



Article Spark Plasma Sintering of Si₃N₄ Ceramics with Y₂O₃–Al₂O₃ (3%–10% wt.) as Sintering Additive

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Abstract: The ceramic samples fabricated by spark plasma sintering of powder mixtures based on silicon nitride (Si₃N₄) were investigated. The powder mixtures were made by wet chemical methods from commercial α -Si₃N₄ powder (the particle size <5 µm) and Y₂O₃-Al₂O₃ sintering additive (3% to 10% wt.). Sintering was carried out at the heating rate of 50 °C/min and the load of 70 MPa until the shrinkage end. The powder mixtures and ceramic samples were characterized by scanning electron microscopy and X-ray diffraction. The shrinkage of the powder mixtures during sintering was analyzed, and the activation energy of sintering was calculated according to the Young-Cutler model. The density, microhardness, and fracture toughness of the ceramic samples were also measured. All samples had high relative densities (98%–99%), Vickers microhardness 15.5–17.4 GPa, and Palmquist fracture toughness, 3.8–5.1 MPa·m^{1/2}. An increase in the amount of sintering additive led to a decrease in the shrinkage temperature of the powder mixtures. The amount of β-Si₃N₄ in the ceramics decreased monotonically with the increasing amount of sintering additive. The shrinkage rate did not decrease to zero when the maximum compaction was reached at 3% wt. of the sintering additive. On the contrary, it increased sharply due to the beginning of the Si₃N₄ decomposition.

Keywords: silicon nitride; spark plasma sintering; ceramics; sintering additive; mechanical properties

1. Introduction

Ceramic materials based on silicon nitride (Si₃N₄) are characterized by a combination of high strength, microhardness, wear resistance, corrosion resistance, and heat resistance. These properties are also retained at high temperatures and under aggressive environmental conditions. In this regard, Si₃N₄-based ceramics are among the most promising structural materials [1]. The Si₃N₄ ceramic products are currently used as the most important components of complex mechanisms in mechanical engineering, the petrochemical industry, power engineering, etc. [2–4]. The ceramics based on Si₃N₄ have also found some special applications due to their good dielectric properties [5].

The covalent nature of the Si–N bonds is the origin of low intensity of diffusioncontrolled processes (sintering, crystallization, coalescence, etc.). For this reason, Si_3N_4 based ceramics are made traditionally in the form of composites containing some sintering additives to facilitate the compaction process [1,2,6,7]. The sintering additive forms a thin layer of the liquid phase at the Si_3N_4 grain boundaries during heating, which contributes to the acceleration of the diffusion processes and the material compaction.

The most commonly used sintering additives for ceramic materials based on Si_3N_4 are metal oxides. The lighter metal oxides form a liquid phase with a lower viscosity. Because of this, the sintering temperature decreases [7,8]. The lower sintering temperature of ceramics correlates with the lower performance properties at high temperatures. In this



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). regard, it is also advisable to add the rare earth metal oxides into the sintering additive (for example, Y_2O_3) [9].

As a rule, the sintering additive does not crystallize in a ceramic sample but forms an amorphous glass phase distributed at the Si_3N_4 grain boundaries. This leads to a decrease in fracture toughness and other mechanical and performance properties of ceramics. The advantage of the Al_2O_3 - Y_2O_3 system is the possibility of the formation of crystalline compounds, for example, yttrium–aluminum garnet (YAG, $Y_3Al_5O_{12}$) [10]. An increase in the proportion of the sintering additive leads to better compaction but reduces the mechanical properties [11]. The main interest of researchers is focused on 5%–15% wt. of the sintering additive Al_2O_3 - Y_2O_3 in Si_3N_4 [12–15]. As a rule, ceramic samples with a lower content of sintering additives have a lower density and low physical and mechanical properties [16,17]. The effect on the compaction of the SiO₂ fraction located on the surface of the Si_3N_4 particles is also noted. [18].

The α -Si₃N₄ phase, which is present in the raw powder material, dissolves in the liquid phase and crystallizes into more stable β -Si₃N₄ during compaction. As a rule, the grains of the β -Si₃N₄ phase in the ceramics have needle-like shapes that affect the mechanical properties positively. It is noted that two-phase α/β -Si₃N₄ ceramics have prospects for a significant reduction in brittleness [19].

