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SPS sintering of nitride ceramics

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Due to the unique properties of ceramics materials based on nitride, it could be used in the broadly understood technique. However, obtaining silicon nitride materials requires it to use the advanced methods of manufacturing, mostly because this material is difficult to sinter. Dense ceramic sinters were obtained from the system $\text{Si}_3\text{N}_4\text{-Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ by applied pulsed current – SPS/FAST method (Spark Plasma Sintering/Field Assisted Sintering Technique). The sintering parameters of the initial mixture were optimized to obtain the highest possible sinter properties, such as: density, Young's modulus, hardness and fracture toughness. In the presented work the influence of pressure and pulse current, used in the SPS/FAST method, on sinterability and on selected physical and mechanical properties of the obtained materials was analyzed. The purpose of introducing the Al_2O_3 and Y_2O_3 additions to the Si_3N_4 matrix was to activate the hard-to-sinter silicon nitride powder and consequently to achieve a high density of the sintered samples. The best properties were characterized by sinter obtained in 1700°C and under pressure 63 MPa; the holding time at sintering temperature was 15 min. The density of the obtained sample has reached 98% theoretical value, and the other parameters were: Young's modulus – 298 GPa, Vickers hardness – 17,7 GPa, fracture toughness – $6 \text{ MPa}\cdot\text{m}^{1/2}$.

KEYWORDS: Si_3N_4 , SPS sintering, Young's modulus, hardness

Introduction

Si_3N_4 silicon nitride is a ceramic material belonging to the so-called technical ceramics. Due to its unique properties, Si_3N_4 matrix ceramics are one of the most popular materials used in the broadly defined technique. Ceramics with a silicon nitride matrix are characterized by good chemical and oxidation resistance, high hardness and surface crack resistance. These materials can work at elevated temperatures, because they retain very good mechanical properties. Due to this, nitride ceramics are widely used in many industries, including aviation, military, chemical, metallurgical, food, fuel, electronics industries, as well as in medicine – nitride ceramics are used to make, for example, machining tools, bearings, engine parts and gas turbines.

Si_3N_4 components are found in dosing valves for chemical pumps and pumps operating at high temperature or aggressive environments. Silicon nitride ensures a longer service life of machinery and equipment, and prevents unnecessary stops and failures – often even entire production lines.

Due to favourable combination of properties of Si_3N_4 matrix ceramics, further modifications to the composition of this group of materials are justified, both in terms of their current and future applications.

Silicon nitride has low self-diffusion rate and is classified as difficult to sinter. Silicon nitride materials in the form of dense sinters with good properties are obtained by free sintering using activators – most often oxides and their mixtures, e.g. MgO , Y_2O_3 , Al_2O_3 . During sintering, activators form the liquid phase and facilitate the consolidation of Si_3N_4 [2, 3]. Due to activators, relatively well-concentrated materials can be obtained by free

sintering. In this method, however, the material's sustaining time at sintering temperature is long (60÷90 min), which causes an increase in grain size and thus deterioration in mechanical properties of the material. To avoid grain growth during sintering Si_3N_4 , various physical factors are used to activate consolidation mechanisms and significantly reduce the total time of the material compaction process. These factors can be e.g. elevated or ultra-high pressure (from 30 MPa to 8 GPa), microwave radiation or pulse current – their impact is used in the processes of sintering with pulse current SPS, microwave sintering and high pressure HPHT (high pressure – high temperature) [4].

Free sintering usually produces sinters with relative density of up to about 96%, while high-pressure sintering HPHT allows materials with density exceeding 99% of the theoretical value to be obtained. However, high density does not guarantee optimal mechanical properties, including Young's modulus or hardness. During sintering HPHT, high stress is created in the material under high pressure, often causing cracking of samples.

The SPS (spark plasma sintering) method is an effective sintering method, combining the advantages of increased pressure, pulse current and a relatively short process time [5]. It uses impulse current to heat the compressed greenbody in the graphite matrix (fig. 1).

The SPS method is gaining more and more popularity because it enables sintering of materials from various groups (metallic, ceramic, composite) – both electrically conductive and insulators – including hard-sintered materials, such as carbides and borides classified as ultra-high melting ceramics, with a melting point above 3000°C (e.g. TaC, TiC, ZrC, NbC, TaB₂, ZrB₂) or silicon nitride. Due to the direct heating of the charge and the short process time, the SPS method is characterized by high energy efficiency, which makes it a cost-effective and ecological technique.

