MECHANICAL PROPERTIES OF Si_3N_4/SiC COMPOSITES WITH VARIOUS ADDITIONS

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Abstract
Different 30Si_3N_4/70vol.%SiC composites, without and with additions of titanium (Ti), titanium diboride (TiB_2) and cubic boron nitride (cBN), were obtained by High Pressure - High Temperature (HPHT) sintering. Density, Young's modulus, hardness, fracture toughness and coefficient of friction were measured. Microstructural (SEM) investigations were also conducted for selected samples. Materials obtained from 30Si_3N_4/70vol.%SiC submicro powders with the addition of 30 vol.% cBN micro powder were characterized by the best combination of Young's modulus, hardness, fracture toughness and coefficient of friction. The microstructures of investigated samples were compact and dense, with the ingredients uniformly distributed in the volume of composite. Such properties predispose 30Si_3N_4/70vol.%SiC+ 30vol.%cBN composites to various advanced engineering applications.

Keywords: ceramic matrix composites (CMC), sintering, acoustic methods, hardness, toughness, tribology

1 Introduction

Silicon nitride has a favorable combination of properties that includes high strength over a broad temperature range, high hardness, moderate thermal conductivity, a low coefficient of thermal expansion, moderately high elastic modulus, and relatively high fracture toughness for a ceramic. Silicon nitride ceramics have reached large-scale production for cutting tools, bearings, turbocharger rotors and a variety of custom wear parts [1, 2, 3].
Silicon carbide has many of the same applications as silicon nitride. Most silicon carbide materials have very high hardness (harder than alumina and silicon nitride) and thus have superior wear resistance [4, 5, 6]. A major disadvantage of SiC ceramic materials is their low fracture toughness, which usually does not exceed about 3.5 $MPa \cdot m^{1/2}$ [7, 8].
In previous studies, attempts have been made to obtain an Si_3N_4/SiC composite characterized by both high hardness and high fracture toughness [9, 10]. The purpose of the presented work is to study the effect of the addition of third-phase particles selected from metals (Ti) or ceramics (TiB_2, cBN) to an Si_3N_4-70vol%SiC system on the mechanical properties of Si_3N_4/SiC composites obtained by the HPHT method. The main goal was to improve the fracture toughness of the investigated materials.

When a particulate second phase is introduced into a brittle matrix, there are several toughening mechanisms that may be operative [11, 12, 13].

E.g. metallic particles are capable of plastic deformation and thus absorption of energy and bridging of a growing crack, resulting in increased strengthening. (**Fig. 1a**) [14]. The addition of titanium particles into an Si_3N_4 – SiC system may cause chemical reaction, and favorable, plastic, ceramic phase type titanium silicon nitride may appear. On the other hand, hard ceramic particles can introduce a favorable stress state, which can cause a toughening effect by crack deflection and crack bifurcation (**Fig. 1b**). Hard particles also improve the hardness and other mechanical properties of the composite as a whole.

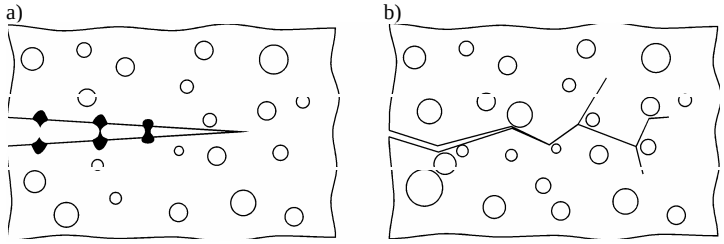


Fig.1 Strengthening mechanisms in ceramic matrix composites with dispersed metallic (a) and ceramic particles (b)

2 Experimental

2.1 Materials preparation

Powders used for the preparation of mixtures are listed in **Table 1**.

Table 1 Powders used for preparation of mixtures.

Powder	Granulation [μm]	Manufacturer	Description
Si_3N_4(1)	0.6	H.C. Starck, Germany	M11-grade, alpha>90%
Si_3N_4(2)	1 – 5	AEE, US	alpha>85%
Si_3N_4(08)	0.1 – 0.8	Goodfellow, UK	alpha
SiC(2)	0.1 – 1	Goodfellow, UK	alpha
SiC(3)	-	AGH, Poland	specific surface 24 m^2/g
TiH_2(1)	<44	Fluka, Switzerland	
TiB_2(4)	2.5 – 3.5	H.C. Starck, Germany	F-grade
BN(M010)	0 – 0.01	Element6, South Africa	Micron+ABN (cubic)
BN(M36)	3 – 6	Element6, South Africa	Micron+ABN (cubic)

The following mixtures were prepared by mixing the appropriate powders in an isopropanol environment using a Fritsch Pulverisette 6 planetary mill.

