

Light element ceramics⁺

K J RAO*, K B R VARMA and A R RAJU

Materials Research Laboratory, Indian Institute of Science, Bangalore
560 012, India

Abstract. An overview of a few structurally important light element ceramics is presented. Included in the overview are silicon nitride, sialon, aluminium nitride, boron nitride, boron carbide and silicon carbide. Methods of preparation, characterization and industrial applications of these ceramics are summarized. Mechanical properties, industrial production techniques and principal uses of these ceramics are emphasized.

Keywords. Silicon nitride; sialon; aluminium nitride; boron nitride; boron carbide; silicon carbide.

1. Introduction

Some of the best known natural ceramics like silica, alumina, and carbon (in its various allotropic forms) are composed of only the light elements of the short periods in the periodic table. The best man-made ceramics such as borides, carbides, nitrides and oxides are also largely made up of light elements. The abundance of these light elements in nature and the extraordinary properties exhibited by a variety of ceramics resulting from their combination provides great attraction for research and development of light element ceramics.

Light element ceramics considered in this review are the stable binary, ternary and polynary ceramic phases obtained by chemical combination of the elements boron, carbon, nitrogen, oxygen, aluminium and silicon. Though alumina is a light element ceramic of great importance, it is not discussed here. Upon considering the volume of work reported in the literature and the proven importance of various light element ceramics, they are discussed in this report in the following order; silicon nitride, sialon, aluminium nitride, boron nitride, boron carbide and silicon carbide. Some of the ternaries and quarternaries related to these binaries are also discussed at appropriate places. Known methods of preparation of each material, particularly as relevant to large-scale manufacture, are first reviewed and then a brief presentation of their significant properties is given. Emphasis is placed on putting together well-documented data related to mechanical properties since light element ceramics are projected the world over as the advanced structural ceramics of the future.

⁺Contribution No. 76 from the Materials Research Laboratory

*For correspondence

2. Silicon nitride

2.1 Methods of preparation

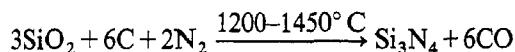
There are several methods in vogue for the preparation of silicon nitride. They include (a) direct nitridation, (b) carbothermal reduction, (c) gas-phase reaction, (d) silicon-sulphur-nitrogen reaction and (e) liquid phase reaction.

2.1a Direct nitridation: A commercially-known nitridation process involves heating of pure Si powder (particle dia < 10 μm) in the temperature range of 1200–1450°C in an atmosphere of NH₃/H₂ or N₂:

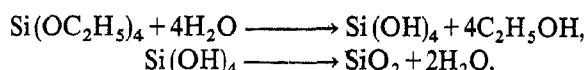


The above reaction is exothermic and the process yields Si₃N₄ lumps which are later crushed and milled to fine size particles. Hirao *et al* (1986) have adopted a method called self-propagating high temperature synthesis (SHS) to prepare fine Si₃N₄. In this process Si powder compacts are burnt in nitrogen at 10 MPa pressure. The method is suitable for obtaining homogeneous Si₃N₄ submicron particles with a uniform size distribution.

2.1b Carbothermal reduction: When a mixture of fine powders of carbon and silica is subjected to carbothermal reduction, followed by nitridation, Si₃N₄ lumps are obtained.



The advantage of this method over direct nitridation is that both SiO₂ and C are more readily available than pure Si. It is always better to obtain the precursor in a finely divided form in order to prepare a final product with tailored properties. A sol-gel process has certain advantages in this context over conventional techniques using powder mixtures. In the sol-gel process, aqueous suspensions of oxides and hydrous oxides are mixed to give a composition corresponding to the required multicomponent ceramic. Szweda *et al* (1981) have examined the nitridation of gel powders in an N₂/H₂ atmosphere. A SiO₂ sol derived from a flame-hydrolyzed material was mixed with C powder (C/SiO₂ = 2:1) and nitrided between 1400 and 1600°C. The product was found to be either α -Si₃N₄ or β -Si₃N₄ depending on the drying process adopted. The final powder has been heated to 600–650°C in air to burn out excess carbon. The sol-gel preparative route uses organic compounds of silicon such as tetraethoxysilane Si(OC₂H₅)₄ which undergoes hydrolysis giving rise to SiO₂.



Hydrolysis leads to substitution of alkoxy groups by hydroxyl groups which further condense into polymerized hydrous oxides. Silica gel thus derived from Si(OC₂H₅)₄ has been nitrided by Hoch and co-workers (Hoch *et al* 1977; Hoch & Nair 1979). Submicron α -Si₃N₄ was obtained by nitriding at 1350°C in NH₃ gas. Preparation of high purity Si₃N₄ from a disilane compound with the general formula R_nX_{6-n}Si₂ (R = H, alkyl, alkenyl, aryl; X = halogen atom, n = 1–5) by hydrolyzing it in the presence of C powder and nitriding the product at 1350–1550°C has been reported.

The product was a pale green powder containing approximately 93% $\alpha\text{-Si}_3\text{N}_4$. Sharma *et al* (1984) and Hanna *et al* (1985) obtained Si_3N_4 by firing rice husk at 1200–1500°C for about 0.5–2 h in an ammonia atmosphere. The silicon nitride produced was in the form of $\alpha\text{-Si}_3\text{N}_4$ with minor amounts of the β -form.

2.1c Gas phase reaction: Prochazka & Greskovitch (1978) have prepared Si_3N_4 powder with particle diameter in the range of 300–2000 Å by allowing SiH_4 to react with NH_3 at 500–900°C at atmospheric pressure. SiCl_4 and SiH_4 react with NH_3 ,



The use of SiCl_4 leads to corrosive by-products while SiH_4 is even more hazardous due to its spontaneous flammability in air. Several workers (Cannon *et al* 1982; Danforth & Haggerty 1983) have employed a CO_2 laser (150 W power, 10.6 μm wavelength) as the heat source with both unfocussed and focussed geometries to prepare Si_3N_4 powder. Here SiH_4 is preferred over SiCl_4 since SiH_4 has an absorption band at 10.6 μm. When SiH_4 was heated with CO_2 laser in the presence of NH_3 , it yielded monodisperse, pure, loosely agglomerated Si_3N_4 powders with a production rate of up to 10 g h⁻¹. Seiji *et al* (1986) have reported the preparation of Si_3N_4 layers at low pressures and temperatures of 800–1300°C using the (CVD) technique. Sugawara *et al* (1986) have employed the ion vapour deposition method (IVD) to prepare Si_3N_4 films. This method involves electron beam evaporation of Si and simultaneous nitrogen ion implantation which gives rise to Si_3N_4 films.

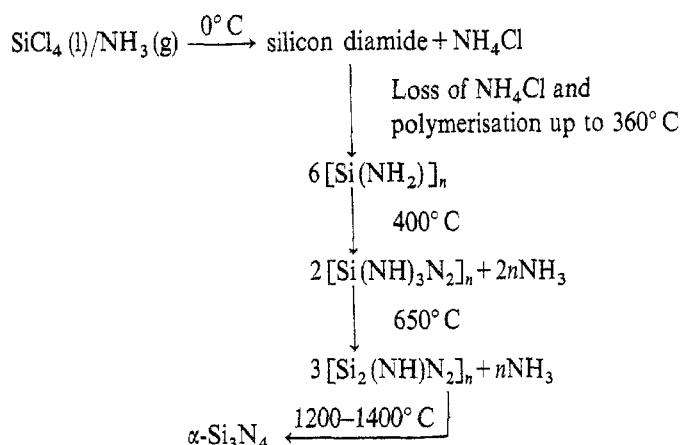
The plasma-activated vapour deposition method (Goodwin 1982) has been used for depositing Si_3N_4 films on substrates. This technique is particularly recommended for use in the electronic industry. Fletcher *et al* (1971, p. 145) achieved 7% conversion of Si powder into Si_3N_4 using 14% N_2 in Ar plasma. 15% conversion to a mixture of α and $\beta\text{-Si}_3\text{N}_4$ was reported by Canteloup & Mocellin (1975). Formation of ultrafine Si_3N_4 powder has been reported in an arc plasma (Segal 1986). Conditions favourable for deposition of Si_3N_4 on steel substrates by the CVD technique have been reported by Fumiyoishi & Hiroyuki (1986).

2.1d Silicon-sulphur-nitrogen reaction: Morgan (1984) has reported that ultrapure Si_3N_4 can be obtained from Cl-free reactants. Si powder was reacted at 900°C in a stream of 10% $\text{H}_2\text{S}/\text{Ar}$ to form SiS_2 . SiS_2 was then reacted with NH_3 at 1200–1450°C to give $\alpha\text{-Si}_3\text{N}_4$. The synthesis of Si-S compounds, specifically silane thiols, silthians and mercaptosilanes has been described by Eaborn (1960, p. 333). Recently, the preparation of Si_3N_4 by the SiS_2 precursor route was reported by Morgan & Pugar (1985). The important role of nitrogen in the preparation of Si_3N_4 and related ceramics has been discussed by Morgan (1986).

2.1e Liquid phase reaction: Mazdiyasni *et al* (1978) have prepared $\alpha\text{-Si}_3\text{N}_4$ in the form of fibre bundles (1.3 μm dia) by pyrolysis of hexaphenyl cyclotrisilazane in nitrogen at 1400°C, while Seyferth *et al* (1983) have shown that the polysilazane oil (H_2SiNH_x) derived from reaction of dichloro-silane and ammonia in dichloromethane could be pyrolyzed in N_2 at 1150°C to get $\alpha\text{-Si}_3\text{N}_4$ fragments.

It is of historical interest to note that Persoz as early as 1830 had obtained a white precipitate from the interaction of SiCl_4 and $\text{NH}_3(\text{g})$ in an inert solvent (benzene) at 0°C. This precipitate was then considered to be silicon tetramide $\text{Si}(\text{NH}_2)_4$ and subsequently confirmed by Lengfeld (1899). Nevertheless the precipitate was unstable

and decomposed at ambient temperatures to give silicon diamide $\text{Si}(\text{NH}_2)_2$ and ammonium chloride. Glemser & Newmann (1903) and Billy (1959) also obtained similar products on carrying out the reactions in liquid ammonia. Recently Segal (1985) has given a series of possible intermediates which are formed during the preparation of α -silicon nitride from silicon tetrachloride and ammonia.



