × 3.8 mm; the surface of the discs flat and parallel to within 0.02 mm; and the roughness of the test surface not more than 0.1 μm Ra. The samples were ground using diamond wheels and polished using diamond slurries. The following test conditions were established:

- ball diameter: 3.175 mm,
- applied load: 4 N,
- sliding speed: 0.1 m/s,
- diameter of the sliding circle: 2-4 mm,
- sliding distance: 100 m,
- calculated duration of the test: 1000 s.

Friction coefficient was calculated from the equation 2:

$$\mu = \frac{F_t}{F_n} \tag{2}$$

where: F_t - measured friction force, F_n - applied normal force.

Microstructure observations of the specimen were carried out using a JEOL JSM-6460LV scanning electron microscope. X-ray diffraction was used both to identify phases.

3. Results and discussion

The results of the mechanical and the physical properties such as: Young's modulus *E*, Vickers hardness *HV1*, apparent density ρ_p, and Poisson's number ν of tested diamond-TiB_2/TiNn composites with different percentage participation of bonding phase (DTiB_2/TiNn10-10 wt%, DTiB_2/TiNn20-20 wt% and DTiB_2/TiNn30-30 wt%) are presented in Table 2.

Table 2.
Selected mechanical and physical properties of tested diamond-TiB_2TiNn composites with different percentage of binding phase (DTiB_2/TiNn10-10 wt%, DTiB_2/TiNn20-20 wt% and DTiB_2/TiNn30-30 wt%)

Material	Vicker's hardness HV1, GPa	Young's modulus E, GPa	Poisson's number ν, -	Apparent density ρ_p, g/cm^3
DTiB_2/TiNn10	35.0	564	0.11	3.42
DTiB_2/TiNn20	31.0	376	0.06	3.53
DTiB_2/TiNn30	20.0	363	0.09	3.68

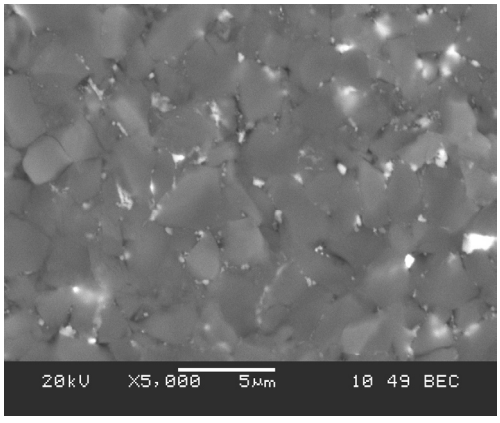
Mechanical properties of the tested diamond-TiB_2/TiNn composites depend on percentage participation of the bonding phase TiB_2/TiNn. The Vicker's hardness HV1 changes in the range 35.0-20.0 GPa, (maximum value exhibits for the diamond-TiB_2/TiNn10 composite with 10wt% of the binding phase). The Young's modulus has similar character of changing and the values of this property are in the range 564-363 GPa (maximum value exhibits for the diamond-TiB_2/TiNn10 composite with 10wt% of the binding phase). Selected mechanical and physical properties of the tested diamond-TiB_2n10 and the diamond-TiB_2/TiNn10 composites such as: Young's modulus *E*, Vicker's hardness *HV1*, apparent density ρ_p, and Poisson's number ν are presented in Table 3.

Table 3.
Selected mechanical and physical properties of tested diamond-TiB_2n10 and diamond-TiB_2/TiNn10 composites

Material	Vicker's hardness HV1, GPa	Young's modulus E, GPa	Apparent density ρ_p, g/cm^3	Poisson's number ν, -
DTiB_2n10	49.7	569	3.35	0.10
DTiB_2/TiNn10	35.0	564	3.42	0.11

The Vicker's hardness (HV1) for tested diamond-ceramic composites with the different composition of binding phase at the same percentage participation of the ceramic phase (10 wt%) depends on composition of the phase. Higher value of the Vicker's hardness (HV1) for the DTiB_2n10 composite is observed. The mixture phase TiB_2/TiN used as the binding phase causes reduction of Vicker's hardness from 49.7 GPa to 35.0 GPa (≈ 30%). The microstructure of the diamond-TiB_2/TiNn10 and the diamond-TiB_2n10 composites surfaces is presented in Figs. 5, 6. In the case of mixture ceramic phase DTiB_2/TiNn, agglomerates of nanocrystallites, with tendency to increasing, depending on the fraction of ceramic phase is observed (Fig. 5b).

a)



b)

