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Preparation of silicon nitride powder from silica and ammonia

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Abstract

Silicon nitride powders were obtained in a reaction of SiO_2 powders with NH_3. The influence of the following parameters on the quality of Si_3N_4 was determined: silica particle size, temperature and furnace heating programme, sample heating time, ammonia flow rate and application of the selected mineralising agents. The powders of silica were characterised by: optical microscopy, SEM, X-ray phase analysis and thermal analysis. The products of the syntheses were tested by: optical microscopy, SEM, X-ray phase analysis, IR spectroscopy and classic quantitative analysis. The investigations resulted in elaboration of a method of preparation of crystalline silicon nitride powders containing more than 96% Si_3N_4. The discussion on the influence of magnesium nitride additive on the Si_3N_4 synthesis process has also been carried out. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Powders; D. Si_3N_4; Synthesis

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1. Introduction

Besides the improvement of preparation and sintering of Si_3N_4 aimed at manufacturing of higher quality ceramics, the search for simpler and more economic synthetic methods of the initial powders seems to be essential. The method of synthesis of Si_3N_4 from SiO_2 and NH_3 could be one of them. The currently applied methods of nitriding of silicon powder with nitrogen or reduction of silicon dioxide with carbon with simultaneous nitriding with nitrogen are either time consuming [1,2] or give products contaminated with carbon or silicon carbide [1,3,4]. Therefore, we have elaborated a method of synthesis of silicon nitride powder from powdered silicon dioxide and gaseous ammonia with no need for the addition of carbon or its compounds. The main goal was to prepare a powder whose grain size was about 1 μm and which contained the maximum possible amount of silicon nitride. The influence of the following parameters on the such defined quality of the silicon nitride powder was investigated: granulation of a substrate, temperature and furnace heating programme, sample heating time, ammonia flow rate and application of the selected mineralising agents added to the silica.

2. Experimental

2.1. Method for silica nitriding

The following reagents were used in the course of the investigations:

- SiO_2 manufactured by Zakłady Rudniki (Poland)
- SiO_2 manufactured by Grace GmbH (Germany)
- SiO_2 manufactured by Aresil (Germany)
- SiO_2 manufactured by Zakłady Ceramiczne in Luboñ (Poland)
- silicon dioxide—gel for chromatography
- ammonia of 99.99% purity manufactured by Zakłady Azotowe Puławy (Poland)
- home made magnesium nitride.

The investigations were carried out in tube furnaces of working volumes of 5 and 250 cm^3 with ammonia flow above the layer of the substrate. The 1–2 mm thick layer of silicon dioxide powder was placed in boats made of alumina and then put into a heating zone of a furnace.

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The furnace was purged with ammonia for about 15 min before the process. The furnace was heated up to the required temperature at a chosen rate and then the temperature was kept for the required time. The following parameters were changed during the investigations: powder grain size, process temperature, heating rate, sample heating time and ammonia flow rate. Pure SiO_2 powder was used at the first stage of the investigations and then in order to improve the reaction yield magnesium nitride was added in amounts of 1–5% w/w. The processes were carried out at temperatures of 1300, 1400, 1450 and 1500 °C, respectively, and then the samples were frozen. The samples were removed from the furnace, ground in a mortar and then analysed according to the described procedure. The information about the intermediate products were used for elaboration of the most probable mechanism of the Si_3N_4 creation.

2.2. Powders characterization

2.2.1. Optical microscopy and SEM

In order to determine the grain size of the powders the samples for microscopic observations were prepared in the following way: the suspension of the powder in pure ethanol (about 5 mg of the powder in 1 ml of the alcohol) was prepared using an ultrasonic bath for homogenisation. Then a drop of the suspension was deposited onto a flat monocrystalline silicon wafer and left to evaporate. The samples were observed in the Neophot 2 metallographic microscope. The automatic system of image analysis was used for determination of the following parameters characteristic of the powder granulation: mean equivalent diameter d_z defined as the diameter of a circle whose area was equal to the area of the projection of the grain on the picture plane and its standard deviation STD (d_z) as well as the parameters characteristic of the grain shape: mean coefficient of elongation $\alpha = d_{max}/d_z$, where d_{max} is the longest chord of the grain projection and the mean coefficient of surface development $\beta = p/\Pi d_z$, where p stands for a perimeter of the grain projection.

The SEM analyses of the powders were also carried out using LEO 1530 scanning electron microscope (Germany).

