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Silicon nitride: synthesis and properties

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Abstract. Methods of preparing silicon nitride and silicon nitride materials as powders and as materials consolidated from the powders, and also as films and coatings, are reviewed. Information on the structure and on the physicochemical properties of silicon nitride materials is analysed and discussed. The bibliography includes 172 references.

I. Introduction

The synthesis of silicon nitride by heating elemental silicon in an atmosphere of nitrogen generated by the decomposition of potassium cyanide was first reported by Balmen in the middle of the last century.[1] Thus, though first synthesised about 150 years ago, silicon nitride (like silicon carbide) has played a leading role among all known refractory compounds (judging by the number of publications, seminars, conferences, etc.) only during the last two decades. The most 'productive' period was the autumn of 1993, when a symposium on silicon ceramics was held in Tokyo in September, the conference 'Silicon nitride 93' was held in Stuttgart in October, and a symposium on silicon ceramics as construction materials was held in Hawaii in November, in spite of the authoritative symposia held in December 1992 and in April 1993 respectively, in the USA, by the Materials Research Society and by the Ceramics Society, aimed at the scientific and the technological aspects of silicon nitride materials. This sustained interest is not fortuitous: it can be attributed to at least two factors. Firstly, to the remarkable properties of silicon nitride (high hardness, good tribological and elastic characteristics, low density, adequate mechanical and thermal stability, inertness towards many aggressive media, unique electrical properties, and readily available starting materials). Secondly, it is stimulated by the relative complexity of silicon nitride as the object of physicochemical research and technological development.

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Whereas the first of these factors accounts for the wide range of possible applications of this compound (in structural, cutting tool, and tribotechnical materials, and also in materials with special physical and physicochemical properties), and therefore for the interest shown by specialists in different disciplines, the second factor explains the need for comprehensive investigations.

One of the most notable contributions was made in the 1950 – 1970s by Samsonov, who reported a comprehensive study of refractory compounds in general and silicon nitride in particular.[1,2] Monographs so far published on this topic are few,[3–5] and deal with aspects which are now obsolete: the more recent information is to be found in journals and in relatively obscure symposia.[6–9] The latest reviews[10–12] deal with specific aspects, and do not consider the overall problem. It should be noted that the chemical and physicochemical aspects are among the most important in the development of modern silicon nitride materials, and that their relevance is increasing continuously.

The aim of the present review is to discuss and generalise as fully as possible the most recent data on the synthesis and properties of silicon nitride in the form of powders and materials made from the powders, and also in the form of films.

II. Powders and their consolidation

1. Synthesis and thermal dissociation

Si_3N_4 powders can be prepared by many of the standard powder technology methods: direct synthesis in its numerous variants, carbothermic reduction, gas – phase synthesis and dissociation reactions, and mechanical comminution as an additional treatment. These methods are listed in Table 1 with some of their modifications.

The main methods of preparing Si_3N_4 powders used recently have relied on mechanosynthesis, now widely used in the preparation of powders of many refractory compounds and intermetallics.[13–15] It has been shown[16] that the use of ammonia during the milling of silicon is much more effective than the use of nitrogen. The hydrogen formed during the dissociation of ammonia reacts with oxygen impurities in the atmosphere and decreases the probability of forming oxynitride surface films, which suppress the nitridation of the silicon particles. Intensive milling of silicon in ammonia for 150 h, followed by vacuum treatment at 800 °C (τ = 8 h), produces α-Si_3N_4, but the product contains 14.22 at.% of oxygen, 1.28 at.% of iron, and 1.99 at.% of titanium. This result is undoubtedly encouraging, but it also makes clear the need for further optimisation of the regimes adopted in the preparation of Si_3N_4 by the mechanosynthesis method.

Table 1. Main methods of synthesis of silicon nitride powders and their variants.

Method	Main reactions	Main variants of the method
Direct synthesis of components	$3Si+2N_2 \rightarrow Si_3N_4$ $3Si+4NH_3 \rightarrow$ $\rightarrow Si_3N_4+6H_2$	Self-propagating high-temperature synthesis (SHS). Plasmachemical synthesis. Mechanosynthesis
Carbothermic reduction	$3SiO_2+6C+2N_2 \rightarrow$ $\rightarrow Si_3N_4+6CO$	–
Gas-phase synthesis	$3SiCl_4+16NH_3 \rightarrow$ $\rightarrow Si_3N_4+12NH_4Cl$ $3SiH_4+4NH_3 \rightarrow$ $\rightarrow Si_3N_4+12H_2$	Plasmachemical synthesis. Laser synthesis
Dissociation (pyrolysis)	$3Si(NH)_2 \rightarrow$ $\rightarrow Si_3N_4+2NH_3$ $(1/n)[SiR_2-NR]_n \rightarrow$ $\rightarrow Si_3N_4+RH+H_2$	Laser induced
Milling	–	–

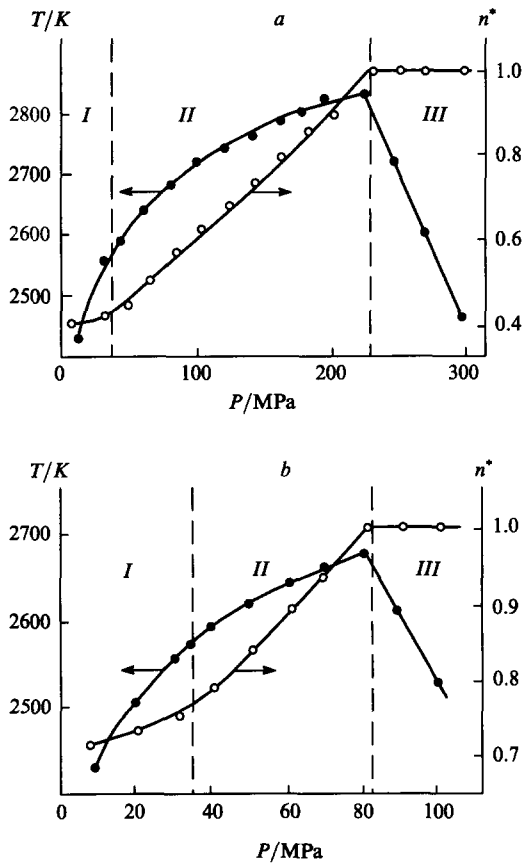


Figure 1. Effect of the nitrogen pressure on the adiabatic combustion temperature and on the extent of reaction of the silicon (n^*). (*a*) Si; (*b*) $Si:Si_3N_4 = 50:50$. Calculated for an assumed porosity of 65%. *I–III* see text.

The kinetics of the interaction of silicon with nitrogen are strongly influenced by the density of defects in the initial powders, as shown by X-ray structural analysis and by ESR and IR spectroscopy methods applied during the milling of silicon.[17] The mechanism of the reaction of silicon with nitrogen has been analysed in detail also by earlier workers,[4,10] and we shall not dwell upon it further here.

Detailed studies of the interaction of silicon with nitrogen during the self-propagating high-temperature synthesis (SHS) of the compound[18–21] have been reported. Fig. 1 shows the dependence on the nitrogen pressure of the calculated adiabatic combustion temperature of silicon and of the extent of reaction. The effect of diluting the initial silicon with silicon nitride, which lowers the nitrogen pressure and the combustion temperature, is also shown. Three regions of the reaction have been defined:[21] in the first (*I*) the rate of combustion is limited by the transport of nitrogen, in the second (*II*) the reaction is controlled by the high-temperature dissociation of the silicon nitride, and in the third region (*III*) rate limitation is provided by the reaction kinetics. In the latter region complete conversion of the silicon into the nitride is observed at the front of the combustion wave ($n^* = 1$).

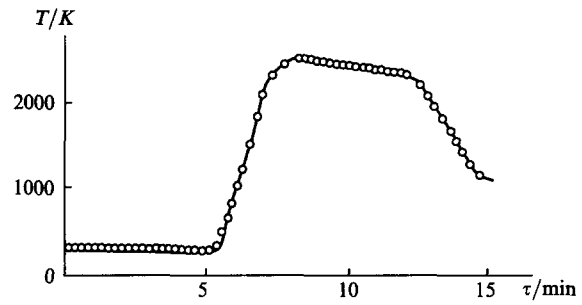


Figure 2. Typical thermogram for the combustion of a mixture of $Si:Si_3N_4 = 50:50$ in nitrogen at a pressure of 50 MPa (porosity 65%).[21]

On the whole these calculations are confirmed by experiment. Fig. 2 shows one of the thermograms obtained in the combustion of silicon (50 mass%) + Si_3N_4 (50 mass%) in nitrogen under a pressure of 50 MPa. The maximum combustion temperature recorded in these experiments (~2500 K) differs by approximately 100–150 K from the calculated values: in view of the approximate nature of the calculations this result can be accepted as fully satisfactory. However, at other temperatures the agreement between the experimental and the theoretical results was not so good.

One of the advantages of the silicon nitride powders prepared by the SHS method is their relatively low oxygen content (0.4%–0.6%).[22] This is due to the use of pure starting materials (semiconductor-grade silicon and thoroughly purified nitrogen). Commercial-grade powders prepared by the SHS method have a much higher content of impurities (for example, their oxygen content is between 1.5% and 2%). Some recent papers[23–25] describe their technological and other properties.

The favourable economic indicators of the SHS method have been discussed by Golubjatnikov et al.,[26] who calculated that for an annual production rate of 50 t by the SHS method the cost of 1 kg of Si_3N_4 powder would be ~US \$28, compared with ~US \$33.7 for material produced by the normal method. Characteristically, in both cases the main contribution to the cost comes from the economically inefficient milling operation.

The tempting idea of preparing silicon nitride powders by the self-propagating combustion of silane–ammonia mixtures without additions of oxygen has not so far been realised.[27] Only the synthesis of silicon oxynitride powders has been reported.

The carbothermic reduction of silicon oxide in a nitrogen atmosphere has long been of interest as a method of using widely available materials including waste products (for example rice husks[28]). However, the powders obtained by this method do not offer a high purity and require additional milling. Their purity can be improved by chemical purification (acid etching) of

the materials.[11] A detailed study of the mechanism of formation of Si_3N_4 under the conditions of carbothermic synthesis (T = 1400–1550 °C, p_N = 0.1–6 MPa) in relation to the properties of the carbon black and of the silicon has been carried out.[29] It was shown that at nitrogen pressures between 2 and 6 MPa the evaporation of the silicon monoxide and the formation of nonequilibrium phases can be largely suppressed, thus bringing the carbon and oxygen content of the reaction products under control. The special features of the carbothermic reduction of silica in nitrogen were discussed also by several contributors to the Stuttgart conference[9] in 1993. For example, it was reported that the well-known Dow Chemical Company (USA) had developed a technology for the carbothermic synthesis of Si_3N_4 which produced a powder of submicron particle size with a high content of the α-phase (>95%) and a relatively small content of oxygen (2%–2.5%) and of carbon (0.3%–0.5%).[30] The moderate cost and the useful technological characteristics of this powder were stressed.

Most of the work reported during the last few years relates to the gas-phase synthesis of silicon nitride, and is mainly aimed at the production of ultrafine powders (UFP) with a particle size of less than 100 nm (usually $d < 20$ nm).[15] The reactions between ammonia and the vapours of silicon tetrachloride or silane, or their derivatives, have been widely studied.[11,31–35] Work aimed at the preparation of carbide nitride powders should also be mentioned.[31,35]

Under appropriate conditions the gas-phase synthesis stimulates homogeneous nucleation, and thus allows silicon nitride to be prepared in the form of UFP. As has been pointed out,[11] the use of silicon tetrachloride or of silane as the starting materials involves some important considerations. On the one hand the low cost of $SiCl_4$ must be weighed against the need to take special steps to remove corrosive side products (NH_4Cl). On the other hand the less easily available silane, which also requires special precautions in handling, gives a better-quality product. Nevertheless silicon tetrachloride is widely used in the industrial production of silicon imide $Si(NH)_2$. This material decomposes at ~1000 °C with formation of amorphous Si_3N_4, which is then annealed to induce crystallisation at 1500 °C.[36]

The most significant results of the studies of gas-phase reactions include the recognition of the special features of the laser-assisted synthesis of silicon nitride as non-agglomerating UFP,[33] and also calculations of the thermodynamic equilibrium in the Si–H–Cl–N system in the temperature range 800 to 2600 K using SiH_4, $SiCl_4$, their many derivatives, and the imide.[37] The pyrolysis conditions in various media (argon, oxygen, nitrogen, helium) of crosslinked organosilicon polymers have also been analysed in detail.[38,39] The formation of various intermediates during these experiments was demonstrated by NMR and IR spectroscopy.

It should be noted that the use of organosilicon polymers of the polysilazane type $\{[SiR_2-NR]_n$ and $[SiR_2-SiR_2-N]_n\}$ as the precursors in the synthesis of UFP of silicon nitride and of its mixtures with silicon carbide is now being widely adopted.[40] Unfortunately, polymeric precursors of Si_3N_4 with the ideal atomic ratio Si : N : C = 3 : 4 : 0 cannot be prepared by the method used successfully for SiC. The traditional plasma methods of synthesising these products are still proving valuable.[31,32,41] Laser technology is used mainly on the laboratory scale. An increasing number of publications on the use of gas-phase reactions in thermal reactors of the flow type is now appearing. Thus, the thermal dissociation of hexamethyldisilazane $Me_3SiNHSiMe_3$ introduced in a stream of helium as the carrier gas (rate 8.55×10^{-3} mol min^{-1}, silazane concentration 16.5 mol%) has been described; some characteristics of the silicon nitride UFP thus obtained are listed in Table 2.[35]

The low density values (up to ~15% lower than in silicon nitride and carbide) and the acceptable agreement between the particle sizes calculated from measurements of the specific surface by the BET method and from transmission electron microscopy (TEM) data are noteworthy. However, the oxygen content of the powders was fairly high. The amorphous powders first obtained were then annealed. Annealing in an argon atmosphere caused crystallisation of cubic β-SiC ($T \approx$ 1300 °C), whereas α-Si_3N_4 was crystallised by an anneal at 1400 °C in a mixture of $NH_3 : H_2$ = 1 : 1.

The residence time of the precursor–gas mixture in a high-temperature reactor 25.4 mm in diameter and ~200 mm long was less than 0.1 s. The extent of conversion increased from 30% to 51% at temperatures between 1100 and 1400 °C. Approximately 2 g of the powder was deposited in 30 min on a rotating drum cooled in liquid nitrogen. It was noted that the preparation of nonagglomerating UFP required a low concentration of the precursor in the carrier gas (which minimises the probability of cluster coalescence in processes of short duration), a fast expansion of gas stream at the outlet from the high-temperature region into a low pressure of inert gas ($10^2 - 5 \times 10^3$ Pa), and rapid cooling of the particles. These assemblies also include special attachments for collecting the powder and for consolidating it in situ at high pressures with complete protection from the surrounding medium.

