Reinforced composite materials based on silicon carbide and silicon nitride

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Abstract. In this work, ceramic materials based on silicon carbide and silicon nitride with an additive were obtained to increase the mechanical and operational properties of fibers and whisker crystals of SiC and Si₃N₄. Studied the basic properties and applications of reinforced materials.

1. Introduction

Dense materials based on silicon carbide is produced by the reaction, liquid phase sintering and hot pressing. Despite the widespread use of methods of manufacturing articles for constructional purposes, each of the methods of producing SiC (Si₃N₄) – materials has both its advantages and disadvantages, which determine their great importance to obtaining products of a wide range of applications.

Reaction-sintered body (imregnation) silicon carbide (SiSiC) the most common form of ceramic materials [1, 2], is prepared by impregnating porous preforms from silicon carbide particles and carbon black technical silicon melt. For SiSiC-keramiki characteristic substantially nonporous structure (P ≤ 0,5 %) material in which main phase grains are silicon carbide primary SiC¹, the phase between them - the secondary carbide SiCII. As a part of the finished product is also present unreacted 5 to 15 % residual silicon. A positive feature of SiSiC-materials is sintering at a relatively low temperature (~ 1600°C) the use of large SiC starting powders, dimensionality stability during sintering. The disadvantages in the material a high content residual silicon, which limits the temperature region of use (Table 1).

A liquid phase-sintered bodies (LPSSiC) obtained by sintering silicon carbide (d₀,5 ≤ 1 μm) with oxide additives (10–20 wt.%) At temperatures 1850–1950°C [3–5]. The resulting materials are more corrosion-resistant and temperature stable (working temperature up to 1450°C in an air atmosphere). However, high temperature sintering, unlike SiSiC and large shrinkage limit number of products manufactured by this method (table 1).

Hot-pressed silicon carbide (HPSiC) and silicon nitride (HPSN) prepared by sintering fine powder α-SiC or β-Si₃N₄ in the presence of small amounts (up to 5 wt.%) of oxides [6, 7]. The resulting material has a higher level of mechanical characteristics (Table 1). The disadvantages of this method
can apply high energy and the inability to obtain articles of complex geometrical shape without additional machining, which limits the industrial manufacture of articles by hot pressing.

Table 1. Physical and mechanical properties and high temperature the ceramic

| Material | $\rho \pm 0.02$ (g/cm$^3$) | $\sigma_{f}^{20} \pm 10$ (MPa) | $\sigma_{f}^{1200} \pm 10$ (MPa) | $\sigma_{comp}^{20} \pm 20$ (MPa) | $K_{IC} \pm 0.2$ (MPa m$^{1/2}$) | $HV \pm 0.2$ (GPa) | Working temperature | Protective atmosphere | Air atmosphere |
|----------|--------------------------|-----------------------------|-----------------------------|-------------------------------|-------------------------------|-----------------|-------------------|-------------------|-----------------|
| SiSiC    | 3.05                     | 400                         | 150                         | 1200                          | 3.5                           | 22              | 1300              | 1200              | 1500            |
| LPSSiC   | 3.20                     | 500                         | 400                         | 2000                          | 5.5                           | 21              | 1600              | 1450              | 1400            |
| HPSiC    | 3.15                     | 750                         | 500                         | 2200                          | 6.5                           | 26              | 1700              | 1500              | 1400            |
| HPSN     | 3.20                     | 900                         | 500                         | 2800                          | 7.5                           | 20              | 1600              | 1400              | 1400            |

$\rho$ – density; $\sigma_{f}^{20}$ – flexural strength, measured at a temperature of 20 °C; $\sigma_{f}^{1200}$ – flexural strength, measured at a temperature of 1200 °C; $\sigma_{comp}^{20}$ – the compressive strength measured at 20 °C; $K_{IC}$ – fracture toughness; $HV$ – Vickers hardness

The purpose is to obtain reinforced structural fibers and whiskers of materials based on SiC and Si$_3$N$_4$ covalent compounds.

2. Materials and Method

The density and porosity of the samples was determined by hydrostatic weighing; Elastic modulus was determined method of measuring the resonant frequency of longitudinal vibrations on the "ZVUK–130"; strength at three-point bending and compression on the installation «Shimadzu AG-300kNX»; Vickers hardness – by pressing into the material of Vickers pyramid, on the hardness installation TR–7r 1; crack resistance coefficient - measuring the length of cracks emanating from Vickers pyramid base. The microstructure was examined using a scanning electron microscope «Quanta 200».

