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PREPARATION OF α-Si_3N_4 POWDER AND CERAMICS REINFORCED BY β-Si_3N_4 WHISKERS

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α-Silicon nitride containing 35—37 wt. % nitrogen, 3—4 wt. % oxygen and 1 wt. % carbon, with a mean particle size of about 1 μm, was prepared by heating the mixture of finely dispersed silica and carbon at 1 500 °C for 7—8 hours in nitrogen flowing at a rate of 40—50 cm^3 *min*$^{-1}$ *(the flow rate related to 1* g *of* SiO_2 *in the initial mixture). α-silicon nitride is formed by precipitation from gaseous* SiO, *and* N_2 *and* CO. *The positive effect of seeding crystals of α-silicon nitride on the reaction rate, the particle size of the product and on its morphology increases with the increasing surface area of the seeding powder.*

A ceramic material exhibiting a fracture toughness of about 6 MPa m$^{1/2}$, *which can be further increased by an addition of β-silicon nitride, was prepared by hot pressing of the silicon nitride powder with additions of yttrium oxide and aluminium oxide. Cutting tools made by grinding the resultant material were tested by intensive machining of cast iron and showed wearing comparable to that of cutting tools manufactured commercially abroad.*

INTRODUCTION

At present, advanced ceramics have been increasingly used in technology not only as a refractory material, but also as a structural one. This is due to their advantageous combination of physical and chemical properties, which is not exhibited by any other materials. These are above all the high melting temperatures, high strength, hardness and Young's modulus and a very good chemical stability and abrasion resistance. These properties are a consequence of chemical bonding and crystal structure of the substances used for preparation of structural ceramic materials. Strong and oriented covalent bonding leads to stable space arrangements of atoms in crystal structures. On the other hand a disability of movement of adjacent atoms leads to brittleness (low fracture toughness) and thermal shock sensitivity which are the main disadvanteges as compared with metals. For these reasons wider application of ceramics for structural purposes so far has been significantly limited. Improvement of reproducibility of the properties has been one of the main goals of recent research. Basically this can be achieved by improvement of methods for powder preparation and for powder densification. Considerable attention is also paid to seeking the ways for suppressing the brittleness of ceramics.

a) Development of preparative methods

The requirements for the properties of powders for ceramics have been reviewed by Barringer and Bowen [1]. The aim is to prepare chemically and phase-pure highly disperse non-aglomerated powders with a particle size smaller than 1 μm, with an isometric shape and a narrow particle size distribution. The surface of the powder particles is frequently treated chemically to create such repulsive forces which would supress spontaneous aggregation, but which would not hinder moulding and compacting. Powders of such properties are potentially capable of providing a green body (prepared by pressing, casting, etc.) with a homogeneous distribution of pores, which is a necessary prerequisite for the creation of a dense ceramic body with a uniform microstructure. If a green body with a wide distribution of grain and pore sizes is sintered, various local rates of densification occur, which leads to creation of stresses in the final material. The formation of large pores that can be hardly eliminated and abnormal grain growth are additional negative effects.

The mechanical properties of ceramics can also be substantially improved by using progressive methods of densification, e. g. medium pressure (up to 10 MPa) [2] or high pressure (up to about 300 MPa) [2—4] hot isostatic pressing of the green body covered by a gas-tight plastic (e. g. glass) container.

b) Increasing the fracture toughness of ceramics

Two basic concepts have been proposed for improving the fracture toughness of ceramics: transformation toughening which exploits the martensitic phase transformation of the tetragonal modification of ZrO_2 to the monoclinic one [5, 6] and reinforcement with whiskers (thin long monocrystals) or fibres dispersed throughout the matrix (composite materials) [6—11].

In the latter method, the toughness of the ceramics is improved by utilizing the high strength and Young's modulus of whiskers and fibres (e. g. of silicon carbide). Such admixtures influence the behaviour of the material during fracture. Under tensile stress the whiskers (fibres) are elongated less than the matrix as a result of their higher Young's modulus. Stresses are concentrated in the whiskers (fibres) and stress concentration in the matrix is therefore reduced. If the matrix nevertheless fails, the material can be held together by the strong whisker (fibre) bridging over the two cracked surfaces (Fig. 1a). If the fracture stress is greater than the whisker strength, the whisker is fractured and the crack can propagate in the matrix (Fig. 1b). When the whisker is stronger than the acting stress and its bond to the matrix is weak, the whisker is pulled out as the crack propagates (Fig. 1c). The process requires the friction in the matrix-whisker boundary to be overcome, and this consumes some of the energy causing the crack propagation. Additional dissipation of energy results from different thermal expansions of the whisker and the matrix. On cooling the material down from the sintering temperature, the whisker and the matrix shrink differently, and the compressive (or tensile, according to a lower or higher thermal expansivity of the whisker) and shear stresses, which are superposed on the external tensile stress, cause the crack deflection (Fig. 1d). During the process, the acting external stress is reduced to an effective value, which will be the smaller the greater the deviation of the direction of crack propagation from the original direction.

The strength and toughness of the material can also be expected to be significantly affected by the uniformity of distribution of inclusions in the matrix.

In the present work finely dispersed powders of α-silicon nitride were prepared by carbothermal reduction and nitriding of silica. The effect of the reaction conditions on the kinetics of conversion of silica to silicon nitride, and on the chemical and phase composition and on the morphology of the products were studied. The silicon nitride powders were compacted by hot pressing into a dense ceramic material. The effect of additions of β-silicon nitride whiskers on the sinterability and toughness of the material was investigated. Cutting tools prepared by grinding of the materials were tested by high-speed machining of cast iron to determine their cutting properties.

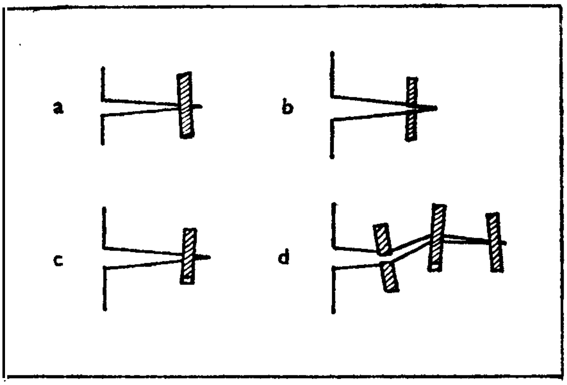

Fig. 1. Mechanisms involved in improving the toughness of ceramics by means of whiskers. a) strong whisker will stop crack propagation (bridging over); b) if the stress at the crackface exceeds the whisker strength, the whisker will break and the crack will go on propagating; c) pull-out of whisker from the matrix; d) deflection of the direction of crack propagation resulting from stresses in the neighbourhood of inclusions.

PREPARATION OF SILICON NITRIDE POWDERS BY CARBOTHERMAL REDUCTION AND NITRIDING OF SILICA

At present, silicon nitride is one of the most important representatives of non-oxidic structural ceramics. The materials prepared on this basis exhibit a favourable combination of low thermal expansion ($\alpha = 3.2$—3.4×10^{-6} K^{-1} at 20—1000 °C) and a good thermal conductivity ($\lambda = 20$—35 $Jm^{-1}K^{-1}s^{-1}$ at room temperature), which contributes to their high thermal shock resistance. Good mechanical stability and mechanical properties at high temperatures (bending strength $\delta = 300$—500 MPa at 1300 °C) make these materials suitable for applications at tempetaures above 1000 °C (up to about 1400 °C), where even the best metallic materials fail.

As indicated above, experience of ceramists allows to conclude that high-grade structural materials can only be made from pure non-agglomerated powders consisting of very small particles of uniform sizes and preferably of isometric shape [1]. Particularly, preparation of materials based on silicon nitride requires very fine powders, as their sintering temperatures are limited due to thermal decomposition of silicon nitride above approx. 1700 °C at nitrogen pressure of 101 kPa [12]. The sintering can also be carried out under higher nitrogen pressures, but such technology is significantly more complicated and expensive. The silicon nitride powder should also contain a high portion of the α-modification (more than about 90 wt. %) as the transformation of α-silicon nitride to the β-form during sintering contributes to improving the mechanical properties of the material [13].