Studies of the milling of silicon nitride are still being reported.[42,43] Contamination of the product from the material of the milling balls and of the lining can be avoided by using piece parts made from silicon nitride, but milling is invariably accompanied by oxygen contamination. This effect is well illustrated by the milling of a powder of H1 grade (produced by H C Stark Co.) in a specially lined attrition mill (Table 3).[42]

Table 3. Some characteristics of a powder of H1 grade from the H C Stark company after milling for 4 h and 12 h.

Milling time/h	S/m^2 g^{-1}	d/nm	O (mass%)
0	8.4	220	0.9
4	20	95	2.1
12	30	60	3.0

Table 2. Effect of the dissociation temperature on the properties of an ultradispersed $SiC_xN_yO_z$ powder.

T/°C	γ/g cm^{-3}	S/m^2 g^{-1}	Particle size d/nm		Composition		
			from BET data	from TEM data	x	y	z
1100	2.614	568	4	10	1.26	0.35	0.61
1200	2.737	555	4	10	1.35	0.40	0.47
1300	2.781	360	6	8	1.45	0.48	0.29
1400	2.783	272	8	6	1.51	0.49	0.28

Notes. γ is the pyknometric density; S is the specific surface.

The use of milled powders increases the density of sintered and hot-pressed samples.

To conclude this section we shall list the various forms of commercially produced silicon nitride: fibres, monocrystals, and SiAlON ceramics. The production and properties of Si_3N_4 fibres have been discussed in recent reviews.[11,44] Almost all the chemical methods listed in Table 1 are applicable to the production of fibres, but they require an additional organisation of the crystallisation processes in the liquid–vapour–crystal or vapour–crystal systems for the successful growth of fibres or of filamentary crystals (whiskers). For example, the formation of fibres by heating silicon imide with small addition of iron or of silicon oxide in an oxygen-free atmosphere at 1200–1500 °C or by high-temperature treatment of polycarbosilane in ammonia has been reported. It has also been pointed out[35] that monocrystalline nanofibres (30–40 nm diameter, length to diameter ratio > 500) can be produced in a very perfect structural state. It was suggested that the growth of these fibres takes place by the formation of liquid microdrops of silicon during the reduction and decomposition of the ultrafine SiC_xN_y powder, followed by dissolution and subsequent crystallisation of the nitride. The formation of single crystals of the α phase (up to 1 μm in diameter, several micrometres in length) was observed also in the synthesis of silicon nitride in the SHS regime at pressures of 10–180 MPa.[21]

Single crystals of α-Si_3N_4 (1–3 μm diameter, 6–10 mm in length) have been obtained[45] by the gas-phase method using the reaction $SiH_x + N_2 \rightarrow Si_3N_4$ with iron as a catalyst: they were used in studies of the physicomechanical properties of these crystals. Crystals of α-Si_3N_4 several millimetres long were produced[46] in a graphite crucible 300 mm in diameter at 1300 °C by the reaction of $HSiCl_3 + N_2 + H_2$ (pressure ~65 Pa). Crystals were isolated from the polycrystalline sample with a diamond cutting tool. It was pointed out that single crystals grown in the $\langle 10\bar{1}0 \rangle$ direction contained far fewer defects (cracks) than monocrystals with a [0001] orientation, though the latter were larger.

The term SiAlON usually refers to compounds formed in the $Si_3N_4-SiO_2-AlN-Al_2O_3$ system and having the general formula $Si_{3-x}Al_xON_{4-x}$. An authoritative review of the properties of these ceramics has recently been published,[47] and we shall not dwell upon them further.

2. Properties of the powders

The compositions and particle sizes of most of the industrial silicon nitride powders and of some samples now being developed are shown in Table 4. These data, collected by the present writer from various publications,[11,22–25,36,48–50] are on the whole consistent with the considerations discussed above on the advantages and disadvantages of the different methods of synthesis. According to Cambier et al.[50] in the late 1980s 18 companies in the USA, Japan, and Western Europe produced ~40 grades of Si_3N_4 powder, of which 35 were made by the direct synthesis method, 3 by the dissociation of the imide, and only one by the carbothermic and one by the gas-phase synthesis method.

An additional comment should be made concerning the specifications placed on the powders. Thus, the content of free silicon, which can be as high as 1%–2%, has to be specified.[25] High concentrations of free silicon are usually found in the powders prepared by nitridation of the silicon. In the prospectuses of the H C Stark Co. the quantity of free silicon in the H1, LC10, and LC12 grades is stated to be not more than 0.1 mass%. The content of metallic impurities is controlled in order to avoid the formation of vitreous phases, which seriously lower the high-temperature strength of silicon nitride materials at the grain boundaries. An associated requirement is the control of the oxygen content, but this effect is also influenced by the activation of the agglomeration process caused by the formation of a liquid phase, which we shall examine below. As was recently pointed out,[51] halogen impurities can also degrade the properties of the powders. In most of the commercial grades of silicon nitride the content of fluorine and chlorine is claimed to be 0.001–0.009 mass%.[36] The phase composition of the powders

Table 4. Composition and size of silicon nitride powders.

Supplier	Grade of powder	Method of synthesis[a]	Composition (mass%)				α-Si_3N_4, (mass%)	S/m^2g^{-1}	$\bar{d}/\mu m$
			N	O	C	Fe+Al+Ca			
H C Stark, Germany	LC12	DS	38.2	1.8–2.1	< 0.2	< 0.015	> 92	19–22	0.6
	LC10	DS	38.2	1.7–2.0	< 0.2	< 0.1	> 94	13–16	0.8
	H1	DS	38.2	1.3–1.8	< 0.5	< 0.16	> 90	7–10	0.9
	GP	GS	38.5	1.1–1.6	< 0.05	< 0.016	> 90	10–13	0.5
Ube Ind., Japan	SN-E10	ID	38.6	1.3	0.1	0.008	97	11	0.55
	SN-A	ID	39.0	0.9	0.2	0.043	88	7	0.65
Toshiba Cer., Japan	A-200 (SN-D)	CS	37.5	2.0	0.9	0.217	98	10.2	0.9
	SN-B	DS	38.2	1.1	0.48	0.16	96	8.5	1.0
Denka, Japan	SN-P21B	DS	38.6	0.3		0.02	92	9	0.7
Institute of Inorganic Chemistry, Latvia	–	PCS (Si)	38	3.1	0.18	0.19	9130		
		PCS ($SiCl_4$)	38.5	1.6	0.07	0.08		45	
Institute of Structural Macro-kinetics, Russia	–	SHS	38.8	1.5–2.2		0.14 Fe	75	3–6	
		SHS	39–39.3	0.4–0.6	< 0.05	< 0.08 Fe	80	1–4	

[a] Here and elsewhere the following symbols are used: DS direct synthesis, GS gas-phase synthesis, ID imide dissociation, CS carbothermic synthesis, PCS plasmachemical synthesis using silicon or silicon tetrachloride as the starting material.

has a marked influence on the microstructure of the sintered and hot-pressed materials. A predominance of the α-phase in the initial powders is thought to be the best composition.

Lastly, properties of UFP related to their agglomeration capacity have attracted special interest in recent development work on nanocrystalline materials.[15,35] The presence of agglomerates affects the formation in the structure of sintered materials of relatively large pores, which degrade the physicomechanical and other properties. More detailed formulations of the requirements on Si_3N_4 powders are continually being proposed, and therefore the data in Table 4 may have to be revised. We should also add that clear criteria for the agglomeration capacity of powders have not yet been formulated.

It follows from the above discussion that the chemical and the phase composition of silicon nitride powders possibly exert a dominant contribution to the final properties of the materials. Not surprisingly, therefore, the distribution of the components in the powders and the special properties of their surface layers continue to be studied in depth. We know that powder surfaces are usually enriched in oxygen; this effect is also seen[4] in Si_3N_4. The most successful recent studies of this type[48,51-57] used various methods of measurement: IR spectroscopy, X-ray photoelectron spectroscopy (XPES), Auger spectroscopy, and others. Szepvolgyi et al.[48] showed that no correlation existed between the overall chemical composition and the particle size of the powders (between 40 and 115 nm). The same workers observed an enrichment of the particle surface by carbon as well as by oxygen. The nitrogen was distributed more or less uniformly over the cross-section. The segregation of oxygen, fluorine, and carbon in the surface layer was observed also by other workers.[52,54-57]

Data on the oxygen content of the powders are of special interest. Possible sources of oxygen include the starting materials and substances specially added to facilitate the sintering process. The presence of oxygen can also be associated with special features of the preparation and pressing technology, and of the conditions under which the powders are stored and treated. In silicon nitride oxygen can be accommodated as so-called lattice oxygen (found in SiO_2 and in oxynitrides of variable composition, such as Si_2N_2O and complex SiAlON ceramics), and also in the composition of hydroxyl groups [$Si(OH)_x$ ($x > 2$)] with different degrees of hydration and of carbonate compounds. The presence of the last two forms was established by XPE spectroscopy.[54] The presence of oxygen in the adsorbed gases (CO, CO_2, water vapour) should also be noted. As reported,[48] the amount of oxygen in the surface layers is 2–20 times greater than in the bulk. According to chemical methods of analysis the oxygen content in the surface was 3–4 times greater than in the bulk.[57] According to calculations based on XPES data the N : Si ratio in the surface layers of powders supplied by the H C Stark company was 0.8–1.0, which differs markedly from the theoretical value of 1.63 but is almost indistinguishable from the value for the oxynitride Si_2N_2O.[58] The most uniform distribution of oxygen is found over the cross-section of carbothermic powders.[36,48]

The large segregations of carbon on the surface are also of interest: they can exceed the bulk content of carbon by a factor of several hundred.[48] The results of studies of the gas evolution during heating of the powders are of interest from this point of view.

The temperature and time dependences of the gas evolution from silicon nitride powders heated in high vacuum, prepared by the SHS method (with an oxygen content of 0.5%) are shown in Fig. 3. We note the dominant presence of carbon monoxide in the desorbed gases, whose evolution effectively ceases after 1.5 h annealing at 1000 °C. (The same treatment was applied to the Si_3N_4 powders to remove adsorbed and other gases before determining the dissociation pressure of the silicon nitride.) Gas evolution was studied also in other samples of Si_3N_4 powder (Table 5). As can be seen, the correlation between the total amount of adsorbed gases and the specific surface, though often observed, is not invariably followed. There is also no regularity in

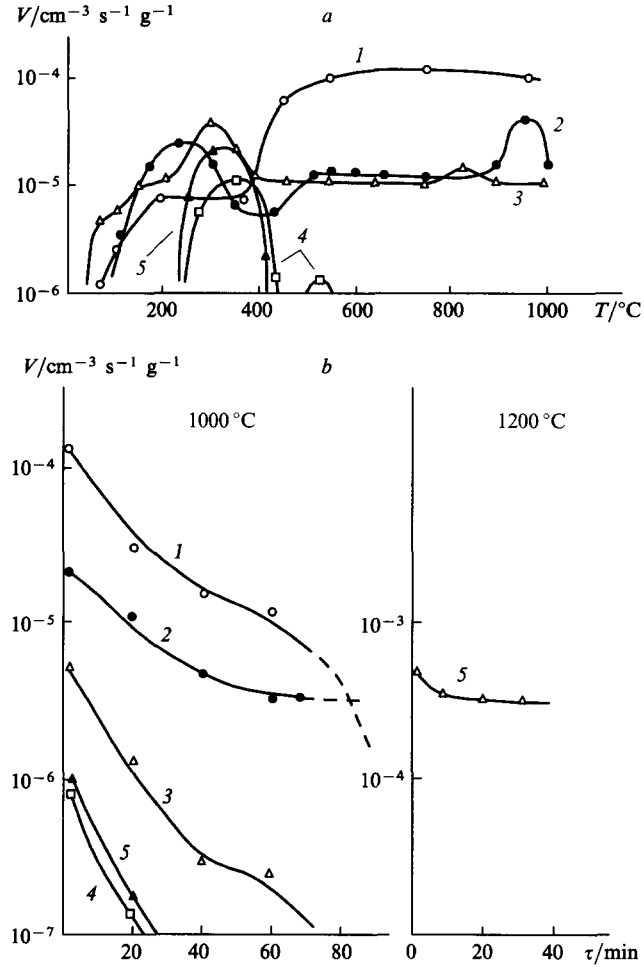


Figure 3. Temperature (*a*) and time dependence (*b*) of the rate of gas evolution during high-vacuum heating of a Si_3N_4 powder prepared by the SHS method.[59] (*1*) CO; (*2*) H_2; (*3*) N_2; (*4*) CO_2; (*5*) N_2.

the temperature at which the rate of gas evolution is a maximum. We know that silicon nitride undergoes hydrolysis when stored in insufficiently pure media. In powders heat treated in vacuum for 1 h at 1200 °C after brief exposure to the air a substantial decrease in the gas content was observed, the desorbed gases consisting mainly of CO.

Thus the results in Table 5 reflect not only the difference in grain size and in the general impurity level of the particles but also the difference between the storage conditions, which were markedly different in the powders listed in Table 4. The role of the storage conditions has been independently confirmed.[48] Whereas the overall level of impurity is determined mainly by the preparation technology, the distribution of the impurities over the cross-section of the particles is controlled by the conditions under which the powders are stored and subsequently handled.

It is important to note that in all the powders the predominant component of the desorbed gases is carbon monoxide (as was also observed, for example, in a study of the gas evolution from titanium nitride powders[63]). This effect can be correlated with the above mentioned segregation of carbon on the surface of the Si_3N_4 particles.[48,54,57] According to Vaivads et al.[54] the carbon can exist on the surface as carbonates and carboxyls.

Table 5 also shows that the temperature of the degassing heat treatment should be about 1000 °C for almost all the powders. However, it is not clear why the dominant species in the desorbed gas below 1000 °C is carbon monoxide, and not carbon dioxide, as could have been expected from the well known equilibrium of the Bell–Boudouard reaction.

Table 5. Parameters of the gas evolution during high-vacuum heat treatment of some silicon nitride powders.[59-62]

Method of preparation	$S/m^2 g^{-1}$	$Q/cm^3 g^{-1}$ (see [a])	Predominant gas concentration (mass%)				Temperature of maximum rate of gas evolution/°C				
			CO	H_2	N_2	H_2O	CO	H_2	N_2	H_2O	CO_2
SHS	0.7	0.9	65	21	10.5	–	500–1000	200–900	300–800	–	–
SHS	1.7	2	see [b]	see [b]	see [b]	–	300–1200	300–1200	300–1200	–	–
SHS	7.1	23.7	62	2.5	23	–	1000	1000	700	–	–
DS	2.5	3.5	see [b]	see [b]	see [b]	–	300	300	300	–	–
PCS	37.5	22.3	see [b]	see [b]	see [b]	–	800–1000	300	800–1000	–	–
PCS	109	263.7	see [b]	see [b]	see [b]	–	700	300	700	–	–
PCS[c]	125	625	59	11	21	7	500–900	500–900	500–900	300–400	300–400
PCS[c] (after annealing for 1 h at 1200 °C)	125	89	79	7	10	6	450–900	450–900	450–900	250–400	250–400

[a] Q is the amount of gas evolved. [b] In the earlier work[60,61] (in contrast to Refs 59, 62, and 63), carbon monoxide and nitrogen were not distinguished in the mass spectroscopy determination of mass number 28. [c] This writer's results, obtained with the help of R A Lyutikov and V I Chukalin.