Mazdiyasni & Cooke (1973) have shown that powder produced from pyrolysis is initially X-ray amorphous and that it is transformed into the β -phase on heating between 1200 and 1400°C for about 8 hours.

2.2 Characterization

The Si_3N_4 powders prepared by various methods have been characterized using high resolution electron microscopy, IR, Raman and X-ray photoelectron spectroscopies. These techniques also yield information about the quality of the preparation and the nature of impurities present in the powders.

Mehmet *et al* (1985) have discussed the usefulness of high resolution electron microscopy in analysing microstructural characteristics of light element ceramics in general. They have also presented evidence of the presence of amorphous phases of Si_3N_4 (also mullite and AlN ceramics) in the grain boundaries. The glassy phase was absent at some grain boundaries in Si_3N_4 and instead a second phase was noticed. The nature and composition of the surface of Si_3N_4 powder were investigated using high voltage - high resolution TEM, XPS and SIMS* by Rahaman *et al* (1986). Both XPS and SIMS studies indicate that oxygen is present as a major impurity. Minor impurities such as Cl, F, C, Fe and Na are also present in the sample. IR absorption and Raman spectroscopic studies (Takase & Tani 1986) have been carried out on sintered Si_3N_4 containing additions of Al_2O_3 and rare earth oxides (Y_2O_3 , CeO_2 , La_2O_3). It is noticed that there is an increase in the widths of the Raman bands in the spectral range of $400\text{--}1100\text{ cm}^{-1}$ as the Al_2O_3 content in Si_3N_4 is increased. It is attributed to the increasing degree of structural disorder in $\alpha\text{-Si}_3\text{N}_4$ network caused by the replacement of Si and N by Al and O respectively. Toshio *et al* (1985) have employed inductively coupled plasma emission spectrometry to determine the impurities present in Si_3N_4 . Nobuo *et al* (1985) have reviewed the possible use of

*Secondary ion mass spectroscopy.

thermal and analytical methods such as DTA, DSC and thermogravimetry in the characterization of ceramics. Use of TEM and electron diffraction for analysing fine ceramics in general has been reviewed by Yoshio (1985).

2.3 Industrial production techniques, properties and uses

Most high performance Si_3N_4 ceramic products rely on the quality of the starting elements, Si and N_2 . However, it is necessary to sinter the products using sintering aids in order to ensure better performance of products. Negita (1985) has discussed the role of sintering aids on the basis of chemical bonding. His studies indicated that electronegativities and ionic radii of the cations in the additives are important parameters which affect the densification of Si_3N_4 ceramics. In general, the majority of Si_3N_4 products are produced either as hot-pressed silicon nitride (HPSN) or as reaction-bonded silicon nitride (RBSN). Hot-pressed Si_3N_4 can be produced by either uniaxial (Vasilos 1977, pp. 367–382) or hot isostatic pressing (Larker *et al* 1975). One generally starts with $\alpha\text{-Si}_3\text{N}_4$ powder along with densification aids such as MgO or ZrO_2 . Depending upon the purity of the starting Si_3N_4 powder, and the type of additives, milling procedures and hot pressing parameters used, one can obtain a very wide range of strength, creep, fracture toughness or oxidation behaviour. Hot-pressed silicon nitride (HPSN) obtained with Y_2O_3 additive possesses typically higher strengths at both room and elevated temperatures. It also possesses better oxidation resistance, fracture toughness and slower crack growth features as compared to MgO -containing HPSN (Gazza *et al* 1978). Si_3N_4 of very high strength has been obtained by Komeya *et al* (1977) with Y_2O_3 and Al_2O_3 as additives and by using the grain boundary crystallization approach.

The fabrication of RBSN components begins with a silicon metal powder preform which is made by slip casting, dry pressing, flame spraying, injection moulding or other techniques. The preform is then nitrided in an atmosphere of pure H_2 or $\text{N}_2 + \text{H}_2$ with either a preselected temperature schedule (Messier & Wong 1974, p. 181) or by using a nitrogen demand cycle (Wong & Messier 1978). This process of nitriding of a Si preform is remarkable for its simplicity but is still imperfectly understood. While the reaction $3\text{Si} + 2\text{N}_2 \rightarrow \text{Si}_3\text{N}_4$ is associated with a 23% increase in the solid volume compared to Si when this reaction is carried out on a preform, there is essentially no change in dimensions (0.1%). The reason for this appears to be that Si_3N_4 is formed in the voids in Si-preforms via a vapour phase or surface diffusion reaction. This procedure is therefore of great importance and can be used in mass production of products to tight dimensional tolerances.

Reaction-bonded silicon nitride can exhibit creep rates significantly lower than those of HPSN (Larsen *et al* 1978). It has also been reported that as a consequence of the reaction bonding process, RBSN is of necessity at least 10% porous which makes it less oxidation resistant than HPSN at intermediate temperatures (McLean 1978) but limits its strength to less than 415 MPa. The quality of products obtained from reaction-bonded silicon nitride has been improved considerably over the past few years. However, when high strength and greater oxidation resistance is required, it would be desirable to have readily sinterable fully dense silicon nitride. This has been the impetus for the development of sintered silicon nitride (SSN).

Sintered Si_3N_4 of at least 95% density has been prepared successfully and it is reported that densities greater than even 99% have been achieved. Gazza *et al* (1978) have recently reviewed the status of SSN. SSN components which are formed by

injection moulding require little machining. It is also possible that sintered Si_3N_4 bodies of over 95% theoretical density may be used as preforms for cladless hot isostatic pressing. Materials like SSN and HPSN are only in the initial stages of development. Sinter densities of $\geq 95\%$ could be obtained by adding only 2 wt% MgO . Products should be targeted to possess a low concentration of sintering aids at high temperatures. HPSN with Y_2O_3 as sintering aid is quite oxidation resistant. A HPSN product prepared from quartz sand and air has been found to be highly resistant to wear and thermal shock even at high temperatures. These are comparable to the Lulea hard metal oxide ceramics, cubic boron nitride and industrial diamonds.

Mechanical properties of both hot-pressed and reaction-bonded Si_3N_4 ceramics have been investigated in detail. Friction and wear properties of hot-pressed Si_3N_4 were studied by Ishigaki *et al* (1986). The friction coefficient was correlated with the fracture toughness of Si_3N_4 . Frictional anisotropy was also observed in hot-pressed Si_3N_4 . Kim *et al* (1986) have carried out wear tests on Si_3N_4 in dry rolling contact at room temperature. The wear rate of Si_3N_4 was found to be less than that of any other ceramic material. Observations of worn out surfaces and wear debris revealed that ceramic materials have two types of wear, one related to real contact area and the other related to Hertzian contact area. Brittle fracture dominates the wear process of ceramic materials in dry rolling contact. Nancy (1986) has recently reported that the microstructural changes associated with creep in Si_3N_4 are due to the operation of both cavitation and crack propagation mechanisms within the bonding phase below plastic deformation temperature of the matrix grains. Bandyopadhyay & French (1986) have reviewed the preparation of Si_3N_4 jet engine components by injection molding. Steinmann (1986) has reviewed crack-formation and propagation in hot-pressed Si_3N_4 during creep and on the durability of Si_3N_4 product as a function of temperature and load. These products have high corrosion resistance, good electrical insulation and are non-magnetic. Kaji & Mamoru (1986) have carried out systematic studies on microstructure and room temperature strength of $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ pressureless sintered compacts. Thermal conductivity and microhardness of Si_3N_4 with and without additives have been studied by Tsukuma *et al* (1981). High pressure hot-pressing of Si_3N_4 without additives was performed by Shimada (1986) using a mixture of $\alpha\text{-Si}_3\text{N}_4$, amorphous Si_3N_4 and $\beta\text{-Si}_3\text{N}_4$ in the ratio 4:1:2 as starting material. Figure 1 shows the variation of microhardness of Si_3N_4 with temperature in these studies.

3. Sialons

3.1 Methods of preparation

The term 'sialon' was chosen to particularize any composition containing elements Si, Al, O and N as major constituents (Oyama & Kamigaito 1971; Jack & Wilson 1972; Oyama 1972; Jack 1976). Sialons can be made by high temperature reaction between silicon nitride or oxynitride and alumina. During the reaction silicon and nitrogen are replaced partially and simultaneously by aluminium and oxygen atoms, respectively. The α' -structure results in M-Si-Al-O-N systems and is derived from the $\text{Si}_{12}\text{N}_{16}$ unit cell by partial replacement of Si^{4+} by Al^{3+} (M is Li, Mg, Ca or Y). All the sialons have the compositions represented by $\text{M}_x(\text{Si}, \text{Al})_{12}(\text{O}, \text{N})_{16}$ where

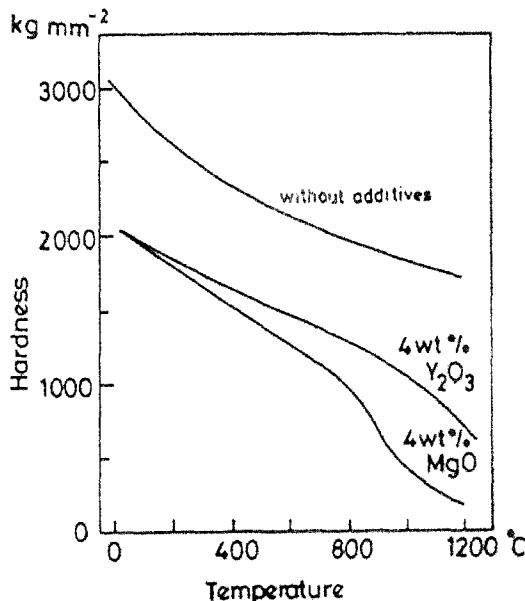
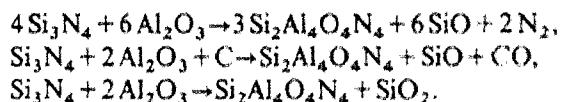


Figure 1. Variation of microhardness of silicon nitride with temperature (adapted from Shimada 1986).

