SILICON NITRIDE CERAMICS

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The first author of this paper, Dr. Tibor Ličko, suddenly died during the manuscript preparation. The paper is composed on his notes and many of ideas and conclusions drawn in present paper are the results of his own work. That is why, I would like to dedicate the paper preferably to him. *Z. Lenčéš*

INTRODUCTION

The world market for ceramic materials is steadily growing and an increase of about 10% is expected up to the end of present decade, [1]. Despite a lower volume of engineering ceramics application comparing to functional one, it's production is expected to be at least doubled compared to the present state. This optimistic forecast is overshaded by not fullfiled expectations concerning the mass use of engineering ceramics already in this decade.

The reasons for failure of engineering ceramics are inherent to the nature of the ceramics itself, these are high brittleness and low reliability. High research potential is devoted into improvement of these properties. Catastrophic propagation of a crack at the load exceeding it's critical value is a consequence of the brittleness of ceramics materials. The reason for this is unsufficient dissipation of the crack tip energy by the accompanied effects, e. g. in metals the mobility of dislocations is high enough to provide plastic deformation. In ceramics this value is uncomparably lower. The crack origins in ceramics are usually microstructural defects, always present in the ceramic body. The reliability of ceramics is also closely connected with the defects. The reliability can be defined as a probability, that the ceramic body will not be destroyed at the undercritical load, i. e. within all the measured samples the defect size and their distribution is almost the same. Each deviation from the similarity of defect size distribution diminishes Weibull modulus (parameter relating to the reliability). For the ceramic materials, which would have their strength close to their maximum, the defect size should be very low, on the level of the microstructure grains, i. e. large grains of microstructure can start to play the role of defects. For such a case the processing route has the highest importance. Two approaches to preparation of high reliable ceramics exist:

- the development of new, progresive technologies which could eliminate the occurence of large deffects,
- the development of new, composite materials.

Present paper tries to touch both approaches with respect to preparation of silicon nitride ceramics and shows the weak points in the processing of silicon nitride based ceramics. Silicon nitride is most familiar ceramic material from the family of the high-tech materials. Both above mentioned approaches to preparation routes of good quality silicon nitride based materials have one common starting point. This is well defined starting powder.

POWDER PREPARATION

Special requirements are made for high grade Si_3N_4 powders which refer to the shaping behaviour, sintering activity, formation of the microstructure and the hereon depending final product properties. The requirements on Si_3N_4 powders are as follows:

Fineness: Approx. 0.5 μm average particle size with a maximum grains below 3 possibly 1 μm, without hard agglomerates. The particle shape should be equiaxed.

Chemical purity: This should be more than 99.9% concerning metallic impurities. Especially low alkaline and alkaline earth contents are required for high performance ceramic parts, where the melting temperature of the grain boundary glassy phase determines the strength. High homogeneity, no heterogenous contaminations. Oxygen is the major accompanying element among the non-metallic impurities. It is bonded on the powder surface in the form of SiO_2 film or disolved in the lattice. Si free contents should be below 0.5%.

Constitution: High α-phase content, more than 95%, is important for a fine crystalline microstructure.

The choice of powder manufacturing methods is focused on advantegous final product properties. The best way to produce high purity Si_3N_4 powders is to start with raw materials which are available in high purity as well as with respect to the economic basis.

Generally, four Si_3N_4 preparation methods are used:

- Carbothermal nitridation of SiO_2, [2–5],
- Gas phase reactions of silane and its halogen derivatives with NH_3, [6, 8],
- Imide processes / liquid phase reactions, [9, 10],
- Direct nitridation of Si, [11].

Also other preparation routes exist, but these four mentioned above are, because of their application, most ellaborated.

