CARBOTHERMAL REDUCTION OF SILICA TO SILICON NITRIDE POWDER

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For Linda

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CERAMICS

"Minerals of variable composition and rather doubtful purity (that) are subjected to an unmeasurable thermal treatment for a period of time just long enough to allow unknown reactions to take place incompletely, yielding the heterogeneous, non-stoichiometric material known by the name of ceramics."

ABSTRACT

The processing conditions for carbothermal reduction of silica to silicon nitride was found to be sensitive to several key processing parameters: namely the intimacy of mixing of carbon and silica, the temperature, the specific high surface area of carbon, the nitrogen gas purity and the action of the nitrogen gas passing through the reactants

Sol-gel processing was found to provide superior mixing conditions over dry mixing, which allowed for complete conversion to silicon nitride at optimum carbon:silica ratios of 7:1. The ideal reaction temperature was found to be in the range of 1500°C to 1550°C. Suppression of silicon oxynitride and silicon carbide was achieved by ensuring that: (a) the nitrogen gas was gettered of oxygen, and (b) that the gas passed through the reactants Thermodynamic modelling of the Si-O-N-C system showed that ordinarily the equilibrium conditions for the formation of silicon nitride are very delicate Slight deviations away from equilibrium leads to the formation of non-equilibrium species such as silicon carbide caused by the build-up of carbon monoxide. Reaction conditions such as allowing nitrogen gas to pass through the reactants beneficially moves the reaction equilibrium well away from the silicon carbide and silicon oxynitride stability regions

The particle size of silicon nitride produced from carbon and silica precursors was of the order of 2-3 μ m and could only be reduced to sub-micron range by seeding with ultra-fine silicon nitride. It was shown that the mechanism of nucleation and growth of unseeded reactants was first nucleation on the carbon by the reaction between carbon, SiO gas and nitrogen (gas-solid reaction), and then growth of the particles by the gas phase reaction (CO, SiO, N₂).

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RESUME

Les conditions de réduction carbothermique de la silice en nitrure de silicium ont ete etudiées. Le processus est sensible a un certain nombre de parametres clés intervenant lors de la fabrication, tels que: le degre de melange du carbone et de la silice, la temperature, la surface specifique du carbone, la purete du gaz d'azote et l'action du gaz d'azote passant à travers les réactifs.

On a trouve que le procedé sol-gel donnait de meilleures conditions de mélange par rapport au melange a sec, permettant la conversion complète du nitrure du silicium avec un rapport optimal carbone/silicium de 7 pour 1. La temperature ideale de reaction était entre 1500°C et 1550°C. L'élimination de l'oxynitrure de silicium et du carbure de silicium à eté obtenu grâce aux mesures suivantes. (a) l'azote a été libéré de son oxygene, et (b) le gaz est passé à travers les reactifs. La modèlisation thermodynamique du système Si-O-N-C a montre que les conditions d'equilibre pour la formation du nitrure de silicium sont tres dificiles a atteindre De faibles écarts par rapport à l'équilibre peuvent conduire a la formation de composés instables tel que le carbure de silicium formé par un empilement de monoxyde de carbone. Les conditions de reaction comme celles permettant le passage du azote a travers les reactifs eloignent l'equilibre des regions de stabilité pour le nitrure et l'oxynitrure de silicium

La taille des particules de nitrure de silicium produites à partir du carbone et de la silice etait de l'ordre de 2-3 µm et ne pouvait être réduite à un niveau inferieur micron que grâce à un ensemencement de particules de nitrure de silicium extra fines. Il a ete demonstré que le mécanisme de gérmination et de croissance des reactifs non ensemencés était d'abord la gérmination sur le carbone par la réaction entre le carbone, le gas SiO et l'azote (reaction vapeursolide), et ensuite la croissance des particules par la reaction de la phase gazeuse (CO, SiO, N_2)

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CHAPTER 1 INTRODUCTION

The past decade has been witness to the rapid development of structural ceramics as potential replacements for more traditional materials such as steels and superalloys. Their attraction stems from their strength, creep and oxidation resistance at high temperatures, well above the limits exhibited by their metallic counterparts. The potential impact of engineering ceramic materials will be to improve the fuel burning efficiency of gas turbine and diesel engines. Other promising applications are in areas where high wear occurs, such as minerals handling and metal processing equipment.

A heat engine is a device that converts heat into work, the operation of which can be modelled by the Carnot cycle. Raising the combustion temperature of the engine increases the conversion efficiency of heat into work. The most obvious application of ceramics in this field are gas turbines and diesel engines. Currently, the operating temperatures of these engines are between 800 and 1000°C, the limiting temperature being the onset of creep of the metal alloys used in the combustion zone. Even small increases in the operating temperature (e.g. 10° C) can lead to major improvements ^{1,2} in the combustion efficiency. In the operation of gas turbines, this has been achieved by the careful design of blades with complex networks of tiny cooling channels which lower the temperature of the metallic components whilst allowing the gas temperature to rise. However, ceramic materials offering much improved high temperature properties would enable the operating temperature to be increased by as much as 100 to 300°C without cooling Nowadays, where energy conservation and, particularly, pollution control are major political issues, the advantage of using high operating temperatures

are two-fold: (a) the higher the operating temperature, the more complete is the combustion. This in turn allows for the use of lower octane fuels and for lower fuel consumption; and (b) greater efficiency leads to a greater power to weight ratio, implying that for a particular power output a smaller engine can be used.

The efficiency of the diesel engine is also limited by the operating temperature of the combustion chamber, and must be cooled in order to maintain a constant temperature. The power to drive the cooling system comes from the engine itself, significantly reducing the power output. In addition, the system adds weight to the engine, reducing the useful power output still further. The greatest disadvantage of having a cooling system is its unreliability. In a study conducted on U.S. army tanks³ and trucks, greater than 50% of all breakdowns were related to problems with the cooling system. Thus, elimination of the cooling system is extremely advantageous, and has become the objective of the development of the Cummins/TARADCOM adiabatic turbo-compound engine program.

These are two examples of the more popular "high tech" applications, but they are not the only ones being considered. Besides heat engines, structural ceramics lend themselves well to low temperature, high wear situations, such as in slurry pumps, cutting blades, tool bits and extrusion dies, to name a few. In many ways, more successful development is to be expected in these fields since part design is less complex and operating conditions are less rigorous than those required for heat engines.

Thus far, it would appear that ceramic materials are the perfect choice for the replacement of metals, and yet very few applications exist where they are commonly encountered. Other than in their traditional applications as refractories and vitreous china, the projections for market growth world-wide for advanced ceramics ranges between \$187 billion (US)⁴ by the year 2000 to \$17 billion $(US)^5$ by 1995. The breadth of these projections indicate that the potential for market growth is large but uncertain. The uncertainty is linked to the inherent nature of ceramics, i.e. metals will fail in a reasonably predictable manner whereas ceramic materials fail unpredictably by brittle fracture. Failure in metals invariably occurs after a period of plastic deformation; thus, in designing for high stress applications, allowance is made for the onset of plastic deformation. With ceramics, there is never any plastic deformation (at least at low temperature), and fracture occurs without warning. This would not be so serious if it was certain that failure would occur above a certain stress condition; however, the point of failure is highly dependent upon the size of defects or flaws in the microstructure. The reliability and reproducibility of ceramic materials is therefore solely dependent on the elimination of critical defects within the microstructure. This is a problem that must be overcome so that ceramic components can be manufactured to be technically reliable and economically competitive.

The reliability of a ceramic component is therefore of prime importance. The most important variables en route to achieving a critical defect-free ceramic will be shown to be directly related to the processing route and, in particular, the starting materials used in fabrication of components.

Reliability, although critical, is not the only drawback of using ceramics, since there are other disadvantages limiting their application. Few ceramics have high enough toughnesses to make them capable of withstanding the shock of impact. Thus, there are problems with their applications as machine tools, an area where high impact resistance is required. These problems are being approached by the incorporation of whiskers ⁶ and fibers in the ceramic matrix, which then act to prevent the propagation of cracks by various mechanisms '.

Some of the ceramic materials being considered for high temperature, structural applications are alumina (Al_2O_3) , zirconia (ZrO_2) , silicon carbide (SiC), and silicon nitride (Si₃N₄). Each of the above materials have quite different properties and are suitable for a number of different applications. In terms of developing good mechanical properties, they are all highly dependent upon the condition of the microstructure which is controlled by the fabrication process of the ceramic body.

Ceramic materials cannot practically be cast into shape in the same way as metals since they only become molten at very high temperatures or never become molten but decompose, as is the case for Si_3N_4 and SiC. This is due to the highly covalent nature of their interatomic bonding. The usual way to consolidate powdered ceramics is by mechanically compacting the powder to form a green body and then heating the body to an appropriate temperature for diffusion to take place, leading to particle-particle bonding and densification. The latter process is known as sintering, and will be discussed in greater detail later.

The occurrence of second phases can be brought about either purposefully (as in liquid-phase sintering), or may result from impurities in the starting powder. Should these phases have low melting points, then the mechanical properties at high temperatures would be greatly reduced. Silicon nitride is an example of where the presence of a second phase is beneficial. Because of its low coefficient of self-diffusion, silicon nitride powder will not sinter and densify satisfactorily. Additions are made to the powder that form an oxynitride liquid phase at high temperatures, which promotes densification and bonds the particles together. In the event that impurities such as iron, sodium or calcium are present, the liquid melting point is reduced through the formation of low melting point eutectics. This, in turn, severely degrades the high temperature mechanical properties of the silicon nitride ceramic⁴. Therefore, the powder characteristics are of critical importance on the route to producing reliable ceramics. Other defects and flaws may be introduced at later stages of fabrication, but if the starting powder is unsatisfactory, then the best mechanical properties that could possibly be achieved by the final monolithic ceramic will always be controlled by the characteristics of the starting powder.

This work deals specifically with the production of silicon nitride powder by carbothermal synthesis. The next two chapters will discuss the physical properties of silicon nitride, its applications in engineering and the primary methods by which quality silicon nitride powders are produced. In respect of the commercial manufacturing of powders, it will be shown how the properties of the powders affect the final properties of the ceramic.

CHAPTER 2 LITERATURE REVIEW

2.1 SILICON NITRIDE

Historically, the first published report concerning the formation of silicon nitride was by Wuller and Deville⁹ in 1857. Surprisingly, this was not accomplished by the reaction between the constituent elements, but from silicon tetrachloride and ammonia. Subsequent work by Sinding-Larson^{10,11}, Mehner ¹²(1896) and Johnson ¹³(1909) went on to form silicon nitride by the direct nitridation of silicon and by the carbothermal reduction of silica.

Other studies^{14,15,16} were conducted to characterize the properties of silicon nitride itself, but interest declined until the 1940's when ceramics were rediscovered as materials that exhibitied superior mechanical properties to metals at elevated temperatures. In 1944, Conway ¹⁷ identified several key areas where ceramics could be used in aircraft propulsion systems and diesel engines.

The main advantages to using ceramics components in gas turbines was seen to be the potential to increase the overall efficiency of the engine by raising the gas temperature at the turbine inlet. The application of ceramics in turbines by this time had already been looked into in Germany¹⁸, where porcelain blades were fitted to a ceramic rotor with a glass as a bonding agent. Sure enough, the engine could be run at increased turbine entry temperatures of ~230°C, but problems arose when no solution could be found to prevent thermal shock when the engine was shut down.

The early stages of development for ceramic components were plagued by failure; a result of a combination of poor mechanical design and unsatisfactory materials. In the early Fifties, silicon nitride was found to have good refractory properties¹⁹ and, as a result, was recommended as a good candidate for engineering applications.

The development of improved ceramic materials like silicon nitride, silicon carbide, and zirconia initiated renewed enthusiasm for Governmentsponsored programs for heat engine development. Japan, the U.S.A., Sweden, Germany and the United Kingdom all have such programs, and have successfully demonstrated engines that can run for many hours without failure. However, problems still arise because the components cannot be produced with intrinsically reliable properties. The reliability is lowered further by impact damage from particles entrained in the gas flow, introducing defects in the ceramic leading to component failure.

Silicon nitride and silicon carbide both have similar high temperature and mechanical properties (Table 2.1). However, silicon nitride is the preferred

	Temp. (°C)	MOR (MPa)	K _{IC} (MPa.m [‡])
Sintered Si_3N_4	$\begin{array}{c} 20\\1300\end{array}$	800 350	3.5-8
Sintered SiC	$\begin{array}{c} 527\\1100\end{array}$	$\begin{array}{r} 450\\ 450\end{array}$	4.1

Table 2.1.Mechanical properties of sintered
silicon nitride and sintered silicon
carbide^{20,21}.

material to work with, since it exhibits greater toughness and can be sintered at lower temperatures than silicon carbide. Initially, the only means of fabricating silicon nitride components was either by hot pressing green compacts of the powder, or by the reaction bonding of silicon metal powder compacts. The hot pressing method is costly and limited to components of simple geometry, whereas reaction bonding can provide complex shapes with good dimensional properties, but the mechanical strength is compromised by residual silicon metal and porosity. The development of silicon nitride based alloys, called Sialons^{22,23} (an acronym for the elemental components of Si,Al, O and N) has meant that fully dense components can now be created by pressureless sintering; this is a less costly alternative to hot pressing, with the additional advantage of allowing the fabrication of complex shapes by processes such as slip and pressure casting, and also injection moulding.

Currently, the tabrication of silicon nitride ceramic components is focussed on these technologies, particularly with respect to the effect of the nature of the starting powders. The following sections will briefly discuss the properties of silicon nitride, the densification processes, and the fabrication routes that can be used to make the silicon nitride powder.

2.1.1 The Structure of Silicon Nitride

The first evaluation of the structure of silicon nitride was carried out by Turkdogan et al.²⁴ who discovered that silicon nitride could exist in two forms: a or β . An initial estimate of the structure by Leslie et al.²⁵ mistakenly proposed that the two forms of silicon nitride were isomorphous and rhombohedral. Later, Vassiliou and Wild²⁶ maintained that the two forms were orthorhombic and hexagonal symmetry although which form was which was not stated. Shortly after this, a more rigorous study was published by Hardie and Jack²⁷, showing that a and β were both hexagonal with differing c dimensions; a being almost twice that of β (Table 2.2). Since this was the case, the differences in structural dimensions were attributed to being the result of a change in stacking sequence from ABCD... for a, to ABAB... in β . These results were later corroborated by Ruddlesden and Popper²⁸.

	a-Si ₃ N4	β -Si ₃ N ₄
а	7.749	7.609
с	5.617	2.911

Table 2.2 Si_3N_4 unit cell dimensions (Å)

Both forms of silicon nitride are comprised of tetrahedra of four nitrogen atoms with a silicon atom located in the center. A single layer of silicon nitride is made up of a ring of six tetrahedra with each nitrogen atom shared between three tetrahedra (Figure 2.1)²⁹. The a unit cell (Si₁₂N₁₆) with stacking sequence ABCD has these planes arranged such that CD is the mirror image of AB, whereas the β phase unit cell (Si₆N₈) is the simple alternation of these layers as ABAB..., isomorphic to the phenacite structure (Be₂SiO₄)²⁹.Both of the structures are hexagonal with space groups P3_{1c} and P6_{3/m} for a and β respectively.

The relationship between the two structures has been discussed frequently, there having been two schools of thought: The first that a was an oxynitride of the approximate composition $Si_{11} 4N_{15}O_{03} 3^{30}$ to $Si_{76}N_{100}O_2 1^{11}$, whereas β is the stoichiometric form, Si_3N_4 ; the second being that a and β were low and high temperature modifications, respectively. The counterargument against the latter was that the reverse transformation of β to a has not been observed. This is presumed to be due to kinetic considerations, i.e. that the reverse transformation will not occur because the solid state diffusion of atomic species is so sluggish at the transformation temperature. An alternative view has been to assume that β silicon nitride is stable at all temperatures and that a is the low temperature, metastable phase³⁷ The measurement of the thermodynamic properties of silicon nitride by Wild et





Figure 2.1: The two polymorphs of silicon nitride.

al.³³ was considered as confirmation that the predominating structure depends upon the oxygen partial pressure; a was stabilized by a high oxygen partial pressure, whereas β by a low oxygen partial pressure. However, a silicon nitride has since been synthesized with very low amounts of oxygen in the structure^{34,35}.

The direct formation of β from a is sluggish, the rate-controlling step being the diffusion of silicon and nitrogen species along the surface layers of the silicon nitride³⁶. This process was found to be accelerated by additions of liquid forming species^{37,38 39} such as magnesia. Studies of partially transformed, hot pressed material revealed that the transformation was a solution-precipitation reaction.⁴⁰

It is now widely accepted that the appearance of the two polymorphs, although still not fully understood, is related to the mechanism by which they are formed. a silicon nitride is the product of vapour phase reaction, as in the reaction between silicon monoxide gas, carbon and nitrogen, whereas β is favoured by the presence of a liquid phase. More recently, Natansohn⁴¹ has confirmed that the transformation of a to β will only occur in the presence of a liquid phase, and is enhanced by the presence of β nuclei prior to transformation.

2.1.2 Densification of Silicon Nitride

There are three main fabrication routes that are typically used to make dense silicon nitride components, namely sintering (SSN), reaction bonding (RBSN) and hot pressing (HPSN). The following will give a brief outline on the principles involved in each of the above forming processes and discuss the advantages and disadvantages in terms of the mechanical properties obtained.

2.1.2.1 Sintering Mechanisms

2.1.2.1.1 Solid State Sintering

Ceramic powders can be compacted into the required shapes by a variety of methods such as uniaxial and isostatic pressing, or slip casting. The powder compacts are known as green bodies, and can contain anywhere from 25% to 60% porosity, which must be removed in order to obtain the physical properties close to that of the theoretically fully dense material.

During sintering, therefore, the changes that occur in the compact are mainly concerned with the reduction in the amount of porosity, that is, the microstructural alterations taking place during the transformation of an originally porous compact into a strong dense ceramic.

Whatever the means by which this occurs, there are two fundamental criteria that must be met for sintering to occur, viz. a material transport mechanism and a source of energy to activate it.

Ashby⁴² identified various routes by which the transport of material could take place and are shown in Figure 2.2. Each one involves the transport of material from a source at the grain boundary to a sink or the neck between particles. The driving force for each process is derived from the particle size. For vapour phase transport, for instance, the energy is derived from the difference in vapour pressure as a function of the surface curvature. Material is transported from the particle surface, which has a positive radius of curvature and therefore high vapour pressure, to the neck, which has a negative radius of curvature and a lower vapour pressure. The smaller the particles are, the greater is the difference in curvature between the surface area and neck, and the greater is the driving force.