$x \geq 2$ and are structurally related to α -and β -silicon nitrides (Hampshire *et al* 1978). Detailed compatibility and phase equilibria studies of sialons have been reported by a number of workers (Jack 1976; Hampshire *et al* 1978; Gauckler *et al* 1975). Jack has included the data obtained from specimens hot-pressed at temperatures ranging from 1550–2000°C in the phase diagram. According to Jack, the β' -sialon region extends from Si_3N_4 to $\text{Si}_{6-x}\text{Al}_x\text{O}_x\text{N}_{8-x}$ with $x=4.2$. β' -sialon forming regions are reported in other systems such as $\text{Si}_3\text{N}_4\text{-Al}_2\text{O}_3\text{-Be}_2\text{SiO}_4$, $\text{Si}_3\text{N}_4\text{-Al}_2\text{O}_3\text{-Li}_2\text{O}$ and $\text{Si}_3\text{N}_4\text{-Al}_2\text{O}_3\text{-MgO}$ etc by Jack (1973), Oyama (1973) & Husbey *et al* (1975). The possible reactions of Si_3N_4 and Al_2O_3 which produce β' -sialon with $x=4$ are



Similar β' -sialon phases were obtained by reacting Si_3N_4 with lithium-aluminium spinel (LiAl_5O_8) and also with magnesium aluminium spinel (MgAl_2O_4). In addition to the sialon phases α' , β' , σ' and χ which were originally reported by Jack (1973, 1976), six unidentified phases nearer to the AlN corner of the $\text{Si}_3\text{N}_4\text{-AlN-Al}_2\text{O}_3\text{-SiO}_2$ system have been prepared by Gauckler *et al* (1975). The complex phase diagram reported by Jack (1976) is shown in figure 2. Aluminosilicate minerals provide a convenient source of β' -sialon phases through the carbothermal reaction. β' -sialon powders prepared by this method have been characterized by Mostaghaci *et al* (1986). The effect of agglomeration in the sialon powder on densification and microstructure development during hot pressing has been examined. Baldo *et al* (1983, p. 437) have reported the preparation of sinterable sialon powders from hydrated silicates of aluminium with carbon and nitrogen. This route is considered to be more economical for preparing sialons. A variety of β' -sialon powders based on natural raw materials such as kaolin, clay, pyrophyllite, sillimanite and kyanite have been reported by Baldo *et al* (1983, p. 437). Table 1 indicates compositions of several natural silicates used as reacting materials.

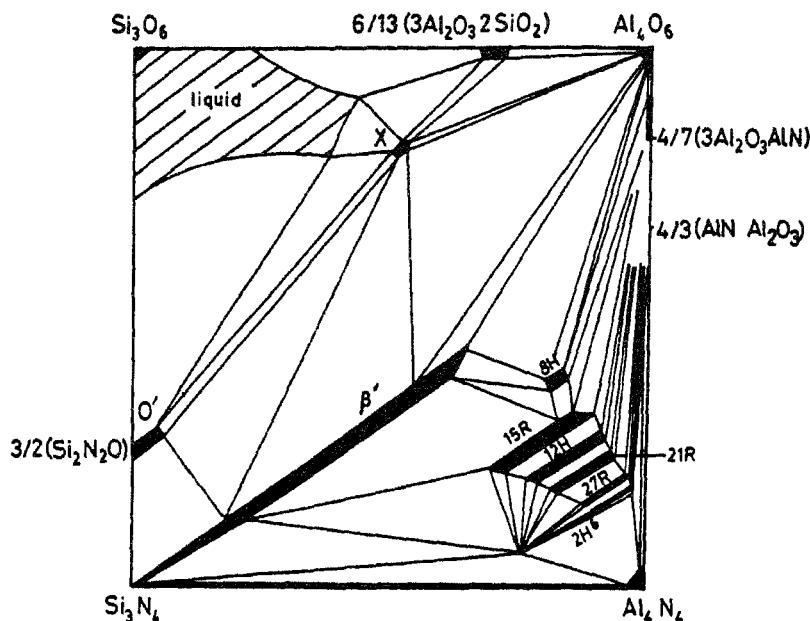
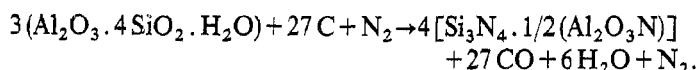


Figure 2. The complex pseudoquaternary phase diagram of Si-Al-O-N system at 1700°C (from Jack 1976).

Approximate compositions of β' -sialons ($\text{Si}_{6-x}\text{Al}_x\text{O}_x\text{N}_{8-x}$) obtained with the above materials are listed below.

<i>Al/Si</i>	<i>x</i>	<i>Sialon composition</i>
0	0	Si_3N_4
1/2	2	$\text{Si}_4\text{Al}_2\text{O}_3\text{N}_6$
1	3	$\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$
2	4	$\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$

A typical carbothermal reaction resulting in the formation of a sialon may be represented as follows.



The preparation of β' -sialon from china clay and coal is described by Higgins & Hendry (1986). It is a chemical reaction in which the important stages are (i) dissociation of kaolinite to mullite and silica, (ii) formation of silicon carbide, and

Table 1. Natural silicate compositions and their ratios.

Silicate	Formula	Ratio (Al/Si)
Silica	SiO_2	0
Pyrophyllite	$\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$	1/2
Kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	1
Kyanite	$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$	2

(iii) simultaneous reduction and nitridation of mullite by carbon and silicon carbide in the presence of nitrogen gas. The reaction rate is controlled by the nitrogen flow rate because of its effect on the removal of carbon monoxide formed by reduction of the oxides. The reaction corresponding to the formation of β' phase is reversible through the control of the carbon monoxide partial pressure. Hanna & Ghoneim (1986) have employed pure kaolin and coked rice hulls ($\text{SiO}_2\text{:C} = 47:52$) for the preparation of sialon. The formation of β' -sialon powder was investigated by firing kaolin and coked rice hulls containing 20, 30, 40 and 50 wt%, at 1300–1500 °C under NH_3 .

Translucent sialon ceramics have been prepared (Nobuyuki 1985) from Si_3N_4 , Al_2O_3 and AlN. The resulting β' -sialon has the formula $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$ and light transmissions of 43 and 70% at wavelength 0.4 and 4 μm , respectively. These translucent materials are useful in making container tubes for high voltage sodium lamps, windows for high temperature vessels and integrated circuit substrates.

3.2 Characterization

Sialons have been characterized using X-ray diffraction analysis (Jack & Wilson 1972; Izumi 1983; Thommy & Bertil 1986; Thompson *et al* 1983, p. 61) and analytical electron microscopy (Thompson *et al* 1983; Izumi *et al* 1984; Bonnel *et al* 1986; Johnson & Hendry 1979). Investigations have been carried out on materials of different compositions prepared under different processing conditions. Greil & Weiss (1983, pp. 359–374) have used TEM to characterize a hot-pressed solid solution material with 11 wt% Al^{3+} and varying oxygen content. With increasing amounts of oxygen, it is found that prismatic grains containing increasing amounts of amorphous phase are formed. Raman studies have been used to determine the changes in force constants which occur when interatomic distances and bonding characteristics are altered (Jack 1976). Magic angle spinning high resolution solid state NMR (MASNMR) has been used to monitor the quantity and co-ordination of aluminium in sialon and other ceramic materials (Fyle & Gobbi 1983). Aluminium and silicon are found to be present as AlO_4 and SiO_4 tetrahedra and as AlO_6 octahedra. It was noted that in addition to SiO_4 tetrahedra, SiO_3N , SiO_2N_2 , SiON_3 and SiN_4 tetrahedra can also be present because each type of tetrahedra can be linked to neighbouring tetrahedra in five possible ways. Sanyal & Mukerji (1986) have used Mössbauer spectroscopic techniques to study the effect of iron on the conversion of clay into β' -sialon. These studies indicate that no Fe is present in the metallic state in sialon.

3.3 Industrial production techniques, properties and uses

Hot-pressing has been widely used in the fabrication of sialon products. Various material combinations listed in table 2 have been pressed at temperatures where simultaneous chemical reaction and densification were found to take place. MgO has been commonly used as an additive to promote densification. The most effective hot-pressing temperature and time appear to be 1650–1750 °C and 30 minutes to 2 hours, respectively. The experimental studies indicated in table 2 illustrate the varied nature of investigations in hot-pressed β' -sialons.

Pressureless-sintering studies have been conducted with various material combinations with and without additives. Sintering was conducted at about one

Table 2. Fabrication of sialon by hot-pressing.