A. 30Si_3N_4/70vol.%SiC composite:

A1) 30 vol.% Si_3N_4(1) + 70 vol.% SiC(2) (submicro: Starck + Goodfellow)

A2) 30 vol.% Si_3N_4(08) + 70 vol.% SiC(2) (submicro: Goodfellow)

A3) 30 vol.% Si_3N_4(2) + 70 vol.% SiC(3) (micro: AEE + AGH)

A4) 30 vol.% Si_3N_4(2) + 70 vol.% SiC(2) (micro: AEE + submicro: Goodfellow)

B. 30Si_3N_4/70vol.%SiC composite + Ti:

B1) 28 vol.% Si_3N_4 (1) + 64 vol.% SiC(2) + 8 vol.% Ti - from TiH_2(1) (submicro: Starck + Goodfellow + micro: Fluka)

C. 30Si_3N_4/70vol.%SiC composite + TiB_2:

C1) 28 vol.% Si_3N_4 (1) + 64 vol.% SiC(2) + 8 vol.% TiB_2(4)

(submicro: Starck + Goodfellow + micro: Starck)

C2) 21 vol.% Si_3N_4(1)+49 vol.% SiC(2)+30 vol.% TiB_2(4)
(submicro: Starck + Goodfellow + micro: Starck)

D. 30Si_3N_4/70vol.%SiC composite + cBN:

D1) 28 vol.% Si_3N_4(1) + 64 vol.% SiC(2) + 8 vol.% cBN(M36)
(submicro: Starck + Goodfellow + micro: E6)

D2) 28 vol.% Si_3N_4(08) + 64 vol.% SiC(2) + 8 vol.% cBN(M010)
(submicro: Goodfellow + nano: E6)

D3) 21 vol.% Si_3N_4(1) + 49 vol.% SiC(2) + 30 vol.% cBN(M36)
(submicro: Starck + Goodfellow + micro: E6)

After drying, the mixtures were preliminarily compressed into pellets of diameter 15 mm and height 5 mm under pressure of ~200 MPa. The green bodies with the addition of TiH_2 were additionally annealed in a vacuum at a temperature of 800°C for 1h in order to remove the hydrogen and obtain pure metallic titanium. The composites were obtained at high pressure (6 GPa) in the temperature range of 790 – 2030°C using a Bridgman-type toroidal apparatus (**Fig. 2**). The sintering temperatures were established experimentally for each composite to obtain crack-free samples with the highest values of density and mechanical properties. Duration of the sintering process was 60 s.

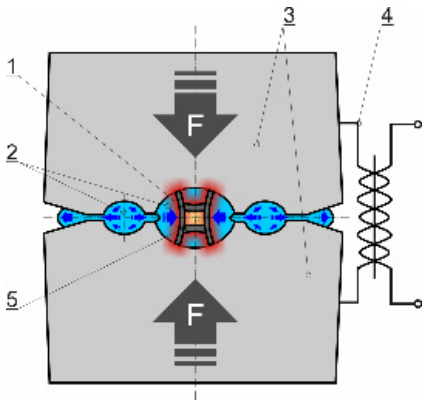


Fig.2 Sintering process in a Bridgman-type HPHT system. Quasi-hydrostatic compression of the preliminary consolidated powders (sample - 1) is achieved as a result of plastic deformation of the gasket material (2) between anvils (3); electrical heating is provided by a high-power transformer (4) and graphite resistive heater (5)

The sintered compacts were subsequently ground to remove remains of graphite after the technological process of sintering and to obtain the required quality and surface parallelism for physical and mechanical studies.

2.2 Methods of investigation

Densities of the sintered samples were measured by the hydrostatic method. The uncertainty of the measurements was below 0.02 g/cm^3, which gave a relative error value of below 0.5 % (excluding measurements of small pieces of broken samples, where error was up to 0.1 g/cm^3, due to their insufficient volume and mass).

Young's modulus of the samples obtained by HPHT sintering was measured based on the transmission velocity of ultrasonic waves through the sample, using a Panametrics Epoch III ultrasonic flaw detector. The velocities of transverse and longitudinal waves were determined as a ratio of sample thickness and relevant transition time. The accuracy of calculated Young's modulus was estimated to be below 2 %.

