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Study of the structure and properties of SiC ceramics

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This paper presents the results of the entropy calculation of the equilibrium constants of chemical reactions at liquid-phase sintering of SiC ceramics with eutectic additives. The composition of the charge for sintering ceramics with nanoadditives forming the liquid phase was determined: MnO_{nano} 1.5 wt. % + Al_2O_{3nano} 2 wt.% + $SiC_{\mu m}$ 94 wt. % + $SiO_{2\mu m}$ 2.5 wt. %. Possible chemical reactions of liquid-phase sintering of ceramics at a temperature of 1800 °C in a weakly reducing CO medium were established. The values of the change in the Gibbs energy for all possible chemical reactions at a sintering temperature of 1800 °C were calculated by the method of entropy calculation of the equilibrium constants. The elements of the liquid phase and reinforcing additives were determined.The elements of the liquid phase and reinforcing additives were determined. The structure and properties of finished sintered ceramic samples were studied. Microstructural analysis of ceramics indicated its grain structure with an average grain size of ~10 μm. The main phase components of the ceramics based on silicon oxide were determined. It was found that the sample consists of three main phases: modification of the ring radical of silicate Si_3O_6, silicon dioxide SiO_2 and anorthoclase $(SiAl)O_4$.

Keywords: silicon carbide, nanoparticles, ceramics, structure, chemical reactions, liquid phase sintering.
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1 Introduction

Rapid development of science and technology results in the need to create fundamentally new materials capable of operating under extreme conditions and increased mechanical loads. Such materials should be resistant to thermal effects, have high density and low porosity, and other features for thermally and mechanically loaded material [1, 2]. The most promising today are ceramic composite materials obtained using modern technologies and the achievements of science and technology [3, 4]. Composite materials are heterophase systems of two or more components, with the preservation of the individual properties of each individual component [5].

The main advantage of ceramic composite materials is a special mechanism of their destruction under the action of loads [6]. In order to increase the strength of the material, reinforcing components are added to the ceramic matrix [7, 8]. Thus, reinforcing components tend to increase fracture toughness by redirecting crack paths, or minimizing crack growth. Thus, the control of the creep of aluminum oxide at elevated temperatures is carried out by introducing other phases – mullite and zirconium dioxide [9].

One of the most difficult tasks in the synthesis of ceramics based on silicon carbide is the creation of temperature and other conditions for its sintering. Since the temperature of solid phase sintering of SiC ceramics is 2100 °C in a CO atmosphere, this technological process requires special high-tech thermal equipment [10, 11]. The introduction of reinforcing additives into the ceramics based on SiC, with a properly selected eutectic, makes it possible to reduce the sintering temperature to 1800 °C and below [12].

The choice of oxide binders for silicon carbide sintering was studied in [13], following the thermodynamic arguments, Al_2O_3, BeO, HfO_2 are the most stable and do not contribute to the decomposition of silicon carbide during sintering. Oxides of zirconium, calcium, magnesium, on the contrary, contribute to the dissociation of SiC into metal and carbon. Suzuki et al. [14] used aluminum oxide to densify silicon carbide. The samples were fired in an oxygen-free environment (an atmosphere of argon or he-

lium with vapors of aluminum, silicon, and carbon is preferable, contributing to better compaction). Fuentes et al. [15] activated SiC sintering with additions of Al_2O_3, CaO, and C. The addition of free carbon in the system, reacting with the calcium aluminate phase, gave a liquid oxycarbide phase, which led to an increase in the density of the material up to 97-99%. Liquid-phase sintering of silicon carbide with Al_2O_3 and/or MgO binders in the temperature range of 1800-2000 °C leads to the appearance of a second phase, which usually lowers the mechanical properties of the material at high temperatures. Such a negative effect indicates the need to reduce the proportion of additives introduced. To reduce the sintering temperature of the samples, ultrafine powders of the initial components are used [16].

To obtain products from powders with nanoadditives, it is necessary to compact them. The main goal of this stage is to keep the grain size in the nano range and get a quality product with minimal defects. The most developed technologies for producing silicon carbide ceramic products are high vacuum pressing, pressure sintering, hot isostatic pressing, etc. [17-21].

Thus, the aim of this study is to develop the composition of the charge for sintering carbide ceramics with nanoadditives that form a liquid phase at a sintering temperature of 1800 °C in a weakly reducing CO atmosphere, as well as the study of the structure and properties of finished sintered ceramic samples.