Starting materials	Additives	Temperature (°C)	Time (min)	Pressure (MN/m ²)	Nature of investigation (Reference)
Si ₃ N ₄ , Al ₂ O ₃ , Li ₂ CO ₃	— ^a	1750	20	29	Solid solubility (Oyama & Kamigaito 1971)
Si ₃ N ₄ , Al ₂ O ₃	—	1700	60	—	Formation, structure and thermal expansion (Jack & Wilson 1972)
Si ₃ N ₄ , AlN, Al ₂ O ₃	—	1730	30	25	Solid solubility (Oyama 1972)
Si ₃ N ₄ , Ga ₂ O ₃ , Al ₂ O ₃	—	1730–1800	20–180	25	Solid solubility and thermal expansion (Jack 1973)
Si ₃ N ₄ , Al ₂ O ₃ , AlN, SiO ₂	—	1760	60–300	30	Phase equilibria and compatibility relation (Arrol 1974, p. 729)
Si ₃ N ₄ , AlN, Al ₂ O ₃ , SiO ₂ , Si ₂ N ₂ O	—	1500–2000	—	—	Phase equilibria, compatibility and structure (Gauckler <i>et al</i> 1975)
Si ₃ N ₄ , Al ₂ O ₃	—	1700	60	15	Microstructure & phase analysis (Drew & Lewis 1974)
Si ₃ N ₄ , Al ₂ O ₃	—	1700	30	—	Phase analysis (Gugel <i>et al</i> 1975)
Si ₃ N ₄ , Be ₃ N ₂ , BeO, SiO ₂	—	1765–1880	60–120	28	Phase equilibria (Hussey <i>et al</i> 1975)
Si ₃ N ₄ , Al ₂ O ₃	—	1650–1850	6–60	25	Sintering, grain growth and phase equilibria (Oyama & Kamigaito 1971)
Si ₃ N ₄ , AlN, SiO ₂	MgO	1750	60	20	Fabrication, chemistry and creep (Lumby <i>et al</i> 1975, p. 283)
Si ₃ N ₄ , Al ₂ O ₃ , AlN, SiO ₂	MgO	1760	—	—	Physical, mechanical and thermal properties (Gauckler <i>et al</i> 1977)
Si ₃ N ₄ , AlN, SiO ₂	MgO	1800	60	15	Formation, microstructure characterization (Lewis <i>et al</i> 1977)
Si ₃ N ₄ , Al ₂ O ₃	—	1500–1700	120	5.5–27.5	Effects of pressure and temperature on sintering (Yeh & Watters 1977)

^adash indicates not reported.

atmosphere of nitrogen to produce bodies with as high as 98% theoretical densities. Various aspects of sintering of sialons have been discussed by Jack and others (Jack 1973; Gugel *et al* 1975; Gauckler *et al* 1978, p. 559; Drew & Lewis 1974). In a special sintering procedure known as 'transient liquid phase sintering' (TLP), sialon of composition Si_{1.4}Al_{1.6}O_{1.6}N_{2.4} was obtained from two pre-reacted compositions, one of which was the X-phase which melts near 1700°C (Baldo *et al* 1983, p. 437). The microstructures of both hot-pressed and sintered-materials consist of β'-sialons as the predominant phase with some isolated porosity and metallic looking phase in a uniform β'-matrix. In some cases isolated grains of the X-phase and a 15R polytype phase were found with sizes varying between 0.2–2 µm (Greil & Weiss 1983, pp. 359–374; Takase & Tani 1984). The grain morphology in both sintered- and hot-pressed

materials was characteristic of the presence of a liquid phase during densification. This liquid phase was retained in intercrystalline spaces during cooling from hot-pressing (Evans & Moulson 1983, pp. 237-243) or sintering temperature (Takase & Tani 1984) and formed a glassy phase at the grain boundaries. Density values of hot pressed β' -sialons vary from 3.09 to 3.16 g/cm³ while the densities of other phases (X and 15 R) have been found to be between 3.05 g/cm³ and 3.08 g/cm³ (Gauckler *et al* 1977).

Most of the mechanical properties reported in the literature refer to β' -sialon in (Si, Al, O, N) systems. Other systems such as (Si, Be, N, O), (Si, Al, Be, N, O) etc, have been examined primarily with respect to solid solubility, phase relationships and structure. The room temperature strength of sintered β' -sialon compares favourably with room temperature strength of sintered Si_3N_4 . On the other hand, the room temperature strength of sintered β' -sialon is considerably lower than that of hot-pressed Si_3N_4 . At high temperature (1370 °C) the strength of sintered β' -sialon is equivalent to or higher than the strength of sintered Si_3N_4 but lower than that of hot-pressed Si_3N_4 (figure 3). Creep behaviour of several hot-pressed sialons have been measured and compared (Baldo *et al* 1983, p. 437) with available data on hot-pressed Si_3N_4 , hot-pressed SiC and reaction-bonded Si_3N_4 . The sintered sialon has a creep rate lower than that of hot-pressed or reaction-bonded Si_3N_4 . Lumby *et al* (1975, p. 283) have noted a strong dependence of creep behaviour on AlN concentration.

Fracture toughness (K_{IC}) values have been reported in the literature for various compositions. Generally, the values are lower than those of hot-pressed Si_3N_4 . Wills *et al* (1977) have suggested that the presence of X -phase should be kept at very low levels and preferably be eliminated completely to improve the fracture toughness of sialons. Lumby *et al* (1978, p. 893) have however observed a high fracture toughness

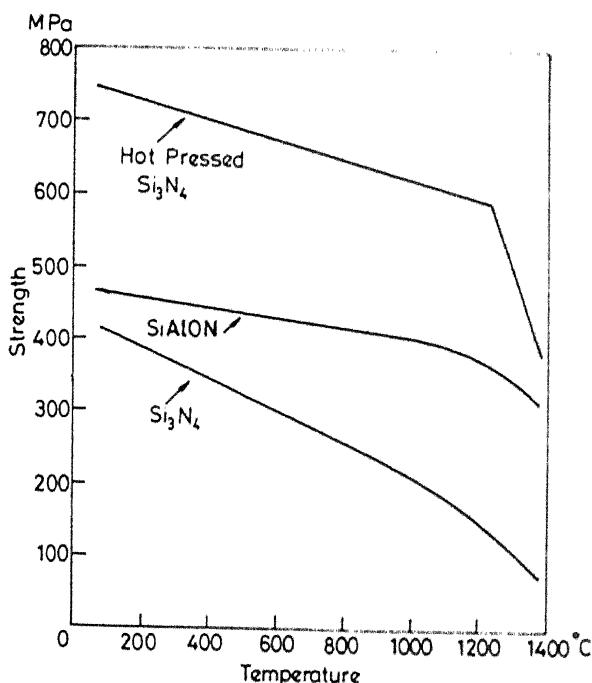


Figure 3. Comparison of strength of silicon nitride and sialon at various temperatures (adapted from Lumby *et al* 1978, p. 893).

value for a pressureless sintered sialon which is similar to that of hot-pressed Si_3N_4 . It has also been suggested that the increase in K_{IC} values at high temperatures is associated with viscous deformation of the grain boundary phase. The variation in K_{IC} values could probably be attributed to variation in sialon composition as well as fabrication and measuring techniques. The oxidation resistance of β' -sialon is better than that of hot-pressed Si_3N_4 (Arrol 1974, p. 729). It has also been observed that the oxidation rate of TLP sintered $\text{Si}_{1.4}\text{Al}_{1.6}\text{O}_{1.6}\text{N}_{2.4}$ is an order of magnitude less than that of hot-pressed Si_3N_4 at 1400°C .

The coefficient of linear thermal expansion of β' -sialon is $2.7 \times 10^{-6}\text{K}^{-1}$ and is less than that of β - Si_3N_4 ($3.5 \times 10^{-6}\text{K}^{-1}$). Gauckler *et al* (1977) have reported an average value of $3.4 \times 10^{-6}\text{K}^{-1}$ which compares with the value for pure β - Si_3N_4 . It has been observed that essentially linear decrease (Gauckler *et al* 1977; Wills *et al* 1977) of the thermal expansion coefficient occurs with increasing Al concentration in sialons. Several investigators (Gauckler *et al* 1977; Lumby *et al* 1978, p. 893) have reported the value of water-quenched thermal shock resistance (ΔT_c) of several sialons. While ΔT_c values for β' -sialons are comparable to those of various silicon carbide ceramics and RBSN, they are considerably lower than that of hot-pressed Si_3N_4 .

Aliprandi (1986) has reviewed sialon ceramics with regard to their suitability in extrusion and drawing of metals. Recently high temperature properties of ceramics in the (Si, Al, O, N) system were studied by Bonnel *et al* (1986). The fracture toughness generally decreases with temperature. Short time annealing raises the toughness at lower temperatures whereas further annealing brings it back to the value characteristic of hot-pressed material. The problems associated with mass transport processes in the oxidation of calcium doped β' -sialon were studied by Chukukere & Riley (1986). The effects of creep on anelastic strain recovery, bulk and surface morphologies of sialon ceramics were examined using 3-point bending creep tests in air at 1200°C and 240 MPa by Besson *et al* (1986). TEM examination showed a marked decrease in the amount of glassy phase in the bulk of the samples after creep. No cavitation was however detected.

4. Aluminium nitride

Aluminium nitride is another useful nitride ceramic which exhibits a number of interesting properties. These include excellent high temperature strength, oxidation and thermal shock resistance and resistance against the attack of liquid metals. It is a good thermal conductor while it is electrically insulating.

4.1 Preparation and characterization

AlN powder is usually synthesized by two methods. The first one which has been widely adopted is direct nitridation of aluminium powder (or Al_2O_3 with C-black or graphite) by heating in a nitrogen or NH_3 atmosphere (Pierre *et al* 1985; Liping *et al* 1986). In the second method a high purity free-flowing AlN powder with low oxygen content is prepared by treating Al_2S_3 with NH_3 or N_2 at $> 1100^\circ\text{C}$ (Ibrahim 1986).

Fumino *et al* (1986) have reported the deposition of amorphous AlN films by a plasma CVD method using a metal organic aluminium source and NH_3 as the starting materials. The powder samples of AlN were characterized using X-ray diffraction and ESCA (Ibrahim 1986). It is found that the particles are associated with high surface concentration of O and grain sizes are of the order of 2000 Å.

4.2 Industrial production techniques, properties and uses

Polycrystalline compacts of AlN have been prepared by several methods such as sintering of pressed powder (Matsue *et al* 1965), reaction sintering of Al-AlN mixture (Taylor & Lenie 1960) and hot-pressing (Komeya & Inoue 1969). Although AlN is difficult to sinter without any flux, Komeya & Inoue (1969) found that very fine powders can be easily sintered though the extent of oxygen impurity in such powders is not known. Sakai & Iwata (1977) used hot-pressing techniques and studied the sintering behaviour and strength of sintered samples with various oxygen contents. Densification has been carried out by hot-pressing (Weston & Carruthers 1973) in an inductively heated graphite die. To avoid reaction between AlN and graphite die at high temperatures, graphite was coated with high purity boron nitride suspended in an aqueous solution of methyl cellulose. Methods of preparing AlN multilayer ceramic substrates for hybrid integrated circuits have been described which are suitable for mass production (Nobuo *et al* 1984; Komeya & Inoue 1974; Billy & Mexmain 1985).