Besides the chemical composition, the sintering kinetics will depend strongly on the particle size distribution for each component, on the method (and the homogeneity) of mixing the powders as well as on the sintering method. Recommendations for sintering additives known from the literature are based on traditional grinding and mixing methods and generally refer to hot pressing [7,18,20,21].

High-speed sintering methods, such as spark plasma sintering (SPS), are currently of particular interest for various materials [22–30]. This is due to the possibility of reducing the sintering time and keeping the grain size in the ceramic samples close to the particle sizes in the initial powders. The interest of researchers in studying the possibilities of the SPS method for sintering the ceramics based on Si₃N₄ has grown in recent years [31–33].

There are increasing requirements for the powder mixtures as a factor determining the homogeneity and physical and mechanical properties of the ceramic samples. Co-deposition methods provide high mixing homogeneity and are used to prepare the mixtures despite the process complexity [17,34–36].

Previous studies have reported the wet chemical methods combined with SPS to produce ceramic samples with a dense and homogeneous microstructure as well as mechanical properties comparable to industrial ceramics [37–39]. Consequently, it was proposed that a decrease in the amount of the sintering additive is possible without loss of ceramic density while ensuring sufficient homogeneity of the sintering additive distribution in the mixture [40].

Thus, the aim of the study was to analyze the effect of the amount of Y_2O_3 - Al_2O_3 sintering additive introduced by wet chemical methods on the sintering kinetics, phase composition, density, microstructure, and mechanical properties of the ceramics based on Si_3N_4 .

In this work, the ceramic samples were obtained by spark plasma sintering, which is a high-speed method. The powder mixtures were synthesized by wet chemical methods, which makes it possible to ensure the homogeneity of the additive distribution. It is assumed that under these conditions it is possible to achieve homogeneous diffusion processes during sintering in the entire volume of the sample and obtain dense ceramics with high mechanical properties and low additive contents (3% wt.).

2. Materials and Methods

The objects of the study were ceramics based on the Si_3N_4 - Y_2O_3 - Al_2O_3 system produced by SPS of the powder mixtures.

The Si₃N₄ powder (abcr GmbH, Karlsruhe, Germany) was used as the raw powder material for the mixture preparation. The particle sizes in the raw material were $\leq 5 \mu m$, and the content of α -Si₃N₄ was $\leq 90\%$ wt. Below, all concentrations are given in % wt.

The preparation of the powder mixtures was conducted using two different wet chemical methods developed previously by our research group: the co-deposition method in the presence of citric acid (the Pechini method) and the spray drying method [34].

Spark plasma sintering of the powder mixtures was conducted using Dr. Sinter model SPS-625 (SPS Syntex, Inc., Tokyo, Japan) in a vacuum. Sintering was performed in a graphite mold (LLC Termokarbon, Vyazma, Russia) with an inner diameter of 12 mm under a uniaxial mechanical load of 70 MPa and a heating rate of 50 °C/min. Graphite molds were covered with graphite felt of 4 mm in thickness to ensure the homogeneity of the temperature field during sintering. A hole with a diameter of 14 mm was cut into the graphite felt for the temperature control. Graphite foil (LLC Termokarbon, Vyazma, Russia) was used to improve the electrical contact of the moving parts of the mold (the punches and the die). The temperature was measured using an optical pyrometer IR-AHS2 (Chino Corporation, Tokyo, Japan) focused on the surface of the graphite mold. The true sintering temperature of the sample was estimated based on preliminary studies [41]. The load was applied to the mold simultaneously with the start of heating. Free cooling was used to cool the ceramic samples. The sintering continued until the end of the stage of the intensive shrinkage of the powder mixture.

The ceramic samples were annealed in a laboratory muffle furnace EKPS-10 (JSC Smolensk SKTB SPU, Smolensk, Russia) to remove the residual graphite foil from the surfaces of the samples. The annealing was performed at 750 $^{\circ}$ C for 2 h.

