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PROPERTIES OF SiC AND Si_3N_4 BASED COMPOSITE CERAMIC WITH NANOSIZE COMPONENT

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Materials with nanosize oxide additive aluminum garnet were obtained by liquid-phase sintering. SiC and Si_3N_4 based materials were sintered at temperatures 100°C below the sintering of materials with addition of micron-size oxide powders. High mechanical properties were obtained: $\sigma_b = 540$ MPa, $K_{1C} = 5.5$ MPa · $m^{1/2}$, $HV = 20.1$ GPa for SiC-based materials and $\sigma_b = 650$ MPa, $K_{1C} = 6.4$ MPa · $m^{1/2}$, $HV = 17.2$ GPa for Si_3N_4-based materials.

Key words: silicon carbide, silicon nitride, nanosize oxides, liquid-phase sintering, mechanical properties.

Silicon carbide and nitride are widely used in industry owing to their unique combination of properties, such as high hardness and mechanical strength, low thermal conductivity and density, and good erosion properties, which makes it possible to use articles made from silicon carbide and nitride as wear-resistant, heat-resistant, and acid-resistant materials operating under extreme conditions of high temperatures and corrosive media. Materials based on SiC and Si_3N_4 can be obtained by reaction and liquid-phase sintering and hot pressing.

High performance indices are obtained for materials made by the latter method; however, the high energy intensiveness and impossibility of obtaining blanks of articles with a complex shape as well as the use of high-density and expensive graphite for the tooling limits the production of materials by this method. Reactive sintering is used to obtain materials with relatively low mechanical strength indices, but technologically and economically it is preferred. Liquid-phase sintering with oxide activating additives is the optimal method in terms of the labor-intensiveness of the process and the mechanical properties obtained.

There exist three basic methods of obtaining dense materials by means of liquid-phase sintering of silicon carbide:

1) sintering of materials with suppression of the interaction between the silicon carbide and the oxides (for example, sintering in a medium of carbon monoxide), leading to the formation of gaseous compounds via the reactions

$$SiC_{(sol)} + Al_2O_{3(sol)} \rightarrow SiO_{(gas)} + Al_2O_{(gas)} + CO_{(gas)};$$

$$SiC_{(sol)} + 2Y_2O_{3(sol)} \rightarrow SiO_{(gas)} + 4YO_{(gas)} + CO_{(gas)}$$

and shifting the equilibrium of the reaction to the left. However, this method of sintering is not used because of the toxicity of the sintering process in a carbon monoxide CO atmosphere;

2) the use of multicomponent (two or more) complex oxide eutectic systems as activators of liquid-phase sintering, which makes it possible to reduce the evaporation of the oxides formed during high-temperature interaction of the initial components; the additional bond energies in multicomponent oxide systems increase the stability of the sintered phases SiC–MeO, and the use of oxides in the eutectic ratio lowers the overall sintering temperature of the material because the liquid phase reaches the requisite flowability at the lower temperature; the following are examples: a mixture of aluminum and yttrium oxides formed at the sintering stage aluminum yttrium garnet $3Y_2O_3 \cdot 5Al_2O_3$ [1 – 3], magnesium and aluminum oxides forming magnesia spinel $MgO \cdot Al_2O_3$ [4];

3) since the dimensional component of the initial powders is an important component for obtaining high mechanical properties of liquid-phase-sintered materials, ultradisperse (nanosize) powders must be used; high density is achieved by using oxide powders (weight content 5 – 15%) with size an order of magnitude smaller than that of silicon

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TABLE 1. Compositions of Ceramic Materials Based on SiC and Si_3N_4

Composition no.	Mass content, %				Theoretical density, g/cm^3
	SiC	Si_3N_4	Oxides		
			Al_2O_3	Y_2O_3	
1	95	–	2.15	2.85	3.27
2	90	–	4.30	5.70	3.33
3	85	–	6.45	8.55	3.38
4	–	95	2.15	2.85	3.26
5	–	90	4.30	5.70	3.33
6	–	85	6.45	8.55	3.37

carbide, which upon mixing maximizes the uniformity of the distribution of the oxide components between the SiC particles.

The aim of the present work is to obtain high-density ceramic materials based on silicon carbide and nitride by means of liquid-phase sintering with highly disperse activating additives aluminum and yttrium oxides.

EXPERIMENTAL MATERIALS AND METHODS

Silicon carbide SiC M40 (VAZ JSC) and Si_3N_4 LC-12 (HC Starck) powders comminuted in a jet mill to particle size $d_{0.5} = 0.8$ μm for SiC and $d_{0.5} = 1.2$ μm for Si_3N_4 were used in this work. The sintering additives for liquid-phase sintering were Al_2O_3 and Y_2O_3 oxide powders manufactured by the Plazmaterm Co.; the powders with specific surface $S_{sp} = 15 - 38$ m^2/g were obtained by plasma-chemical synthesis. The oxides were taken in the ratio forming aluminum-yttrium garnet at the sintering stage. The compositions of the materials and their theoretical densities are presented in Table 1.

