Sintering and physico-mechanical properties of materials based on silicon nitride nanoscale powders

IOP Conf. Series: Materials Science and Engineering **848** (2020) 012068 doi:10.1088/1757-899X/848/1/012068

Sintering and physico-mechanical properties of materials based on silicon nitride nanoscale powders

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Abstract. Obtained a high-density material (ρ = 3,28 g/cm^3, a porosity of 1,4 %) on the basis of silicon nitride powder by liquid phase sintering nanoscale. Displaying pressing pressure on the density of sintered materials the based silicon nitride. The process of pattern formation material during sintering. The main physico-mechanical characteristics: the density, porosity and grain size of the solid phase, the modulus of elasticity, flexural strength, fracture toughness ratio, Vickers hardness.

1. Introduction

Oxygen-free ceramics belongs to the brittle materials do not exhibit macroscopic ductility and fracture when loaded up to the dissociation temperature of the compounds. This phenomenon makes it possible to create a unique class of structural materials with high hardness, strength and stability of mechanical properties in a wide range of temperatures, exceeding significantly the properties of metal alloys [1].

Silicon nitride is widely used in industry due to its unique combination of physical and mechanical properties such as high hardness and mechanical strength, low thermal conductivity and good erosion properties that allows to apply the product of Si_3N_4 as a wear-resistant, heat-resistant and acid resistant materials, working in extreme conditions of high temperature and aggressive environments. Materials made of silicon nitride can be prepared by various methods: reaction sintering, activated sintering, chemical vapor deposition and hot, hot isostatic pressing. High properties are achieved at the materials produced by the last two methods, however, a large energy consumption, inability to obtain articles of complex shapes and low productivity limit the reception of materials by this method on an industrial scale. reaction sintering method is impossible to obtain dense materials with a porosity of less than 5 vol. %. Using the method of chemical precipitation from the gaseous phase leads to materials with nearly the theoretical density, but due to the technological difficulties their production is extremely difficult. The optimal method is the liquid-phase sintering with oxide dopant, which results in a material with high mechanical properties, with less energy consumption and processing cost [2]. For materials with a high level of mechanical properties necessary to use fine powders, what is feasible with the additional process step of grinding, however, to produce particles of less than 0,5 microns is extremely difficult. Using the silicon nitride nanoscale powders (n-Si_3N_4) allows to obtain dense materials with maximum mechanical characteristics, but complicates the intermediate preparation materials.

As the sintering additives are used as individual oxides of Al_2O_3, Y_2O_3, MgO and their eutectic mixture. The most common activating additive is a mixture of components Al_2O_3 and Y_2O_3 in a ratio of yttrium aluminum garnet [3–10]. Among the active energy-oxides can also include Li2O, BeO, MgO, CaO, Ce_2O, ZrO_2 and their double oxide mixture introduced into the materials on the based silicon nitride in the form of starting components and in the form of binary eutectic compounds.

The aim is the preparation and study of physico-mechanical properties of high density ceramic materials based on nano powder nitride silicon by liquid-phase sintering.

2. Materials and Method

We used a nanosized powder plasmochemical Si_3N_4 (OOO «Plazmotherm», Russia) with a particle size d = 50–80 nm and a silicon nitride obtained by CVC (ISMAN Sciences, Russia), ground in a planetary mill to a size $d_{0,5}$ = 1 μm. Nanosize powder has a high content of silicon and oxygen impurities – 0,8 and 1,7 wt. %, respectively. In the course of storage due to the high activity of n-Si_3N_4 adsorbs oxygen on the surface, forming a thin SiO_2 film, which during the sintering react with oxide additives to form a fusible silicate melts. The compositions of the materials investigated in the work shown in Table 1.

Table 1. The compositions of the ceramic materials of silicon nitride.