The conversion of silica to silicon nitride was studied in [14—26]. At 1400 to 1500 °C, weakly aggregated silicon nitride powders with a particle size of about 1 μm, containing less than 3 wt. % oxygen and about 1 wt. % carbon, and with α-phase content of 90—95 wt. % were prepared. However, the potential of the process has obviously not yet been fully exhausted. It can be assumed that better undestanding of the processes of products formation will allow to prepare silicon nitride powders with improved chemical and phase purity and morphology.

Thermodynamics and kinetics

At carbothermal reduction and nitridation of silica silicon nitride is formed according to the overall reaction:

$$3\,SiO_2(s) + 6\,C(s) + 2\,N_2(g) \rightleftharpoons Si_3N_4(s) + 6\,CO(g) \qquad (1)$$

$$K_1(1430\,°C) = 2.84 \times 10^{-3},$$

where K_1 is the equilibrium constant of reaction (1). Because of the low value of the equilibrium constant, it is necessary to perform the reaction in flowing nitrogen in order to ensure efficient removal of the liberated carbon monoxide from the reaction system.

Reduction of silicon dioxide to silicon monoxide is generally regarded as the first step in the mechanism of reaction (1):

$$SiO_2(s) + C(s) \rightleftharpoons SiO(g) + CO(g) \qquad (2)$$

$$K_2(1430\,°C) = 5.23 \times 10^{-4},$$

$$SiO_2(s) + CO(g) \rightleftharpoons SiO(g) + CO_2(g) \qquad (3)$$

$$K_3(1430\,°C) = 7.32 \times 10^{-8}.$$

Komeya and Inoue [14] assumed that in the second step, the gaseous silicon monoxide reacted with nitrogen on the surface of carbon particles:

$$3\,SiO(g) + 2\,N_2(g) + 3\,C(s) \rightleftharpoons Si_3N_4(s) + 3\,CO(g) \qquad (4)$$

$$K_4(1430\,°C) = 1.99 \times 10^{7}.$$

Such a reaction can proceed rapidly until the entire surface of the carbon particles becomes covered with a layer of the product. The subsequent reaction would then proceed only after diffusion of the gaseous reactants through the layer. In such an instance the morphology of the silicon nitride should be similar to that of the initial carbon particles. However, such a similarity was not proved experimentally. In spite of this, other authors also assumed such reaction mechanism [18, 21, 26]. On the other hand, examination of the morphology of the product allowed Zhang and Cannon [20] to assume that silicon nitride is formed from gaseous reactants:

$$3\,SiO(g) + 2\,N_2(g) + 3\,CO(g) \rightleftharpoons Si_3N_4(s) + 3\,CO_2(g) \qquad (5)$$

$$K_5(1430\,°C) = 5.46 \times 10^{-5}.$$

Carbon dioxide is then reduced by the excess carbon present in the reaction system:

$$CO_2(g) + C(s) \rightleftharpoons 2\,CO(g) \tag{6}$$
$$K_6(1430\,°C) = 7.14 \times 10^3.$$

The authors [20] noticed the uniform particle size of the silicon nitride and suggested that supersaturation of silicon monoxide required for the nucleation of silicon nitride can only be attained in the initial stages of the reaction, which leads to the formation of a virtually single generation of crystals.

The reaction system silica—carbon—nitrogen may also produce silicon carbide:

$$SiO_2(s) + 3\,C(s) \rightleftharpoons SiC(s) + 2\,CO(g) \tag{7}$$
$$K_7(1430\,°C) = 0.126,$$
$$Si_3N_4(s) + 3\,C(s) \rightleftharpoons 3\,SiC(s) + 2\,N_2(g) \tag{8}$$
$$K_8(1430\,°C) = 0.709.$$

The equilibrium constants of reactions (7) and (8) increase with increasing temperature. i. e. the thermodynamic conditions for the formation of silicon carbide are also improved. The limit temperature, above which silicon carbide begins to form, is about 1440 °C for 101 kPa of nitrogen. Above this temperature, the product of reaction performed under normal nitrogen pressure will always contain silicon carbide, the amount of which will depend on the temperature and the kinetics of the formation of silicon carbide and silicon nitride. By optimizing the reaction conditions and using additions of crystallization nuclei of α-silicon nitride into the initial mixture of silica with carbon, Mori et al. [17] prepared α-silicon nitride powder with a silicon carbide content lower than 3 wt. %. According to the equilibrium (8), the formation of silicon carbide can be suppressed by increasing the partial pressure of nitrogen. The authors of [17] also found that an addition of crystallization nuclei has a positive effect not only on the chemical and phase purity of the product, but also on the kinetics of conversion of silica to silicon nitride, as well as on reducing the mean grain size of the silicon nitride produced.

Experimental

The experimental techniques were described in detail in [23]. Three types of high-purity silica were used in the preparation of the mixtures:

1. amorphous dense particles with a medium grain size of 50 nm, $S_{BET} = 50\ m^2g^{-1}$ (Aerosil OX-50, Degussa GmbH, FRG),
2. porous xerogel, $S_{BET} = 80\ m^2g^{-1}$ (Reachim, USSR),
3. finely ground quartz with a particle size below 5 μm, $S_{BET} = 5\ m^2g^{-1}$.

The carbon was in the form of high-purity acetylene carbon black with a specific surface area $S_{BET} = 80\ m^2g^{-1}$ (P-1250, VEB Stiskstoffwerk Piesteritz, GDR).

Four different types of silicon nitride were introduced as crystalline nuclei into the initial mixtures of silica and carbon. Their characteristics are listed in Table I.

The initial mixtures with a 1 : 1 weight ratio of silica to carbon (molar ratio 1 : 5), containing 0—20 wt. % of crystallization nuclei of silicon nitride, were homogenized by grinding in an agate planetary mill for 20 minutes. The reaction mixtures were prepared with a 2.5-fold excess of carbon, to suppress sintering and growth of

Table I

Data on silicon nitride powders used as seeding crystals in carbothermal synthesis of silicon nitride

Si_3N_4	Chemical composition (wt. %)			Content of α —Si_3N_4 (wt . %)	S_{BET}/m^2g^{-1}
	N	O	C		
S-72[1] ÚACH	36.4	2.20	1.40	100	3.5
LC12[2] Starck	38.6	1.84	0.19	95	20.9
IPM[1] Kiev	37.1	1.70	0.50	98	8.0
PCHS[3] Riga	34.1	5.88	0.195	30-α/20-β/50-amorph.	22.3

[1] Prepared by carbothermal reduction and nitridation of SiO_2

[2] Prepared by nitridation of silicon

[3] Prepared plasmochemically

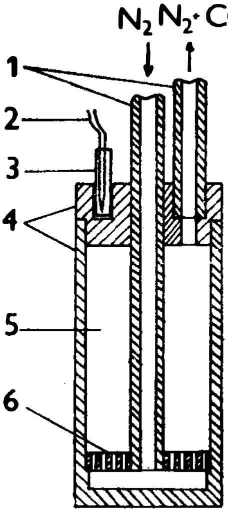

Fig. 2. Graphite reactor; 1 — inlet and outlet tube, 2 — thermocouple, 3 — protective corundum tube with one end closed, 4 — crucible with closure, 5 — reaction mixture, 6 — perforated bottom.

silicon dioxide grains. The reaction mixtures were heated at 1350—1550 °C for 2—10 h in a graphite reactor designed so as to ensure forced flow of nitrogen through the reaction mixture and efficient removal of carbon monoxide from the reactor (Fig. 2). The reactor was placed in a protective alumina tube heated by an adapted laboratory chamber furnace. The charge weight was varied from 5 to 15 g (most frequently 13 g), the rate of flow of nitrogen was varied over the range of 50—250 cm^3min^{-1} (at room temperature), which corresponded to 20 to 100 cm^3min^{-1} per 1 g of SiO_2 in the charge. The extent and kinetics of the reduction was followed continuously by measuring the concentration of carbon monoxide in the gas flowing out of the reactor, using an IR analyzer of CO (Infralyt 4, VEB Junkalor Dessau, GDR). After reaction, the non-reacted excess carbon was removed by oxidation in air atmosphere at 650—700 °C for 4—10 h. The morphology of the powders was studied by electron microscopy. The phase composition of the product was established by X-ray diffraction analysis. The oxygen content in the samples was determined by activation neutron analysis, and that of carbon by the LECO method. The nitrogen content was determined by titration after an absorption of ammonia (in 1.5 % solution of trihydrogenboric acid H_3BO_3) liberated during alkaline melting of the product in excess powdered sodium hydroxide and calcium oxide (1 : 1 by weight) at 700 °C for 1 hour.

