Silicon nitride ceramics with light-melting sintering additive in CaO-TiO2 system

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Abstract. The aim of this work was to obtain Si3N4/SiC composites, where silicon nitride served as the matrix, and the silicon carbide content varied from 3 to 50 wt.%. To reduce the sintering temperature (hot pressing) of the ceramic, it is used a sintering additive of calcium aluminate eutectic. The charge was prepared as follows: the silicon nitride powder was mixed with 10 wt.% sintering calcium aluminates, then the charge was added over 100 % of silicon carbide in an amount of 3, 5, 7, 10, 15, 20 and 50 wt.% in a planetary mill. Ceramic materials were hot pressed at 1660°C, the pressure was 30 MPa for 60 minutes in N2 atmosphere. The 10 wt.% SiC composite has highest properties: 3.16 g/cm3 density, 650 MPa bending strength, 22 GPa microhardness.

1. Introduction

Different types of structural ceramics compete with each other. In the case of silicon nitride for ball bearings, its combination of properties gives advantages over others. Silicon nitride has a unique combination of properties: high wear resistance, low density, low weight, wide operating temperature range, high resistance to oxidation or corrosion. This complex of properties allows to use silicon nitride products in many industries ranging from agriculture to electronics and aerospace [1-4].

Structural ceramics ensures the fulfillment of strict requirements that are imposed in the engineering, medical, environmental and manufacturing industries. Direct replacement of metal parts for ceramic is increasingly common in industry due to ceramics outstanding properties. Of course, ceramic products have several disadvantages due to the fragility and problems of fastening or mounting on the support. It is often necessary to consider various aspects of the system as a whole. Industrial ceramics cannot be welded or bolted to the right place, ceramics require more complex and careful fastening systems. Ceramics are highly heat resistant and hard due to these properties, engineers prefer ceramics with
metals and polymers. The competition between these types of materials continues with varying success. There are a number of examples when ceramic products are replaced with metal ones, often for reasons of cheapness.

There is a search for ways to reduce the final cost of products made of silicon nitride ceramics continues. One of the ways to reduce costs is the use of sintering additives with a lower melting point than those have used in industry analogues. However, a decrease in sintering temperature may lead to a decrease in the main material properties. It is necessary to develop a sintering additive, one will reduce the sintering temperature up to 150-200°C while the properties of the resulting ceramics will not change.

The preparation of full density Si$_3$N$_4$ ceramics is difficult due to the high dissociation during sintering. Therefore, to obtain full density silicon nitride ceramic, additives are needed. It is contributed to the compaction of samples at below the temperature which silicon nitride starts to dissociate. Most often, alumina, yttrium and magnesium oxides, and their mixtures are used to densify the ceramics [5]. Unfortunately, the use of above refractory oxides increases the cost of the final products due to the high sintering temperature.

The studies were carried out to obtain low-melting sodium and yttrium oxides for the synthesis of dense and durable ceramics based on silicon nitride at 1600-1700°C [6, 7]. We have also previously conducted studies on the use of a sintering additive in the CaO-Al$_2$O$_3$ system of eutectic composition with a melting point of 1597°C [8]. The materials obtained had high strength characteristics: relative density up to 98%, bending strength up to 850 MPa at room temperature, bending strength up to 400 MPa at 1400°C, microhardness up to 19 GPa [9].

The aim of this research was to study the effect of a low-melting sintering additive of CaO-TiO$_2$ eutectic composition system (a melting point of 1454°C) and to analyze the properties of silicon nitride ceramics.

2. Results and discussion

The commercially available silicon nitride powder («Plasmotherm» LLC) is represented by well-crystallized fibrous particles of silicon nitride. An average size is about 3-4 µm in length and up to 200 nm thick (Figure 1). The powder contented α-Si$_3$N$_4$ ≥ 95 % and specific surface is 9.2 m$^2$/g.

![Figure 1. SEM micrographs α-Si$_3$N$_4$ powder](image-url)
Sintering additive was prepared by sol-gel method of calculating 25 mol% CaO : 75 mol% TiO$_2$ (Figure 2). Tetraethoxide (C$_2$H$_5$O)$_4$Ti (> 98% Merck), isopropyl, ethyl alcohols and mineral acids were used to prepare the sol.

The calculated amount of calcium oxide was introduced into the sol in the form of acidic solutions of calcium salts (chlorides or nitrates). The temperature of the additive synthesis was determined by DTA (STA 409 Luxx with mass spectrometer QMS 403 C Aëolos by Netzsch). The synthesis temperature additive lies in the range of 870-900°C (Figure 3).

Si$_3$N$_4$ powder was introduced into the liquid sol with vigorous stirring on the basis of a given amount of sintering additive (7 and 10 wt.%). Gelation of a sol containing hydrated CaO – TiO$_2$ particles on silicon nitride powders was carried out in air, and the gels in the resulting mixtures were aged at room temperature. The removal of tetraethoxytitanium hydrolysis and calcium salts from a mixed sol, deposited on Si$_3$N$_4$ (water, alcohols and acids) was carried out by heat treatment in a muffle furnace at
900°C. In this case, the synthesized additive is evenly distributed over the volume of the charge. The additive grain size is 50-120 nm (Figure 4).

![SEM micrographs of α-Si3N4 and sintering additive powder mix](image)

**Figure 4.** SEM micrographs of α-Si3N4 and sintering additive powder mix

Samples from the resulting mixture were molded blanks in the form of cylinders. The molding was performed by cold uniaxial two-sided pressing in a steel mold at 100 MPa with 3 wt.% addition of 10% aqueous solution of polyvinylpyrrolidone.

Ceramic materials were hot pressed at 1500-1600°C, a pressure was 30 MPa, for 60 minutes long in an N₂ atmosphere.

For dense ceramics used hot pressing furnace Thermal Technology Inc. high temperature experts, model HP20-3560-20. To identify the phase and chemical composition were used X-ray diffraction analysis (XRD 6000 SHIMADZU diffractometer, CuKα radiation, λ = 1.5406 Å, scanning speed 20 = 2 deg/min). The samples phase composition was identified using the PDF-2 database, JCPDS-ICDD (Set 1-2002). The surfaces of the samples were studied on a Tescan Vega II SBU scanning electron microscope with an embedded INCA Energy X-ray microanalysis system (SEM). The conductive coating (gold) application was performed using a Q150R Quorum Technologies sputtering unit. Density was measured by the Archimedes method in water. The flexural strength three bending test were studied by Intron 5581 test machine. The microhardness test was studied by Micro-hardness Tester 401/402 MVD.

The best properties had samples with 10 wt.% sintered at 1600°C. Mechanical strength was 350 MPa, density 3.06 g/cm³, microhardness 17.4 GPa.
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