Number of composition	Content $5Al_2O_3{\cdot}3Y_2O_3$, wt. %	Content of nanosized Si_3N_4, wt. %	Contents micron Si_3N_4, wt. %
1	15	0	85
2	15	5	80
3	15	10	75
4	15	15	70
5	15	20	65
6	15	25	60
7	15	40	45
8	15	60	25
9	15	75	10
10	15	85	0

As a sintering additive, a mixture of Y_2O_3 and Al_2O_3 oxides (OOO «Plazmotherm», Russia), particle size d = 30–50 nm, in a ratio forming step of sintering yttrium aluminum garnet (YAG) [11]. A liquid phase-sintered materials based on silicon nitride ceramic prepared by techniques [12], the method comprising preparing the batch molding of the samples at different pressures (25; 50; 75; 100 MPa), high temperature drying and sintering.

To increase the bulk density of the n-Si_3N_4 powders and oxides repeatedly briquetted and granulated. The starting powders in a predetermined ratio (Table 1) were stirred in a drum mixer. The polyethylene glycol used as a temporary process binder. Sintering was performed at 1780 °C in N_2 atmosphere with isothermal exposure for 40 min.

density of the samples was determined by hydrostatic weighing. Porosity was measured using an optical microscope Meiji Techno IM 7200 and computer image analyzer. The elastic modulus was determined by excitation of the resonant vibrations on the installation Zvuk–130. Three-point bending strength was measured on installation ShimadzuAG–300kNX. Hardness and fracture ratio was determined by introducing into the material and measuring the Vickers pyramid diagonals print size and originating from cracks on its corners microhardness PMT–3M. The microstructure and grain size of the solids was investigated by the scanning electron microscope Tescan Vega 3. Equipment granted «Engineering Center» SPSIT.

3. Results and discussion

Obtaining ceramics of high quality with a maximum level of mechanical properties is possible while achieving high density (close to the theoretical). The sintering process may be controlled by selection of dispersion, particle morphology. For silicon nitride retardation characteristic of diffusion processes, as in the lattices covalent compounds suppressed processes diffusion-viscous flow responsible for the mass transfer and seal the solid-state sintering. Sintering can significantly intensify the introduction of additives, which at a certain temperature (below the sintering temperature of ceramics) form at the grain boundaries primary liquid phase component. To accelerate the seal material may also be reducing the size of the precursor particles, using nanoscale particles during sintering which reduces the diffusion path and increasing the mass transfer [13].

Sintering mechanism includes: a seal of the particles by the method of solid-phase sintering; education fusible silicates and glasses; redistribution Si_3N_4 particles in the presence of a silicate liquid phase; dissolving α-, β-Si_3N_4 in the silicate melt by the interface and their recrystallization from the melt in the form β-Si_3N_4. It plays an important role as the formation on the particles Si_3N_4 layer of a solid solution (phase Si–Al–O–N, known as «sialon») due to dissolution of nitride in the yttrium aluminum garnet, which is described by the formula $Si_{6-Z}Al_ZO_ZN_{8-Z}$ ($z = 0 \div 4{,}2$) [5]. During sintering Si_3N_4 with oxides based on aluminum are formed in the solid solutions Si_3N_4 Al_2O_3 (β_1- and X_1-phase), the latter being located in a bundle between the Si_3N_4 grains and β'-phase. β'-phase growth occurs by recrystallization of Si_3N_4 by the melt corresponding to the composition X_1-phase which is formed at a temperature over 1700 °C. The interaction of these elements leads to the formation of wurtzite structures (O-phase), apatite structure compounds (H-phase) and a solid solution of Y_2O_3 in the Si_2N_2O (Y-phase). Daylight α'→β' sialon to as α→β Si_3N_4 observed for the presence of liquid phase.

Thus, when the silicon nitride sintered with the oxides formed multiphase materials, whose structure is determined by the following factors: the composition and phase dispersion of Si_3N_4; type and oxide content, liquid phase sintering temperature and duration of high-temperature exposure [14].