2 Materials and methods

The microstructure and point elemental analysis of the samples were studied using a scanning electron microscope with a JSM-6390LV, 2007 energy-dispersive microanalysis attachment with a resolution of up to 3 nm in high vacuum.

The value of the apparent density was determined according to GOST 2409-95 “Refractories. Method for determining apparent density, open, total and closed porosity, water absorption”. The dried sample was weighed, evacuated, and saturated with a liquid that wets the sample but does not interact with it. Then the test sample was weighed in the saturating liquid and in air. Based on the weightings and the value of the true density of the material, the apparent density was calculated with an accuracy of ± 0.001%, open and total porosity, and water absorption – with an accuracy of ± 0.0001%.

The determination of the microhardness of the samples was carried out using the indentation method using the Vickers method. A diamond pyramid was used as an indenter; the pressure force was 500 N.

X-ray phase analysis of powders and samples was carried out using an X’PertPRO X-ray diffractometer (PANanalytical, 2005).

3 Results and discussion

In order to select reinforcing and liquid-phase additives for SiC ceramic sintering, it is necessary to select the optimal ratio, amount and calculate the eutectic of impurities promoting ceramic sintering at a temperature of 1800 °C in a weakly reducing CO atmosphere. The significant affinity of aluminum for oxygen, as well as the cubic lattice of the synthesized yttrium aluminum garnet, make it possible to prevent the carbidization of the complex oxide up to a temperature of 2040 °C [22-25]. Metals that form oxides of the cubic system have the highest affinity for oxygen. This suggested that yttrium oxide in the form of a complex compound with aluminum oxide, for example, yttrium-aluminum garnet, which has a cubic crystal lattice, may be resistant to carbidization above 1850 °C. Oxides thermodynamically allowed for use as additives are reduced by carbon: CaO – at 2050 °C, MgO – 2060 °C, Al_2O_3 – 1980 °C. Since the melting point of nanosized particles of powders in comparison with the micron size of particles of the same substance decreases, then the maximum allowable temperature for the synthesis of ceramics by the method of liquid-phase sintering will be 1800-1850 °C.

Taking into account the analysis and review of literature data, the composition of the charge for sintering carbide ceramics with additives that form the liquid phase has been developed:

$$MnO_{nano}\ 1.5\ wt.\ \% + Al_2O_{3nano}\ 2\ wt.\ \% + SiC_{\mu m}\ 94\ wt.\ \% + SiO_{2\mu m}\ 2.5\ wt.\ \%.$$

In the process of liquid-phase sintering of ceramics of the specified composition, the following chemical reactions are possible:

$$2SiO_2 + SiC \rightarrow 3SiO + CO \quad (1)$$

$$Al_2O_3 + SiC \rightarrow SiO + Al_2O + CO \quad (2)$$

$$MnO + SiC \rightarrow Mn + SiO_2 + CO \quad (3)$$

$$Al_2O_3 + SiO_2 \rightarrow Al_2(SiO_3)_3\ (Al_2O_3SiO_2) \quad (4)$$

$$SiO_2 + 2SiC \rightarrow 3Si + 2CO \quad (5)$$

$$MnO + SiO_2 \rightarrow MnO_2 + SiO \quad (6)$$

During the sintering of ceramics in a weakly reducing CO environment, the possible chemical reactions are:

$$Al_2O_3 + CO \rightarrow Al + CO_2 \quad (7)$$

$$SiO_2 + CO \rightarrow SiO + CO_2 \quad (8)$$

$$SiC + CO \rightarrow SiO_2 + C \quad (9)$$

To determine the possibility of interaction of these elements during sintering, one can use a simplified calculation, the so-called entropy method for calculating equilibrium constants, based on the Gibbs-Helmholtz equation:

$$A = Q + T\frac{dA}{dT} \quad (10)$$

one of the forms of which, for standard conditions, is the equation:

$$\Delta G_T^0 = \Delta H_{298}^0 - T\Delta S_{298}^0 \quad (11)$$

$$\Delta H_{298}^{\circ}(reaction) = \\ = \sum n_i \cdot \Delta H_{298}^{\circ}(products) - \\ - \sum n_i \cdot \Delta H_{298}^{\circ}(initial\ compounds) \quad (12)$$

n_i are stoichiometric coefficients.