CARBOTHEMAL NITRIDATION OF SiO_2

The price of the starting products for the carbothermal nitridation, which are silica and carbon, is relatively low. That is why this method seems to be favourable for the industrial production of Si_3N_4 powder. The process of Si_3N_4 powder formation follows the reaction, [2]:

$$3SiO_2(s) + 2N_2(g) + 6C(s) \longleftrightarrow Si_3N_4(s) + 6CO(g)$$

The carbothermal nitridation is usually performed at temperatures below 1500°C depending on reactivity of raw material and furnace system used. Lot of work was done on the effect of temperature, nitogen flow rate and quality of initial substances on the reaction and properties of its products [4, 5, 12]. The thermodynamics of this process and all possible acompanying reactions are also described in [5]. Positive effect of seeding of the starting reaction mixture with the Si_3N_4 seeds is also ellaborated [13]. It was found that the reduction of SiO_2 by C 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 SiC grows rapidly. and at 1555°C the SiC is the dominant component of the product. The nitrogen flow rate influences the course of reaction. The low flow rates slow down the reduction of silica, and local crystallization of SiO_2 is observed, at high flow rates of nitrogen, increasing amount of silicon tend to escape from the reactor in the form of SiO. As an optimum nitrogen flow rate was found 40–50 $cm^3\ min^{-1}$ of nitrogen per 1 g of SiO_2. An addition of finely dispersed Si_3N_4 powder to the starting mixture of SiO_2 and C promotes conversion of SiO_2 to Si_3N_4 and reduces the mean particle size of the product. The powder prepared according to these procedure is shown in Fig. 1. Si_3N_4 powders produced via the carbothermal nitridation are characterized by high α-phase content of > 95%. Typical carbon content as low as 0.4% may be achieved. This powder can be further processed by milling to desirable fineness and by wet chemical purification the metallic or non-metallic (oxygen) impurities can be reduced.

GAS PHASE REACTION WITH NH_3

Various gas-phase systems have been used for the preparation of Si_3N_4 powders: $SiCl_4$-NH_3 [7,14], SiH_4-NH_3 [6, 8, 14], $SiCl_4$-N_2-H_2 [15]. SiF_4-NH_3 [16], SiH_2Cl_2-NH_3 [17], $SiBr_4$-NH_3 [18]. These systems are frequently used for the deposition of thin films, more recently powders were also prepared by gas-phase reaction [6, 8, 19, 20]. As an example for such a preparation of Si_3N_4 powder following reaction can be utilized, [8]:

$$3\ SiH_4 + 4\ NH_3 = Si_3N_4 + 12\ H_2$$

Generally, this route yields the amorphous Si_3N_4 powders. These are very fine ranging from 0.05 to 0.8 μm with respect to the reaction conditions, Fig. 2. Reaction is performed in the temperature range from 600 to 1400°C. As a main impurity oxygen was identified in the fraction from 2 to 4%. Also the stoichiometry of the product is dependent on the reaction conditions. Amorphous Si_3N_4 powder with a slight hyperstoichiometry of nitrogen was obtained at a NH_3/SiH_4 ratio 8 to 12 between 800 and 1000°C. Powder prepared at 1400°C was partially crystalline, containing about 10% of α-Si_3N_4.

DIIMIDE DECOMPOSITION

Silicon tetrachloride and ammonia react according to the equation:

$$SiCl_4 + 6\ NH_3 = Si(NH)_2 + 4\ NH_4Cl$$

to an intimate mixture of ammonium chloride and so called silicon diimide.

In principle the liquid phase reaction of $SiCl_4$ with NH_3 can be performed in three different ways:

- $SiCl_4(l) + NH_3(l)$,
- $SiCl_4(g) + NH_3(l)$,
- $SiCl_4(l) + NH_3(g)$.

In all three cases an intimate mixture of fine particulates of silicon diimide and ammonium chloride is formed with specific surface areas of some 100 m^2/g. After extraction or evaporation of ammonium chloride amorphous Si-N compounds with approximate composition between $Si(NH)_2$ – Si_2N_3H – Si_3N_4 are formed. Complete crystallization may be achieved beyond 1250°C dependent on the other reaction conditions like time, atmosphere, type and amount of contaminations. The amorphous intermediates are typically contaminated by residual chloride of the order of 1 wt%. The Si_3N_4 powder formed in crystallization process consists of agglomerates of fine particles predominantly spherical in shape, but needles or coarse hexagonal prisms may be obtained, too. In the final step a fine powder is produced by milling.

DIRECT NITRIDATION OF Si

The direct synthesis of Si_3N_4 from the elements is an old method, by which coarse β-Si_3N_4 had been produced for the use as refractory materials since a long time already.

High-purity α-Si_3N_4 powder can be produced by suitable pure and fine Si-powders and by the control

of the exothermal nitridation reaction. Si-powders of 99 to 99.99% purity and commonly below 100 μm fineness are used and are nitrided in batches or contineous production.