Materials with a large number of n-Si_3N_4 achieve maximum density under the molding pressures of 50–75 MPa. Nano powder has a large specific surface, so the high-density materials prepared therefrom molding at lower pressures. According to [15] in the silicon nitride sintered α-phase Si_3N_4 completely transformed into β phase. This process is active in the temperature range 1100–1400 °C, when the density reaches only 60–65 % of the density of the sintered material. By increasing the sintering temperature goes into step increases densification rate, which is accompanied by a maximum shrink material.

Compressed to the optimum density of the samples have a high sintering density (97–98 % of theoretical for the latter two compounds) (Figure 1). Increasing the density of samples with increasing content of n-Si_3N_4 because nanoscale powders during sintering is achieved by high-density packing of the particles and increases the mass transfer of material from the surface to the grain boundaries. The radius of the particles is comparable with the diffusion layer thickness therefore activated sintering and is accompanied by volumetric shrinkage. When smaller n-Si_3N_4 content greater molding pressure necessary to obtain the best properties of materials. This trend is observed for formulations 1–3 samples for which the maximum density is achieved with a molding pressure of 100 MPa. Sample compositions 4 and 5 show the highest density value is already at a molding pressure of 75 MPa, wherein the further increase in pressure led to a decrease in density. With increasing concentration of n-Si_3N_4 (formulations 6–10) the maximum density is achieved with a molding pressure of 50 MPa. The highest density of the material at 75 % n-Si3N4 and 10 % micron-Si_3N_4 (Figure 1). Thus, it can be concluded that the nanoscale powder is not only increases the density of the sintered samples, but also intensifies the process of particle compaction.

An important parameter in the design of composite materials is porosity, which value is considerably affect the mechanical properties (see Table 2).

As seen from Table 2, by increasing the content of n-Si_3N_4 composed of the composite material porosity decreases, which is well supported by data reported for density (Figure 1). Table 2 also shows the dimensions of the grains of silicon nitride. The structure consists of elongated grains, and a

reinforcing material imparting good mechanical properties to it (Figure 2). In the final stage of sintering the structure material is significantly increased content of elongated grains with clear-cut length to diameter ratio different 3÷5.

On the strength of the materials affected by the presence of structural defects (dislocations, impurity atoms pores and microcracks). The presence of the first two types of defects increases the overall strength of the material and reduces its last two. High speed cooling of the plasma during the synthesis of nanoscale silicon nitride particles results in a considerable concentration of lattice defects and, as a result, high activity of the powder. The appearance of significant amounts of edge and screw dislocations due to the kinetic characteristics of the process producing n-Si_3N_4. As shown in Table. 2, the total porosity of the materials based on n-Si_3N_4 does not exceed 2–3 %, resulting materials have a high strength level (Figure 3)