The equilibrium constant of a chemical reaction at a temperature of 1800 °C was calculated using tables of standard values. For a given temperature, at a $\Delta G_T^0 < 0$ reaction is possible; when the $\Delta G_T^0 > 0$ reaction is impossible; when $\Delta G_T^0 = 0$ the system is in equilibrium.

Based on the above equations (1-12), the main thermodynamic quantities for chemical elements and compounds involved in the technological process of liquid-phase sintering were determined (Table 1).

Based on the data in Table 1, the values of the change in the Gibbs energy were calculated – ΔG_T^0 for all possible chemical reactions, at a sintering temperature of 1800 °C in a weakly reducing CO atmosphere (Table 2).

Table 1 – Thermodynamic values for chemical elements and ceramic compounds of the composition: MnO_{nano} 1.5 wt. % + Al_2O_{3nano} 2 wt. % + $SiC_{\mu m}$ 94 wt. % + $SiO_{2\,\mu m}$ 2.5 wt. %

Compound	T_{melt}, °C	ρ, g/cm³	$\Delta H_{,298\ K}$, kJ/mol	S, kJ/mol
SiC	2830	3.22	− 66.1	16.61
SiO_2	1710	2.65	− 910	41.84
SiO	17 02	2.13	− 92.9	211.6
Si	1414	2.33	0	18.82
MnO	1245	7.21	− 385.1	61.5
MnO_2	535	5.08	− 521.5	53.1
Mn	1517	7.21	0	32.0
Al_2O_3	2044	4.0	− 1675.7	50.9
Al_2O	—	—	− 148.6	264.6
Al	660	2.69	329.1	164.4
CO_2	78	0.0019768	− 393.51	213.67
CO	−205	0.00125	− 110.52	197.54
C	3600	2.25	715.1	157.99
$Al_2(SiO_3)_3 (Al_2O_3SiO_2)$	1860	3.23	− 166.2	20

Table 2 – Calculation of the change in the Gibbs energy, which determines the possibility of a spontaneous reaction at T = 1800 °C

Chemical reaction	ΔG, kJ/mol	Possibility of the reaction
$2SiO_2 + SiC \rightarrow 3SiO + CO$	− 460305	Reaction is possible
$Al_2O_3 + SiC \rightarrow SiO + Al_2O + CO$	− 1255325	
$MnO + SiC \rightarrow Mn + SiO_2 + CO$	− 401218	
$Al_2O_3 + SiO_2 \rightarrow Al_2(SiO_3)_3 (Al_2O_3\, SiO_2)$	− 153209.5	
$SiO_2 + 2SiC \rightarrow 3Si + 2CO$	− 779622	
$MnO + SiO_2 \rightarrow MnO_2 + SiO$	− 333819	
Sintering in carbon monoxide (CO)		
$Al_2O_3 + CO \rightarrow Al + CO_2$	− 267309	Reaction is possible
$SiO_2 + CO \rightarrow SiO + CO_2$	− 384816	
$SiC + CO \rightarrow SiO_2 + C$	29667	Reaction is impossible

Thus, taking into account the decrease in the melting temperature of nanosized particles of Al_2O_3 and MnO powders, we can assume the formation of a liquid phase proceeds according to reactions in Table 1. Based on the values of the melting temperature and the end products of chemical reactions, SiO_2, SiO, Si and MnO will contribute to the formation of the liquid phase.

Samples of silicon carbide ceramics obtained by liquid-phase sintering were studied to establish their physical and mechanical properties and structural features. The results of physical and mechanical properties are shown in Table 3.

According to the results of testing the physical and mechanical properties, it was found that the studied ceramic sample reaches a microhardness of 2450 kgf/mm^2, which is an average value found in the literature, while the sintering temperature of ceramic samples obtained by other authors is higher on average by 20%. The density of the sample obtained by us, 3.11 g/cm^3, corresponds to the lower limit of previously encountered data in the literature. According to the experimental results, the open porosity was 0.8%, which also corresponds to the limits of previous studies by other authors. The resulting ceramic material has sufficient density and low porosity, while the use of additives of eutectic compositions of oxide systems with different temperatures of formation of the eutectic melt made it possible to study the effect of these additives on the temperature of compaction and hardening. These studies are relevant for obtaining SiC materials of a granular structure at a relatively low firing temperature while maintaining high mechanical properties.

