Construction ceramics from silicon nitride with calcium aluminates additives received by the sintering method in the SHS-reactor

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Abstract. The paper considers preparation of a strong and dense ceramics based on silicon nitride by sintering in a SHS reactor. As a sintering agent, an additive was used in the Al₂O₃-CaO system. The content of the additive varied from 5 to 15 wt. %. It is established that an increase in the amount of silicon introduced into the initial charge increases the strength characteristics of the material due to the formation of secondary silicon nitride during sintering.

1. Introduction

Silicon nitride is one of the most promising high-temperature materials. Silicon nitride and materials based on it have a high operating temperature up to 1400-1750°C, wear resistance, chemical inertness, high (especially silicon nitride) strength and crack resistance [1, 2]. Therefore, the appearance of these materials made it possible to raise the issue of replacing metal products with ceramic ones for operation in extreme thermomechanical conditions, for example, in the hot zone of gas turbine and piston engines. The replacement of carbide and other types of cutting tools with a more efficient ceramic tool continues, ceramics favorably differs from them, for example, in the field of processing of cast iron or superalloys. Currently research is being conducted to use nitride and silicon carbide products in virtually all industries in developed countries. They have already found wide application in aerospace, metallurgy, chemical, electronic and other industries [3, 4].

There are several methods for obtaining ceramics from silicon nitride: firing in a nitrogen medium without applying pressure, reaction sintering, hot pressing (GP), hot isostatic sintering (HIP). The listed methods are the most applicable in industry. High properties are obtained from the materials synthesized by the latter two methods, however, the high energy intensity and the impossibility of obtaining blanks of complex shapes, as well as the use of high-density and expensive graphite as a press tool, makes it possible to obtain Si₃N₄ ceramic. It is impossible to obtain dense materials with a porosity of less than 5 vol. % by the method of reaction sintering. The chemical deposition method
from the gas phase leads to the practically theoretical density production. However, their mass production is difficult because of technological difficulties [5].

In this work, a different method of calcination was used. Ceramic blanks were sintered in the process of self-propagating high-temperature synthesis (SHS). The SHS method is based on the fact that the heat released by the exothermic reaction, due to energy transfer, heats the substance neighboring layers, excites the reaction in them and leads to self-propagating combustion process occurrence. This method has not found wide application in the production of silicon nitride products yet, but it has prospects for implementation. Previously, ceramic materials based on silicon nitride in the firing mode of SHS were obtained [6]. Yttrium-aluminum garnet and mullite were used as sintering additives. In this paper, calcium aluminate was used as a sintering additive, which had already been used to produce nitride-silicon ceramics [7]. The aim of the work was obtaining a durable, strong silicon nitride ceramic with the calcium aluminate addition by firing in SHS reactor and studying the physicochemical and mechanical properties of sintered materials.

2. Materials and Method

Silicon nitride and aluminum nitride powders had been obtained by self-propagating high-temperature synthesis (SHS) (ISMAN RAS) and were used as starting materials. The well crystallized fibrous Si$_3$N$_4$ powder was obtained by the SHS method. An average size at a length was about 2 μm and a thickness up to 200 nm after grinding in a planetary mill (Figure 1). The content of α-silicon nitride was not less than 95%, the specific surface area of the powder was 8.2 m$^2$/g.

The sintering additive (eutectic composition 33.5 wt.% CaO + 66.5 wt.% Al$_2$O$_3$) was selected on the basis of phase equilibrium data in the Al$_2$O$_3$-CaO system (Figure 2). It was used commercially powders Al(OH)$_3$ («Labteh») and CaCO$_3$ («Labteh») to synthesise the sintering additive. The powders were mixed in a planetary mill with zirconium oxide balls in an alcohol medium (mass ratio material: balls = 1:5), the resulting powder was dried and wiped through 0.063 mm sieve cells). The mixture was calcined at 1200°C for two hours to obtain the desired phase composition additive. The additive was disaggregated in a planetary mill in acetone medium for 30 minutes after synthesis. According to X-ray the synthesis of calcium aluminate supplements does not go completely under these conditions. There are the Ca$_{12}$Al$_{11}$O$_{33}$ phase presented in addition to the main phases of CaAl$_2$O$_4$ and CaAl$_4$O$_7$. Therefore the additional heat treatment was carried out for 4 hours, it ensures the production of the required composition eutectic mixture (Figure 3). The commercially available technical silicon powder KR00 was used in the experiments (GOST 2169-69).