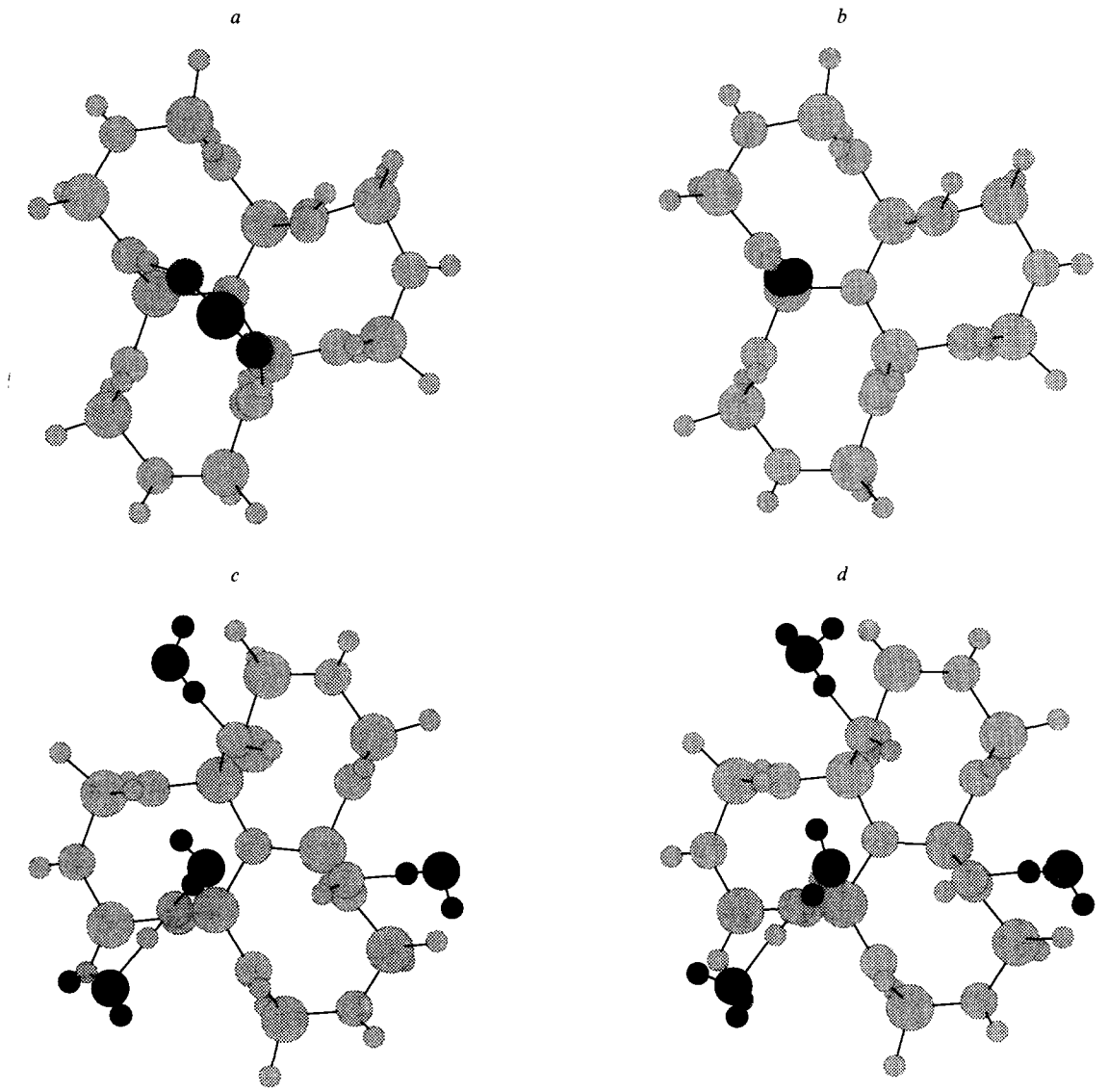


Figure 4. Schemes of the location (top view) of molecules of various adsorbates on the silicon nitride surface. (*a*) CO_2; (*b*) CO; (*c*) H_2O (4 molecules); (*d*) NH_3 (4 molecules). The adsorbate molecules are shown as filled circles. This figure was kindly supplied by N V Goncharova and E F Sheka.[66]

A complex picture of the structure of the surface layers of silicon nitride powders from different producers was observed in a study of these materials by the inelastic neutron scattering method.[64,65] An analysis of the spectra revealed the presence in the surface regions of the powders produced in a 'chlorine' plasma of adsorbed complexes of the NH_4Cl type, and also of NH_3 and HCl. In the case of powders produced by direct nitridation the presence of hydroxyl groups and water is suggested. Quantum-chemical calculations showed that silanol and silamine groups are the principal functional groups of the reaction centres on the surface.[66] Schemes of the proposed arrangement of CO_2, CO, H_2O, and NH_3 molecules on the silanol centres of the Si_3N_4 surface are shown in Fig. 4.

Other impurities also have been detected on the surface of Si_3N_4 and SiC particles: iron, aluminium, calcium, and sodium.[67] However, on the whole we must acknowledge the need for further systematic studies in this direction, using a range of modern methods and carefully standardised materials at all stages (preparation, storage, and applications of the powders).

We shall conclude our discussion of the powders by reexamining their relative costs. A figure of ~US \$30 per 1 kg has been stated.[26] This was independently confirmed,[68] and a cost of \$115 was quoted for 1 kg of UFP of Si_3N_4 ($d \approx 0.017$ μm) produced by laser synthesis. It was stressed that the main contribution (~96%) to the cost of the Si_3N_4 powders came from the cost of the silane. Thus the range \$30–115 is typical of the cost of Si_3N_4 powders (including the UFP materials); for carbothermic powders it can be even lower than \$30.

3. Consolidation

Consolidation processes (compaction, sintering, hot pressing, high-energy methods such as static or dynamic high pressures) are used to prepare silicon nitride materials having a prescribed density. In this context we must allow first of all for the covalent nature of the bonds in Si_3N_4, which accounts for the high brittleness, the high temperature of the brittle–ductile transition, and the low diffusional mobility of the material.

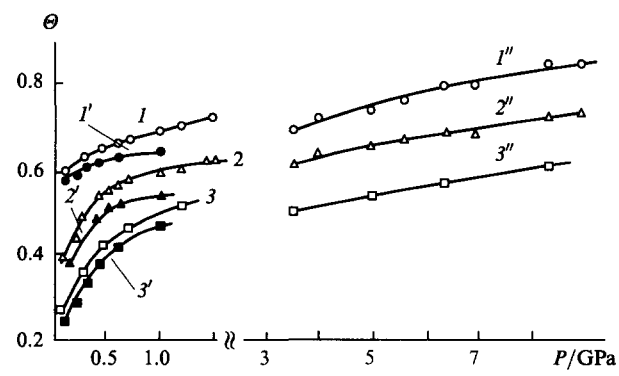


Figure 5. Pressure dependence of the relative density (Θ) in the compaction of Si_3N_4 samples of different granularity.[70] *1–3* compaction in the hydrostat; *1′–3′* compaction in standard dies; *1″–3″* compaction in high-pressure apparatus; d/μm: *1, 1′, 1″* 1; *2, 2′, 2″* 0.05; *3, 3′, 3″* 0.017.

Figs 5–7 show the results of a study of compaction over a wide range of pressure and temperature, and also of the sintering of Si_3N_4 powders.[61,69–73] As can be seen from Fig. 5, even at very high pressures (~9 GPa) samples with a relative density greater than 0.85 cannot be obtained at room temperature. The poor compressibility of Si_3N_4 is associated with a poor plasticity. In the case of UFP the limiting relative densities fall to 0.6–0.7 as a result of the negative effect of the interparticle friction. Only the use of combined high temperatures and pressures result in full densification, when the granularity effect of the powder is to a large extent suppressed (see Fig. 6). Sintering without the

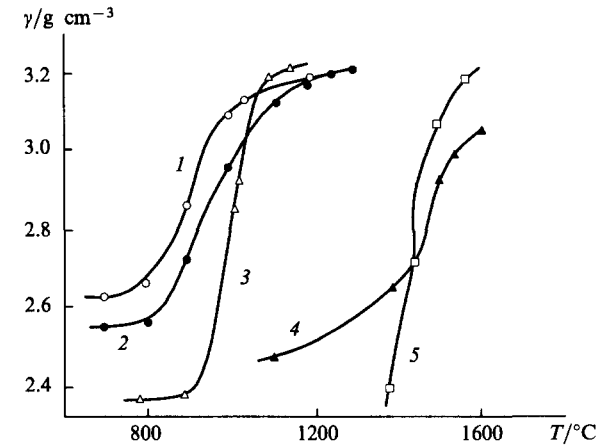


Figure 6. Effect of the compaction temperature and pressure on the density of Si_3N_4 powders of different granularity.[71–73] d/μm: (*1*) 1.1; (*2*) 0.75; (*3*) 0.05; (*4*) 0.45; (*5*) 0.08; P/GPa: (*1–3*) 8.5; (*4,5*) 3.

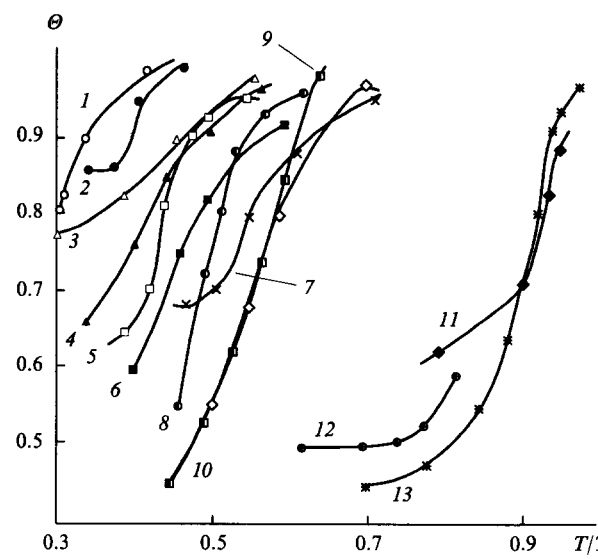


Figure 7. Temperature dependence of the densification during the sintering of various powders.[69,71,72] (*1*) ZrO_2; (*2*) TiN; (*3*) TiO_2; (*4*) Ni; (*5*) CaF_2; (*6*) Mo; (*7*) ZrC; (*8*) MgO; (*9*) WC; (*10*) AlN; (*11*) B; (*12*) Si_3N_4; (*13*) Si.

application of external pressure should produce a temperature of active densification greater than 0.85 T_m in silicon nitride as in other covalent solids (for example, boron and silicon) (see Fig. 7). This conclusion, previously formulated by me,[4,69,71] was recently confirmed by Kryl'.[74] It is interesting to note that whereas in powders of metals, alloys, intermetallics, and ionic compounds the transition to UFP is accompanied by a substantial lowering of the sintering temperature (see Fig. 7) in UFP with covalent bonds this effect is practically undetectable.

Because of the poor sintering properties of Si_3N_4 powders various oxides are added to them (Al_2O_3, MgO, Y_2O_3, singly or in combination) in order to form a liquid phase and thus to accelerate the sintering and hot pressing of the powders.[4] This artifice is used mainly in the hot isostatic pressing variant, which has been widely discussed (see, for example, Refs 69 and 75–79). The liquid phase is formed at high temperatures by the interaction between the added oxides and the films of silica and of oxynitrides present on the surface of the powder particles. The oxygen content of the initial powder plays a limiting role, and it is usually held at the 1%–2% level, though under these

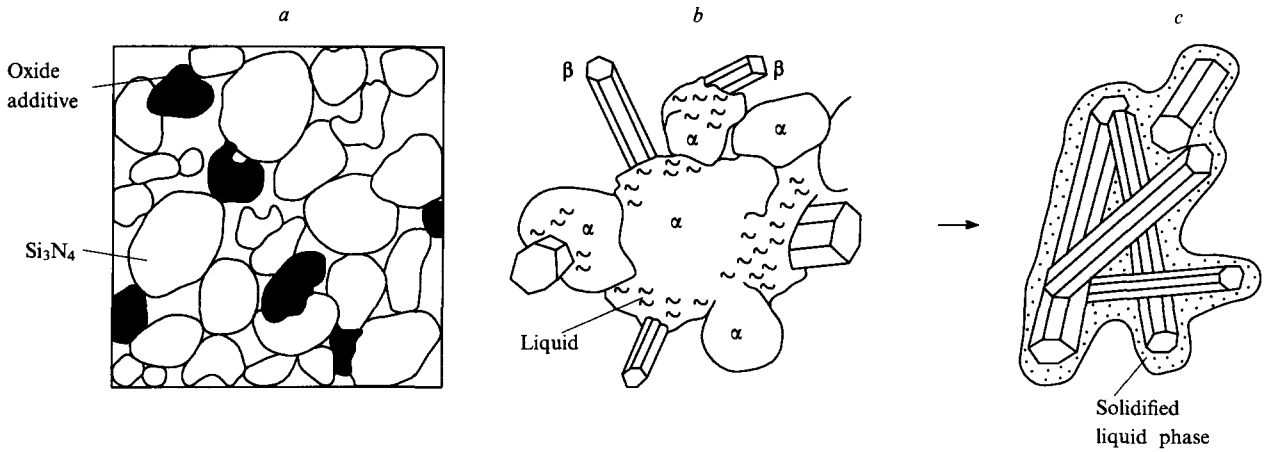


Figure 8. General scheme for the formation of a microstructure during the liquid-phase sintering of silicon nitride materials.[10] (*a*) initial powder; (*b*) α→β transformation; (*c*) microstructure of the densified sample.