Results and discussion

The effect of temperature, nitrogen flow rate and the quality of initial substances on the reaction and the properties of its products was discussed in detail in the previous study [23].

It was found that the reduction of silica by carbon in flowing nitrogen starts at 1150 °C, and the maximum rates of conversion were found at 1470—1510 °C. At higher temperatures the proportion of silicon carbide grows very rapidly, and at 1555 °C the carbide is the dominant component of the product. The quality of the initial silicon dioxide has no substantial effect on the kinetics of the process and on the properties of the product. This obviously holds only when the SiO_2 powders are sufficiently chemically pure (content of cationic impurities less than 0.01—0.05 wt. %), as was the case of substances used in the present study.

The nitrogen flow rate over the range of 20—100 $cm^3 min^{-1}$ per 1 g SiO_2 does not influence significantly the course of the reaction. However, at lower flow rates the reduction of silicon dioxide and the formation of silicon nitride will slow down, and local crystallization of silica in the form of cristoballite was observed in the charge. At higher flow rates of nitrogen, increasing amounts of silicon tend to escape from the reactor in the form of silicon monoxide.

In the optimum regime of synthesis (1500 °C, time of isothermal dwell 7—8 h, nitrogen flow rate 40—50 cm^3min^{-1} per 1 g of SiO_2 in the initial mixture [23], the α-silicon nitride obrained contained 35—37 wt. %.nitrogen, 3—4 wt. % oxygen

Table II

Conditions during carbothermal synthesis of silicon nitride

Exp.	Seeding crystals of silicon nitride	wt. % of addition	Time* at 1510 °C/h
75	—	0	8
76	IPM	5	6.6
79	IPM	20	3
80	IPM	10	4.2
93	S-72	10	5.8
94	PCHS	10	3.5
95	LC12	10	4.5

*Time required for attaining virtually zero concentration of CO in the gas passing out of the reactor

Table III

Chemical composition and specific surface area of the products of carbothermal reduction and nitridation of SiO_2

Product	Content (wt. %)			S_{BET} (m^2g^{-1})
	N	O	C	
75	27.4	14.1	1.2	3.5
76	34.6	2.9	1.1	4.7
79	38.1	2.8	0.6	4.8
80	37.9	3.3	1.0	5.2
93	36.3	2.9	1.2	3.8
94	33.0	3.8	2.7	6.9
95	36.4	3.6	0.5	9.2

and 1 wt. % carbon. The product consisted of uniform crystals about 1 μm in size (Fig. 3a).

The effect of crystallization nuclei on the reduction and on the quality of products was investigated in further experiments. 0, 5, 10 and 20 wt. % of silicon nitride seeding crystals were added to 13 g silica (Aerosil OX-50) and acetylene carbon black mixture. The reaction temperature was 1510 °C. Heating rate over the interval 20—1300 °C was 10 °C min^{-1}, above 1300 °C it was 5 °C min^{-1}. The nitrogen flow rate was kept at 250 cm^{3}min^{-1}. Data on the experiments and some characteristics of the products are summarized in Tables II and III.

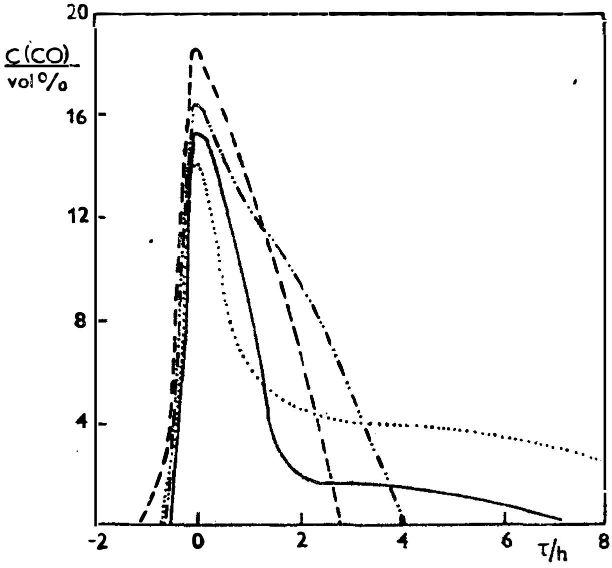

Fig. 4. Effect of the amount of IPM silicon nitride seed on the rate of liberation of CO during carbothermal reduction and nitridation of silicon dioxide; .... 0 wt. %, ———— 5 wt. %, —..—..—..— 10 wt. %, — — — 20 wt. %.

The effect of the amount of seeding crystals on the reaction rate, expressed as the dependence of CO concentration on time is plotted in Fig. 4. The diagram demonstrates clearly the positive effect of seeding the reaction mixture with crystallization nuclei on the rate of converscon of silica to silicon nitride. The shape of the curve indicates a high reaction rate particularly in the stage just before attaining the temperature of isothermal dwell and during its first minutes. A wide region with a practically constant reaction rate is observed in the subsequent stage with samples with addition of no and 5 mass% of seeding crystals, respectively.

The initial high reaction rate probably corresponds to the first step of the reaction, where reduction of silica by carbon, reaction (2) can take place. The reaction (2) can occur till a close contact between the solid reactants is retained. Because of an intensive evolution of silicon monoxide favourable conditions for nucleation and crystal growth of silicon nitride are stated in this reaction stage. However, from the beginning the surface of forming silicon nitride crystals is small and an evolution of silicon monoxide can exceed the amount that can be consumed for the silicon nitride growth. The excess silicon monoxide then departs from the reaction zone, or can oxidize to silicon dioxide according to equations (2) and (3). Recrystallization and formation of coarse crystals of silicon dioxide may then slow down its conversion to silicon nitride. If crystallization nuclei of silicon nitride are present in the reaction mixture from the beginning of the reaction, this creates substantially more favourable conditions for the consumption of silicon monoxide and for the growth of silicon nitride. In this respect, additional intensification of the process will depend on the surface area of the crystallization nuclei introduced.

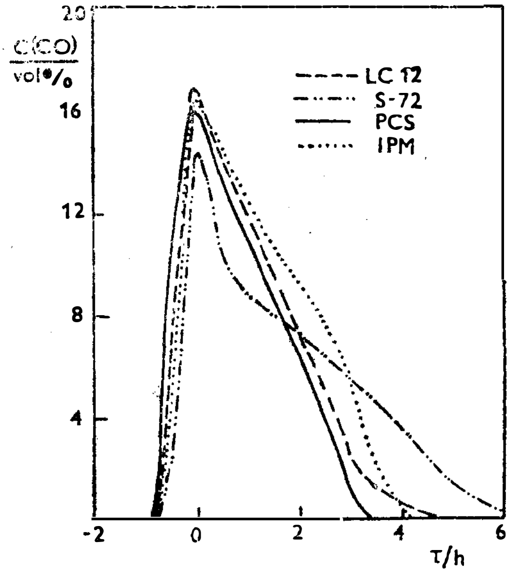

Fig. 5. Effect of various types of seeding crystals of silicon nitride on the rate of liberation of CO during carbothermal reduction and nitridation of silicon dioxide; -------- *10 wt. % of LC12,* —·—·—·— *10 wt. % of S-72,* ——— *10 wt. % of PCS,* .... *10 wt. % of IPM.*

The effect of various types of silicon nitride used in the seeding of the reaction mixtures is shown in Fig. 5. The rate of conversion obviously increases with increasing specific surface area of the crystallization nuclei introduced. However, there is an exception with silicon nitride powder prepared plasmochemically. This behaviour can be explained by its crystallization and changes in specific surface area in the course of heating up to the reaction temperature. The increase in the number of crystallization nuclei leads to considerable shortening of the time required for virtually complete conversion of silica to silicon nitride, and has also a positive effect on the smaller particle size of the products (Table III, Fig. 3a, b, c). Fig. 3d shows the morphology of a product prepared in the optimum regime. The narrow distribution of particle sizes was achieved by controlling the rate of silicon monoxide evolution.

