RIGA TECHNICAL UNIVERSITY

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ELABORATION OF SINTERING TECHNOLOGY OF SILICON NITRIDE BASED NANOCOMPOSITES

Doctoral thesis summary

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CONFIRMATION

I confirm that I have developed the present Doctoral Thesis, which is submitted for consideration at Riga Technical University for scientific degree of the doctor of engineering chemistry. The Doctoral Thesis has not been submitted at any other university for the acquisition of a scientific degree.

Nataļja Žilinska ....

Datums ....

The thesis is written in Latvian, contains an introduction, literature review, methodological part, experimental part, conclusions and bibliography with 140 references. The thesis consists of 129 pages, 72 figures and 31 tables.

Topicality of theme. One of the tasks of material sciences is to create new materials, whose physical-chemical and mechanical properties are able to serve the growing requirements for technical and scientific challenges, or to simplify the existing technology. Silicon nitride-based ceramics have a very wide range of applications, from electronics and finally to the aviation, space and automotive industries [1].

Silicon nitride and oxynitride ceramics characterize [2]:

- high mechanical strength at high temperatures;
- good thermal conductivity;
- chemical resistance in an oxidizing atmosphere, acids;
- stability in metals (Al, Mg, Zn, Pb) alloys;
- high thermal shock resistance;
- low coefficient of thermal expansion;
- high wear resistance and low coefficient of friction.

The formation of silicon nitride was reported a century ago. However silicon nitride ceramics were only obtained by hot pressing in 1961. Significant achievements in silicon nitride ceramic production and applications have been explored during the past 30 years, making great progress in using of ceramic materials in the economy. All the above-mentioned positive silicon nitride material properties arise only if the material is fully dense. Silicon nitride is a covalent compound with low diffusion activity; therefore, fabrication of a dense material with conventional compacting methods is practically impossible. Partially this problem can be solved by using a variety of hot pressing techniques, and sintering in high nitrogen pressure or by using different sintering enhancing additives and nanosize powders.

Aim of the work and tasks.

Aim of promotion work is to clarify the sintering relationships of silicon nitride based particulate nanocomposites compared with composites prepared from industrial powders and to determine the received materials parameters (properties and microstructure), depending on the used additives and sintering technique.

To reach aim of promotion work the following tasks have to be solved:

1. to elucidate the relationship of Si_3N_4-Al_2O_3-Y_2O_3 nanopowders composites sintering by conventional sintering, hot pressing and sintering in solar furnace in comparison with composites prepared from the industrial powders;
2. to clarify the influence of TiN, ZrO_2 un SiC nanopowders additives on Si_3N_4-Al_2O_3-Y_2O_3 nanocomposite materials microstructure formation and mechanical properties improvement;
3. to clear up an effect of introduction mode of sintering additives on the Si_3N_4-SiC nanopowders microstructure formation by hot pressing;
4. to develop α-, β- sialons compacting technique and determinate mechanical properties of compacting materials;
5. to give a recommendations for selection the best composition of particulate nanocomposites and sintering methods.

Scientific novelty.

The complex studies of silicon nitride-based ceramic were developed, using different sintering methods, defined relationships, that involved of production of particulate nanocomposites, it's dispersity, compositions, homogeneity, sintering techniques, temperature of process with ceramic density, microstructure, phase composition and mechanical properties.

The advantages of one-step plasmachemical synthesis of Si_3N_4 based nanocomposites for activation of sintering were found. Fine grain microstructure formation and increasing of mechanical properties of composites prepared from mixtures of nanopowders, compared with industrial powders were demonstrated. Significant Si_3N_4 ceramic bending strength increasing provide an extended β - Si_3N_4 or β - sialons crystal formation at a temperature of 1600 to 1750 ^{0}C.

Practical significance.

Practical significance of promotion work is simplified technology of preparation raw silicon nitride-based particulate nanocomposite for ceramic materials. The application of nanocomposites provides decreasing of sintering temperature by conventional sintering, compared with industrial powder composites. The developed ceramic composite uniformity, density and presence of elongated crystal provides increasing of the mechanical properties of materials at operating temperature of 1000 ^{0}C.

Practical application.

The results of promotion work were applied within a framework of ES project "TRANSNANOPOWDER" for the anti-friction material and the dry friction ball bearing. Elaborated silicon nitride ceramic and sialon were applied for processing tools and for the manufacture of high temperature construction materials within framework projects of "NANOCERAM" and "CARCIM".

Approbation of study results.

The results of promotion work were presented at 20 international scientific conferences. The research results have been summarised and published in 23 internationally referenced publications.

LITERATURE REVIEW

Items on crystalline structure and properties of Si_3N_4, phase transition [4] production methods of traditional and nanopowders of silicon nitride, methods of ceramics production as well as on properties of Si_3N_4 – containing ceramics and possible applications has been reviewed.

Besides Si_3N_4 a very significant group of its compounds, so called sialons are known. Sialons are solid solutions isostructural with **α-** and **β-** Si_3N_4, respectively. When the part of Si and N is replaced with Al and O in **β-** Si_3N_4, solid solution is formed called **β-** sialon. The common formula of **β-** sialon is $Si_{6-z}Al_zO_zN_{8-z}$, where „z" can change from 0 to 4,2. The second solid solution is **α-** sialon formed on the basis of the **α**-Si_3N_4 structure. The formula of this solid solution is $M_xSi_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$, where M is the metal ion with the valence of **p+** and **x = m/p**, but **m** characterises the number of Si-N bonds in **α-** Si_3N_4, which are replaced by the Al-N bonds, and **n** characterises the amount of Si-N bonds replaced by the Al-O bonds [5].

At present besides the traditional methods of silicon nitride synthesis the known methods of nano- Si_3N_4 production are: mechanochemical synthesis (high energetic milling) [6], laser synthesis [7] and plasma synthesis [8].

Silicon nitride and Si_3N_4-based composite powders are used for obtaining of constructional ceramics. At present a rapid increase of ceramic constructional materials application is prospective following also the increase of the volume of output. Due to high temperature durability (strength), chemical stability and low specific weight of silicon nitride based materials it has been possible to develop ceramic combustion engine with the temperature of working cell up to 1400 ^{o}C and to increase for 1,5 times the coefficient of efficiency, to reduce significantly the fuel consumption and the pollution of environment as a result of better combustion of the fuel. In equipments of nuclear energy silicon nitride ceramics is used for the shells of heat-eliminating elements, but in thermonuclear power industry – as the heat and electric insulation material of the first wall of the plasma chamber.

Due to the typical covalent bonding of Si_3N_4 it is not really possible to obtain dense ceramics by the classical method of sintering – the heating of pressed powders. The main reason for this is extremely low diffusion rate of silicon and nitrogen (at 1400 ºC the diffusion rate of silicon is D_{Si} ~0,5x10^{-19} m^2·s^{-1} and of nitrogen D_N ~6,8x10^{-10} m^2·s^{-1}) in the volume or on the surface of Si_3N_4 grains [9].

The mass transfer in volume or diffusion through the grain boundary surface is necessary in the compacting process, but because the diffusion is thermally activated process, high sintering temperatures are necessary for obtaining of the dense material [10]. Unfortunately, Si_3N_4 decomposes at high temperatures. Therefore the sintering promoting additives are used ensuring the process at the presence of the liquid phase and therefore increasing the diffusion rate through the phase grain surfaces.