2.2.2. Thermal analysis

At the initial stage the thermal analysis methods were used for determination of the temperatures of the starting points of the silicon dioxide nitriding process depending on the SiO_2 grain size. The OD 102 derivatograph (Hungary) was used.

2.2.3. X-ray phase analysis

The X-ray studies were carried out by means of the powder diffractometry (XPD) with application of the CuK_α ($\lambda = 1.54056$ Å) radiation. The HZG-4 diffractometer (Germany) was used.

2.2.4. IR spectroscopy

The infrared spectroscopy (Specord IR 75 spectrophotometer, Germany) of the silicon nitride powder synthesised in the reaction of silicon dioxide with ammonia allows for preliminary estimation of the nitride concentration in the Si_3N_4–SiO_2 mixture [5]. The measurements were carried out with application of the standard KBr pellet procedure. This method is also valid in the case when one or both components of the mixture are amorphous, that makes the X-ray analysis difficult. It has been demonstrated that this method can be useful for samples containing more than 20% nitrogen and its precision is ±4% w/w of nitrogen (the stoichiometric concentration of nitrogen in silicon nitride is 40% w/w). Despite these limitations this method can be efficiently used for the fast preliminary determination of the nitrogen concentration in a sample. The high determination threshold has got no meaning in the case of a synthesis of pure silicon nitride since the nitrogen concentration should be very close to the stoichiometric value of 40%.

2.2.5. Classic quantitative analysis

In the method of the classic quantitative analysis [5,6] the weighted aliquot (0.2–0.3g) of the Si_3N_4–SiO_2 mixture was dissolved in a PTFE pressure vessel in a mixture of sulphuric and hydrofluoric acids within 48 h. Then NaOH was added to the prepared solution and a distillation was carried out. The created ammonia was absorbed in a titred HCl solution and then analysed by titration. The nitrogen content in the analysed sample was calculated from the amount of the ammonia generated.

3. Results and discussion

3.1. Preliminary investigations

The silicon dioxide manufactured by the Zakłady Rudniki was used both in the form of the standard grade powder as well as the pneumatically fractionated material in order to get finer grains. The mean diameter of the grains was measured by the optical microscopy with the digital image analysis and the results obtained are presented in Table 1.

All the above described powders appear in an agglomerated form. These substrate powders have been studied by means of X-ray diffractometry proving their amorphous structure. Fig. 1 presents an example distribution of a substrate powder grain size obtained by means of optical microscopy with digital image analysis.

During the preliminary investigations the thermal analysis methods were used in order to determine the

Table 1
Particle sizes of the various powders of silica

Silica powder	Powder particle size (μm)
Manufactured by the Aresil company	0.1
Fractionated powder manufactured by the Zakłady Rudniki	0.5
Manufactured by the Zakłady Rudniki	1.95
Manufactured by the Grace company	2.95
Manufactured by the Zakłady Ceramiczne in Luboñ	1
Chromatography gel	8

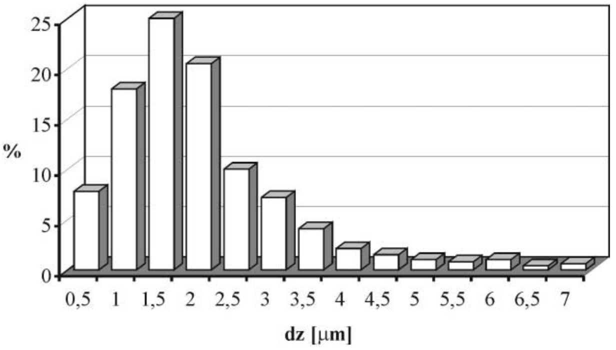

Fig. 1. Grain size distribution of the substrate powder (SiO_2 manufactured by Zakłady Rudniki, Poland).

temperature of the starting point of the reaction. The powders of the mean grain size of 8, 1, 0.5 and 0.1 μm were studied. The results of the analyses are presented in Fig. 2.

The nitriding reaction of SiO_2 runs according to the following equation:

$$3SiO_2 + 4NH_3 \rightarrow Si_3N_4 + 6H_2O \quad (1)$$

and involves a loss of mass. In the case of the 8 μm powder no effect is observed up to 1500 °C. For the 4 μm diameter particles the reaction starts at 1300 °C. The powders of 0.5 and 0.1 μm begin the nitriding reaction at 1250 and 1200 °C, respectively. The mass decrements registered on the thermograms were low and corresponded to the conversion degrees not exceeding a few per cents. Fig. 3 presents the relation between the starting temperature of the nitriding reaction and the particle size. DTA studies showed no peak for the reaction of silica nitriding. However, TG analysis showed that the reactions (with the mass loss) start at different temperatures depending on the particle size.

