Composite material Si$_3$N$_4$/SiC with calcium aluminate additive

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Abstract. The aim of this work was to obtain Si$_3$N$_4$/SiC composites, where silicon nitride served as the matrix, and the silicon carbide content varied from 3 to 50 % by weight. To reduce the sintering temperature (hot pressing) of the ceramic, a sintering additive of calcium aluminate eutectic. The charge was prepared as follows. The silicon nitride powder was mixed with 10 wt.% sintering calcium aluminate. Then the charge was added over 100 % of silicon carbide in amount of 3, 5, 7, 10, 15, 20 and 50 % by weight in a planetary mill. Ceramic materials were obtained by hot pressing at a temperature of 1660°C, a pressure of 30 MPa, for 60 minutes in an atmosphere of N$_2$. The highest properties were achieved on the material with 10 wt.% SiC: density of 3.16 g/cm$^3$, bending strength 650 MPa, microhardness 22 GPa.

1. Introduction

Among all the high-temperature ceramic materials, Si$_3$N$_4$/SiC composite ceramic has received great attention due to their high mechanical properties, termo-stability, tribological properties, especially because of high toughness, heat conductivity, thermostat and low coefficient of linear expansion (CLE). This composite saved it mechanical properties up to high temperature ($\geq 1500^\circ$C), it is of great interest for various fields of engineering applications [1, 2]. The most valuable properties of silicon carbide and nitride are due to these materials are dominated by a covalent bond type, and materials are characterized by low self-diffusion coefficients, which leads to low compaction of ceramics on their basis. The sintering additives are used for a good compaction of materials based on nitride and silicon carbide [3-5]. There is a large group of composites based on Si$_3$N$_4$ or SiC with reinforcing additive, which improved properties: hardness, thermal conductivity, bending strength and fracture toughness [6-8]. Silicon carbide has a lower resistance to molten salts and metals than silicon nitride [9]. It is possible to obtain materials capable of operating in oxidizing media at temperatures 1750-1950 K using SiC-Si$_3$N$_4$ composites [10]. Such additives improve both mechanical properties, resistance to chemically aggressive media and electrical conductivity, it makes it possible to use them as abrasives, wear-resistant refractories and thermistors. The most usual used additives are a mixture of alumina and yttrium oxide in a ratio of 3:2 corresponding to the composition with the lowest...
eutectic melting point in $Y_2O_3$-$Al_2O_3$ system (1826°C) [11-15]. It allows the sintering of SiC-based materials in the high-temperature furnace with a slight overheating of the oxides to increase their fluidity at a temperature of 1930°C.

There are known works on the creation of Si$_3$N$_4$/SiC composite materials. The SiC and Si$_3$N$_4$ industrial powders from different manufacturers were used as the starting materials in [16]. The SiC: Si$_3$N$_4$ ratio was 70:30 mol%. The authors increased the ceramics crack resistance from 3.5 to 6 MPa*m$^{-1}$ by introducing 30 mol% Si$_3$N$_4$ into SiC matrix. Samples were obtained by HP at a temperature of $T = 1810^0$C.

Works are known where Si$_3$N$_4$ is the matrix. It was shown Si$_3$N$_4$ (66.7 vol%)-SiC (27.5 vol%)-Al$_2$O$_3$-Y$_2$O$_3$ (2.3 vol%) the material obtained by hot pressing at $T=1820^0$C had the following properties: density 3.23 g/cm$^3$, bending strength 661.3 MPa, Vickers hardness 1810 HV, crack resistance 4.4 MPa*m$^{-1}$ [17].

The aim of this research was to obtain Si$_3$N$_4$/SiC composites, where silicon nitride acted as a matrix and the silicon carbide content varied from 3 to 50 wt. %.

2. Materials and Method

The commercially available silicon nitride powder (Plasmotherm LLC) (Figure 1a), industrial silicon carbide powder (Volzhsky Abrasive Plant LLC) (Figure 1b) was used as a starting component.