Fully densified AlN has a microhardness value of 150 on the Vicker's scale which is comparable to those of silicon oxynitride and Si_3N_4 . The strength of AlN at room temperature is greater than that of RBSN but decreases when temperature increases and reaches a stable value between 800–1400°C. At 1400°C the strength is of the same order as that of other nitrides (Lecompte *et al* 1983, pp. 293–298). Trontelj & Kolar (1975, p. 39) have shown that with 99 AlN-1 Ni (wt%) powders, dense compounds could be sintered having a bend strength of 300 MN/m². Komeya & Inoue (1971) have studied the properties of AlN containing Y_2O_3 prepared by pressureless sintering. The highest value of the strength (328 MN/m²) could be obtained with a composition of 75 AlN-25 Y_2O_3 . AlN with single oxide additives such as Li_2O , CaO , MgO , SiO_2 , B_2O_3 , NiO , Cr_2O_3 (1 wt%) has been used to study the sintering effect. Complete densification has been achieved through sintering under nitrogen at comparatively low firing temperatures (Schwetz *et al* 1983, pp. 245–252). McCauley & Corbin (1979) have shown that it is possible to reactively sinter Al_2O_3 with 27–40 mol% AlN to form a single phase cubic oxynitride spinel. The resultant material has a unique combination of properties and possesses mechanical properties very similar to Al_2O_3 of similar grain size. The final product, AlON, is optically isotropic.

Kazuo *et al* (1986) have reported that AlN mixed with 3 wt% strontium oxalate hot-pressed at 1800°C under a pressure of 300 kg/cm² has a thermal conductivity of 58 W/mK. The effect of sintering parameters such as pressure, particle size and temperature of AlN powders (coated with a thin film of Al_2O_3) on the densification rate was investigated in order to determine the sintering mechanism of AlN (Gossain *et al* 1985). Effect of CaO additives on electrical conductivity of hot-pressed AlN ceramic was studied by Zulfequar & Kumar (1986). A review on heat conducting aluminium nitride boards have been presented by Nobuo & Kazuo (1986).

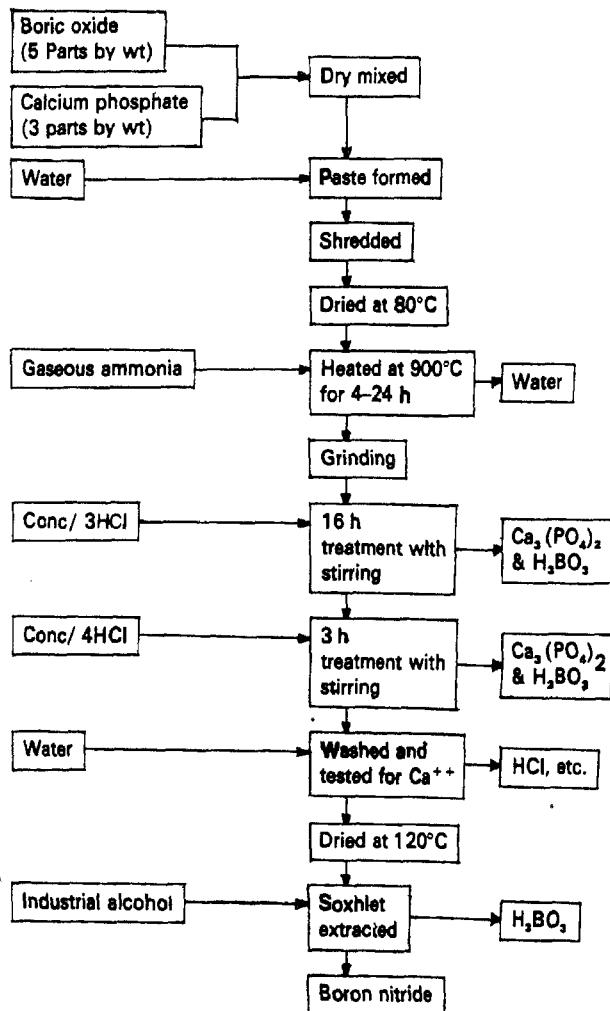
5. Boron nitride

Lately, boron nitride has been recognized as a potential material for use at high temperatures. There is a marked similarity between BN and carbon, as they are isoelectronic. Boron nitride is known to exhibit three polymorphic modifications;

hexagonal graphite type (*h*-BN), cubic zinc blende type (*c*-BN) and wurtzite type (*w*-BN).

5.1 Methods of preparation

Various methods of preparation of BN have been described in the literature (Giardini 1953). Sorrel & McCartney (1986) have reviewed the history of development, method of manufacture, properties and application of *c*-BN ceramics. Fujio & Kozo (1986) have reported the preparation of hexagonal BN. In this process borax and melamine are heated at 150°C in an N₂ atmosphere for about 1 h and cooled in the same atmosphere overnight. The powder is washed with HCl and water and dried at 100°C for 2 h when white BN powder with 90.6% yield is obtained. A summary of known methods of preparation of hexagonal boron nitride is given by Ingles & Popper (1960, pp. 144–167) and the preparation of powder by the reaction of a mixture of boric oxide and calcium orthophosphate with ammonia at 900°C is discussed in detail. A flow sheet for the preparation of boron nitride powder from boric oxide and ammonia (Ingles & Popper 1960, pp. 144–167) is given below.



Cubic BN in general is synthesized from *h*-BN under high pressure-high temperature conditions, typically 65 kbar and 1700°C. The General Electric Company of America has succeeded in the preparation of *c*-BN from *h*-BN by applying very high pressure (60,000 atm) at a high temperature (1600°C) (Wentorf 1957). *w*-BN is also synthesized from *h*-BN employing even higher pressure, mostly by a shock process which involves a shear mechanism. The conversion of *h*-BN to *c*-BN is kinetically a difficult process, even in the thermodynamically stable regime of *c*-BN. This is due to the high activation barrier involved. Therefore the transformation is usually carried out in the presence of some catalyst material which lowers the activation barrier. *c*-BN compacts are synthesized at high temperature and pressure with suitable binders (Hibbs & Wentorf 1974; Fukunaga *et al* 1978, p. 328; Rapoport & Nadin 1985).

5.2 Industrial production techniques, properties and uses

c-BN is an industrially important hard material, useful in abrasive and cutting tool applications. New methods for easier and more economical production are therefore constantly sought. Rapoport & Nadin (1985) have examined mechano-chemical processing which can provide some extra activation to *h*-BN powder and assist in its conversion to *c*-BN. AlN was chosen as an additive to *h*-BN in view of its reported role as a catalyst in the conversion of *h*-BN to *c*-BN. Akashi & Sawaoka (1986) have prepared compacts of cubic boron nitride with 94% theoretical density and a Vickers microhardness value of 30.3 GPa from coarse *c*-BN powder by a shock compaction technique. According to them the mechanical and chemical properties of cubic boron nitride are very similar to those of diamond except for reduced reactivity with ferrous materials at high temperatures. Sintered *w*-BN compacts were characterized (Singh 1987) with regard to their different crystalline phases, which are formed at high temperatures and pressures, composition and particle size distribution. The cubic BN consists of particles with sharp blade edges and well-developed (111) faces and it is useful as a cutting and grinding material. Lavrenko & Alekseev (1986) have studied the oxidation resistance of BN samples obtained by various methods using thermogravimetric analysis, DTA and IR spectroscopy.

Composite materials were prepared using sialon and 5–20 vol % BN fibres by hot-pressing. The products had high thermal shock resistance and were used for the manufacture of special rings for horizontal continuous casting of steel (Peizhi *et al* 1986). The DC conductivities of hexagonal boron nitride and BN-containing composites were measured as a function of temperature up to 2400°C. The results confirm that at high temperatures BN is an intrinsic semiconductor with an energy gap of 6.2 ± 0.4 ev (Frederikse *et al* 1985).

The mechanical and chemical stability and the high electrical resistivity of hexagonal boron nitride at high temperatures (2500°C) makes this compound a principal candidate for use as microwave windows in re-entry vehicle communication systems. However hexagonal boron nitride sublimes at 2500°C (Ingles & Popper 1960, pp. 144–167).

6. Boron carbide

Boron carbide which has a high melting point is among the refractory carbides. The

commercial importance of refractory carbides is mainly due to their extreme hardness.

6.1 Preparation

Boron carbide was initially produced in an electric furnace by Joly (1883) and Moissan (1894). For the production of pure boron carbide on an industrial scale, boric acid, which is available in high purity and in adequate amounts, is generally used. The formation of boron carbide from B_2O_3 is represented by the equation



Recently boron carbide has been prepared by high temperature reaction involving boric oxide and carbon (Ramamurthy 1985; Seiji 1986).

6.2 Characterization

Boron carbide has already been known for 50 years, since its crystal structure was elucidated by Laves (1934–35). The elementary cell was described by Silver & Bray (1959) on the basis of NMR investigations. The B-C phase diagram has been described in detail by Samsonov (1958 a, b, c). X-ray data were used by Samsonov and coworkers for generating the phase diagrams. Metallographic investigations were also carried out along with measurements of density, hardness and electrical resistance.

6.3 Properties, industrial production techniques and uses

The most important property of boron carbide is its extraordinary hardness. After diamond and cubic boron nitride (the so-called Borazon), boron carbide is the hardest industrial material known. However, hardness values of boron carbide are reported in different ways in the literature (Knoop 1939). Figure 4 shows the

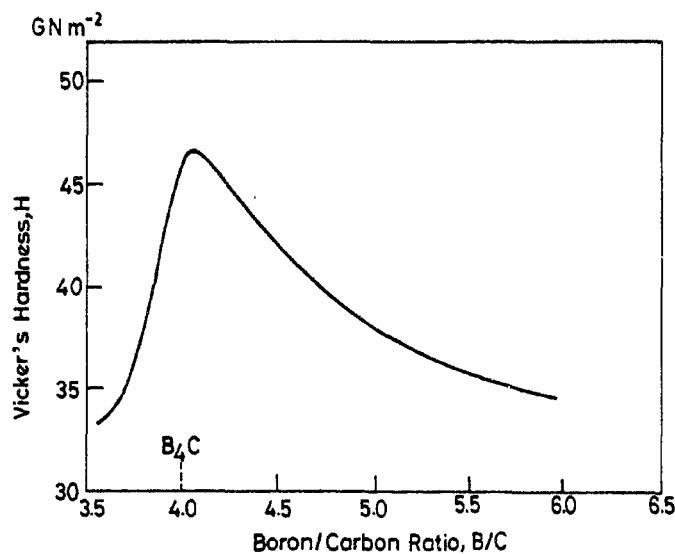


Figure 4. Vicker's hardness as a function of B/C ratio for boron carbide (adapted from Niihara *et al* 1984).