- 1. Surface diffusion
- 2. Bulk diffusion
- 3. Vapour diffusion
- 4. Grain boundry diffusion

Figure 2.2: Paths for material transport during sintering.

Similarly, during solid state sintering, the driving force results from the difference in free energy or chemical potential between the free surfaces of the particles and the points of contact between them. Once again, the smaller the particle size, the greater this energy difference becomes. Surface and vapour diffusion via routes 1 and 3 respectively in Figure 2.2 result in pore closure but not removal since there is no bulk material transport to enable closing of porosity. However, with bulk diffusion occurring by routes 2 and 4, material is removed from the interface between the two particles and transported to the pore. This causes the centres of particles to move closer together with the elimination of porosity, which is seen, on a macroscopic scale, as shrinkage.

2.1.2.1.2 Liquid phase sintering

Liquid phase sintering, as the name implies, requires the presence of a viscous liquid phase in between the particles at the sintering temperature. It is the liquid itself that acts as the means of material transport. Providing the liquid wets the surface of the particles, substantial capillary pressures are developed which aid densification by particle rearrangement and increase the particle/particle contact pressure. This latter effect increases the rate of material transport by solution and reprecipitation^{40,43}, and can also improve particle rearrangement through plastic deformation and creep processes.

2.1.2.2 Sintered Silicon Nitride

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The ability of a ceramic powder to densify is therefore directly dependent upon the particle size to provide a driving force for densification. However, whether or not the ceramic material will densify depends upon the ability of the species that are present to diffuse via one of the routes proposed in Figure 2.2. Ceramic materials are highly covalent so that the interatomic bonding, rather than being diffuse as in metals and ionic materials, is short and highly directional. This means that self diffusion as a means of material transport is limited⁴⁴. Interatomic bonds are neither purely ionic nor purely covalent, but are to a greater degree one or the other of the two extremes. Pauling⁴⁵ derived a semi-empirical relationship in order to estimate the ionic nature of solids. Taking alumina and silicon nitride as examples, the degree of ionic character exhibited by both materials are ~60% and <20%, respectively. It is not surprising then that alumina sinters more readily than silicon nitride. Attempts at measuring the self-diffusion coefficients in materials⁸ have shown that the values obtained for alumina are several orders of magnitude higher than for silicon nitride (Table 2.3).

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Material	Diffusion Species	Temperature (°C)	Diffusion Coefficient (cm ² .sec ⁻¹)
Al_2O_3	Al O	$\begin{array}{c} 1500 \\ 1400 \end{array}$	$ \begin{array}{r} 2x10 & 12 \\ 5x10 & 13 \end{array} $
a-Si ₃ N ₄	Si N	$\begin{array}{c} 1400 \\ 1400 \end{array}$	8x10 12 1x10 19
β -Si ₃ N ₄	N	1400	1x10-16

Table 2.3. Self diffusion coefficients for Al_2O_3 and Si_3N_4

Studies⁴⁶ on the sintering characteristics of pure silicon nitride powder showed that it was practically impossible to obtain any densification; even hot pressing did not improve matters. More recently, Danforth et al.⁴⁷ were able to fabricate fully dense pure silicon nitride by hot pressing using extremely fine powders (17 nm) with very low oxygen contents. Solid state sintering of silicon nitride is therefore possible but the complexity of the process required to produce such high quality powders is extremely costly, and so makes the process impractical.

Thus, liquid phase sintering has become the more popular means of enhancing material transport during the sintering of silicon nitride. Deeley et al.⁴⁸ found that densification of hot pressed and reaction bonded silicon nitride could be accomplished with the addition of small quantities of MgO. First reports of sintering of silicon nitride were documented by Terwilliger and Lange⁴⁹. Other liquid forming single and multi-component systems were developed from hot-pressing, such as $Y_2O_3 + Al_2O_3$ and $Y_2O_3 + MgO$. One very important contribution was the simultaneous discovery of the SiAlON system (Figure 2.3) by Jack et al.²² and Oyama et al.²³ in two separate investigations. Typical additions to Si₃N₄ are Al₂O₃, AlN, SiO₂, and, more recentlly, Y_2O_3 .

2.1.2.3 <u>Sintered Sialons</u>

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The Si-Al-O-N system has become one of the most widely investigated systems, especially those with Y_2O_3 additions. One of the disadvantages of using a liquid phase is that it limits the high temperature mechanical properties to below those of the softening temperature of the glassy phase. By devitrifying the glass into an ordered crystalline structure, the melting point increases, making the grain boundary phase more refractory. In the case of the Y-Si-Al-O-N system, yttrium aluminogarnet ($Y_3Al_5O_{12}$ or YAG) is the highest melting point, crystalline phase that can be derived from the glass; Gazza⁵⁰ reported improvements in low and high temperature creep resistance by heat treatment of Y-Si-Al-O-N.



Figure 2.3: The Si-Al-O-N phase diagram (1700°C).
The alternative to changing the nature of the glassy phase is to eliminate the liquid phase altogether by ensuring that the glassy phase and the silicon nitride are intersoluble. This is the principle used in the hot pressing of silicon nitride with $BeSiN_2^{51}$. However, the amount of work done in this field is minimal, presumably due to the highly toxic nature of beryllium compounds.

2.1.2.4 <u>Alternative Production Routes for Silicon Nitride Component</u> Fabrication

2.1.2.4.1 Hot pressing

Hot pressing (HPSN) is an alternative means of supplying pressure rather than relying on the capillary pressure alone, as is the case with pressureless sintering. Figure 2.4 is a schematic of a typical hot press. Essentially. it consists of a high temperature graphite die and punch enclosed in a gas-tight high temperature furnace. Since the operation is usually carried out at temperatures close to 2000°C, the die and punch are protected from oxidation by conducting the operation in an inert gas atmosphere. Further protection is given by coating the die and punch with boron nitride, which also prevents reaction with the powder material being pressed. Pressure is supplied by means of a hydraulic press with a water-cooled platten.

In order to hot press silicon nitride, small additions of sintering aids such as magnesia or yttria must be made in order to promote liquid formation and hence sintering. By the simultaneous application of temperature and pressure, 100% densification can be achieved, which is accompanied simultaneously by the transformation of equiaxed a to acicular β grains. These β grains, rather than being randomly oriented, become preferentially aligned perpendicular to the pressing axis⁵². This accounts for the anisotropy



Figure 2.4: Schematic of a Hot-press.

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of the mechanical and thermal properties seen parallel and perpendicular to the hot pressing direction.

Unfortunately, hot pressing can only be applied to a limited number of applications, i.e. shapes that have only a single axis of symmetry like blocks, cylinders or rings. Other more complex shapes made of hot pressed silicon nitride must be machined at great cost using diamond tooling.

The geometric limitations of hot pressing have been overcome by the development of hot isostatic pressing techniques (HIPing). Pressure is applied to the article by the application of gas pressure and can be used for densifying powder compacts and previously sintered components. Powder compacts of complex geometry must first be sealed in a deformable can, as seen in Figure 2.5, using a material such as silica or tantalum that is easily deformable at the sintering temperature. When pressure (100-200 MPa) is applied at high temperatures, the coating or cladding material deforms as the compact shrinks. This is more often referred to as cladded hipping, whereas the hipping of previously sintered components is termed cladless. The merits of using the latter method means that both the sintering and hipping can be carried out in the same furnace, and with lower pressure requirement(10MPa).

2.1.2.4.2 Reaction Bonded Silicon Nitride (RBSN)

Reaction bonded silicon nitride is a particularly attractive process for making monolithic components since complex, near-net shapes can be made with little or no shrinkage occurring during nitridation.

RBSN is made by the direct nitridation of silicon. Powdered silicon is consolidated into blocks of billets by a variety of techniques such as isostatic pressing or slip casting, and then partially sintered in argon at $\sim 1300^{\circ}$ C to



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Figure 2.5: Cladded HIPping.

increase the strength. The preform can then be readily machined to the shape of the required products. After shaping, the component is reaction bonded in a nitrogen atmosphere at temperatures between 1200 and 1450°C. The resulting product is close to the required tolerances (within 0.1%). With a porosity content of approximately 20%, the remainder is silicon nitride (60 to 90% a, with the balance being β), and residual unreacted silicon. Moulson⁵³ has detailed in depth the mechanisms involved in the production of commercial RBSN, and need not be discussed here.

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2.1.3 <u>The Influence of Powder Characteristics on Sintering and</u> <u>Mechanical Properties</u>

The previous sections have discussed the means by which ceramics, and in particular, silicon nitride can be produced, but of key importance is the development of a high strength reliable material.

Table 2.4 shows some typical room temperature four-point flexure strength, and toughness data for reaction bonded (RBSN), hot pressed (HPSN) and sintered silicon nitride (SSN). From these data, HPSN has in most

Material	Relative Density (%)	Flexure Strength (MPa)	KIC (MPa.m [‡])
RBSN	69-84	200-350	1.7-2.8
HPSN	100	620-900	4.0-7.2
SSN	98-99	799-900	3.5-8.0

Table 2.4. Mechanical Properties of Silicon Nitride.

respects the best properties, but is impractical for the manufacture of complex shapes. On the other hand, RBSN has excellent dimensional stability but the poorest mechanical properties and also poor oxidation resistance⁵³. Within these two extremes then, sintered silicon nitride is a good compromise between high strength and dimensional tolerances, with the added benefit of the ability to make complex shapes. Clearly then, the choice of the fabrication route cannot be based solely on the process that provides the most superior mechanical properties. Therefore, selection is made by optimizing the cost of production, strength and shape complexity for a particular application. The mechanical properties already detailed before suggest that SSN can develop the highest toughness, which is of great significance to the manufacturers of tool bits and other mechanical parts. The following discussion on silicon nitride powders will be related to their effects on the properties of SSN

2.1.3.1 Powder Requirements

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The mechanical properties of any ceramic are highly dependent upon the nature of the microstructure. The occurrence of defects such as pores or second phases can act as sites for crack nucleation. In 1920, Griffith⁵⁴ derived an expression in terms of the material's fracture toughness, $\sqrt{E_Y}$, and the defect size such that:

$$\sigma_f = A \left(\frac{E_Y}{c}\right)^{\frac{1}{2}}$$
(2.1)

where σ_f is the fracture stress, E the Young's Modulus of the material, γ the energy required to create new surfaces, c is the defect size, and A is a constant dependent on the defect geometry. A more general relationship has been presented by Evans & Tappin⁵⁵ to take account of crack geometries, but the principle remains the same.

In terms of a ceramic material, the quality and reproducibility of the mechanical properties is directly related to the size of the largest defect

present. During the fabrication process of a ceramic, care must be taken in order to prevent the introduction of microstructural flaws resulting during sintering of the powder, from impurities (dust, lint, and extraneous material), and also introduced as machining flaws. The mechanical properties seen in Table 2.4, when viewed in conjunction with the relative density, clearly show how closely related they are to the condition of the microstructure.

The flexure strength as a function of temperature for silicon nitride (Figure 2.6⁵⁶) bears out much the same relationship, with the strength being greatly reduced above 1200°C.

2.1.3.1.1 Particle Size

The particle size must be extremely small $(<1\mu m)$ in order to provide the high surface free energy that acts as the driving force for densification. Since diffusion coefficients of silicon and nitrogen in silicon nitride are extremely low, the required diffusion distances for sintering can be decreased by using ultrafine powders, as discussed earlier.

2.1.3.1.2 Particle Size Distribution

The question of which is the best particle size distribution to have, i.e. narrow or broad, is a controversial one since different benefits can be gained from both. Simply put, a broad distribution results in high green densities and low shrinkage upon firing, but the degree of shrinkage is not necessarily uniform. A narrow distribution powder on the other hand, is difficult to compact, giving poor green densities and large but uniform shrinkage upon firing

The differences in shrinkage between the two distributions comes from the efficiency of packing of the powder particles. Assuming ideal packing, mono-



Figure 2.6: 3-Point MOR strengths of silicon nitride ceramics.

size spherical particles could give an ideal green density of 74%. Perfect packing might be achieved over a short range but, over the long range, disruptions in the ordering in the form of voids and packing defects occur⁵⁷ in a similar manner to the modelling of dislocations, vacancies and grain boundaries by the bubble raft⁵⁸ analogy. This means that a large amount of porosity (~40%) may have to be removed in order to achieve full densification. Therefore, higher green densities can be achieved using a broad distribution where small particles can fill up the extra void space, thus leading to much less overall shrinkage. However, inhomogeneities in the particle size distribution within the green compact cause localized differential shrinkage when sintering. Thus small cracks and voids can open up as a result of the stresses induced in the regions of variable particle size.

Another problem with having a broad particle size distribution is that large grains will grow at the expense of the adjacent smaller grains. The grain size must be kept as small as possible since large grains are detrimental to the mechanical strength. The existence of large grains in a fine grained microstructure are viewed as being similar to that of inclusions in an otherwise homogeneous matrix⁵⁹. Large stresses can develop at the interface between the inclusion and the interface as a result of mismatch in expansion coefficients of two materials given by Equation 2.2^{60} :

$$\sigma_{r} = -2\sigma_{t} = -\frac{(\alpha_{m} - \alpha_{l})\Delta T}{\frac{1 + v_{m}}{2E_{m}} + \frac{1 + 2v_{l}}{E_{l}}} \left(\frac{R}{r^{*}}\right)^{3}$$
(2.2)

where $\sigma_r = radian stress$

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 σ_t = tangential stress

i = inclusion

- m = matrix
- a = thermal coefficient of expansion
- v = Poisson's ratio
- E = Young's modulus
- R = Inclusion radius
- r^* = radial distance from inclusion
- ΔT = difference between ambient temperature and the temperature prior to the onset of stress relaxation

In some cases, these stresses alone can be large enough to initiate a crack which, in itself, becomes a critical flaw upon loading. In addition, if the elastic moduli of the inclusion and matrix differ, then the inclusion also becomes the source of stress concentration⁶¹ when the matrix is subjected to an applied stress. Failure in ceramics caused by inclusions is seen as being a complex combination of the residual stress due to thermal expansion mismatch and stress concentration.

In general, the thermal expansion coefficients seen in non-cubic single crystals are anisotropic, whereas the overall expansion coefficient of a randomly oriented, fine grained, polycrystalline material is isotropic. Thus, in much the same ways as for inclusions, large grains can produce large interfacial stresses and also result in stress concentration.

A broad particle size distribution can therefore lead to enhanced grain growth, with large grains growing at the expense of the smaller ones. This state of affairs need not arise if all of the particles were much the same size as in a narrow size distribution.

Barringer et al.⁶² have postulated that the advantages of monosized powders are:

- 1. Ease of processing uniform microstructures, resulting in greater control of the sintered grain size and porosity.
- 2. Modification of sub-micron powder surface properties so that dispersion in a liquid phase and subsequent deposition as an ordered green body can be achieved.

By adopting these views, the authors suggest that liquid phase sintering, primarily responsible for particle rearrangement, becomes unnececessary when uniform microstructures are possible with monosized particles. The alternative view is held by Sacks et al.⁶³ and Gauthier et al.⁶⁴ who have investigated the use of wide and selected bimodal distributions of ceramic powders. In the former study, broad and narrow distributions of alumina powders resulted in much the same sintered microstructure.

The densification of silicon nitride requires the presence of a liquid phase, not only for particle rearrangement, but also for the dissolution of a and precipitation of β . So that there may, in fact, be little advantage to using a monosized powder; a wider distribution would, therefore, have the advantage of higher green density, green strength and reduced porosity, although there is no absolute proof of this.

A contributing factor to the green density is particle morphology: particles with high aspect ratios, when randomly oriented, will pack very inefficiently in the green state with large amounts of residual porosity⁶⁵. This has become a particular problem when trying to incorporate whiskers into ceramic matrices in order to improve the fracture toughness characteristics. The whiskers become agglomerated with large amounts of unfilled void space within the aggregate. However, with respect to non-composite ceramics, the ideal particle morphology is equiaxed rather than completely spherical. It

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has been suggested⁶⁶ that equiaxed particles pack more efficiently due to their slight irregularities.

2.1.3.1.3 The Effect of The α - β Transformation

The mechanical properties and, in particular, the fracture toughness of fully dense silicon nitride is derived from the acicular nature of its microstructure⁶⁷ This comes about as a result of the transformation of equiaxed a particles to acicular β particles during the densification process. The β particles are nucleated on pre-existing β particles in the α phase, which grow at the expense of α via the liquid phase. The aspect ratio of β that develops is dependent upon the initial quantity of pre-existing β , assuming that growth only occurs parallel to the prismatic axis. The relationship between the aspect ratio (R) and the α/β ratio in the starting powder has been suggested by Lange ⁶⁸ as being:

$$R = 1 + \frac{\alpha}{\beta} \tag{2.3}$$

Therefore, high a-silicon nitride powders are required for fabrication, but it is noted that this relationship breaks down when α/β , whereupon it is thought that heterogeneous nucleation of β (presumably on α) is supposed to predominate.

2.1.3.1.4 Powder Impurities and Their Effects on Sintering and Mechanical Properties

Direct comparisons between the commercially available silicon nitride powders are difficult to make due to the great variability in the occurrence of particular elemental species. Depending on which method is used to make a particular powder, this allows for the introduction of elemental species characteristic of that process.

The most common impurity is oxygen, in the form of silica, and is usually a result of the direct oxidation of the particle surface. Silica has a higher free energy of formation than values often quoted for silicon nitride and, as such, the oxidation product of the latter will always be silica. It is well understood⁶⁹ that this reaction takes place quite readily at room temperature in the presence of air or humid atmospheres, although the kinetics are quite slow. However, powders such as those produced by plasma synthesis, with particle sizes well below the sub-micron range (<30nm), are even more susceptible to oxidation due to their highly reactive nature. A more recent study⁷⁰ has suggested that oxygen may also be contained within the particles themselves and is very much dependent upon the preparation process that was used; a high internal oxygen content is characteristic of direct nitridation and carbothermal reduction processes, whereas decomposition of silicon diimide (section 2.1.4) is the opposite. The oxygen content in itself is not detrimental to the high temperature performance of the ceramic since it is a principal constituent in silicon nitride-based alloy systems, such as the Si-Al-O-N system. Instead, allowance can be made for the oxygen already present in the silicon nitride powder when calculating the additions necessary for a particular sialon composition. The major source of the degradation in the high temperature mechanical properties arises from the reaction of the silica, associated with the silicon nitride, interacting with other impurities in the powder

Impurities such as iron and alkali elements like sodium, potassium and calcium, can all form silicates with significantly lower melting points (e.g FeSiO₃ with $T_m = 1150$ °C; Na₂Si₂O₅, $T_m = 874$ °C)⁷¹than say a Y-Si-Al-O-N

glassy phase ($T_m \approx 1500 \ ^{\circ}C^{72}$), the intergranular liquid phase present in many Y-Sialon materials. Therefore, at high temperatures, low melting point phases in the grain boundaries reduce the viscosity of the glassy phase and lead to enhancement of creep processes.