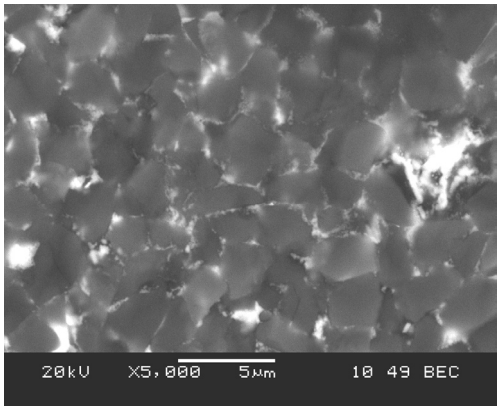
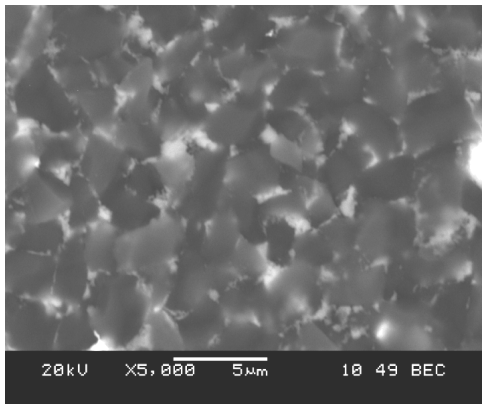


Fig. 5. SEM micrographs of a surface of the diamond-TiB_2/TiNn composites at 5000x magnification: a) DTiB_2/TiNn10, b) DTiB_2/TiNn20 (titanium diboride and titanium nitride-grains in white colour)

The uniformly distributed of the TiB_2n phase (white grains) with agglomerates in diamond matrix is observed as well (Fig. 6b).

a)



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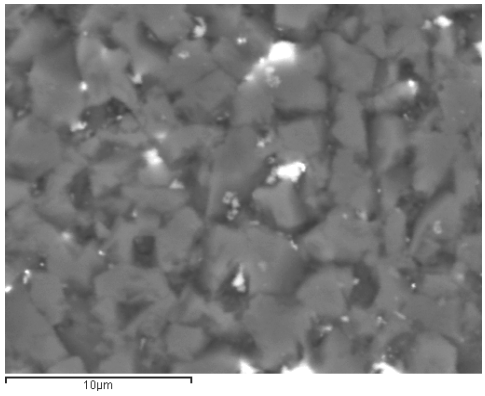
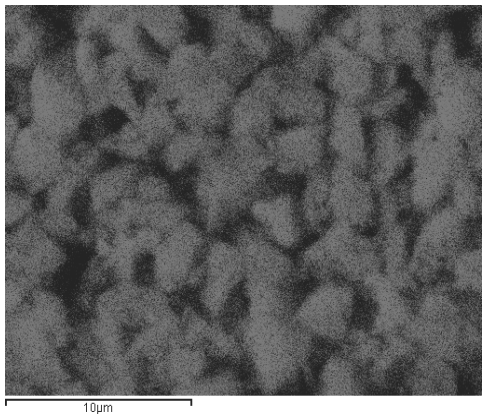


Fig. 6. SEM micrographs of a surface of the tested diamond composites at 5000x magnification: a) $DTiB_2$/TiNn30; b) $DTiB_2n10$ (titanium diboride-grains in white colour)

Mapping of Ti and C dispersion in the $DTiB_2n10$ composite is presented in Fig. 7.

The X-ray diffraction analysis for the characterization of the tested diamond ceramic composites were made as a completion study. The Rietvelda method with X'Pert Plus programme was used for quantitative phase analysis of tested diamond-ceramic composites. The Philips program APD-3.5B-Fit profile allows observation of the weight percentage content of revealed phases. X-ray diffraction analysis of tested ceramic composites is presented in Fig. 8 a,b.

a)



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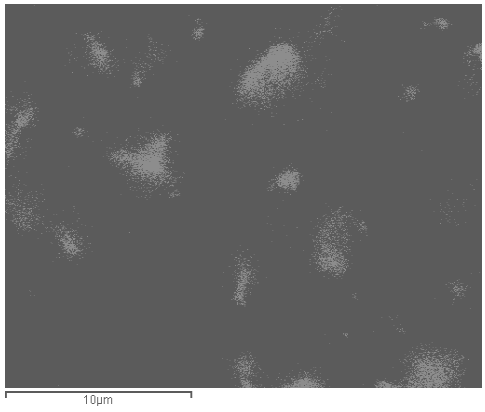

Fig. 7. EDS analysis of the $DTiB_2n10$ composite-mapping of dispersion: a) C; b) Ti