PREPARATION OF MATERIALS BASED ON SILICON NITRIDE BY HOT PRESSING

With respect to the low values of diffusion coefficients of silicon nitride structural elements in solid state even at high temperatures, the preparation of silicon nitride based ceramics expose some specific features. The decomposition of silicon nitride at nitrogen pressure of 100 kPa under relatively low temperatures is another factor dictating the specific conditions of silicon nitride sintering.

For these two reasons, materials based on silicon nitride are prepared by sintering with additives forming a liquid phase at the sintering temperature. The liquid phase positively influences the densification (helps rearangement and speeds up diffusion) and partially suppresses the thermal decomposition of silicon nitride. On the other hand, the residual amount of the amorphous phase at the grain boundaries degrades the high-temperature mechanical properties of silicon nitride. For these reasons the sintering of silicon nitride should be conducted under conditions ensuring a minimum amount of liquid phase arising on sintering, but allowing the maximum density of the product to be attained. These two contravertial requirements are met succesfully by the hot pressing method.

Experimental

The morphology of silicon nitride powder used for the preparation of the materials is shown in Figs. 6a, b. The chemical composition and specific surface area of the powders are given in Table IV. A mixture of yttrium oxide (99.99 wt.%) and alumina (99.99 wt.%) at a molar ratio of 3 : 5, corresponding to the composition of yttrium-aluminum garnet, was used as an additive forming a liquid phase at the sintering temperature. The oxides were added in the form of aqueous solution of yttrium nitrate and aluminum nitrate into an aqueous suspension of silicon nitride. Yttrium hydroxide and aluminum hydroxide were co-precipitated by adding a suitable amount of urea. The suspension was heated for 1 hour at 100 °C and then homogenized for 24 hours in ethanol. The total amount of the mixture of yttrium oxide and aluminium oxide in the 3 : 5 molar ratio in the initial powders of silicon nitride was 8 wt. %. To the powders prepared in this way, 0, 5, 10 and 20 and 30 wt. % of β-silicon nitride whiskers were added. The morphology and aspect ratio distribution of the whiskers are shown in Fig. 7. The high-purity whiskers with an oxygen content of 0.8 wt. % and the content of other impurities lower than

Table IV

Chemical composition and specific surface area of the initial powders of silicon nitride employed in the preparation of material by hot pressing

Designation	Manufacturer	Chemical composition (wt. %)			S_{BET} (m^2g^{-1})
		N	O	C	
I	H.C. Starck Berlin-W	38.4	1.6	0.49	9.9
II	ÚACH	37.1	2.8	0.44	5.5

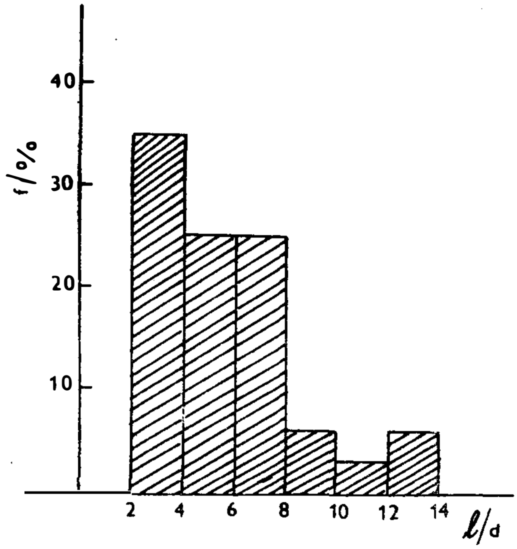

Fig. 7. Whiskers of β-silicon nitride used in the preparation of initial mixtures. b) distribution according to aspect ratio (f — frequency vs. aspect ratio — l/d).

300 ppm were prepared by the SHS method (self-propagating high-temperature synthesis), at the Institute of Structural Macrokinetics of the Soviet Academy of Sciences, Chernogolovka. The whiskers were added to initial powders I and II according to the schematic diagram shown in Fig. 8. The green compacts were prepared by cold pressing under 100 MPa in a press with a piston diameter of 12 mm; the resulting pellet thickness was about 5 mm. The sintering was performed in a hot press with a graphite die heated by a graphite meander element. Nitrogen was used as protective atmosphere. The design of the equipment is descibed in detail in [27]. The compacts were sintered in a boron nitride powder bed at 1750 °C under a pressure of 39 MPa. In the course of sintering, the pressure was applied at 1500 °C and released after the hot pressing cycle at 1000 °C. The relative densities of compacts before and after sintering were determined by weighing the specimens in mercury. The change in the pellet thickness in the course of hot pressing

was recorded by a dilatometer. The fracture toughness of sintered specimens was determined by the indentation method, using Vickers's pyramide indentor under a load of 1000 N. The coefficient of fracture toughness K_{1C} was calculated according to the equation [20, 29]:

$$K_{1C} = Ha^{1/2} (E/H)^{2/5} 10^{Y}. \tag{9}$$

where H is the Vickers's hardness, a is one half of the length of the diagonal of Vickers's impression, Y is a function of the expression log $[(l + a)/a]$, l is the half mean crack length and E is the Young's modulus of elasticity, its value was estimated 300 GPa with respect to the values for materials of similar composition [30].

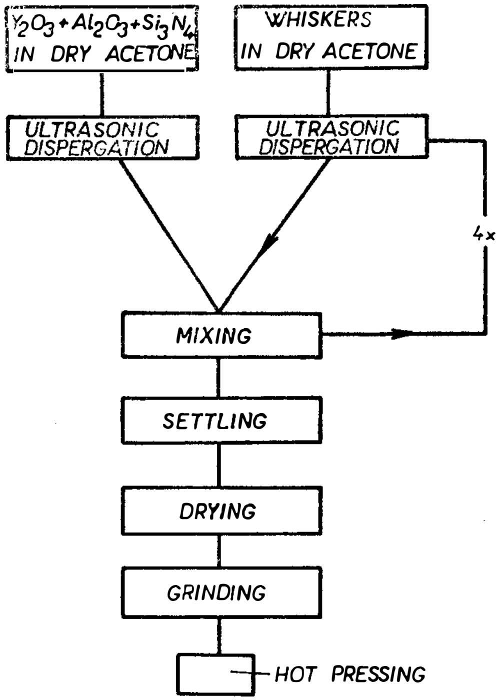

Fig. 8. Schematic diagram of the preparation of initial mextures.

Results and discussion

The dependence of the ceramic materials density vs. isothermal hot pressing time dwell at 1750 °C and pressure of 39 MPa is shown in Fig. 9. The diagram proves that the whiskers of β-silicon nitride significantly influence the densification only at additions of 30 wt. % of whiskers in powder I. Smaller amounts of β-silicon nitride whiskers do not significantly influence the densification curves. The effect of another phase (in the present case of β-silicon nitride whiskers) on the sinterability of composites can be expressed by the ratio of the matrix stress relaxation rate to the rate of matrix densification [31—33]. A high value of this ratio is advantageous, since in such case the composite will densify similarly to the matrix without any addition of another phase. In the case of application of inclusions with a thermal expansion coefficient close to that of the matrix one can assume that the matrix will be more capable to absorb the stresses resulting from the

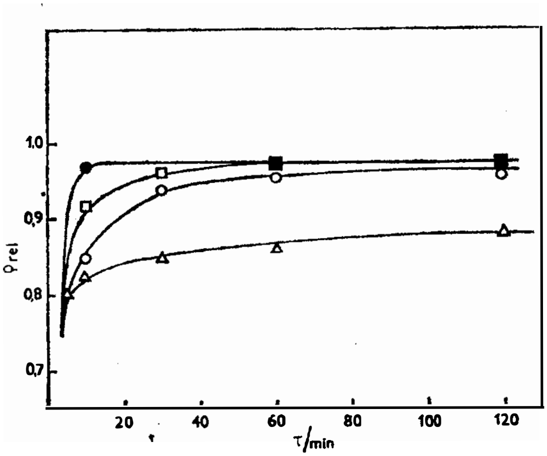

Fig. 9. Density of materials, ϱ_{rel}*, vs. isothermal holding* τ *during hot pressing;*

Addition of β-Si_3N_4 *whiskers:*	Si_3N_4 *powder:*
■ . . . *0 wt.%, 5 wt.%;*	*I (H. C. Starck)*
○ . . . *10 wt.%, ... 30 wt.%;*	
● . . . *0 wt.%, 10 wt.%, 20 wt.%*	*II (ÚACH SAV).*