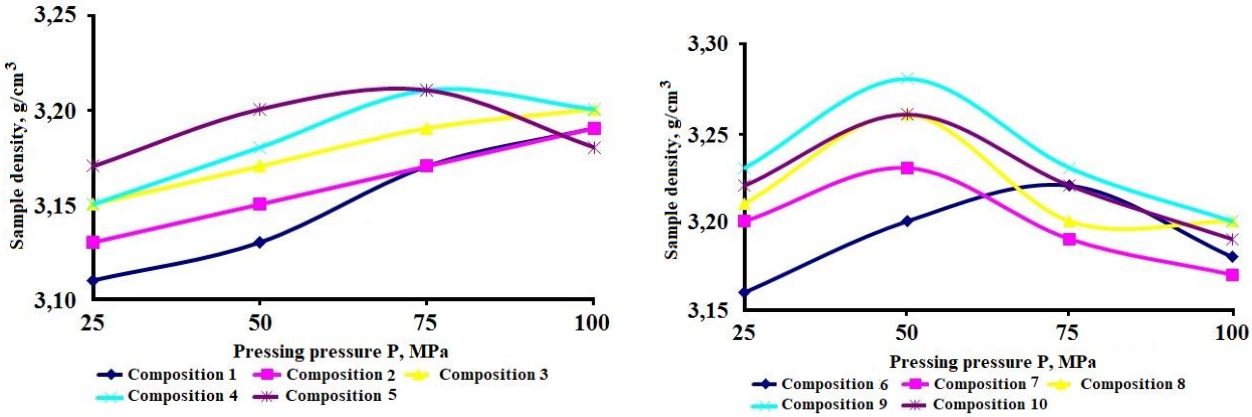

Figure 1. The dependence of the density of the sintered samples of different compositions by molding pressure.

Table 2. The values of porosity and grain size of materials based on silicon nitride.

№ composition	Porosity P (± 0,1),%	The pore size, microns		Grain size d_{max}, μm
		P_{max}	P_{min}	
1	3,5	13,2	1,2	5,1
2	3,3	12,7	1,4	4,7
3	3,1	10,4	1,2	4,8
4	2,5	11,9	1,1	4,4
5	2,6	10,6	0,8	3,9
6	2,1	11,3	1,1	4,0
7	2,0	9,4	1,2	3,1
8	1,8	8,8	1,0	2,9
9	1,4	7,5	0,8	1,8
10	1,1	3,1	0,5	0,3

The module of elasticity of materials is a function of the strength and also depends on the structural defects, i.e. the density and the bulk porosity. The paper [16] studied materials based on n-Si_3N_4 and concluded that by increasing the concentration of nano-sized powder of ceramics density increases.

Virtually all the compositions curves are extreme character with a maximum at the optimal properties of the molding pressure. A trend increase in the modulus of elasticity with increasing content of nano-sized Si_3N_4 powder composed of materials (Figure 4). Since the modulus depends directly on the density, the more denser materials at the maximum amount of n-Si_3N_4, showed a high level of properties (Figure 4).

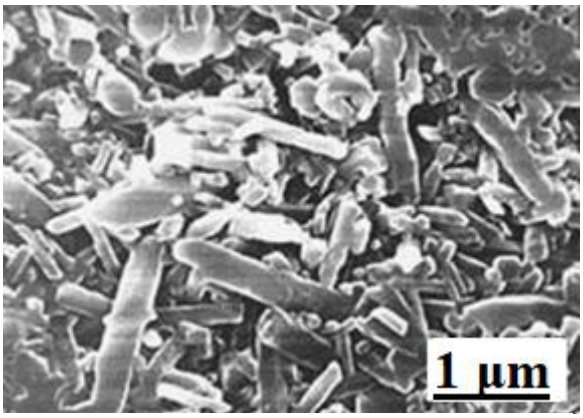

Figure 2. Etched microstructure of the section of the sintered Si_3N_4-material.

