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CERAMICS ON THE BASIS OF NANODISPERSE SILICON NITRIDE PREPARED AT 1850 °C BY HOT PRESSING

UZ SILĪCIJA NITRĪDA NANOPULVERU BĀZES AR KARSTO PRESĒŠANU 1850 °C TEMPERATŪRĀ IEGŪTĀ KERAMIKA

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Introduction

According to [1] there are two approaches to improve the mechanical properties of ceramics: one is the control of microstructure and another is the fabrication of composite. The microstructure of material can be significantly changed, by using nanosized compounds and their composites for preparation of materials. The distinctive properties of nanophase materials are low temperature plasticity, high diffusion coefficient and high solubility. Owing to good corrosion resistance and mechanical characteristics silicon nitride based ceramics are promising candidate for structural materials [2]. However, its use has been limited by its relatively low fracture toughness and the fact that its mechanical properties degrade at temperatures above 1200 °C. As it was shown in research [3], if nanosized Si_3N_4 powders and composites (Si_3N_4-Me_2O_3, Si_3N_4-SiC) are used, high mechanical properties remain up to 1400 ^oC and higher temperatures.

It is well known that properties of silicon nitride ceramics could be increased by addition of a second nano-phase. Flexural strengths of up to 1,5 GPa were attained for material Si_3N_4-25 vol.% SiC, while the hardness increased to 19 GPa from 15 GPa for monolithic Si_3N_4 [4]. Advantages of Si_3N_4-TiN composite powders have been described in [1].
Ceramic materials on the basis of silicon nitride are widely used in different fields, including cutting tools and high temperature construction materials for application at temperatures up to 1400 – 1500 ^oC in motor works, aircraft and aerospace (details of internal-combustion engines and gas-turbines, ball and sliding-bearings for exploitation at the extreme conditions etc.) [5].
Therefore, the aim of this investigation was to compare sintering, microstructure and properties of nanosized Si_3N_4-Me_2O_3 composite powder and its mixture with the second phase by means of hot pressing at 1850 ^oC as a compacting method. Si_3N_4-$6Y_2O_3$-$3Al_2O_3$ was used as a basic powder and its mechanic mixtures with other nanopowders (Si_3N_4-SiC, ZrO_2, TiN) as well as composite powder Si_3N_4-TiN.

Experimental

Fine powders of Si_3N_4-$6Y_2O_3$-$3Al_2O_3$-, Si_3N_4-TiN- system as well as dopants (Si_3N_4-SiC, ZrO_2, TiN) were formed by the plasma chemical synthesis method [6]. Chemical content of products is given in the Table 1.
The average particle size of the nanosized composites is in the range of 30-60 nm (Fig. 1). The Si_3N_4-$6Y_2O_3$-$3Al_2O_3$ powders have irregular shape. The plasma produced Si_3N_4-TiN and Si_3N_4-SiC consists from TiN and SiC powders coated with layer of Si_3N_4.

Table 1.

Chemical and phase composition and size distribution of used nanosized powders

The used powders	Chemical composition									Phase composition	SSA, m^2/g	d_{50}, nm
	Si	Y	Al	Zr	Ti	Si_{free}	N	C	O			
Si_3N_4-$6Y_2O_3$-$3Al_2O_3$	53,2	4,8	1,5	-	-	0,6	35,3	-	4,6	crystallinity 20%; $\alpha/\beta \approx 1$	65	35
Si_3N_4-TiN	52,8	-	-	-	7,5	0,7	37,2	-	2,3	amorphous Si_3N_4, weak TiN	60	40
Si_3N_4-SiC	66,7	-	-	-	-	0,8	4,2	26,2	2,0	β-SiC; amorphous Si_3N_4	36	60
ZrO_2	-	-	-	73,8	-	-	0,5	-	25,7	70% teragon., 30% monoclin.	30	40
TiN	-	-	-	-	77,1	-	22,3	-	1,8	TiN cubic	40	30