Halogens such as chlorine and fluorine are also seen as undesirable impurities. Both of these elements, but more particularly chlorine, are thought to inhibit the dissolution of nitrogen⁷³ in the intergranular glassy phase. This, in turn, retards the a to β transformation which takes place by solution precipitation reaction via the liquid phase. In some Y-Si-Al-O-N compositions, the formation of the crystalline intergranular phase known as N-YAM solid solution (Y₄Al₂O₉-Y₄Si₂O₇N₂)₅₅ is inhibited by the presence of chlorine, in favour of amorphous Y₂SiO₅ glass. This is seen as being direct evidence that the nitrogen solubility is greatly reduced by the presence of chlorine. The lack of nitrogen in the glassy phase results in a drop in the viscosity and softening temperature of the grain boundary phase, and consequently decreases the high temperature properties of the material

Fluorine has been observed to have an additional effect⁷⁴ on the surface chemistry of silicon nitride powders in that such powders are difficult to disperse in aqueous media. This is of prime importance in fabrication processes such as slip casting, where powder consolidation must proceed via well dispersed, as opposed to flocculated particles.

Carbon is another impurity that has been reported as having a deleterious effect on the high temperature mechanical properties of silicon nitride based ceramics. It is usually associated with silicon nitride powders produced by carbothermal reduction of silica, but can also be introduced during milling operations which use carbide milling media Initially, it was thought that carbon reduced the oxidation resistance of grain boundary crystalline phases such as N-melilite, produced in hot pressed Y-Sialons⁷⁵. However, Hampshire and Jack⁷⁶ showed that it was N-melilite itself that caused the poor hightemperature oxidation resistance; the specific volume change occurring during oxidation of N-melilite is about 30%. It was found that the carbon reacts with the surface silica on the silicon nitride powder, resulting in the evolution of SiO gas which therefore moves the overall composition into a phase field containing N-melilite. Thus, when using silicon nitride powders with significant carbon contents, the additive content must be adjusted such that N-melilite formation is avoided.

2.1.4 Silicon Nitride Powder Production Routes

Silicon nitride can be produced by several different routes. Commercially, the most important has been the direct nitridation of silicon^{''7,78,79} by:

$$2S\iota_{(s)} + 2N_{2(\sigma)} = S\iota_{3}N_{4(s)} \qquad 1450^{\circ}C \tag{2.4}$$

This is the method used by H.C. Starck Gmbh. of Germany in the manufacture of their range of powders. The reaction between silicon and nitrogen is highly exothermic, and extreme care must be taken to control the reaction temperature to prevent the melting of the silicon powder. Should the reaction get out of control and the silicon melt, complete nitridation becomes virtually impossible. Despite careful control of the temperature, the a-silicon nitride so formed is heavily agglomerated and must be milled in order to obtain fine powders. The milling procedure is one of the principal sources of iron and tungsten contamination, arising from the milling media.

The powders are purified by treatment with hydrogen fluoride, which serves to remove residual silicon and silica in addition to iron. In so doing, the powders can become contaminated with fluorine, the effects of which were mentioned earlier.

Another alternative is to proceed via a vapour phase reaction, between either silicon tetrachloride or silane and ammonia, by one of the following reactions:

$$3S_{i}Cl_{4(g)} + 4NH_{3(g)} = S\iota_{3}N_{4(s)} + 12HCl_{(g)}$$
(2.5)

or

$$3S\iota H_{4(g)} + 4NH_{3(g)} = S\iota_3 N_{4(g)} + 12H_{2(g)}$$
(2.6)

Using the correct reaction conditions, very fine amorphous silicon nitride can be produced. The limitations on production are either equipment corrosion problems, as with Reaction 2.5, or the prohibitively high cost of silane gas. Various methods have been developed despite these drawbacks by either using a simple tube furnace⁸⁰ design or by making use of laser or gas plasmas^{81,82} to drive the reactions. Powders formed using these last two methods are characteristically ultrafine (<1µm) and amorphous; once again, the capital outlay for the process equipment is high, but the powders produced also tend to have high oxygen contents in the form of a surface layer of silica As was previously stated, the particles are so fine that they readily react with oxygen or moisture in the atmosphere and, therefore, must be kept and processed under an inert gas atmosphere.

Another method similar to Reaction 2.5 is the production of silicon diimide⁸³ at zero degrees celcius as Reaction 2.7:

$$SICl_{4(l)} + 6NII_{3(l)} = S_{(NH)} + 4NH_{4}Cl_{(s)} \qquad (0^{\circ}C)$$
(2.7)

Once the ammonium chloride is removed with liquid ammonia, the silicon diimide is first given a polymerization heat treatment, and then pyrolyzed at 1100°C in nitrogen to produce amorphous silicon nitride. Subsequent heat treatment at temperatures greater than 1430 °C converts this to a-silicon nitride. This met¹ d is the route taken by UBE Industries Ltd.⁸⁴ and Ford Motor Co⁻⁵⁵ duce fine silicon nitride powders. The UBE-SNE10 powder is advet¹ d as having a low chlorine content of 100 ppm (Braue et al.⁷² obse deleterious effects due to chlorine at approximately 400 ppm), low exygen content of 1.2wt.%, and a measured average particle size of 0.2µm. This is by all accounts an excellent powder, but the major drawback in production is the elimination of oxygen from the system in Reaction 2.7, which is costly in terms of equipment and running costs.

Other pyrolyzation techniques for the production of amorphous silicon nitride powders involve the controlled decomposition of organosilicon compounds⁸⁶ such as polycarbosilane and methylchloropolysilanes. These routes are not popular because of the high cost of the precursor materials. It is reasonable to suppose that production costs would decrease if there were sufficient demand.

CHAPTER 3

CARBOTHERMAL REDUCTION OF SILICA

3.1 BACKGROUND

The previous chapter outlined the different methods that are currently available for making silicon nitride; however, none of these processes necessarily produces the "ideal" powder. Instead, there is usually at least one drawback to each of the processes (including carbothermal reduction) in terms of purity and particle size of the silicon nitride produced, the cost of the precursors, or even the production costs. The selection of the processing route becomes a choice between the price of the powder and the inherent disadavantages of using that powder to fabricate monolithic ceramic components.

When considering carbothermal reduction, the resulting silicon nitride powder will more than likely be contaminated with excess carbon and probably have a high oxygen content. However, from the point of view of starting materials, carbothermal reduction of silica to silicon nitride would appear to be one of the most cost-effective options available; carbon and silica are two of the most abundantly available materials, particularly silica. It is estimated that 45.16% of the Earth's upper mantle consists of silica

At the turn of the century, carbon was well known for its properties as a strong reducing agent and was in great demand in the iron and steel industry. It is not surprising that carbothermal reduction of silica was among one of the first methods used to make silicon nitride. In 1896 the first patent for the process was granted to Mehner¹² of Germany, shortly followed in 1909 by Johnson¹³ and 1910 by Sinding-Larsen¹⁰. Much of the interest in silicon nitride was more as an intermediate step in the production of ammonia than for its ceramic properties. However, this was short-lived due to the discovery of the Haber process for making ammonia.

At the present time, Toshiba is the only company producing powders by this method commercially, the most widely used powders being those derived from the direct nitridation of silicon, and from the imide process. Monolithic ceramic articles made from carbothermally produced silicon nitride are usually found to have poor mechanical properties⁷⁷, however recent work⁴⁷ would indicate that superior mechanical properties can also be developed from these powders.

3.2 THE REACTION

In principle, the carbothermal reduction of silica is a relatively simple reaction a mixture of silica and carbon is heated at the appropriate temperature in nitrogen for a sufficient period of time and the reaction proceeds according to:

$$3S_{lO_{2(s)}} + 6C_{s,j} + 2N_{2(g)} \rightarrow S\iota_{j}N_{4(s)} + 6CO_{(g)}$$
(3.1)

This only describes the overall reaction, and stoichiometric mixtures of silica and carbon do not necessarily result in silicon nitride. Under the correct conditions, the chief reaction stages as initially proposed by Lee et al.³⁹ were as follows:

Silica is reduced by carbon to silicon monoxide gas and carbon monoxide:

$$S_{iO_{2(s)}} + C_{si} = S_{iO_{(g)}} + C_{(g)}$$
 (3.2)

whereupon more silica is reduced by carbon monoxide in the reaction:

$$S\iota O_{2(s)} + CO_{(g)} = S\iota O_{(g)} + CO_{2(g)}$$
(3.3)

with carbon monoxide being regenerated by reaction:

Å

$$C_{(g)} + CO_{2(g)} = 2CO_{(g)}$$
(3.4)

Silicon nitride is formed by the reaction between silicon monoxide gas and nitrogen with carbon as:

$$3S_{i}O_{(g)} + 3C_{(g)} + 2N_{2(g)} = S_{i}N_{4(g)} + 3CO_{(g)}$$
(3.5)

which will be referred to as the gas-solid reaction. One possible alternative to this is the formation of silicon nitride via the following gas phase reaction:

$$3S\iota O_{(g)} + 3CO_{(g)} + 2N_{2(g)} = S\iota_3 N_{4(g)} + 3CO_{2(g)}$$
(3.6)

The rapid rate of reaction to form silicon nitride, as seen by Szweda⁹⁰, was thought to be due to the reaction between silica and carbon monoxide (Reaction 3.3.), since this would be more rapid than for silica and carbon. Higgins⁹¹, who conducted work on the carbothermal reduction of kaolinite to sialon (a similar system to Si-O-N-C, but also containing aluminium) found that as the CO content of the reaction gas (N₂) increased to 16%, Sialon formation decreased, and was replaced by silicon carbide. By increasing the carbon monoxide content still further to 18%, silicon carbide formation was completely suppressed; the only residual remaining phases being multite and amorphous silica. By making parallel comparisons between the two systems, since the two are quite similar, it would appear from Higgin's work that the carbon monoxide partial pressure must be maintained at a low level in order to maximize the formation of silicon nitride. Alternative or additional steps to the formation of Si_3N_4 have also been proposed. For example, Lee and Cutler⁹² suggested silicon carbide as an intermediate step in the formation of silicon monoxide gas according to the reaction sequence:

$$SiO_{2(s)} + 3C_{(s)} \rightarrow SiC_{(s)} + 2CO_{(g)}$$

$$(3.7)$$

(0,0)

and then

$$2SiC_{(s)} + SiO_{2(s)} + 2N_{2(g)} \rightarrow Si_{3}N_{4(s)} + 3CO_{(g)}$$
(3.8)

or

$$S_{iC_{(g)}} + S_{iO_{2(g)}} = 3S_{iO_{(g)}} + CO_{(g)}$$
 (3.9)

However, no other studies have ever reported seeing silicon carbide in incompletely reacted products containing silicon nitride and so that would appear to be an unlikely reaction step, unless Reaction 3.8 was very rapid. Other studies^{93,94} have reported silicon carbide as an intermediate phase in the production of SiO gas, but these were all done under inert atmosphere.

Barnitskaya et al.⁹⁵ state that pure silicon nitride cannot be obtained from carbon, silica and nitrogen alone: they report that the maximum amount of silicon nitride attainable is only a few percent, the balance being silicon carbide. In order to obtain a higher yield of a-silicon nitride, small additions of iron were made to their starting material. As a result, they proposed that silicon nitride grew from a molten intermediate compound - a form of iron carbosilicide - by a complex series of reactions. This is quite contrary to Siddiqi and Hendry ³¹ who have shown that iron impurities promote the formation of silicon carbide, not silicon nitride.

3.2.1 Back Reactions

In addition to the reactions stated above, there are several possible back reactions that must be considered for completeness and they are shown below

$$SiO_{(g)} + CO_{(g)} = SiO_{2(s)} + C_{(s)} = (\Gamma \le 1500 \ \text{C})$$
 (3.10⁵⁰)

$$3StO_{(g)} + CO_{(g)} = 2StO_{2(s)} + StC_{(s)}$$
(3.1197.98)

$$2SiO_{(g)} = Si_{(g \text{ or } l)} + SiO_{2(s)}$$
(3.12%)

$$SiO_{(g)} + 2C_{(s)} = SiC_{(s)} + CO_{(g)}$$
 (3.13%)

$$SiO_{(g)} + 3CO_{(g)} = SiC_{(s)} + 2CO_{2(g)}$$
(3.14⁹⁹)

A further reaction was suggested by Hendry and Jack ¹⁰⁰ whereby silicon nitride reacts with oxygen, a frequent impurity in the nitrogen feed gas, i.e.,

$$2S\iota_{3}V_{4(s)} + 3O_{2(g)} = 6S\iota O_{(g)} + 4N_{2(g)}$$
(3.15)

This is similar to the volatilization of silicon nitride seen 5^{22} during the liquidphase sintering of Si₃N₄ and of Sialons, where silicon nitride reacts with silica in the liquid as:

$$St_{3}N_{4(s)} + 3StO_{2(l)} = 6StO_{(g)} + 2N_{2(g)}$$
(3.16)

and results in the formation of gas porosity and even bloating of the component during firing. The forward reaction sequence and the possible back reactions that can also occur illustrate the complex nature of the Si-O-N-C system. Since all of the above reactions are either gas phase or gas-solid reactions, then by application of Le Chatelier's Principle(section 4.2 1.2), their equilibrium positions are strongly dependent upon the partial pressures of carbon monoxide, silicon monoxide and nitrogen gases. That being the case, the outcome of carbothermal reduction is very sensitive to the manner in which the reaction is conducted. Such considerations are: (i) the nitrogen gas purity and flow rate, (ii) starting material purity, (iii) the degree of precursor mixing, and (iv) powder compaction.

3.2.2 Reaction Time and Temperature

For laboratory scale experiments, based on either weight $loss^{90}$, XRD 90,101 or nitrogen content 102 of the final powders, the reaction time for the production of silicon nitride has been found to be close to five hours. Lee et al. 92 report the reaction time as being closer to three hours from weight loss experiments, however, these results were influenced by small additions of iron (5wt%).

Regarding the reaction temperature, there is a great deal more discrepancy[.] The lowest temperature stated for the reaction was 1350°C by Cutler^{10.3} apparently in the production of silicon nitride from rice hulls. A number of other investigations^{101 104,105} have placed the reaction temperature at 1400°C or higher still, between 1450-1470°C by Figush & Liko¹⁰⁶, Mori et al ¹⁰². Siddiqi et al.³¹ and Szweda et al.⁹⁰ recognize a higher temperature of 1500°C as being more appropriate.

At temperatures in excess of these, β -silicon carbide is always the predominant phase with several reports^{90–107} defining the minimum temperature required for 100% silicon carbide formation as 1600°C. The low

temperature of reaction seen by Cutler was explained by Hendry and Jack ¹⁰⁰ to result from the activity of carbon derived from rice husks being much higher than unity. This, when applied to Reaction (3.17), with the thermodynamic data considered,

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$$3S_{i}C_{(s)} + 2N_{2(g)} = S_{i_{3}}N_{4(s)} + 3C_{(g)}$$
(3.17)

would lead to a decrease in the temperature required to produce silicon nitride.

Another consideration that must be taken into account is the purity of the starting material. Rice husks are not necessarily a high-purity source of carbon, and typically they have mineral impurities such as sodium, potassium, iron and calcium which must be removed prior to nitriding ¹⁰⁸ The presence of these impurities and their effects on the nitridation kinetics are not known.

As discussed in the previous section, the Si-O-N-C system is very sensitive to variations in the partial pressures of the gaseous species, such as carbon monoxide and silicon monoxide. The ways in which these partial pressures vary depend upon the manner in which the experiments are carried out. Examples of such variables are the actual gas flow rate or velocity and the ability of the gas to flow through the reactants. The latter is related to the size and shape of the crucible, which can affect how much of the flowing gas bypasses or short-circuits the reactants. Other constraints, such as powder compaction into pellets, could have similar consequences by restricting the free flow of gas through the reactants. Variations in parameters such as these may bare affected the results of previous research work. One case in point is the broad range of reaction temperatures reported, these may be due to any of the reasons mentioned above, or even the way in which the temperature was measured. Precise details concerning the experimental set-up and procedure are rarely reported, and so it is often difficult to compare one set of data to another.

3 2.3 The a to β Silicon Nitride Transformation

The form of silicon nitride produced during carbothermal reduction is usually reported as being predominantly a with trace amounts of β (~5-10%). Most report that the a content of the resulting powders are at least 95% since 5% is the minimum detection limit for most X-ray diffraction equipment, the method generally used for phase analysis.

Hendry and Jack¹⁰⁰ showed that the development of a in preference to β was directly related to the partial pressure of the SiO gas: the limit being approximately 0.07 atm. A high β (>5%) product was obtained at lower SiO gas partial pressures, which could be fully transformed to β by a second step involving the heat treatment of the product at 1500°C in a 80%N₂:20%H₂ reducing atmosphere. This was thought to be due to the removal of the surface layer of silica remaining on the silicon nitride which is presumed to prevent the α to β transformation. However, it is well established (Section 2.1.1) that the α to β transformation always requires the presence of a liquid phase. Therefore, the mechanism for the α to β transition discussed by Hendry and Jack¹⁰⁰ is somewhat unclear and may in fact be incorrect, based on more recent work.

3.2.4 Starting Materials

3.2.4.1 <u>Silica</u>

Fine particle silica is produced in a number of different ways and can be used as a precursor for carbothermal reduction. One of the most common forms used is fumed silica.¹⁰⁹ made by the pyrolysis of silicon tetrachloride in a flame of hydrogen and oxygen. The resulting powders are extremely pure since silicon tetrachloride precursor is a liquid and can be purified with relative ease. The particle sizes of the powders are also extremely fine although they are not of uniform shape; instead, they have a reticular structure made up of chains of very small particles that are fused together (see Chapter 6-1, Figure 6.1). Typically, fumed silicas have a highly active surface, making them extremely hydrophilic. The surface chemistry of silica will be discussed birefly in Section 3.2.6.1 on silica sols. A more complete discussion is given by $ller^{110}$

Other alternative precursors are silica sols and powders which can be made either by the hydrolysis of silicon compounds or by the neutralization of soluble silicates with acids. The former method, first developed by Stober et al.¹¹¹, is accomplished by hydrolyzing a lower alkyl silicate (typically tetraethyl orthosilicate (TEOS)) in an alcohol medium containing water and ammonia. This material was used by Zhang and Cannon¹⁰¹ as the source of silica for carbothermal reduction. However, one disadvantage with using organosilicate routes is that the maximum solids loading of the final silica in the sol is very low (~10%).