Metal oxides are generally used as sintering additives, for example, Y_2O_3, Al_2O_3, MgO, ZrO_2, CaO, SrO, or oxide mixtures with non-oxide compounds, for example, AlN, ZrN and Mg_3N_2.

The amount and composition of additives is mainly established empirically. Additives must form eutectics with Si_3N_4 at the temperature, which is lower than sintering temperature.

The amount and composition of the additives effect not only the sintering parameters (temperature, pressure, time, atmosphere), bet also the composition and microstructure of the final products; they significantly determine many properties of the Si_3N_4 ceramics [9, 10]. At present generally appreciated for sintering of silicon nitride ceramics is the composite Si_3N_4 - 6 wt.% Y_2O_3 - 3 wt.% Al_2O_3, which promotes the obtaining of dense material and the formation of high-temperature phases on the grain boundary surface.

Si_3N_4/SiC materials have been obtained by the hot pressing [11 - 13]. Increased durability is the advantage of Si_3N_4/SiC-containg ceramics in comparison with the silicon nitride ceramic [14, 15]. This can be explained by the fact that the particles of SiC are impeding the abnormal grain growth. This effect increases with the decrease of the grain size and with the increase of the volume part of SiC.

A lot of methods has been developed for obtaining of the compact material (abbreviations for Si_3N_4):

- reactive sintering – RBS (reactive bonded Si_3N_4 – RBSN);
- non-pressure sintering – S (sintered Si_3N_4 – SSN);
- sintering at increased gas pressures – GPS (sintered Si_3N_4 – GPSN);
- hot pressing – HP (hot pressed Si_3N_4 – HPSN);
- hot isostatic pressing – HIPS (hot isostatic pressed Si_3N_4 – HIPSN).

Some non-traditional compacting methods have been appeared at present: microwave sintering, plasma spark sintering, sintering in the furnace of solar energy. The main advantage of these methods is high sintering rate and the shortness of the process restricting the grain growth in the material. Nevertheless, except for the diversity of the applied sintering methods and significant progress in the development of silicon nitride containing ceramics, the regularities of nanosized composite sintering are not sufficiently being investigated and obtained results are often contradictory.

PREPARATION OF SAMPLES AND RESEARCH METHODS

Nanopowders of silicon nitride and Si_3N_4 containing composites. Nanopowders of silicon nitride and Si_3N_4 containing composites (Si_3N_4-6%Y_2O_3-3%Al_2O_3, Si_3N_4-Y_2O_3-Al_2O_3-AlN, Si_3N_4-AlN, Si_3N_4-SiC un Si_3N_4-TiN), as well as other powders used in investigations – Al_2O_3, Y_2O_3, ZrO_2, TiN, AlN – were made by the method of plasmachemical synthesis based on evaporation of the raw powders in high frequency nitrogen plasma (average mass temperature is of 5000 – 6000 K) with the following condensation (freezing) of reaction products in the form of nanoparticles from gas/vapour phase [16, 17]. The characteristics of synthesized nanopowders and composites are given in Table 1.

Table 1

Chemical and phase composition of nanopowders used in composites

Powder composition	Chemical composition, wt %								Phase content	SSA, m^2/g
	Si_3N_4	Al_2O_3	Y_2O_3	ZrO_2	TiN	SiC	$Si_{free.}$	O		
Si_3N_4–$6Y_2O_3$–$3Al_2O_3$	88,6	3,0	6,0	-	-	-	0,5	-	α-, β- un am. Si_3N_4	65
Si_3N_4-SiC	10,6	-	-	-	-	86,4	0,8	2,0	β-SiC; am. Si_3N_4	36
Si_3N_4-TiN	88,0	-	-	-	9,0	-	0,7	2,3	am. Si_3N_4, TiN (sign)	60
TiN	-	-	-	-	98,2	-	-	1,8	TiN cub.	40
ZrO_2	-	-	-	99,5*-		-	-	-	70% tetrag., 30% monocl.	30
Al_2O_3	-	100	-	-	-	-	-	-	δ–, Θ–Al_2O_3	50
Y_2O_3	-	-	100	-	-	-	-	-	30 % cub., 70% monocl.	20

*the rest are adsorbed gases

The synthesized Si_3N_4 nanopowder is characteristic with particles of irregular form with the average particle size of 30-40 nm and the specific surface area of the powder is of 50-70 m^2/g. Powder consists of α- and β- Si_3N_4 (mainly in the proportion 1:1) and the XRD-amorphous part. The content of the amorphous phase is dependent on the specific surface area and is in the range of 60-80 wt. %.

The composite containing 6 wt. % Y_2O_3 and 3 wt.% Al_2O_3 (the specific surface are was of 65-70 m^2/g, corresponding to the average particle size of 30-35 nm) was used as Si_3N_4–Y_2O_3–Al_2O_3 powder composite in investigations. Nanopowders of Si_3N_4-SiC, TiN, ZrO_2, TiN- Si_3N_4 were used to establish their significance in the sintering process of Si_3N_4–Y_2O_3–Al_2O_3 nanocomposite and improvement of ceramics properties.

Nanopowders of Si_3N_4-TiN and Si_3N_4-SiC produced in plasma consist of the particles of TiN and SiC and more fine particles of Si_3N_4. More refractory phase (SiC or TiN) is mainly coated with the fine layer of Si_3N_4. Characteristic feature of plasma-synthesized composites is low degree of crystallization of Si_3N_4 and Al_2O_3. .

Nanocoposites containing silicon carbide. Nanopowders of Si_3N_4-SiC with differing SiC content (series A and B) and their composites with oxide additives (Si_3N_4-SiC – Al_2O_3 – Y_2O_3) as well as separate oxides Al_2O_3 un Y_2O_3 (all produced in high frequency plasma) were used for investigations. Characteristics of produced powders are given in Table **2** (for Al_2O_3 and Y_2O_3 – in Table 1). For experiments of high pressure hot pressing two other composites of SiC-Si_3N_4 (series C) with differing content of free carbon were used. These used composites of nanopowders consist of β-SiC and more fine, mainly XRD amorphous Si_3N_4.