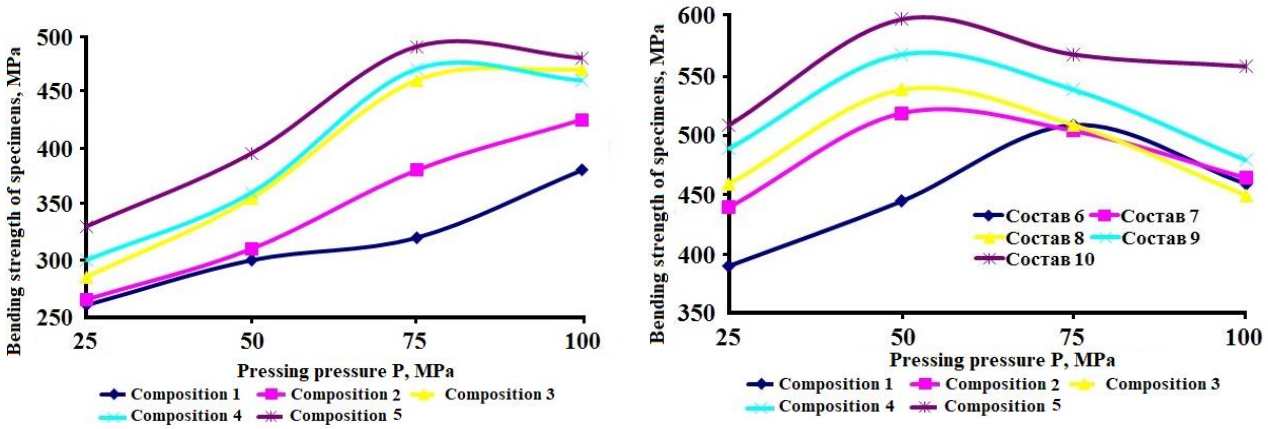

Figure 3. The dependence of the bending strength of samples of different compositions by molding pressure.

An important characteristic of composite materials is the ratio of fracture toughness (K_{1C}) (Fig. 5), which also depends on the density and on the presence of defects in the structure (porosity) in the bulk material. In [17] it is shown that by increasing the density of ceramics based on Si_3N_4 its K_{1C} values increase. Great influence on the mechanical properties of materials has materials based on silicon nitride nature intergranular phase. Since yttrium oxide additive increases the viscosity of the material, and alumina softens it somewhat. The value K_{1C} brittle ceramics can be enhanced by introducing the dispersed second phase inclusions. In [18, 19] has shown that when administered in the ceramics based on silicon nitride, a small amount of TiN increases its fracture toughness ratio of 1,5 times. According to [20, 21], with increasing concentration of n-Si_3N_4 volume percentage of the pores is reduced, thereby reducing the likelihood of local crack propagation and improving the value of K_{1C} (Figure 5). The materials are destroyed in accordance with the intergranular mechanism (destruction of grain bonded).

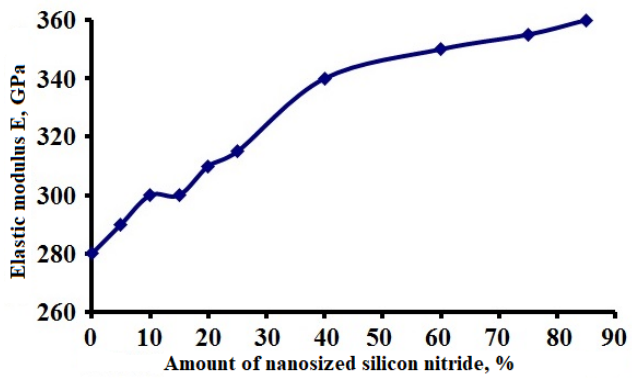

Figure 4. Dependence modulus of elasticity the material of the amount of n-Si_3N_4

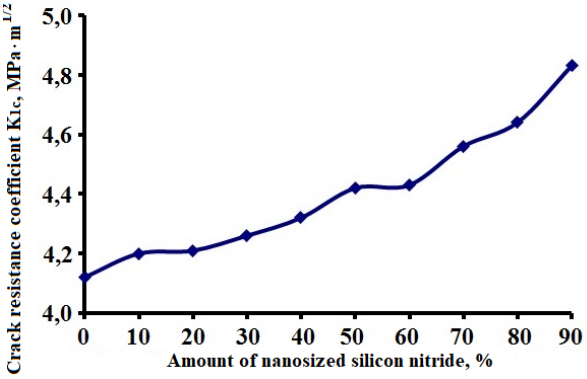

Figure 5. Dependence crack resistance the material of the amount of n-Si_3N_4

According to [22–24], the introduction of whiskers carbide, silicon nitride into the composition of a material based on silicon nitride, significantly increases its strength properties. Daylight α→β-Si_3N_4 grains elongated promotes crystallization, due to which the strength is increased.

