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The selection of phase composition of silicon nitride ceramics for shaping with the use of EDM machining

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Properties

ABSTRACT

Purpose: The purpose of this study is the selection of phase composition of Si_3N_4 matrix ceramics with the addition of conducting phases so as to make shaping of those materials possible by means of electro discharge machining (EDM). Silicon nitride matrix materials with the addition of oxide phases (Al_2O_3, MgO, ZrO_2) and conducting phases (TiB_2, TiN) were sintered by the method of SPS (Spark Plasma Sintering). Additionally the effect of oxide phases on silicon nitride sintering capacity, the value of electric resistance of nitride ceramics depending on the addition of a conducting phase and the effect of sintering parameters on selected features of produced materials were determined.
Design/methodology/approach: Materials were sintered with the use of a SPS device marked with FCT-HP D 5. Apparent density ρ_p was measured by the hydrostatic method. Hardness was determined by the Vicker's method at the load of 980.7 mN with the use of a Future Tech Corp digital hardness tester FM7. For the purpose of those tests a surface was prepared with the use of a Struers cutting grinder ACUTOM. Measurements of Young's modulus for sintered samples were carried out using a ultrasonic method of transverse and longitudinal wave speed measurement with the use of a Panametrics Epoch III detector. Resistance measurement was done with the use of Wheatstone and Thomson technical bridges.
Findings: The addition of titanium nitride had no effect on the reduction of electric resistance of Si_3N_4 matrix ceramics. The lack of electric conductivity of those materials is the result of used additions influencing sintering capacity, mainly magnesium oxide. Si_3N_4 matrix materials with the addition of titanium diboride are characterised by low electrical resistance with high physical and mechanical features maintained. Electric conductivity of those materials and the initial electro discharge cutting attempts prove that it is possible to shape Si_3N_4 matrix ceramic materials with the addition of a TiB_2 phase with the use of EDM process.
Practical implications: The use of EDM will enable the production of elements with complicated shapes (impossible to achieve by other shaping methods) from ceramic materials (with Si_3N_4 matrix).
Originality/value: By the appropriate selection of a conducting phase addition it is possible to increase electric conductivity of silicone nitride matrix ceramics, for which it is possible to shape products by means of electro discharge machining.
Keywords: Silicon nitride; Spark plasma sintering; Mechanical properties; Electrical properties

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1. Introduction

Ceramic materials belong to structures with ionic and covalent bonds. As opposed to metals, energy states of electronic charge carriers capable of invoking current conductivity (that is state belonging to a conductivity thread) are empty in the case of substances with ionic and covalent bonds. Electrical conductivity occurs solely as a result of (thermal or optical) excitation of electrons with lower energy states whereby the executed work must be higher than forbidden energy values. It can be assumed that for the majority of ceramic materials with ionic bonds and additionally with high purity there are no charge carriers [1]. Electrical features of polycrystalline and multiphase ceramic materials can be modified by means of composition and intergranular boundary structure and material surface modification, e.g. by way of layer deposition.

It is possible to distinguish three mechanisms giving technical ceramics (eg. Al_2O_3; ZrO_2+Y_2O_3; Si_3N_4; SiC) electrical conductivity [1, 2, 3]:

- natural electrical continuity by free electrons,
- doping during the process of production by means of natural electrical conductors (e.g. TiC; TiN; CaO; Si; TiB_2; B_4C, metallic phases) or by means of phases increasing ionic conductivity at high temperatures (e.g. Al_2O_3 or $Nd_2Ti_2O_7$ as the second phase in ZrO_2 based electrolyte),
- introduction of alien atoms (La; Mg; Ca; Y).

Ceramic materials are characterized by a number of positive mechanical features (high hardness and strength in a vast temperature range, oxidising and corrosive environment influence resistance, also at high temperatures, thermal shock resistance) and are commonly used in different areas of life [4]. Taking into consideration specific technical (oxide or nitride) ceramics features and possibilities which appear thanks to the electro discharge machining, tests aiming at the increase of technical ceramics electrical conductivity are fully justified and intentional. Ceramic parts with complicated shapes shaping can be carried out by the use of electro discharge machining assuming that the machined material is characterised by the appropriate electrical conductivity. The introduction of natural electrical conductors TiN, TiC, Ti(C,N) or TiB_2 into the matrix improves the multiphase ceramics conductivity. It gives a possibility to be used for such materials of electric discharge machining (EDM), and in final effect to make elements with very complicated shapes [5-10]. At present EDM technology is commonly used for shaping of steel [11] and ceramic materials superhard after high pressure sintering [12].