The initial powders in the requisite ratio (see Table 1) were mixed in an ethyl alcohol medium in a drum mixer in 40 h. A 2% solution of organic binders was used as the plasticizer. The suspension was dried in a vacuum cabinet; the powder was granulated and pressed, by means of semi-dry molding, into samples for determining the physical-mechanical properties. The samples were dried, sintered in a vacuum furnace at temperature 1850°C (SiC-based materials) and 1700°C (Si_3N_4-based materials) in a nitrogen atmosphere with 1-h isothermal soaking.

The density and porosity of the samples were determined by hydrostatic weighing. The relative density was determined on the basis of a calculation of the theoretical density. X-ray phase analysis was conducted with a DRON-3M diffractometer with CuK_α radiation ($\lambda = 1.54158$ Å) and a Ni filter. A Quanta 200 electron microscope was used to investigate the microstructure and perform microphotography of the fracture. Young's modulus was determined on a Zvuk-230 apparatus. A Shimadzu AG-300kNX rupture machine was used to determine the strength in bending. The Vickers hardness was measured with a TP-7p-1 hardness tester under loads up to 1 kg. The fracture toughness of the materials was determined according to the length of cracks emanating from the diagonals of Vickers indentation.

RESULTS AND DISCUSSION

Conventionally, materials made from liquid-phase sintered silicon carbide (LPSSiC) and liquid-phase sintered silicon nitride (SSN) are obtained from powders comprised of micron-size covalent silicon and nitride carbides and oxides [5 – 7], which in the preparation of the molding powder mixing of the initial components results in nonuniformity of the oxide particle distribution between the silicon carbide and nitride particles. Ultradisperse oxide components, whose particle size is an order of magnitude smaller than that of the primary SiC and Si_3N_4 powders, can be uniformly distributed between them, which makes it possible to obtain homogeneous powder mixtures sintered to maximum compaction.

The high activity of disperse oxide powders results in synthesis of YAG and the appearance of a liquid melt at temperature 200 – 300°C lower than in the synthesis of micron Al_2O_3 and Y_2O_3 powders and their sintering with SiC. Liquid-phase sintering of silicon carbide is accomplished in several stages: synthesis of oxides, softening and appearance of YAG liquid, contraction of the centers of the primary particles into the liquid (main shrinkage of the material), slipping of particles along the boundaries toward one another, dissolution of the smaller particles in the liquid, and mass transport of material through the liquid onto the surface of larger particles (Oswald enlargement) [8]. Sintering of Si_3N_4 is accomplished similarly; however, in using Al_2O_3-baswed oxides a SiAlON layer forms on the surface of the silicon nitride particles [9].

The shrinkage of the material is determined by the amount and composition of the liquid phase and increases as oxides grow. The initial particles of silicon carbide, comminuted in a jet mill [10], comprise rounded particles of powder which were formed by the particles rubbing against one another. This shape of the SiC particles makes it possible to obtain more complete compaction of the material in the molding process, which determines the high post-sintering density of the material (Table 2). The relative density of the materials obtains by introducing 15% mass fraction of the sintering additive — 98.8% for materials based on SiC and 97.9% for material based on Si_3N_4. Even though LPSSiC and SSN sinter at temperature 100°C lower than materials comprised of micron-size powders [5, 6, 9, 10], the samples obtained are characterized by high shrinkage and density, which shows the correctness of the choice of the sintering regime.

The porosity is the opposite density index of sintered materials. As the mass content of the oxide component of the additive increases (to 15%), the porosity decreases to 1.7%

TABLE 2. Physical and Mechanical Properties of Sintered Materials Based on SiC and Si_3N_4

Composition no.	Sh ± 0.3, %	ρ_{rel} ± 0.2, %	P ± 0.2, %	E_{elas} ± 10, GPa	σ_b ± 15, MPa	K_{1C} ± 0.2, MPa · $m^{1/2}$	HV ± 0.3, GPa
1	19.8	95.3	5.3	330	430	4.2	21.2
2	20.4	98.1	2.8	380	470	4.9	20.5
3	20.8	98.8	1.7	370	540	5.5	20.1
4	18.3	94.6	5.8	320	560	5.1	18.3
5	19.9	96.7	4.2	350	620	5.8	17.8
6	20.4	97.9	3.1	345	650	6.4	17.2

Notations: Sh) shrinkage; ρ_{rel}) relative density; P) porosity; E_{elas}) modulus of normal elasticity; σ_b) strength in bending; K_{1C}) cracking resistance; HV) Vickers hardness.

for materials based on SiC and 3.1% for materials based on Si_3N_4. In using micron-size oxide powders it is impossible to attain a uniform distribution of the oxides between the particles of silicon carbide or nitride, and therefore fill all pores between the particle and obtain as a result of sintering LPSSiC material with porosity below 2 – 3% [11] and SSN material with porosity below 4 – 5% [12].