The dependencies of the powder shrinkage on the heating temperature L(T) were recorded during sintering using a built-in dilatometer of Dr. Sinter model SPS-625. The contribution of the empty mold $L_{empty}(T)$ was subtracted when processing the results. This contribution was determined during the preliminary experiments. The theoretical densities of the ceramics were estimated from the given Si_3N_4 - $Y_3Al_5O_{12}$ ratio for each mixture composition:

$$\rho_{th} = \frac{1}{\frac{\mathsf{m}_{\mathrm{Si}_3\mathrm{N}_4}}{\rho_{\mathrm{Si}_3\mathrm{N}_4}} + \frac{m_{\mathrm{YAG}}}{\rho_{\mathrm{YAG}}}} \tag{1}$$

where *m* is the mass fraction of Si₃N₄ and yttrium-aluminum garnet (YAG) (yttriumaluminum oxide system in the initial powder compositions) and ρ is the theoretical phase density. The density for Si₃N₄ is 3.20 g/cm³ and for YAG is 4.55 g/cm³. Thus, the theoretical densities for samples containing additives of 3%, 5%, 8.5% and 10% wt. are 3.227, 3.245, 3.266 and 3.292 g/cm³, respectively.

The analysis of the sintering kinetics was carried out according to the procedure described in [41].

The density of the ceramics was determined by hydrostatic weighing in distilled water using CPA 225D (Sartorius, Göttingen, Germany) analytical balance.

The surfaces of the ceramic samples were ground with diamond discs using the Secotom-10 machine (Struers, Copenhagen, Denmark). This surface treatment step was performed to remove the heterogeneous surface layers and to reduce the surface roughness [42]. The initial heights of the ceramic samples were 4 mm. The layers about 100 μ m in thickness were removed during the sample surface preparation [43].

The Vickers microhardness (H_V) was determined with a 60 A+ EVO microhardness tester (ATM Qness GmbH, Mammelzen, Germany) at a load of 2 kg. The fracture toughness coefficient (K_{IC}) was determined by the Palmquist method based on measuring the maximum crack lengths from the Vickers indenter edges:

$$K_{IC} = 0.016P \sqrt{\frac{E}{c^3 H_V}} \tag{2}$$

where *c* is the crack length (m), *E* is Young's modulus (GPa), H_V is the microhardness (GPa), and *P* is the load (N). The Young's modulus for silicon nitride is about 300 GPa.

The X-ray diffraction (XRD) measurements of the powders and ceramics were performed using the XRD-7000 diffractometer (Shimadzu, Kyoto, Japan) (CuK α radiation, the wavelength $\lambda = 1.54$ Å, 30 kV/40 mA). Scanning was performed in the Bragg-Brentano geometry in the range of angles $2\theta = 15^{\circ}-60^{\circ}$ with the step of 0.04° and the exposure time of 1 s. The qualitative phase analysis was carried out using the PDF-2 database (ICDD, 2012). The quantitative phase analysis was carried out by the Rietveld method using "Diffrac.TOPAS" software (Bruker, Karlsruhe, Germany) with the cif-files from the ICSD database (2016): α -Si₃N₄ (N 16752) and β -Si₃N₄ (N 8263) [44]. The uncertainties of this method for the materials based on Si₃N₄ were estimated experimentally [45].

The microstructures of the ceramic samples were studied using JSM 6490 scanning electron microscope (JEOL, Ltd., Tokyo, Japan) with an INCA 350 energy dispersive microanalyzer (Oxford Instruments, Abingdon, UK).

3. Results

3.1. Preparation of Powder Mixtures

The mixture compositions were based on the ratio of Si_3N_4 - Y_2O_3 - Al_2O_3 . The molar ratio of the components of the oxide system was 3:5, which corresponds to the stoichiometry of yttrium-aluminum garnet $Y_3Al_5O_{12}$ (YAG) [46]. The fractions of the sintering additive were 3%, 5%, 8.5% and 10% (Table 1). The mixtures were prepared (I) by spray drying method and (II) by co-deposition method in the presence of citric acid according to the procedures developed earlier [34].

 Table 1. Description of powder mixtures.

Sample	Mixture Synthesis Method	Additive $(Y_2O_3-Al_2O_3)$, % wt.
I-3 I-5 I-8.5 I-10	Ι	3 5 8.5 10
II-3 II-5 II-10	П	3 5 10