N_2, N_2/H_2 or NH_3 gases and gas mixtures, respectively are used as nitridation gases. Reaction conditions are similar as for preparation of reaction bonded silicon nitride (RBSN) materials which will be described later in detail. As the nitridation product is strongly agglomerated a milling is necessary for production of fine powders. Finer high-quality powders are chemically purified to remove impurities from mill wear, in Fig. 3 the commertially available Si_3N_4 powder prepared in such a way is shown. Using high purity Si-powders and sophisticated processing finest powders and powders including high α-phase with metallic impurities below 100 ppm can be produced – comparable to powders from the imide-process or the gas phase method.

Four main silicon nitride powder production methods were introduced in the previous part, carbothermal nitridation of SiO_2, gas phase reactions, imide process and direct nitridation of Si. Depending on starting materials and the powder manufacturing performance these methods allow to produce a wide ranges of powder qualities. In general, all above described powder production routes (in their advaced form) are able to produce silicon nitride powders with properties fullfiled the requirements mentioned in the beginning of this part, i. e. the fine powders with free surface up to 15 m^2/g or more, high volume fraction of alpha phase > 95 wt%, low content of free silicon < 0.1 wt%, the content of other metalic impurities < 0.2 wt% (for the imide process and gas phase reaction this is much lower < 0.02 wt%), and carbon impurity < 0.2 wt%. Oxygen content of powders prepared by these routes can be suppressed below 2 wt%. The selection of the powder for fabrication of a ceramic body depends mainly on the proposed purpose of application of the ceramic body, on the sintering method and on the price of the starting powder. The last mentioned factor seems to be the major objection for the wider application of cearamic parts in the engineering.

PROCESSING OF Si_3N_4 BASED CERAMICS

Pure, fine and non-agglomerated starting Si_3N_4 powder is sufficient but not necessary condition for the ceramics with excellent mechanical properties. The processing route is of the same level of importance because the defects introduced will have catastrophic consequences on the ceramic part during its performance. That is why the great effort is devoted to the development of the processing routes which will secure the preparation of the ceramic materials with microstructures included low-size deffects (not larger than the size of the grains the microstructure consists of). The following parts of present paper will deal with the most popular techniques applied in the preparation of silicon nitride bodies determined for structural application.

REACTION BONDED Si_3N_4

Reaction bonded silicon nitride (RBNS) is prepared by heat treatment of silicon powder compacts in a flowing or static atmosphere of N_2, cracked NH_3 or N_2/H_2 mixture, at a temperature below the melting point of silicon (1410°C). Completion of nitridation is often carried out at temperatures up to 1450°C in order to shorten the overall long time required (tens of hours). The exothermic conversion of Si to Si_3N_4 is accompanied by a theoretical weight gain of 66.6% and volume expansion of 22%, but there are no dimensional changes. This attractive feature is caused by the expansion of formed new material into surrounding pores. The pore sizes decreases two or three orders of magnitude during the nitriding process [21]. The undesirable remaining porosity is about 10–20%. This problem can be partially solved with using a fine (0.3 μm), high-purity starting silicon powder diluted with Si_3N_4. The method enables very complex shapes to be made, but component thickness is limited due to separation of reactants with Si_3N_4 . To start the nitriding reaction from the centre of compact (by using a suitable heating, e. g. microwave heating) can help in solving of this problem.

Despite the complexity of the nitridation process, a number of factors influencing the nitridation of silicon are well established [22–24]. For conventional purity materials and process conditions, the dominant mechanism of α-Si_3N_4 formation is the chemical vapor deposition (CVD) process, while β-Si_3N_4 forms by a gas – liquid catalyst – solid reaction [22]. Minor amount of α-Si_3N_4 forms by reaction between solid silicon and nitrogen [23]. Metallic impurities in the silicon powder, particularly iron, have a pronounced acceleratory effect on the reaction rate by devitrification and disruption of the protective silica film [22, 25, 26] and by formation of liquid phase ($FeSi_x$) or through their catalytic effect on the nitrogen atmosphere. The other additives such as Mn, Co, Ni, Pd or Pt, promoting the nitridation have been also reported [27, 28]. Florides and oxides of Fe, Mn, Ni, Co, Cu, or V are patented as catalysts for silicon nitride formation [29, 30]. An acceleratory effect is also observed when hydrogen is added (4–10 vol%) to the nitriding gas [31, 32]. A long nitriding time, one of the disadvantages of this method (higher price of the product), can be shortened by the use of a mentioned additives. However, their amount cannot be high (>2wt %), because in particulate form they have