The results of microstructural analysis of the obtained sample of SiC ceramics are shown in Figure 1.

Table 3 – Physical and mechanical properties of the resulting ceramic sample

Material	Apparent density, g/cm^3	Micro-hardness, kgf/mm^2	Open porosity, %	Total porosity, %	Closed porosity, %	Water absorption, %
Test sample	3.11	2450	0.8	0.34	0.33	0.03
Literature data [17-20]	3.12 – 3.17	2345-2855	0.5-1.2	-	-	-

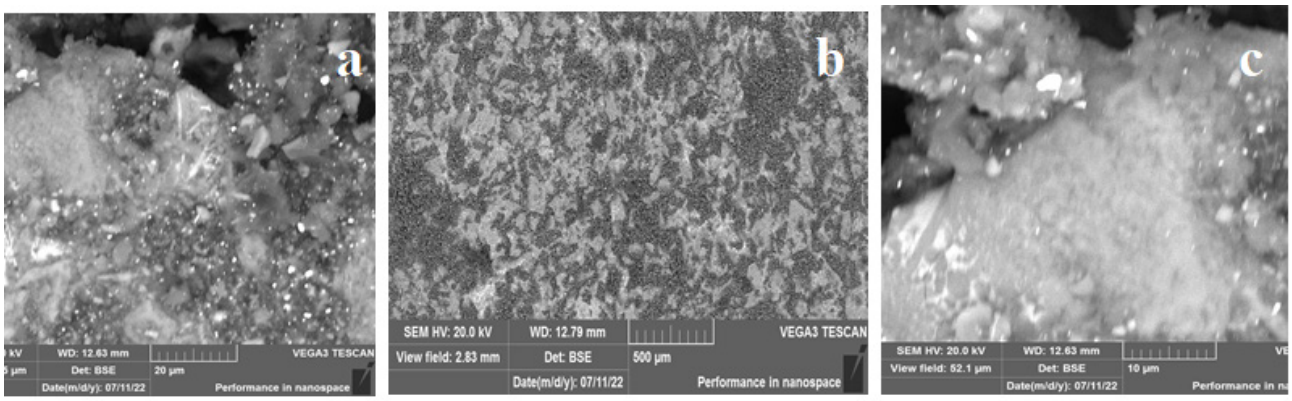

Figure 1 – Microstructure of a sample of SiC ceramics:
a – homogeneous grain structure; b – presence of small pores; c – grain microstructure

The ceramic microstructure is represented by a homogeneous grain structure with an average grain size of ~10 µm (Figure 1a,c). Separate grains of the second phase were not revealed. In the structure of ceramics, the presence of small pores is also observed, apparently formed due to the transformation of the crystal structure and shrinkage of impurity phases during sintering (Figure 1b).

The analysis indicates the presence of C in the composition of ceramics with its content of ~ 57% of the total composition, Al ~ 0.6%, Mn ~ 0.6%, Si ~ 15%, which corresponds to the presence of introduced eutectic additives .

X-ray phase analysis of the sample is shown in Figure 2.

XRD analysis showed that the test sample consists of three main phases, this is a modification of the ring radical of silicate Si_3O_6, silicon dioxide SiO_2 and anorthoclase $(SiAl)O_4$ (Table 4).