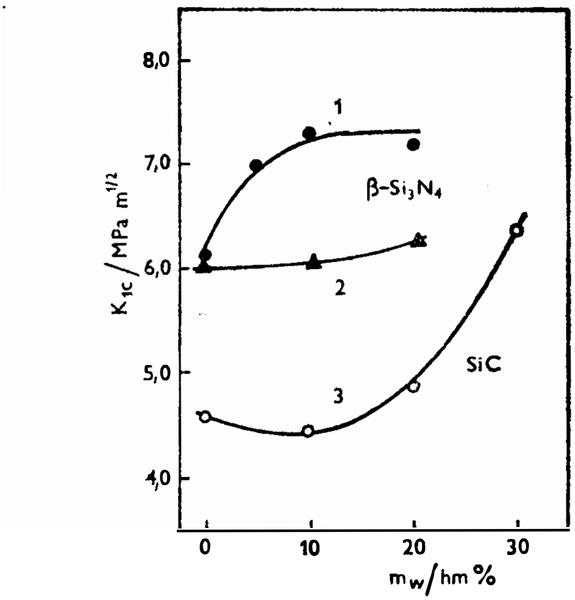

Fig. 10. The coefficient of fracture toughness of the materials, K_{1c}*, vs. the content of whiskers,* m_w*; 1 — initial powder I (H. C. Starck), 2 — initial powder II (ÚACH SAV), 3 — ref. [30].*

presence of inclusions, than in the case when the thermal expansion coefficients are different. For example, application of silicon carbide whiskers in a matrix of silicon nitride will substantially slow down the sintering process [30]. A comparison of the rates of densification of compacts prepared from powders I and II speaks in favour of powder II, which is obviously a result of its advantageous morphology. The particles of powder II (Fig. 6b) are isometric, of quasispherical shape, which is very convenient in the first stage of hot pressing (rearrangement of particles). The compact will attain a dense arrangement in a shorter time than in the case of initial powder I, whose particles have sharp edges, projections and the wide distribution of particle sizes. The fracture toughness curves calculated, according to the equation (9) in terms of the content of β-silicon nitride whiskers, are shown in Fig. 10 for materials prepared from powders I and II. The relative densities of all the compacts tested, whose fracture toughness coefficients K_{IC} are given in Fig. 10, were higher than 0.96. Fig. 10 also shows the K_{IC} values for ceramics with a matrix of silicon nitride reinforced by whiskers of silicon carbide [30]. A comparison of all three curves indicates that the materials with whiskers of β-silicon nitride prepared in the present study show a comparable or higher fracture toughness compared to materials reinforced by whiskers of silicon carbide. The content and composition of additions producing a liquid phase was identical for all the materials mentioned. Fig. 11 shows the loss in weight of compacts during hot pressing in terms of the content of β-silicon nitride whiskers. The values are given for the isothermal dwells at which the compacts attained a density higher than 0,96. The positive effect of an elevated content of whiskers on the loss in weight is obvious.

Reinforcing of ceramics by whiskers involves several mechanisms which may be effective separately or simultaneously in the course of crack propagation through the material (Fig. 1). Whisker pull-out from the matrix is possible when the stress transmitted to the whisker exceeds the strength of the whisker-matrix interphase. The whisker-matrix interfacial strength depends on the coefficient of friction and on the stress acting perpendicularly to the interface parallel with

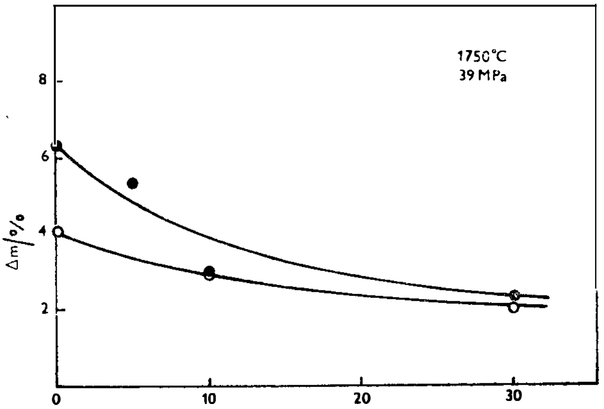

Fig. 11. The wieght loss of the material, △ m, during hot pressing, vs. the content of β-Si_3N_4 *whiskers,* m_w.

the longitudial axis of the whisker. This stress is a function of the difference between the coefficients of thermal expansion of the matrix and the whiskers. If these two values are very close, as is in the case of using β-silicon nitride whiskers, the stress is minimal or zero and pull-out from the matrix can occur. Figs. 12a, b show the imprints of β-silicon nitride whiskers pulled out from the matrix during catastrophic propagation of a crack for both types of materials. This means that in that case the tensile stress acting on the whisker was smaller than the tensile strength of the whisker, but greater than the whisker-matrix interfacial strength. The pull-out of whiskers from the matrix appears to be one of the most important mechanisms influencing the toughness of composites. Lundberg et. al. [34] found that if the bond between silicon carbide whiskers and the matrix is very strong compared to the tensile strength of the whisker, the pull-out of whiskers is not observed, and the fracture toughness decreases slightly with increasing content of whiskers.

The deflection of the direction of the expanding crack is documented in Fig. 13. Faber and Evans [35] found that rod-shape inclusions are most advantageous for changing the direction of crack propagation. They demonstrated that the toughness of composite increases with increasing aspect ratio of whiskers. In the present study, the β-silicon nitride added contained not only high-aspect ratio crystals, but also three-dimensional particles (Fig. 14a) and, moreover, the whiskers also formed agglomerates (Fig. 14b). It can therefore be assumed that these two forms occurring in the material either did not contribute at all, or contributed very little to improving the fracture toughness.

The materials prepared from powders I and II without addition of β-silicon nitride whiskers were ground to the form of cutting tools at the DIAS Turnov State Enterprise. The cutting properties of the tools were tested at the Research Institute of Machine Tools in Prague. The tests were carried out on the cast iron

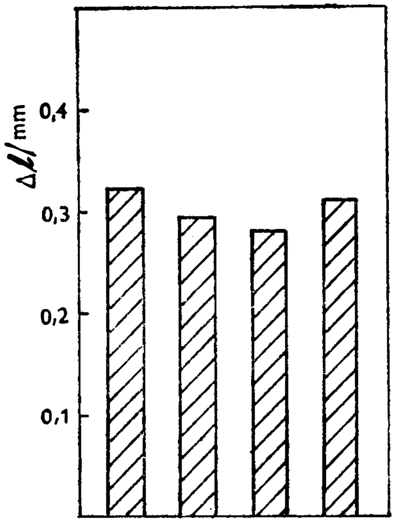

Fig. 15. Maximum wear of cutting tools, Δl*, during cutting tests;* A_1 *— material prepared from initial powder I (H. C. Starck),* B_1 *— material prepared from initial powder II (ÚACH SAV),* R_1 *— Silinit (USSR), SL100 — Feldmühle (FRG).*

specimens with a hardness of 210 to 235 HB under the folloving machining conditions: cutting speed 300 m min^{-1}, feed 0.875 mm per revolution, engagement depth 1.5 mm, net time of engagement 3 min. The wearing results are shown in Fig. 15, for the sake of comparison with the results for tools made by world manufactures (SL 100 — Feldmühle, F. R. G.; Silinit R 1 — U. S. S. R.). The performance properties of the materials prepared in this study are comparable to those of the commercial products mentioned above.

CONCLUSIONS

1. An addition of finely dispersed silicon nitride powder to the initial mixture of silica and carbon promotes conversion of silicon dioxide to silicon nitride during carbothermal synthesis of silicon nitride and reduces the mean particle size of the product.
2. Larger surface areas of the seeding powder promote the effects given in paragraph 1.
3. An isometric shape of grains of the initial silicon nitride powder facilitates reorganization of particles in the initial stages of sintering by the hot pressing method, which substantially shortenes the time required for the preparation of a dense material.
4. The fracture toughness of materials based on silicon nitride prepared by hot pressing can be improoved by an addition of 5—20 wt. % of β-silicon nitride whiskers.

Aknowledgement

The authors wish to express their thanks to the workers of DIAS Turnov State Enterprise, where the variuos specimens were ground into the shape required, and also to the personnel of VÚOSO in Prague, were the materials were tested for their cutting behaviour.