Hardness of selected samples was determined by the Vickers method using a digital Vickers Hardness Tester (FUTURE-TECH FV-700). Five hardness measurements, with indentation loads of 2.94, 9.81 and 98.1 N, were carried out for each sample. Standard deviations of HV values were relatively high but usually no more than 5 % of the average values.

Indentation fracture toughness was calculated from the length of cracks which developed in a Vickers indentation test (with indentation load - 98.1 N) using Niihara's equation (Eq. 1):

$$\frac{K_{IC}\varphi}{H\sqrt{a}}\left(\frac{H}{E\varphi}\right)^{\frac{2}{5}}=0.129\left(\frac{c}{a}\right)^{-\frac{3}{2}} \quad (1)$$

where: K_{IC} - critical stress intensity factor, ρ - constrain factor, H - Vickers hardness, E - Young's modulus, a - half of indent diagonal, c - length of crack.

Microstructural observations were carried out on the densified materials using a JEOL JXA-50A Scanning electron Microscope equipped with back scattering electron (BSE) imaging.

In ball-on-disc tests, the coefficients of friction for contact with an Si_3N_4 ball were determined using a CETR UMT-2MT (USA) universal mechanical tester. In the ball-on-disc method, sliding contact is produced by pushing a ball specimen onto a rotating disc specimen under a constant load. Tests were carried out without lubricant. The loading mechanism applied a controlled load F_n to the ball holder (**Fig. 3**) and the friction force was measured continuously during the test using an extensometer. 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.

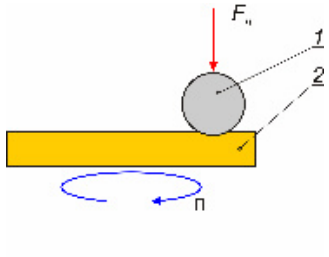


Fig.3 Material pair for the ball-on-disc method: 1 – Si_3N_4 ball; 2 – sample (disc)

The size of the disc-shaped samples was ~13.5 x 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 test samples were ground using diamond wheels and polished using diamond slurries.

The following test conditions were established: ball diameter 2 mm; applied load 4 N; sliding speed 0.1 m/s; diameter of the sliding circle 2 - 5 mm; sliding distance 100 m, calculated duration of the test 1000 s. Friction coefficient was calculated as a quotient F_f / F_n, where F_f is the measured friction force, and F_n is the applied normal force.

3 Results and discussion

Density and Young's modulus of various $30Si_3N_4$/70vol.% SiC composites sintered at different temperatures with and without additions of Ti, TiB_2 and cBN phases are presented in **Table 2**.

Table 2 Physical-mechanical properties of the best samples selected from different modifications of Si_3N_4/SiC composites