The neutralization of soluble silicates with acids results in the form known as precipitated silica. Sodium silicate is the most common precursor and, when suitably diluted and acidified, becomes a sodium stabilized sol of silicie acid. The colloidal particles of silicie acid are then grown into a precipitate by further additions of sodium silicate and acid. A variety of methods are available to obtain precipitated silica powders with very different characteristics¹¹² such as purity, surface area and morphology. The major disadvantage in their use as precursors for silicon nitride production is the presence of residual sodium (typically 0-1-1%), the deletereous effect of sodium on high temperature properties of silicon nitride were discussed earlier (Chapter 2.1.3.1.4). One option is to use an ammonium silicate as the starting material, but this tends to result in a more costly product. Despite this, many varieties of high surface area precipitated silicas are now commercially available and prepared in a similar manner to the above; these are advertized as having low sodium content (e.g. Degussa FK320DS precipitated silica<0.5%Na).

Very little published work on carbothermal reduction reports the use of precipitated silica, possibly due to sodium contamination; one exception is that of Hendry and Jack¹⁰⁰ who, in subsequent studies ^{90,31}, went on to work with fumed silicas.

One interesting source used by Perrera¹⁰⁵ was the precipitation of colloidal silica from the geothermal waters of Wairakei, New Zealand. The particles were colloidal in size ($<2\mu$ m) and contained only very small quantities of iron and sodium (Fe<0.006%, Na \approx 0.3%, Ca \approx 0.07%).

3.2.4.2 <u>Carbon</u>

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Carbon can be obtained in a variety of forms and from numerous different sources, e.g. carbon blacks, charcoal, coke, pitch and from starch and other organic compounds. Carbon blacks are made from the partial combustion of residual aromatic hydrocarbons; usually the heavy residue from the distillation of crude oil. The grade or fineness of the product is dependent upon the extent of oxidation of the final product.

Carbon black powders also have extremely fine particles, and are similar to fumed silica in that they form aggregates of primary particles (Figure 3.1)¹¹³. Each primary particle is itself made up of concentric layers of crystallites, as shown schematically in Figure $3.2(a)^{114}$. The surface area of the particles can



Figure 3.1: TEM micrograph of a typical carbon black.



100Å NORMAL PARTICLE



(b)

(a)

Figure 3.2: Schematics of carbon black particles.

be increased by a secondary processing stage after formation. The porosity produced in the primary particles is directly related to the amount of oxygen used to oxidize the powder. The crystallites which have a high aspect ratio preferentially oxidize perpendicular to their long axis, and since they are all aligned concentrically in each primary particle, the oxidation process causes channels to open up (Figure 3 2(b)). Therefore, the surface area of the powders can be varied according to the degree of oxidation.

Carbon blacks have been by far the most popular form of carbon used in the research of the carbothermal reduction process; they are extremely fine powders that can be readily mixed with other powders in either the dry state or in some dispersing medium (see Section 3.2.6).

Another source of carbon is pyrolyzed starch, which has been investigated by Zhang and Cannon¹⁰¹ and found to be reasonably satisfactory for the production of silicon nitride. However, starch gives a poor yield of carbon (approximately 15%) due to the high oxygen content of the starch molecule. Much better yields of carbon can be obtained from other organic sources. One such material is polyacrylonitrile (PAN) which has a carbon yield of around 50% and is the most preferred precursor in the manufacture of carbon fibers. This source of carbon has been the basis of the patent issued to Toray¹¹⁵ for the carbothermal reduction of silica to silicon nitride and also the subject of similar work by Sugahara et al.¹¹⁶ in the carbothermal reduction of Montmorillonite.

Production of silicon nitride from other sources of carbon, such as from pine tar and pitch, have recently been the subject of patents issued in France¹¹⁷ and Germany¹¹⁸. The previous section showed that rice hulls are a good source of silica, but they will also yield carbon by thermal decomposition of the cellulose, which makes up 80 wt.% of the husk However, cellulose having similar carbon and oxygen content to starch also has a poor yield of carbon of around 15%. At best, the ratio of carbon:silica (3:1) satisfies the stoichiometric requirement for the formation of pure silicon nitride; whether or not this is satisfactory will be discussed later.

3.2.5 Mixing of Precursors

There are two options available for the mixing of silica and carbon: either by mixing the powders mechanically in the dry state, or by dispersing the two materials in a liquid medium to form a sol, and then driving off the liquid to form a solid gel.

It is assumed that much of the literature available on carbothermal reduction relates to the dry-mixing of silica and carbon powders since in many cases no mention is made of the mixing conditions. The first study into the relative merits of dry mixing and sol-gel processing was conducted by Szweda et al.⁹⁰ who used a water-based sol to disperse carbon black and fumed silica. This method could produce silicon nitride high in a (85%) with small amounts of β silicon nitride (5%), silicon carbide (5%), and silicon oxynitride (5%). The presence of silicon oxynitride was thought to be related to the residual moisture content of the dried gel producing a significant partial pressure of oxygen during the reaction. In comparison, the dry-mixed precursors resulted in silicon nitride consisting entirely of the a phase.

The sol-gel approach was therefore seen as a useful method of handling silica and carbon, but not necessarily a good route regarding the formation of a quality silicon nitride powder. No mention was made of the use of other dispersing liquids that could be used to form a sol that would reduce the occurrence of secondary phases such as silicon oxynitride.

3.2.5.1 Silica Sols

The surface chemistry of silica has been reviewed in great depth by Her^{1,3}, so that this review will only be concerned with those facts pertinent to the current work.

Silica, and especially fumed silica, owe much of their complex chemistry to the nature of the surface of the primary particles. Fumed silica has a surface consisting of three different groups: siloxane groups, hydroxyl and hydrogen bonded hydroxyl groups, each shown schematically in Figure 3.3. The siloxane groups, being non-polar, are hydrophobic but can hydrogen-bond with water as shown in Figure 3.4. The hydroxyl groups become attached during the pyrolyzation process and are hydrophilic, as are the hydrogen-bonded hydroxyl groups that become attached by the reaction with water. The latter can bind adjacent to the primary hydroxyl groups or directly with the siloxane groups. The presence of these surface groups makes the silica particles capable of hydrogen-bonding with other materials like liquids so that, provided the particles are small enough ($< 0.1 \mu m$), they can form stable colloidal dispersions as a result of this bonding, to form a sol.

The dispersing liquids can be categorized ¹¹⁹ into three main groups: Group I for polar hydrogen-bonding liquids; Group II for medium polar mediumhydrogen bonding liquids; and Group III for non-polar non-hydrogen bonding liquids.

Examples of Group I liquids are water, the lower alcohols (ethanol, butanol) and short-chain polyalcohols. Group II is the broadest category consisting of the higher alcohols, some oils, plasticizers and resins. Group III are mineral oils and hydrocarbon solvents such as benzene, toluene, hexane and mineral spirits.



Figure 3 3: Surface characteristics of fumed silica.



Figure 3.4: Bonding of siloxane groups with water.

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It is believed that fumed silica more readily forms hydrogen bonds with the Group I liquids rather than itself, whereas in Group II, and particularly in Group III, this occurs to a lesser extent and the silica joins up to form networks, which increases the viscosity of the sol The outcome is that greater solids loading can be achieved with Group I liquids for a given viscosity than Group II or III liquids This means that silica can be used in a variety of liquid systems to adjust its rheological properties according to their end use, e.g. as additives to paints, foods, toothpaste, etc.

Further reference will be made to fumed silica/liquid systems in the discussion.

3.2.5.2 Carbon Dispersion

Carbon blacks do not have the same surface properties as silica; this being the case, they do not hydrogen bond readily with liquid systems and so do not form a stable sol However, the carbon particles are so fine that it takes a long period of time before they will settle out, thus additions of carbon can be made to a silica sol prepared by the methods just described, without any noticeable separation. This is one approach to preparing intimate mixtures of silica and carbon and was the method used by Szweda et al.⁹⁰.

The alternative to this it to dissolve a high carbon yielding organic polymer in a suitable solvent, and then disperse the silica in the solvent/polymer mixture to form a sol. This is the method used by Toray¹¹⁵ and others ¹¹⁶ where PAN is dissolved in, for example, an organic solvent, and once dissolution is complete, silica can be dispersed in the mixture and dried to a gel at 80-120°C. The PAN silica gel is then partially oxidized in air at 220-350°C, whereupon the PAN polymer undergoes oxidative degradations which alters its chemical composition to that of a higher carbon content; a process known as cyclization. Once this process is complete, the pellets are heated in a nitrogen atmosphere at a temperature of 1500°C, by which time the cyclized PAN has completely decomposed into carbon, and carbothermal reduction of the silica can then take place to form silicon nitride.

The ultimate difference between the two methods of preparing sols described here can be seen in two ways: either as silica particles coating carbon particles, as in the first method, or as carbon coating the silica particles in the second method. The interpenetration of PAN into layered minerals such as montmorillonite (Na₀₋₃₃(Al₁₋₆7Mg₀₋₃₃0[Si₄]O₁₀(OH)₂.nH₂O) to form intercalation¹¹⁶ compounds is seen as another example of this latter method. In principle, a sol-gel technique offers superior mixing conditions betwen two components on a molecular scale than any other technique. On the other hand, dry mixing of materials, although able to provide good mixing on a macroscopic level, could not possibly hope to attain separation of small agglomerated powder particles as can be achieved during sol-gel processing.

3.2.6 Carbothermally Produced Silicon Nitride Powder Morphology

Ideally for the manufacture of monolithic ceramics, silicon nitride particles are required to be equiaxed, but not necessarily spherical, have a narrow size distribution and be less than 1 μ m in diameter. Only in very few publications can the final product truly be called particulate. In most cases, the silicon nitride is very fibrous or consisting of straight whiskers¹⁰² or, in others, the silicon nitride forms as convoluted ribbons ^{90,31,102}. When individual particles are seen, they appear almost hexagonal in cross-section^{101,105,106} and approximately 2-3 μ m in diameter. The fact that they are hexagonal in crosssection suggest that they are single crystals. Mori et al ¹⁰² observed that the difference between the particulate and ribbon morphologies was related to the
nitrogen content of the powder products; the fibrous particles having a low nitrogen content and the hexagonal particles having a high nitrogen content.

The only other instances where particles have been produced was when the silica and carbon mixtures were seeded with very fine $(0.5\mu m)$ a silicon nitride particles, the effect of which will be discussed in the next section.

327 Seeding

The practice of seeding is common to a variety of chemical, metallurgical and ceramic processes for the purpose of increasing the rate of reaction and, to a certain extent, controlling the ultimate particle size and/or particle morphology.

Some examples are the Sherritt-Gordon process¹²⁰ for the production of nickel from complex sulphide ores (Fe-Co-Ni-Cu). The ores are leached with ammonia at 105 °C and 8 atm. to precipitate and remove iron hydroxide (Fe(OH)₃) and then boiled to reprecipitate copper sulphide. Nickel is then reduced from the ammoniacal solution by treatment with hydrogen at a pressure of 15 atm. at 170 °C. Even under these conditions, nickel will not readily precipitate unless the liquid is seeded with fine nickel powder. The same is true of the Mond Process¹²¹, where nickel carbonyl vapour is decomposed to carbon monoxide and the nickel deposited on nickel shot.

Seeding is used for grain refinement of aluminium¹²², where small additions of AlTi₃ crystals are inocculated into the molten metal bath short¹y before casting. The efficacy of this is dependent upon the time between the addition and casting, since the crystals themselves will eventually dissolve in the melt; a phenomenon known as fading.

Other metallurgical applications of seeding are the growth of single crystals from molten metals, often known as crystal pulling. Most of the methods involve the relative motion between a seed crystal such that a single crystal is literally pulled from the melt. This technique known as the Czochralski method¹²³ is the most reliable and fastest route for the production of large single crystals such as silicon

Two of the most common applications of seeding in the ceramic industry are the precipitation of aluminium hydroxide (Al(OH)₃) in the Bayer process 1,4 , and the devitrification of glasses to form glass ceramics¹²⁵

In the Bayer process, bauxite is leached with sodium hydroxide to obtain a sodium aluminate solution which, by itself, is gelatinous and difficult to handle. Aluminum hydroxide can be precipitated from the solution by the addition of an excess of seed Al(OH)₃ particles. The precipitated product is then dried and calcined through a number of transition phases to form a-Al₂O₃ (corundum).

The crystallization of glass ceramics such as lithium aluminosilicate (LAS), is carried out using TiO₂ additions as a nucleating agent. This is carried out to promote the nucleation of grains or crystals within the glass itself. In the absence of nucleating agents, nucleation occurs readily at the surface. This is a result of localized differences in the coordination of ions between the surface and the bulk glass which creates a high energy state where devitrification can readily occur. This leads to the formation of large directional columnar grains growing inwards from the surface, with a high incidence of void space, resulting in poor mechanical properties. Nucleating agents therefore promote a fine equiaxed grain structure with much improved isotropic mechanical properties

All of these examples serve to illustrate that the nucleation of a particular compound or structure in a system is enhanced by the addition of nucleating agents. This process, more often referred to as heterogeneous nucleation as opposed to homogeneous nucleation, is discussed in greater detail in the next section

3271 Classical Nucleation Theory

When a new phase initially forms as a product of a reaction, the new phase invariably occurs as a small nucleus of atoms, either within or on the surface of the originating phase. The formation of the nucleus requires a certain amount of work, W, that must be done in order to bring enough atoms together to make a nucleus. Given that there are N sites where nucleation could occur within the system, the number of nuclei that actually form (n) can be approximated by: 26

$$n = \operatorname{Nexp}\left(-\frac{W}{k\Gamma}\right) \tag{3.18}$$

if the nucleus is small, tending towards the size of an atom, then nucleation can take place equally well anywhere within the system, a state referred to as homogeneous nucleation. The work done in creating a nucleus is really the change in Gibbs free energy (ΔG) due to the formation of that nucleus. ΔG is the sum total of the free energy changes resulting from the volume energy of condensation, ΔG_{v} , and surface area (or energy required to create a new surface). ΔG_{o} , of the nucleus. The free energy change for a cluster of atoms of radius r is given by:

$$\Delta G = 4\pi r^{2} r + \frac{4}{3}\pi r^{3} \Delta G \qquad (3.19)$$

where γ is the surface energy. This relationship is illustrated in Figure 3.5 of ΔG_1 as a function of the radius. When the nucleus size is small, the free energy due to the surface area dominates, but for larger radii, the volume free energy



Figure 3.5: Free energy of nucleus formation as a function of nucleus radius.

dominates, such that ΔG_r is highly dependent upon the size of the nucleus. The relationship shows ΔG as a maximum at a value of:

$$r_c = -\frac{2\gamma}{\Delta G_c}$$
 and $\Delta G_c = \frac{16}{3} \frac{\pi \gamma^3}{\Delta G_c^2}$ (3.20)

which is termed the critical radius size. Clusters of atoms, often referred to as embryos, smaller than this size are unstable and will tend to disappear. A cluster of atoms, with a radius of r_c , is capable of continued growth, but stable growth actually ensues when this critical cluster size is greater than this.

This relationship, which is known as the capillarity theory ^{127,128}, is applied to all systems in which nucleation takes place, whether it be the nucleation of grains from molten metal or the deposition of a material from the vapour phase. In either case, the critical nucleus size and therefore the activation energy is dependent upon undercooling, superheating and supersaturation effects.

Homogeneous nucleation is a rare occurrence. In reality - as in situations like that of molten metal in a crucible or mold - nucleation of chemical reactions, as in the evolution of CO in steelmaking or solidification, will usually occur at sites such as defects in the crucible surface or at impurities within the melt. In these situations, the free energy of nucleation (ΔG_n) is much lower than that required for nucleation by the system alone. In effect, the activation energy barrier, A_o , (Figure 3.5) is decreased by the presence of a suitable nucleating surface.

3.2.7.2 Vapour to Solid Nucleation

For deposition from the vapour phase, the critical radius size is dependent upon the degree of supersaturation of the vapour phase; lower supersaturations call for a higher critical radius size since:

$$\Delta G_{\nu} = \left(-\frac{kT}{V}\right) ln\left(\frac{P}{P_{e}}\right)$$
(3.21)

where ΔG_v is the Gibbs free energy per unit volume, V, of condensed phase from the supersaturated vapour with pressure, P, to the equilibrium vapour pressure, P_e.

Figure 3.6 is a schematic for the situation where nucleation is taking place heterogenously on a surface from the vapour phase where γ_{VS} , γ_{Vn} and γ_{Sn} are the surface energies for the interfaces between the vapour-solid, vapournucleus and solid-nucleus. For a nucleus that wets a flat nucleus site the degree of wetting can be represented as a function of angle, θ :

$$\gamma_{\nu n} \cos(\theta) = \gamma_{\nu s} - \gamma_{sn} \tag{3.22}$$

where θ is the contact angle between the nucleus and the vapour such that as θ tends towards zero, the nucleus will completely wet the nucleation site. When $\theta = 180^{\circ}$, no wetting occurs and the solid will not nucleate on the surface, and conditions then favour homogeneous nucleation. ΔG_r in Equation 3 19 can be rewritten for heterogeneous nucleation as:

$$\Delta G_{r,het} = V_n \Delta G_v + A_{vy} Y_{vs} + A_{vn} Y_{vn} + A_{vn} Y_{vn}$$
(3.23)



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Figure 3.6: Heterogeneous nucleation on a solid substrate.

where V_n is the volume of the nucleus and A_{sv} , A_{sn} , A_{vn} are the respective surface areas for the solid-vapour, solid-nucleus, vapour-nucleus interfaces The activation energy for heterogenous nucleation can be expressed as¹²⁸:

$$\Delta G_{\text{erit net}} = \frac{16\pi \sqrt{^3}}{3\Delta G_{\phi}^2} \left[\frac{2 - 3\cos^2\theta + \cos^3\theta}{4} \right]$$
(3.24)

$$= \Delta G_{crit,hom} f(0)$$

Hence, for complete wetting $(\theta = 0)$, there is no activation energy $(\Delta G_{crit,het} = 0)$ barrier, and as θ increases towards 180° , the activation energy approaches the value for homogeneous nucleation. Complete wetting conditions can be achieved by seeding the system with particles of the same phase as the nucleation site. Whether a material will act as a beterogeneous nucleation surface depends upon there being a similarity in both the chemistry of the two materials, and also a high degree of lattice registry - greater than 85% between the high order lattice planes.