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PRÍPRAVA PRÁŠKU α-Si_3N_4 A KERAMIKY SPEVNENEJ WHISKRAMI β-Si_3N_4

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Ohrevom zmesi jemnedisperzného oxidu kremičitého a uhlíka pri teplote 1500 °C počas 7—8 h v prúde dusíka s prietokom 40—50 cm^3 min^{-1} (prietok vztiahnutý na 1 g SiO_2 vo východiskovej zmesi) sa pripravil α-nitrid kremíka s obsahom dusíka 35—37 hm . %, kyslíka 3—4 hm . % a uhlíka 1 hm . % a strednou veľkosťou častíc okolo 1 μm. α-nitrid kremíka vzniká zrážaním z plynných reaktantov SiO, N_2, CO. Pozitívny vplyv prídavku kryštalizačných zárodkov α-nitridu kremíka na rýchlosť reakcie, zníženie veľkosti častíc a morfológiu produktu rastie s rastúcim povrchom očkovacieho prášku.

Z prášku nitridu kremíka s prídavkom oxidu ytritého a oxidu hlinitého sa horúcim lisovaním pripravil keramický materiál s lomovou húževnatosťou okolo 6 MPa $m^{1/2}$, ktorú možno zvýšiť prídavkom whiskrov β-nitridu kremíka. Z materiálu sa vybrúsili rezné doštičky, ktorých opotrebovanie pri intenzívnom opracovávaní zliatiny je na úrovni opotrebovania rezných doštičiek vyrábaných komerčne v zahraničí.

Obr. 1. Mechanizmy zhúževnatenia keramického materiálu whiskrami; a) pevný whisker zastaví šírenie trhliny (premostenie), b) ak napätie v čele trhliny prevýši pevnosť whiskra, whisker sa pretrhne a trhlina sa šíri ďalej, c) vyťahovanie whiskra z matice, d) odklon smeru šírenia sa trhliny v dôsledku napätí v okolí inklúzií.

Obr. 2. Grafitový reaktor; 1 — prívodná a vývodná trubička, 2 — termočlánok, 3 — ochranná korundová kyveta, 4 — téglik s uzáverom, 5 — reakčná zmes, 6 — perforované dno.

Obr. 3. Morfológia typických produktov syntézy; a) bez kryštalizačných zárodkov (produkt S-72), b) s prídavkom 10 hm . % S-72, c) s prídavkom 10 hm.% LC12, d) s prídavkom 5 hm. % IPM a úpravou režimu ohrevu, *Obr. 4. Vplyv množstva kryštalizačných zárodkov nitridu kremíka IPM na rýchlosť uvolňovania CO pri karbotermickej redukcii à nitridácii oxidu kremičitého;* .... 0 *hm.* %, ——— 5 *hm.* %, —..—..—..— 10 *hm.* %, --------- 20 *hm.* %.

Obr. 5. Vplyv rôznych druhov kryštalizačných zárodkov nitridu kremíka na rýchlosť uvolňovania CO *pri karbotermickej redukcii a nitridácii oxidu kremičitého;* --------- 10 *hm.* % *LC12,* —..—..—..— *10 hm.* % *S-72,* ——— *10 hm.* % *PCS,* ....*10 hm.* % *IPM.*

Obr. 6. Východiskové prášky nitridu kremíka použité na prípravu materiálov horúcim lisovaním. a) I (H1, H.C. Stark), b) II (ÚACH SAV).

Obr. 7. Whiskre β-nitridu kremíka použité na prípravu východiskových zmesí$_I$ a) mikrofotografia b) rozdelenie podľa štíhlosti (f — početnosť vs štíhlosť — 1/d).

Obr. 8. Schéma prípravy východiskových zmesí.

Obr. 9. Závislosť hutnosti materiálov, ϱ_{rel} *od izotermickej výdrže horúceho lisovania,* τ.

Prídavok β-Si_3N_4 *whiskrov:*	*prášok* Si_3N_4*:*
■ . . . *0 hm.* %, *5 hm.* %;	
○ . . . *10 hm.* %; Δ . . . *30 hm.* %;	*I (H.C. Starck)*
● . . . *0 hm.* %, *10 hm.* %;, *20 hm.* %	*II (ÚACH SAV)*

Obr. 10. Závislosť koeficientu lomovej húževnatosti materiálov, K_{1c} *od obsahu whiskrov,* m_w. *1 — východiskový prášok I (H. C. Starck), 2 — východiskový prášok II (ÚACH SAV), 3 — práca [30].*

Obr. 11. Závislosť úbytku hmotnosti materiálu, Δm *pri horúcom lisovaní od obsahu whiskrov* β-Si_3N_4, m_w.

Obr. 12. Odtlačky whiskrov β-nitridu kremíka po ich uvoľnení z matice.

Obr. 13. Mikrofotografia dokumentujúca cik-cakový tvar šírenia trhliny.

Obr. 14. Mikrofotografia inklúzií;
a) veľká častica bez význačného rozmeru
b) aglomerát

Obr. 15. Maximálne opotrebovanie rezných doštičiek, Δl *pri rezných skúškach;*
A_1 *— materiál pripravený z východiskového prášku I (H. C. Starck),*
B_1 *— materiál pripravený z východiskového prášku II (ÚACH SAV),*
R_1 *— Silinit (ZSSR),*
SL100 — Feldmühle (NSR).

ПРИГОТОВЛЕНИЕ ПОРОШКА α—Si_3N_4 И КЕРАМИКИ, УПРОЧНЕННОЙ ВИСКРАМИ β—Si_3N_4

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Нагревом смеси тонкодисперсного оксида четырехвалентного кремния и углерода при температуре 1500 °C во время 7—8 часов в потоке азота с протоком 40—50 см^3 мин$^{-1}$ (проток в соотношении на 1 г SiO_2 в исходной смеси) получили α-нитрид кремния, содержащего 35—37 % по весу азота, 3—4 % по весу кислорода и 1 % по весу углерода со средним размером частиц около 1 μм. α-нитрид кремния образуется осаждением из газообразных реактантов SiO, N_2, CO. Оказывается положительное влияние добавки кристаллических зародышей α-нитрида кремния на скорость реакици, понижение размера частиц и морфологию продукта и оно растет с повышающейся поверхностью заправочвого порошка.

Из порошка нитрида кремния с добавкой оксида трехвалентного итрия и оксида трехвалентного алюминия горячим прессованием получили керамический материал с трещиностойкостью около 6 МПа м$^{1/2}$, которую можно повысить добавкой вискров

β-нитрида кремния. Из материала отшлифовали резцы, изношенность которых при интенсивной обработке сплава находится на уровне изношенности резцов, приготовленных для продажи за границей.

Рис. 1. *Механизмы повышения трещиностойкости керамического материала вискрами. а) прочный вискер останавливает распространение трещины, б) когда напряжение в передней части трещины оказывается выше прочности вискра, вискер разрывается и трещина распространяется дальше, в) вытягивание вискра из матрицы, г) отклонение направления распространения трещины в результате напряжения в близости включений.*

Рис. 2. *Графитовый реактор; 1 — подводная и отводная трубки, 2 — термопара, 3 — защитная корундовая кюветта, 4 — тигель с вентилем, 5 — реакционная смесь, 6 — решетчатое дно.*

Рис. 3. *Морфология типических продуктов синтеза: а) без кристаллических зародышей (продукт S-72), б) с добавкой 10 % по весу S-72, в) с добавкой 10 % по весу LC 12, г) с добавкой 5 % по весу I PM и с приспособленным режимом нагрева.*

Рис. 4. *Влияние количества кристаллических зародышей нитрида кремния IPM на скорость выделения CO при карботермическом восстановлении и нитридизации оксида четырехвалентного кремния. : ...... 0 % по весу, ——— 5 % по весу, — . .— 10 % по весу — — — — — 20 % по весу.*

Рис. 5. *Влияние разных видов кристаллических зародышей нитрида кремния на скорость выделения CO при карботермическом восстановлении и нитридизации оксида четырехвалентного кремния: — — — — — — — 10 % по весу LC 12, — . .— 10 % по весу S-72, — — — — — — 10 % по весу PCS ...... 10 % по весу IPM.*

Рис. 6. *Исходные порошки нитрида кремния, используемые для приготовления материалов горячим прессованием: а) I(H1, H. C. Starck), б)* II (ИНХ САН).