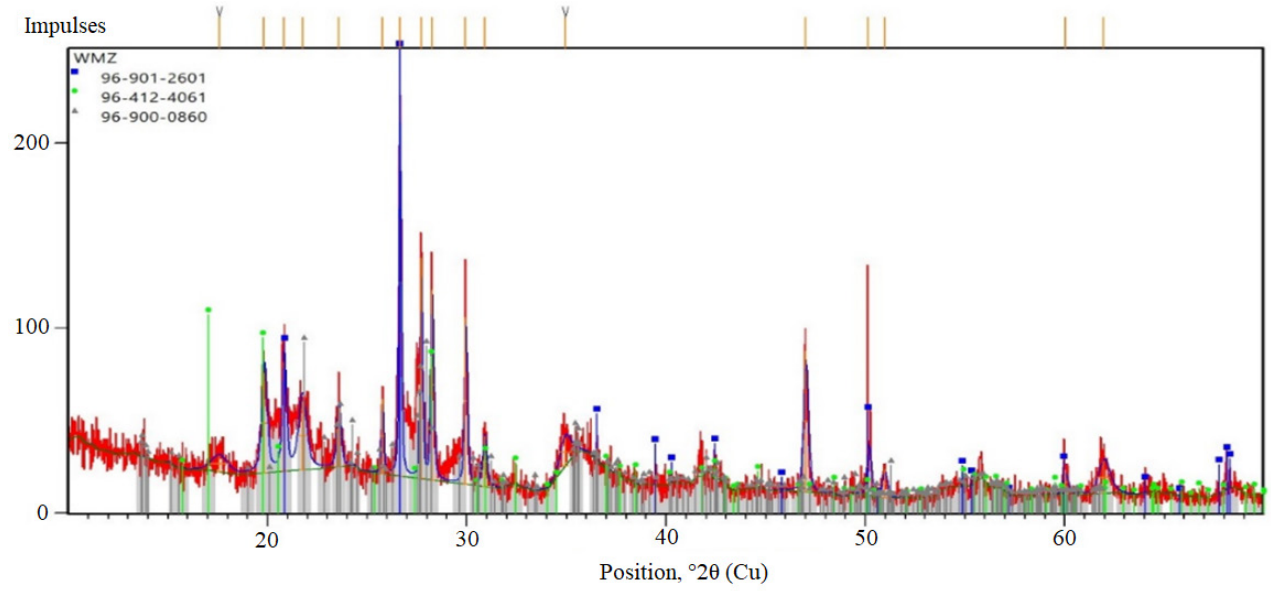

Figure 2 – X-ray spectrum of SiC ceramics sample

Table 4 – PDF cards and phase identification

Card number	Connection name	Offset, [°2θ]	Scale factor	Chemical formula
96-901-2601	Quartz	0.000	1.008	$Si_{3.00}O_{6.00}$
96-412-4061	SiO_2	0.000	0.342	$O_{24.00}Si_{12.00}$
96-900-0860	Anorthoclase	0.000	0.293	$Al_{2.00}Si_{6.00}Na_{1.70}K_{0.30}O_{16.00}$

4 Conclusions

Despite the existence of a wide range of ceramic materials for various purposes, developed based on SiC, the high energy and resource consumption of their manufacture makes it necessary to search for ways to create new types of materials. One of the main solutions is the use of various additives in conjunction with the dispersion of the starting materials. The synthesis of ceramics based on SiC requires high temperatures, and sintering without additives at 2150-2200°C does not allow obtaining dense products due to low diffusion coefficients and high volatility of SiC at these temperatures.

The composition of the charge for sintering carbide ceramics with nanoadditives that form a liquid phase has been developed: MnO_{nano} 1.5 wt. % + Al_2O_{3nano} 2 wt. % + $SiC_{\mu m}$ 94 wt. % + $SiO_{2\mu m}$ 2.5 wt. %. The possible chemical reactions during the liquid-phase sintering of ceramics at a temperature of 1800 °C were determined. The values of the change in the Gibbs energy for all possible chemical reactions at a sintering temperature of 1800 °C were calculated by the method of entropy calculation of the equilibrium constants. The elements of the liquid phase and reinforcing additives were determined.

The main physical and mechanical properties of the ceramic sample obtained by liquid-phase sintering at a temperature of 1800 °C were established: characteristics of water absorption, open, total and closed porosity, density and microhardness.

Microstructural analysis of ceramics indicates its grain structure with an average grain size of ~10 μm. The presence of small pores, apparently formed because of the transformation of the crystal structure and shrinkage of impurity phases during sintering, was also recorded in the ceramic structure. Based on the results of XRD analysis, the main phase components of the ceramics based on silicon oxide were determined. It was found that the sample consists of three main phases: modification of the ring radical of silicate Si_3O_6, silicon dioxide SiO_2 and anorthoclase $(SiAl)O_4$.

Such ceramic composite SiC material can have a wide range of applications: as parts of body armor, internal combustion engines and gas turbine engines, cutting tools, ceramic bearings, working units of pumps, nozzles and burners, equipment for firing ceramic products, chemically resistant parts of pipelines, heat exchangers operating in an aggressive environment, heaters of various grain compositions and sizes to obtain temperatures in furnaces in the range up to 1400-1500°C in air.

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