As it was presented in the study [7] the introduction of ceramics based on Si_3N_4 titanium nitride in the amount of 30 vol.% to 40 vol.% ensures good conductivity and production by means of electro-discharge machining of gas compressors rotors. The introduction of conducting additions in the amount of from 30-40% changes not only electrical conductivity but also mechanical features and abrasive wear resistance [13].

The study shows [14] the resistance measurement results of Si_3N_4 ceramics with the addition of TiN in the amount of 25 vol.%, made by SPS sintering. Ceramics made in this way was characterized by significantly better electrical features in comparison to the ceramics made by the traditional method (pressing and conventional sintering). As it was presented in this study the content of a conducting phase (TiN) in a TiN/Si_3N_4 composite designed for further machining by the EDM method can be reduced to the value of 10%. A significant aspect in the preparation of Si_3N_4 matrix ceramics with conducting additions (e.g. TiN) is not only the conducting phase content but also method of making itself (free sintering, sintering by the method of SPS, HP, HIP). Extended time of sintering of such materials facilitates a phase change of α-Si_3N_4 into β-Si_3N and a slight deterioration of mechanical features.

Electro discharge machining can be used in the case of materials resistance of which is not higher than 100 Ωcm [2, 14]. With the appropriate mechanical features maintained, the increase in a carbide or nitride phase in low conductivity ceramics is justified, because the effectiveness of EDM process increases [15].

2. Experimental procedure

The following powders were used for mixtures preparation:

- Si_3N_4 powder − α M11 variety by Starck with the average grain size of 0.6 μm,
- ZrO_2-Y powder − by Starck with the average grain size of 0.5 μm,
- MgO powder − by Reachim,
- Al_2O_3 powder – A16SG by ALCOA with the average grain size of 0.7 μm,
- TiN powder − by Starck with the average grain size from 1.3 to 1.9 μm,
- TiB_2 powder − by Starck with the average grain size from 1.5 to 2.5 μm.

Mixtures with the following compositions were prepared from the above-mentioned powders (powder content in mixtures is in volume %):

Si_3N_4 + 1.8% MgO + 1.1% ZrO_2,
70% (Si_3N_4 + 1.8% MgO + 1.1% ZrO_2)+30% TiB_2,
70% (Si_3N_4 + 1.8% MgO + 1.1% ZrO_2)+30% TiN,
Si_3N_4 + 1.9% MgO + 3.4% ZrO_2 + 1.7% Al_2O_3,
70% (Si_3N_4 + 1.9% MgO + 3.4% ZrO_2 + 1.7% Al_2O_3) +30%TiB_2,
70% (Si_3N_4 + 1.9% MgO + 3.4% ZrO_2 + 1.7% Al_2O_3)+ 30% TiN.

Materials were sintered by the method of SPS (Spark Plasma Sintering) with the use of a device marked with FCT-HP D 5.

Mixtures for Si_3N_4 based ceramics making were prepared in two stages. The first stage was comprised making of base mixtures: Si_3N_4 with additions: MgO+ZrO_2 and MgO+ZrO_2+Al_2O_3. Mixtures were prepared in a Pulversite 6 mill using a bowl and balls made from Si_3N_4 and with the addition of isopropanol. In the case of the mixture with MgO and ZrO_2 addition, the mill rotary speed was equal to 200 r/min and milling time was equal to 60 minutes. The rotary speed used during the mixture with MgO,

ZrO_2 and Al_2O_3 addition milling was equal to 400 r/min, milling time was also extended to 240 minutes.