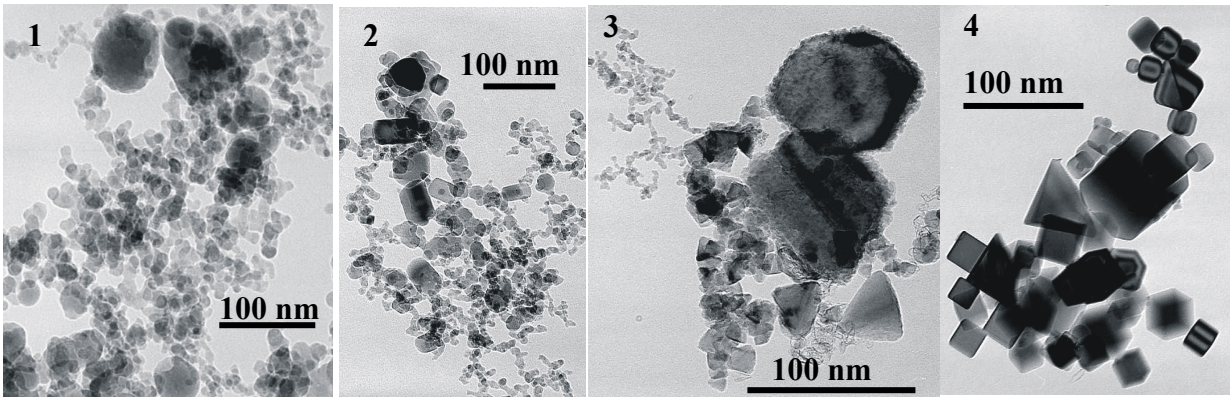

Fig. 1. *Characteristic shape of particles of used nanopowders:*
1 - Si_3N_4-6Y_2O_3-3Al_2O_3; 2 - Si_3N_4-TiN; 3 - Si_3N_4-80 wt. % SiC; 4 – TiN.

Characteristic feature of plasmachemical nanosized powders are low degree of crystallinity. The degree of crystallinity of Si_3N_4 in the Si_3N_4-6Y_2O_3-3Al_2O_3 and Si_3N_4-TiN systems reaches only 20% and ratio of α/β-Si_3N_4 is close to one. The presence of oxide phases has not observed. In the Si_3N_4-SiC system the silicon nitride is X- ray amorphous, but silicon carbide is presented by well crystalline β-SiC.

Starting Si_3N_4-6Y_2O_3-3Al_2O_3 composite powders were mixed with 10 wt. % of second nanophase (Si_3N_4-SiC, ZrO_2, TiN) and mixed for 15 hours in ball mills. Polyethylene vessels and silicon nitride grinding balls were used. Isopropyl alcohol was used as a dispersion medium. After mixing, the sample was treated for 1 h with ultrasound and mixed additionally for 2 h in ball mills. The starting powder (Si_3N_4 -6%Y_2O_3 -3%Al_2O_3), as well as the mixture of plasma prepared Si_3N_4-TiN nanocomposite with 3 wt. % of Al_2O_3 (“Alcoa”) and 6 wt. % of Y_2O_3 (“Nanophase”) were prepared in the similar way.

The obtained mass was dried at 80 °C and sieved through a 200 μm sieve. Prepared powders were compacted by hot pressing at 1850 °C for 2 hours in nitrogen. The loading pressure was 30 MPa and temperature rising rate was 10°/min. All powders were sintered under the same conditions.

Discs with the diameter of 65 mm and 6 mm of height were obtained, from which bars of size 5x5x45 mm were cut for bend strength investigations.

Chemical composition of powders (N, C, Si_{free}, Y, Al, Ti) was determined by chemical analysis. Particle morphology was observed with a transmission electron microscope (TEM), but ceramic structure – with a scanning electron microscope (SEM). Crystalline phases were analyzed by X-ray diffraction (XRD).

Sintered specimens were analyzed by the Archimedes density measurement, X-ray diffraction and SEM observation. Hardness (load: 1 kg) and fracture toughness (load: 10 kg) were measured by the Vickers indentation technique (by Evans and Tanaky). Bending strength was determined by the three-point method at the room and at the 1000 °C temperature.

Results and discussion

The properties of monolithic composites prepared via hot pressing at 1850 °C are summarized in Table 2. Nanopowder of Si_3N_4-6%Y_2O_3-3%Al_2O_3 is marked with "A", but with "B" - the nanopowder of Si_3N_4-TiN with addition of 6 wt. % Y_2O_3 and 3 wt. % Al_2O_3.

Table 2.