$\text{Si}_3\text{N}_4\text{-Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ composite mixture made using commercial nano- and micro-powders were sintered by SPS. The sintering process was optimized and the properties of the materials obtained were determined: apparent density, Young's modulus, Vickers hardness, and surface crack resistance.

Fig. 1. SPS sintering system– sintering chamber with prepared charge

Research material and methodology

The following powders were used to prepare the mixtures:

- Si_3N_4 from H.C. Starck – medium grain size 0.5÷0.7 μm (grade M11),
- Al_2O_3 by ALCOA – medium grain size 0.3÷0.6 μm (grade A16SG),
- Sigma Aldrich Y_2O_3 nano-powder – with an average grain size <50 nm.

The following mass fractions of individual components were preserved in the mix: 88% Si_3N_4 , 6% Al_2O_3 and 6% Y_2O_3 . The mix was homogenized in a Fritsch Pulverisette 6 planetary mill using a grinding bowl (250 ml capacity) and grinders (5 mm diameter) made of silicon nitride. The rotational speed was 200 rpm and the homogenization time was 1 hour. Isopropyl alcohol was used as wetting medium. The mix was then dried at 100°C for 5 h. The mixes were pre-pressed at a pressure of 110 MPa in a 20 mm diameter graphite matrix and

then placed in the SPS chamber. Sinters with a height of approx. 5 mm were obtained. The samples were sintered at a temperature in the range of $1450 \div 1700^\circ\text{C}$ at a pressure of 63 MPa; holding time at sintering temperature was 4 and 15 min. Sintering was carried out under an argon atmosphere. The SPS sintering device is schematically shown in fig. 2.

Fig. 2. Diagram of the SPS device

Phase analysis of the materials was performed by X-ray diffraction (XRD) on an Empyrean II diffractometer from PANalytical, using filtered $\text{Cu K}\alpha$ radiation ($\lambda_{\text{Cu}} = 1.5406 \text{ \AA}$). HighScore Plus software and ICDD-PDF4 + 2016 databases were used to identify the phases.

The microstructure analysis of composites was carried out using a scanning microscope (SEM) JSM-6460LV from JEOL, equipped with an EDS INCA X-act Energy 350 X-ray spectrometer from Oxford Instruments.

The density of samples was determined by the hydrostatic method in accordance with PN-EN 623-2 standard [6], and the Young's module – by the ultrasonic method with the use of the Panamatrix EPOCH 3 flaw detector. Longitudinal and transverse wave velocities were determined using sample thickness and the time of passage of the ultrasonic pulse through material. The ultrasonic method is one of the non-destructive methods for determining the elastic constants of materials.

Hardness measurements were made with the Vickers Hardness Tester FLC-50VX by FUTURE-TECH using a load of 9.81 N (1 kg).

Fracture toughness of samples was determined by the Vickers indenter method. The marks were created under a load of 294.3 N (30 kg). Because the ratio of crack length to half the diagonal of the impression was greater than 2.5, it was classified as a radial crack.

Results

Phase composition analysis

Fig. 3 shows examples of diffraction patterns of silicon nitride sinters obtained at 1550°C and 1700°C . Analysis of the phase composition showed the presence of the α and β phase Si_3N_4 . The diffractograms did not show reflections from sintering activators. The number of α and β phases in the samples varies depending on the sintering temperature.

The phase composition and the share of the β phase in silicon nitride in the entire cross-section of sintering optimization temperature are presented in tab. I.

Proportion of Si_3N_4 β phase in the material varies from 18% to 89% with increasing temperature and sintering time extension. The $\alpha \rightarrow \beta$ transformation is a phenomenon usually occurring at temperatures above 1400°C , favourably affecting the homogeneity of the microstructure and mechanical properties of the material (e.g. resistance to cracking or hardness) [7, 8].

Fig. 3. Analysis of the phase composition of the samples ($\text{Si}_3\text{N}_4\text{-Al}_2\text{O}_3\text{-Y}_2\text{O}_3$)

TABLE I. Phase composition of sinters based on Si_3N_4

Sample	Phase composition [wt. %]	
	α Si_3N_4	β Si_3N_4
1550°C/4'	82	18
1600°C/4'	75	25
1650°C/4'	65	35
1700°C/4'	39	61
1700°C/15'	11	89

Microstructure of sinters

The microstructure is shown in fig. 4. Si_3N_4 grains in sintered silicon nitride are poorly visible, because they are small in size. Still, it can be said that the material is very well compacted. The porosity in the material is not visible in the microstructures.