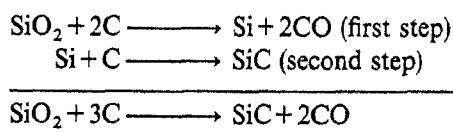
Vicker's hardness as a function of the B/C ratio for boron carbide. It appears that the hardness values range from 20–80 kN/mm² and lie between the hardness values of corundum and diamond. Lipp (1965) has presented an interesting review on the physico-chemical properties and reactivity of boron carbide.

7. Silicon carbide

Silicon carbide was first artificially produced and later discovered in the natural state. The mineralogical name of silicon carbide is moissanite. Moissan (1905) discovered hexagonal silicon carbide interlaced with diamond in the meteoric iron found in the Diablo Canyon (Arizona). Several authors (Kaypov & Baymuratov 1970) have reported the occurrence of Moissanite since 1950 in various volcanic rocks in the Soviet Union. About a decade ago, it was reported that silicon carbide along with some other compounds was detected in the gaseous phase of certain stars (Friedmann 1969; Gilman 1969; Lefevre 1970). SiC occurs most probably in the circumstellar space of cool stars that contain carbon and oxygen in almost equal proportions (Gilman 1969), the presence of silicon carbide was detected by absorption spectral analysis (Lefevre 1970). Acheson developed a process for the manufacture of silicon carbide on an industrial scale in 1891. The process is frequently mentioned in the literature as the Acheson process. Silicon carbide is produced batchwise in an electric furnace by high temperature solid phase reaction of coal and quartz sand. The production of silicon carbide even today is carried out exclusively by this process. Efforts (Lanyi 1955, p. 284) have been made over the past eight decades to produce silicon carbide on an industrial scale by improved methods. It is rather difficult to evaluate either the present situation or the current trends of development precisely because of the nonavailability of complete research literature on SiC production. However, a few standard methods of producing SiC are discussed below.

7.1 Methods of preparation

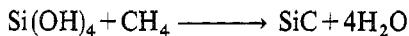
For the production of industrial SiC, silica and carbon are used as basic materials along with various additives: saw dust, sodium chloride and also other modifying components. The correct proportion of raw materials, their pretreatment, optimum grain size, applied additives and modifying components etc. are discussed in the literature (Acheson 1896, 1912; Dadape *et al* 1947; Tomonari 1956). The formation of silicon carbide can be summarized (Ruff 1935) in the following two steps,



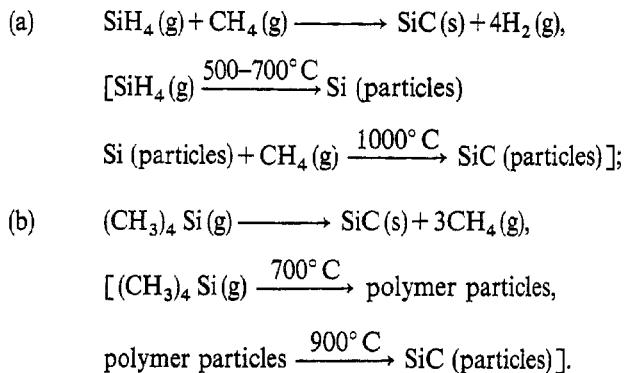
Production of silicon carbide starting from silicon and coal, silicon tetrachloride, trichloro silane, alkyl silanes and aluminium silicates etc. have been described in the early literature. Silicon carbide has been prepared from carbon tetrachloride and alkyl silanes in a hydrogen atmosphere on a glowing carbon rod at a temperature above 1700°C (Pring & Fielding 1909). It is also possible to obtain silicon carbide from a mixture of silicon tetrachloride and toluene using hydrogen as a carrier gas

on fibres of carbon using thallium carbide or zirconium carbide as crystal growth promoting agents (Agte & Moers 1931). Aluminium silicates have been used as starting materials instead of silica (Hayakawa 1949).

Hoch & Nair (1978, pp. 33–40) have reported the preparation of ultrafine powders of SiC from organometallic complexes. The process can be represented by the following equation,



Fine powders of β -SiC were obtained by the vapour phase reaction of a SiH_4 - CH_4 system at about 1400°C and by the thermal decomposition of $(\text{CH}_3)_4\text{Si}$ in hydrogen atmosphere above 1000°C (Okabe *et al* 1979). The formation processes of SiC particles in these reaction systems are summarized as follows



Silicon carbide whiskers can be made by a variety of methods. The most economical one is the carbothermic reaction of SiO_2 and carbon, which are constituents of ground rice hulls (Lee & Cutler 1975). Sharma *et al* (1984) have produced such whiskers and characterized them by transmission electron microscopy. Another method is the gas-phase reaction of SiCl_4 , chlorosilane and/or silane in a carbonaceous atmosphere in the presence of Fe and Cr as catalysts (Mazdiyasni & Zangvil 1985). The effect of covalent bond additives, such as AlN, BN and BeO on the structural stability of SiC has been studied by Zangvil & Ruh (1985).

The detailed structure of silicon carbide has been given by Dietzel *et al* (1960) & Ueltz (1972, p. 1). The crystal structure and mechanical properties of green and black silicon carbides have been discussed by Gasilova & Saksonov (1966, p. 50).

Thermal and chemical properties of silicon carbide which include thermal expansion, thermal conduction and reaction of silicon carbide with various other chemicals have been summarized in the literature. Silicon carbide is attacked at high temperatures by gaseous fluorine, chlorine and hydrogen. It is resistant to mineral acids and is attacked only by a mixture of hydrogen fluoride and nitric acid and/or concentrated phosphoric acid at temperatures above 200°C .

7.2 Industrial production techniques, properties and uses

Silicon carbide based ceramic materials include hot-pressed SiC (HPSiC), reaction-bonded SiC (RBSiC), sintered SiC (SSiC), silicon carbide/silicon composites and chemical vapour deposited SiC (CVD-SiC).

Hot-pressed SiC can be formed with various densification aids, but only the HPSiC

prepared by utilizing Al_2O_3 additive has been considered for high performance engine applications (Prochazka 1975, p. 171). HPSiC is not as strong as HPSN at low temperatures, however, it retains useful strength up to $\sim 1400^\circ\text{C}$.

Reaction-bonded silicon carbides cover a wide range of compositions and manufacturing processes (Alliegro 1974). Typical examples of these materials include UKAEA/BNF Rofel, KT, NI-430, NI-435 and Ford siliconized silicon carbide. Each material is formed by a unique proprietary process. In general, a plastic body is formed by SiC powder, graphite and a plasticizer. In some variants of this process, SiC powder and a char-forming plastic binder are used (Whalen *et al* 1978). A variety of experimental gas turbine components such as combustors or stators, have been made by this route. Since these materials and the processes are easily adopted to mass production techniques and since the products possess good shape retention, there is a strong incentive to use them for the production of automotive components.

Sintered silicon carbide is a recent development. The pressureless sintering of SiC to full density was thought untenable until Prochazka demonstrated that with boron and carbon additions, β -SiC could be sintered to a maximum density at 2000°C (Prochazka 1974). He also demonstrated that sintered β -SiC could be formed into useful shapes by slip-casting, die-pressing and extrusion. Distribution of the carbon additive and exaggerated grain growth of α -SiC were found to interfere with densification. Coppola & McMurtry (1976) have developed sintered α -SiC partly in an effort to eliminate the problems associated with β - α transformation. The β -SiC structure appears stronger than α -SiC. Bending strengths of α and β forms are of the order of 300–450 MPa (Larsen *et al* 1983, pp. 695–710). The temperature variation of the bending strengths of α and β SiC is shown in figure 5.

Reaction-formed SiC/Si composites developed by Hillig (1974) are the first engineering composite ceramic/ceramic materials which offer the possibility of low cost structural components. In this process, the molten silicon reacts with graphite to form polycrystalline SiC fibres in a silicon matrix. This material has been used in a

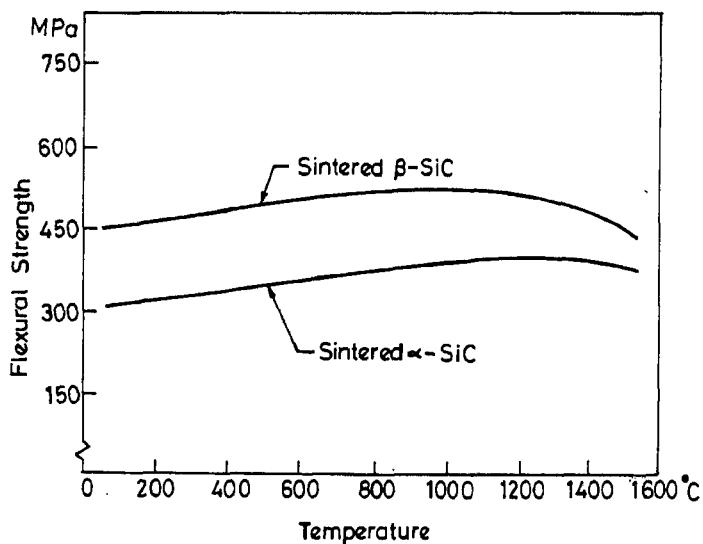


Figure 5. Flexural strength of silicon carbide materials as a function of temperature (adapted from Larsen *et al* 1983, pp. 695–710).

combustion chamber liner application at temperatures above 1400°C (Coppola & McMurtry 1976), although it is still in a very early stage of development.