Properties of monolithic composites

Sample	ρ, g/cm^3	$P_{op.}$, %	Mechanical properties of sintered body			
			σ_{20}, MPa	σ_{1000}, MPa	HV_1, GPa	k_{1c}, MPa.m$^{1/2}$
A	3,27	0,1	1052	1020	16,8	5,65
A+10 wt.% ZrO_2	3,24	0	827	762	15,7	6,11
A+10 wt.% SiC	3,20	0	732	-	17,1	4,97
A+10 wt.% TiN	3,23	0	885	833	15,9	6,00
B	3,22	0,1	976	964	16,9	5,81

The microstructures of sintered bodies are shown in Fig. 2.
The phase composition of obtained ceramics is given in Fig. 3. The phase analysis of obtained materials shows the presence of β-Si_3N_4 in all samples as well as the other phase – respectively ZrO_2, β-SiC and TiN in appropriate samples.
The sintered bodies of the Si3N4-6Y2O3-3Al2O3 and Si3N4-6Y2O3-3Al2O3 +SiC have maximum density among prepared ceramics. Additives of TiN, ZrO_2 introduced in silicon nitride composites by mechanical mixing decreases the density of Si_3N_4 based ceramics. Low density (92%) have reached by hot pressing of plasma prepared Si_3N_4-TiN composite with oxide additives, possibly due to non-homogeneous mixing of components.

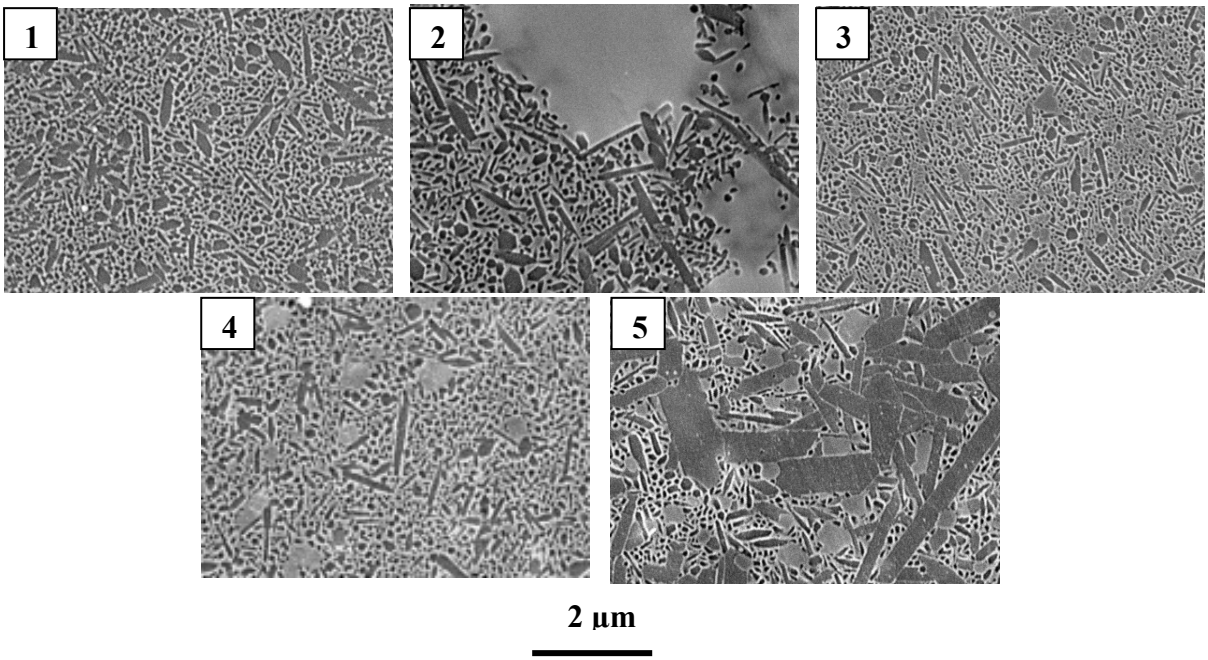

Fig. 2. *Microstructure of samples A (1), A+10 wt.% ZrO_2 (2), A+10 wt.% SiC (3), A+10 wt.% TiN (4) and B (5).*