Sample composition	Sintering Temp. Range	*TempOptimal For(Properties) /description	Density		Youngs modulus		Poisson's ratio	Hardness		Fracture toughness
Vol%	°C	°C	g/ccm	% of theor.	GPa	% of theor.	-	HV_1	HV_{10}	$MPa \cdot m^{1/2}$
A. $30Si_3N_4$/70SiC composite										
A1) $30Si_3N_4$(1)+70SiC(2) (submicro:Starck+Goodfellow)	1450-2030	*1880 (ρ, E, HV)*	*3,18*	*99*	*377*	*92*	*0,19*	*2970*	*2400*	4,9
		1690 (K_{IC})	3,14	98	363	87	0,19	2630	2240	*5,6*
A2) $30Si_3N_4$(08)+70SiC(2) (submicro:Goodfellow)	1650-1810	1810 /cracks	3,13	97	368	89	0,20	2772	2268	5,7
A3) $30Si_3N4$(2)+70SiC(3) (micro:AEE+AGH)	1450-1880	1450 /small cracks	3,02	94	243	58	0,16	1880	1510	4,6
A4) $30Si_3N_4$(2)+70SiC(2) (micro:AEE+submicro:Goodfellow)	1650-1810	*1810 (ρ, E, HV)*	*3,10*	*97*	*368*	*90*	*0,20*	*2748*	*2392*	5,6
		1730 (K_{IC}) /small cracks	3,06	95	345	84	0,20	2576	2278	*6,0*
B. $30Si_3N_4$/70SiC composite + Ti										
B1) $28Si_3N_4$(1)+64SiC(2)+8Ti(1) (submicro:Starck+Goodfellow+micro:Fluka)	790-1810	*790 (ρ)*	*3,21*	*97*	119	31	0,13	-	-	-
		1170 (E)	3,13	94	*176*	*46*	0,10	-	-	-
C. $30Si_3N_4$/70SiC composite + TiB_2										
C1) $28Si_3N_4$(1)+64SiC(2)+8TiB_2(4) (submicro:Starck+Goodfellow+micro:Starck)	1650-1810	*1810 (ρ, E)*	*3,27*	*99*	*381*	*90*	0,20	2488	2364	4,2
		1690 (K_{IC})	3,23	97	356	84	0,18	2526	2324	*6,1*
C2) $21Si_3N_4$(1)+49SiC(2)+30TiB_2(4) (submicro:Starck+Goodfellow+micro:Starck)	1650-2150	*1810 (ρ, HV)*	*3,55*	*99*	374	83	0,17	*2564*	*2318*	5,8
		1730 (K_{IC})	3,50	97	374	83	0,17	2390	2260	*6,4*
D. $30Si_3N_4$/70SiC composite + cBN										
D1) $28Si_3N_4$(1)+64SiC(2)+8BN(M36) (submicro:Starck+Goodfellow+micro:E6)	1650-1950	1950 /cracks	3,17	98	387	86	0,19	2850	2408	6,4
D2) $28Si_3N_4$(08)+64SiC(2)+8BN(M010) (submicro:Goodfellow+nano:E6)	1730-1880	1880 /cracks	3,07	95	379	84	0,17	-	-	-
D3) $21Si_3N_4$(1)+49SiC(2)+30BN(M36) (submicro:Starck+Goodfellow+micro:E6)	1650-1950	*1810 (ρ, E) /cracks*	*3,88*	*118*	*473*	*84*	0,18	3038	2612	7,4
		1880 (HV, K_{IC})	3,80	116	457	82	0,18	*3190*	*2790*	*7,5*

*Optimum temperature for selected properties, e.g. *1690 (K_{IC})* - the best fracture toughness.

Among the composites sintered without additional phases, the highest degree of densification and best mechanical properties were demonstrated by composite A1, obtained from submicron powders 30 vol.% Si_3N_4(1) + 70 vol.% SiC(2) (submicro: Starck + Goodfellow) (Table 2). The A1 composites were obtained in the temperature range of 1450-2030 °C. The samples sintered at the temperature of 1880 °C reached the highest values of relative density (99%), Young's modulus (377 GPa) and hardness (2970 HV_1) with the K_{IC} coefficient of 4.9 $MPa \cdot m^{1/2}$. The samples sintered at the lower temperature - 1690 °C reached the highest value of K_{IC} (5.6

MPa·m$^{1/2}$) wit the decreasing of relative density, Young's modulus and hardness (Table 2). Composite A1 was selected for modification by the addition of third phase particles.

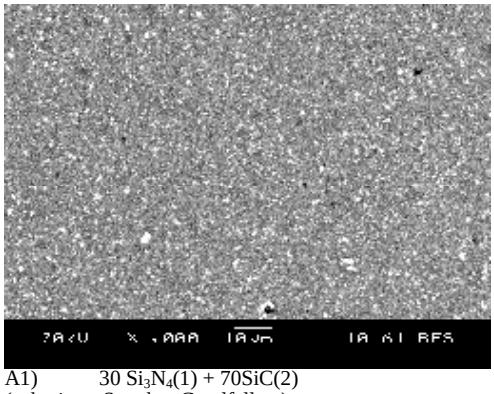
Modification of the 30Si_3N_4/70vol.%SiC composite by the addition of titanium was unsuccessful. Samples from series B1, with the addition of 8% Ti introduced in the form of TiH_2, sintered at low temperatures, were characterized by a very low Young's modulus, whilst all the samples sintered at temperatures above ~1200 °C were cracked.

Composites with the addition of titanium diboride were characterized by a high degree of densification, a high Young's modulus and improved K_{IC} as compared to the unmodified composite. No improvement in hardness was observed (Table 2). Composites modified by the TiB_2 particles were sintered in the temperature ranges of 1650-1810 °C for composition C1(8%TiB_2) and 1650-2150 °C for composition C2(30%TiB_2) respectively. For both group of composites containing TiB_2 phase a similar trends as in the case of unmodified composites are observed. There is the sintering temperature at which samples have the highest density, Young's modulus and hardness, and temperature about 100-200 °C lower from them at which materials are characterized by the highest K_{IC} coefficient. Material C2, with the addition of 30 vol.% TiB_2, shows the highest value of K_{IC} (6.4 MPa·m$^{1/2}$) and moderate hardness (2390 HV_1).