deleterious effects on the strenght of products. Low strenght of RBSN products is the biggest disadvantage of the material prepared by this method. It depends on the microstructure and phase composition of RBSN. The phase composition can be affected except of heat treatment and metal addition also by added gas into nitrogen. Hydrogen promotes the formation of the α-Si_3N_4. The reaction between SiO_2 (s) and H_2 (g) is a source of SiO (g), which is subsequently nitrided to form α-Si_3N_4. On the other hand, in the presence of argon or helium the β/α ratio is increased substantially. Helium and argon encourage the formation of atomic nitrogen, this reacts to form β-Si_3N_4 almost exclusively [26, 27]. Si_3N_4 addition to the silicon powder compact influences the final phase composition and densification of the product. The ideal amount of Si_3N_4 seeds is about 5 –10 wt %[33]. At the same time improved fracture toughness is observed in these materials [34].

The nitridation of Si-Si_3N_4 powder compacts (at 1250–1400°C) containing additions of Y_2O_3, Al_2O_3 or MgO and their subsequent sintering (at 1850°C) is also described [35–37]. The material prepared by this technique is sintered reaction bonded silicon nitride (SRBSN), having a better mechanical properties than RBSN. The amount of additions is up to 10 wt% and the resultant sintering shrinkage is typically 4–7% [38]. Recently, there has been some interest in surface chemistry of starting silicon powder which has a substantial effect on the nitriding kinetics. Kramer et al. [39] showed that Si powders produced by the laser-induced decomposition of SiH_4 have surface characterized by Si-H and Si-H_2 bonding. The reaction of these powders with N_2 to form RBSN occurs at lower temperatures and it is much faster than for conventional powders. Nitrogen adsorption begins at approximately 700°C [40]. Nearly complete conversion (samples 13 mm in diameter, 1 mm thick) was obtained after 1h of nitridation at 1150°C but at 1250°C, the necessary time was less than 10 minutes [41]. The SiH_4-derived RBSN materials, prepared under oxygen free conditions exhibit 10 times less weight gain after oxidation at temperatures up to 1400°C for 50h and higher strengths (500–870 MPa) in comparison with commercial RBSN due to high purity, small diameter of pore channels (0.03μm) and highly perfect microstructure [42]. The other way for obtaining better mechanical properties is preparation of RBSN – based composites such as RBSN/SiC, RBSN/TiN, and RBSN/Al_2O_3 [43] or infiltration of the porous RBSN compacts with various metals and alloys [44]. Ductile metal-reinforcements considerably increase the fracture toughness of RBSN matrix. In the case of ceramics addition the particulate reinforcements take place.

DENSIFICATION OF Si_3N_4

Self-diffusion in covalently-bonded solids such as nitrides, oxinitrides or carbides of silicon is poor, surface and grain boundary diffusion is correspondingly slow (e. g. grain boundary diffusion for SiC is $D_{gb}/m^2s^{-1} = 7 \times 10^{-5} \exp[-611/RT]$) and these compounds dissociate rather than melt at normal pressure. At low temperatures the atomic mobility is therefore too low for densification and at high temperatures, where appreciable atomic mobility is obtained, they begin to decompose. However, the movement of particles and transport of material towards a state of consolidation can be facilitated by providing a liquid phase at temperatures below those a which significant decomposition occurs. Such a process is called liquid-phase sintering. A liquid-phase sintering model developed by Kingery [45] has been applied to describe the densification of nitrogen ceramics by Hampshire and Jack [46] and others. The densification models of Beere [47] and of Bowen et al. [48], which present a different interpretation of the mechanisms of liquid-phase sintering to that of Kingery, have been applied for example by Rahaman et al. [49] and Mostaghaci et al. [50]. Although these models differ in the details of the mechanism of rate control proposed, all require stages of particle rearrangement by grain-boundary sliding and of solution and reprecipitation of solid phases in the liquid. The requirements for densification are therefore agreed to be (i) an appreciable amount of liquid, (ii) wetting of the solids by the liquid and (iii) appreciable solubility of the solid in the liquid.