Рис. 7. *Вискры β-нитрида кремния, используемые для приготовления исходных смесей: а) микрофотосъемка, б) разделение (f — частность) в зависимости от отношения длины к диаметру l/d.*

Рис. 8. *Схема приготовления смесей.*

Рис. 9. *Зависимость плотности материалов, ϱ_{rel} от изотермической выдержки горячего прессования, τ:*

добавка α — Si_3N_4 *вискров:*	*порошок* Si_3N_4:
□ ... *0 % по весу 5 % по весу*	I (H. C. Starck)
○ ... *10 % по весу;* △ ... *30 % по весу*	
● ... *0 % по весу, 10 % по весу, 20 % по весу*	II (ИНХ САН)

Рис. 10. *Зависимость коэффициента трещиностойкости материалов, K_{Ic} от содержания вискров, m_w: 1 — исходный порошок* I (H. C. Starck), *2 — исходный порошок* II (ИНХ САН), *3 — работа* [30].

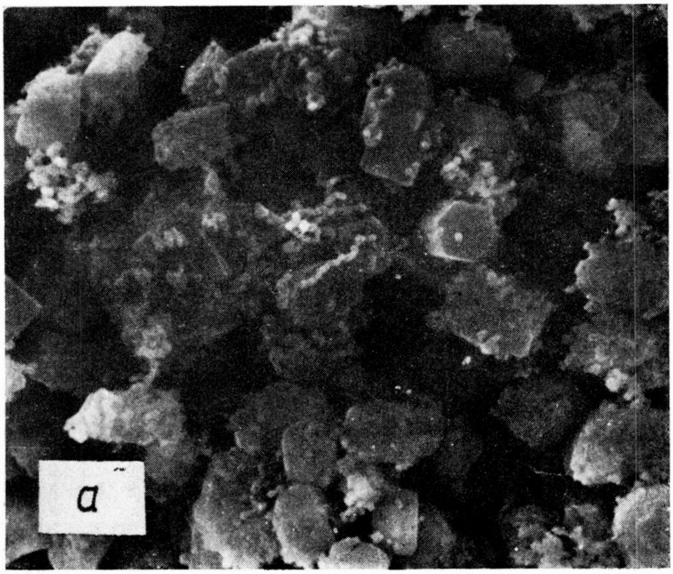
Рис. 11. *Зависимость весовой убыли материала, Δm при горячем прессовании от содержания вискров* β-Si_3N_4, m_w.

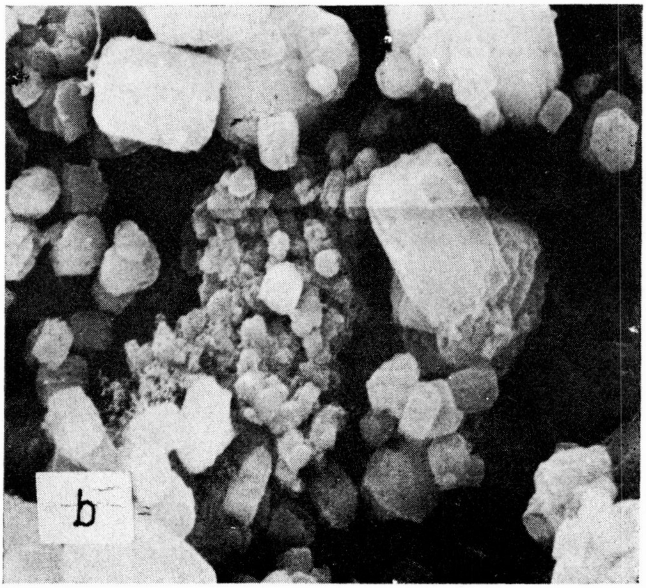
Рис. 12. *Следы от вискров β-нитрида кремния после их удаления из матрицы.*

Рис. 13. *Микрофотосъемка, показывающая зиг-заговую форму распространения трещины.*

Рис. 14. *Микрофотосъемка включений а) крупная частица без значительного размера, б) агломерат.*

Рис. 15. *Максимальное изношение резцов, Δl при резательных испытаниях:* A_1 ... *материал, приготовленный из исходного порошка* I (H. C. Starck), *B* ... *материал, приготовленный из исходного порошка* II (ИНХ САН), R_1 ... *силинит (СССР)*, SL 100 ... Feldmühle (*ФРГ*).


a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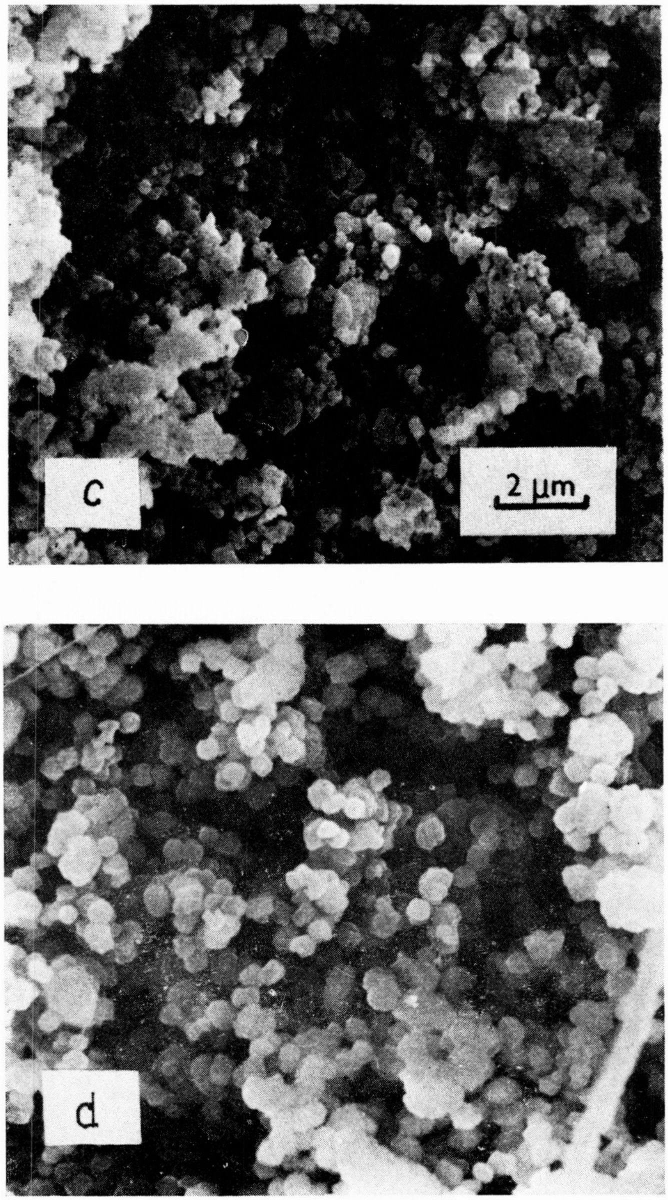
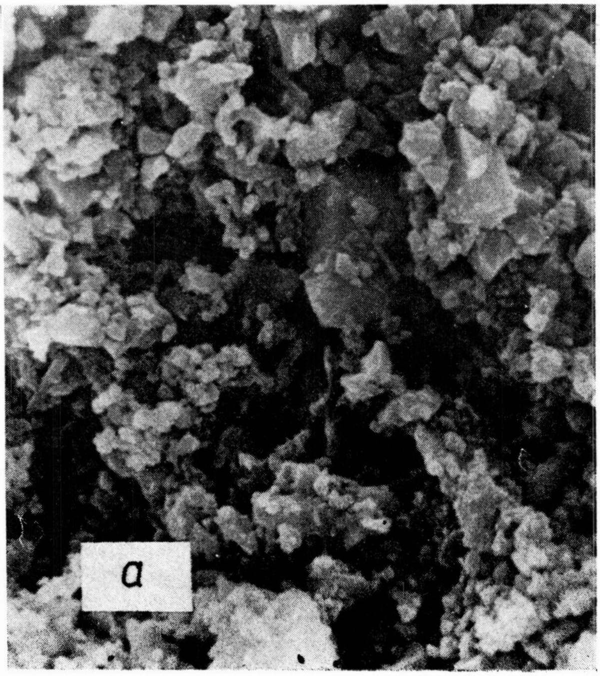