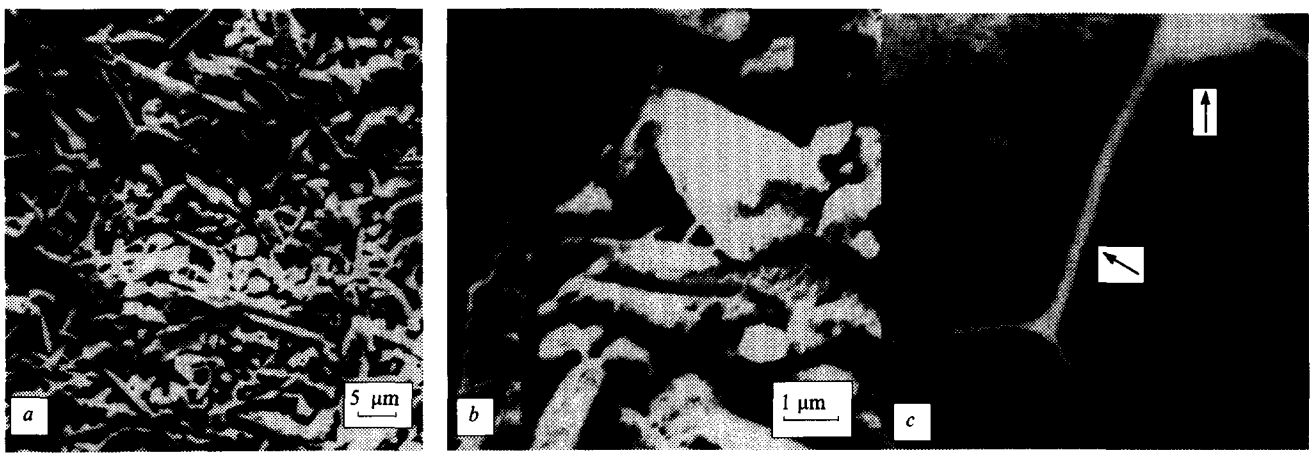


Figure 9. Microstructures of Si_3N_4 obtained in an optical (*a*), a scanning electron (*b*), and a transmission electron microscope (*c*).[10]

conditions the high-temperature strength and creep indices may undergo undesirable changes. Undoubtedly in this case the high-temperature consolidation is complicated by the dissociation of the silicon nitride. Consideration of the complex crystallographic processes associated with the crystallisation of the amorphous phases, the α→β transformation, and the crystallisation from the melts, and also for the normal shrinkage and recrystallisation during sintering and isostatic hot pressing, shows that the nature of the physicochemical mechanism of formation of the structure and properties of silicon nitride materials is far from being trivial.

The mechanism of the liquid-phase sintering and of the isostatic hot pressing has been analysed in many papers.[4,10,11,48,79–81] A general scheme of structure formation during liquid-phase sintering is shown in Fig. 8, while Fig. 9 shows real microstructures obtained by optical microscopy, scanning electron microscopy, and transmission electron microscopy.[10]

Suttor and Fischman[80] have quantified some features of the sintering mechanism. Fig. 10 shows the effect of temperature on the density and on the amount of β phase during the sintering of Si_3N_4 containing 10 mol% of (1:1) $Al_2O_3 + Y_2O_3$.[80] As can be seen from this figure, a significant change in density begins at 1400 °C (the temperature of the ternary eutectic in the $SiO_2-Al_2O_3-Y_2O_3$ system is 1350 °C). A relative density of 0.93 is reached at the temperature (T = 1650 °C), when the α→β transformation is only 23% complete. Microstructural studies of

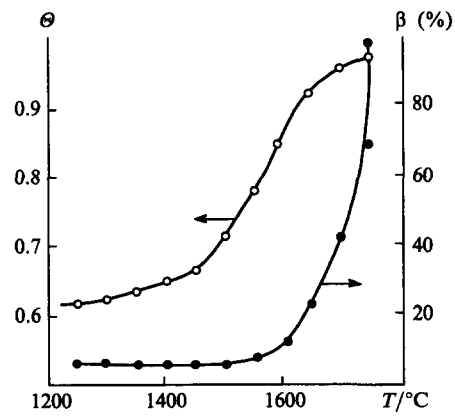


Figure 10. Effect of temperature on the relative density and on the content of β phase during the sintering of Si_3N_4 + 5% Al_2O_3 + 5% Y_2O_3 (see Ref. 80).

quenched samples showed that the characteristic columnar structure (elongated grains of the β phase, see Figs. 9*a* and 9*b*) is formed only during the closing stage of the sintering. Comparing the kinetic coefficients calculated from the experimental data with those of Kingery's theory of liquid-phase

sintering showed that under practical conditions a more complex mechanism must be postulated. NMR was used in a study[81] of the role of additives during sintering, which accounted for the distribution of the elements (^{29}Si, ^{27}Al, ^{25}Mg, ^{89}Y) in the different component phases.

The activating effect of additives of REE oxides (La_2O_3, CeO_2, and others) and of yttrium oxide drew attention to the possibility of finding an active influence on the formation of the so-called self-reinforced fibre structures and of increasing the strength and crack resistance parameters of the material at room temperature and above.[82-85] Thus, fracture toughness values K_{Ic} = 8–9 MPa $m^{1/2}$ have been obtained for the composition Si_3N_4 + 1% Al_2O_3 + 5% CeO_2, exceeding almost two-fold the normal values for silicon nitride materials.[82] The length of individual elongated grains in the structure of these compositions reached 40–50 μm. The bending strength (σ) at room temperature and at 1300 °C for the composition Si_3N_4 + 2% Al_2O_3 + 5% Y_2O_3, into which the additives were introduced by chemical mixing, was 1084 ± 49 and 722 ± 38 MPa respectively, which is also much higher than ordinary values. This effect is attributed to high-melting silicates, which are deposited at the grain boundaries in small quantities.[83] The following parameters have been reported[84] for hot-pressed Si_3N_4 + (8–10%) Y_2O_3 powders synthesised in a plasma: σ(20 °C) = 650–900 MPa, σ(1400 °C) = 550–780 MPa, K_{Ic} = 6–10 MPa $m^{1/2}$. Higher values were obtained for Si_3N_4 doped with oxides of the rare-earth metals: σ(~1500 °C) ≈ 800 MPa (see Takahashi et al.[85]).

Even from this brief survey it is clear that the concepts of grain boundary engineering are of great importance in the development of silicon nitride materials: this is a relatively new area in materials science,[86] which is only now beginning to be applied to silicon nitride. Some aspects of the recrystallisation of silicon nitride have been analysed in detail.[87,88] TEM was used[89] to examine the behaviour of the Si_3N_4 structure at high temperatures and pressures (T = 1300–2300 °C, p = 7.7 GPa). The development of plastic deformation with formation of a high density of dislocations and fragmentation of the larger grains was observed (at T = 1300–1500 °C), and also dynamic recrystallisation, produced both by the migration of grain boundaries and by the rotation of fragments (at T > 1500 °C). The formation of a microstructure is completed by collective recrystallisation, which proceeds rapidly at 2100–2300 °C.

Several studies of the crystallisation of amorphous Si_3N_4 have been published.[36,90-94] Fig. 11 shows the kinetic plots for the crystallisation of the α phase as equiaxial grains from an amorphous powder prepared by the ID method.[36] The calculated activation energy of the process was 890 kJ mol^{-1}. As can be seen from the figure, the crystallisation of Si_3N_4 is completed at 1440 °C. At higher temperatures we observe the formation of the α phase as needle-like grains, and carrying out the process under high nitrogen pressures (up to 100 MPa), at which gas-transport reactions are suppressed, shifts the temperature of the incipient formation of needle-like grains to the region of 1800–2000 °C.[91] Under high-pressure conditions the crystallisation of amorphous Si_3N_4 sets in at lower temperatures: ~800 °C at P = 5 GPa.[90] During sintering and hot pressing the amorphous powders are more inert than the crystalline powders: their active densification temperatures are shifted into even higher temperature ranges, but this effect is almost completely compensated by the use of activating oxide additives.[90,92] The crystallisation of a mixture of amorphous ultrafine powders of Si_3N_4 + SiC begins at 1500 °C and is completed at 1600–1700 °C, i.e. at higher temperatures than for the undoped silicon nitride.[94]

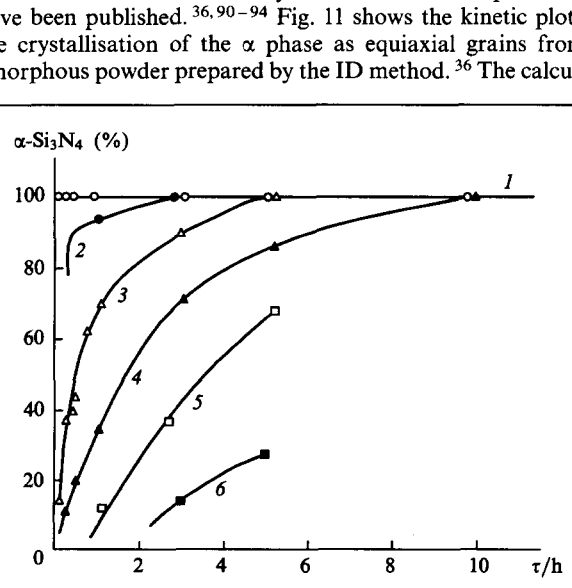


Figure 11. Kinetics of the crystallisation of α-Si_3N_4 from an amorphous powder prepared by the ID method.[36] T/°C: (*1*) 1440; (*2*) 1430; (*3*) 1420; (*4*) 1400; (*5*) 1385; (*6*) 1360.

Studies of the consolidation of Si_3N_4 by the shock compaction method have been reported.[95-97] It is claimed that samples with a relative density of 0.99 were obtained from powders of SN-E10 grade (see Table 3) at pressures of ~40 GPa and temperatures of ~1200 K; their hardness was H_V ~ 23 GPa, and their grain size (calculated from TEM data) was 50–60 nm.[97] The suggested densification mechanism includes plastic deformation and surface melting of the particles.

In conclusion we should note one of the earliest methods of consolidation of silicon nitride materials: reactive sintering. However, this method is rarely studied at present because it does not produce high-density articles. We shall only refer to one report[98] of the use in reactive sintering of fine silicon powders prepared by the laser treatment of silane, which markedly shortened the time of the process.

A relatively new method (infiltration by chemical deposition from the vapour phase, 'chemical vapour infiltration') has not yet found extensive application in the preparation of silicon nitride because of the presence of residual porosity in the final product and because of phase interactions. The use of this method to prepare composite materials of the graphite fibre–silicon nitride type has been reported.[99]

III. Films, coatings, and layers

Both chemical (CVD) and physical (PVD) methods of deposition from the gas phase are used, in different variants, to produce silicon nitride films, coatings, and layers. SiF_4 (or SiH_4, $SiCl_4$)–NH_3–H_2 mixtures are most commonly used. The thermodynamics and kinetics of the deposition of thin layers (up to ~1 μm) of Si_3N_4 have been discussed in monographs[3,5] from the standpoint of problems in microelectronics. Japanese workers[4,100] obtained coatings and layers of polycrystalline and of monocrystalline (as well as amorphous) Si_3N_4 up to 3–4.5 mm thick by deposition from $SiCl_4$–NH_3–H_2 mixtures onto graphite substrates at 1200–1500 °C. Fig. 12 shows the effect of the total gas pressure on the temperature limits of the deposition of the above forms of silicon nitride.

In recent years chemical deposition has been carried out mainly in a high-frequency plasma discharge: the main variants are called plasma assisted and plasma-enhanced CVD processes (PACVD and PECVD respectively). The effect of the power of the high-frequency (13.56 MHz) discharge on the thickness of the coating deposited from a SiF_4–NH_3–H_2 mixture has been studied.[101] The increase in thickness was substantial: at a power of 400 W the thickness increased by more than 50% and reached 700 μm. This result can be explained in terms of the increase in the electron temperature produced by the increased power of the plasma. A high electron temperature increases the rate of dissociation of the gas molecules characterised by a high bond energy, thus increasing the concentration of the corresponding free radicals. Since the bond energy of the SiF_4 molecule (~600 kJ mol^{-1}) is much higher than the bond

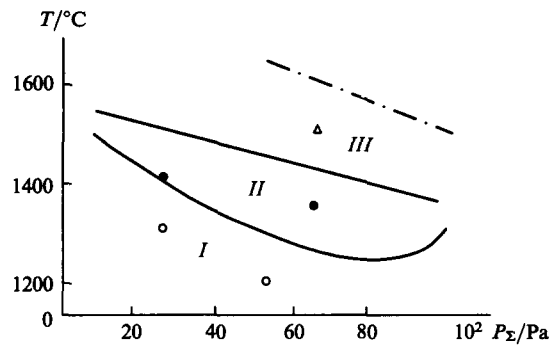


Figure 12. Regions of existence of amorphous (*I*), polycrystalline (*II*), and monocrystalline deposits (*III*) of Si_3N_4 (see Ref. 100). The points denote some specific regimes used to prepare amorphous or polycrystalline samples of size 10 × 40 × 1(3) mm and single crystals 2–3 mm long. The broken line shows the upper limit of the possible formation of deposits. P_Σ is the total pressure of the mixture of gases ($SiCl_4$ + NH_3 + H_2).

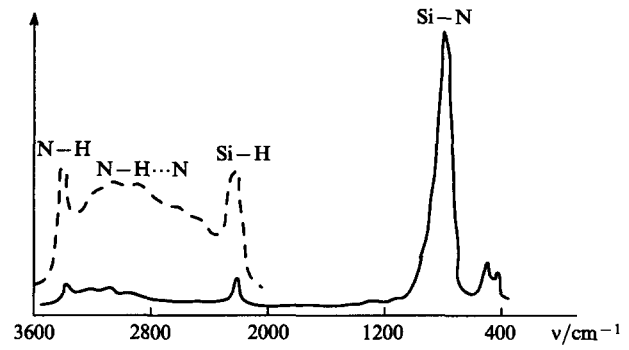


Figure 13. IR spectra of a film of Si_3N_4 0.8 μm thick prepared by PECVD at 293 K (see Ref. 105).

energy of NH_3 (~435 kJ mol^{-1}) it is assumed that the relative number of radicals containing silicon is higher in PECVD.

The optimisation of the regimes used in the deposition of Si_3N_4 films from SiH_4–NH_3–N_2–H_2 mixtures under PECVD conditions has been examined.[102,103] In particular, it was shown that when the power of the high-frequency discharge is increased the residual stresses in the films change sign and are converted from tensile (up to ~270 W) into compressive stresses (>270 W); hydrogen in the gas phase has a similar effect. Table 6 shows the results of an analysis of the composition of films prepared under different conditions.[103] The width of the forbidden gap (E_{gopt}), one of the most important characteristics of these films when used as isolating elements in semiconductor devices and in thin-film field effect transistors in liquid-crystal display systems, is also given in Table 6. As can be seen, the Si:N ratio, the concentration of hydrogen in the films, the presence of Si–Si bonds, and the E_{gopt} parameter show a complicated dependence on the power of the discharge and on the composition of the gas mixture. The use of stoichiometric nitride films, deposited under conditions of minimum residual compressive stress, is recommended.