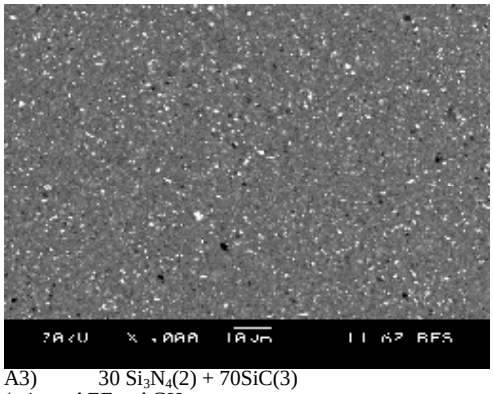
Composites for the D series were modified by the addition of cubic boron nitride in the form of micro- and nano-particels. Composites with the addition of micro-particles of cBN were sintered in the temperature range of 1650-1950 °C while the composites with the addition of nano-particles of cBN were sintered in the temperature range of 1730-1880 °C. Composites from series D3, modified by the addition of 30 vol.% cBN micropowder, showed the highest degree of densification, equal to 118% of theoretical density – an EDS analysis showed a high content of tungsten carbide and zirconium dioxide from the vessel and grinding media used for the preparation of the mixtures – the best mechanical properties and the lowest percentage of cracked samples (Table 2). Samples for this series, obtained at the temperature of 1880 °C are characterised by the Young's modulus of 457 GPa, Vickers hardness of 3190 HV_1 and the fracture toughness of 7.5 MPa·m$^{1/2}$.

SEM microstructures of 30Si_3N_4/70vol.%SiC with and without the addition of TiB_2 and cBN are presented in **Fig. 4**.

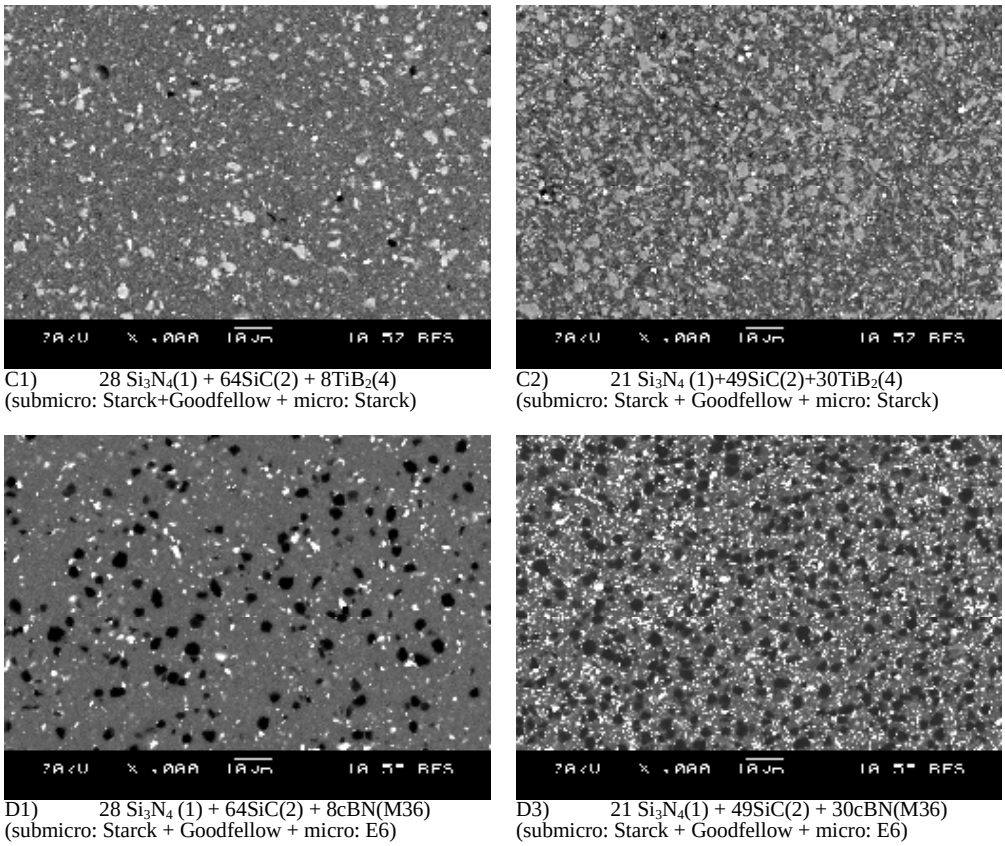
The microstructures of investigated samples are compact and dense, with the ingredients uniformly distributed in the volume of composite. This demonstrates successful blending, using a planetary mill; EDS analysis, however, showed a high content of tungsten carbide and zirconium dioxide from the vessel and grinding media used to prepare the mixtures (white areas visible in the microstructures (Fig. 4).