Table 2

Chemical composition and particle size of used SiC containing nanopowders

Series of experiments	Nanopowders	Chemical composition, masas %						SSA, m^2/g
		SiC	Si_3N_4	Al_2O_3	Y_2O_3	Si_{free}	C_{free}	
A	SiC-Si_3N_4	10,0	85,5	-	-	0,6	-	53
A	SiC-Si_3N_4-Al_2O_3-Y_2O_3	8,0	78,0	7,0	3,6	0,8	1,9	55
B	SiC-Si_3N_4	80,0	11,5	-	-	0,8	8,0	60
B	SiC-Si_3N_4	87,7	9,5	-	-	0,3	0,3	40
B	SiC-Si_3N_4-Al_2O_3-Y_2O_3	70,0	16,0	7,4	3,6	0,6	2,0	45
C	SiC-Si_3N_4	74	18	-	-		8,0	50
C	SiC-Si_3N_4	80	20				0	40

Sialons forming nanopowder composites. For making of sialons of different compositions the following nanocomponents were used: individual nanopowders Si_3N_4, AlN, Al_2O_3, Y_2O_3 and nanocomposites Si_3N_4-AlN *(90%Si_3N_4-10%AlN, 73%Si_3N_4-27%AlN)*, AlN-Y_2O_3 *(90%AlN-10%Y_2O_3)*, Si_3N_4-AlN-Al_2O_3-Y_2O_3. Their characteristics are given in Table **3.**

Table 3

Chemical composition and particle size of nanopowders used for production of sialons

Powder composition	Chemical composition, wt. % *					SSA,m^2/g	d_{50}, nm
	Si_3N_4	AlN	Al_2O_3	Y_2O_3	Si_{free}		
Si_3N_4	98,1	-	-	-	0,7	65	40
AlN	-	97,0	-	-	-	40	50
Si_3N_4-27%AlN	71,1	27,1	-	-	0,4	75	30
Si_3N_4-10%AlN	88,0	9,7	3,9	-	0,6	50	40
AlN-Y_2O_3	-	89,1	-	9,8	-	30	60
Si_3N_4- AlN-Al_2O_3-Y_2O_3	83,7	8,0	2,6	4,1	1,3	70	30

* - the deficit in the weight balance is oxygen adsorbed from the air

Composites of industrially produced powders. For comparing of sintering processes along with the preparation of samples from nanopowders also industrial powders were used and the composites of the same composition as from nanopowders were made from them. They are shortly characterised in Table **4.** The crystallization degree of silicon nitride from company UBE is of 99% and it contains 97% of α- Si_3N_4. The letter R has been added to the nomenclature of samples made from industrial powders.

Table 4

Characteristics of industrial powders used in research

Compound	Grade	Company	SSA, m^2/g	d_{50}, µm	Purity
α-Si_3N_4	SN-10E	UBE	10	2,0	O<2,0%; Cl, Fe < 100 ppm; Ca, Al <50 ppm
AlN	Grade B	H.C.Starck	2 - 4	2,0 – 4,5	Fe< 50 ppm; O <1,5 ppm
Al_2O_3	A16SG	Alcoa Chemie GmbH	8-10	0,4 – 0,5	
Y_2O_3	Grade C	H.C.Starck	10-16	0,9	

Processing of samples for sintering. For investigation of the role of the additives of the second phase in silicon nitride composites, the nanocomposition

Si_3N_4 - 6 % Y_2O_3 – 3 % Al_2O_3 was selected as the main composite of silicon nitride and used as the reference composite. The additive of 10 wt. % of TiN, ZrO_2 or SiC (in the form of 90 % SiC – 10 % Si_3N_4) nanopowders was used as the second phase. Composites were mechanically mixed in the ball mills. In a similar way the mixture from Si_3N_4 - 10 % TiN with the additives of Y_2O_3 and Al_2O_3 was made.

For Si_3N_4-SiC composites the effect of the mode of sintering additives attachment on compacting and properties of the material was investigated. Three different approaches of production this powder composite (mixture with 3,5 % Y_2O_3 and 7 % Al_2O_3) were used: 1) mechanical mixing of individual nanocomponents (SiC-Si_3N_4 and oxide additives) in the ball mills; 2) chemical precipitation of oxides from solutions on the surface of Si_3N_4-SiC nanoparticles; 3) simultaneous synthesis and mixing of SiC-Si_3N_4 and oxides additives during the plasma synthesis.

For chemical precipitation of oxides additives, nanoparticles of Si_3N_4-SiC produced in plasma were dispergated by the ultrasound in ethanol and mixed with the solution of aluminium and yttrium nitrates. Precipitation was controlled by the adding of NH_4OH. The obtained mixture was washed and hydroxides decomposed by heating in the argon.

Two series of samples were made for sialons: at first separate investigations were made in the free chosen places in the range of existence of sialons (series A) and after it systematic investigations in all the range of existence of sialons were made (series B).

Compositions of series A sialons in the phase diagram [18] $Si_{12}N_{16}$ – $Al_{12}O_{12}N_4$ – $Y_4Al_{12}N_{16}$ (Fig. **1.a.**) were chosen in the line Si_3N_4 –$Y_2O_3{\cdot}9AlN$ (samples A1-A5), and in all the range of sialons (samples A6-A10), in order to find the dependence of sintering temperature and properties of materials on composition and to chose the optimum compositions for the needs of particular applications.

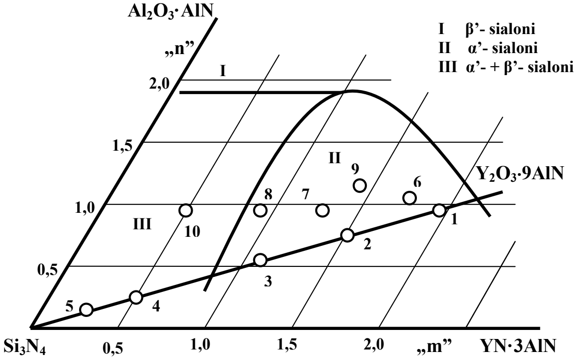

Fig. 1.a. The location of series A samples in the phase diagram of the system Y-Si-Al-O-N

Nanocomposite samples (A1…A5) were made from Si_3N_4 and nanocomposite 10 % Y_2O_3 – 90 % AlN. It means that the content of Y_2O_3:9AlN decreases with the increase of samples' number (serial number). Sample A3*, which corresponds to composition A3 was made from nanopowders of Si_3N_4-AlN and Y_2O_3. Samples from A6 to A10 are with higher oxygen content and in the phase diagram are located outside of the line Si_3N_4 –Y_2O_3·9AlN. These samples were made from nanocomposites Si_3N_4-AlN (samples from A6 to A8) and Si_3N_4-AlN-Al_2O_3-Y_2O_3 (samples A9 and A10) and a small amount of AlN, Y_2O_3 and Al_2O_3 powders additives for the correction of composition. The letter R has been added to the nomenclature of samples of the same composition made from industrial powders: A1R ... A10R.

In the second series of experiments (series B) 18 Y-containing α- sialon composites of different compositions were made corresponding to the formula $Y_{m/3}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ or near the range of α- sialon existence. These composites are shown in the phase diagram $Si_{12}N_{16}$ – $Al_{12}O_{12}N_4$ – $Y_4Al_{12}N_{16}$ **(Fig. 1.b)**. Therefore the final composites can consist either of the single phase α- sialon, or of the composite of α- + β- sialons in accordance with the phase diagram [18].

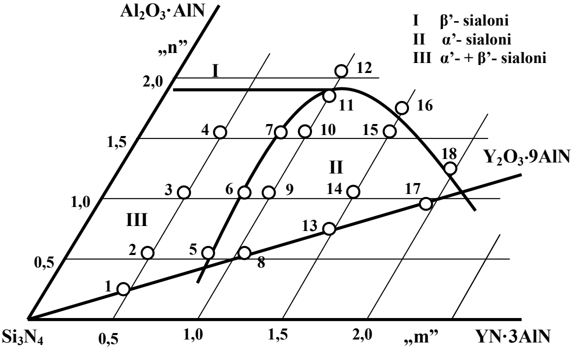

Fig. 1.b. The location of series B samples in the phase diagram of the system Y-Si-Al-O-N

Nanocomposite Si_3N_4 – 27 wt.% AlN as well as Al_2O_3, Y_2O_3 and Si_3N_4 nanopowders' additives for correction of composition were used for making of samples of series B.