The importance and applicability of liquid phase sinterng models to the sintering of Si_3N_4-based ceramics was found to decrease when the complexity of this process was realized. The main reason is probably hidden in the phase transformation from α to β phase, which proceeds together with desnification. It means that there is not only material transport providing densification (neck growth, pore anihilation), but also material transport providing phase transformation.

Despite above mentioned models, also model for solid state sintering have been developed [51–53] and can be applied in the case when no sintering aids are introduced. On the other hand among these, the model of Haviar et al. [53, 54] could provide valuable data for densification also in presence of liquid phase, because it is based on data determined during the densification of real powder compact.

In the case of sintering of silicon nitride, it's densification is always accompanied by phase transformation of α to β phase. Hampshire and Jack [46] have shown the relevance of this transformation to the densification process for different sintering additives.

Brook et al. [55] however, do not consider transformation to be a necessary factor for densification and this is supported by recent studies of the sintering of pre-prepared silicon oxinitride and SIALON powders [50]. On the other hand it was also shown that phase transformation in silicon nitride ceramics can proceed without presence of liquid phase at sintering temperature and thus without densification [56].

The onset of densification by liquid-phase sintering depends on the sintering additive used and on the indigenous impurities present in the powder through their effect on the temperature of liquid formation. Subsequent rate of densification is related to liquid viscosity and wetting characteristics. Furthermore, the liquid character and composition will change with time and temperature and for liquid-phase sintering an external applied pressure (hot/hot-isostatic pressing) is merely additive to the effective pressure derived from capillary forces [57]. It has been pointed out [58] that as solid state mechanisms, liquid phase sintering is frequently hindered by vapourization and volatilization process which results in large weight losses.

In hot/hot-isostatic pressing this problem is less evident than in pressureless sintering due to the closed system employed. However, in an open system or a flowing gas system volatilization durin sintering is a particular problem and several studies have been devoted to indentify the causes [59–62]. Sintering of non-oxide ceramics is therefore a complex balance of factor likely to enhance densification through liquid phase mechanisms and those which by decomposition of the solid compounds inhibit consolidation. Specifications of sintering conditions for non-oxide ceramics must address all these factors. The sintering system will thus comprise of (i) compositions specified for the powder and liquid-phase dinsifying additives, (ii) the composition of gas in which the sintering is carried out, and (iii) the temperature.

Alumina, yttria and combination of them are mostly used as densification additives. The densification comprise of pressureless sintering, hot pressing, hot-isostatic pressing and sinter-hipping. The disadvantage of pressureless sintering is that material often contains defects (mainly in the form of pores), resulting in lower mechanical properties. Such defects, originating from non-uniform densification process are mostly not present in hot pressed materials. The disadvantage of hot pressing is that this method is restricted to simple shapes only and is not suitable for mass production. In hot-isostatic pressing, the powder compact has to be encapsulated and encapsulation has to survive the temperature up to 1900°C and pressure about 200 MPa. To overcome the difficulties with hot-isostatic pressing, the method called sinter-hip was developed. Here the powder compact is sintered to the closed porosity at lower gas pressure of nitrogen, pressure is rised when the closed porosity in the sintered body is achieved. The pressure then acts hydrostatically, promoting further densification.

The additives, which form with silica, present on the surfaces of silicon nitride starting powders the liquid phase, remain after the cooling in the product as a vitreous grain boundary phase. The glassy phase is deteriorating the high temperature mechanical properties of the material. There are generally two ways how to overcome this problem. First one is the devitrification of the glassy phase, while the second one is to dissolve the densification additives in the silicon nitride. This effort leads to the preparation of SIALONs [63]. SIALONs are solid solutions based on Si_3N_4, [64]. The solid solution in α-Si_3N_4 is called α-SIALON and is commonly characterized by the formula $Me_xSi_{12-m+n}Al_{m+n}O_nN_{16-n}$. The relation $m = px$ is valid where p is the valency of cation Me. The cation can be Li, Mg, Ca, Y and rare-earth metals except La, Ce, Pr and Eu [65]. Two substitution mechanisms may act; the first is when n(Si+N) is replaced by n(Al+O). The second is further replacement of mSi by mAl, the electron balance being retained by incorporation of xMe into the α-Si_3N_4 structure. The limits of x and n are from the intervals <0.33;0.67> and <.013;0.31>, respectively.