Problems of hydrogen and other impurities in films of Si_3N_4 have a long history. Many different methods have been used to characterise the films: IR spectroscopy (in different variants), XPES, Auger spectroscopy, RBS, Raman spectroscopy, etc.[3,5,102–105] Fig. 13 shows the IR spectrum of a film of Si_3N_4 deposited from a SiH_4–NH_3–N_2 mixture at 293 K in the plasma of a high-frequency discharge (450 kHz).[105] The peaks at 825, 2215, 3000, and 3400 cm^{-1} correspond to the vibrations of the Si–N, Si–H, N–H...N, and N–H bonds. Traces of oxygen and carbon (~1 at.%) were detected in these films by Auger spectroscopy. IR and XPE spectroscopy methods were used to study the composition of SiN_xC_y coatings prepared by deposition from an $SiCl_4$–CCl_4–N_2–H_2 mixture at 1100–1700 °C onto a tungsten filament.[104] It was found that under these conditions (for example, at a deposition temperature of 1185 °C) the composition of the coatings corresponds to the formula $SiN_{0.8}C_{0.2}$, and that silicon carbide, silicon, and silicon nitride are undetectable.

The thermodynamics of the deposition of condensed phases in the Si–N–C–H system at temperatures up to 2800 K have been discussed by Varlamov et al.[106] It was shown that 'pure' silicon nitride (without codeposition of other condensed phases) is formed in the presence of an excess of nitrogen (N:Si>1.5) at relatively low temperatures ($T < 1100$ K). The regions of coexistence of different phases for C:Si = 4 and H:C = 225 are shown in Fig. 14. The thermodynamics of the formation of Si_3N_4 in the Si–N–Cl–H system have been analysed by Kruis et al.[37]

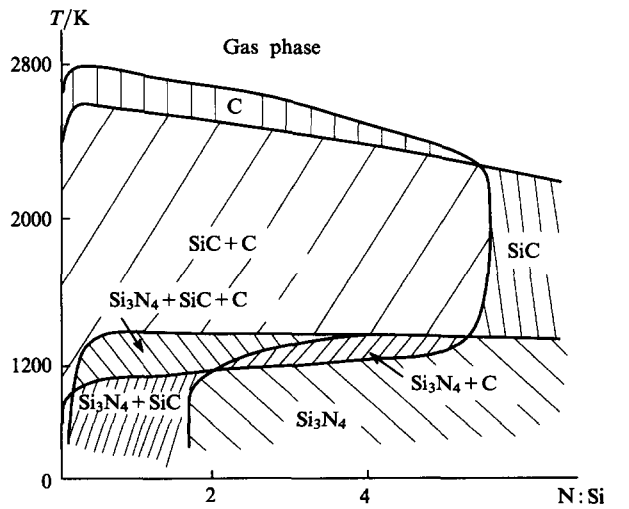


Figure 14. Regions of existence of condensed phases in the Si–N–C–H system with C:Si = 4 and H:C = 225 (total pressure 10^5 Pa).[106]

Table 6. Results of analyses of amorphous films of Si_3N_4 by Rutherford back scattering (RBS) and XPE spectroscopy methods.[103]

Deposition regime		E_{gopt}/eV	Si:N (from RBS data)	Concentration of components (XPES) (at.%)		
W/W	H_2:H_2+N_2 (%)			Si_3N_4	SiNH	Si–Si
100	100	4.1	0.98	76	13	11
400	100	5.6	0.78	76	15	9
300	50	5.3	0.90	85	5	10
300	0	5.3	0.75	90	0	10

Various PVD methods have also been actively applied to the preparation of silicon nitride films. They include a.c. and d.c. sputtering (in different variants), ion-beam deposition (including ion implantation), etc.[107-112] Si_3N_4 films prepared by d.c. sputtering have a columnar structure.[110] The effect of oxygen on the composition and properties of films prepared by r.f. sputtering was analysed by Volkov and Satunkina.[112] A new theory of ion-beam deposition (or ion beam assisted deposition, IBAD) identifies the effect of various technological factors on the composition and certain other properties of silicon nitride films prepared by evaporating silicon and bombarding the amorphous films with nitrogen ions.[109]

IV. Structure and properties

1. Crystal structure and nature of the bond

The crystal structure and the nature of the bond in silicon nitride have been discussed in detail by many workers (see, for example, Refs 3–5 and 10), and therefore we shall dwell on them only in the most general terms, mentioning some new results.

As we know, silicon forms only one chemical compound with nitrogen: Si_3N_4, which exists in two modifications (α and β). Silicon nitride crystallises in the trigonal (α) and the hexagonal crystal system (β). The crystals have identical structures of the Be_2SiO_4 type (phenacite). The main structural element in silicon nitride, as in many silicates, is the tetrahedron 'SiN_4'. A set of three of these tetrahedra share a common nitrogen atom, being arranged with angles of 120° between the tetrahedra. The structures of the α and β modification differ in the arrangement of the tetrahedra along the *c* axis, and therefore they contain different numbers of formula units in the unit cell. The structure of silicon nitride and its main parameters are shown in Fig. 15 and Table 7.

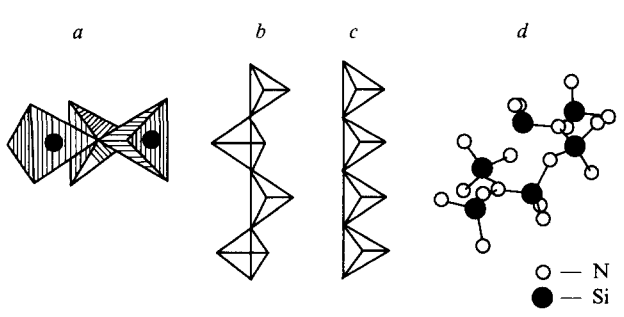


Figure 15. Structure of silicon nitride.[4] (*a*) group of three 'SiN_4' tetrahedra; (*b*) scheme of the arrangement of tetrahedra along the *c* axis in the α phase; (*c*) ditto in the β phase; (*d*) unit cell of β-Si_3N_4.

The special aspects and the mechanism of the α→β transformation have been widely discussed in the literature.[4,10,11,113] It was shown that only the α→β transition is possible: the reverse transition does not take place. This indicates a monotropic transition, and shows that the α→β transition can be classified as a transformation in the second coordination sphere, in which the mutual location of groups of atoms (tetrahedra) is changed but the structure within these groups stays unchanged. A calculation of the Madelung energy showed that above $T = 293$ K the β phase is more stable than the α, which again confirms the monotropic nature of the α→β transformation.[114]

The temperature and the detailed aspects of the α→β transition are still not entirely clear: we know, for example, that heating α-Si_3N_4 samples prepared by gas-phase deposition does not induce the transition at temperatures below 1800 °C.[4] It was pointed out[46] that hot isostatic pressing of the α single crystals at 1600 (P = 5 GPa) and at 2200 °C (P = 70 MPa) is also not accompanied by an α→β transformation. At the same time additions of oxides (MgO, Al_2O_3, Y_2O_3, and others) to activate the sintering and hot pressing processes (see Fig. 10) activate also this transformation as a result of liquid-phase crystallisation. An intensification of polymorphic transformations as a result of dissolution–deposition processes in the presence of a liquid phase is also characteristic of transitions of the rearrangement type in the second coordination sphere. Lastly, under high-pressure conditions (8.5 GPa) the α→β transformation begins at 800 °C and is completed at 1200 °C.[61,115] As was stated above, high pressures also lower the crystallisation temperature of amorphous silicon nitride.[90] However, on the whole we should stress the need for further studies in this area. The structure of amorphous films has been discussed in monographs.[3,5]

NMR is an effective method of localising various structural states and of producing a phase analysis of Si_3N_4, especially if the sample is rotated through the so-called magic angle.[81,116] Its main advantage over the traditional X-ray phase analysis (XPA) is the possibility of identifying not only the crystalline modification but also the amorphous phase, and of localising the position of the other elements (^{13}C, ^{15}N, ^{25}Mg, ^{27}Al, ^{89}Y, ^{189}La), as was stated above in the context of the sintering problem. Fig. 16 shows the forms of the ^{29}Si NMR spectral lines for the different modifications of silicon nitride.[116] As can be seen the NMR method offers information on both the α and the β modification, as well as the amorphous phase.

Though the covalent or covalent–ionic character of the bonds in silicon nitride has long been recognised, a clarification of the details of the electronic structure of this compound remains a topic for discussion.[117-121] Fig. 17 shows a general scheme of the transformation of the atomic orbitals of silicon and nitrogen during the transition to the electronic states of silicon nitride.[119] The conduction band is formed mainly from the 3*s* and 3*p* states of the silicon, and the *s* and *p* states of the nitrogen give rise to the valence band. Of course, this is a simplified picture of the electronic structure of silicon nitride, whose details are being determined by quantum-chemical calculations and by an experimental study of the emission and absorption spectra by various methods (XPES and others). The results of a calculation of the density of states in Si_3N_4 by the tight binding approximation and the corresponding spectroscopic data are shown in Fig. 18. The electronic structure of Si_3N_4 is controlled mainly by the local short-range order, and therefore the α and the β modification and the amorphous phase have almost identical pictures of the density of states. According to quantum-chemical calculations[119] the width of the optical gap is 5.3 eV, which is fairly close to the experimental results (see Table 6). The constitution and the electronic structure of the Si–H and N–H bonds and the defect states in amorphous silicon nitride films (α-SiN_x:H) have been

Table 7. Crystal structure and density parameters of Si_3N_4 (see Ref. 4).

Modification	Space group	Lattice parameters/nm			Length of Si–N bond/nm	Number of formula units in cell	X-ray density/g cm^{-3}
		a	*c*	*c*/*a*			
α	$P31c$	0.78183	0.55914	0.715	0.1715–0.1759	4	3.148
β	$P6_3$	0.7595	0.29023	0.382	0.1704–0.1767	2	3.211

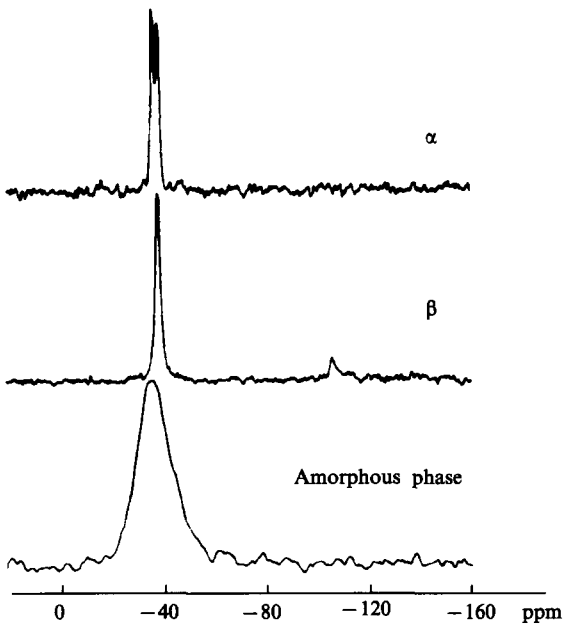


Figure 16. Forms of the NMR spectral lines of ^{29}Si for different modifications of Si_3N_4 (see Ref. 116).

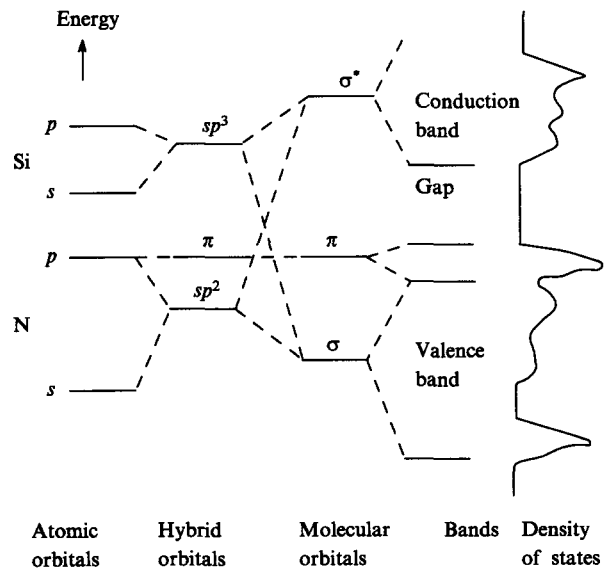


Figure 17. Scheme of the transformation of the atomic orbitals of nitrogen and silicon into the band structure of Si_3N_4 (see Ref. 119).

studied in depth.[119-121] The contribution of the ionic component to the bond energy of Si_3N_4 was estimated to be between 30% and 50%.[114,119]

Calculations of the band structure in β-Si_3N_4 and in the hypothetical compound β-C_3N_4 have been reported.[118] In silicon nitride the crystal structure parameters and the bulk elastic modulus based on these calculations were satisfactorily consistent with experimental data. A substantial amount of charge transfer towards the nitrogen atoms and a higher ionicity contribution were also observed in Si_3N_4 as compared with SiC and C_3N_4.

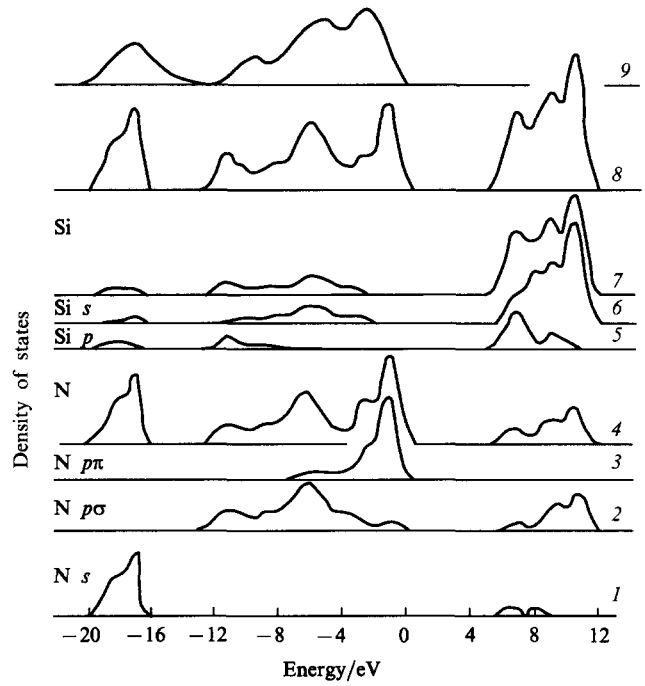


Figure 18. Calculated partial (*1*-*7*) and total (*8*) densities of states for β-Si_3N_4, and results obtained by the photoemission method (*9*) for amorphous films.[119]

2. Phase equilibria and physicochemical properties

The silicon-nitrogen phase diagram has been known for more than 30 years, and very few changes have been made during this period. Fig. 19 shows the diagram calculated for a pressure of 10^5 Pa.[122] Unfortunately, variants of this diagram for pressures above 10^5 Pa have not been produced. For a long time the melting point (T_m) of silicon nitride was given as ~1900 °C in standard handbooks, this being the temperature at which the dissociation pressure of the compound reaches ~10^5 Pa.