All investigated composites were made by weighing samples with the preciseness of 0,001g and mechanically mixed for 15 hours in ball mill. Only for mixing of series B sialons the planetary mill was used. Polyethylene vessel and silicon nitride balls were used. Isopropanol was used as dispersion medium. For ordinary sintering 2 wt.% of stearic acid was added to mixtures for better compacting properties. In the HP and SPS processes plasticizer was not used. After mixing the mixture was treated with ultrasound for 1 hour to prevent the repeated formation of aggregates and for 2 hours mixed in ball mill. Also plasmochemically made nanocomposites, for example, Si_3N_4 -6%Y_2O_3 -3%Al_2O_3, were treated in the same way.

After mixing composites were dried at 80 ºC and sieved through 200 µm sieve. For sintering in the conventional furnace (sintering without pressure) or in the solar energy furnace samples were pressed (pressure of 200 MPa) 15 mm in diameter and 7-8 mm in height. Stearic acid was burned out at 600 ºC in nitrogen. The density of the pressed samples form nanopowders was of 40-48 % (the density of Si_3N_4–$6Y_2O_3$–$3Al_2O_3$ nanocomposites did not exceed 33 - 36 %), but for samples made form industrial powders - 50 - 57 %.

Methods of preparing of ceramic materials:

1) Traditional pressureless sintering. In the process of convenient pressureless sintering samples were annealed in nitrogen atmosphere at the temperature range of 1000-1750 ºC, isothermal holding time was 2 hours, heating rate was 10º/min. Until 1000 ºC the process was carried out in vacuum in order to maximal release of particle surface from adsorbed gases, mainly oxygen. Samples were cooled together with the furnace.

2) Hot pressing. Powders were sintered at such conditions: nitrogen atmosphere, heating rate 10°/min. and pressure of 30 MPa. Sintering temperatures was 1750, 1800, 1850 un 1910 °C, isothermal sintering dwell time was 1 or 2 hours.

3) High pressure hot pressing. Compact materials were made in the high pressure hot pressure equipment (pressing pressure up to 10 GPa and sintering temperature up to 1800 °C). Sample (2 mm in diameter, 3 mm in height) was pressed into the rhenium capsule and MgO cylinder, where the W/Re thermo-couple was also installed. All this unit was inserted into the MgO containing ceramic octahedron surrounded by 8 cubic WC units. This construction transferred the pressure from the press to the sample. Samples were pressed to the necessary pressure during 3,5 hours and hold at this pressure for 2 hours. Then the pressure was reduced till normal during 15 hours. Samples were heated at the maximum pressure (heating rate 100 °C/min, dwell time up to 10 min.).

4) Sintering in the solar energy furnace. Heating rate until sintering temperature (1600 – 1750 ^{o}C) was in the range from 30 to 180 ^{o}C/min. Dwelling time at sintering temperature in nitrogen was from 10 to 60 min.

5) Spark plasma sintering (SPS). SPS was made by two different equipments. SiC containing samples were compacted by the equipment HP D 25/1, which operated at temperatures up to 1900 ^{o}C, heating rate of 200 ^{o}/min, pressing pressure of 30 MPa and nitrogen pressure in operating chamber of 40 mbar, pulsation mode of 10/5/1/0 ms. The diameter of samples was 40 mm. Equipment SPS-825.CE was used for compacting of sialons: heating rate up to 1600 °C was 100 ^{o}/min, from 1600 °C to 1700 °C – 50 °/min, isothermal dwelling time at 1700 °C – 5 min, pressing pressure 30 MPa. Sintering was made in vacuum. The electric current pulsation rate was 14 impulses per second.

Research methods of nanopowders and materials.

The chemical composition of powders (N, C, Si_{free}, Y, Al, Ti) was estimated by the chemical analysis. The specific surface of powders was estimated by the BET method of argon adsorption- desorbtion method.

Size and morphology of particles was estimated by the transmission electronic microscope (TEM) Philips CM20.

Phase content of powders and sintered samples was estimated by the XRD analysis (DRON-3 and Advance D8, Bruker AXS).

The Archimedes method was used to estimate the density of sintered samples and open porosity. The density of sintered SiC samples was measured also by the mercury immersion method.

Microstructure of sintered samples was analysed by the scanning electron microscope (SEM) (Hitachi, S4800 and Supra 40VP, Zeiss, HR-SEM.

Hardness of samples (HV_1, load 9,8 N and HV_5, load 49 N) and fracture toughness (K_{1c}, load 98 N) were estimated by the Vickers method, bending strength by the three-point method at room temperature and at 1000 °C. After sintering samples were cut in bars of 5x5x45 mm, grinded and polished.

REZULTS AND DISCUSSION

1. Preparing of ceramics in systems Si_3N_4-Me_2O_3 and Si_3N_4-Me_2O_3 – modifier

Results of pressureless sintering of Si_3N_4-containing nanopowders. The sintering regularities of plasma-synthesized Si_3N_4 – 6%Y_2O_3 – 3%Al_2O_3 nanocomposite were estimated and compared with sintering of the industrial powders. Changes of relative density of nano- Si_3N_4 – 6%Y_2O_3 – 3%Al_2O_3 samples during pressureless sintering process are shown in Fig. **2**.

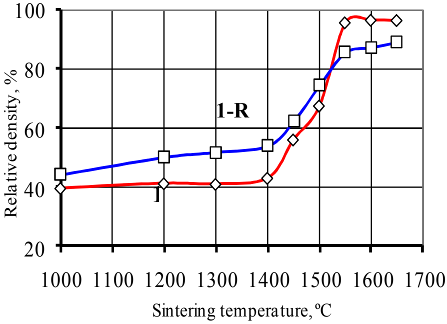

Fig. 2. The dependence of relative density of Si_3N_4–6%Y_2O_3–3%Al_2O_3 samples on sintering temperature: 1- nanocomposite, 1-R- composite from industrial powders.

The relative density of samples did not change up to 1400 °C: the starting density of the sample from nanopowders (sample **„1”**) was only 39,8%, but from industrial powders (sample **„1-R”**) – 49,7%. With the rising of sintering temperature the density of samples increases very rapidly and the maximum density of sample from nanopowders is reached already at 1550 °C. For obtaining of the dense material from industrial powders even the temperature of 1650 °C was not sufficient (density was not higher than 88%). The difference in the density of sintered samples follows from the differing particle size and so the activity of the used powders as well as from the differing way of the composite preparation.

Crystallization (for nanopowders) and phase transfer processes take place simultaneously with the compacting of material. For silicon nitride ceramics from industrial powders the explicit α-/β- Si_3N_4 phase transfer is being observed at 1500-1550 °C (Fig. **3.**). For nanopowders the crystallisation (formation of α- and β- Si_3N_4) of amorphous silicon nitride at temperatures up to 1400 °C takes place. The α-/β-Si_3N_4 phase transition for nanopowders is being observed at 1400-1450 °C.

Changes of density, microstructure and also the phase transfer during sintering is a factor of changes of also the mechanical properties of material (hardness HV_1 and fracture toughness K_{1c}) (Fig. **4.**).