3. The results and discussion

Conventionally, structural materials consisting of covalent compounds reinforced structure can be divided into three types: 1) Reinforced fiber (SiC$_f$) SiSiC-materials; 2) hot-pressed materials based on SiC and Si$_3$N$_4$, reinforced whisker (SiC$_w$ and Si$_3$N$_4w$); 3) Materials based on SiC and Si$_3$N$_4$ advanced samoamirovannoy structure during sintering.

1) randomly distributed fibers SiC$_f$ are in the «SiC–C»-preform, which are impregnated with a silicon melt. The maximum density after impregnation of the porous billet can not be obtained, and in the contact areas SiC$_f$ is the surface porosity (Figure 1). For reinforced SiSiC-materials used fibers SiC, as a continu-ous filament, obtained by pyrolysis polikarbolanovoy thread (Japan) with a diameter $d = 140$ mm, which were crushed to size (length) $l = 0.5–1.0$ mm and introduced into the composition of the feedstock composition SiSiC-material.

With increasing content SiC$_f$ composed material increases its porosity and strength properties are reduced, but fracture toughness value is increased (to 12 vol. % SiC$_f$). With further increase of the content SiC$_f$, due to increased porosity, reduced level of mechanical properties (Table 2).

Figure 1. Microstructures SiSiC-material: a – 4 % vol. SiCf; b – 12 % vol. SiCf
Table 2. Physical-mechanical properties of the reinforced ceramic

| Material | Fibers SiC<sub>f</sub> | Whiskers | ρ ± 0,02 (g/cm<sup>3</sup>) | σ<sub>fl</sub> ± 10 (MPa) | σ<sub>comp</sub> ± 20 (MPa) | K<sub>IC</sub> ± 0,2 (MPa m<sup>1/2</sup>) | HV ± 0,2 (GPa) |
|----------|----------------------|----------|-----------------------------|-------------------------|-------------------------------|-------------------------|----------------|
| SiSiC    | 4 %                  | –        | 2,92                        | 950                     | 2300                          | 8,0                     | 22,0          |
|          | 8 %                  | –        | 2,85                        | 850                     | 2200                          | 7,0                     | 24,0          |
|          | 12 %                 | –        | 3,12                        | 320                     | 900                           | 5,0                     | –             |
|          | – 4 % SiC<sub>W</sub>|          | 3,00                        | 400                     | 1200                          | 4,0                     | 20,0          |
| HPSiC    | – 8 % SiC<sub>W</sub> |          | 3,07                        | 900                     | 2200                          | 7,5                     | 20,5          |
|          | – 12 % SiC<sub>W</sub>|         | 3,20                        | 1000                    | 2800                          | 8,5                     | 19,0          |
|          | – 4 % Si<sub>3</sub>N<sub>4w</sub>|     | 3,15                        | 1100                    | 2800                          | 9,0                     | 18,0          |
|          | – 16 % Si<sub>3</sub>N<sub>4w</sub>|   | 3,05                        | 970                     | 2550                          | 8,2                     | –             |

2) In the hot-pressed materials based on silicon carbide and nitride are introduced up to 25 vol. % SiC<sub>W</sub> and Si<sub>3</sub>N<sub>4w</sub>. Unlike reinforced fibers SiC<sub>f</sub> materials SiSiC hot-pressed materials are formed to a higher density. With increasing quantities SiC<sub>W</sub> and Si<sub>3</sub>N<sub>4w</sub>, increases the level of mechanical properties of materials, despite the slight decrease in density. When administered whiskers > 10 vol. % increased porosity materials and reduced level of mechanical properties (Table 2). The micrographs of the microstructure of whiskers and hot-pressed materials with addition SiC<sub>W</sub> and Si<sub>3</sub>N<sub>4w</sub> shown in Figure 2 and Figure 3.