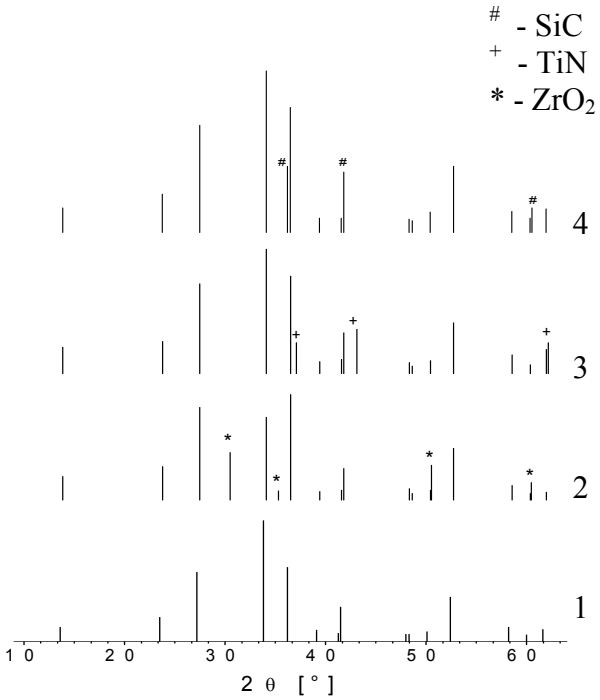

Fig. 3. *Phase composition of sintered materials: 1 – sample A (β-Si_3N_4); 2 – A+10%wt. ZrO_2; 3 – A+10%wt. TiN; 4 – A+10wt.% SiC.*

The studies of microstructure show that in comparison with the materials prepared at 1800 °C [7], in materials sintered at 1850°C the amount of rod-like crystals and their length increase significantly. The sintered body of synthesized Si_3N_4 composite-powder (sample A) exhibited a fine-grained microstructure with small elongated grains. Grains size are mainly of 0,2-0,5 μm and there are a lot of rod-like crystals with the diameter of 0,2-0,4 μm and length of 1,5-3 μm (l/d = 4-10).

The same finely grained structure with characteristic rod-like crystals is observed also in the case of ceramics with the ZrO_2 addition. In this material a separate, homogeneously distributed ball-shaped ZrO_2 containing inclusions with a size up to 5 μm can be observed.

The samples containing SiC additive have finer microstructure than sample A. It means that SiC inhibits grain growth of Si_3N_4, which agrees with data [8].

More elongated rod-like crystals with the diameter of 0,1-0,5 μm and the length up to 5 μm are observed in silicon nitride ceramics with the additive of TiN. The TiN containing silicon nitride ceramics exhibits a little increased amount at rod-like β-Si_3N_4 grains in comparison with Si_3N_4-$6Y_2O_3$-$3Al_2O_3$ ceramics. This observation is consistent with suggestion that fine TiN inclusions works as nuclei accelerating the growth of elongated β-Si_3N_4 grains [8].

Differing from the mechanical mixture of Si_3N_4 and TiN, in the material prepared from Si_3N_4-TiN nanocomposition synthesized in plasma (sample B) there are significantly more such a coarse Si_3N_4 grains and they are distributed in matrix from finely grained Si_3N_4.

The increasing of fracture toughness of silicon nitride ceramics with ZrO_2 additives can be explained by appearing of tensile stresses due to expansion of ZrO_2 determined by phase transition. The other reason can be the presence of separate coarse grains of ZrO_2 because it has been proved that the development of some coarse grains in ceramic microstructure can improve the fracture energy [9]. The enhanced fracture toughness of silicon nitride ceramic

with TiN additives can be a result of formation of rod-like β-Si_3N_4 particles and of appearing of residual stresses caused by different thermal expansion coefficients of Si_3N_4 ($2,8x10^{-6}$/°C) and TiN ($9,3x10^{-6}$/°C) [10].
The higher value of bending strength, especially at high temperature of sample B in comparison with the sample A+ 10 wt.% TiN prepared by mechanical mixing with similar chemical and phase composition can be explained by more homogeneous distribution of TiN particles in Si_3N_4 matrix in plasma prepared composite.
Figure 4 shows the polished surface of samples "A" and "B" with a crack propagated by the Vickers indentation. Cracks are a little bit zigzag-shaped. The zigzagged crack means the crack deflection by rod-like grains contained in this specimen. This is the reason for the increase in fracture toughness.