A sintering additive of calcium aluminate eutectic composition with a melting point of 1600°C was used to reduce the sintering temperature (hot pressing) of the ceramic [18].

The sintering additive (eutectic composition 33.5% by weight CaO + 66.5% by weight Al$_2$O$_3$) was prepared by the solid-phase synthesis method from the Al(OH)$_3$ (chemically pure grade) and CaCO$_3$ (chemically pure grade) (Figure 1c) [19].

The charge was prepared as follows. Silicon nitride powder was mixed with 10 wt.% calcium aluminate sintering additives, then silicon carbide was added to the charge in an amount of 3, 5, 7, 10, 15, 20 and 50 wt.% over 100%. The powders were mixed in a planetary mill in isopropyl alcohol medium for 30 minutes, then dried and granulated. Samples were prepared in the form of disks (25 mm diameter) charge by the semi-dry pressing method from the received.

Ceramic materials were obtained by hot pressing at 1650°C, a pressure was 30 MPa, for 60 minutes long in an N$_2$ 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 was used (XRD 6000 SHIMADZU diffractometer, CuK$\alpha$ radiation, $\lambda = 1.5406$ Å, scanning speed 20 = 2 deg/min). The phase composition of the samples was identified using the PDF-2 database, JCPDS-ICDD (Set 1-2002). Morphology and structural features of the samples were studied by scanning electron microscopy (electron microscope NVision 40, Carl Zeiss). Density was measured by the Archimedes method using water. The flexural strength three bending test were studied by Instron 5581. The microhardness test was studied by Micro-hardness Tester 401/402 MVD.
3. Results and discussion

The samples structure and properties were studied after sintering.

Preliminary studies were carried out on silicon nitride with 10 wt.% sintering additives of the chosen composition without the silicon carbide addition samples. As a result of the silicon nitride and calcium aluminates interaction Ca-sialon is obtained [18, 19]. The samples were dense, the bending strength was 450 MPa, the microhardness 19 GPa (table 1). The introduction of silicon carbide up to 10 wt. % in the charge leads to an increase in the density (3.16 g/cm³) and the mechanical properties of the ceramic (bending strength 650 MPa, microhardness 22 GPa). This is due to the silicon nitride crystals have a defective structure, so they are poorly compacted during the sintering process. Crystals of silicon carbide serve as a finely dispersed filler in the silicon nitride matrix and lead to the compaction of the material. With an increase in the content of silicon carbide more than 10 wt.% density and mechanical properties begin to decrease, this indicates that the resulting intergranular Ca-sialon phase is not sufficient to compact the resulting ceramic. Density and mechanical properties
decrease due to an increase in the silicon carbide concentration more than 10 wt.%. This suggests that the resulting intergranular Ca-sialon phase is not sufficient to compact the resulting ceramic.

**Table 1.** The starting compositions, sintering parameters, density, microhardness and flexural strength of the Si$_3$N$_4$/SiC ceramics.

| Samples   | Composition, wt.% | Sintering parameters (°C/min) | Density (g/cm$^3$) | Microhardness (GPa) | Flexural strength (MPa) |
|-----------|-------------------|-------------------------------|-------------------|-------------------|-------------------------|
| SiSINC-0  | Si$_3$N$_4$:90, Al$_2$O$_3$-CaO:10, SiC:0 | 1660/60                      | 3.10              | 19.0              | 450                     |
| SiSINC-5  | Si$_3$N$_4$:90, Al$_2$O$_3$-CaO:10, SiC:5  | 1660/60                      | 3.13              | 20.5              | 565                     |
| SiSINC-10 | Si$_3$N$_4$:90, Al$_2$O$_3$-CaO:10, SiC:10 | 1660/60                      | 3.16              | 22                | 650                     |
| SiSINC-20 | Si$_3$N$_4$:90, Al$_2$O$_3$-CaO:10, SiC:20 | 1660/60                      | 2.98              | 19.3              | 490                     |
| SiSINC-30 | Si$_3$N$_4$:90, Al$_2$O$_3$-CaO:10, SiC:30 | 1660/60                      | 2.76              | 16.2              | 370                     |
| SiSINC-50 | Si$_3$N$_4$:90, Al$_2$O$_3$-CaO:10, SiC:50 | 1660/60                      | 2.62              | 15.9              | 330                     |