Hardness is rising in proportion to the density of material. Fracture toughness as well as bending strength is effected by the microstructure of material – the presence of needle-shaped crystals increases especially the bending strength of materials.

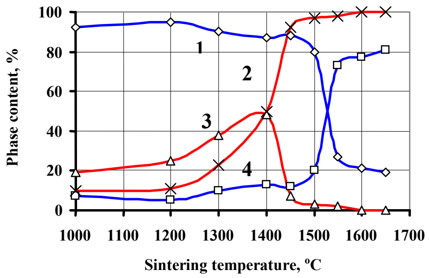

Fig. 3. Changes of phase composition of Si_3N_4–6%Y_2O_3–3%Al_2O_3 powders composite during sintering for samples **„1”** (2,3) and **„1-R”** (1,4):1,2 - α-Si_3N_4, 3,4 - β-Si_3N_4

These results are in good correspondence to that obtained for materials produced by the method of hot pressing at 1600 and 1850 °C: HV_1 is respectively 17,2 and 16,8 GPa, but the fracture toughness is (4,7 and 5,7 MPa.m$^{1/2}$) and bending strength is (560 and 1150 MPa).

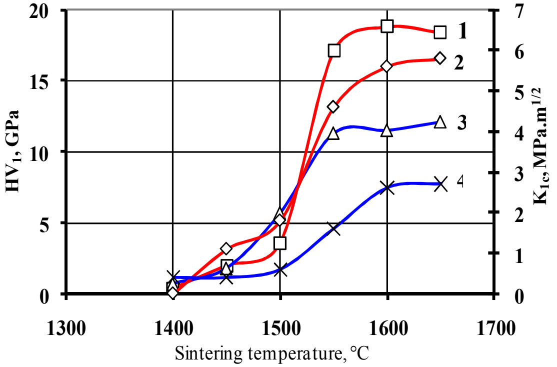

Fig. 4. Changes of material properties (hardness HV_1 (1,3) and fracture toughness K_{1c} (2,4)) depending on sintering temperature for Si_3N_4–6%Y_2O_3–3%Al_2O_3 materials **„1"** (1,2) and **„1-R”** (3,4)

In comparison with the ceramics from industrial powders the sintering of nanocomposites at 1600 °C ensures the increase of fracture toughness more than two times and up to 50% raise of hardness determined by differing density, microstructure and phase composition.

Sintering of silicon nitride containing nanopowders in solar furnace. Sintering research in the solar energy furnace was made by using the same Si_3N_4 – 6 %Y_2O_3 – 3%Al_2O_3 nanocomposite. One of the aims of the research was to find, how the sintering of material and microstructure effected by the temperature rising rate, which in the solar energy furnace is possible more high in comparison with the traditional furnace.

The sintering temperature of 1600 °C is not sufficient to sinter the Si_3N_4–6%Y_2O_3–3%Al_2O_3 nanocomposite (sample **„1”**) – after sintering for 10 minutes the changes of sample density are insignificant and also after the sintering for 60 minutes the sample has not been fully sintered (Tab. **5**.), but at 1700 °C already relatively dense ceramics has been formed.

Table 5

The dependence of relative density (ρ) and hardness (HV_1) of samples **„1"** on sintering parameters (starting density was 39,8 %)

Heating rate, °C/min	Isothermal holding time, min	1600 °C		1700 °C		1750 °C	
		ρ, %	HV_1, GPa	ρ, %	HV_1, GPa	ρ, %	HV_1, GPa
180	10	45,4	3,0±0,3	94,0	12,7±0,3	96,1	17,8±0,6
180	30	-	-	-	-	95,5	18,7±0,8
180	60	85,1	8,0±0,4	94,9	17,4±0,5	96,1	17,8±0,5
30	60	-	-	-	-	95,7	17,6±0,4

It is not possible to obtain dense material from industrial powders even at 1750 °C after isothermal dwelling for 60 minutes.

Generally the density and mechanical properties after sintering of nanocomposites at 1750 ^{0}C for 10 – 60 minutes in the solar energy furnace are analogical to that obtained by the non-pressure sintering of nanocomposites at 1600 – 1650 ^{0}C. The obtained results give an evidence that sintering in the solar furnace could be perspective for obtaining of low-sized materials of high purity.

Research of hot pressing of materials containing Si_3N_4 nanopowders. Hot pressing (widely used for sintering of industrial Si_3N_4 powders) was applied for Si_3N_4-6%Y_2O_3-3%Al_2O_3 composites of the previously mentioned composition. The research was performed at two sintering modes: at 1600 °C and 1850 °C, the isothermal dwelling time was of 2 hours. Pressing pressure was of 30 MPa. Properties of materials are given in Table **6.**

Table **6**

Mechanical properties of Si_3N_4-6%Y_2O_3-3%Al_2O_3 composites obtained by the hot pressing method

Sample	Sintering temperature, °C	Density, g/cm^3	P_{open}, %	Bending strength, MPa	E, GPa	K_{1c}, MPa·m$^{1/2}$	HV_1, GPa
1	1600	3,18	0,3	560±80	-	4,7±0,3	17,2±0,5
1-R		2,80	11,5	-	-	-	11,8±4,5
1	1850	3,27	0	1150±160	346±15	5,7±0,4	16,8±0,5
1-R		3,25	0	940±48	262±17	-	16,4±0,6

The density of the sample obtained at 1600 °C from nanopowders is near to the theoretical. Materials have high hardness, but not a very high bending strength because there are no needle-shaped crystals in nanostructure. They are generally formed at temperatures about 1700 °C. This temperature is too low for industrial powders to obtain dense material with a good properties.

After sintering at 1850 °C the microstructure of materials obtained from nanopowders and industrial powders differs significantly (Fig. **5.**) – in both cases we can observe significant amount of elongated (needle-shaped) grains, but for nanopowders the size of these grains are significantly smaller (100 - 200 nm, individual grains up to 400 nm in diameter) and the elongation degree of grains is higher (l/d up to 10) in comparison with the sample from industrial powder. This is also the reason of increased mechanical properties of material, especially bending strength (Table **6**).

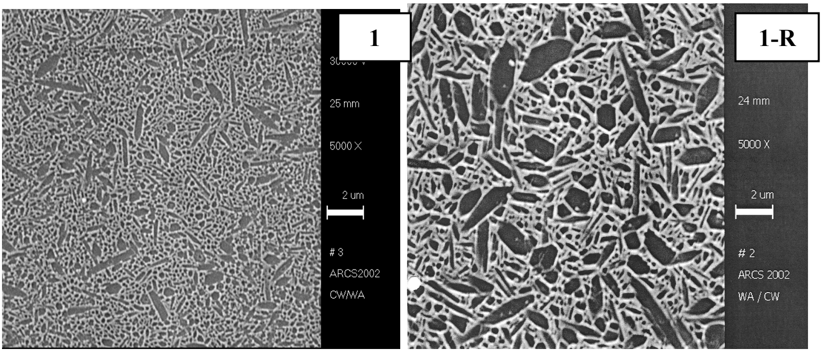

Fig. 5. Microstructure of ceramics obtained from nanopowder (**„1"**) and industrial powder (**„1-R"**) by the hot pressing method at 1850 °C

Dense Si_3N_4-6%Y_2O_3-3%Al_2O_3 ceramics from nanopowders can be obtained already at 1600 °C (both by the non-pressure sintering and hot pressing), but at this temperature recrystallization and formation of needle-shaped β- Si_3N_4 crystals are insignificant. Therefore bending strength and also fracture toughness of materials obtained at temperatures until 1600 °C do not reach maximum values. But this cannot be related to hardness – it is the highest for nanopowder samples obtained at these temperatures. (Table **6**).