A1) 30 Si_3N_4(1) + 70SiC(2)
(submicro: Starck + Goodfellow)



A3) 30 Si_3N_4(2) + 70SiC(3)
(micro: AEE + AGH



C1) 28 Si_3N_4(1) + 64SiC(2) + 8TiB_2(4) (submicro: Starck+Goodfellow + micro: Starck)

C2) 21 Si_3N_4 (1)+49SiC(2)+30TiB_2(4) (submicro: Starck + Goodfellow + micro: Starck)

D1) 28 Si_3N_4 (1) + 64SiC(2) + 8cBN(M36) (submicro: Starck + Goodfellow + micro: E6)

D3) 21 Si_3N_4(1) + 49SiC(2) + 30cBN(M36) (submicro: Starck + Goodfellow + micro: E6)

Fig.4 SEM microstructures of selected 30Si_3N_4/70vol.%SiC composites with and without the addition of TiB_2 and cBN

A comparison of mean curves of friction coefficient for various kinds of 30Si_3N_4/70vol.%SiC composites, with and without the addition of cBN and TiB_2, is presented in **Fig. 5**.

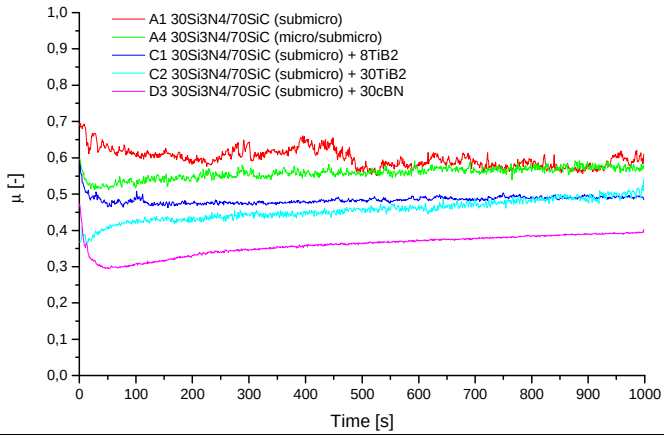


Fig.5 Coefficient of friction of selected 30Si_3N_4/70vol.%SiC composites with and without the addition of TiB_2 and cBN (mean curves).

High coefficients of friction generate thermal stress, which is detrimental to the wear behavior of materials. Hard ceramic bodies – possessing high fracture toughness and low coefficients of friction – used in mechanical systems that involve high loads, velocities and temperatures, will reduce costs and be less harmful to the environment. Obtaining coefficients of friction below 0.2 is unlikely since, under non-lubricated conditions, current dual-phase ceramics typically have coefficients of friction of 0.5–0.8 [15].
Unmodified composites had the highest coefficients of friction. Average values of friction coefficient for materials A1 and A4 were 0.60 and 0.56 respectively. Composites modified by the addition of a TiB_2 phase were characterized by intermediate values of friction coefficient. Average values of friction coefficient for materials C1 and C2 were 0.48 and 0.46 respectively. The composite with the addition of 30% cBN was characterized by the lowest average coefficient of friction, at only 0.36.

4 Conclusions

Various modifications of $30Si_3N_4/70SiC$ (volume ratio) composites, with additions of Ti, TiB_2 and cBN, obtained by HPHT sintering, were investigated.
Composites modified by the addition of Ti show deterioration of properties in comparison with the unmodified composites.
Composites modified by the addition of TiB_2 show only a partial improvement of properties in comparison with the unmodified composites.
Composites modified by the addition of 30% cBN micropowder are characterized by the best combination of Young's modulus, hardness, fracture toughness and coefficient of friction. Such properties predispose $30Si_3N_4/70$vol.%SiC + 30 vol.% cBN composites to various advanced engineering applications. Wear tests and cutting tests (intended in the future) will show the range of applications of this material in machining.

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