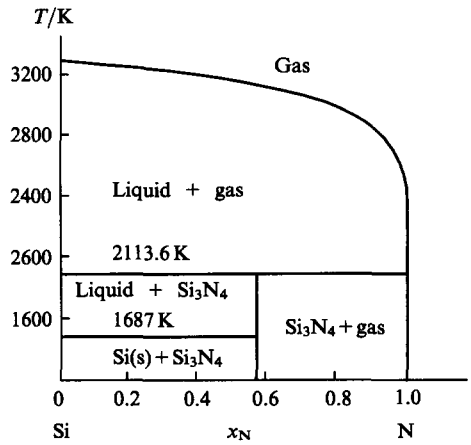


Figure 19. Silicon-nitrogen phase diagram calculated for a pressure of 10^5 Pa (see Ref. 122).

An attempt to determine the melting point was made by me earlier.[4,69,123,124] A value of $T_m \approx 2600$ °C was obtained by using the correlation between the melting point and the elastic modulus. An analysis of the diffusional mobility in silicon carbide and silicon nitride gave a similar value ($T_m \approx 2700$ °C). An analysis of data on the sintering of Si_3N_4 (see Fig. 7) suggested an intermediate value of T_m (2650 °C), which led to fully acceptable results.

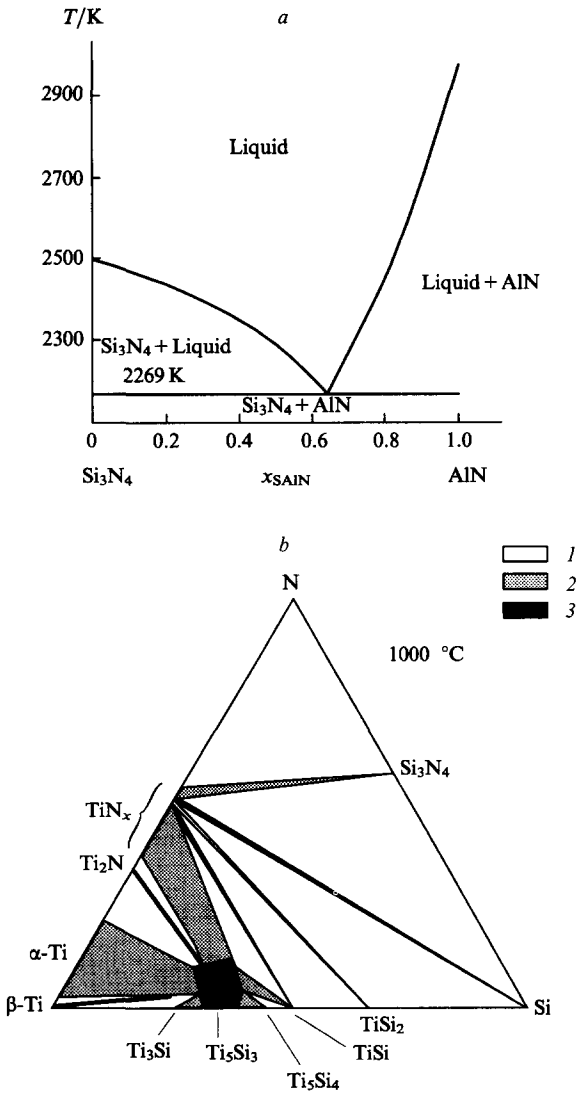


Figure 20. Calculated phase diagrams for Si_3N_4 + AlN (*a*) and Ti–N–Si (*b*).[122,133] Regions in the isothermal section: (*1*) three-phase; (*2*) two-phase; (*3*) region of existence of Ti_5Si_3.

Other workers adopted the following values of T_m in calculations of the phase diagram and of the isostatic hot pressing diagrams: ~2400 °C;[125,126] ~2330 °C;[122,127] 2564 °C.[78] It was pointed out[127] that the value $T_m \approx$ 2330 °C was calculated by comparing the properties of BeO and ZnO (see Weiss's thesis[128]). The entropy of melting of Si_3N_4 was given as 80.5 J K^{-1} mol^{-1}. An experimental determination of the melting point of Si_3N_4 under high nitrogen pressures showed that in the pressure region 120–198 MPa this parameter varies between ~2290 and ~2500 °C, and that the melting is incongruent.[129] Thus our estimates of T_m have been confirmed on the whole, but the need for further and more exact experimental determinations of the melting point has not disappeared.

Information on the phase diagrams of Si_3N_4 can be found in many publications (for example in Refs 4, 122, 125–128, 130–134). Computational methods are now widely applied, and have been used (for example) to construct the diagrams for Si–N–O (see Refs 126 and 130), Si–C–N–O (see Refs 130 and 131), Si–Al–N (see Refs 122 and 125), Si–M–O–N, where M = Al, Mg, Y, Ce, Ti (see Refs 130, 132, 133), and others. The regions of existence of the condensed phases in the Si–N–C–H system were shown above in Fig. 14.[106] In Fig. 20 we show as an example the Si_3N_4–AlN (see Ref. 122) and Ti–N–Si diagrams (see Ref. 133), calculated ignoring the gas phase (whose role, however, is substantial in the first of these systems). Experimental data on the polythermal sections of these and other diagrams for systems including Si_3N_4 are few.

Until recently data on the dissociation of silicon nitride were mostly inferred from results obtained at relatively low temperatures (up to 1500–1700 °C). In the writer's laboratory this temperature was increased to 2000 °C, and the samples included powders prepared by DS, GS, and SHS methods (see Table 4).[58,59,62,135] In Table 8 we show some of the results obtained in this way; Fig. 21 illustrates the temperature

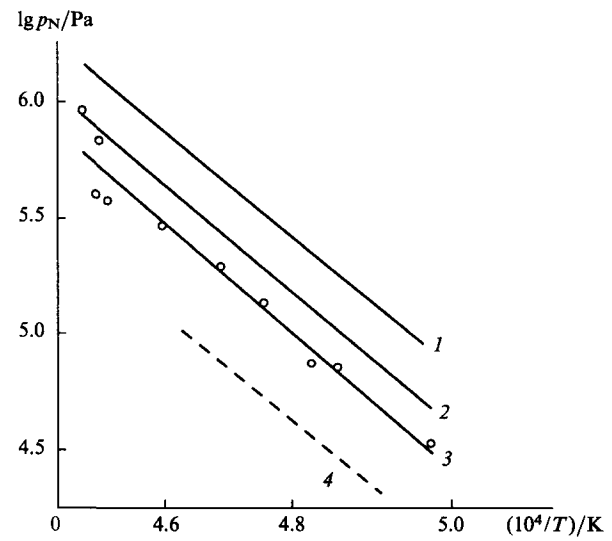


Figure 21. Temperature dependence of the dissociation pressure of silicon nitride. (*1*) GS powder (see Table 8); (*2*) DS powder; (*3*) SHS powder;[58,59] (*4*) from Ref. 136.

Table 8. Thermodynamic properties of silicon nitride.

Method of preparation	Composition (mass%)					$\lg p_N(Pa) = A - B/T$		$-\Delta_f H_{298}$/ kJ mol^{-1}	$\Delta_f G_T$/ kJ mol^{-1}	T/K (p_N = 10^5 Pa)
	O	C	Fe	Al	Ca	A	$10^{-3}B$			
GS	1.6	0.021	0.0043	0.0006	0.0002	16.13	22.30	763(II) 763.4(III)	$-854+0.426T$	2005
DS	1.25	0.15	0.0045	0.03	0.004	15.92	22.37	752(II) 775(III)	$-856+0.418T$	2050
SHS	0.5	0.05	0.08	–	–	15.93	22.76	795(II) 803.6(III)	$-871+0.418T$	2084

dependence of the dissociation pressure of silicon nitride. The effect of the composition of the powders, and in particular of the oxygen content, on the dissociation pressure is evident. Some results published more than 30 years ago [136] and included in most of the standard handbooks [137,138] were obtained in a manometric study of the monovariant equilibrium in the $Si-Si_3N_4-N_2$ system using pure components (99.95% Si, and Si_3N_4 in the form of a nitrided layer with a purity of 99.94%) at nitrogen pressures up to 10^4 Pa. The results of our experiments on the determination of the dissociation pressure by using powders were higher, which we attribute to the effect of oxygen though the detailed mechanism of this effect is not yet clear. This is because before the determination of the dissociation pressure all the powders were degassed to remove adsorbed gases (see Fig. 5 and Table 3), i.e. a substantial part of the oxygen was eliminated. However, the proportion of remaining (lattice) oxygen and its distribution in the surface layers and in the bulk of the particles, and therefore the mechanism of the effect of oxygen on the dissociation pressure, need to be more accurately determined.

It should be noted that no singularities associated with the $\alpha \rightarrow \beta$ transition can be seen in the $\lg p_N = f(T)$ plots, probably because of the close similarity between the thermodynamic properties of these modifications. The results of the determination of the dissociation pressure (see Fig. 21) also suggest that more attention should be paid to the oxygen content in the determination of the melting points and the ignition temperatures in the $Si-N_2$ system (see the already mentioned reports, [21,129] and Figs 1 and 2), because it can affect the dissociation pressure by a substantial factor and erroneously identify the character of the melting.

Values of the enthalpy and of the Gibbs free energy of formation of silicon nitride are shown in Table 8. The values of $\Delta_f H_{298}$ were calculated by the writer by the second and the third law of thermodynamics from data on the dissociation of Si_3N_4. As we know, the agreement between $\Delta_f H_{298}$ values calculated in this way and their closeness to independently obtained calorimetric data confirm the validity of the evaporation or dissociation effects. Only one paper [139] on the calorimetric determination of the heat of formation of Si_3N_4 ($\Delta_f H_{298}$ = 787.8 kJ mol^{-1}) has been published so far. Thus our results appear to be reasonably good, though the need for further studies is evident.

Values of the specific heat and entropy, and also of the thermodynamic functions of silicon nitride over a wide range of temperatures have been reported, [140,141] but no allowance was made for the purity of the samples.

The self-diffusion parameters of silicon nitride have been studied in several laboratories. [142-145] These results are shown in Table 9. The higher diffusional mobility in the β phase as compared with the α phase is noteworthy. The practical problems met in the study of diffusional processes in silicon nitride were analysed by Kunz et al. [144] Comparing the results obtained by different workers [145] reveals a difference of 2-4 orders of magnitude in the absolute values of D. A TEM study of dislocation loops [146] gave an estimate of the diffusion coefficient of the vacancies of $\sim 10^{-18}\ m^2\ s^{-1}$ (T = 1700 °C), which is more than 5 orders of magnitude greater than the value of the same coefficient obtained [142] by extrapolation to this temperature. Therefore the need for further detailed studies of the self-diffusion over a wide range of temperatures and using monocrystalline samples is obvious.

Problems of oxidation and corrosion resistance in silicon nitride materials have recently achieved prominence, and call for a special discussion. Related problems are dealt with in several monographs, handbooks, and reviews, [147-152] and we shall only briefly mention these sources. It should be noted that materials based on Si_3N_4 have undergone substantial corrosion when under stress, and that both tensile and compressive stresses can influence the oxidation processes. [152,153] It is also evident that the dissociation and the oxidation of silicon nitride at high temperatures are two factors which seriously limit the application of materials of this type above 1500-1600 °C. [154] Therefore further studies of the high-temperature thermodynamics of Si_3N_4 in conjunction with corrosion tests under the same conditions, including the development of satisfactory coatings, are urgently needed.

Data on the contact angles and on the energy parameters of wetting of silicon nitride materials by liquid metals and alloys have been reported. [4,147]

3. Physicochemical aspects of the high-temperature strength

Some information on the mechanical properties and structure of silicon nitride has already been given above in the discussion of the consolidation of these materials (see Figs 8 and 9). More detailed information on the physico-mechanical properties can be found in various monographs, handbooks, and reviews, [4,6-12,155-158] in addition to the many original papers in scientific journals, and therefore a complete analysis of this problem goes beyond the scope of the present review. Some of the characteristics obtained recently for single crystals of the α modification are listed in Table 10. [44-46] As can be seen, some properties of the single crystals have been redefined and made more specific, [45,46] though it should be noted that the results of Ref. 45 apply to thin fibres.

Table 9. Parameters of the self-diffusion in silicon nitride.

T/°C	Component	D_i/$m^2\ s^{-1}$ (see [a])	Method	Notes	Ref.
1200-1410	Nitrogen	$1.2 \times 10^{-16}\exp(-233.2/RT)$ $6.8 \times 10^{2}\exp(-777.5/RT)$	Isotope exchange	α-Si_3N_4 β-Si_3N_4	142
1230-1450	Nitrogen	$2 \times 10^{-15}\exp(-132.7/RT)$ $4 \times 10^{-4}\exp(-212.8/RT)$	Nuclear microanalysis	Bulk diffusion in the β phase Grain boundary diffusion in the β phase	143
1400-1600	Silicon	$(0.45-2) \times 10^{-19}$	Spectrometric analysis	α-Si_3N_4	144
900-1300	"	$6 \times 10^{-10}\exp(-183/RT)$	Processing of data obtained by hot isostatic pressing	Effective grain boundary diffusion in (α + β)-Si_3N_4	145

[a] The activation energy is given in kJ mol^{-1}.

Table 10. Some physicochemical characteristics of α-Si_3N_4.

Parameter	Value[a]	Ref.
Young's modulus, GPa	550–750	45
	(380)	44
Tensile strength, GPa	30–50	45
	(3–11)	44
Temperature of the transition from the brittle to the ductile state, °C	1760–1820 (> 1800)	46
Slip system at 1820 °C	$\{1\bar{1}01\}\langle 11\bar{2}0\rangle$ ($\{1\bar{1}01\}[0001]$)	46
K_{Ic}/MPa $m^{1/2}$	1.5–2.0	46
H_V $[P = (2-5)H]$/GPa	34 ± 5 $\{1\bar{1}00\}$	
	(32–36)	
	26 ± 5 (0001)	
	(26–28)	46

[a]The values shown in parentheses are known for single crystals and polycrystals,[4] and also for whisker crystals.[44,46]

The temperature dependence of the hardness for two crystallographic planes is shown in Fig. 22. For the (0001) plane these results are similar to those reported earlier.[100] The high values for the $(1\bar{1}00)$ and $(11\bar{2}0)$ plane denote a substantial anisotropy of the hardness. Furthermore the high-temperature hardness values for monocrystalline Si_3N_4 are much greater than those for polycrystalline and for amorphous samples, even ignoring the values for silicon nitride containing oxide impurities.[77,100,158,159] At 1400–1500 °C the hardness of silicon nitride exceeds that in all the data previously reported for other substances, as was first pointed out by Niihara and Hirai.[100]

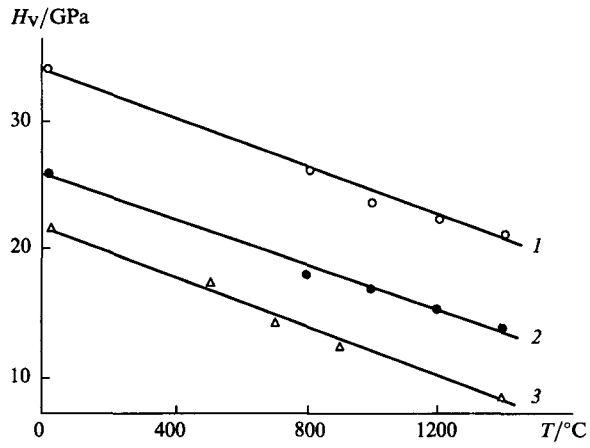


Figure 22. Temperature dependence of the hardness for the $\{1\bar{1}00\}$ (*1*) and (0001) (*2*) of a single crystal,[46] and for a sample of Si_3N_4 containing 2–4.6 mass% of O (*3*).[159] Data for relationships (*1*) and (*2*) were kindly supplied by I E Reimanis.[46]

In this section we shall confine ourselves to an analysis of only a limited number of the physicochemical aspects of the high-temperature strength, in view of the wide range of possible applications of Si_3N_4 in high-temperature technology. In this context problems of impurity effects are of major importance.