The experiments were made on production of Si_3N_4-containg ceramics by the hot pressing method to check on the effect of the second phase on the properties of silicon nitride ceramics. Nanocomposite Si_3N_4–6%Y_2O_3–3%Al_2O_3 (sample signed with **„1"**) was use as the reference system. The additives of 10 wt% of ZrO_2, SiC (respectively, composite of 90 wt.% SiC – 10 wt.% Si_3N_4) and TiN nanopowders were used to find the effect of the second phase on the microstructure and properties of material. Additionally also plasma-synthesized Si_3N_4 – 10 wt% TiN nanopowders composite mechanically mixed with 6 wt% Y_2O_3 and 3 wt% Al_2O_3 nanopowders (sample **„SN-TN"**) was used. Hot pressing was made at two temperatures - 1800 and 1850 °C. Properties of these samples are summarised in Table **7** and Table **8.**

Table 7

Mechanical properties of materials hot pressed at 1800 °C

Sample	ρ, %	P_{open}, %	Mechanical properties			
			σ_{20}, MPa	σ_{1000}, MPa	HV_1, GPa	K_{1c}, $MPa.m^{1/2}$
„1”	96,1	0,2	610	554	17,0	4,8
„1” + 10 % ZrO_2	92,5	0,1	640	629	17,3	5,0
„1” + 10 % SiC	96,7	0,1	692	-	18,8	5,0
„1” + 10 % TiN	93,5	0,1	655	437	17,9	5,1
„SN-TN”	88,6	1,3	785	753	18,3	5,6

Table 8

Mechanical properties of materials hot pressed at 1850 °C

Sample	ρ, %	P_{open}, %	Mechanical properties			
			σ_{20}, MPa	σ_{1000}, MPa	HV_1, GPa	K_{1c}, $MPa.m^{1/2}$
„1”	99,1	0,1	1080	1020	16,8	5,7
„1” + 10 % ZrO_2	93,8	0	827	762	16,7	6,1
„1” + 10 % SiC	97,3	0	732	-	18,1	5,3
„1” + 10 % TiN	94,0	0	885	833	16,9	6,0
„SN-TN”	91,7	0,1	976	964	17,9	5,8

Modifying additives ensure improvement of separate properties, for example, addition of ZrO_2 or TiN increases K_{IC}, addition of SiC increases hardness. The effect of modifying additives on mechanical properties of ceramics from nanosized powders is less than for ceramics from industrial silicon nitride powders as it has been referred in literature, because is more significantly impacted by the decreased density of sintered samples.

2. Obtaining of Si_3N_4-SiC ceramics

Pure silicon carbide ceramics is a high temperature construction material in common with ceramics from silicon nitride. It is endurable for a long time until temperatures up to 1700 °C [19]. By the process of plasmachemical synthesis and using nitrogen plasma, it is possible to produce Si_3N_4-SiC nanocomposite, where the SiC content can be change in the range from 0 to 90 wt%. One of the tasks of this research was to find the sintering possibilities of such nanopowders and the optimal ways for adding of sintering additives.

Sintering of Si_3N_4-SiC composites by the common sintering methods is really impossible because the temperature over 1800 °C is necessary for sintering of SiC, but at these temperatures Si_3N_4 already decomposes. Therefore sintering at the increased nitrogen pressure (prevents decomposition of Si_3N_4) [20] or hot pressing is used for compacting of such composites. Hot pressing and SPS methods were used in this research.

Si_3N_4-SiC nanocomposites of two compositions were used for experiments: with 10 wt% of SiC (A series) and with 80 wt% of SiC (B series), and three different methods of oxide additives injecting (Table **9**). In order to evaluate and to compare the sintering possibility of nanopowders, simultaneously composites of the same composition were made from industrial powders. The methods of composite obtaining are given in Table **9.**

Dense ceramics with fine-grained microstructure has been obtained by the hot pressing method from Si_3N_4-SiC nanocomposites with Al_2O_3 and Y_2O_3 sintering additives. For samples with low content of SiC compacting conditions are similar as for pure Si_3N_4 – sintering temperature is about 1750 °C. Bending strength of obtained samples (σ_{3p} ~ 690 MPa) is lower than for pure nitride ceramics, but hardness is high (HV_1 = 19 GPa).

Higher temperatures are necessary to sinter samples containing a lot of SiC (series B). At 1850 °C samples were obtained with density of 3,13-3,19 g/cm^3 and good mechanical properties (σ_{3p} = 580-610 MPa, K_{1c} = 5,1- MPa·m$^{1/2}$, HV_1 = 19,4 - 20,0 GPa). Density, microstructure and mechanical properties of composite samples prepared with different methods (chemical precipitation of oxide additives on the surface of nanoparticles and plasma synthesis) are similar, but the less labour consuming process is plasma synthesis of nanocomposites because synthesis and mixing of components is integrated in a one-stage process.

Table 9

Characteristics of Si_3N_4-SiC composites

Symbol	Sample	Method of the composite preparation
A (${Si_3N_4}$-SiC (90:10) - Al_2O_3 - Y_2O_3)		
A1	Si_3N_4-SiC + Al_2O_3 + Y_2O_3	Mechanical mixing
A2	Si_3N_4-SiC-Al_2O_3 - Y_2O_3	Plasma synthesis
A3	Si_3N_4+SiC+Al_2O_3+ Y_2O_3	Mechanical mixing of industrial powders
B (Si_3N_4-SiC (20:80) - Al_2O_3 - Y_2O_3)		
B1	Si_3N_4-SiC+Al_2O_3+ Y_2O_3	Mechanical mixing (C_{free}= 8 wt%)
B2	Si_3N_4-SiC+Al_2O_3+ Y_2O_3	Mechanical mixing (SiC without C_{free})
B3	Si_3N_4-SiC-Al_2O_3 - Y_2O_3	Plasma synthesis
B4	Si_3N_4-SiC-Al_2O_3 - Y_2O_3	Chemical precipitation of oxides
B5	Si_3N_4+SiC+Al_2O_3+ Y_2O_3	Mechanical mixture of industrial samples

Composites containing industrial SiC do not form dense structure at the performed compacting conditions, therefore the mechanical properties of samples are falling behind of such of nanocomposite samples.

Characteristics of samples prepared by the SPS method are similar to that obtained by the hot pressing method. The activation of sintering due to the impact of strong current impulse ensures very fast run of the SPS process, but simultaneously determines also a rapid growth of grains.

When compacting SiC-containing samples at high pressures, materials with a very high microhardness (up to 35 GPa) were obtained; this is proposed to be due to the formation of over-stoichiometric SiC [21]. When free carbon containing samples are compacted at high pressure, diamond microcrystals are formed, so such a material can be useful for development of high durability cutting tools.