3.2.7.3 Seeding with Silicon Nitride

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The seeding process has been used for producing silicon nitride by lnoue et al.¹²⁹ and Figush and Licko¹⁰⁶, both of whom report a reduction in the ultimate particle size of the silicon nitride. Inoue also noticed that the addition of small quantities (~1wt.% Si₃N₄) of seed crystal reduced the amount of residual silica to undetectable levels and increase the reaction kinetics. Thus, it would appear that the addition of seed silicon nitride is acting as a heterogeneous nucleating site for silicon nitride, although no mention of the manner in which this occurs is made.

CHAPTER 4

THERMOCHEMISTRY OF THE SI-O-N-C SYSTEM

4.1 THERMOCHEMICAL DATA

Holistic approaches to the thermochemistry of the Si-C N-C system have rarely been undertaken, mainly due to the lack of reliable data for some of the species involved, e.g. silicon nitride and oxynitride. Less complex ternary systems have been studied, such as the Si-O-C system by Nagamori et al.¹³⁰ and Si-O-N system by Hendry¹³¹ and Blegan³⁶.

The thermodynamic properties of a silicon nitride were studied first by Matignon¹³², Henke and Brantley¹³³, Satoh¹³⁴ and Phelke and Elliott¹³⁵, and was for a long time, the only data available (Table 4.1). The preferred estimation by Chase et al. (JANAF)¹³⁶ of the data being the heat capacity, determined by Satoh, and the standard enthalpy of formation ($\Delta H^{\circ}_{f,298}$) and the entropy (ΔS°_{298}) after the work by Phelke and Elliot. The basis for this data from earlier editions of the JANAF Tables¹³⁷ have not changed and were originally called into question by Wild et al.³³ since it was apparent that the a-silicon nitride used by Phelke & Elliott was impure and contained significant quantities of the β -phase.

Further work by Colquhoun¹³⁸ on the nitridation of silicon in an iron-14wt. % silicon alloy determined a series of relationships for the Gibbs free energy (ΔG°) as a function of temperature for a and β silicon nitride and silicon oxynitride (Table 4.1). Their data, backed up by previous work by Wild³³, suggested that a silicon nitride was in fact a form of oxynitride, having a range of oxygen substitution from Si₁₁ $_4N_{15}O_{0.3}$ to Si₁₁ $_5N_{15}O_{0.5}$. In contrast, the β -phase consisted entirely of silicon and nitrogen in the stoichiometric ratio of Si₃N₄. The a to β transformation has already been discussed (Section 2.1.1) and it has been shown that a can exist with less than the theoretical amount of oxygen substitution in the lattice stated above — Furthermore, a will not transform readily to β without the presence of a liquid phase to act as a means of material transport for the phase change.

By using a similar technique to that of Colquhoun et al¹³⁸, Blegan³⁶ also evaluated the thermodynamic properties for β silicon nitride and silicon oxynitride (Table 4.1). However, the data were found to differ significantly from those of the former authors. Hendry¹³¹ proposed that these differences were a result of using the activities of silicon in iron from different sources and went on to standardize their results based on the Fe Si activity data reviewed by Chart¹³⁹ As a result, a much better agreement was obtained between the different sets of data (Table 4.1). However, Hendry¹¹¹ derived a preferred equation for β -Si₃N₄ using an experimentally measured value derived by Wood¹⁴⁰ for the room temperature enthalpy of formation ($\Delta H'_{1.998}$) This was combined with the heat capacity (C_p) data for a silicon witride, presumably assuming that the heat capacity of a and β are similar, if not the same. Based upon this data, Hendry was able to produce a predominance diagram for the Si-O-N system. The heat capacity and entropy at 298K of β silicon nitride have more recently been evaluated experimentally by Koshchenko and Grinberg^{141,142}.

Other studies of silicon oxynitride by Ryall¹⁴³, Colquhoun¹³⁸ and Ehlert¹¹⁴ were evaluated in great detail by Fegley¹⁴⁵ (Table 4.1). These data are thought to be the most reliable values available and are, in part, verified by Koshchenko and Grinberg¹⁴⁶, whose measured value for S²₁₉₈ is in very close agreement with the value estimated by Fegley (Table 4.1).

Phase	Author	ΔGʻτ (KJ'mol)	ΔΗ ^e f 298 (KJ/mol)	S°298 (J/mol K)	Cp (J/mol K)				Ttange
					8	b	c	d	(K)
0-S13N4	Phelke' ⁿ	-735+75 3T	736	104 7	120 406	42 579	-36 546	-4 458	1612 2000
	Colquboun ¹³	-820+0367	-820	44.4	•				
	Hendry ¹³¹	-1167.3 + 0.534T	-1167.3	-154 4					
	Saton ¹³⁴				74 5	112 769	-6 046	-28 662	298-2000
β-S.3N4	Colquhoun ¹³⁸	-808 + 0 376T	-808	63 5					
	Blegan ³⁶	-954 + 0 451T	-954						
	Hendry ¹³¹	-987+049T	-987	-50.5					
	Hendry ¹³¹ (cf Wood)	-925 + 0 45T	-925 2	-10 5					
	Koschenko ¹⁴¹			64 2	103 92	65 429	-26 039	-11 571	298-2000
S12N2O	Colquhoun ¹³⁸	883 + 0 285T	-883	47.3					
	Blegan ³⁶	-948 1+0 254T	-948						<u> </u>
	Hendry ¹³¹	-658+0 130T	-658	200					
	Fegley ¹⁴⁵		-9477±51	45 35±0.4	113.9	9 668	-44 610	0 650	298-2500
	Koshchenko ¹⁴⁶		1	44 26					5-300

Table 4.1: Thermochemical data for a, β silicon nitride and silicon oxynitride

Silicon carbide, in contrast to silicon nitride and silicon oxynitride, has been studied far more thoroughly. As such, the best assessment of the thermodynamic data for the α and β SiC phases can be found in the JANAF Thermodynamic Data Tables¹³⁷

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More recently, some studies of the Si O N-C system have been published based on some of the above data. Wada¹⁴⁷ investigated the phase stabilities of the system (and in particular β -silicon nitride) in relation to the activity of carbon at high temperatures, to be used principally as a guide to better understand the sintering of silicon nitride and silicon carbide ceramics and composites. Ekelund et al.¹⁴⁸ have studied the phase stabilities of silicon nitride, silicon oxynitride and silicon carbide during carbothermal reduction at high pressures. How closely this work can be related to actual practice of carbothermal reduction is not clear since the experiments were carried out in a stagnant nitrogen atmosphere in order to approach equilibrium conditions In general, it seems that silicon nitride formation is reliant upon a great excess of nitrogen gas through the reactants.

Thermodynamic data for other phases such as silica, silicon monoxide gas and silicon carbide for the present study have been taken from the literature (Appendix I) and need not be discussed here

Having reviewed some of the more pertinent thermodynamic data for the Si-O-N-C system, it is clear that the values for a and β silicon nitride are far from certain – Silicon oxynitride has received more attention and, although still not certain, the data proposed by Fegley is regarded as a very good estimation.

4 2 THERMODYNAMIC MODELLING OF THE SI-O-N-C SYSTEM

Until more accurate thermodynamic data for a and β silicon nitride become available, an alternative means of assessing the existing data must be tried. One method of doing this would be to somehow simulate or model a complete system using the accepted thermodynamic data for each of the species involved. In that way, different data for a particular phase, in this case silicon nitride, can be tried and the outcome compared with the products of a real system

The calculations from such a model could become quite cumbersome for a system consisting of a number of different elements, and the subsequent possible compound and reaction combinations. Calculations of this nature are therefore well suited to being adapted to use on a computer

Fortunately, there is no need to design different models for individual systems; instead, there now exist generic computer-based systems designed specifically for thermodynamic calculations of this nature. One of the more popular and powerful systems is the F*A*C*T system, a brief description of which follows in the next section – With this sytem, it is possible to do this kind of modelling but, as with any thermodynamic calculation, the results produced refer to equilibrium conditions and take no account of any kinetic considerations.

The object of using this was to try to study the system as a whole, rather than speculate a possible sequence of reactions, as has been the strategy employed in past studies. In so doing, it was hoped that a better understanding of the variables affecting carbothermal reduction could be achieved and, in addition, try to ascertain a working set of thermodynamic data for a and β silicon nitride.

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4.2.1 The F*A*C*T System

F*A*C*T (Facility for the Analysis of Chemical Thermodynamics) is a mainframe computer-based system designed to be used for the more commonly encountered thermodynamic calculations. Developed by Bale, Pelton and Thompson¹⁴⁹, the F*A*C*T system has a wide range of capabilities which include the calculation of

- 1. Reaction heat balances
- 2. Isothermal/isobaric property changes (ΔH , ΔG , etc.)
- 3. Elemental or compound vapour pressures
- 4. Equilibrium products of complex multi-phase chemical reactions.
- 5. Predominance diagrams
- 6. Binary, ternary and quaternary phase diagrams.

Each of these functions are quite specific in their own right, the outputs of which can be combined together in order to form the basis for the modelling of chemical reactions and systems.

The system has a large database of thermodynamic properties for over 5000 elements and compounds that can be accessed by the user in calculations. However, the user may also specify his or her own preferred data in order to assess data from other sources.

The two most applicable facilities of the program to the present work were the calculation of equilibrium products for the Si-O-N-C system (EQUILIB) and the calculation of predominance diagrams (PREDOM).

4.2.1.1 <u>Thermodynamic Principles</u>

The F*A*C*T program requires, for each species, the enthalpy of formation at 298.15K, $(\Delta H^{\circ}_{t,298})$, the absolute entropy at 298.15K (S°_{298}) , and constants specifying the temperature dependence of the heat capacity $(C_{\rm p})$,

with the temperature range over which this applies. In this particular case, the heat capacity is given by

$$C_{1} = a + 1 - 10^{-3} b T + 1 + 10^{7} T = (+1 + 10)^{-9} T T$$
(4.1)

where a, b, c and d are the polynomial coefficients describing the heat capacity of the phase, element or compound

Therefore, the Gibbs energies of reaction, the enthalpies of reaction and the entropy change for the reaction can be applied using the relationships between ΔG , ΔH and ΔS for any reaction as,

$$\Delta G_{I} = \Delta H_{I} - \Gamma \Delta S_{J} \tag{4.2}$$

where $\Delta G = \Delta H_{-}$ and ΔS^{+} are the standard free energy, enthalpy, and entropy changes at temperature T, respectively – For a reaction such as Reaction 4.3 carried out at temperature T

$$\Lambda + B \Rightarrow \Lambda B \tag{4.3}$$

$$\Delta H = \Delta H_{maxAB} + \Delta H_{maxA} + \Delta H_{298B} + \left[\frac{I}{298}C_{AB}\frac{dT}{dT} + \int_{298}^{T}C_{A}\frac{dT}{dT} + \int_{298}^{T}C_{A}\frac{dT}{dT} + \int_{298}^{T}C_{A}\frac{dT}{dT}\right]$$

$$= \Delta H_{208} - \int_{-208}^{-1} \Delta C_{2} t T$$
(4.4)

which is otherwise known as Kirchoff's Law. The change in absolute entropy, ΔS_{11}^{+} , is calculated in a similar manner, where.

$$\Delta S_{T} = S_{208,AB} - S_{208,A} - S_{208,B} + \left| \frac{\Gamma}{298} \frac{C_{20A}}{\Gamma} \right| I\Gamma - \left| \frac{T}{298} \frac{C_{2A}}{T} \right| dT - \left| \frac{\Gamma}{298} \frac{C_{2B}}{T} \right| d\Gamma$$

$$\Delta S_{1} = \Delta S_{\text{MAS}} = 1 \frac{\Delta C_{1}}{m_{\text{MS}} - l} dT$$
(4.5)

This series of relationships forms the basis of many thermodynamic calculations on the F*A*C*T system

Often, the standard enthalpies of formation at 298K and absolute entropies for a compound do not exist, and must be estimated from relationships between the Gibbs free energy of formation, ΔG , and the temperature, such that.

$$\Delta G = -C + m\Gamma \tag{1.6}$$

where -C is the heat of formation term ($\Delta H_{(298)}$, and *m* is the change in absolute entropy (- ΔS°_{298}). This relationship assumes that the ΔC_p for the reaction is either negligible or zero, which is often not true but, under such circumstances, this method is a good approximation. However, in order that the calculations be carried out by F*A*C*T as efficiently as possible, estimations or even other data for the heat capacity must be included

4.2.1.2 Le Chatelier's Principle

While discussing the thermodynamic principles involved in the $F^*A^*C^*T$ system, it is convenient to mention the thermodynamic basis that LeChatelier's Principle describes. The principle is often stated in order to qualitatively estimate the change in the equilibrium position of a chemical reaction when changes are made to the partial pressures of the constituent gaseous reactants or products.

LeChatelier's Principle states that "when a system which is at equilibrium is subjected to the effects of an external influence, the system moves in that direction that tends to nullify the effects of the external influence"¹⁵⁰ This can be demonstrated in two ways; either in terms of a phase change due to an increase in temperature, or as a phase change due to an increase in pressure.

Consider a two-phase system such as water in equilibrium with water vapour at 100°C:

$$H_{2}O_{11} = H_{2}O_{12} \tag{4.7}$$

If the heat input into the system is increased (the external influence), then the system will work to nullify that effect by transforming more water into steam, a transformation that absorbs heat. In so doing, the temperature remains constant at 100° C since the heat that would otherwise have raised the temperature has been used to transform water into steam. The reverse is also true, i e cooling the system results in the condensation of the steam with a release of the energy used to create it. In so doing, the removal of heat from the system (the external influence) is countered by the heat evolved from the phase change from steam to water (referred to as latent heat) and the system remains at 100° C.

The influence of pressure on the equilibrium position can best be shown with a different example, where there is a change in the number of moles, as in the equilibrium between nitrogen dioxide (NO₂) and dinitrogen tetroxide (N₂O₄) such that:

$$2NO_{2(g)} = N_2 O_{4(g)} \tag{4.8}$$

In this case, the eqilibrium will respond to a change in the pressure by working to nullify the effect. One mole of any gas occupies the same volume $(22.4 \text{ dm}^3 \text{ at STP})$ Thus, in this instance there is a halving in the number of moles in the formation of N₂O₄, and therefore a halving in the volume that

the gas occupies. An increase in the pressure will then favour the production of N_2O_4 since by decreasing the volume, the effect of an external pressure increase is nullified. The converse is true if the pressure is decreased, and the formation of nitrogen dioxide is favoured

LeChatelier's Principle can therefore be used as a qualitative means of assessing how an equilibrium will respond to external influences in temperature an pressure

This can be shown in a more quantitative manner¹⁵⁰. The Gibbs energy difference (ΔG°) between $NO_{2(g)}$ and $N_{2}O_{4(g)}$ can be expressed in terms of the equilibrium constant, K_{p} , at a fixed temperature, as:

$$\Delta G^{\circ} = RT \ln K \tag{4.37}$$

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where R is the universal gas constant and T is the temperature which is, by definition, independent of pressure – However, as has been shown above, the reaction equilibrium expressed in terms of the number of moles is dependent upon the pressure. Therefore, Reaction 4.8 becomes:

$$K_{\gamma} = \frac{p_{N_2O_4}}{p_{NO_5}} \tag{(4.10)}$$

where $p_1 = X_1P$ and p_1 and X_1 are the partial pressure and mole fraction of species *i* and *P* is the overall pressure of the system. Thus

$$K_{p} = \frac{X_{V_{2}O_{4}}}{X_{VO_{2}}^{2}P^{2}} = \frac{X_{V_{2}O_{4}}}{X_{VO_{2}}^{2}P} = K_{z}P^{-1}$$
(4.11)

where K_x is the equilibrium constant expressed as mole fractions. Since K_p is always constant, K_x will vary according to the overall pressure. By increasing the pressure, K_x must also increase, which is only accomplished by increasing the mole fraction of N_2O_4 and decreasing the mole fraction of NO_2 . Therefore, the reaction is shifted towards the products.

In more general terms, the K_p for a reaction such as \cdot

$$aA + bB = cC + dD \tag{4.12}$$

can be expressed as:

$$K_{p} = \frac{p_{C}^{\prime} p_{D}^{d}}{p_{\Lambda}^{a} p_{B}^{b}} = \frac{X_{C}^{c} X_{D}^{d}}{X_{\Lambda}^{a} X_{B}^{b}} - \frac{p^{c} p^{d}}{p^{a} p^{b}} = K_{\chi} p^{c+d-a-b}$$
(4.13)

References to LeChatelier's Principle will be made in order to qualitatively demonstrate the effects on the equilibrium of a particular reaction by either altering the overall pressure of the system or the partial pressure of one of the reactants or products.

4.2.1.3 Program EQUILIB

Program EQUILIB of the F*A*C*T system calculates the products of a given set of reactants at specified temperatures and pressures, along with values constraints at equilibrium. This is accomplished by iteratively optimizing the number of moles of the selected products in order to obtain the most negative Gibbs free energy for the system. It is well understood that equilibrium conditions persist when the Gibbs free energy (ΔG) is at a minimum. In effect, what the program is able to do is to consider the chemical environment as a whole. The only other alternative to this would be to calculate the ΔG for each possible reaction, and optimize the system for the

minimum ΔG . By the very nature of this method, this is impractical and tedious, not to mention that if one critical reaction happens to be overlooked, the whole calculation becomes invalid Therefore, the method employed in EQUILIB is the most efficient route for predicting the equilibrium conditions resulting from a particular set of reactants.

The major advantage to using a system like this is that thermodynamic calculations are no longer conducted for single reactions in isolation of other compounds that are stable under the same conditions. Instead, the program takes an overall approach to the problem, considering all the possibilities.