It has long been recognised that the presence of oxide additives, introduced in order to activate sintering and hot pressing processes, is accompanied by the formation of liquid interlayers during heating, which in its turn leads to a substantial lowering of the strength indices at temperatures above 1100–1200 °C. The formation of silicate or oxide nitride phases at the grain boundaries and at triple joints has been established by electron microscopy (see Fig. 9).[10] Analyses of the effects of various additives (MgO, Al_2O_3, Y_2O_3, SiO_2, SiC, and REE oxides) on the high-temperature and other properties have been reported by several workers (see, for example, Refs 4, 76, 85, 160–165). We can distinguish at least two approaches to improving the high-temperature behaviour. Firstly the use of silicon nitride powders without oxide additives,[51,77,160,163,166] and secondly the use of a special doping designed to avoid the formation at grain boundaries of vitreous low-melting phases and to encourage the formation of high-temperature crystalline compounds (see, for example, Refs 56, 85, 165).

In a high-temperature study of the strength, rate of propagation of subcritical cracks, elastic modulus, and internal friction it was shown that silicon nitride without added oxides can retain its mechanical properties up to 1450 °C.[51,77,166] It was also pointed out that calcium and halogen impurities play an important role in the high-temperature degradation of the strength, and that the presence of these impurities affects the crystallisation and the behaviour of the silicate phases.

As was pointed out above, oxygen impurities are invariably found in silicon nitride powders. It was shown[85] that samples of Si_3N_4 containing 3.4 mass% of oxygen (in which the oxide nitride Si_2N_2O was detected by XPA in addition to the α phase) retained their strength at the level of ~600 MPa at 1600 °C. However, the microstructure of these samples did not contain the characteristic columnar β crystals (see Figs 8 and 9), and the overall level of strength and crack resistance in this case (as also found by other workers)[51,77,166] was low. According to one report[165] substantial additions of yttrium oxide (up to 15–18 mass%), like additions of other REE oxides,[85] improve both the level and the retention of the strength: at 1400–1500 °C we have σ = 800–850 MPa, the fracture surface being characterised by transgranular features and the K_{Ic} value reaching 13 MPa $m^{1/2}$. These high indices are associated with the formation of a complex Y–Si oxynitride having a high melting point (1850 °C) and with the formation of columnar crystals 7–10 μm long and having a diameter of 0.2–0.7 μm. It is also interesting to note that according to microprobe measurements the distribution of yttrium in the structure was uniform.

The findings mentioned above offer only an empirical outline of new developments in heat-resisting silicon nitride materials. Other data include the effect of the surroundings on the mechanical properties,[148,149,152] the problem of compatibility of the components in composite materials,[12,167] and problems of high-temperature superplasticity.[162,168,169] All these conclusions underline the importance of the concept of controlling the grain boundaries in silicon nitride, as was mentioned above. Unfortunately the nature of the boundaries in these materials has been studied only on a very limited scale.

V. Conclusion

Because of their many desirable physicochemical and physico-mechanical characteristics materials based on Si_3N_4 are finding increasingly wide applications in ordinary industry and in industrial chemical equipment, electronics, turbine construction, and other parts of modern technology.[6–9,170] One of the most promising scientific areas for the application of these materials is in high-temperature techniques. It is thought that the striking progress in the measurement of the melting point could lead to the creation of a new generation of silicon nitride refractory materials, working at temperatures of ~2000 °C. The results shown in Fig. 22 also suggest major possibilities for the use of Si_3N_4 as a material for cutting tools, allowing an increase in the temperature of the cutting site and in the corresponding machining parameters. Of course, these forecasts assume the solution of many nontrivial research and construction technology problems, some of which are mentioned above. Another recent

review[154] also deals with problems in the fundamental study of the creation of a new generation of refractory ceramic materials for use at temperatures up to ~2000 °C.

Silicon nitride is far from having been fully studied as an objective of physicochemical research, and has continued to attract the attention of researchers. Because of the very large number of publications and of the shortage of space, our treatment of some aspects of the silicon nitride problems has been unavoidably superficial. The results of studies carried out mainly during the past 5–10 years have been selectively considered. Again we must stress the large number of publications and the important results obtained in the synthesis of the material and in the study of its high-temperature properties. Recent data on the properties of films of silicon nitride and oxynitride have been reviewed by Habraken and Kuiper.[171] It should also be noted that the unique properties of silicon nitride have allowed the prediction[118] of the new compound carbon nitride, which is now being studied intensively in thin film form.[172]

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References

1. G V Samsonov *Nemetallicheskie Nitridy* (Nonmetallic Nitrides) (Moscow: Metallurgiya, 1969)
2. G V Samsonov, O P Kulik, V S Polishchuk *Poluchenie i Metody Analiza Nitridov* (Preparation and Methods of Analysis of Nitrides) (Kiev: Naukova Dumka, 1978)
3. V I Belyi, L L Vasil'ev, V A Gritsenko, A S Ginovker, S M Repinskii, S P Sinitsa, T P Smirnova, F L Edel'man *Nitrid Kremniya v Elektronike* (Silicon Nitride in Electronics) (Novosibirsk: Nauka, 1982)
4. R A Andrievskii, I I Spivak *Nitrid Kremniya i Materialy na Ego Osnove* (Silicon Nitride and Materials Based on It) (Moscow: Metallurgiya, 1984)
5. A V Rzhanov (Ed.) *Silicon Nitride in Electronics* (Amsterdam: Elsevier, 1988)
6. D A Bonnel, T Y Tien (Eds) *Preparation and Properties of Silicon Nitride Base Materials* (Aedermannsdorf: Trans. Tech. Publ., 1989)
7. S Somiya, M Mitomo, M Yoshimura (Eds) *Silicon Nitride-1* (London: Elsevier Appl. Sci, 1989)
8. I-W Chen, P F Becher, M Mitomo, G Petzow, T-Sh Yen (Eds) *Silicon Nitride Ceramics — Scientific and Technological Advances* Vol. 287 (Pittsburg: Mater. Res. Soc., 1993)
9. M J Hoffmann, P F Becher, G Petzow (Eds) *Silicon Nitride'93* (Aedermannsdorf: Trans. Tech. Publ., 1993)
10. G Ziegler, J Henrich, G Wotting *J. Mater. Sci.* **22** 3041 (1987)
11. H Lange, G Wötting, G Winter *Angew. Chem., Int. Ed. Engl.* **30** 1579 (1991)
12. Yu G Gogotsi *J. Mater. Sci.* **29** 2541 (1994)
13. E G Avvakumov (Ed.) *Mekhanokhimicheskii Sintez v Neorganicheskoi Khimii* (Mechanochemical Synthesis in Inorganic Chemistry) (Novosibirsk: Nauka, 1991)
14. P H Shingu (Ed.) *Mechanical Alloying* (Aedermannsdorf: Trans. Tech. Publ., 1992)
15. R A Andrievskii *Usp. Khim.* **63** 431 (1994) [*Russ. Chem. Rev.* **63** 411 (1994)]
16. A Calca, J S Williams, P Millet *Scr. Metall. Mater.* **27** 1835 (1992)
17. T S Bartnitskaya, M V Vlasova, V B Zelyavskii, N G Kakazei, A V Kurdyumov, L L Sukhikh, V I Chistyakov *Poroshk. Metall.* (11) 1 (1993)
18. A S Mukas'yan, V M Martynenko, A G Merzhanov, I P Borovinskaya, M Yu Blinov *Fiz. Goreniya Vzryva* **22** 43 (1986)
19. A S Mukas'yan, B V Stepanov, Yu A Gal'chenko, I P Borovinskaya *Fiz. Goreniya Vzryva* **26** 45 (1990)
20. A S Mukasyan, I P Borovinskaya *Int. J. Self-Propag. High-Temp. Synth.* **1** 55 (1992)
21. M Skibska, A Szulc, A S Mukasyan, V A Shugaev, A A Shiryaev *Int. J. Self-Propag. High-Temp. Synth.* **2** 247 (1993)
22. A G Merzhanov *Int. J. Self-Propag. High-Temp. Synth.* **2** 113 (1993)
23. S Yu Sharivker, I P Borovinskaya, G A Vishnyakova, Yu N Barinov, A S Mukas'yan, A M Knyazik *Poroshk. Metall.* (11) 16 (1992)
24. S Yu Sharivker, I P Borovinskaya, A S Mukas'yan, V V Karpov *Poroshk. Metall.* (3) 3 (1993)
25. Ya A Kryl', O N Kaidash, E Yu Pavlov *Sverkhtverd. Mater.* (3) 23 (1993)
26. K Golubjatnikov, G Stangle, R Spriggs *Am. Ceram. Soc. Bull.* **72** (12) 96 (1993)
27. R G Aivazyan, V V Azatyan, V I Kolachev, V I Rubtsov *Fiz. Goreniya Vzryva* **30** (4) 85 (1994)
28. A S Vlasov, A I Zakharov, O A Sarkisyan, in *Tugoplavkie Nitridy i Materialy na Ikh Osnove* (Refractory Nitrides and Materials Based upon Them) (Ed. T Ya Kosolapova) (Kiev: Inst. Polym. Mater. Akad. Nauk Ukr., 1992) p. 72
29. M Ekelund, B Forslund *J. Am. Ceram. Soc.* **75** 532 (1992)
30. G A Cochran, C L Conner, G A Eisman, A W Weimer, D F Carroll, S D Dunmead, C J Hwang, in *Silicon Nitride'93* (Eds M J Hoffmann, P F Becher, G Petzow) (Aedermannsdorf: Trans. Tech. Publ., 1993) p. 3
31. H J Lee, K Eguchi, T Yoshida *J. Am. Ceram. Soc.* **73** 3356 (1990)
32. F Allaire, S Dallaire *J. Mater. Sci.* **26** 6736 (1991)
33. R A Bauer, J G M Becht, F E Kruis, B Scarlett, J Schoonman *J. Am. Ceram. Soc.* **74** 2759 (1991)
34. S C Danforth *Nanostruct. Mater.* **1** 197 (1992)
35. W Chang, G Skandan, S C Danforth, B H Kear *Nanostruct. Mater.* **4** 507 (1994)
36. T Yamada *Am. Ceram. Soc. Bull.* **72** (5) 99 (1993)
37. F E Kruis, B Scarlett, R Bauer, J Schoonman *J. Am. Ceram. Soc.* **75** 619 (1992)
38. K E Gonsalves, P R Strutt, T D Xiao *J. Mater. Sci.* **27** 3231 (1992)
39. D Bahlout, M Pereira, P Goursat, N S Chooing Kwet Yive, R J B Corriu *J. Am. Ceram. Soc.* **76** 1156 1163 (1993)
40. M Peuckert, T Vaahs, M Bruck *Adv. Mater.* **2** 398 (1990)
41. G M Kheidemane, Ya P Grabis, T N Miller *Izv. Akad. Nauk SSSR, Neorg. Mater.* **15** 595 (1979)
42. W G Schmidt *Interceram.* **40** 15 (1991)
43. S G Malghan, D B Minor, L-S H Lum *Powder Technol.* **67** 201 (1991)
44. T F Cooke *J. Am. Ceram. Soc.* **74** 2959 (1991)
45. K Huttinger, T W Pieschnick *J. Mater. Sci.* **29** 2879 (1994)
46. I E Reimanis, H Suematsu, J J Petrovic, T E Mitchell *J. Am. Ceram. Soc.* (1995) (in the press)
47. T Ekstrom, M Nygren *J. Am. Ceram. Soc.* **75** 259 (1992)
48. J Szepvolgyi, I Bertoti, I Mohai-Toth, E Gilbdart, F L Riley, M Patel *J. Mater. Chem.* **3** 279 (1993)
49. Advertisement *Am. Ceram. Soc. Bull.* **70** 181 (1991)
50. F Cambier, A Leriche, E Gilbart, R Brook, F Riley, in *The Physics and Chemistry of Carbides, Nitrides, and Borides* (Ed. R Freer) (Dordrecht: Kluwer, 1990) p. 13
51. I Tanaka, K Igashira, H-J Kleebe, M Ruhle *J. Am. Ceram. Soc.* **77** 275 (1994)
52. Yu M Shul'ga, V M Martynenko, T M Moravskaya, I P Borovinskaya, A G Merzhanov, Yu G Borod'ko *Poroshk. Metall.* (1) 48 (1984)
53. P S Kislyi, L S Posun'ko, V G Malogolovets *Poroshk. Metall.* (5) 83 (1988)
54. Ya K Vaivads, T N Miller, A A Kuzyukevich, I Beroti, T Sekei, M Lukach *Poroshk. Metall.* (3) 80 (1990)
55. G N Komratov, Yu M Shul'ga *Poroshk. Metall.* (3) 5 (1992)
56. S Natansohn, A E Pasto, W J Rourke *J. Am. Ceram. Soc.* **76** 2273 (1993)
57. G Kaiser, H Schubert *J. Eur. Ceram. Soc.* **11** 253 (1993)
58. R A Andrievskii, Yu F Khromov, R A Lyutikov, S A Zhmurov, E A Galkin, R S Yurkova *Zh. Fiz. Khim.* **68** 5 (1994)
59. R A Andrievskii, R A Lyutikov *Zh. Fiz. Khim.* (1995) (in the press)
60. R A Andrievskii, M A Leont'ev *Poroshk. Metall.* (8) 9 (1984)
61. M A Leont'ev, Candidate's Thesis in Technical Sciences, M V Lomonosov Moscow Institute of Fine Chemical Technology, Moscow, 1990
62. R A Andrievski, in *Materials by Powder Technology. PTM'93* (Ed. F Aldinger) (Oberursel: Informationsgesellschaft, 1993) p. 649