Fig. 4. Microstructure of sinters obtained by the SPS method (1650°C/4'/63 MPa)

Selected physical and mechanical properties

Results of measurements of selected physical and mechanical properties of silicon nitride sinters obtained by the SPS method at different temperatures are presented in tab. II. The analysis of sinter density and modulus of elasticity confirms the positive effect of pressure (63 MPa) and pulse current. As part of the author's previous research [7], the Si_3N_4 material was obtained by free sintering at 1680°C for 60 min (holding time at sintering temperature). The maximum sinter density that could be obtained at that time and Young's modulus were

3 g/cm³ and 241 GPa, respectively. For comparison: when sintering by SPS, already at 1550°C, the density was higher and amounted to 3.18 g/cm³. The Si₃N₄ sintering process by the SPS method was optimized to ensure the highest density and Young's modulus (fig. 5).

The density and Young's modulus of sinters increases with increasing temperature. The optimization process proceeded to a temperature of 1700°C, in which the holding time at sintering temperature was extended from 4 to 15 min. The longer sintering time resulted in additional sinter compaction and an increase in its Young's modulus of elasticity.

TABLE II. Selected properties of materials based on Si₃N₄

Sample	Density [g/cm ³]	Young's modulus E [GPa]	Hardness HV [GPa]	Crack resistance K_{IcHV} [MPa·m ^{1/2}]
Si ₃ N ₄ -Al ₂ O ₃ -Y ₂ O ₃				
1450°C/4'	2.62 ± 0.01	-	-	-
1500°C/4'	2.85 ± 0.01	219 ± 2	-	-
1550°C/4'	3.18 ± 0.01	296 ± 6	17.6 ± 0.3	4.9 ± 0.2
1600°C/4'	3.21 ± 0.01	299 ± 7	17.2 ± 0.1	4.9 ± 0.2
1650°C/4'	3.22 ± 0.01	299 ± 6	16.2 ± 0.9	5.2 ± 0.1
1700°C/4'	3.21 ± 0.01	294 ± 6	16.3 ± 0.4	5.4 ± 0.2
1700°C/15'	3.24 ± 0.01	298 ± 5	15.4 ± 0.2	6.0 ± 0.2

Fig. 5. Optimization of the sintering process for Si₃N₄ material by the SPS method:
a) density, b) Young's modulus

Fig. 6. Selected mechanical properties of the Si₃N₄ sinter obtained by the SPS method:
a) hardness, b) fracture toughness

The sinter had the highest hardness obtained at 1550°C (fig. 5a), and the best resistance to surface cracking – sinter obtained at 1700°C for 15 minutes (fig. 5b).

The hardness of Si_3N_4 samples decreases as the sintering temperature increases, while the surface crack resistance increases. These changes are caused by changes in the phase composition (transformation $\alpha \text{Si}_3\text{N}_4 \rightarrow \beta \text{Si}_3\text{N}_4$) and the microstructure of the sintered material – there is grain growth associated with an increase in temperature and prolonged sintering time. Material with increased density and crack resistance was obtained.

The research showed a large application potential of silicon nitride materials. The composite obtained has a crack resistance level of $K_{\text{ICHV}} 6 \text{ MPa}\cdot\text{m}^{1/2}$. The possibility of using this type of materials for the production of cutting blades seems particularly attractive.

Conclusions

- It has been shown that the degree of phase transformation of $\alpha \text{Si}_3\text{N}_4$ into $\beta \text{Si}_3\text{N}_4$ increases with increasing temperature and sintering time extension and reaches a maximum of 71% for the considered process parameters. Due to the phase transformation, the fracture toughness increased from 4.9 to $6 \text{ MPa}\cdot\text{m}^{1/2}$.
- Due to the SPS method, the time and material sintering temperature can be significantly reduced, which can bring measurable economic benefits. For example, to obtain ceramics based on Si_3N_4 by free sintering, a temperature of 1680°C is required, and the total process time – including the stages of heating, sintering and cooling the charge and furnace – is up to several hours, while in the case of the SPS method sintering takes place at 1550°C, and the total process time is just tens of minutes. Of course, it should be taken into account that the charge in free sintering processes is usually much larger/more numerous than in SPS processes, therefore the unit cost of sinter is relatively low. In many situations it is necessary to quickly obtain small elements – then the SPS method is more effective.
- The resulting sinters with a silicon nitride matrix, which are characterized by a high degree of compaction and good mechanical properties, are especially useful for the production of cutting blades intended for the demanding machining of difficult-to-machine super alloys, such as Inconel. Such ceramics can also be used to produce wear-resistant, small machine and equipment components, e.g. ball bearings or matrix inserts, improving their service life.

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