Fig. 3. Morphology of typical synthesis products; a) without seeding crystals (product S-72), b) with an addition of 10 wt. % of S-72, c) with an addition of 10 wt. % of LC12, d) with an addition of 5 wt. % of IPM and using an adjusted heating regime.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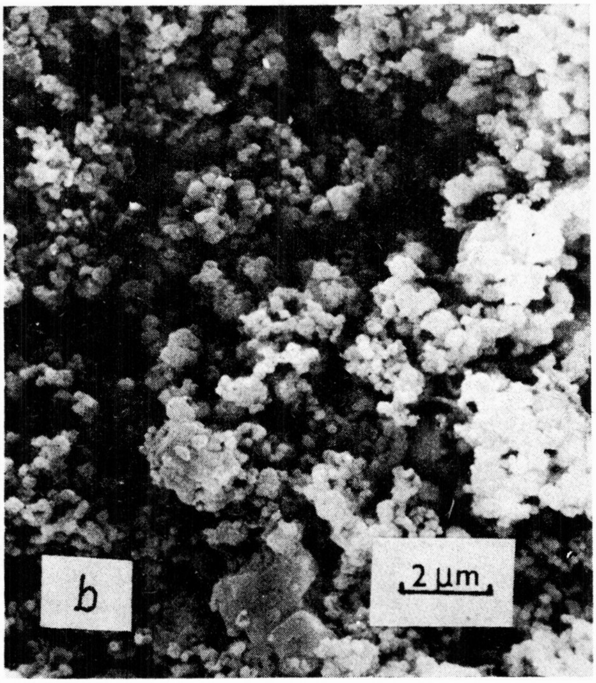

Fig. 6. Initial powders of silicon nitride employed in the preparation of materials by hot pressing a) I (H1, H. C. Starck), b) II (ÚACH SAV).

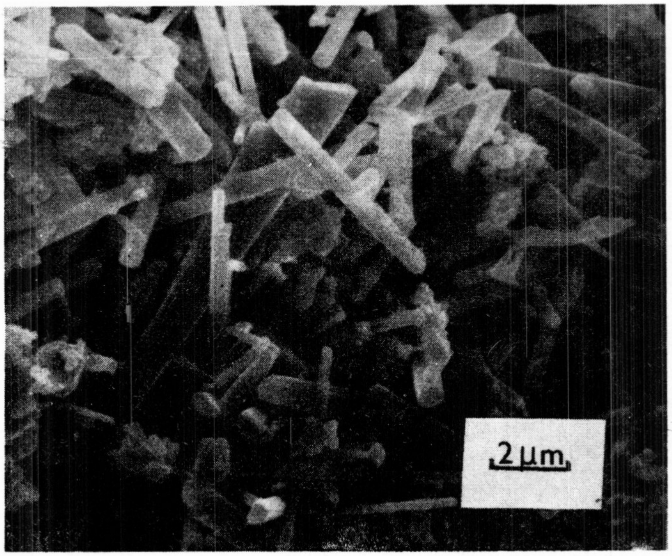

Fig. 7. Whiskers of β-silicon nitride used in the preparation of initial mixtures. a) micrograph.

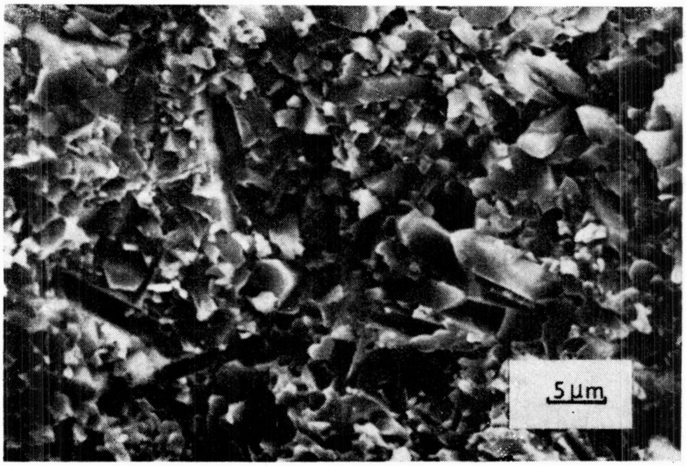

Fig. 12. Imprints of β-silicon nitride whiskers after their pulling out from the matrix.

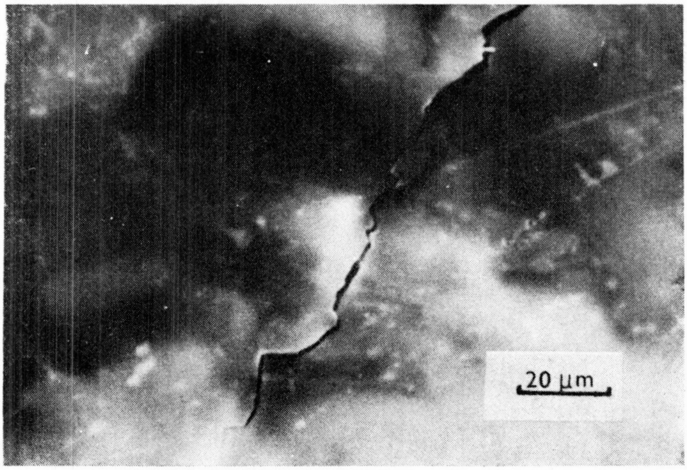

Fig. 13. A micrograph showing the changing direction of crack propagation.

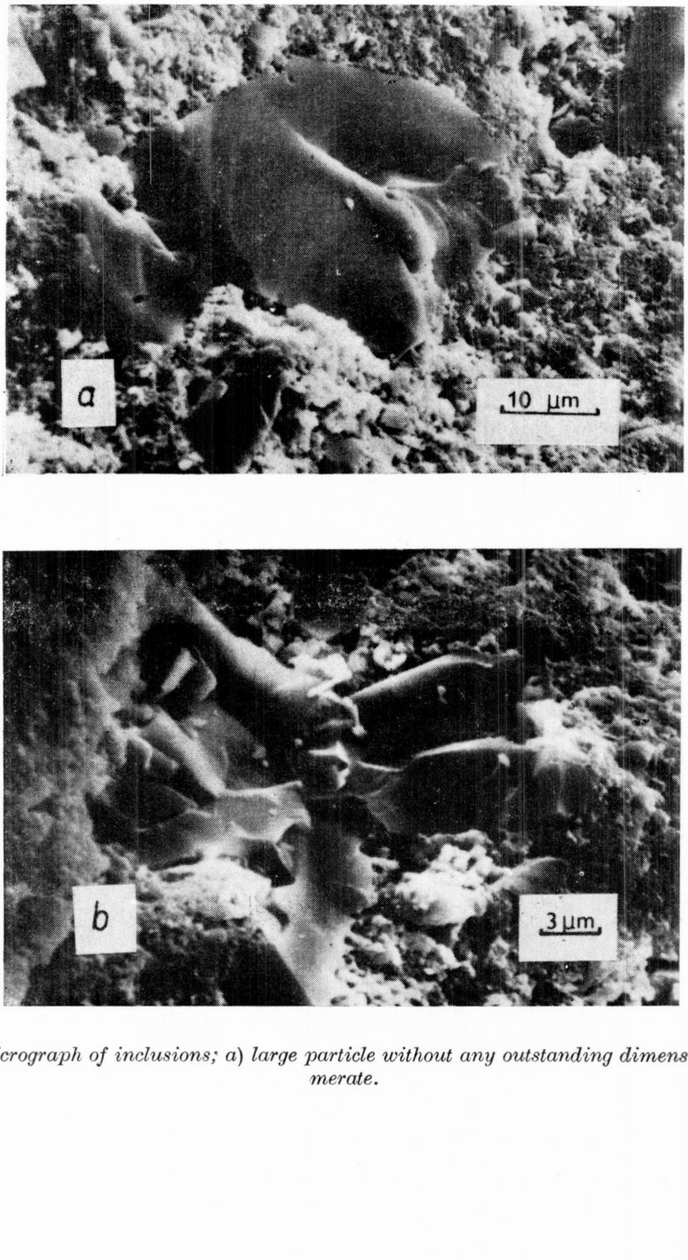

Fig. 14. A micrograph of inclusions; a) large particle without any outstanding dimensions, b) agglomerate.