β-SIALONs are characterized by the formula $Si_{6-z}Al_zO_zN_{8-z}$, where z is from the interval <0;4.2>, [63]. As the formula suggests, they are formed when zSi is replaced by zAl and zN is replaced by zO. The unit cell of β-SIALON is expanding linearly with the amount of substitution, [66].

The advantage of SIALONs is that SIALON-forming additives form the liquid phase during SIALON-forming process, which promotes also the densification [64, 67, 68]. Due to the formation of SIALON the liquid is consumed. The most problematic on the preparation of SIALON materials is to find a balance between SIALON formation, which results in decreasing the amount of liquid phase and densification, [68].

To provide better and more uniform densification the extra additives, e. g. yttria are normally added. The processing parameters as temperature and pressure (when present) regime are therefore of upmost iportantance.

MICROSTRUCTURE AND SOME MECHANICAL PROPERTIES

As was recently shown the silicon nitride based materials expose strong correlation between room temperature mechanical properties and microstructure [69–72]. From this point of view the preparation of well defined composite-like microstructures of Si_3N_4 based ceramics is desired.

Two basic approaches to reach this aim are performed: (i) Preparation of β-Si_3N_4 – Si_3N_4 composites by introduction of β-Si_3N_4 whiskers into the starting mixture prior to sintering, microstructure of such a ceramics is shown in Fig. 4. (ii) Preparation of self-reinforced Si_3N_4 ceramics by growth of needle-like β-Si_3N_4 grains within the microstructure during the sintering process, microstructure of such a ceramics is shown in Fig. 5.

The first approach (i) leads to the improvement of the fracture toughness with increasing content of the β-Si_3N_4 whiskers, from 6 to 7.3 MPa.m$^{1/2}$, [73]. The major disadvantage of this approach is that to reach full densification, even by hot pressing, is almost impossible for the whisker addition above 20 wt%. The difficulties are connected also with random distribution of β-Si_3N_4 whiskers within the starting powder, the optimum procedure is described in [74]. The whisker agglomerates degrade the bending strength of such a ceramics. Improved processing resulted in absence of whisker agglomerates and the strength increased to 930 MPa, that means increase of almost 40%.

The second approach (ii) allows to prepare great variety of microstructures with different mechanical properties [75]. Self-reinforced Si_3N_4 materials are in majority of cases prepared by gas pressure sintering, which can be taken into the category of sinter-hip with moderate pressures of nitrogen, up to 10–15 MPa. For such a ceramics high values of fracture toughness up to 12 MPa.m$^{1/2}$ were achieved with the moderate bending stength about 790 MPa, [71]. As is shown in [71, 72] the fracture toughness increases with increase of mean particle size of the self-reinforced microstructure and vice versa, the bending strength increases with their refinement. This antagonistic relation between the strength and fractrue toughness led to the conclusion that each particular case the compromise between both of above mentioned properties with respect to the proposed of purpose application should be found, [72]. Recent results show [76] that also very fine microstructures can expose high fracture toughness, more than 8 MPa.m$^{1/2}$. The necessary condition for reaching this value is to choose the starting powder and sintering conditions in such a way that the final microstructure consists of large volume fraction of fine needle-like β-Si_3N_4 grains with high aspect ratio > 4, with diameter well below 1 μm.

The direction towards refinement of the microstructure is in coincidence with the effort of Niihara et al. [77] who prepared among others also Si_3N_4-SiC nanocomposites which expose enhanced fracture toughness and bending strength. These properties are unchanged up to high temperatures of testing conditions (1500°C). The problem ceramic nanocomposites is discussed in [1] in more detail.

CONCLUSIONS

The necessity of use of fine and pure powders with desired α/β ratio was recognized already in seventies. Since then, the R/D effort is focused to:

i) improvement of mechanical, specially high temperature properties,
ii) improvement of reliability,
iii) decreasing the cost.

Despite considerable impovements, e. g. bending stength at 1400°C has been during last decade increased by 100%, there is still believed to be potential for it's further development, and almost the same is concerning reliability. Among the various densification techniques, gas pressure sintering (sinter-hip) is mostly preferred. The highest contribution to the cost of silicon nitride products is caused by the raw material. That is why in order to decrease the price, cheaper powders should emerge on the market. However, this seems to be a close-loop problem. To produce cheaper powders, higher amounts should be fabricated. To start mass production of Si_3N_4 parts, cheaper powders should be on the market. In this situation, the only unknown parameter is time. The authors believe, that silicon nitride is so superior material, that it's further exploitation is only question of time.