An example of how the data, reactants and products are entered into the program for silicon, oxygen, nitrogen and carbon is given in Appendix I. Some of the optional features that were used are:

- 1. The suppression of printing of species occurring below a certain cut-off concentration.
- 2. The extrapolation of temperature. Very often, thermodynamic data is specified for a phase over a stated temperature range. The choices of the most stable phase for a given temperature being the most suitable species that also has a temperature range that covers that temperature. The data can be extrapolated beyond the range, but not with any certainty.
- 3. Fixing activities in the product equilibrium. This can be used to determine the amounts of reactants required in order to achieve fixed concentrations or activities of particular product species. Care has to be taken such that in fixing a number of product activities that the Phase Rule is still obeyed

The program has other facilities for the treatment of other systems such as ideal and non-ideal solutions, and aqueous systems which are either not considered or required in the present work.

4 2.1 4 Program PREDOM

The concept of the predominance diagram was popularized by Kellogg and Basru^{1,1,1} as an aid to visualizing the ranges of stabilities for metal-oxygensulphur systems. Since then, they have become an important tool for assessing the reaction conditions for many other systems. The authors of the F*A*C*T program have reviewed¹⁵² the use and calculation of predominance diagrams in detail, and proposed a new, efficient method for the calculation of the diagrams, that particularly lends itself to the basis of a computational algorithm

Essentially, a predominance diagram is a representation of all the compounds of a selected "base element" that are stable in relation to the partial pressures (activities) or ratios thereof of other species. These species must not contain the base element. An example of the Fe-S-O system is given in Figure 4.1, where iron is the base element and the stability ranges of the compounds of iron are shown in relation to the partial pressures of SO₂ and O₂. In systems containing more than three elements, values of additional variables must be fixed (one for each extra element) in order for the diagram to be calculated.

The boundaries between the phases are not strictly phase boundaries, except where two adjacent phases are in the condensed state. In the instance where two gas phase regions are adjacent to one another, the boundary between them is the locus of points of equal partial pressures of these gases. Each field therefore contains the predominating gas (hence the name) with a lesser concentration of the gas from the adjacent field.



Figure 4.1: The Fe-S-O Predominance diagram (627 °C).

CHAPTER 5

SCOPE OF THE INVESTIGATION

When the work for this thesis was begun in May 1986, the original aim was to try to produce high-quality β -sialon ceramic powders from novel precursors. Although several studies^{91,153-157} have been carried out on the carbothermal reduction of aluminosilicate minerals to β' -Sialons and oxynitrides, problems exist with the characteristics of the end-product, the powders produced tended to consist of hard agglomerates requiring milling in order to produce a sinterable product. The milling operation is almost always a source of major contamination, by the wear and abrasion of the grinding media.

The starting point for this work was to investigate sol-gel processing as a means of mixing the precursor (Al₂O₃, SiO₂, C, Y₂O₃, etc.) on a fine scale. Nitriding studies were then to be undertaken to ascertain the optimum conditions for producing high-quality powders (if that could be achieved) Initially, nitriding experiments were carried out on silica and carbon, reproducing the work done by Szweda⁹⁰, in order to become familiar with the process. However, it soon became clear from the results obtained from these tests, that the details concerning the formation of quality powders, as opposed to those with mixed morphologies and purity, were somewhat lacking in the literature. Since silicon nitride powder is produced commercially by carbothermal reduction, it is assumed that much of the technical information is withheld in the proprietary domain. In addition, nothing has been discussed concerning the problems associated with the scale-up from small laboratory preparation to larger scale production. Rather than continue with the direct production of β '-Sialon, it was decided that it would be best to carry on with the investigation into silicon nitride production. The former project was seen as having too many variables to optimize Therefore, starting off simply with silicon nitride and working up to more complex systems with subsequent projects was seen as a better course of approach to the problem.

The scope of the investigation was firstly to investigate the role played by the following variables on carbothermal reduction of silica to silicon nitride:

1. the molar ratio of carbon:silica.

2. the precursor mixing conditions used.

3. the surface areas of the silica and carbon.

4. powder treatment prior to reaction (pelletized vs. loose powder).

5. the optimum reaction temperature.

The aim was to optimize these variables and determine the effect that they had on the degree of conversion of silica to silicon nitride, and also the effect on the particle size and morphology produced.

The Si-O-N-C system was modelled thermodynamically using the F*A*C*T system. The thermodynamic data existing in the literature for silicon nitride was assessed for its validity by comparing the calculated results of carbothermal reduction to the results obtained from experimentation. Conditions for the formation of non-equilibrium phases could then be determined and related to experimental results.

Using the results obtained from the preliminary results, a study into the effect of seeding was carried out to try to produce micron to sub-micron sized powder. Having made small quantities of silicon nitride powder and determined the optimum reaction conditions, an attempt was made at making larger quantities, to identify the problems involved with scale-up.

CHAPTER 6

EXPERIMENTAL PROCEDURE

The experimental procedure for the preparation and study of silicon nitride powder was divided into six key areas:

1. precursors

2. precursor mixing

3. nitridation

4. substrate deposition

5. powder analysis and characterization

6. bulk powder preparation

These stages were undertaken in order to examine the critical processing parameters for silicon nitride production.

6.1 PRECURSOR POWDERS

This study was carried out using high-purity carbon blacks and fumed silicas, all of which were provided by the Cabot Corporation. Their physical and chemical characteristics are summarized in Table 6 1. The powders are all high purity, the highest impurity content being found in the high surface area carbon black (Monarch 1300), which had relatively high levels of cyanides (6.33 ppm) and phenols with significant trace amounts of nickel (16.4 ppm) and chromium (11.8 ppm).

Weight losses of all of the above powders were ascertained by heating them under the same conditions that were used for the nitridation reaction at 1400°C in nitrogen scrubbed of oxygen with a linear gas flow rate of 31 cm/min. In every case, the weight losses of all of the powders were much greater than the volatile content given by the manufacturer. For the silica,

		Surface Area (m²/g)	Particle Size (µm)	Bulk Density (g/cm ³)	Impurity Content (ppm)	Major Impurity	Volatile s (%)	Actual wt loss (%)
Silica	EH-5	380	.007	.04	38	H ₂ O	2.5	5.1
	M-5	200	.014	.04	38	H ₂ O	2	4.2
	LM-130	130	.021	.05	38	H ₂ O	1.0	3.9
Carbon black	M-1300	500	.013	.29	58	CN,Ni,Cr	9.5	17.7
	M-1000	343	.016	.26	38	CN,Ni,Cr	9.5	-
	M-880	220	.016	.13	15	CN,Ni,Cr	1.5	0.7
	M-800	210	.017	.24	9	CN,Ni,Cr	1.5	5.2

 Table 6.1 Precursor powder characteristics

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this is likely to be due to the removal of water, since ultra-fine fumed silicas are extremely hydrophilic, readily picking up moisture from the atmosphere The carbon blacks lost a great deal more volatile material than the product data sheet would suggest. Since mixtures of silica and carbon were prepared by a sol-gel method, it could not be determined what effect the addition of propanol (the dispersing medium) would have on the weight loss due to moisture. However, the weight loss of carbon black was more significant as much of the weight loss was due to the evolution of cyanides and phenols Therefore, this was taken into account when calculating the molar carbon:silica ratios.

The silica powders all have extremely high surface areas, which implies a very small particle size, but the nature of the ultimate particles is far from being uniform. Instead, each silica particle is an aggregate of branched chains of primary particles that have become fused together, as seen in Figure 6.1.

6.2 PRECURSOR MIXING

The mixing of the silica and carbon powders was accomplished by either dry mechanical mixing (dry mixing) or by a sol-gel route. The dry mixing comprised of combining correct ratios of silica and carbon in a dry plastic washbottle with a number of alumina grinding balls (10 mm diameter), ard shaken vigorously by hand for ten to fifteen minutes, or until no more white particles of silica could be discerned. The sol-gel mixing route was carried out as per the flow chart seen in Figure 6.2

The silica and carbon black in the correct molar ratios were blended for fifteen minutes in a laboratory blender with iso-propanol (reagent-grade). The ratio of silica:iso-propanol was kept constant at 15g:500 mL so that the



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Figure 6.1: Electron micrograph of a CAB-O-SIL fumed silica particle (Courtesy Cabot Corp)¹⁰⁹



Figure 6.2: Schematic of powder mixing.

sol did not become too viscous. After blending, the sol was dried at 120°C in a drying oven until a friable gel remained. The gel was then ground to a loose powder, either using a pestle and mortar or by dry blending for a few seconds. The two types of powders were quite different from each other: The blended powder was much finer and free-flowing compared to the powder ground by hand. The latter, although also being a loose powder, had soft agglomerated lumps due to the compacting nature of grinding with a pestle and mortar

The loose powders were, in some cases, compacted into pellets of 1 cm diameter by approximately 1 cm in height with a uniaxial pressure of 56 MPa. Pellets formed at lower pressures were too fragile to pick up, whereas if this pressure was exceeded, the pellets would shatter upon removal from the die.

6.2.1 <u>SEEDING</u>

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Seed particles were added along with the carbon and silica. Fine grained a-silicon nitride (UBE SN-E-10) with a particle size of $\sim 0.5 \,\mu$ m or whiskers(inhouse preparation) were made as seed additions to the silica and carbon mixtures. The amount added was determined according to the weight ratio of seed silicon nitride with respect to the starting silica content, which ranged from 5 wt.% to 50 wt.% of silicon nitride seed.

6.3 <u>NITRIDATION</u>

All nitriding experiments were carried out in an inert atmosphere vertical tube furnace shown schematically in Figure 6.3. The inner tube diameter was 63.5 mm, with a hot zone of $\sim 100 \text{ mm}$.

The gas used was high-purity nitrogen which, unless otherwise stated, was maintained at a linear flow rate of 31 cm/min. The nitrogen was also purged of oxygen by passing the gas through a titanium sponge getter, at a



Figure 6.3: Nitriding Furnace.

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temperature of 800°C, prior to nitriding. To prevent back diffusion of air from the gas outlet into the furnace, the exhaust gas passed through a gas bubbler filled with rotary vacuum pump oil.

In order to eliminate oxygen from the system before nitriding, the furnace was flushed three times with nitrogen using a rotary vacuum pump. Once the furnace had been flushed, the crucible containing the reactant was slowly raised over a period of twenty minutes into the hot zone of the furnace.

The crucibles were made of either high-purity alumina or graphite. Figures 6 4(a) and (b) are photographs of the alumina and graphite crucible. Figure 6.4(c) shows the arrangement of the holes in the base of the graphite crucible, which allowed the gas to flow freely over the reactants. The reactants were prevented from falling out of the crucible by a thin layer of graphite felt (PAN-derived) over the base, as can be seen in Figure 6.5.

After nitridation, the powder was heated in air in a muffle furnace at 800°C for one hour in order to remove the excess carbon (decarburization).

64 <u>SUBSTRATES</u>

In order to hold substrates above the bed of reactants in the flow of any gases given off, a support was made out of graphite that was capable of holding three substrate discs. Figure 6.6 is a photograph of the substrate support and three different substrates in position on the crucible.

The substrate materials were 20 mm discs of graphite*, alumina**, boron nitride^{*}, sintered silicon nitride, and isopressed a-silicon nitride[§] The sintered silicon nitride contained $\sim 10\%$ grain boundary glass. The a and β -

^{*}Speer Canada, Grade 3499

^{**}Coors, Colorado, U S A , A98

⁻Carborundum

^{*}UBE Industries, Japan, a-SNE-10



Figure 6.4: (a) Alumina Crucible.

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Figure 6.4: (b) Top view of the graphite crucible, (c) base of graphite crucible



Figure 6.5: Loading of the crucible.

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Figure 6.6: Crucible with carbon, boron nitride and alumina substrates in position.

silicon nitride discs were both uniaxially pressed and the former was then isostatically pressed at 350 MPa

6.5 <u>ANALYSIS</u>

6.5.1 X-ray Diffraction (XRD)

X-ray diffraction was used for the quantitative phase analysis of the nitrided powders. An American Instruments X-ray generator was used to provide CuKa radiation, with an accelerating voltage of 40 kV ($\pm 0.1\%$) and a beam current of 20 mA ($\pm 0.1\%$). A Philips Automatic Powder Diffractometer system was used to produce XRD patterns over a scan range of 20 from 15° to 45°, at a rate of 1°/minute. This particular range was used such that all of the strongest diffraction peaks from all of the possible phases could be detected. Samples were prepared by lightly pressing the powders into a sample holder.

The intensity and 20 data were acquired and stored using a Philips APD 1700 computer system (Digital Micro-PDP 11). The raw data could then be corrected for systematic error using the silicon nitride JCPDS-XRD pattern data as an internal reference standard. KCl could also have been used as an external standard, but since the powders were only produced in small quantities, contamination had to be avoided. Error correction was not always necessary since the strong diffraction peaks of the phases could be readily recognized. In instances where phase analysis was difficult, the corrected XRD pattern was compared with the JCPDS reference patterns data base resident on the computer using the "Search and Match" feature of the software.

Quantitative analysis using XRD patterns relies on the principle that the intensity of the diffraction peaks of one phase in a mixture of phases depends upon the proportion of that phase in the mixture¹⁵⁸. The relationship between

the diffracted peak intensity and the concentration of a particular phase is not necessarily linear, but is dependent upon the absorption coefficient of the mixture which, itself, varies with the mixture composition.

The intensity of the diffracted beam for a single phase material is given by:

$$I = \left(\frac{I_o A \chi^3}{32\pi r}\right) \left(\left(\frac{\mu_o}{4\pi}\right)^2 \frac{e^4}{m^2}\right) \left(\frac{1}{V^2}\right) \left(|F|^2 p \left(\frac{1+\cos^2 2\theta}{\sin^2 \theta \cos \theta}\right)\right) \left(\frac{e^{-2m}}{2\mu}\right)$$
(6.1)

where

Ι	=	integrated intensity/unit length of the diffraction line	m	=	mass of an electron
Io	=	incident beam intensity	V	=	volume of unit cell
Α	=	incident beam cross- sectional area	F	=	structure factor
λ	=	incident beam wavelength	р	Ξ	multiplicity factor
r	=	radius of diffractometer circle	θ	-	Bragg angle
μο	=	4пх10-7 mKg C-2	e-2m	=	temperature factor
е	=	charge on an electron	μ	=	linear absorption coefficient

This equation can be greatly simplified since all the quantities involved are constant, except for the concentration of the phases under scrutiny and the absorption of the mixture, μ_m , such that Equation 6.1 can be reduced to:

$$I_{i} = \frac{K_{1}C_{i}}{\mu_{m}} \tag{6.2}$$

where C is the concentration of the phase, and i denotes the phase in question. K_1 is therefore a constant and is unknown since I_0 is also unknown, but will cancel out if I_1 is taken as a ratio of some known reference line. This ratio can be used to determine the concentration of ι^{th} phase in three ways,

namely the external standard method, the direct comparison method, and the internal standard method. The external method is only suited to binary mixtures, whereas the internal and direct methods can be used to determine concentrations in multi-component mixtures. Either of the remaining two methods would be satisfactory for the quantitative phase analysis for the present study if it was not for the presence of amorphous silica in many of the samples. Most of the constants, such as the Structure factor (F), etc., involved in Equation 6.1 for a and β silicon carbide and silicon oxynitride, can be found in the literature, but these, of course, do not exist for amorphous materials. For this reason, the quantitative phase analysis was made on the basis of the selected integrated peak heights for both crystalline and amorphous phases alone, i.e. not taking into account the absorption coefficients of the mixture or structure factors, etc. The apparent weight percent (w₁) of any phase was therefore calculated according to:

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$$W_{\iota} = \frac{I_{\iota}}{\sum_{\iota=1}^{n} I_{\iota}}$$
(6.3)

where I_1 is the integrated peak intensity for a selected diffraction line of the ith component. Although not strictly true, this was a reasonable approximation since it was never required to know the exact composition of the mixture. Rather, this form of semi-quantitative analysis was used to see trends in the development of a-silicon nitride by varying the process conditions.

The diffraction peaks selected were $a-Si_3N_4$ (201), $\beta-Si_3N_4$ (101), $\beta-SiC$ (002), cristobalite (101), and the Si_2N_2O doublet peak (002)(200) which

mainly occurs as a single broad peak. The area of the amorphous silica band was measured between 15° and 37.5°.

The integrated peak heights were measured from the XRD pattern using a Zeiss IBAS Image Analyzer The peaks had to be traced by hand so that the system could measure the peak area; therefore, this process became one of the major source of uncertainty in the analysis (Appendix II).

The measurement of the amorphous silica band was the hardest to quantify, mainly because the peak was not clearly defined.

6.5.2 Chemical Analysis

Oxygen analysis of the silicon nitride powders produced was carried out by Spectrochemical Laboratories, Inc., Pittsburg, PA., using the inert gas fusion method (Leco TC130).

6.5.3 Specific Surface Area Measurement

The surface area measurements of the nitrided powders were carried out using a Quantasorb area-meter. The measurement of the area is based upon the differential thermal conductivity of a He/N₂ mixture before and after adsorption of N₂ onto the surface of the powders at 77K.

6.5.4 Particle Size Analysis

The particle size distribution was measured using a Micromeritics Sedigraph 5000D. The operating conditions are listed in Table 6.2. Samples of silicon nitride powder were dispersed in water containing 0.1 volume percent of Darvan C* to act as a dispersant. Dispersion was aided by

^{*} R.T Vanderbilt Co , Inc USA

immersing the beaker containing the mixture of powder and water in an ultrasonic bath for 15 minutes.

Temperature (°C)	31		
Water Density ($\rho_0 \ g/cm^3$)	0.9954		
Water Viscosity (n cp)	0.7840		
Sample Density (p_g/cm ³)	3.19		
Rate Setting ⁺	õ93		

Table 6 2 Operating parameters for the Sedigraph 5000D

⁺ Calculated from Sedigraph data sheet

6.5.5 Scanning Electron Microscopy

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Prepared powder samples were examined using a JEOL JSM-T300 Scanning Electron Microscope. Powder samples of silicon nitride had to be sputter coated with a gold/palladium mixture for eight minutes in order to prevent charging.

Qualitative chemical analysis was accomplished using a Tracor Northern 5400 Energy Dispersive Spectrosocopy (EDS) unit. The lowest atomic number that could be detected was sodium.

Light element analysis was carried out at JEOL U.S.A., Boston, with a JEOL JSM-840A, in conjunction with a Kevex Delta 4 EDS, with a Quantum ultra-thin window detector. In this case, the lowest atomic number resolution was nitrogen.