The results of research are corresponding to the opinion from [22], that mechanical properties of ceramics from Si_3N_4-SiC nanocomposites at the room temperature are not significantly better than that of Si_3N_4 ceramics. However at high temperatures (1400 °C and more) long-lasting mechanical properties of SiC-containing ceramics increase due to the changes of oxidation mechanism [23, 24]. The protective layer of Si_2N_2O forms under the oxide layer decreasing the volume defects (the migration of additives towards the surface) and formation of pores.

3. Development of sialon materials

Pressureless sintering of sialon materials. First investigated sample was plasma-synthesized α-/β- sialon with composition **A10** (Fig. 1.a.). The particle size of sialon starting powder is of higher importance for sintering than in the case of nitride composites (Fig. **6**) – sialon materials obtained from industrial powders sinter at significantly higher temperatures than silicon nitride with additives.

The process of sialon nanopowder sintering begins at already 1300 ºC, but the maximum density sample reaches at 1500 ºC; this temperature is lower than sintering temperature of Si_3N_4 nanocomposites. Sintering of industrial powders begins only from 1500 ºC and at 1650 ºC the obtained density of material is only 70%.

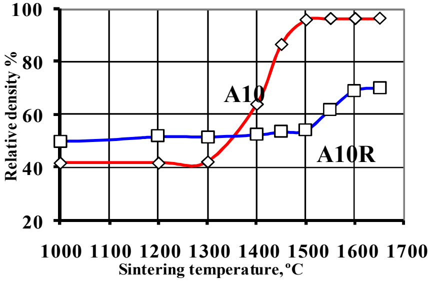

Fig. 6. Dependence of the relative density of **A10** sialon material from nano- (A10) and industrial powders (A10R) on sintering temperature.

Changes of density and microstructure as well as phase transition during sintering effect also changes of mechanical properties of material (hardness HV_1 and fracture toughness K_{1c}) (Fig. **7**). Hardness increases proportionally to the density of material.

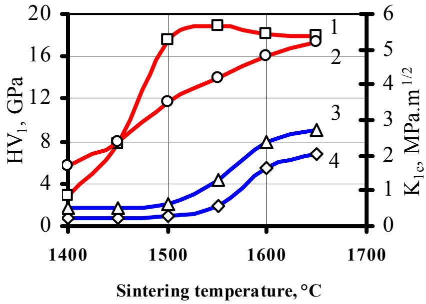

Fig. 7. Changes of sialon material **A10** composition hardness HV_1 (1,4) and fracture toughness K_{1c} (2,3) on sintering temperature for materials **A10** (1,2) and **A10R** (3,4).

When maximum density has been reached (sintering temperatures over 1500 °C), hardness of samples from nanopowders does not increase, but, on the contrary, begins to go slightly down. This can be explained by the grain growth and the formation of elongated β–sialon crystals at high temperatures [25, 26], but the presence of these crystals is a reason for increase of the fracture toughness.

Compacting of sialons in a solar furnace. The aim of the sintering of samples in a solar energy furnace was to intensify the sialon sintering process and to get more fine-grained structure of the compacted material by high temperature rising rate and short sintering time. α-/β- sialon composite **A10** was used for experiments (used already in the previous chapter). The obtained results are presented in Tables **10** and **11.**

Sintering of α-/β- sialon nanopowders went on at significantly lower temperatures in comparison with of Si_3N_4 – 6% Y_2O_3 – 3% Al_2O_3 nanocomposite (sintering temperature of 1600 °C was not sufficient for total sintering of this) and the relative density of 95% was reached already after sintering at 1600 °C (Table **10**).

Table 10

The dependence of relative density of sialon sample on sintering parameters (starting density of the pressed sample is of 40,8 %)

Heating rate, °C/min / isothermal holding time, min	1600 °C	1700 °C	1750 °C
180 / 10	93,3	97,7	95,4
180 / 30	-	-	95,9
180 / 60	95,7	95,7	96,1
30 / 60	-	-	95,2

Table 11

The dependence of mechanical properties of sialon samples on sintering parameters

Heating rate, °C/min / isothermal holding time, min	1600°C		1700°C		1750°C	
	HV_1, GPa	K_{1c}, $MPa.m^{1/2}$	HV_1, GPa	K_{1c}, $MPa.m^{1/2}$	HV_1, GPa	K_{1c}, $MPa.m^{1/2}$
180 / 10	15,3±0,3	-	16,8±0,5	5,1	16,9±0,3	6,2
180 / 30	-	-	-	-	17,9±0,4	-
180 / 60	16,6±0,7	4,8	16,8±0,7	-	18,2±0,5	7,2
30 / 60	-	-	-	-	17,5±0,4	7,4

It is difficult to obtain large-sized samples in the solar energy furnace because of great temperature gradient, therefore the bending strength was not measured, but it is known that the formation of needle-shaped crystals significantly increase the bending strength [27, 28].

The mechanical properties of samples in these experiments depend mainly on their density, which is relatively high for all sialon samples in the temperature range of the performed research. The density of these samples practically does not depend neither from the temperature rising rate, nor from sintering time therefore hardness is high for all samples (Table **11**). The increase of the fracture toughness with the rising of the sintering temperature can be explained because of the formation of elongated (needle-shaped) crystals over 1700 ^{o}C as it was in the case of silicon nitride.

Compacting of sialons by the method of hot pressing.

The research was made for sialon samples **A6**, **A7**, **A9**, **A10 and A9R**, the last sample was prepared from industrial powders.

The microstructure of sialon materials depends on chemical composition, as it can be seen from Fig. **8** and **9**: β-silicon nitride and β-sialon has characteristic needle-shaped structure. Therefore these materials has high bending strength (Table **12**), moreover also at high temperatures.

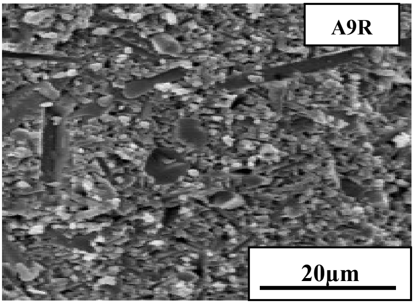

Fig. 8. Microstructure of material hot pressed at 1910 °C from industrial powders

The structure of α-sialons can differ, depending on composition, but there are less needle-shaped crystals therefore the bending strenght is less, whereas hardness is considerably higher then for silicon nitride materials (sample **SiN** for comparison). Grains of materials obtained by the hot pressing are relatively big (0,5 - 1,0 µm), but the length of needle-shaped crystals for individual composites is up to 5 - 10 µm (they are longer than for sialon composites with similar composition after sintering at temperatures untill 1700 °C [29].

When the temperature of hot pressing is increased the needle-shaped structure becomes more characteristic and the bending strength increases but hardness decreases.