*over 100 wt. %

Crystalline phases of these Si$_3$N$_4$/SiC ceramics were examined using XRD (Figure 2). The crystalline phases at 1660°C were SiC (JCPDS Card No. 42-1360), β-Si$_3$N$_4$ (JCPDS Card No. 33-1160), tetragonal phase Si$_3$N$_4$ (JCPDS Card No. 40-1129).

![Figure 2. XRD patterns of Si$_3$N$_4$/SiC ceramics](image)

4. Conclusion
The aim of the research was increase in the mechanical properties of silicon nitride (Si$_3$N$_4$)-silicon carbide (SiC) composite. The first part of the research was devoted to silicon nitride powder mixture with 10 wt.% calcium aluminates sintering additive. The second was to obtain composite with addition over 100% silicon carbide into the charge in an amount of 3-50 wt.%. Ceramic materials were obtained by hot pressing at 1660°C, 30 MPa pressure, for 60 minutes in N$_2$ atmosphere. The highest
properties were achieved on the material with 10 wt.% SiC: density of 3.16 g/cm³, bending strength 650 MPa, microhardness 22 GPa.

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5. References

[1] Shevchenko V Ya and Barinov S M 1986 Technical ceramics (Moscow: Metallurgiya) p 277
[2] Garshin A P, Gropyanov V M, Zaytsev G P and Semyonov S S 2003 Ceramics for mechanical engineering (Moscow: Nauchtekhlitizdat) p 384
[3] Tatarko P, Kašiarová M, Dusza J, Šajgalík P 2013 Journal of the European Ceramic Society 12 2259
[4] Perevislov S N and Nesmelov D D 2016 Glass and Ceramics 7-8 249
[5] Perevislov S N 2013 Glass and Ceramics 7-8 265
[6] Endo H, Ueki M, Kubo H 1991 Journal of Materials Science 26 3769
[7] Kyeong-Sik C, Young-Wook K, Heon-Jin C, June-Gunn L 1996 Journal of Materials Science 31 6223
[8] Kornaus K, Grabowski G, Raczka M, Zientara D, Gubernat A 2017 Processing and Application of Ceramics 4 329
[9] Samsonov G V 1976 Refractory compounds. Directory (Moscow: Metallurgiya) p 560
[10] Probst H B 1980 American Ceramic Society Bulletin 2 205
[11] Perevislov S N, Lysenkov A S, Titov D D, Tomkovich M V 2017 Inorganic Materials 2 220
[12] Santos C, Ribeiro S, Strecker K, Suzuki P A, Kycia S, Silva C R M 2009 Ceramics International 1 289
[13] Kim J-S, Schubert H, Petzow G 1989 Journal of the European Ceramic Society 5 311
[14] Samanta A K, Dhargupta K K, De A K, Ghatak S 2000 Ceramics International 8 831
[15] Candelario V M, Nieto M I, Guiberteau F, Moreno R, Ortiz A L 2013 Journal of the European Ceramic Society 10 1685
[16] Klimešzyk P, Jaworska L, Urbanovich V 2011 Acta Metallurgica Slovaca 2 90
[17] Blugan G, Hadad M, Graule T, Kuebler J 2014 Ceramics International 40 1439
[18] Kargin Yu F, Lysenkov A S, Ivicheva S N, Solntsev K A, Zakharov A I., Popova N A 2010 Inorganic Materials 7 799
[19] Lysenkov A S, Kargin Yu F, Titov D D, Petrakova N V, Ivicheva S N, Zakharov A I, Popova N A, Zakorzhvskii V V, Borovinskaya I P and Melnikova I S 2018 IOP Conf. Ser.: Mater. Sci. Eng. 347 012040