CHAPTER 7 RESULTS AND DISCUSSION

7.1 OPTIMIZATION OF THE CARBON :SILICA RATIO

7.1.1 Preparation: Dry-mixing vs. so'-gel processing

The stoichiometric requirement for carbon and silica for the carbothermal reduction of silica to silicon nitride is 2:1, according to the reaction:

$$3S\iota O_{2(s)} + 6C_{(s)} + 2N_{2(g)} = S\iota_{3}\iota V_{4(s)} + 6CO_{(g)}$$
(7.1)

However, previous work by Szweda et al.⁹⁰ and Mori et al.¹⁰² has indicated that greater molar ratios of 4:1 to 10:1 are required to obtain the maximum yield of silicon nitride. Whether this is a chemical requirement or due to maximizing the dispersion of silica within the mixture has not been made clear, and was the initial aim of this investigation.

Figure 7.1 shows how the percentage of silicon nitride present in the final powder varies with the molar carbon:silica ratio, using the highest surface area carbon and silica (Monarch 1300 and EH5), and using an alumina crucible; the reaction time was maintained at 5 hours. The figure shows results for powders prepared by both of the processing routes (dry mixing and sol-gel) and were either compacted into pellets or left as loose powders. Considering the dry mixed powders first, the maximum amount of silicon nitride that could be produced was approximately 30-40%, at a ratio of 10:1, irrespective of the powder compaction conditions. Similar results are obtained for sol-gel derived mixtures in the pelletized condition, but a marked improvement is seen in the silicon nitride yield, with almost complete conversion (within limits of uncertainty) for the same powder, in the loose condition at a ratio of 10:1. This would suggest that there are two



Carbon:Silica Ratio

Figure 7.1: Weight % silicon nitride produced vs. carbon:silica ratio in the alumina crucible (closed symbols = loose powder, open = pellets)

considerations that are playing an important role: The first, and foremost, is the intimacy of the mixture, and the second is the free diffusion of gases within the reactants.

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When using the alumina crucible, the nitrogen gas would tend to flow past the crucible and, therefore, by-pass the reactants. Therefore, a similar set of experiments using the sol-gel derived powders was carried out under the same conditions, but this time using a graphite crucible with a perforated base (Section 6.3). Figure 7.2 shows how the estimated weight percent of silicon nitride varies with the carbon:silica ratio for the sol-gel prepared powder, using the alumina and graphite crucibles. The ratio required to produce complete conversion has been reduced from 10:1 to 7 1, and has also greatly improved the silicon nitride content of ratios as low as 4:1. The flow of gas through the reactants would therefore appear to greatly improve the reaction between the gases and the reactants. Other possibilities that could be affecting the reaction conditions are the oxygen-gettering effects of the graphite crucible, or even the removal of excess gaseous species such as silicon monoxide gas by the flow of gas. These topics will be discussed in greater detail later.

The results shown in Figure 7.1 and 7.2 are not in accordance with those of Szweda⁹⁰, whose data suggests that dry mixed powders provide more complete conversion over a five-hour period than for sol-gel derived material Figure 7.3 shows a comparison of the data obtained in this work with that of Szweda The major discrepancies between these results can perhaps be accounted for by the technique used to evaluate the compositions of the resultant powders. No mention is made of how the quantitative phase analysis was accomplished, nor was there any mention of the residual amorphous silica content of the powders produced. The present study took account of all phases present,



Carbon:Silica Ratio

Figure 7.2: Weight silicon nitride vs.Carbon:silica ratio



Carbon:Silica Ratio

Figure 7.3 Weight% silicon nitride vs. carbon:silica ratio

including the amorphous silica content, however all the figures were only concerned with the silicon nitride content (for a complete analysis of the phases seen in Figures 7.1. and 7.2 see Appendix II).

The difference in the technique used for analysis between this study and Szweda's⁹⁰ would not necessarily explain why dry-mixed materials have the advantage over sol-gel processed materials. Szweda suggested that an excess of carbon was required in order to counteract the effect of high moisture content in his material, which raised the oxygen partial pressure sufficiently to cause the formation of silicon oxynitride. The major difference between this work and that carried out by Szweda was that iso-propanol was used instead of water as the dispersing medium. The iso-propanol molecule contains much less oxygen (8.3 at.%) than water (30at.%) and, in addition has a lower dipole moment (water = 1 86, iso-propanol = 1.66)¹⁵⁹. The latter means that propanol forms a weaker hydrogen bond with the silica than does water, indicating that iso-propanol would be more easily driven off during the drying process. In the light of these observations, definite benefits could possibly be gained by using dispersing liquids which contain little or no oxygen, such as hexane. These liquids commonly come under the classification of Group III liquids for the dispersion of silica (Section 3.2.6.1). A dispersing liquid such as hexane would therefore eliminate a possible source of oxygen, but there are other drawbacks to using Group III liquids. Since these liquids are non-polar, the tendency is for the silica to hydrogen-bond with itself rather than with the liquid and, therefore form a networked structure of silica particles The overall effect is that non-polar liquid/silica systems become viscous at lower solids loading than polar Groups I and Group II liquids.

To summarize, the results presented in this study show that there are definite advantages to using a sol-gel precursor processing route over mechanical mixing, particularly when using non-aqueous sol systems such as iso-propanol. Therefore, the complete conversion of silica to silicon nitride is reliant upon the intimate mixing of reactants, and on the free flow of nitrogen through the reactants.

7.2 <u>THE CARBON:SILICA RATIO AND ITS EFFECT ON SILICON</u> NITRIDE YIELD

The previous section dealt with maximizing the silicon nitride content in the final powder over the occurrence of other phases such as residual silica (amorphous and crystalline), silicon oxynitride and silicon carbide. The ideal conditions for the occurrence of only silicon nitride need not necessarily be the same as those that result in the greatest yield. It is reasonably well established that the first stage in carbothermal reduction is the evolution of silicon oxide gas from the reaction between silica and carbon:

$$SiO_{2(s)} + C_{(s)} = SiO_{(g)} + CO_{(g)}$$
(7.2)

In a system where nitrogen is allowed to pass through the reactants, gaseous species such as silicon oxide, are able to escape from the reaction bed and react elsewhere, such as on the crucible or furnace walls. Thus, if more carbon were to be present, it might be expected that the loss of silicon oxide would be reduced.

By measuring the weight losses that occurred in the series of experiments used in Figure 7.2, it was possible to estimate the amounts of silica loss as silicon monoxide gas (Appendix III). These results have been plotted in Figure 7.4 for reactions carried out in the alumina and graphite crucibles. The figure shows that, for the alumina crucible, the loss of silica as SiO steadily increases to a maximum of $\sim 20\%$ at ratios between 4:1 and 7:1,



Figure 7.4: Silica weight loss as SiO gas vs. carbon:silica ratio

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decreasing again to 10% at a ratio of 10:1. When using the graphite crucible, the weight loss reaches a maximum of 32% at 2:1, and then steadily decreases close to 10% for ratios of 7:1 to 10:1.

At low ratios of 1.1, in both cases, the evolution of SiO gas is low. This is thought to be due to the sintering of silica particles, which causes a reduction in the surface area of the silica, enveloping the carbon and preventing the escape of SiO gas. With the graphite crucible, greater weight losses are seen at low ratios because the gas flowing through the reactants carries away SiO gas, whereas with the alumina crucible, this is less likely to occur. At higher carbon:silica ratios, it would be expected that the weight losses in the carbon crucible would almost always be greater than those for the alumina crucible, due to the loss of SiO gas. Surprisingly, quite the reverse occurs. It would appear that allowing nitrogen gas to flow through the reactants enhances the reaction, allowing SiO gas to react with nitrogen/carbon or nitrogen/carbon monoxide, for enhanced conversion to silicon nitride. In addition, the amount of carbon also plays an important role since it is not until higher carbon.silica ratios of 10:1 are used that near complete conversion occurs in the alumina crucible

An excess of carbon appears to have a two-fold effect. Firstly, as a means of minimizing the amount of silica-silica contact by dilution, thus preventing sintering of the silica and slowing the reaction; and secondly, as an important participant in the reaction to form silicon nitride. Exactly how the latter is affected by the quantity and characteristics of the carbon is not clear, but by having a larger proportion of carbon, a larger surface area is available that could improve nucleation.

Other studies of carbothermal reduction report a wide range of carbon:silica ratios from 4 to $6:1^{90}$ 105 to between 15 to 20:1.102.104; differences

which the present study shows could be due to the conditions under which experiments are conducted, although these have not been stated in the past.

7.2.1 Silicon Carbide Formation

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When using the alumina crucible, traces of β -silicon carbide were often found, irrespective of whether the reactants were in the form of pellets or loose powders In contrast, when using the graphite crucible, no silicon carbide was ever detected. Thus, it was supposed that the formation of silicon carbide was prevented by the action of nitrogen gas sweeping through the powder bed. Reaction 7.3 is one possible reaction that can lead to the formation of silicon carbide:

$$3SiO_{(g)} + CO_{(g)} = 2SiO_{2(g)} + SiC_{(g)}$$
(7.3)

The action of the nitrogen sweeping through the powder bed would flush the gaseous species, like carbon monoxide and silicon monoxide, away from the reaction zone By Le Chatelier's Principle, the equilibrium would be moved towards the reactants' side of Reaction 7.3, thus preventing the formation of silicon carbide. Therefore, the occurrence of silicon carbide in the reaction products formed in the alumina crucible can be seen as being due to a localized build-up of SiO and CO gases in the reaction bed; a situation unlikely to occur in the graphite crucible because of the flow of nitrogen through the reactants. The likelihood of this reaction taking place will be discussed later in the section on thermochemistry.

7.2.2 Silicon Oxynitride

The limiting oxygen partial pressure below which the formation of silicon oxynitride is prevented during carbothermal reduction has been determined to be in the region of 10⁻²⁰ atm. at an ambient pressure of 1 atm^{3b} In order to avoid the formation of silicon oxynitride, all the possible sources of oxygen must be eliminated from the system. Szweda⁹⁰ found that silicon oxynitride only formed in sol-gel derived material, and presumed that this was due to the high water content of the starting materials that provided the source of oxygen.

In the present work, it was suspected that the source of oxygen was due to the alumina crucibles that were used initially. With reference to the predominance diagram for the Al-O-N system shown in Figure 7.5 calculated by the F*A*C*T system, it can be seen that for a nitrogen partial pressure of 1 atm., as long as alumina is present, the partial pressure of oxygen over the alumina must be greater than 10-17 atm., i.e. alumina can form gaseous suboxide species plus oxygen by the following reaction:

$$Al_2O_{3(5)} = Al_2O_{2(g)} + \frac{1}{2}O_{2(g)}$$
(7.4)

This partial pressure of oxygen is at least four orders of magnitude greater than the minimum oxygen partial pressure required to form silicon oxynitride. Making use of a graphite crucible eliminates this source of oxygen and possibly acts as a getter for any extra oxygen in the system arising from the alumina work tube and nitrogen feed gas. However, it was found that the use of a graphite crucible alone was not sufficient to prevent the formation of silicon oxynitride when using nitrogen feed gas that had not been scrubbed of oxygen. Titanium sponge at 800°C was used as a getter to remove traces of oxygen and water. By using this as a gas pre-treatment stage, the amount silicon oxynitride formed became negligible. This means that neither high silica to carbon ratios nor graphite crucibles are satisfactory in their own right as getters for this system.



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Figure 7.5: Al-O-N Predominance Diagram.

By using flowing, oxygen-free gas, it was possible to dilute the oxygen evolved from the alumina furnace tube. In addition, if the gas can flow freely through the reactants, the excess oxygen can be swept away as it evolves.

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7.3 <u>SILICON NITRIDE FORMATION AS A FUNCTION OF</u> <u>TEMPERATURE</u>

The temperature at which silicon nitride forms has been reported to occur at 1350°C, 1400°C, 1450°C and 1500°C as discussed in Section 3.2.3, and that exceeding these temperatures brings about the formation of silicon carbide. The reason for the wide variation could well be due to experimental set up, such as furnace design, the means of temperature measurement, and the type of crucible used. Since there is such a large discrepancy in the literature about the reaction temperature, a series of experiments were carried out to determine the optimum temperature range for the apparatus used in this work.

The experiments were all carried out using high surface area carbon black (Monarch 1300) and high surface area silica (EH-5), with a carbon:silica molar ratio of 10:1. The reaction time was taken as 5 hours, since other work^{90,101,102} has shown that the nitrogen concentration of product powders reaches a maximum after this residence time.

Figure 7.6 is a plot of the weight percent of the phases present, such as silicon nitride and silicon carbide, with temperature, the remainder being amorphous silica and cristobalite, not shown in this figure. At low temperatures, betwen 1300°C and 1450°C, very little silicon nitride is observed; the predominant phase being amorphous silica. By increasing the temperature to 1500°C, the only detectable phase is a-silicon nitride, which



Figure 7.6: Variation in weight percent of α -Si₃N₄ and β -SiC with temperature.

persisted through to a temperature of 1550° C. At higher temperatures, β -silicon carbide is formed in preference to silicon nitride.

This shows that there is a very limited temperature range over which silicon nitride will form, and is in good agreement with Szweda's⁹⁰ work. This is not surprising since the experimental set-up in the present investigation is very similar.

7.4 THE EFFECT OF SURFACE AREA OF THE STARTING MATERIALS

High-purity carbon blacks and silicas could all be obtained with varying surface areas (Section 5.1), and it was therefore possible to investigate whether the surface areas (implying particle size) of either the carbon or silica had any effect on the production of silicon nitride.

Figures 7.7 and 7.8 show how the proportion of silicon nitride in the powders produced varies with the surface areas of the carbon and silica. There are two sets of data presented in each figure: one for sol-derived powders in the loose state, the other for the same set of powders in pellet form. From Figure 7.7, it is clear that the surface area of the carbon black is of key importance in the formation of silicon nitride, whether in the loose or pelletized state. The highest yields are always obtained with the highest surface area carbon (M1300). In contrast, Figure 7.8 shows that there is no noticeable effect of the silica surface area aiding the reaction.

In what way the surface area improves the reaction cannot be shown here, since either the evolution of silicon monoxide gas by the reaction of silica and carbon (Reaction 7.5) or the nucleation of silicon nitride on the carbon via the gas/solid reaction (7.6) are the two possible rate limiting steps:



Figure 7.7: Weight % silicon nitride vs carbon surface area. (EH-5=■, M-5=●, LM-130=▲, filled = loose empty = pellets).



Figure 7.8: Weight % silicon nitride vs. silica surface area

$$S_lO_{j(s)} + C_{j} = S_lO_{j(a)} + CO_{aj}$$
(7.5)

$$3S\iota O_{(s)} + 3C_{(s)} + 2N_{2(\mu)} = S\iota_3 N_{4(s)} + CO_{(\mu)}$$
(7.6)

Neither of these can easily be separated at this point, but will be discussed at greater length later (Section 7.8.4).

Zhang and Carnon¹⁰¹ conducted a similar study to this one, although they used carbons, in the form of lamp black and pyrolyzed starch, mixed with organically precipitated silicas (from TEOS). They came to much the same conclusion that a high carbon surface area was the most important factor, although the silica surface area was also seen to have a similar effect, but to a lesser extent.

In earlier work, Lee & Cutler⁴⁹ showed that the silica particle size does have a very significant effect, but this was conducted on powder with much lower surface areas, ranging from 0 01 m²/g to 2m²/g, implying particle diameters of 200 μ m down to 1 5 μ m. The powders used in the present study all had extremely high surface areas, between 130m² g to 380m²/g. Therefore, the reaction appears to be more affected by a comparatively larger particle size than by ultra-fine silicas.

The fact that no significant benefit during nitridation is being derived from the high surface area silicas would suggest that perhaps the silica powder particles were sintering and consolidating before reaching the optimum nitriding temperature. However, despite the fact that a high surface area plays no major function in the outcome of the reaction, a high surface area silica is still required in order to become adequately dispersed as a sol. Advantages are to be gained from using the highest surface area silica available, since the highest solids loading of silica sols can be achieved.

7.5 PARTICLE SIZE AND MORPHOLOGY

In the Section 2.1.2.1, the importance of particle size and morphology of ceramic powders was discussed, particularly the effect that the particle morphology has on the green density, and the particle size as the source of the driving force for sintering. Ideally, the particles should be equiaxed polyhedra (not purely spherical) and submicron in size. There are a number of parameters which could possibly have an effect on the final powder particle characteristics, such as temperature, carbon to silica ratio, precursor powder treatment, and the surface areas of the precursor materials.

The following experiments were carried out, using optimum powder preparation conditions unless otherwise stated, i.e. sol-derived powders in the loose state.

7.5.1 Temperature

The effect of temperature in terms of the yield of silicon nitride has already been shown to be most satisfactory in the temperature range of 1500°C to 1550°C. At temperatures lower than this, amorphous silica was the predominant species present, and above 1550°C, silicon carbide. Micrographs of samples treated at various temperatures should therefore reflect the changing nature of the powder.

Figures 7.9(a)-(d) is a series of micrographs showing how a very fine, reticulated silica structure at low temperature progresses through to a mixed morphological stage of silicon nitride particles and amorphous silica.





Figure 7.9 : Powder Microstructure at (a) 1350°C, and (b) 1500°C.



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Figure 7.9: Powder Microstructure at (c) 1550°C, and (d) 1600°C.

(c)

(d)

Uniform particles of silicon nitride develop between 1500°C and 1525°C, and finally at 1600°C a very fine structure of silicon carbide is seen.

Thus, the morphology of the powder produced over this range of temperatures is characteristic of the phases that are present, rather than being solely dependent on the temperature. Between 1500° C and 1525° C, silicon nitride is the only phase present, and there is no significant variation in the particle size that results, which remains consistant around 3-4µm. This is too large a particle size to be considered as a good sinterable material and must somehow be reduced to within the 1 µm range.

7.5.2 Carbon:Silica Ratio

The preliminary experiments on optimization of the carbon:silica ratio and the ideal carbon surface area have shown how the formation of silicon nitride is dependent upon the amount and nature of the carbon used. Therefore, it might be expected that the particle size and morphology of the powder produced would also be affected by the same variables or characteristics. Only the use of highest surface area carbon black (M1300) resulted in complete conversion to silicon nitride. Thus, the characteristics of the silicon nitride powder produced could only be observed over a range of carbon to silica ratios using this form of carbon.