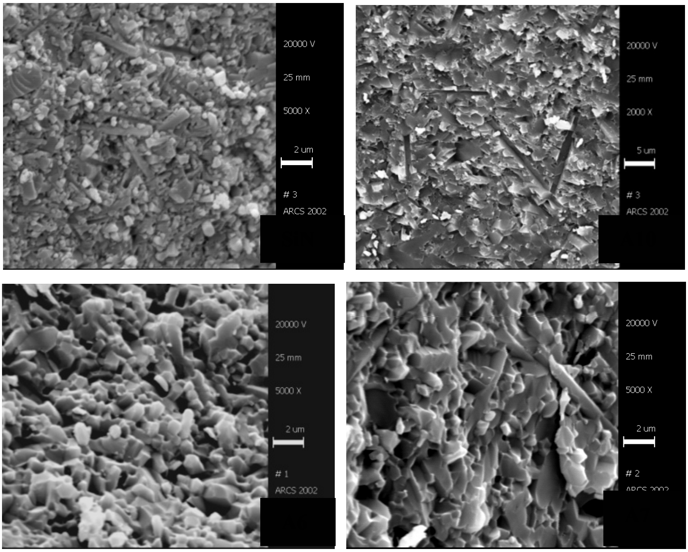

Fig. 9. Microstructure of samples hot pressed at 1800 °C (composition at Fig. **1a**)

Table 12

Characteristic of sialon ceramics obtained by the hot pressing (N_2, 2 h)

Sample	T, °C	ρ, g/cm^3	P_{open},%	HV_1, GPa	σ_{20}, MPa	E_{20}, GPa	σ_{1000}, MPa	E_{1000}, GPa	K_{1c},MPa·m$^{1/2}$
SiN	1800	3,17	0,2	17,0±0,2	590±40	235±5	554	135	4,4±0,2
	1850	3,27	0	16,8±0,5	1150±160	312±7	-	-	-
A10	1800	3,20	0,6	20,0±0,7	715±15	215±15	-	-	-
	1910	3,22	0	17,6±0,5	760±10	335±15	755	181	-
A6	1800	3,33	0,1	21,9±0,5	345±20	244±14	-	-	-
	1910	3,31	0	20,8±0,7	520±15	342±23	-	-	5,5±0,3
A7	1800	3,26	0,2	21,1±0,8	535±25	247±12	221	140	-
	1910	3,26	0	20,2±0,5	620±30	331±3	-	-	4,0±0,2
A9	1800	3,23	0,2	20,4±2,5	525±30	-	-	-	-
	1910	3,28	0	20,9±0,8	690±40	-	-	-	7,0±0,3
A9R	1910	3,30	0	20,8±0,7	700±70	248±10	-	-	7,1±0,3

Complex research of series B sialons by the method of SPS compacting. The results of SPS experiments are summarised in Table **13**. The temperature of beginning of shrinkage is marked with $T_{beg.}$, but the temperature of the end of shrinkage with T_{end}. Changes in XRD analysis (XRD maximum {hkl = 321} shift from β- Si_3N_4 peak to the β-sialon peak) is marked with “XRD shift”.

As follows from Table **13**, both the temperature of beginning of shrinkage and the end of shrinkage decreases by the increase of amount of sintering additives in composite (with the increase of coefficients „m” and „n” in the formula of α-sialons) and approaching to the region of α- sialons. Dense samples in the region of α- sialon were obtained at 1400-1500 °C.

Practically all sialon composites were sintered to the theoretical density until 1550 °C by the SPS compacting method. Open porosity of all samples was 0%.

Table 13

Characteristics of samples sintered by the SPS method

Nr.	$T_{beg..}$ [°C]	T_{end} [°C]	ρ [g/cm^3]	$P_{open.}$ [%]	HV_5 [GPa]	K_{1c} [MPa.m$^{1/2}$]	XRD shift. 2Θ [°]
B1	1300	1600	3,16	0	16,6±0,7		0
B2	1200	1580	3,14	0	16,5±0,7		0,15
B3	1200	1550	3,16	0	16,1±0,8		0,20
B4	1200	1550	3,13	0	16,3±0,2		0,20
B5	1160	1490	3,15	0	15,6±0,5		0,05
B6	1150	1520	3,16	0	15,8±0,2	4,2±0,2	0,15
B7	1120	1480	3,16	0	15,6±0,7		0,25
B8	1200	1550	3,24	0	16,1±0,9		0,20
B9	1200	1560	3,15	0	15,9±0,3	5,7±0,3	0,25
B10	1100	1520	3,24	0	15,9±0,5		0,35
B11	1050	1480	3,14	0	16,7±0,5		0,40
B12	1050	1450	3,12	0	16,3±0,9		0,40
B13	1060	1500	3,21	0	16,6±0,6	6,4±0,3	0,30
B14	1070	1480	3,27	0	17,5±0,8		0,45
B15	1000	1430	3,19	0	15,5±0,7		0,40
B16	1000	1400	3,27	0	16,3±0,7		0,45
B17	1000	1420	3,34	0	16,9±0,7		0,45
B18	1000	1420	3,22	0	16,9±0,9		0,65

It is obvious from the phase analysis of sintered samples that in applied compaction conditions all samples consist only of the β- sialon phase with changing chemical composition (differs the shift of the peaks). Exception is only the sample B1 containing also a small amount of Si_2N_2O phase besides β- Si_3N_4. Sintering temperature and especially the short sintering time at the mentioned experimental conditions are not sufficient for formation of α- or α-/β- sialon phases corresponding to the phase diagram.

SUMMARY

1. The dependence of phase composition, microstructure and mechanical properties of ceramics obtained from Si_3N_4-containg nanosized and industrial powders on composition of raw materials, particle size, preparation of composite and sintering method was estimated by applying of non-pressure sintering, hot pressing, SPS process and sintering in solar energy furnace.
2. Application of plasma-synthesized Si_3N_4-Y_2O_3-Al_2O_3 nanocomposites ensures obtaining of dense ceramics by the non-pressure sintering and hot pressing beginning from the temperature of 1600 ^oC, in contradistinction from application of industrial powders.
3. Properties of obtained Si_3N_4-Y_2O_3-Al_2O_3 nanocomposite ceramics (HV_1 = 16,8 – 18,0 GPa, K_{1c} = 5,6 – 5,7 MPa·$m^{1/2}$, σ_{20} = 1150 MPa, σ_{1000} = 1020 MPa) are significantly better than those of ceramics produced from industrial powders and the reason of this is density of ceramics, microstructure and formation of elongated grains, because their presence increases fracture toughness and bending strength.
4. Addition of modifying nanodopants (ZrO_2, TiN, SiC) to the silicon nitride nanocomposites improves individual properties of ceramics, for example, ZrO_2, TiN dopants increase fracture toughness, SiC – hardness.
5. Ceramics with a very high microhardness (35 GPa) has been obtained by the hot pressing of SiC containing nanocomposite at high pressure (8 GPa) and in the presence of free carbon the formation of diamond micrograins has been observed.
6. Preparation of nanocomposites in plasma by combining synthesis and mixing of nanocomponents is an effective method for production of raw materials for silicon nitride based ceramics.
7. Applied methods of production of materials can be successfully used for sintering of dense sialon ceramics of variable composition possessing excellent mechanical properties. After complex research it has been find that the best properties possess to the composites having index value „m” =1,0 –1,8 and „n” = 0,9 –1,2 in the general formula $Y_{m/3}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$.
8. Properties of dense sialon ceramics depend on phase composition and microstructure: formation of α-, β- sialons, isoaxial or elongated grains, which are supported by the increase of sintering temperature until 1700 ^0C.

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