The dependence of the compressive strength of the number of silicon nitride powder nano shown in Figure 6. Flexural strength and compressive hot-pressed materials may reach 900–1000 MPa and 1500–1700 MPa [25, 26] that 2,0–2,5 times higher than the strength values of the liquid-phase-sintered ceramics of micron powders. In this paper were obtained by liquid phase sintering materials based on n-Si_3N_4 with properties σ_b = 600 ±15 MPa; σ = 1720 ±20 MPa.

For test materials, the Vickers hardness is slightly lower than for ceramic based powders micrometer Si_3N_4 (Figure 7). Hardness heterophase materials is determined by the method of additive between the hardness phases within them. During sintering Si_3N_4 particles partly dissolve into the oxide bonded, forming a "Sialon" phase, reducing the overall hardness of the material.

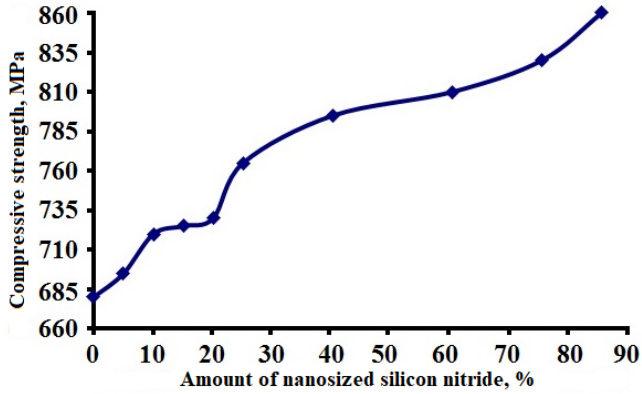

Figure 6. The dependence of the compressive strength materials from amount of n-Si_3N_4.

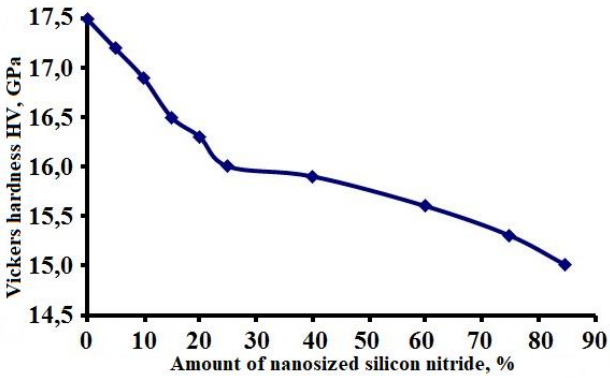

Figure 7. Dependence of Vickers hardness materials on the amount of n-Si_3N_4.

Thus, using a liquid-phase sintering of silicon nitride, the method was able to obtain materials with a sufficiently high level of mechanical properties that allow to recommend it for use in various fields of industry – in the production of sliding bearings, balls for rolling bearings, end seals for centrifugal pumps, of the cutting tool, abrasive nozzles, turbine blades and refractory products.

4. Conclusion

Obtained a high-density material (ρ = 3,28 g/cm^3) based nonorazmernogo silicon nitride powder by liquid phase sintering. The process of pattern formation material during sintering, as well as physical and mechanical characteristics. Maximum properties obtained at high material (85%) content of

nanoscale silicon nitride: ρ = 3,20 ± 0,02 g/cm^3; P = 1,1±0,1%; E = 320±10 GPa; σb = 600±15 MPa; σ = 1720±20 GPa; K_{1C} = 4,8 ± 0,1 MPa·m$^{1/2}$; HV = 15,2 ± 0,1 GPa. Maximum properties in materials based on nanoscale powders are obtained at the optimal (50–75 MPa) pressure molding.

Acknowledgments
This work was supported by RNF (Grant № 18–79–00246 «Investigation of the effect of various additives on the complex dielectric and mechanical properties, and kinetics of liquid phase sintering advanced ceramic materials based on silicon nitride»).

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