In the second stage powders of the materials designed to increase electrical conductivity, that is TiB_2 and TiN, were added to the prepared base mixtures. Mixtures with conducting phases were also milled in a Pulversite 6 mill using a bowl and balls made from Si_3N_4 and with the addition of isopropanol. The mill rotary speed was equal to 200 r/m and milling time was equal to 60 minutes. After being dried, the mixtures were granulated with the use of a sieve with mesh width of 0.9 mm.

Materials designed for sintering with the use of an SPS device were initially pressed in a graphite die at the pressure of 30 MPa and the used parameters of sintering for individual materials are presented in Table 1.

Table 1.
Materials sintering process parameters

Composition	Force	Temp.	Time
	kN	°C	min.
Si_3N_4-MgO-ZrO_2	11	1550	10
Si_3N_4-MgO-ZrO_2-TiB_2	11	1550	5
	11	1550	10
Si_3N_4-MgO-ZrO_2-TiN	11	1550	5
	11	1550	10
Si_3N_4-MgO-ZrO_2-Al_2O_3	11	1350	10
	11	1450	10
	11	1500	10
	11	1550	10
	11	1600	10
	11	1650	10
Si_3N_4-MgO-ZrO_2-Al_2O_3-TiB_2	11	1550	10
Si_3N_4-MgO-ZrO_2-Al_2O_3-TiN	11	1550	10

Apparent density ρ_p was measured by the hydrostatic method. Hardness was determined by the Vickers method at the load of 980.7 mN with the use of a Future Tech Corp digital hardness tester FM7. For the purpose of those tests a surface was prepared with the use of a Struers cutting grinder ACUTOM. Measurements of Young's modulus for the sintered samples were carried out by means of ultrasonic method of transverse and longitudinal wave speed measurement with the use of a Panametrics Epoch III detector.

Resistance measurement was done with the use of technical bridges: Wheatstone MMW-5 type and Thomson TMT-5 type.

3. Results and discussion

The influence of sintering temperature on Si_3N_4-MgO-ZrO_2-Al_2O_3 ceramics density is presented in Fig. 1. Compaction of Si_3N_4 matrix ceramics depending on used additions MgO-ZrO_2 or MgO-ZrO_2-Al_2O_3 is presented in Fig. 2. Compaction of Si_3N_4 ceramics depending on used additions facilitating sintering capacity and conducting phases is presented in Fig. 3 and in Fig. 4.

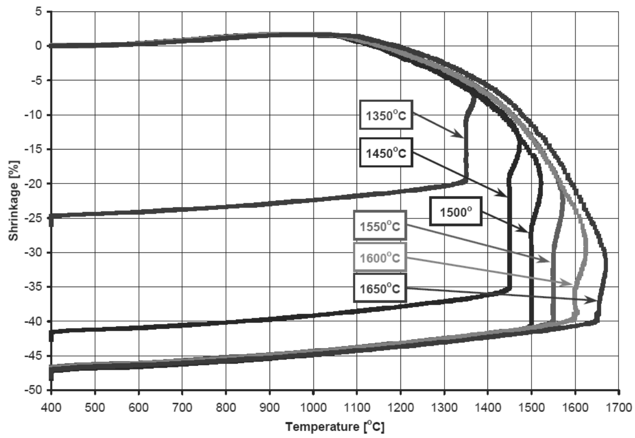

Fig. 1. The effect of sintering temperature on Si_3N_4-MgO-ZrO_2-Al_2O_3 samples density

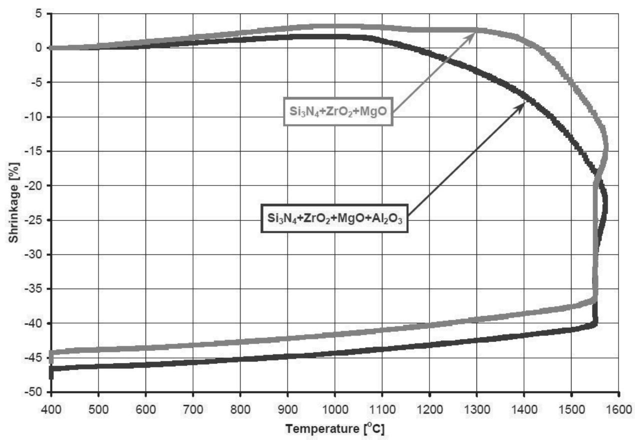

Fig. 2. Compaction of Si_3N_4 matrix samples with different oxide phases additions

