Si$_3$N$_4$ ceramics with sintering additive of MnO-TiO$_2$

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Abstract. Ceramic samples based on Si$_3$N$_4$ were obtained and studied using a sintering additive in the MnO-TiO$_2$ system of eutectic composition, which was accepted and applied to the surface of silicon nitride by the sol-gel method. Ceramic samples were obtained by hot pressing at 1650 °C and 1750 °C. Phase composition, thermo-physical and mechanical properties were studied. The microstructure of the resulting ceramics was also studied.

1. Introduction
Usage of ceramic materials for structural parts manufacture is becoming more popular. The advantages of ceramics over analogues (metals, polymers) are a wide range of types of ceramics and properties they have. Largely, ceramics properties depend on the types of additives and methods of preparation, sintering and compaction only in the presence of sintering additives in the case of high-temperature kinds of ceramics.

It is known that the silicon nitride compound has a predominantly covalent type of bond, which makes this material resistant to thermal, mechanical shock and corrosive environments. The presence of covalent bonds also indicates the difficulty of obtaining silicon nitride ceramics, which is high sintering temperatures (over 2000 °C). To solve this problem, various sintering additives are used based on metal oxides of the eutectic composition Y$_2$O$_3$-Al$_2$O$_3$, MgO, MgO-Y$_2$O$_3$-Al$_2$O$_3$, etc., depending on the type of additive [1-4]. Kargin et al. [5] investigated the effect of the eutectic sintering additive CaO-Al$_2$O$_3$-AlN on silicon nitride ceramics; it was found that the onset sintering temperature is 1375 °C with the addition of 10 wt. % of the sintering additive. Lysenkov et al. also studied low-melting sintering additives of the CaO-TiO$_2$ and CaO-Al$_2$O$_3$ compositions for Si$_3$N$_4$ ceramics obtaining. The sintering temperature was 1600-1650 °C by hot pressing [6-8].

In this research, ceramic samples based on silicon nitride with sintering addition MnO-TiO$_2$ were obtained and studied. Processes of liquid phase sintering condition the choice of sintering additive MnO-TiO$_2$. These processes provide the complete compaction and sintering at lower temperatures. Moreover, using additive have a lower melting temperature comparing the mentioned analogues.

2. Experiment

2.1. Raw materials
For receiving ceramic samples, raw powders were used: commercial alpha-phase silicon nitride (Plasmotherm) with a particle size up to 2 μm, sintering additive MnO-TiO$_2$ (TiO$_2$ 64,5 wt. % - MnO 35,5 wt. %) with eutectic melting 1290 °C (Figure 1).
Sintering additive MnO-TiO₂ was obtained and inflicted on the Si₃N₄ grain surface by the sol-gel method. The total quantity of sintering additive MnO-TiO₂ was 7 wt.%. The obtained mixture has been heated treated at a temperature of 80 °C for 2 hours. The dried powder was pre-granulated and formed at a load pressure of 30 MPa.

To get dense ceramics used hot pressing furnace Thermal Technology Inc. high-temperature experts, model HP20-3560-20. Continuous shrinkage measurement was performed by a dilatometer (NETZSCH DIL 402 C/7 up to a temperature of 2000°C). To identify the phase and chemical composition was used, X-ray diffraction analysis was used (XRD DRON-3 diffractometer, CoKα radiation, λ = 1.79020 Å, scanning speed 2θ = 2 deg/min). The phase composition was identified using COD database [10, 11]. Morphology and the samples’ structural features were studied by scanning electron microscopy (SEM) (electron microscope Tescan Vega II SBU). Density and open porosity were measured by the Archimedes method using water. The flexural strength three bending tests were studied by Instron 5581. The microhardness test was investigated by Micro-hardness Tester 401/402 MVD.

2.2. Dilatometry
Dilatometric analysis of the sample of Si₃N₄ with MnO-TiO₂ was carried out and optimal firing mode, initiate sintering temperature was determined 1569 °C. The sintering curve of Si₃N₄ with MnO-TiO₂ ceramic is in figure 2. Following the results obtained, ceramics were obtained by hot pressing at a temperature of 1650 °C at a pressure of 30 MPa and isothermal holding for 1 hour. To study the behavior of the components and the properties of the ceramics, samples were also obtained at a higher temperature of 1750 °C.
Figure 2. Sintering curve of Si$_3$N$_4$-7\%MnO-TiO$_2$ ceramic.

2.3. Mechanical properties

Table 1 shows the properties of ceramic samples 1650 °C and 1750 °C. The resulting ceramics have 70\% and 67\% relative density. This is due to the presence of organic phases. Presence of organic phases because of the sol-gel obtaining method of raw powders. It is assumed that to increase the samples' density, the powder's preliminary heat treatment is required to remove organic substances.

Table 1. Properties of ceramic samples Si$_3$N$_4$ with 7 wt.\% MnO-TiO$_2$.

| Temperature, °C | Density, g/cm$^3$ | Hardness HV, GPa | Strength, MPa |
|-----------------|-------------------|------------------|---------------|
| 1650            | 2.46 (70 \%)      | 2.87±0.4         | 130±26        |
| 1750            | 2.34 (67 \%)      | 2.27±0.6         | 82±24         |

2.4. XRD

On figure 3 are XRDs of ceramic samples 1650 °C and 1750 °C. In the case of 1650 °C ceramic, the presence of residual oxide phases MnO and TiO$_2$ was revealed, however, oxide phases interact with Si3N4 more intensively and thoroughly with the formation of complex nitride compounds (Ti$_{0.75}$Si$_{0.25}$)N and (Ti$_{0.6}$Mn$_{0.4}$)N during temperature increase up to 1750 °C.
Figure 3. XRD of ceramic samples obtained 1650 °C and 1750 °C.

2.5. SEM
Figure 4 shows SEM captures of ceramics microstructures. The coarse fraction corresponds to the silicon nitride phase with 1-3 µm. The additive grains are smaller, about 100 nm.

Figure 4. SEM captures of ceramics: a – Si₃N₄ with 7 wt.% MnO-TiO₂ (1650 °C), b – Si₃N₄ with 7 wt.% MnO-TiO₂ (1750 °C).
3. Conclusions
Ceramic samples based on Si$_3$N$_4$ with the addition of sintering additive in the eutectic system of MnO-TiO$_2$ were obtained using sol-gel synthesis in the concentration of 7 wt. %. Sintering was carried out by the hot-pressing method. It was established that ceramic obtained at 1650 °C contains residual oxides of manganese and titanium as sintering additive. Simultaneously, during temperature increase up to 1750 °C sintering additive fully interacts with silicon nitride to form compounds (Ti$_{0.75}$Si$_{0.25}$)N and (Ti$_{0.6}$Mn$_{0.4}$)N. All samples had low relative density of 70 % approximately. This is due to obtaining and applying the MnO-TiO$_2$ additive by the method of sol-gel synthesis, where organic substances were used. During firing, pyrolysis occurs with the formation of gases; due to this process, the density decreases and pores are formed in the ceramic volume. It is planned to carry out the preliminary firing of the original powder to increase ceramics' density.

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