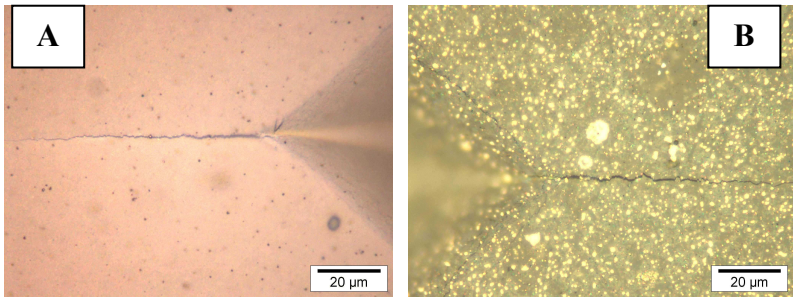

Fig. 4. *The polished surface of samples A and B with a crack propagated by the Vickers indentation.*

Conclusions

Evaporation of Si, Ti, Al_2O_3, Y_2O_3 raw powders in radio-frequency nitrogen plasma in the presence of ammonia ensure production of Si_3N_4-$6Y_2O_3$-$3Al_2O_3$ and Si_3N_4-TiN nanosized homogeneous composites with average particle size of 35-50 nm.
Bulk materials with fine-grained microstructure and relative density of 92-99 % have been prepared by hot pressing at 1850 °C.
Nanopowder (TiN, SiC, ZrO_2) additives gives the possibility to change the structure and mechanical properties of silicon nitride ceramics.
Mechanical properties of samples obtained after hot pressing at 1850 °C differs from those obtained at 1800 °C with increased mechanical properties and the most significant increase of properties has been observed for Si_3N_4-$6Y_2O_3$-$3Al_2O_3$ without addition of the second phase.
Due to the complex of properties of prepared materials they could be applied as construction materials for action at high temperatures or probably as wear resistant material, for example, in ball-bearings for acting at the specific conditions (high temperatures, vacuum, without lubricants).

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N. Zilinska, I. Zālīte, J. Grabis. Uz silīcija nitrīda nanopulveru bāzes ar karsto presēšanu 1850 °c temperatūrā iegūtā keramika.

Viens no ceļiem, kā mainīt keramikas materiālu īpašības, ir nanoizmēra izejas pulveru un to kompozīciju pielietošana materiālu ieguvē. Uz silīcija nitrīda bāzes veidotiem materiāliem ir virkne labu īpašību (mehāniskā izturība gan istabas temperatūrā, gan temperatūrās līdz 1400 °C, laba korozijas izturība u.c.), kas nodrošina to praktisku pielietojumu dažādās rūpniecības nozarēs. Pastāv iespēja izmainīt Si_3N_4 keramikas īpašības ievadot sastāvā otru nanofāzi.

Darba mērķis bija noskaidrot otrās fāzes (SiC, ZrO_2, TiN nanopulveri) ietekmi uz nanokompozīcijas Si_3N_4-6%Y_2O_3-3%Al_2O_3 saķepšanu, struktūru un īpašībām, veicot karsto presēšanu 1850 °C temperatūrā.

Pētījumi parādīja, ka vairumā gadījumu otrās fāzes piedeva pārveido keramiskā materiāla mikrostruktūru un īpašības.

N. Zilinska, I. Zalite, J. Grabis. Ceramics on the basis of nanodisperse silicon nitride prepared at 1850 °c by hot pressing.

One of the ways for modification of ceramic materials properties is application of nanosized compounds and their composites for preparation of materials. Materials based on silicon nitride possess several good properties (mechanical strength both in the room and in the temperatures until 1400 °C, good corrosion resistance and other), ensuring their practical application in different branches of industry. The possibility exists to change the properties of Si_3N_4 ceramics by addition of a second nanophase.

The aim of investigation was to find the effect of the second phase (SiC, ZrO_2, TiN nanopowders) on sintering, structure and properties of nanocomposite Si_3N_4-6%Y_2O_3-3%Al_2O_3 by hot pressing at 1850 °C.

It was shown by studies that addition of the second nanophase mostly changes microstructure and properties of material.

Н. Жилинска, И. Залите, Я. Грабис. Керамика на основе нанопорошков нитрида кремния, полученная горячим прессованием при 1850 °с.

Одним из способов влияния на свойства керамических материалов при их получении является применение исходных нанопорошков и их композиций. Создаваемые на основе нитрида кремния материалы обладают рядом превосходных свойств (механическая прочность при комнатной температуре и температурах до 1400 °С, хорошая коррозионная стойкость и др.), обеспечивающих их

применение в различных отраслях промышленности. Существует возможность менять свойства керамики из Si_3N_4 путем ввода в состав дополнительной (второй) нанофазы (SiC, ZrO_2, TiN).
Цель представленной работы была выяснить влияние второй фазы на спекание, микроструктуру и свойства материала на основе Si_3N_4-6%Y_2O_3-3%Al_2O_3 при горячем прессовании при 1850 °C.
Исследования показали, что в большинстве случаев наличие второй фазы влияет на микроструктуру и свойства керамики.