The sintering additive was introduced into the Si₃N₄ powder by spray drying method (I) using a mixture of Al₅(NO₃)₃(OH)₁₂ and Y(OH)₂(CH₃COO) sols. Al₅(NO₃)₃(OH)₁₂ sol was obtained by dissolving pre-hydrolyzed aluminum isopropylate (Al(i-OC₃H₇)₃, 99.99% purity, made on site) in nitric acid (HNO₃, 99.9999% purity, Khimreaktiv, Nizhniy Nov-gorod, Russia). Y(OH)₂(CH₃COO) sol was produced by dispersing the Y₂O₃ nanopowder in acetic acid (CH₃COOH, 99.9% purity, Khimreaktiv, Nizhniy Novgorod, Russia). The Y₂O₃ nanopowder was obtained by self-propagating high-temperature synthesis from commercial yttria (99.99% purity, Polirit, Moscow, Russia) [47,48]. The aqueous suspension contained 52.5% wt. in terms of the solid phase of Si₃N₄ and YAG. Ammonium polyacrylate Dispex 4040 (BASF, Ludwigshafen, Germany) (in the amount of 1.5% wt.) was introduced additionally for stabilization. The suspension was dried by spray drying at 150 °C after mixing in a Pulverisette 6 planetary mill (FRITSCH, Idar-Oberstein, Germany) with the Y₂O₃ balls.

The Pechini method (II) consists of the formation of citrate gels from solutions of yttrium nitrate $(Y(NO_3)_3 \cdot 6H_2O, 99.9\%$ purity, Vekton, Saint-Petersburg, Russia) and aluminum nitrate $(Al(NO_3)_3 \cdot 9H_2O, 98\%$ purity, Vekton, Saint-Petersburg, Russia) with the addition of citric acid $(C_6H_8O_7 \cdot H_2O, 99\%$ purity, Vekton, Saint-Petersburg, Russia) [49]. Citric acid solution was added to the aqueous solution of yttrium and aluminum nitrates in such an amount that the molar ratio of citric acid to the total content of nitrate ions was 1:1. Si₃N₄ powder was added to the resulting solution and dried with continuous mixing to the thick gel state. Afterward, the gel was annealed sequentially at 350 and 500 °C for 2 h.

Figure 1 shows the microstructure of the synthesized powder mixtures.



Figure 1. SEM images of the powder mixture with different amounts of the sintering additive: (**a**,**b**) 3% wt.; (**c**,**d**) 5% wt.; (**e**) 8.5% wt.; (**f**,**g**) 10% wt.

The results of the scanning electron microscopy (SEM) investigations demonstrate a high degree of homogeneity of the powder mixtures and the absence of large (>5 μ m) agglomerates of the sintering additive. As a rule, the spray drying method ensures no formation of spherical agglomerates [37].

The I-8.5 powder mixture was investigated by transmission electron microscopy (TEM). The faceted Si_3N_4 crystal grains and the sintering additive distributed on their surfaces are visible in the TEM image (Figure 2). Thus, the realization of the expected contamination of each particle of the Si_3N_4 powder by the sintering additive is shown.



Figure 2. TEM image of the I-8.5 powder mixture.

The diffraction peaks from the α -Si₃N₄ and β -Si₃N₄ crystalline phases are present in the diffraction patterns of both the powder mixtures and the raw powder material. There are no diffraction peaks corresponding to the oxide phases. This suggests an amorphous structure of the oxide phases [34]. The content of β -Si₃N₄ is 10% wt.

3.2. Compaction (Sintering) of Powder Mixtures

Seven samples of ceramics were produced. The compaction behavior is represented in Figure 3 by the shrinkage and shrinkage rate measured in the course of sintering.



Figure 3. Cont.



Figure 3. Shrinkage and shrinkage rate vs temperature during SPS of the powder mixtures with different amounts of the sintering additive: (**a**) 3% wt.; (**b**) 5% wt.; (**c**) 8.5% wt.; (**d**) 10% wt.

The analysis of the measured shrinkage cures for the powder mixtures indicates slow shrinkage in the temperature range from 900 to 1400 °C. The beginning of the intensive shrinkage stage takes place at 1400–1500 °C and is not affected by the sintering additive amount. At the same time, the higher the sintering additive amount, the lower the shrinkage end temperature. The shrinkage end almost corresponds to the beginning of the decomposition of Si₃N₄ for the samples with an additive content of 3%–5% wt. This is reflected as a sharp increase in shrinkage at temperatures above 1800 °C.

Figure 4 presents the plots of the vacuum level in the SPS chamber vs. temperature for the I-3, I-5, II-3, and II-5 samples. One can see that the pressure in the chamber increases at temperatures above 1800 °C. This result confirms the beginning of the decomposition of Si_3N_4 at these temperatures.



Figure 4. Vacuum level for the studied samples with an additive content of 3%–5% wt.