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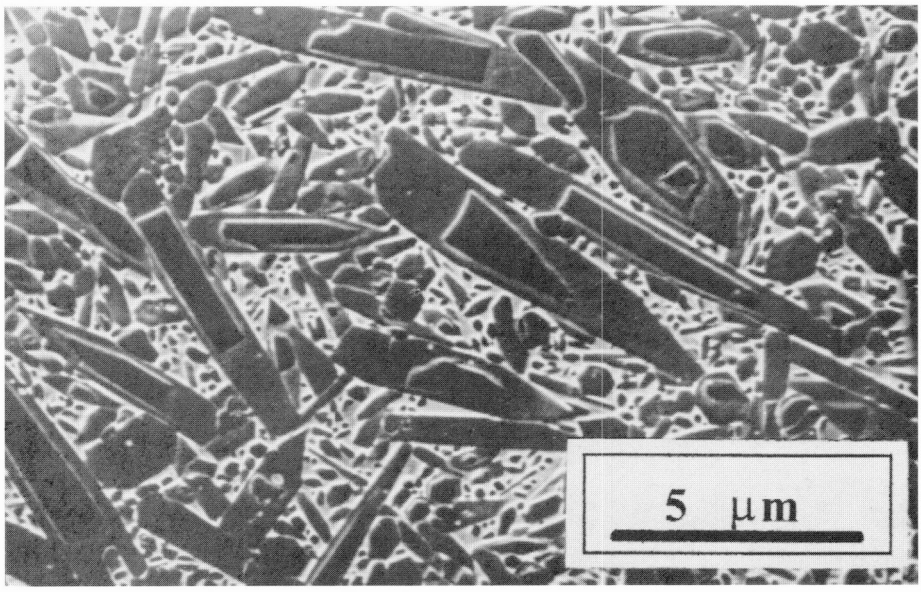

Fig. 4. Microstructure of the β-Si_3N_4 – whisker-reinforced Si_3N_4, prepared by hot-pressing in house, bar = 5 μm.

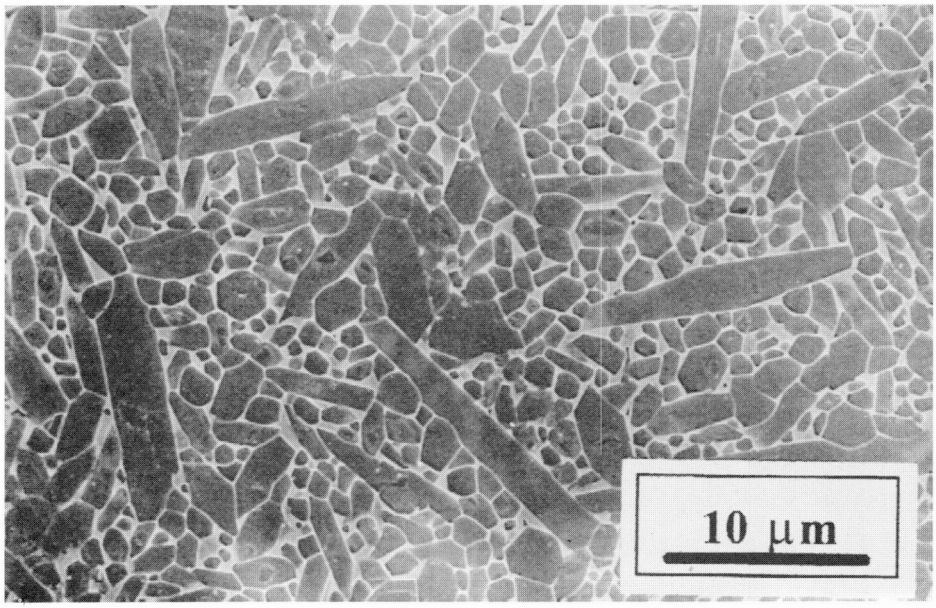

Fig. 5. Microstructure of self-reinforced Si_3N_4, prepared by gaspressure sintering in house, bar = 10 μm.