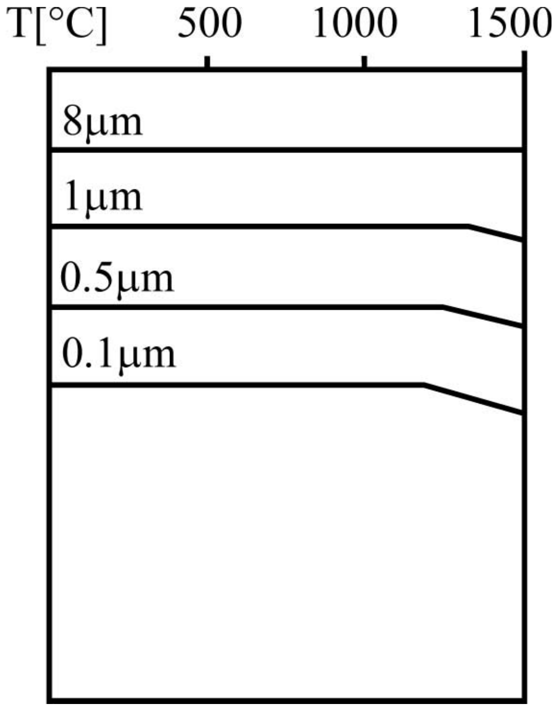

Fig. 2. TG curves of various grain size SiO_2 powders in ammonia.

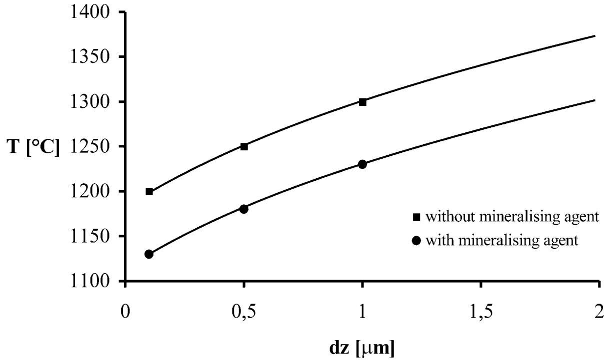

Fig. 3. Dependence of temperature of the starting point of nitriding on grain size.

3.2. Synthesis without the addition of a mineralising agent

The attempts to synthesise silicon nitride without the addition of mineralising additives were performed at the first stage of the investigations. The preliminary series of experiments was carried out in the smaller furnace (the reactor working volume of 5 cm^3 and 10 mm in diameter) within the temperature range of 1200–1500 °C and times from 0.5 to 1.5 h. It was observed, that at heating rates exceeding 20 °C/min the samples sintered before nitriding. The optimal heating rate was set to 10 °C/min. No silicon nitride was detected by the X-ray powder diffraction in the reaction products obtained at temperatures below 1400 °C and process times shorter than 1 h. The IR spectra have not revealed the bands characteristic of silicon nitride. These facts indicated that the concentration of silicon nitride in the product mixture was below 20%, therefore, the conversion degree was low. During these experiments it was observed that there was an ammonia flow limit below which sintering of the silica took place. These limits amounted to 25 or 400 l/h for the furnaces of the volume of 5 or 250 cm^3, respectively. The sintering of the silica resulted in a significant decrease of the specific area of the powder and finally reduction of its reactivity.

Further experiments were carried out at temperatures above 1400 °C, taking into account the limit flow of ammonia. Tables 2 and 3 illustrate the influence of grain size and time on the results of the nitriding process.

The low nitrogen concentration in the reaction products was observed at this stage of the investigations.

3.3. Synthesis with the addition of magnesium nitride

In order to improve the obtained results, the addition of a mineralising agent was applied. Among the substances like lithium, aluminium, calcium and magnesium in metallic or nitride forms, magnesium in the form of magnesium nitride was chosen. The following criteria were used to choose the mineralising agent:

- magnesium in the form of MgO is added to silicon nitride as the activator in the sintering process, therefore, its presence does not lower the functional quality of the manufactured powder;
- magnesium nitride can be easily comminuted into grains of the size comparable to the substrate that facilitates preparation of a homogeneous mixture with silica.