CVD-silicon carbide in contrast to CVD-Si₃N₄ has been produced in bulk. Fabrication capability of gas turbine components including radial and axial rotors has also been demonstrated. CVD-SiC has proven to be an outstanding creep- and oxidation-resistant material. Its major drawback from an automotive application point of view is likely to be the cost. This process may be useful in coating SiC ceramics formed by more conventional routes. A sintered body consisting of SiC and AlN has 90% theoretical density, specific resistance of 1–10⁴ ohm/cm (at room temperature), excellent bending strength and oxidation-resistance. It is useful for heaters, electrical resistors and temperature sensors.

8. Concluding remarks

The ceramics discussed in this article are the most important materials currently in demand for advanced and emerging technologies. Large volume ceramic applications appear to be round the corner in the automotive industry. Adiabatic engines made from advanced ceramics such as Si₃N₄ have the demonstrated ability to save power upto 20–30% which is too attractive to ignore by a world faced with an imminent energy crunch.

A variety of advanced technologies also make continuous demand on super hard materials for cutting tools and materials which are capable of standing extremes of temperature, pressure and chemical environment. Metals and alloys have been found to be incapable of answering these challenges, thus making ceramics the only candidates in the field; a ceramic age appears to have been ushered in. As pointed out earlier light element ceramics constitute choice materials for further development and exploration. Nature has distributed the light elements so evenly on our planet that they are there for all progressive countries to harvest for their own benefit.

References

- Acheson E G 1896 BRD Patent 85197
- Acheson E G 1912 US Patent 1014199
- Agte C, Moers K 1931 *Z. Anorg. Allg. Chem.* 198: 233–243
- Akashi T, Sawaoka A B 1986 *J. Am. Ceram. Soc.* 69: c78–80
- Aliprandi G 1986 *Metall. Ital.* 78: 405–411
- Alliegro R A 1974 *Ceramics for high performance applications* (eds) J J Burke, A E Gorum, R N Katz (Chestnut Hill, Mass: Brook Hill) chap. 13
- Arrol W J 1974 *Ceramics for high performance applications* (eds) J J Burke, A E Gorum, R N Katz (Chestnut Hill, Mass: Brook Hill)
- Baldo J B, Pandolfelli V C, Casarini J R 1983 *Ceramic powders* (ed.) P Vincenzini (Amsterdam: Elsevier Scientific Publ. Co.)
- Bandyopadhyay G, French K W 1986 *J. Eng. Gas Turbine Power* 108: 536–539
- Besson J L, Streicher E, Chartier T, Goursat P 1986 *J. Mater. Sci. Lett.* 5: 803–805
- Billy M 1959 *Ann. Chim.* 4: 795–851
- Billy M, Mexmain J 1985 *Sprechsaal* 118: 245–249
- Bonnel D A, Ruehle M, Tien T Y 1986 *J. Am. Ceram. Soc.* 69: 623–627
- Cannon W R, Danforth S C, Flint J H, Haggerty J S, Marra R A 1982a *J. Am. Ceram. Soc.* 65: 324–330
- Cannon W R, Danforth S C, Haggerty J S, Marra R A 1982b *J. Am. Ceram. Soc.* 65: 330–335
- Canteloup J, Mocellin A 1975 *Spec. Ceram.* 6: 209–222

- Chukukere F N, Riley F L 1986 *Mater. Sci. Forum* 7: 307-316
- Coppola J, McMurtry C H 1976 Substitution of ceramics for ductile materials in design, National Symposium on Ceramics in the Service of Man, Carnegie Institution, Washington DC
- Dadape V V, Kane G P, Sathe P K 1947 *J. Sci. Ind. Res. (India)* B6: 123-127
- Danforth S C, Haggerty J S 1983 *J. Am. Ceram. Soc.* 66: c58-59
- Dietzel A, Jagodzinski H, Scholze H 1960 *Ber. Dtsch. Keram. Ges.* 37: 524
- Drew P, Lewis M H 1974 *J. Mater. Sci.* 9: 261-269
- Eaborn C 1960 *Organosilicon compounds* (London: Butterworths)
- Evans J R G, Moulson A J 1983 *Progress in nitrogen ceramics* (ed.) F L Riley (Dordrecht: Martinus Nijhoff)
- Fletcher F J, Ibrahim J, Kerry I M 1971 *Symposium on electrochemical engineering* (London: Inst. Chem. Eng.)
- Frederikse H P R, Kahn A H, Dragoo A L, Hosler W R 1985 *J. Am. Ceram. Soc.* 68: 131-135
- Friedmann C 1969 *Physica* 41: 139-143
- Fujio M, Kozo K 1986 *Jpn. Kokai Tokyo Koho JP* 61, 111, 904
- Fukunaga O, Endosh T, Akashi M, Osawa T, Yamaoka S 1978 Proc. Int. Symp. of Factors in Densification and Sintering of Oxide and Nonoxide Ceramics, Japan, p. 328
- Fumino H, Tsuyoshi T, Isaco O, Yasuo N 1986 *Ext. Abstr. Conf. Solid State Devices Mater.* 18: 663-666 (*Chem. Abstr.* 1987, 106: 42449r)
- Fumiyoji M, Hiroyuki K 1986 *Kinzoku Hyomen Gijutsu* 37: 401-405
- Fyfe C A, Gobbi G C 1983 *Polyhedron* 3: 1267-1269
- Gasilova E B, Saksonov Yu G 1966 *Karbid Kremniya* (ed.) I N Frantsevich (Kiev: Navkova Dumka)
- Gauckler L J, Boskovic S, Naik I K, Tien T Y 1978 *Ceramics for high performance applications II* (eds) J J Burke, E N Lenoe, R N Katz (Chestnut Hill, Mass: Brook Hill)
- Gauckler L J, Lukas H L, Petzow G 1975 *J. Am. Ceram. Soc.* 58: 346-347
- Gauckler L J, Prietzel S, Bodemer G, Petzow G 1977 *Nitrogen ceramics* (ed.) F L Riley (Leiden: Noordhoff)
- Gazza G E, Knoch H, Quinn G D 1978 *Am. Ceram. Soc. Bull.* 57: 1059-1060
- Giardini A A 1953 *US Bur. Mines Inf. Circ.* No. 7664: 13
- Gilman R C 1969 *Astrophys. J.* 155: L185
- Glemser V O, Newmann P 1903 *Z. Anorg. Allg. Chem.* 298: 134
- Goodwin C A 1982 *Ceram. Eng. Sci. Proc.* 3: 109-119
- Gossain A, Didier B, Michel B, Sop H K, Pierre L 1985 *Rev. Chim. Miner.* 22: 473
- Greil P, Weiss J 1983 *Progress in nitrogen ceramics* (ed.) F L Riley (Dordrecht: Martinus Nijhoff)
- Gugel E, Petzenhauser I, Fickel A 1975 *Powder Metall. Int.* 7: 66-67
- Hampshire S, Park H K, Thompson D P, Jack K H 1978 *Nature (London)* 274: 880-882
- Hanna S B, Ghoneim N M 1986 *Interceram* 35: 42-45
- Hanna S B, Mansour N A L, Taha A S, Abd-Allah H M A 1985 *Br. Ceram. Soc. Trans. J.* 84: 18-21
- Hayakawa Y 1949 *J. Electrochem. Assoc. Jpn.* 17: 147
- Hibbs L E Jr, Wentorf R H Jr 1974 *High Temp. High Pressures* 6: 409
- Higgins I, Hendry A 1986 *Br. Ceram. Soc. Trans. J.* 85: 161-166
- Hillig W B 1974 *Ceramics for high performance applications* (eds) J J Burke, A E Gorum, R N Katz (Chestnut Hill, Mass: Brook Hill) chap. 52
- Hirao K, Miyamoto Y, Kozumi M 1986 *J. Am. Ceram. Soc.* 69: c60-61
- Hoch M, Nair K M 1978 *Materials science research* (eds) Palmour Hayne III, R F Davis, T M Hare (New York: Plenum) Vol. 11
- Hoch M, Nair K M 1979 *Am. Ceram. Soc. Bull.* 58: 187
- Hoch M, Thompson A L, Houck J, Nair K M 1977 *J. Power Bulk Solids Technol.* 1: 34
- Husbey I C, Lukas H L, Petzow G 1975 *J. Am. Ceram. Soc.* 58: 377
- Ibrahim S 1986 *PCT Int. Appl. No.* 86, 06, 360
- Ingles T A, Popper P 1960 *Special ceramics* (ed.) P Popper (London: Heywood)
- Ishigaki H, Kawaguchi I, Iwasa M, Toibana Y 1986 *J. Tribol.* 108: 514-521
- Izumi F 1983 *Adv. X-ray Chem. Anal., Jpn.* 14: 43
- Izumi F, Mitomo M, Bando Y 1984 *J. Mater. Sci.* 19: 3115-3120
- Jack K H 1973 *Br. Ceram. Soc. Trans. J.* 72: 376-384
- Jack K H 1976 *J. Mater. Sci.* 11: 1135-1158
- Jack K H, Wilson W I 1972 *Nature (London)* 238: 28-29
- Johnson P M, Hendry A 1979 *J. Mater. Sci.* 14: 2439-2445