The shrinkage end is reached at temperatures of 1650-1700 °C for the samples with an additive content of 8.5%-10% wt. (I-8.5, I-10, II-10). This is reflected in the shrinkage by reaching the plateau. The sintering temperatures calculated using the approach reported earlier [41] and the relative densities for the ceramic samples manufactured are given in Table 2.

Sample	Sintering Temperature, °C Measured Density, g/cm ³		Relative Density, %
I-3	1920	3.221	99.8
I-5	1930	3.229	99.5
I-8.5	1740	3.243	99.3
I-10	1730	3.226	98.0
II-3	1920	3.214	99.6
II-5	1880	3.222	99.3
II-10	1710	3.226	98.0

Table 2. Sintering temperature, measured, and relative densities of the ceramic samples.

The density values for the ceramic samples confirm the formation of a high-density structure. The lowest relative density (98.0%) was achieved for the ceramics with the highest sintering additive content. The ceramic samples with densities of at least 99.3% were obtained from the powder mixtures containing 3%–8.5% wt. of the sintering additive.

3.3. Microstructure of Ceramic Samples

Figure 5 shows the results of SEM investigations of the ceramic samples.



Figure 5. SEM images of the ceramic samples with different amounts of the sintering additive: (**a**,**b**) 3% wt.; (**c**,**d**) 5% wt.; (**e**) 8.5% wt.; (**f**,**g**) 10% wt. The arrows point to the elongated β -Si₃N₄ grains.

The results of the SEM image analysis (Figure 5) demonstrate a lower porosity for samples containing smaller amounts of the sintering additive, in accordance with the ceramic density reported. The images of samples with smaller amounts of the sintering additive (Figure 5a–d) show the elongated β -Si₃N₄ grains up to 1 µm in thickness and up to 5 µm long (marked by arrows in Figure 5). The ceramic samples made from the

powder mixtures synthesized by spray drying (Figure 5a,c,e,g) have no visible pores or the content of these is insignificant in all cases. At the same time, the sintering additive inclusions manifested as the light spots (due to the presence of yttrium in the composition of these ones) are distributed along the triple joints of the grains. The sintering additive is practically invisible at the grain boundaries at the resolution of the equipment available.

The equiaxial grains were observed preferentially in the SEM images obtained for samples with 10% wt. of sintering additive (Figure 5e,g). The porosity is characteristic of all ceramic samples obtained from the powder mixtures produced by method II (Figure 5b,d,e). In addition, the porosity increases with increasing the sintering additive amount.

Moreover, Figure 5 shows that an increase in the sintering additive content leads to a reduction in the average grain size. This is probably due to the fact that the shrinkage end occurs at a lower temperature at an increased sintering additive amount in the powder mixture. In this case, the α -Si₃N₄ phase is still quite stable [8]. Accordingly, the grain growth of the β -Si₃N₄ phase is less intense than at higher temperatures.

3.4. Phase Composition and Mechanical Properties of Ceramics

Figure 6 shows the diffraction patterns from the ceramic samples.



Figure 6. Diffraction patterns from the ceramic samples with different amounts of the sintering additive in the powder mixtures synthesized by method I (**a**) and by method II (**b**).

Only the α -Si₃N₄ (PDF № 01-071-6479, ICSD № 16752, P31c, a = b = 7.754(1) Å, c = 5.610(1) Å, V = 292.11(1) Å³) and β -Si₃N₄ (PDF № 01-071-0623, ICSD № 8263, P6₃, a = b = 7.595(1) Å, c = 2.902(1), V = 144.99 Å³) phases are present in the ceramic samples according to the presented diffraction patterns. The quantitative phase composition of the samples studied and the mechanical properties of the ones are presented in Table 3.

Sample	α -Si ₃ N ₄ , % wt.	β -Si $_3N_4$, % wt.	H_V , GPa	K_{IC} , MPa·m ^{1/2}
I-3	_	100	16.5 ± 0.4	3.8 ± 0.3
I-5	-	100	16.4 ± 0.4	4.4 ± 0.3
I-8.5	58 ± 2	42 ± 2	16.1 ± 0.4	4.0 ± 0.3
I-10	66 ± 2	34 ± 2	17.4 ± 0.4	5.1 ± 0.3
II-3	_	100	15.8 ± 0.4	5.1 ± 0.3
II-5	-	100	15.5 ± 0.4	4.0 ± 0.3
II-10	20 ± 2	80 ± 2	16.5 ± 0.4	4.2 ± 0.3

Table 3. Phase composition and mechanical properties of the ceramic samples.

