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Phase homogeneity of Si3N4-based ceramic materials produced by spark plasma sintering

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Ceramics obtained by spark plasma sintering of powder compositions of Si_3N_4 was studied by the method of layer-by-layer X-ray diffraction analysis. The effect of carbon diffusion in the surface layers of the sintered ceramics from the graphite mold was observed. The homogeneity of the ceramic phase composition along the depth of the sample was shown. Therefore, a uniform distribution of the temperature field inside the sintered sample was concluded.

Keywords: silicon nitride, ceramics, spark plasma sintering, X-ray diffraction.

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Silicon nitride (Si_3N_4) based ceramic material possesses high physical and mechanical properties: strength, hardness, as well as corrosion resistance and refractory quality [1].

Due to the covalent nature of bonds in Si_3N_4, the diffusion processes during sintering have low intensity, thus it is difficult to produce ceramics from pure Si_3N_4 [2]. To resolve this problem, sintering additives of various compositions are used, e.g. the $Y_2O_3-Al_2O_3$ [3] system. In the process of sintering the α-Si_3N_4 phase is dissolved in the phase of sintering additive, and then it crystallizes in the form of β-Si_3N_4. The intensity of this transition can be controlled by varying the percentage and composition of the sintering additive, as well as conditions of the sintering [4].

To produce fine-grained ceramics, the method of spark plasma sintering, SPS is gaining popularity [5]. High speed of heating provokes overheating of the surface and arising of temperature gradient inside the workpiece, which can result in inhomogeneous running of the sintering process. It was shown that in the process of SPS an intensive diffusion of carbon from graphite parts of the mold inward the workpiece can occur, which leads to arising of carbon-bearing phases near the workpiece surface [6,7].

The purpose of this study is to investigate homogeneity of phase composition of the Si_3N_4 based ceramics sintered at different temperatures. The presence of phase inhomogeneity will allow making conclusion about the presence of temperature gradient inside the ceramic workpiece in the process of sintering and the effect of carbon diffusion from graphite parts of the mold.

The role of initial material was played by industrial powder of Si_3N_4 (purity 99.6%, 90 wt% α-Si_3N_4 + 10 mass% β-Si_3N_4, average particle size $< 5\,\mu$m, Alfa Aesar, Germany). The $Y_2O_3-Al_2O_3$ sintering additive (with a mole ratio of 3:5) was introduced into the Si_3N_4 initial powder in the form of precursor in an amount of 5 and 10 mass % (specimens № 1 and 2, respectively) expressed as oxide [8].

Powder mixtures were sintered on the Dr. Sinter model SPS-625 (SPS Syntex, Japan) in a graphite mold with an inner diameter of 12 mm. The speed of heating to sintering temperatures of 1880 and 1710°C for specimens № 1 and was 100°C/min. The applied uniaxial stress was 70 MPa. Relative density of ceramic specimens measured by the Archimedes method was 99 and 96%, respectively.

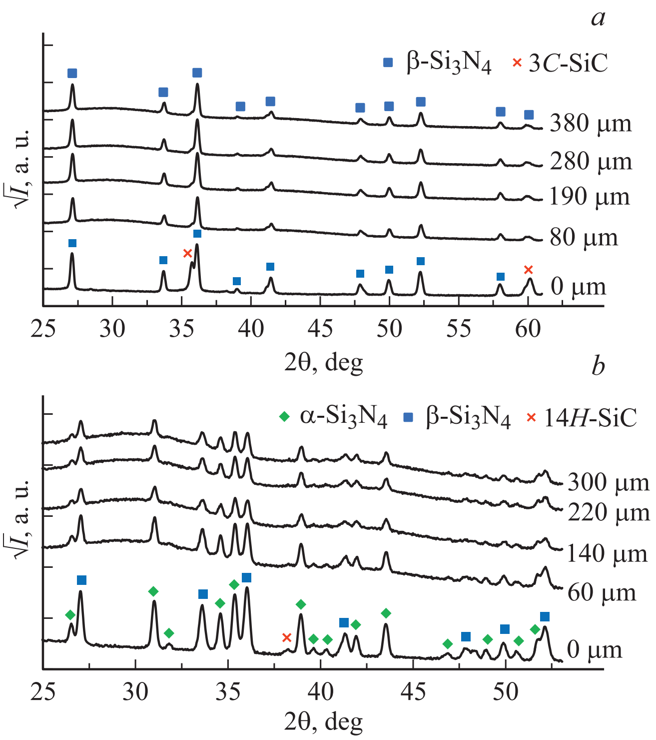
Microstructure of the ceramics was investigated using a JEOL JSM-6490 scanning electron microscope. The microstructure of specimen № 1 demonstrates clearly distinctive elongated grains of β-phase Si_3N_4 with a length of up to $5\,\mu$m. In triple points pores can be seen with a size of not more than $0.1\,\mu$m.