The silicon nitride, silicon and sintering additive (7, 10 and 15 wt.%) were mixing in a planetary mill. The 15 and 30 wt.% elemental silicon were introduced into the starting charge over the 100 wt.%. The introduction of elemental silicon is associated with partial reaction sintering due to the resulting material (secondary silicon nitride) increases in volume and fills internal pores [9].
Figure 2. Diagram of the CaO-Al$_2$O$_3$ system.

Figure 3. XRD patterns and SEM micrograph of CaO-Al$_2$O$_3$ powder

The samples formed in 50x5x5 mm balks and 70x20x5 mm plates by the semi-dry uniaxial two-sided pressing method. The balks were placed inside the charge in the SHS reactor along the combustion front (Figure 4). The ratio of the fill components was 45:55 (Si-$\beta$-Si$_3$N$_4$). The weight of the backfill was 5 kg. Samples were heated to 1900°C for 120 seconds in the SHS reactor, the holding time at this temperature was approximately 150 seconds, then the reactor was cooled. The entire process from samples loading to extraction was about 2 hours.
Figure 4. Location of samples in the SHS reactor

The X-ray diffraction analysis was used to identify a phase of the chemical composition (XRD 6000 SHIMADZU diffractometer, CuKα radiation, λ = 1.5406 Å, scanning speed 2θ = 2 deg/min). The phase was identified using the PDF-2 database, JCPDS-ICDD (Set 1-2002). The microstructure and phase composition were examined on an electron microscope (Supra 50 VP (LEO, Germany) with an INCA Energy + Oxford microanalysis system with a prefix for local X-ray spectroscopy). Density was measured by the Archimedes method using water. The flexural strength three bending test were studied by Instron 5581.

3. Results and discussion
The structure and ceramic properties of these samples were studied after sintering. Preliminary studies were carried out on silicon nitride with a different calcium aluminate concentration without silicon addition. The samples were porous and a low density (Table 1). The balks with 7 wt.% sintering additive composition had 26.5% open porosity. In view of this, up to 30 wt.% Si was added to the starting charge. It was noted above, addition 30 wt.% Si into the starting charge led to reduce the closed porosity and increased the grain size due to the secondary silicon nitride formation.

As can be seen in Table 1, the silicon addition reduces the number of closed pores, increased density and bending strength up to 540 MPa.

Table 1. The starting compositions, sintering parameters, density, open porosity and flexural strength of the Si$_3$N$_4$ ceramics

| Samples     | Composition, wt. % | Sintering parameters (°C/sec) | Density (g/cm$^3$) | Open porosity (%) | Flexural strength (MPa) |
|-------------|--------------------|-------------------------------|-------------------|------------------|------------------------|
|             | Si$_3$N$_4$ | Al$_2$O$_3$-CaO | *Si | * |                             |                          |
| SHS-1       | 93 | 7 | - | 1900/150 | 2.49 | 26.58 | 123 |
| SHS-2       | 90 | 10 | - | 1900/150 | 2.55 | 19.87 | 245 |
| SHS-3       | 85 | 15 | - | 1900/150 | 2.62 | 10.75 | 366 |
| SHS-Si-1    | 93 | 7 | 30 | 1900/150 | 2.93 | 5.97 | 195 |
| SHS-Si-2    | 90 | 10 | 30 | 1900/150 | 2.99 | 3.26 | 510 |
| SHS-Si-3    | 85 | 15 | 30 | 1900/150 | 3.05 | 2.78 | 540 |

*over 100 wt. %
4. Conclusion
Thus, a ceramics based on silicon nitride with a different calcium aluminate concentration (sintering additive) was obtained using the firing method in low-pressure reactor SHS (SHS-30). The ceramics properties with 15 wt.% sintering additive (without the introduction of silicon): flexural strength up to 350 MPa and density of 3.03 g/cm$^3$ at room temperature. The best properties were flexural strength up to 540 MPa and density of 3.09 g/cm$^3$ at room temperature ceramics based on silicon nitride with 15 wt.% calcium aluminates and by adding 30% Si with the following properties.

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