According to the results of the X-ray diffraction analysis, the ceramic samples were found to contain the α -Si₃N₄ and β -Si₃N₄ crystalline phases only. Only the β -phase is present in the samples obtained with the amount of the additive of 5% wt. or less.

The α -Si₃N₄ phase content is higher in the samples with higher amounts of sintering additive and, accordingly, lower sintering temperatures.

The results of mechanical tests demonstrated the Vickers microhardness above 15.5 GPa for all ceramic samples studied. Moreover, the mechanical properties were higher for the samples made by method I (among those with equal amounts of sintering additive). The highest microhardness was achieved at the highest values of the sintering additive amount. The high microhardness and fracture toughness of the sample I-10 (Figure 5e) are probably due to the synergistic effects of both elongated needle-shaped β -Si₃N₄ grains, which increase the fracture toughness and a significant number of α -Si₃N₄ grains, which have higher microhardness as compared to the β -phase [7,8].

4. Discussion

Some features were revealed in the analysis of the sintering curves presented in Figure 3. A temperature-dependent shrinkage curve of a sample is shown schematically in Figure 7. Two points on the temperature axis should be noted in addition to the characteristic temperatures of the shrinkage beginning (900 °C) and the intensive shrinkage beginning (1400–1500 °C). The temperature T_s characterizes the end of the intensive shrinkage stage when the highest density of the sample is reached, T_d is the beginning of the decomposition of Si₃N₄. The temperature T_d may depend on the sintering mode (in particular, on the pressure inside the mold) at temperatures $T \ge 1800$ °C [50].



Figure 7. Schematic representation of the shrinkage of a sample based on Si₃N₄.

The increase in the shrinkage at the temperatures above 1800 °C is due not to compaction but to the Si_3N_4 decomposition (along with the increase in vacuum pressure). This was confirmed also by comparison of the densities of the sample with 5% additive contents. The difference in the sintering temperatures for samples I-5 and II-5 was 50 °C:

1930 and 1880 °C, respectively. The shrinkage of the sample I-5 in the temperature range 1880 \div 1930 °C was 0.2 mm. However, the relative density values for the I-5 and II-5 ceramic samples were close (Table 2). Therefore, it is assumed that the decomposition of Si₃N₄ occurred on the surface of the I-5 sample only and the sample bulk retains its densification. The temperature T_s was lower for the samples with higher sintering additive contents. Consequently the difference (T₁-T₂) was greater at higher sintering additive contents.

Consequently, the difference (T_d - T_s) was greater at higher sintering additive contents. The temperatures T_d and T_s were almost the same for samples with the additive content of 3% regardless of the method of its introduction into the powder mixture (Figure 3). For this reason, a sharp increase in the shrinkage rate instead of saturation starts at 1800 °C. Thus, it should be expected that a lower sintering additive content in the Si₃N₄-based ceramics will also lead to an increase in the shrinkage rate due to the decomposition of Si₃N₄ (at ~1800 °C) before the end of shrinkage.

The relationship between the sintering temperature, the phase composition of the samples, and the sintering additive content in the mixture for the samples under study is illustrated in Figure 8.



Figure 8. Dependence of the α -Si₃N₄ amount in the ceramic sample and the sintering temperature on the sintering additive amount.

The complete phase transition α -Si₃N₄ $\rightarrow \beta$ -Si₃N₄ does not occur in the ceramic samples with the sintering additive content of 8.5% wt. or more.

The α/β ratio of the Si₃N₄ phases is mainly affected by the sintering temperature and, to a lesser extent, the amount of the sintering additive [7,33,51,52].