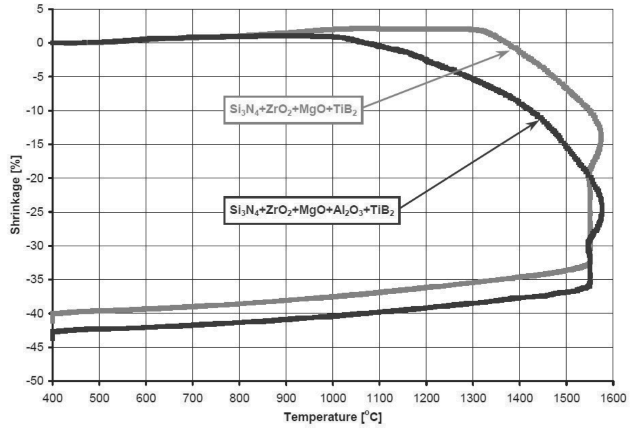

Fig. 3. Compaction of Si_3N_4 matrix samples with a TiB_2 conducting phase addition

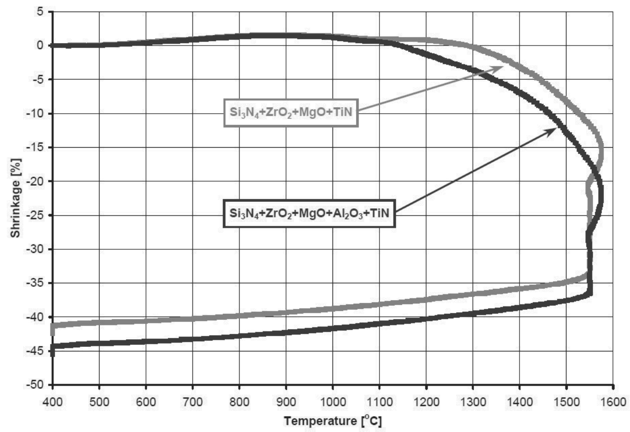

Fig. 4. Compaction of Si_3N_4 matrix samples with a TiN conducting phase addition

Selected features (density, Young's modulus, hardness HV1, electrical conductivity) of powders included in the composition of individual mixtures are presented in Table 2. Features of Si_3N_4 matrix ceramics with oxide phases additions and with conducting phases additions after sintering by the method of SPS are included in Table 3.

Initially chosen sintering parameters of Si_3N_4 ceramics with oxide phases allow obtain high density materials. The result of density measurements, Young's modulus and Vickers hardness of materials with a MgO-ZrO_2 and MgO-ZrO_2-Al_2O_3 additions were equal to accordingly: 3.16 g/cm^3 and 3.25 g/cm^3, 315 GPa and 313 GPa and 2011 HV1 and 1954 HV1. The increase in sintering temperatures and heating time result in a transition of α-Si_3N_4 into β-Si_3N_4, which involves insignificant hardness and Young's modulus reduction. Partial phase transition can be the cause of lower hardness (1876 HV1) and Young's modulus (304 GPa) of Si_3N_4-MgO-ZrO_2-Al_2O_3 mixture sintered at the temperature of 1650°C. It must be added that in view of short heating times the transition of a phase α into β does not occur as intensively as with other sintering methods eg. HP or free sintering. From the entered Si_3N_4-MgO-ZrO_2-Al_2O_3 mixture compaction curves (Fig. 1 and Fig. 2) it is apparent that the beginning of sintering connected with the formation of a low melting SiO_2-MgO-ZrO_2-Al_2O_3 phase occurs at the temperature of 1000°C. From that temperature the sample volume reduction and beginning of sintering process are noticeable. Partial oxidation of silicon nitride surface has a positive influence on the formation of a low melting glassy phase and on sintering capacity. In the case of Si_3N_4-MgO-ZrO_2 mixture the process of a glassy phase formation occurs in two stages, the first one at the temperature of 1000°C, the second at the temperature of 1300°C.