- Joly F 1883 *Compt. Rend.* 97: 456
- Kaji H, Mamoru K 1986 *Funtai Oyobi Funmatsuyakin* 33: 210–215 (*Chem. Abstr.* 1986, 105: 10186m)
- Kaypov A D, Baymuratov M N 1970 *Izv. Akad. Nauk. Kaz. SSR, Ser. Geol.* 27: 68
- Kazuo U, Makoto K, Toru K 1986 *Chem. Express* 1: 511–514
- Kim S S, Kato K, Hokirigawa K, Abe H 1986 *J. Tribol.* 108: 522–526
- Knoop F 1939 *J. Res. Natl. Bur. Stand.* 23: 39–61
- Komeya K, Inoue H 1969 *J. Mater. Sci.* 4: 1045
- Komeya K, Inoue H 1971 *Br. Ceram. Soc. Trans.* 70: 107–113
- Komeya K, Inoue H 1974 *J. Am. Ceram. Soc.* 57: 411
- Komeya K, Tsuge A, Hasimoto H, Kubo T, Ochiai T 1977 Gas Turbine Soc. of Japan, Tokyo joint gas turbine conference, Paper No. 65
- Lanyi B 1955 *Elektrotermikus Eljarasok (Electrochemical processes)* (Budapest: Akademiai Kiado)
- Larker H T, Adlerborn J, Bohman H 1975 Fabrication of dense Si_3N_4 parts by hot isostatic pressing, SAE 770335
- Larsen D C, Adams J W, Ruh R 1983 *Progress in nitrogen ceramics* (ed.) F L Riley (Dordrecht: Martinus Nijhoff)
- Larsen D C, Bortz S A, Ruh R, Tallan N M 1978 *Ceramics for high performance applications II* (eds) J J Burke, E N Lenoe, R N Katz (Chestnut Hill, Mass: Brook Hill) chap. 36
- Laves N 1934–35 *Götting Ges.* 2, VI 1: 57–
- Lavrenko V A, Alekseev A F 1986 *Ceram. Int.* 12: 25–
- Lecompte J P, Jarrige J, Mexmain J 1983 *Progress in nitrogen ceramics* (ed.) F L Riley (Dordrecht: Martinus Nijhoff)
- Lee J, Cutler I B 1975 *Am. Ceram. Soc. Bull.* 54: 195
- Lefevre J 1970 *Astron. Astrophys.* 5: 37–44
- Lengfeld F 1899 *Am. Chem. J.* 21: 531
- Lewis M H, Powell B D, Drew P, Lumby R J, North B, Taylor A J 1977 *J. Mater. Sci.* 12: 61–74
- Liping H, Xiongzhang H, Xiren F, Baozhen S 1986 *Guisnanyan Xuebao* 14: 332
- Lipp A 1965 *Tech. Rundsch.* 14: 28–33
- Lumby R J, North B, Taylor A J 1975 *Special ceramics-6* (ed.) P Popper (Manchester: Br. Ceram. Res. Assoc.)
- Lumby R J, North B, Taylor A J 1978 *Ceramics for high performance applicaitons II* (eds) J J Burke, E M Lenoe, R N Katz (Chestnut Hill, Mass: Brook Hill)
- Matsue S, Komeya K, Matsuki Y 1965 *Yogyo Kyokaishi* 73: 82
- Mazdiyasni K S, Cooke C M 1973 *J. Am. Ceram. Soc.* 56: 628–633
- Mazdiyasni K S, West R, David L D 1978 *J. Am. Ceram. Soc.* 61: 504–508
- Mazdiyasni K S, Zangvil A 1985 *J. Am. Ceram. Soc.* 68: c142–144
- McCauley J W, Corbin N D J 1979 *Am. Ceram. Soc. Bull.* 62: 476–479
- McLean A F 1978 *Ceramics for high performance applications II* (eds) J J Burke, E N Lenoe, R N Katz (Chestnut Hill, Mass: Brook Hill) chap. 1
- Mehmet S, Ilhan A, Gareth T 1985 *Mater. Sci. Res.* 19: 167
- Messier D R, Wong P 1974 *Ceramics for high performance applications* (eds) J J Burke, A E Gorum, R N Katz (Chestnut Hill, Mass: Brook Hill)
- Moissan H 1894 *Compt. Rend.* 118: 556
- Moissan H 1905 *Compt. Rend.* 140: 769
- Morgan P E D 1984 *Mater. Res. Soc. Symp. Proc.* 32: 213
- Morgan P E D 1986 *J. Mater. Sci. Lett.* 5: 372
- Morgan P E D, Pugar E A 1985 *J. Am. Ceram. Soc.* 68: 699–702
- Mostaghaci H, Fan Q, Riley F L, Bigay Y, Torre J P 1986 *Br. Ceram. Soc. Trans.* 7. 85: 12–16
- Nancy T 1986 *J. Mater. Res. Soc. Symp. Proc.* 62: 435
- Negita K 1985 *J. Mater. Sci. Lett.* 4: 417–418
- Niihara K, Nakahira A, Hirai T 1984 *J. Am. Ceram. Soc.* 67: C13–14
- Nobuo I, Akihiko I, Yasuyuki S 1984 *Int. Hybrid Micro-electron* 7: 49–53
- Nobuo I, Kazuo S 1986 *Densi Zairyō* 25: 40–46
- Nobuo K, Aszmu S, Nobuyasu M 1985 *Seramikkusu* 20: 920
- Nobuyuki K 1985 Jpn. Kokai Tokyo Koho JP60, 19, 064
- Okabe Y, Hojo J, Kato A 1979 *J. Less Common Met.* 68: 29–41
- Oyama Y 1972 *Jap. J. Appl. Phys.* 11: 15–72
- Oyama Y 1973 *Jpn. J. Appl. Phys.* 12: 500–508

- Oyama Y, Kamigaito O 1971 *Jpn. J. Appl. Phys.* 10: 1637
Peizhi G, Wanmer S, Hong C, Weiru Z 1986 *Gui Suanyan Xuebao* 14: 369
Pierre L, Florence M, Gossan A, Michel B 1985 *Rev. Chim. Miner.* 22: 534
Pring J N, Fielding W 1909 *J. Chem. Soc.* 95: 1497–1506
Prochazka S 1974 *Ceramics for high performance applications* (eds) J J Burke, A E Gorum, R N Katz (Chestnut Hill, Mass: Brook Hill) chap. 12
Prochazka S 1975 *Special ceramics-6* (ed.) P Popper (Manchester: Br. Ceram. Res. Assoc.)
Prochazka S, Greskovitch C 1978 *Am. Ceram. Soc. Bull.* 57: 579–581
Rahaman M N, Boiteux Y, DeJonghe L C 1986 *Am. Ceram. Soc. Bull.* 65: 1171–1176
Ramamurthy S 1985 *J. Mater. Sci. Lett.* 4: 603–605
Rapoport E, Nadiv S 1985 *J. Mater. Sci. Lett.* 4: 34–36
Ruff O 1935 *Trans. Electrochem. Soc.* 68: 87
Sakai T, Iwata M 1977 *J. Mater. Sci.* 12: 1659–1665
Samsonov G V 1958a *Ukr. Khim. Zh.* 24: 659
Samsonov G V 1958b *J. Phys. Chem.* 32: 2424
Samsonov G V 1958c *Technol. Buntmet.* 29: 367
Sanyal A S, Mukerji J 1986 *J. Mater. Sci. Lett.* 5: 787–788
Schwetz K A, Knoush R, Lipp A 1983 *Progress in nitrogen ceramics* (ed.) F L Riley (Dordrecht: Martinus Nijhoff)
Segal D L 1985 *Chem. Ind.* 544
Segal D L 1986 *Br. Ceram. Trans.* 1: 184–187
Seiji M 1986 *Kogyo Zairyo* 34: 21
Seiji M, Noriyuki I, Tatsuhiko H 1986 *J. Mater. Sci.* 21: 3836–3842
Seyferth D, Wiseman G H, Prudhomme C 1983 *J. Am. Ceram. Soc.* 66: c13–14
Sharma N K, Williams W S, Zangvil A 1984 *J. Am. Ceram. Soc.* 67: 715–720
Shimada M 1986 *Am. Ceram. Soc. Bull.* 65: 1153–1155
Silver A H, Bray P J 1959 *J. Chem. Phys.* 31: 247–253
Singh B P 1987 *J. Mater. Sci.* 22: 495
Sorrel C C, McCartney E R 1986 *Mater. Forum* 9: 148–161
Steinmann D 1986 *Sprechsaal* 119: 562
Sugawara F, Ajioka T, Ichikawa F, Ushio S 1986 *Mater. Res. Soc. Symp. Proc.* 54: 535–540
Szweida A, Hendry A, Jack K H 1981 *Proc. Br. Ceram. Soc.* 31: 107
Takase A, Tani E 1984 *J. Mat. Sci. Lett.* 3: 1058–1060
Takase A, Tani E 1986 *Am. Ceram. Soc. Bull.* 65: 1597–1600
Taylor K M, Lenie C 1960 *J. Electrochem. Soc.* 107: 308–314
Thommy E, Bertil A 1986 *Chem. Ser. A* 26: 33–35
Thompson D P, Korgul P, Hendry A 1983 *Progress in nitrogen ceramics* (ed.) F L Riley (Dordrecht: Martinus Nijhoff)
Tomonari T 1956 *J. Electrochem. Soc. Jpn.* 24: 27
Toshio T, Yoshinori U, Akira T 1985 *Nagoya Kogya Gijutsu Shikensho Hokoku* 34: 235
Trontelj M, Kolar D 1975 *Special ceramics-6* (ed.) P Popper (Manchester: Br. Ceram. Res. Assoc.)
Tsukuma K, Shimada M, Koizumi M 1981 *Am. Ceram. Soc. Bull.* 60: 910–912
Ueltz H F G 1972 *Proc. Int. Grinding Conf.* (ed.) M C Shaw (Pittsburg: Carnegie Press)
Vasilos T 1977 *Nitrogen ceramics* (ed.) F L Riley (Leiden: Noordhoff)
Wentorf R H Jr 1957 *J. Chem. Phys.* 26: 956
Weston R J, Carruthers T G 1973 *Proc. Br. Ceram. Soc.* 22: 197
Whalen T, Koakes J E, Terner L L 1978 *Ceramics for high temperature applications II* (eds) J J Burke, E M Lenoe, R M Katz (Chestnut Hill, Mass: Brook Hill) chap. 9
Wills R R, Stewart R W, Wimmer J M 1977 *Am. Ceram. Soc. Bull.* 56: 194–196
Wong P, Messier D R 1978 *Am. Ceram. Soc. Bull.* 57: 525–526
Yeh H C, Watters W J 1977 Effects of pressure and temperature on hot pressing of sialon, NASA TM-78945
Yoshio B 1985 *Seramikkusu* 20: 1117–1126
Zangvil A, Ruh R 1985 *Mater. Sci. Eng.* 71: 159–164
Zulfequar M, Kumar A 1986 *J. Mater. Sci. Lett.* 5: 1230–1232