In the microstructure of specimen № 2, in addition to the elongated grains of β-Si_3N_4 phase, there are equiaxed grains, probably α-Si_3N_4. Between the grains, the phase of sintering additive can be distinguished with a thickness of $\sim 0.1-0.2\,\mu$m, as well as pores with a size of up to $0.5\,\mu$m.

The initial height of specimens was 4 mm. The surface of sintered specimens was successively abrasing machined by diamond disks in a Struers Secotom-10 machine. Height of specimens was measured by micrometer.

X-ray diffraction experiments were carried out using XRD-7000 diffractometer (Shimadzu, Japan) (CuK_α, $\lambda = 1.54$ Å). Conditions diffraction experiment were as follows: Bragg–Brentano geometry, „wide slot mode", angle range $2\theta = 15-70°$, scanning step 0.04°, exposure time 2 s.

According to the performed evaluations, the attenuation of [X-ray intensity CuK_α in Si_3N_4 by e times takes place at a depth of about $40\,\mu$m. Thickness of the removed layer at each stage was not less than $60\,\mu$m to make it possible the



Areas of diffraction patterns of specimens № 1 (*a*) and 2 (*b*) depending on thickness of the removed layer.

studying of the layer that knowingly did not contribute to the result at the previous stage.

The qualitative phase analysis was carried in Diffrac.EVA software (Bruker, Germany) using the data from PDF-2 data bank (2012). The quantitative phase analysis was carried out by the Rietveld method in Diffrac.TOPAS software (Bruker, Germany) using cif-files from the ICSD bank (2016): # 16752 (α-Si_3N_4), 8263(β-Si_3N_4), 28895 (3C-SiC), 42859 (14H-SiC). The absolute error of determining mass fractions of the phases for both specimens by the Rietveld method is not more than 1 mass % (according to preliminary experiments).

The figure shows results of layer-by-layer X-ray diffraction studying of specimens № 1 and 2 depending on thickness of the layer removed from their surfaces. The first experiment (0 μm) is performed for an unmachined ceramic surface.

Phase composition of the surface of specimen № 1 (see Figure, *a*): 77 mass% β-Si_3N_4 (PDF # 01-071-0623) and 23 mass% 3C-SiC (PDF # 01-073-1665). The formation of SiC phase on the surface of specimen № 1 is caused by the carbon diffusion inward the sintered specimen due to its direct contact with the mold. The presence of silicon on the specimen surface is related to the surface overheating. This overheating resulted in partial decomposition of Si_3N_4 to Si with a release of nitrogen. It is known that the decomposition of Si_3N_4 is possible from $T > 1600°C$ [2]. In underlying layers only crystalline phase of β-Si_3N_4 can be found.

It follows from the analysis of X-ray diffraction patterns of specimen № 2 (see Figure, *b*) that on the unmachined surface, in addition to peaks of the β-Si_3N_4 phase, there are peaks that characterize the α-Si_3N_4 phase (PDF # 01-071-6479), which has not transformed to the β-phase because of lower sintering temperature. Also, the 14H-SiC phase (PDF # 01-089-2215) is found on the surface.

Phase composition of the surface of specimen № 2: 54 mass % α-Si_3N_4, 42 mass% β-Si_3N_4 and 4 mass % SiC. At a depth of 60 μm mass fractions of α- and β-phases Si_3N_4 are equal to 56 and 42 mass%, respectively. Also, a peak of SiC (2 mass%) is observed at this depth. In deeper layers of specimen № 2 mass fractions of α-Si_3N_4 and β-Si_3N_4 phases remain unchanged within the measurement accuracy and are equal to 57 and 43 mass %, respectively.

The unchanged phase composition of ceramics suggests a homogeneous distribution of the sintering additive and temperature over the volume of specimens starting from a depth not more than 140 μm.

Thus, in this work we have demonstrated that in the process of spark plasma sintering of Si_3N_4 powder a diffusion of carbon to surface layers (less than 80–140 μm) of the sintered ceramic can occur from the graphite mold where the powder is sintered. The presence of silicon carbide on the specimen surface confirms the surface overheating. Starting from a depth of about 80 μm the layers of ceramic material are characterized by homogeneity of the α- and β-Si_3N_4 phases ratio within the measurement accuracy that allows making a conclusion about homogeneity of the temperature distribution inside the specimen.

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Conflict of interest

The authors declare that they have no conflict of interest.

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