Table 2
Influence of grain size on reaction products; no mineralising agent added

Number of sample	Grain diameter (μm)	Nitrogen concentration (%)	Phase composition of the product according to XPD
1	0.1	29.,4	α Si_3N_4
2	0.1	35.4	α Si_3N_4
3	0.1	21.3	Amorphous sample
4	0.1	22.8	α Si_3N_4
5	0.5	34.9	α Si_3N_4
6	0.5	27.7	α Si_3N_4
7	0.5	27.0	α Si_3N_4 (weak reflexes)
8	0.5	10.1	α Si_3N_4 (traces)
9	1	32.14	α Si_3N_4
10	1	16.4	α Si_3N_4 (weak reflexes)
11	1	–	SiO_2
12	8	1.8	SiO_2

Process parameters: temperature 1450 °C, process duration 3 h, ammonia flow 5 cm/s, layer thickness 1–2 mm, reactor diameter 60 mm (capacity 250 cm^3).

Table 3
Influence of time on reaction products; no mineralising agent added

Number of sample	Reaction time (h)	Nitrogen concentration (%)	Phase composition of the product according to XPD
1	0.5	–	SiO_2
2	1	19.2	SiO_2 + α Si_3N_4 + Si_2N_2O
3	3	34.9	α Si_3N_4
4	3	29.3	α Si_3N_4
5	3	9.3	SiO_2 + α Si_3N_4 (traces)
6	4.5	9.5	Amorphous sample
7	6	33.9	α Si_3N_4
8	16	38.8	α Si_3N_4

Process parameters: temperature 1450 °C, ammonia flow 5 cm/s, grain size 0.5 μm, substrate layer thickness 1–2 mm, reactor diameter 60 mm (capacity 250 cm^3).

Magnesium nitride was added in amounts of 1–5% w/w.

The studies of the nitriding reaction by means of the thermal analysis methods demonstrated that the 5% additive of magnesium nitride lowers the temperature of the starting point of this reaction by about 70 °C (Fig. 3).

The experimental series was performed in the analogous conditions as without the mineralising additive i.e. at temperatures above 1400 °C and the ammonia flow rates exceeding the limit value.

Tables 4 and 5 illustrate the influence of time and concentration of the mineralising agent on the composition of the product mixture.

The analysis of the above results shows the clear abrupt increase of the reaction yield with the added amount of magnesium nitride. The concentration below 2% does not improve the reaction yield. However, when 2–3% of the mineralising agent was added the reaction yield strongly increased. The further increase of magnesium nitride concentration did not influence the composition of the reaction product. Thirty per cent of the introduced magnesium was found in the solid products of the reaction in the form of MgO. The influence of time on the process is similar to the case without the mineralising additive. However, the significantly higher conversion degrees are obtained at equivalent conditions (higher nitrogen content in the mixture) when the mineralising agent is added. In this part of the

Table 4
Influence of time on reaction products; mineralising agent added

Number of sample	Reaction time (h)	Nitrogen concentration (%)	Phase composition of the product according to XPD	Remarks
1	1	19.0	SiO_2 + Si_2N_2O	5 mm
2	1.5	23.4	SiO_2 + Si_2N_2O + β,α Si_3N_4	5 mm
3	3.0	34.2	β and α Si_3N_4	
4	3.0	36.8	β and α Si_3N_4	
5	3.5	36.3	β and α Si_3N_4	
6	3.5	34.3	β and α Si_3N_4	2.5% Mg_3N_2
7	6	32,8	β and α Si_3N_4	
8	7	34.9	β and α Si_3N_4	
9	7	36.8	β and α Si_3N_4	

Process parameters: temperature 1450 °C, mineralising agent concentration 5% w/w (if not marked), ammonia flow 5 cm/s, grain size 0.5 μm, substrate layer thickness 1–2 mm (if not marked), reactor diameter 60 mm (capacity 250 cm^3).