The sintering of Si_3N_4 is a three-stage process accompanied by a phase transformation according to [53]. The dissolution of α -Si₃N₄ in the sintering additive melt and deposition as the β -phase occurs at high temperatures [54,55]. Thus, a larger amount of melts and lower shrinkage end temperatures prevent complete phase transformation. It is assumed that a higher sintering temperature at equal sintering additive content indicates a more homogeneous sintering additive distribution. Based on the regularity of the decrease in the sintering temperature with increasing the sintering additive content, the formation of local inhomogeneities in the powder mixture will reduce the sintering temperature on average. In this regard, the formation of the local inhomogeneities in the powder mixture will reduce the sintering temperature on average. The Young-Cutler model was used to analyze the kinetics of high-speed sintering of powders at the stage of intensive shrinkage (T > 1400 °C). This model describes the initial stage of non-isothermal sintering of spherical particles under conditions of simultaneous processes of bulk and grain boundary diffusion and plastic deformation [56]:

$$\varepsilon^2 \left(\frac{\partial \varepsilon}{\partial t}\right) = \frac{2.63\gamma \Omega D_v \varepsilon}{kT d^3} + \frac{0.7\gamma \Omega b D_b}{kT d^4} + \frac{A p \varepsilon^2 D}{kT}$$
(3)

where ε is the relative powder shrinkage, γ is the surface free energy, D_v is the bulk diffusion coefficient, D_b is the grain boundary diffusion coefficient, d is the grain size, p is the pressure, D is the plastic deformation diffusion coefficient.

According to [56], the slope of the temperature dependence of shrinkage plotted in the axes

$$\left(YC \equiv ln\left(T\frac{\partial\varepsilon}{\partial T}\right); \frac{T_m}{T}\right) \tag{4}$$

corresponds to the effective sintering activation energy mQ_{s1} where *m* is a coefficient depending on the dominant sintering mechanism: m = 1/3 for the grain boundary diffusion, m = 1/2 for the bulk diffusion, and m = 1 for the viscous flow (creep), T_m is the melting point taken equal to Si₃N₄ decomposition temperature ~1800 °C.

The analysis of the results shows the effective activation energy of SPS (mQ_{s1}) at the stage of intensive shrinkage for Series II ceramics to be ~ 12 ± 4 kT_m (Figure 9).





It should be noted also that the value of the SPS activation energy for the fine-grained ceramics can be calculated within the pore diffusion dissolution model described in [41]. In this approach, the activation energy Q_{s2} can be determined from the slope of the dependence:

$$BD \equiv \left(ln \left(ln \left(\frac{\alpha \rho}{\rho - 1} \right) \right) \right) = f \left(\frac{T_m}{T} \right)$$
(5)

where $\alpha = 0.5$ is the compaction coefficient of powder billet, ρ is the relative density.

The calculations showed that there is no difference (within the uncertainty) in the values of the sintering activation energy Q_{s2} for all ceramic samples studied: $Q_{s2} = (11 \pm 3) kT_m$ (Figure 10).

The close values of $mQ_{s1} = (12 \pm 4) kT_m$ and $Q_{s2} = (11 \pm 3) kT_m$ mean that the value of *m* in the Young-Cutler model is close to unity ($m \sim 1$). According to [56], it means that the hardening process of Si₃N₄-Y₂O₃-Al₂O₃ powder mixtures at the stage of intensive shrinkage of SPS is controlled by the viscous (plastic) flow of the oxide phase.



Figure 10. Analysis of the sintering activation energy within the pore dissolution model on the example of the II-5 sample.

5. Conclusions

The powder mixtures based on the Si_3N_4 powder (the particle size <5 µm) and Y_2O_3 -Al₂O₃ (3:5) sintering additive were prepared by spray drying method and by the codeposition method in the presence of citric acid (Pechini method). The sintering additive contents were 3%, 5%, 8.5% and 10% wt.

The ceramic samples were produced from the powder mixtures using spark plasma sintering (SPS). A homogeneous distribution of the sintering additive (Y₂O₃-Al₂O₃) in the powder mixture was shown to be possible using wet chemical methods. The Vickers microhardness of the ceramic samples was (16.5 \pm 0.4) GPa, and the Palmquist fracture toughness was (5.1 \pm 0.4) MPa·m^{1/2}.

This study has shown the possibility of obtaining high-density nonporous ceramics by sintering the powder mixtures with the sintering additive content of 5% wt. or less.

The results of this investigation show the sintering kinetics in SPS of Si_3N_4 -based ceramics change significantly when decreasing the sintering additive amount. The shrinkage rate does not decrease to zero at the maximum compaction but starts to increase sharply, which corresponds to the beginning of the decomposition of Si_3N_4 .

Using the Young-Cutler model and diffusion pore dissolution model, the main mechanism of the powder compaction during the intensive shrinkage stage was shown to be the viscous material flow.

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