63. R A Andrievskii, R A Lyutikov, O D Torbova, V I Torbov, V G Vil'chinskii, O M Grebtsova, E P Domashneva, A A Eremenko, A Z Rakhmatullina *Neorg. Mater.* **29** 1641 (1993)
64. I Markichev, E Sheka, N Goncharova, I Natkaniec, A Muzychka, V Chukalin, V Khavryutchenko, E Nikitina *Physica B* **198** 200 (1994)
65. E Sheka, V Khavryutchenko, E Nikitina, I Natkaniec, I Markichev, N Goncharova, V Chukalin *J. Electron Spectrosc. Relat. Phenom.* **67** 133 (1994)
66. N V Goncharova, E A Nikitina, V D Khavryuchenko, E F Sheka *Zh. Strukt. Khim.* (1995) (in the press)
67. M N Rahaman, Y Boiteux, L C De Jonghe *Am. Ceram. Soc. Bull.* **65** 1171 (1986)
68. J M Schoenung *Am. Ceram. Soc. Bull.* **70** (1)112 (1991)
69. R A Andrievskii, M A Leont'ev, A V Bragin *Izv. Akad. Nauk SSSR, Neorg. Mater.* **20** 2055 (1984)
70. R A Andrievskii, S E Zeer, M A Leont'ev, in *Fizikokhimiya Ul'tradispersnykh Sistem* (Physical Chemistry of Ultradisperse Systems) (Ed. I V Tananaev) (Moscow: Nauka, 1987) p. 197
71. R A Andrievskii *Poroshkovoe Materialovedenie* (Powder Materials Technology) (Moscow: Metallurgiya, 1991)
72. R A Andrievski *J. Mater. Sci.* **29** 614 (1994)
73. R A Andrievski *Int. J. Powder Metall.* **30** 59 (1994)
74. Ya A Kryl' *Sverkhtverd. Mater.* (2) 22 (1993)
75. S Greskovich *J. Am. Ceram. Soc.* **64** 725 (1981)
76. G Wötting, G Ziegler *Ber. Dtsch. Keram. Ges.* **65** 471 (1988)
77. I Tanaka, G Pezzoti, T Okamoto, Y Miyamoto, M Koizumi *J. Am. Ceram. Soc.* **72** 1656 (1989)
78. J Sleurs, R C Piller, M F Ashby, R W Davidge *Silik. Ind.* **(1–2)** 25 (1992)
79. Ya A Kryl' *Vysokotemperaturnoe Gazostaticheskoe Uplotnenie Nitrida Kremniya* (The High-Temperature Gas-Static Densification of Silicon Nitride) (Kiev: Naukova Dumka, 1993)
80. D Suttor, G S Fischman *J. Am. Ceram. Soc.* **75** 1063 (1992)
81. K J D Mackenzie, R H Meinhold *J. Mater. Chem.* **4** 1595 (1994)
82. E Tani, S Umebayashi, K Kishi, K Kobayashi, M Nishijima *Am. Ceram. Soc. Bull.* **65** 1311 (1986)
83. A Bellosi, G N Babini, in *Silicon Nitride'93* (Eds M J Hoffmann, P F Becher, G Petzow) (Aedermannsdorf: Trans. Tech. Publ., 1993) p. 117
84. T Millers *Mater. Sci. Eng., A. Struct. Mater., Prop. Microstruct. Process.* **168** 171 (1993)
85. T Takahashi, M Isomura, Y Endoh, Y Furuse, in *Silicon Nitride'93* (Eds M J Hoffmann, P F Becher, G Petzow) (Aedermannsdorf: Trans. Tech. Publ., 1993) p. 225
86. B Ralph *Univ. Wales Rev.* **4**, 29 (1988)
87. M Mitomo, M Tsutsumi, H Tanaka, S Uenosono, F Saito *J. Am. Ceram. Soc.* **73** 2441 (1990)
88. G Petzow, M J Hoffmann *Mater. Sci. Forum* **113–115** 91 (1993)
89. N V Danilenko, G S Oleinik, N P Semenenko *Poroshk. Metall. (8)* 5 (1992)
90. V Shimada, N Ogawa, M Koizumi, F Dachille, R Roy *Am. Ceram. Soc. Bull.* **58** 519 (1979)
91. P S Kislyi, Ya A Kryl', A A Svirid, V I Chukalin, V N Troitskii *Izv. Akad. Nauk SSSR, Neorg. Mater.* **27** 1646 (1991)
92. G T Burns, J A Ewald, K Mukherjee *J. Mater. Sci.* **27** 3599 (1992)
93. T Wang, L Zhang, C Mo *Nanostruct. Mater.* **4** 207 (1994)
94. Y-L Li, Y Liang, Z-Q Hu *Nanostruct. Mater.* **4** 857 (1994)
95. J J Petrovich, B V Olinger, R B Roof *J. Mater. Sci.* **20** 391 (1985)
96. T Akashi, A Sawaoka *J. Mater. Sci.* **22** 1031 (1987)
97. H Hirai, K Kondo *J. Am. Ceram. Soc.* 77 487 (1994)
98. B W Sheldon, J Szekely, J S Haggerty *J. Am. Ceram. Soc.* **75** 677 (1992)
99. R D Veltri, F S Galasso *J. Am. Ceram. Soc.* **73** 2137 (1990)
100. K Niihara, T Hirai *Powder Metall. Int.* **16** 223 (1984)
101. C Gomez-Alexandre, O Sanchez-Garrido, J M Martinez-Duart, J M Albella *J. Mater. Sci.* **26** 4683 (1991)
102. Y Okada, Sh Nakajima *Appl. Phys. Lett.* **59** 1066 (1991)
103. I Kobayashi, T Ogawa, S Hotta *Jpn. J. Appl. Phys.* **31** 336 (1992)
104. A G Varlamov, Yu M Grigor'ev, T M Moravskaya, Yu M Shul'ga *Zh. Neorg. Khim.* **36** 1544 (1991)
105. V I Zakhar'in, N M Rubtsov, V I Rubtsov, Yu M Shul'ga *Thin Solid Films* **216** 268 (1992)
106. A G Varlamov, A A Shiryaev, Yu M Grigor'ev *Izv. Akad. Nauk SSSR, Neorg. Mater.* **27** 1222 (1991)
107. W Posadowski *Thin Solid Films* **69** 149 (1980)
108. C J McHargue, in *Structure–Property Relationships in Surface-Modified Ceramics* (Eds C J McHargue, R Kossowsky, W O Hofer) (Dodrecht: Kluwer, 1989) p. 253
109. J K Hirvonen *Mater. Sci. Rep.* **6** 217 (1991)
110. B Himmel, J Claudius, T Gerber, C Reinhold *J. Non-Cryst. Solids* **162** 136 (1993)
111. O Knotek, F Loffler, W Beele, in *Silicon Nitride'93* (Eds M J Hoffmann, P F Becher, G Petzow) (Aedermannsdorf: Trans. Tech. Publ., 1993) p. 275
112. V T Volkov, L F Satunkina *Thin Solid Films* **247** 145 (1994)
113. V K Sarin *Mater. Sci. Eng. A, Struct. Mater., Prop. Microstruct. Process.* **105/106** 151 (1988)
114. R Grun *Acta Crystallogr. B* **35** 800 (1979)
115. R A Andrievski, Yu S Konyaev, M A Leontiev, G I Pivovarov, in *High Pressure Research* Vol. 1 (Gordon and Breach, 1989) p. 329
116. G R Hatfield, K R Carduner *J. Mater. Sci.* **24** 4209 (1989)
117. I A Brytov, V A Gritsenko, Yu P Kostikov, E A Obolenskii, Yu N Romashchenko *Fiz. Tverd. Tela* **26** 1685 (1984)
118. A Y Liu, M L Cohen *Phys. Rev. B* **41** 10727 (1990)
119. J Robertson *Philos. Mag. B, Phys. Condens. Matter Electron. Opt. Magn. Prop.* **63** 47 (1991)
120. V A Gritsenko, Yu P Kostikov, L V Khramova *Fiz. Tverd. Tela* **34** 2424 (1992)
121. Ch Mo, L Zhang, C Xie, T Wang *J. Appl. Phys.* **73** 5185 (1993)
122. M Hillert, S Jonsson *CALPHAD, Comput. Coupling Phase Diagr. Thermochem.* **16** 199 (1992)
123. R A Andrievski *Sci. Sinter. (Issue 2)* **20** 49 (1988)
124. R A Andrievskii, in *Tugoplavkie Soedineniya. Poluchenie, Struktura, Svoistva i Primenenie* (Refractory Compounds. Preparation, Structure, Properties, and Application) (Ed. T Ya Kosolapova) (Kiev: Izd. Akad. Nauk Ukr. SSR, 1991) p. 54
125. L Kaufman *CALPHAD, Comput. Coupling Phase Diagr. Thermochem.* **3** 279 (1979)
126. L Kaufman, F Hayes, D Birnie *High Temp.-High Press.* **14** 619 (1982)
127. M Hillert, S Jonsson, B Sundman *Z. Metallk.* **83** 648 (1992)
128. J Weiss, PhD Thesis, Univ. of Stuttgart 1980; quoted after Ref. 127
129. A V Kostanovskii, A V Evseev *Teplofiz. Vys. Temp.* **32** 26 (1994)
130. J Weiss, H L Lukas *Mater. Sci. Forum* **47** 43 (1989)
131. H Wada, M-J Wang, T-Y Tien *J. Am. Ceram. Soc.* **71** 837 (1988)
132. M Hillert, S Jonsson *Z. Metallk.* **83** 720 (1992)
133. S Sambasivan, W T Petuskey *J. Mater. Res.* **9** 2362 (1994)
134. A E McHale (Ed.) *Borides, Carbides, and Nitrides. Phase Equilibria Diagrams* (Westerville: Am. Ceram. Soc., 1994)
135. R A Andrievski, R A Lyutikov, Yu F Khromov, in *Silicon Nitride'93* (Eds M J Hoffmann, P F Becher, G Petzow) (Aedermannsdorf: Trans. Tech. Publ., 1993) p. 369
136. R Pehlke, J Elliott *Trans. Metall. Soc. AIME* **215** 781 (1959)
137. O Karlson *Bull. Alloys Phase Diagr.* **11** 569 (1990)
138. JUNAF Thermochemical Tables *J. Phys. Chem. Ref. Data* **14** (Supll.1) 1583 (1985)
139. J Wood, G Adams, J Mukeryi, J Margrave, in *Third International Conference on Chemical Thermodynamics, IUPAC, Austria, 1973* Vol. 1, p. 115
140. V I Koshchenko, Ya Kh Grinberg *Izv. Akad. Nauk SSSR, Neorg. Mater.* **18** 1064 (1982)
141. V I Koshchenko, Ya Kh Grinberg, R V Koshchenko *Izv. Akad. Nauk SSSR, Neorg. Mater.* **21** 244 (1985)
142. K Kijima, S Shirasaki *J. Chem. Phys.* **65** 2668 (1976)
143. A R Cooper, L D Major *US NTIS Rep. AD-A-069004* 1979; quoted after Ref. [144]
144. K P Kunz, V K Sarin, R F Davis, S R Bryan *Mater. Sci. Eng. A, Struct. Mater., Prop. Microstruct. Process* **105/106** 47 (1988)
145. R A Andrievskii, G M Vol'dman, M A Leont'ev *Izv. Akad. Nauk SSSR, Neorg. Mater.* **27** 729 (1991)
146. Ch M Wang, F L Riley, F Castro, I Iturriza *J. Am. Ceram. Soc.* **76** 2136 (1993)
147. A D Panasyuk, V S Fomenko, G G Glebova *Stoikost' Nemetallicheskikh Materialov v Rasplavakh* (Stability of Nonmetallic Materials in Melts) (Kiev: Naukova Dumka, 1986)

148. V A Lavrenko, Yu G Gogotsi *Korroziya Konstruktsionnoi Keramiki* (Corrosion of Structural Ceramics) (Moscow: Metallurgiya, 1989)
149. Yu G Gogotsi, V A Lavrenko *Corrosion of High-Performance Ceramics* (Berlin: Springer, 1992)
150. A H Heuer, V L K Lou *J. Am. Ceram. Soc.* **73** 2785 (1990)
151. Yu G Gogotsi, M Yoshimura *MRS Bull.* **19** 39 (1994)
152. Yu G Gogotsi, Doctoral Thesis in Chemical Sciences, Institute of Problems of Science of Metals, National Academy of Science of Ukraine, Kiev, 1995
153. Yu G Gogotsi, G Grathwohl *J. Am. Ceram. Soc.* **76** 3093 (1993)
154. R Raj *J. Am. Ceram. Soc.* **76** 2147 (1993)
155. F L Riley (Ed.) *Progress in Nitrogen Ceramics* (Hague, Netherlands: Martinus Nijhoff, 1983)
156. T Ya Kosolapova, T V Andreeva, T B Bartnitskaya, G G Gnesin, G N Makarenko, I I Osipova, E V Prilutskii *Nemetallicheskie Tugoplavkie Soedineniya* (Nonmetallic Refractory Compounds) (Moscow: Metallurgiya, 1985)
157. G G Gnesin *Beskislorodnye Keramicheskie Materialy* (Oxygen-free Ceramic Materials) (Kiev: Tekhnika, 1987)
158. R A Andrievskii, I I Spivak *Prochnost' Tugoplavkikh Soedinenii i Materialov na Ikh Osnove* (Strength of Refractory Compounds and Materials Based upon Them) (Chelyabinsk: Metallurgiya, 1989)
159. R A Andrievski, in *Proceedings of the 13th International Plansee Seminar* Vol. 2 (Eds H Bildstein, R Eck) (Reutte: Metallwerk Plansee, 1993) p. 580
160. G Pezzotti, I Tanaka,T Okamoto *J. Am. Ceram. Soc.* **73** 3039 (1990)
161. K I More, D A Koecter, R F Davis *Ultramicroscopy* **37** 263 (1991)
162. T Rouxel, F Wakai, K Izaki *J. Am. Ceram. Soc.* **75** 2363 (1992)
163. K Sato, K Tanaka, Y Nakano *J. Am. Ceram. Soc.* **76** 2042 (1993)
164. T Rouxel, F Wakai *Acta Metall. Mater.* **41** 3203 (1993)
165. I I Tkacheva *Ogneupory* (2) 13 (1994)
166. I Tanaka, G Pezzotti, K-I Matsushita, Y Miyamoto, T Okamoto *J. Am. Ceram. Soc.* **74** 752 (1991)
167. J-L Huang, Sh-Y Chen, M-T Lee *J. Mater. Res.* **9** 2349 (1994)
168. I-W Chen, Sh-L Hwang *J. Am. Ceram. Soc.* **75** 1073 (1992)
169. R A Andrievski, V T Ivannikov, V S Urbanovich, in *Silicon Nitride'93* (Eds M J Hoffmann, P F Becher, G Petzow) (Aedermannsdorf: Trans. Tech. Publ., 1993) p. 445
170. R N Katz *Interceram.* **41** 231 (1992)
171. F H P M Habraken, A E T Kuiper *Mater. Sci. Eng. R. Rep.* **12** 123 (1994)
172. S A Uglov, V E Shub, A A Beloglazov, E N Lubnin, E D Obraztsova, A S Chernikov, V I Ionov *Fiz. Khim. Obrab. Mater.* (6) 68 (1994)