3) The widespread in the industry as a structural material was sintered silicon nitride. During the sintering process occurs growth of reinforcing structure SSN grains (Figure 4a), which gives increased strength properties of the sintered material [8]. The disadvantage can be considered SSN decrease in hardness compared with LPSSiC-materials. Sintered silicon nitride has been successful as a structural material working in extreme conditions of erosive environments (hot gas streams at elevated temperature – 1400 °C) (Table 3).

![Figure 2. Micrographs whiskers: a – SiC<sub>W</sub>; b – Si<sub>3</sub>N<sub>4w</sub>](image1)

![Figure 3. The microstructure of materials: a – HPSiC+8 vol. % SiC<sub>W</sub>; b – HPSN + 16 vol. % Si<sub>3</sub>N<sub>4w</sub>](image2)
Figure 4. Photomicrographs of materials: a – SSN; b – RSSN

Reaction-sintered (nitrided), silicon nitride (RSSN) obtained sintered material consisting of a composition «Si₃N₄–Si» in N₂ atmosphere at a temperature ≥ 1600 °C. In the process of nitriding, a structure consisting of grains of silicon nitride bonded thin elongated grains Si₃N₄ (analogs whiskers) (Fig. 4b). RSSN-materials are resistant to high temperatures. Reinforced structure during sintering makes it lasting the material up to work to high temperatures (1400 °C) (Table 3). RBSN the advantages include lower sintering temperatures, little shrinkage, the use of coarse raw powders and the possibility of forming large products of complex geometric shape.

Table 3. Physical and mechanical and high-temperature properties of hot-pressed materials

| Material | ρ±0.02 (g/cm³) | σₙ300±10 (MPa) | σₙ1200±10 (MPa) | σₖ₂0±20 (MPa) | Kₑ ±0.2 (MPa·m½) | HV ±0.2 (GPa) | Working temperature | Protective atmosphere | Air atmosphere |
|----------|----------------|----------------|----------------|---------------|-----------------|--------------|-------------------|---------------------|------------------|
| SSN      | 3.18           | 650            | 400            | 1700          | 6.0             | 18           | 1450              | 1350                |                 |
| RSSN     | 2.85           | 300            | 250            | 1300          | 4.5             | 16           | 1600              | 1500                |                 |

Adding to the initial particles consisting of powder α-SiC, a small amount of β-SiC powder leads at a temperature> 1600 °C to activate the growth of elongated grains (Figure 5). Grain growth is carried out by β → α phase transition silicon carbide. The presence of α-SiC powder in the starting material increases the rate of β → α junction, which is fully completion at the extended sintering time (≥ 4 h).

Figure 5. The microstructure of the sintered body 90 wt. % β-SiC + 10 wt. % YAG, at different sintering durations: a – 1 h; b – 8 h

SiC-grain growth speed is determined by particle size of the main phase and the amount of oxides. The growth of elongated grains in the process of β → α phase transition reduces the material strength. Fracture toughness is inversely related to strength (see Table 4). Materials with large grains can be destroyed on the mechanism of grain fracture, thereby defining a high mechanical properties self-reinforcing coarse grain SiC-ceramic.

Materials without the addition of β-SiC has low values $K_{IC}$. The reinforced ceramics crack occurs in contact with an elongated grain encloses it or pass through it, breaking the grain and loses speed, which is characteristic for the mechanism of grain fracture of ceramics [9].
Table 4. Physico-mechanical properties self-reinforcing ceramics based on SiC

| Material   | Contents YAG (wt. %) | Duration of sintering time (h) | $\rho \pm 0.02$ (g/cm$^3$) | $\sigma_{fl} \pm 20$ (MPa) | $K_{IC} \pm 0.2$ (MPa-m$^{1/2}$) |
|------------|----------------------|--------------------------------|-----------------------------|-----------------------------|----------------------------------|
| 5 wt. %    |                      | 1                              | 3.23                        | 505                         | 4.5                              |
| $\alpha$-SiC + | 10                      |                                | 3.20                        | 470                         | 4.8                              |
| 85 wt. %   |                      | 4                              | 3.15                        | 420                         | 5.4                              |
| $\beta$-SiC |                      | 8                              | 3.10                        | 380                         | 6.0                              |

4. Conclusions
Applying the methods of reinforcing fibers carbon and silicon carbide and growth of elongated grains during sintering using different technology of dense ceramic materials, or adjusting the particle size distribution of the material or structure can receive new product with complex mechanical and performance properties.

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