The following characteristics were chosen to determine the elastic and mechanical properties: Young's modulus, strength in transverse bending, cracking resistance, and Vickers hardness (see Table 2).

Structural defects (porosity) and the amount of the sintering additive influence Young's modulus (since Young's modulus of oxides is an order of magnitude smaller than in silicon carbide and nitride). The increase of E_{elas} for the composition 2 is associated with the production of material with higher density (see Table 2). As the mass content of the oxides increases from 10 to 15% in the composition of the material, the elastic modulus of LPSSiC decreases in spite of the lower porosity. A similar behavior is observed for SSN material.

The strength in bending also depends on the structural defects. For LPSSiC and SSN materials the strength increases monotonically with mass content of the oxide additive increasing from 5 to 15% (see Table 2). A uniform distribution of the high-dispersity oxide components between the SiC and Si_3N_4 grains gives materials with strength 20% higher for LPSSiC and 30% for SSN than by using micron oxide powders [9, 10].

The structure of LPSSiC material consists of fine grains of silicon carbide, primarily of irregular shape, and an intergrain phase (aluminum-yttrium garnet) (see Fig. 1*a*). In sintering silicon nitride based material, α-Si_3N_4 transforms into β-Si_3N_4, and this transformation is accompanied by intense growth of silicon nitride grains. Sintered SSN comprises a self-reinforced ceramic material with elongate grains of silicon nitride (see Fig. 1*b*), possessing high porosity and cracking resistance compared with LPSSiC.

A crack appearing in SSN material propagates primarily along silicon nitride grains (intercrystallite fracture), since the hardness of the primary phase (grains) is greater than the intergrain hardness. Reaching an 'elongate' grain, the crack goes around it, thereby increasing the travel distance and the cracking resistance of materials as compared with LPSSiC (see Table 2).

The hardness of the composite material is determined by the hardness of its constituent phases, and as the oxide content in the material increases, the hardness decreases from 21.2 to 20.1 GPa for LPSSiC material and from 18.3 to 17.2 GPa for SSN material (see Table 2). The hardness of the latter material is lower than that of LPSSiC; this is associated with the synthesis of an SiAlON layer, which is less hard than the grains of the primary phase, on the surface of Si_3N_4.

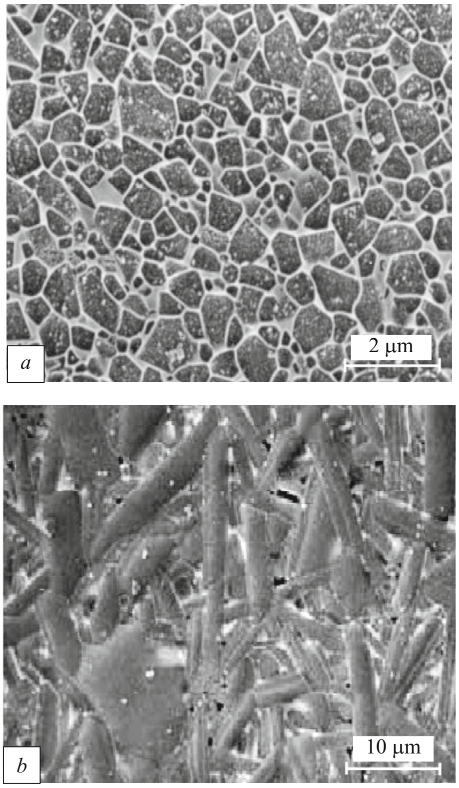

Fig. 1. Microstructure of composite materials based on silicon carbide and nitride with 10 wt.% YAG: *a*) LPSSiC material; *b*) SSN material.

CONCLUSIONS

Silicon carbide and nitride based composite materials were obtained by means of liquid-phase synthesis. High-dispersity nanosize oxide powders in the ratio of aluminum-yttrium garnet were used as sintering-activating additives. The high dispersity of the oxide powders makes it possible, by mixing the SiC–MeO mixture, to obtain a homogeneous mixture that sinters at a temperature 100°C below the sintering temperature of materials made from micron powders. The mechanical properties of the sintered materials are 20% higher compared with LPSSiC materials and 30% higher compared with SSN materials obtained using micron-size oxide powders.

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