Table 5
Influence of mineralising agent concentration on reaction product

Number of sample	Catalyst concentration (%)	Nitrogen concentration (%) by IR	Nitrogen concentration (%) by classic analysis	Phase composition of the product according to XPD	Furnace capacity (cm^3)
1	1	0	–	SiO_2	5
2	1	0	–	SiO_2	5
3	2	0	–	SiO_2	5
4	2.5	40	–	β and α Si_3N_4	5
5	2.,5	39	34.3	β and α Si_3N_4	250
6	3	31	–	β and α Si_3N_4	5
7	5	40	–	β and α Si_3N_4	5
8	5	33	–	β and α Si_3N_4	5
9	5	40	36.3	β and α Si_3N_4	250
10	5	38	34.2	β and α Si_3N_4	250
11	5	40	36.8	β and α Si_3N_4	250

Process parameters: temperature 1450 °C, process duration 3–3.5 h, ammonia flow 5 cm/s, grain size 0.5 μm, substrate layer thickness 1–2 mm, reactor diameter 10 and 60 mm (capacity 5 and 250 cm^3).

investigation the creation of the oxynitride Si_2N_2O is observed only at low conversion degrees (short times and a thick layer of the substrate) and the results are highly reproducible.

Figs. 4 and 5 present the SEM images of the reaction products at magnifications of 5 and 50 thousand times, respectively.

Fig. 4 presents a general outlook of the powder. The individual grains of the size not exceeding 1 μm are agglomerated, that can give an impression of higher grain size when a microscope of lower resolution is used. More information is given by Fig. 5 due to the higher magnification applied. Fig. 5 presents separate crystals of the shape of elongated prisms that is characteristic of the β phase [7]. These crystals are about 200–500 nm in size which means that they definitely fulfil the assumed criterion of the particle diameter. The lumps that can also be seen comprise probably much smaller grains of Si_3N_4. This assumption is supported by the results of the chemical analysis of the powder giving the result of 95% of silicon nitride.

In addition the particle size distribution obtained by the method of optical microscopy with digital image analysis is presented in Fig. 6. The comparison of these

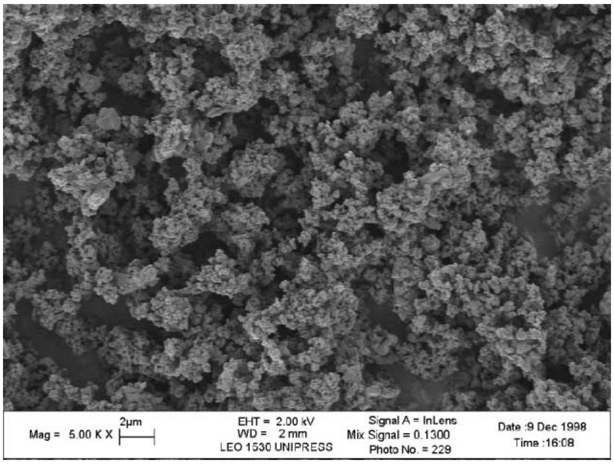

Fig. 4. SEM image of the obtained powder. Agglomeration of the powder is visible.

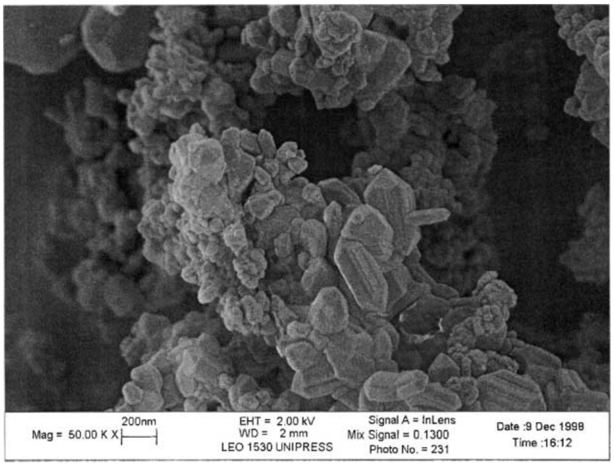

Fig. 5. Fraction of the agglomerate of the obtained powder showing β-Si_3N_4 single crystals.

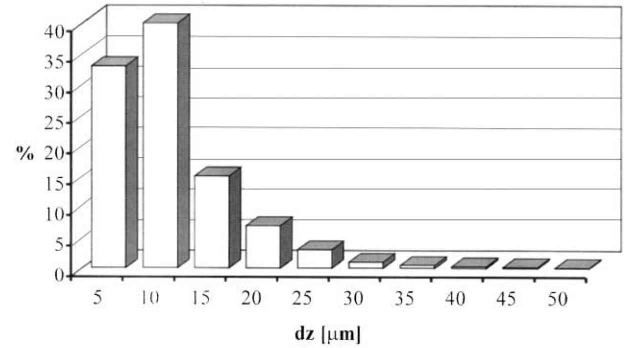

Fig. 6. Grain size distribution of the product powder obtained by optical microscopy.

results with the SEM images indicates clearly that the obtained distribution is related to the agglomerated particles of the silicon nitride powder.