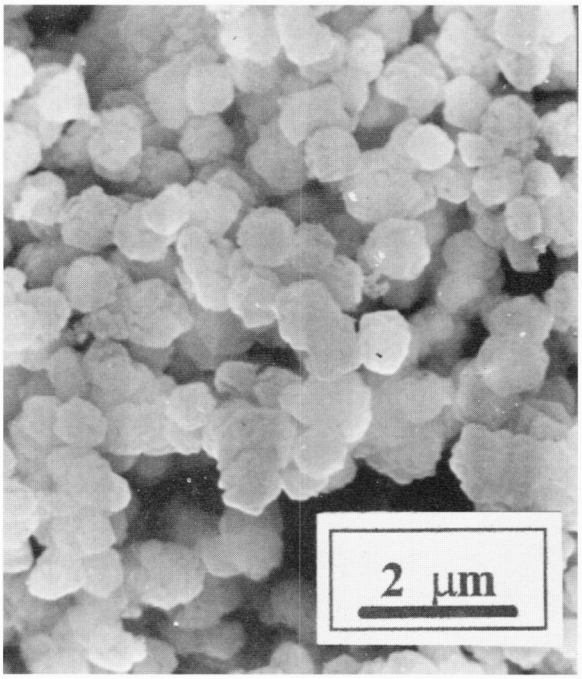

Fig. 1. Microphotograph of the powder prepared by carbothermal nitridation of SiO_2, prepared in house, bar = 2 μm.

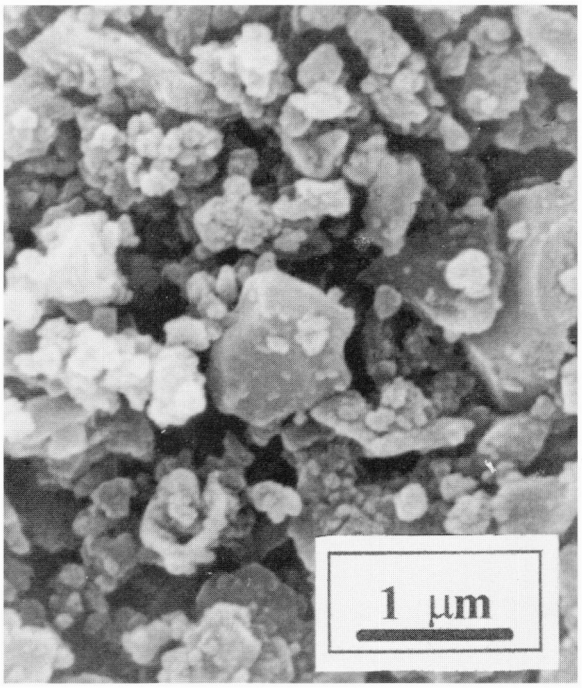

Fig. 3. Microphotograph of the powder prepared by direct nitridation of Si, grade H-1, commercially available from H. C. Starck, Goslar, Germany, bar = 1 μm.

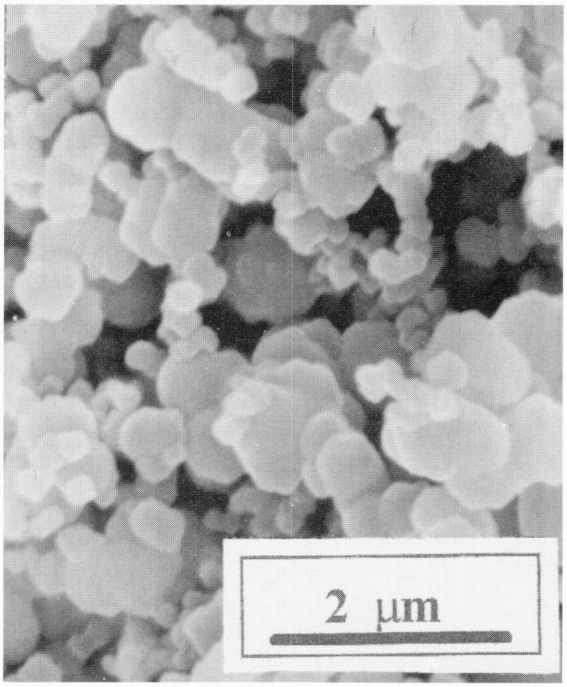

Fig. 2. Microphotograph of the powder prepared by gas phase reaction of SiH_4 with NH_3, prepared in house, bar = 2 μm.