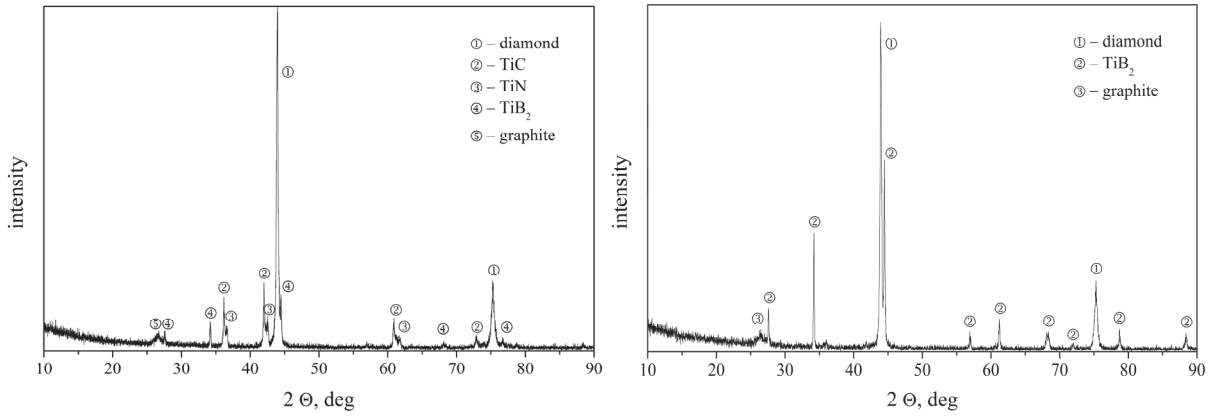

Fig. 8. X-ray diffraction analysis of the tested ceramic composites: a) $DTiB_2$/TiNn10 specimen, b) $DTiB_2n10$ specimen

X-ray diffraction presented in Fig. 8a indicates for $DTiB_2$/TiNn10 specimen: 88.6 wt% diamond, 1.7 wt% TiB_2, 1.6 wt% TiN, 2.8 wt% TiC, 0.3 wt% Ti(C,N) and for $DTiB_2$n10 specimen (Fig. 8b) indicates: 88.0 wt% diamond and 7.6 wt% TiB_2. The exemplary curves representing measurements of the friction coefficient for the $DTiB_2$n10 and the $DTiB_2$/TiNn10 samples at the Si_3N_4 ceramic ball and the 100Cr6 steel ball contact are presented in Fig. 9.

The values of the friction coefficient strongly depend on ball material. The differences of the friction coefficient values in the range of the tested composites with various phase composition at the contact with the same ball materials are small. The values of the friction coefficient μ of the tested composites at the contact with the Si_3N_4 ceramic ball exhibit lower values (μ=0.15-0.11) in comparison with the values of the same composites at the contact with the 100Cr6 steel ball (μ=0.61-0.56). The $DTiB_2$/TiNn10 composite reveals four-times higher values of friction coefficient at the contact with the 100Cr6 steel ball than at the contact with the Si_3N_4. The same character of the friction coefficient change is observed for the $DTiB_2$n10 composite. The $DTiB_2$n10 composite indicates five-times higher values of friction coefficient at the contact with the 100Cr6 steel ball than at the contact with the Si_3N_4 ball.

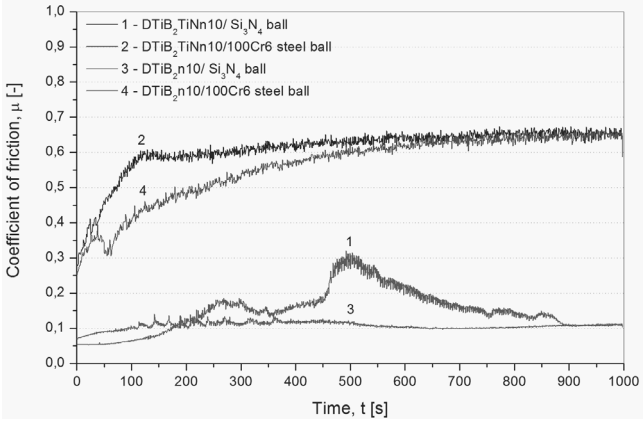

Fig. 9. Coefficient of friction of selected the $DTiB_2$/TiNn10 and the $DTiB_2$n10 specimens

4. Conclusions

In this work the effect of reduction powder size from submicron scale to nano scale of phase components in titanium diboride and titanium diboride-nitride on selected mechanical properties has been reported. Two diamond-ceramic composites with the TiB_2n and the TiB_2/TiNn binding phases were used. Analysis of the results of the mechanical and the physical properties such as: Young's modulus *E*, Vickers hardness *HV1*, apparent density ρ_p, and Poisson's number ν of tested diamond-TiB_2/TiNn composites with different percentage fraction of bonding phase: 10 wt%, 20 wt% and 30 wt% allow on the optimal percentage fraction of ceramic binding phase. The Vicker's hardness (HV1) for tested diamond-ceramic composites with the different composition of binding phase at the same percentage fraction of the ceramic phase (10 wt%) depends on composition of the phase. The mixture phase TiB_2/TiN used as the binding phase causes reduction of Vicker's hardness from 49.7 GPa to 35.0 GPa (≈ 30%). The further tests base on diamond-ceramic composites with 10 wt% fraction of binding phase. The X-ray diffraction carried for the $DTiB_2$/TiNn10 specimen indicates of 2.8 wt% TiC and 0.3 wt% Ti(C,N). The values of the friction coefficient strongly depend on ball material. The $DTiB_2$/TiNn10 composite reveals four-times higher values of friction coefficient at the contact with the 100Cr6 steel ball than at the contact with the Si_3N_4 ball. These investigations allow enhance possibility of using this materials as burnishing tools and rational use of existing ceramic tools.

Acknowledgements

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