Si_3N_4 matrix materials with additions of conducting phases (TiB_2 and TiN) were sintered at the temperature of 1550°C. As earlier attempts at Si_3N_4 matrix materials sintering proved, according to the parameters included in Table 1 the sintering time at the temperature of 1550°C should be not shorter than 10 minutes. Samples sintered at the temperature of 1550°C in the time of 5 minutes were characterised by low density, Young's modulus and Vickers hardness, as it is apparent from the results included in Table 3.

Volume fraction of individual conducting phases in mixtures was equal to 27% to 30%. However, it must be added that good electrical conductivity was demonstrated only by Si_3N_4 matrix materials with the addition of TiB_2. Si_3N_4-TiN materials were characterised by high electrical resistance exceeding 5000 kΩ. From the literature data [19] it is apparent that the lack of electrical conductivity can be caused by a low melting glassy phase being a phase linking individual grains of Si_3N_4 and isolating conducting phases grains. The entered resistance measurements results do not confirm this thesis because a low melting glassy phase should isolate a TiN phase grains to the same degree as TiB_2 grains, more particularly as partial oxidation of those phases leads to the formation of, among others, titanium oxide TiO_2, and in the case of titanium diboride also a low melting B_2O_3 phase. Some explanation of achieved results can be that the lack of electrical resistance of materials with the addition of TiN occurs only in materials containing more than 1 vol.% of MgO. The results presented in Table 4 indicate that Si_3N_4 or Al_2O_3 matrix materials with similar conducting phase (TiN, Ti(C,N)) content, but with lower MgO content, demonstrate electrical resistance at the level of 10^{-1} Ω (lower by a number of orders of magnitude). Relatively high content of MgO and a TiN phase leads to the formation of spinel marked with Mg_2TiO_4 which emerging on the surface of titanium nitride grains effectively isolates grains and influences a significant increase in material electrical resistance. TiN as well as MgO are characterized by identical crystal structure (cF8).

Si_3N_4 based materials with the addition of TiN, apart from high electrical resistance, are characterised by good mechanical features. Si_3N_4-MgO-ZrO_2-TiN material was characterised by density at the level of 3.56 g/cm^3, Young's modulus equal to 305 GPa and hardness 1700 HV1. Si_3N_4-MgO-ZrO_2-Al_2O_3-TiN material was characterised by density equal to 3.84 g/cm^3, Young's modulus equal to 341 GPa and hardness exceeding 1900 HV1.

Table 2.
Materials features included in the composition of individual mixtures [2, 16, 17]

Features	Component					
	Si_3N_4	MgO	ZrO_2-Y	Al_2O_3	TiB_2	TiN
Melting Temperature, K	2170	2890	2950	2130	3270	3203
Density, g/cm^3	3.25	3.48-3.58	5.98	3.90-3.99	4.52	5.40
Young's modulus E, GPa	280-310	250-320	210	300-420	510-575	450
Poisson's Ratio	0.25	0.36	0.29-0.30	0.22-0.26	0.327	0,22
Hardness, GPa / *HV0.5	16	700*	1250*	1700-2000*	33	18-21
Electrical resistance, Ω·cm	10^{12}	$>10^{14}$	10^{12}	$5·10^{14}$	$20.4·10^{-6}$	$25·10^{-3}$

Table 3.
Physical and mechanical features of Si_3N_4 materials after SPS sintering