In order to test the applicability of the powders for practical purposes hot pressed ceramics were made out of them as well as coatings on steel surfaces were prepared by means of the plasma spraying method. The hot pressed ceramics appeared to be good cutting tools for cast iron and the layers exhibited good adhesion to steel and high resistance against abrasion and corrosion.

3.4. *Influence of the mineralising agent on the reaction*

The intermediate products—$MgSiN_2$ and Si_2N_2O, were observed when the reaction was performed with the 5% addition of magnesium nitride. These products were detected when the reaction carried out at 1400 °C was frozen after 1 h. At the same time it was found that silicon-magnesium nitride $MgSiN_2$ was created in a reaction of a stoichiometric mixture of silica and magnesium nitride in an atmosphere of ammonia. When the sample is heated at 1300–1400 °C magnesium oxide is present in the product mixture besides silicon-magnesium nitride. However, silicon nitride does form at 1450 °C after a 3 h heating. Silicon-magnesium nitride decomposes into silicon nitride and magnesium nitride at temperatures exceeding 1400 °C [8]. It was also demonstrated that the addition of silicon nitride to silica resulted in the higher conversion degree in comparison to the nitriding process of pure SiO_2. In this case the creation of silicon oxynitride, Si_2N_2O, was observed as the intermediate product. The analysis of the above information allows for the following conclusion concerning the detailed run of the reactions.

At the first stage of the process, at temperatures from 1300 to 1400 °C the creation and decomposition of magnesium silicon nitride plays the main role. As the effect of this process, the initial amount of silicon nitride is synthesised [reactions (2) and (3)]. The magnesium nitride recovered in the process (3) reacts with the next portions of SiO_2. A part of the created magnesium nitride reacts with the produced water vapour that leads to formation of magnesium oxide [reaction (4)] that does not take part in further chemical reactions.

The dominating process above 1400 °C is the synthesis reaction of silicon nitride with silicon oxynitride being the intermediate product [reaction (5)]. First, the thermodynamically preferred α phase is created. Then, in the presence of magnesium compounds, a recrystallisation takes place that results in formation of the β phase. This process is analogous to the one occurring during the sintering.

$$3\,SiO_2 + Mg_3N_2 + 4\,NH_3 \rightarrow 3\,MgSiN_2 + 6\,H_2O \quad T = 1400\ ^\circ C \tag{2}$$

$$3\,MgSiN_2 \rightarrow Mg_3N_2 + Si_3N_4 \quad T > 1400^\circ C \tag{3}$$

$$Mg_3N_2 + 3\,H_2O \rightarrow 3\,MgO + 2\,NH_3 \quad T = 1400\ ^\circ C \tag{4}$$

$$3\,SiO_2 + 4\,NH_3 \xrightarrow{Si_3N_4} (Si_2N_2O) \longrightarrow Si_3N_4 + 6\,H_2O \quad T = 1450\ ^\circ C \tag{5}$$

The proposed run of the process has been confirmed by the X-ray determination of the indicated intermediate products in the product mixtures created at the given temperatures of the reactions.

4. Conclusions

A powder containing 90–96% of silicon nitride in the product mixture was obtained in the reaction of silicon dioxide with ammonia in the presence of magnesium nitride. Magnesium nitride (3–5% w/w) was added to the silicon dioxide powder of the grain size of 0.5 μm. The reaction was carried out at the temperature of 1450 °C for at least 3.5 h. The obtained powder of the grain size of 0.5–1 μm contained β-Si_3N_4 as the predominant component. Magnesium nitride plays a double role in the studied process. First it lowers the temperature of the starting point of the reaction and leads to the creation of the initial amounts of silicon nitride. Then it converts into magnesium oxide. On the other hand magnesium compounds support the recrystallisation process of the synthesised silicon nitride from α into the β phase.

The above described method of the preparation of silicon nitride powder from silicon dioxide and ammonia is economic and easy to perform. The obtained product is suitable to obtain high density Si_3N_4 ceramics and deposit layers by means of the plasma spraying method.

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