Composition	Sintering parameters	Density		Young's modulus		Poisson's Ratio	Hardness	Resistance
	temp.-time	apparent	relative	measured	relative			
	°C/min.	g/cm^3	%	GPa	%	-	HV1	Ω
Si_3N_4-MgO-ZrO_2	1550/10	3.16	95.4	315	97.3	0.26	2018	$>5·10^6$
Si_3N_4-MgO-ZrO_2-TiB_2	1550/5	3.06	81.3	207	61.5	0.2	702	$1.69·10^5$
	1550/10	3.34	88.7	302	89.7	0.21	1522	$1.05·10^1$
Si_3N_4-MgO-ZrO_2-TiN	1500/5	3.29	80.1	223	62.2	0.23	990	$1.23·10^6$
	1550/10	3.56	86.7	305	85.1	0.24	1737	$>5·10^6$
Si_3N_4-MgO-ZrO_2-Al_2O_3	1350/10	2.41	70.1	109	33.8	0.23	-	$>5·10^6$
	1450/10	3.00	87.3	243	75.3	0.24	1399	$>5·10^6$
	1500/10	3.23	94.0	317	98.2	0.26	2035	$>5·10^6$
	1550/10	3.25	94.6	313	97.0	0.25	1954	$>5·10^6$
	1600/10	3.25	94.6	309	95.8	0.26	1996	$>5·10^6$
	1650/10	3.24	94.3	304	94.2	0.26	1876	$>5·10^6$
Si_3N_4-MgO-ZrO_2-Al_2O_3-TiB_2	1550/10	3.51	91.6	318	94.7	0.22	1918	$8.45·10^{-1}$
Si_3N_4-MgO-ZrO_2-Al_2O_3-TiN	1550/10	3.84	90.7	341	94.4	0.25	1955	$>5·10^6$

Table 4.
Electrical resistance of selected Si_3N_4 and Al_2O_3 matrix ceramic materials with additions of TiN, TiB_2, Ti(C,N) conducting phases

Material	Phase composition, vol. %								Resistance, Ω
	Si_3N_4	TiN	TiB_2	Ti(C,N)	Al_2O_3	Y_2O_3	ZrO_2	MgO	
Si_3N_4-TiB_2	67.6	-	30.4	-	-	-	0.7	1.3	$1.05·10^1$
Si_3N_4-TiB_2	65.2	-	29.9	-	1.2	-	2.4	1.3	$8.45·10^{-1}$
Si_3N_4-TiN	70.6	27.3	-	-	-	-	0.8	1.3	$>1.23·10^6$
Si_3N_4-TiN	65.2	29.9	-	-	1.2	-	2.4	1.3	$>5·10^6$
Si_3N_4-TiN	53.7	38.5	-	-	5.3	2.5	-	-	$3.14-5.57·10^{-1}$
Al_2O_3-TiN	-	32.6	-	-	66.9	-	-	0.5	$2.26-8.42·10^{-1}$
Al_2O_3-Ti(C,N)	-	-	-	24.5	73.9	-	1.4	0.2	$6.75-24.9·10^{-2}$

Si_3N_4 based materials with the addition of TiB_2 demonstrated the minimal value of electrical resistance ($1.05 \cdot 10^1$ Ω) as in the case of Si_3N_4-MgO-ZrO_2-TiB_2 and ($8.45 \cdot 10^{-1}$ Ω) for Si_3N_4-MgO-ZrO_2-Al_2O_3-TiB_2 material. These materials were characterised by accordingly the following features: density 3.34 g/cm^3 and 3.51 g/cm^3, Young's modulus 302 GPa and 318 GPa and hardness 1522 HV1 and 1918 HV1.

4. Conclusions

The study presents the results of mechanical and electrical feature tests of Si_3N_4 matrix ceramics sintered by means of the SPS method. Titanium nitride or titanium diboride was added in order to improve electrical conductivity of Si_3N_4 ceramics. Obtained materials were characterized by good physical features, high Young's modulus and Vickers hardness. Young's modulus of materials sintered at the temperature of 1550°C in the time not shorter than 10 minutes exceeded the value of 300 GPa, irrespective of used additions. Vickers hardness of individual materials was included in the range of 1500 to 2020 HV1. However, the minimum value of electrical resistance was characteristic of materials in which the addition of TiB_2 was used. The addition of titanium nitride had no influence on the reduction of electric resistance of Si_3N_4 matrix ceramics.

The lack of electric conductivity of those materials is the result of used additions, mainly magnesium oxide, which influence on sintering capacity. High electrical resistance is characteristic for materials containing more than 1 vol.% of MgO. Relatively high content of MgO and a TiN phase leads to the formation of spinel marked with Mg_2TiO_4.

Si_3N_4 matrix materials with the addition of titanium diboride are characterized by low electrical resistance with high physical and mechanical features maintained. Electric conductivity of those materials and the initial electro discharge cutting attempts prove that it is possible to shape Si_3N_4 matrix ceramic materials with the addition of a TiB_2 phase with the use of EDM process.

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