Figures 7.10(a)-(d) is a series of micrographs of powders produced from different molar ratios of carbon to silica (2:1, 4:1, 7:1, 10:1), at a temperature of 1500°C. At a carbon to silica ratio of 2:1, the particles are of very irregular sizes, and have a large proportion of whiskers. XRD patterns show that there is a substantial quantity of amorphous silica present, but it is not clear from this micrograph what form it takes. Increasing the ratio to 4:1 improves particle morphologies a little, but still shows the presence of whiskers. Only



(a)



Figure 7.10: Powder Microstructure at carbon:silica ratios of (a) 2:1, and (b) 4:1.



Figure 7.10 : Powder Microstructure at carbon:silica ratios of: (c) 7:1, and (d) 10:1.

at 7:1 did the final powder consist almost entirely of silicon nitride particles. Increasing the ratio further to 10.1 did not change noticeably the size or morphology of the resulting powder.

Therefore, the optimum carbon to silica ratio that determines the best particle morphology is 7:1. It is possible to go to higher ratios, but there is little advantage to doing this since there is no significant effect on the grain size or morphology. The effect that the silica:carbon ratio has on the particle characteristics has never been discussed in much detail in the literature, presumably because there is, in fact, little or no significant interdependence.

7.6 PRECURSOR POWDER TREATMEN'T

7.6.1 Mixing

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The two previous sections have both used sol-derived powders in the loose condition; however, dry-mixed powders will be briefly discussed here in order to show the advantages of using the sol-gel route.

Figures 7.11(a) and (b) show the powders resulting from dry-mixed and sol-gel mixed precursors after heat treatment. The dry-mixed route produces convoluted tapes or ribbons of silicon nitride which are approximately 1 μ m wide and also very large particles, possibly silica. In comparison, the same carbon to silica ratio (10:1) mixed through the sol-gel route produced powders that consisted of equiaxed particles of a-silicon nitride.

Previous work¹⁰² in this field have mostly shown the occurrence of convoluted tapes of silicon nitride, even from sol-gel routes ^{90,31}, and it has been suggested that these powders could be further ground in order to obtain a small, relatively equiaxed particle size. However, there have been no reports as to the sintering characteristics of such a powder or how effective



Figure 7.11 : Silicon nitride powders derived from: (a) Dry-mixed materials and (b) Sol-gel processed materials

this communution procedure is in producing a powder with the required characteristics.

Powders produced by the method used in this work by the sol-gel route described would have the advantage of not requiring a grinding stage, which often results in the pick-up of impurities from the grinding media. Even though the particle size in this case is quite large ($\sim 4\mu m$), ways of reducing this still further will be discussed later

Exactly why particles should form in preference to ribbons is not clear, but at this stage it was thought to be related to the degree of inter-mixing, since dry-mixing is much less efficient than dispersion in a sol. However, this cannot be the only factor involved since Szweda et al.⁴⁰ and Siddiqi et al.⁴¹ both used the sol preparation route (although water-based) and still reported the formation of tapes and ribbons.

7.6.2 The Effect of Pelletizing

So far, the results seen in this chapter have shown that there is a definite advantage to using loose powders rather than powders that have been compacted into pellets: The yield of silicon nitride was greatly improved when using loose powders as opposed to pellets. This was explained as being due to the inability of gaseous species such as N_2 , CO, CO₂ and SiO gas to freely permeate within the reactants. However, the use of pellets was found to be quite beneficial when trying to ascertain how silicon nitride forms in the reaction zone.

It was noticed that the silicon nitride tended to form on particular surfaces within the pellet, as shown by the schematic and photograph in Figure 7.12,. These surfaces were, in fact, capping defects brought about by the pellet pressing operation. It was presumed that nitrogen could easily penetrate into



Figure 7.12: Cross section through a pellet.

the pellet via these channels, but not so readily into the bulk of the pellet, which would explain the high residue of silica and the low yield of silicon nitride.

By studying these surfaces after nitridation, it is possible to see the way in which silicon nitride is formed, and relate this to the formation in loose powders.

Figure 7.13 is a micrograph of one of these surfaces for high surface area carbon and silica (M1300 & EH-5), showing clumps of silicon nitride approximately 50 µm in diameter which, when magnified further (Figure 7.14), can be seen to be agglomerates of discrete particles. The fact that clumps form would suggest that the first step in the process is the nucleation of primary silicon nitride within the pellet and then further heterogeneous nucleation on the primary silicon nitride to form clumps. This relates well with Section 7.4, which showed that a high carbon surface area was required in order to obtain the highest yield of silicon nitride, and adds credence to the suggestions that the carbon is the active nucleation site. Therefore, it would appear that the first silicon nitride to form is nucleated on the carbon

By using a carbon with a lower surface area (M880), and a high surface area silica (M-5), clumps still form in the capping defects of the pellet, but their size and morphology are quite different. Figure 7.15 shows that the clumps are now fewer in number and much larger, approximately 300 μ m in diameter, and the make-up of each clump consists of convoluted ribbons of material (Figure 7.16). The greater size of the clumps and their diminished numbers indicate that the number of nucleation sites for reaction during nitridation has decreased, which, for a lower surface area carbon, might be expected. It cannot necessarily be said that the morphology of the silicon nitride is directly related to the surface area of the carbon, but a similar sort



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Figure 7.13: a-silicon nitride clumps on the pellet defect surface.



Figure 7.14: Close-up of a clump of silicon nitride.


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Figure 7.15: Clumps of particles on the defect surface of a low surface area carbon pellet.



Figure 7.16: Enlargement of a clump seen in Figure 7.15

of particle morphology is seen for products resulting from loose powder precursors. Figure 7.17 is a micrograph of the product of a sol-derived loose powder of M-800 carbon and EH-5 silica, showing a mixed morphology of large particles and fine ribbons of silcon nitride.

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Szweda⁹⁰ and Siddiqi³¹ believed that the growth of convoluted ribbons, as opposed to whiskers, is due to the silicon nitride reaction being "physically constrained by the environment", the tortuosity of each ribbon being a route or channel through the carbon/silica aggregate. However, by taking a reacted pellet initially consisting of high surface area silica (EH-5) and carbon (M-1300), and sectioning it longitudinally (Figure 7.18), clumps of particles can be seen within the capping defects. The fact that the defect is wider than the clumps (some clumps bridge the defect) shows that the individual particles are hardly constrained by the surrounding material.

Mori et al.¹⁰² proposed that the different morphologies were related to the nitrogen content of the final powder. High nitrogen contents were typical of particulate powders, whereas low nitrogen contents were typical of ribbon morphologies. However, since this was based on bulk nitrogen analysis, it is not certain whether the low nitrogen content was due to large amounts of unreacted silica, or silica that is closely associated with the a-silicon nitride.

The oxygen content, in relation to the particle morphology, was studied in this work using powders derived from low and high surface carbon mixtures. Figures 7.19(a) and (b), and 7.20(a) and (b) show the micrographs and light element EDS analyses for the particulate powder (high surface area carbon) and ribbon morphology (low area carbon) powder. The analyses qualitatively show that particulate powders contain very little oxygen and, ipso-facto, must contain very little silica. On the other hand, the EDS spectra for the ribbon morphology powder has a much stronger oxygen peak, with nitrogen being



Figure 7.17: Product of loose powdered precursors made up of high surface area silica (EH-5), and low surface area carbon (M-800).



Figure 7.18: Electron micrograph of a longitudinal section through a pellet showing clumps of particles bridging the capping defect.



Figure 7.19: (a) Micrograph of particulate silicon nitride, and (b) its EDS spectra.



Figure 7.20: (a) Micrograph of ribbon silicon nitride, and (b) its EDS spectra.

apparent only as a very slight overlap with the oxygen peak. The aluminum peak and part of the oxygen peak seen in both spectra come from the aluminum SEM stub that the powder was mounted on. Whether or not the high oxygen content is manifested as silica, as suggested by Peuckert and Greil,⁷⁰ or even as a non-stoichiometric silicon oxynitride as Wild el al. ³ have indicated cannot be shown here. However powder morphologies like this can be largely regarded as being highly contaminated with oxygen.

Szweda⁹⁰ and Siddiqi³¹ believed that ribbon morphologies like this were silicon nitride, and that a grinding process would produce a satisfactory powder. In the light of the above results, this assumption would be incorrect.

7.6.3 Effect of Grinding of Gels on the Silicon Nitride Particle Size

It was stated in Chapter 6.2, on experimental procedures, that the gels derived from sols of carbon and silica were either ground by hand in a pestle and mortar, or crushed in a high-speed stainless steel blender for a few seconds. Powders produced by the latter method were very much lighter and more free-flowing than those produced by hand. The difference between the two methods became very obvious when examining the powder produced after nitriding in the loose condition (using high surface area carbon and silica). Figure 7 21(a) and (b) show a significant difference in the grain size between the two powders produced: the blended carbon/silica powder produced particles of around 2 μ m, whereas the powder ground by hand in a pestle and mortar produced particles between 4-5 μ m.

The decrease in particle size suggests that more nucleation is taking place in the blended powder than in the powder ground by hand. Therefore, by blending the carbon/silica gel, a greater surface area is made available for nucleation

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Figure 7.21 (a): Silicon nitride powder formed from gels crushed in a pestle and mortar.



Figure 7.21 (b): Silicon nitride powder formed from gels broken down in a blender.

Crushing the carbon/silica gel by hand breaks up the large particles, but the fine particles so formed become compacted on a small scale. Therefore, the structure of a hand-ground gel is less open than a blended gel. This manifests itself as a difference in the tap density for the same weight of material, the blended powder has a tap density of almost twice that of the hand-ground powder.

7.7 SUBSTRATE EXPERIMENTS

The purpose of conducting the following set of experiments was to determine which materials are critical to the formation of silicon nitride. The substrates used were disks of alumina (Al₂O₃), boron nitride (BN), graphite, sintered silicon nitride and isostatically pressed a-silicon nitride powder. Alumina and boron nitride were chosen as substrates since they were expected to be inert in the deposition reaction likely to occur.

The substrates were placed above a bed of reactants in a crucible in groups of three, as shown in Figure 6.4 (Chapter 6) All of the substrate experiments were carried out at 1500°C for 5 hours in flowing nitrogen under conditions that would maximize the evolution of SiO gas. This was previously determined from the plot of silica lost (as SiO gas) as a function of carbon silica ratio (Figure 7.4), where the maximum SiO gas evolution was observed at a molar ratio of 2:1. In each experiment, three different substrates were used, such that direct weight gain/loss comparisons could be made between each material. The results are summarized in Table 7.1. To obtain the net weight gains of each substrate, allowances have been made for natural weight losses occurring in the substrates with no reactants present in the crucible.

Substrate	Net wt. gain (+) loss()
С	+2.9 to 3.1
BN	-52.1 to -36.0
Al_2O_3	5.6 to -4.4
Sintered Si_3N_4	+0.3 to $+0.9$
a-Si ₃ N ₄	+31.6 to $+33.1$

Table 7.1.Net weight gains/losses for the
substrate materials (mg)

Considering the first three materials in the table, i.e. C, BN, and AlgO₃, the data show that carbon substrates have a significant weight gain, whereas alumina and, more noticeably, boron nitride, have moderate to substantial weight losses. Visual inspection, alone, was sufficient to see that the surface of the carbon substrate facing towards the reaction bed was covered in a fine white deposit, as shown in Figure 7.22. Figures 7.23(a) and (b) show typical surfaces of the alumina and boron nitride, respectively, which indicates no sign of any deposit on their surfaces. The only noticeable change was in the alumina substrate, which had discoloured from a brilliant white to a pale brown colour. Assessment of the cause of the weight loss of the alumina substrates is thought to be a result of sub-oxide (Al₂O₂) formation at the grain boundaries. This is a well-known phenomenon, particularly useful in the thermal etching of ceramics to reveal details of the microstructure. Figure 7.24 shows the alumina grains of one of the heat treated alumina substrates, clearly standing in relief.

The weight loss of the boron nitride substrates is harder to explain, but is possibly due to reactions between B_2O_3 , CaO (remnants from the boron nitride fabrication process) and SiO gas. Exactly what process is causing this net weight loss in the presence of SiO gas is unknown, but it does show that



Figure 7.22: Carbon substrates (clockwise from the left) (a) Asreceived, (b) No reactants, (c) With reactants



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Figure 7.23: (a) Boron nitride before (left) and after reaction



Figure 7.23: (b) Alumina substrates before (left) and after reaction.



Figure 7.24: Alumina surface after heat treatment.

boron nitride, under these circumstances, is not inert. Microscopically, (Figures 7.25), there is little change in the condition of the surface, except for a few large particles. These contain calcium and silicon, possibly being a form of calcium silicate, that suggests a reaction between CaO and SiO gas

The deposit on the carbon substrates was found by XRD to be entirely asilicon nitride, and all in the form of whiskers, as shown in the micrograph in Figure 7.26. The silicon nitride whiskers are arranged in clumps. Figure 7.27 shows a small clump where many whiskers are nucleated from one spot on the carbon surface. Exactly how these whiskers grow or why they grow in preference to particles is uncertain. Whisker growth from the vapour phase has been observed in many ceramic systems, and is invariably seen as a vapour-solid-liquid (VSL) reaction whereby the growing whisker is precipitated from a liquid globule at the tip. The liquid is often caused by the presence of an impurity which is thought to act as a catalyst. For example, hafnium carbide and nitride¹⁶⁰ whiskers form from a liquid phase rich in nickel, similarly for lanthanum hexaboride¹⁶¹. Silicon carbide whiskers are also reported³¹ as having a similar deposition reaction, where the whiskers are precipitated from an iron silicide liquid phase present on the tips. Whiskers can also be formed in metals, an example being tin¹⁶², although the whiskers in this instance are thought to grow from the root through a mechanism involving diffusion and strain effects

The growth of whiskers in general is widely believed to take place via the addition of atoms or molecules to a screw dislocation emerging at the tip (or at the root, as is the case with tin); the presence of the liquid is a means of material transport from the vapour to the nucleation sites^{16d}

In the present study, no globules are seen on the tips of the whiskers (Figure 7.28), so it would appear to be a direct deposition from the gas phase.



Figure 7.25: Boron nitride substrate after heat treatment



Figure 7.26: A micrograph of a-silicon nitride whiskers formed on a graphite substrate.



Figure 7.27: Multiple whiskers growing from a single point on the graphite substrate.



Figure 7.28: The tip of a silicon nitride whisker grown on a graphite substrate.

The growth could be occurring from the root of the whisker, but there is no evidence for or against this. The whiskers themselves all grow with the whisker axis parallel to the c axis of the silicon nitride unit cell¹⁰⁴. If the growth theory is correct, this would mean that the Burgers vector of a screw dislocation would also have to exist in this direction along the whisker axis.

Sintered silicon nitride (Sialon) substrates ilso formed a white layer of whiskers, as shown in Figure 7 29(a) The amount of whiskers that formed was dependent upon the number of sintered silicon nitride substrates present on top of the crucible, doubling the number of substrates could almost double the amount of whiskers. Microscopy revealed (Figure 7 29(b)) that the whiskers themselves were not straight, as with the carbon substrate, but appeared tangled and intermixed, with occasional particles. Not enough whiskers were ever collected in order to obtain a satisfactory XRD pattern to identify the phases present, nor did EDS reveal any elements other than silicon and possibly aluminum.

It was thought that the whiskers, in this case, were grown from the intergranular glassy phase which, at 1500°C, is a liquid, and that the whiskers would themselves be a Sialon phase, possibly β '-solid solution

The largest net weight gains were seen on the iso-pressed a-silicon nitride substrate, but visual and microscopic examination showed no whisker growth, and there appeared to be no appreciable difference between the asreceived and reacted substrates (Figures 7.30(a) and (b)). Since the substrate is made from a silicon nitride powder that has a particle size in the sub-micron range ($\sim 0.5 \,\mu$ m), new particles growing on the surface of the substrate particles or growth of these original particles by accretion of silicon nitride from the gas phase, would be difficult to distinguish from the original material. A means



Figure 7.29 (a): Sintered silicon nitride As-sintered (left), and after reaction.



Figure 7.29 (b): The morphology of whiskers grown on the sintered silicon nitride.

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Figure 7.30 (a): Iso-pressed a-silicon nitride before reaction.



Figure 7.30 (b): Iso-pressed a-silicon nitride after reaction.

of observing the growth of silicon nitride from the gas phase will be detailed in the next section on seeding of carbothermal reduction

In summary, these experiments have shown that there are two critical steps in the formation of silicon nitride in carbothermal reduction of silica: (1) nucleation will only take place on a carbon surface, indicating the gas/solid reaction (Eq. 7.5); and (2) once nucleation has taken place, particle or whisker growth takes place by the deposition of silicon nitride via the gas phase reaction (Eq. 7.6). The gas phase reaction will not take place on relatively inert substrates such as alumina and boron nitride, but only appears to proceed on a pre-existing a-silicon nitride surface.

7.8 <u>SEEDING</u>

Past observations of seeding of carbon/silica mixtures with fine silicon nitride seed particles have shown that the particle size of the a-silicon nitride produced is much smaller than for powders produced from unseeded materials. Inoue et al ¹²⁹ carried out a series of experiments with a variety of different silicon nitride seed contents, ranging from zero to 50 wt % of seed to silica. The present investigation used a similar range of seed contents to do a comparative study and observe how the particle size develops with seed content. The only difference between this work and that of Inoue et al. was that the reaction temperature was kept at 1500°C instead of 1350°C used in their study

All of the experiments with different seed ratios gave high yields of asilicon nitride (from XRD analysis), but it was also noticed that the proportion of β -silicon nitride became more prevalent than in unseeded materials as the seed content increased. The as-received UBE powder (SN-E-10) that was used as the seed material had a significant quantity (~5-8%) of β -silicon nitride⁴². Thus, it is supposed that the β -silicon nitride seen after carbothermal reduction was a residue of the seed material.

7.8.1 Particle Size

The results of median particle size (d_{50}) , the powder surface area, and the cumulative particle size distribution in Table 7.2 and Figure 7.31 show how the addition of seed material reduces the particle size. The unseeded material

Seed content (%)	d50 (µm)	Surface area (m²/g)
unseeded	4 5	2.15
5	2 5	4 8
50	2.5	47

Table 7 2. Silicon nitride particle sizes and surface areas of seeded and unseeded precursors.

has a very broad distribution with a mean particle size of 4.5 μ m, which is relatively large compared with the sub-micron range required for a ceramic powder with good sintering characteristics. The aduition of only 5% silicon nitride seed greatly reduces the median particle size to 2.5 μ m, narrows the size distribution considerably, and more than doubles the powder surface area. In contrast, raising the seed content to 50% does nothing to reduce the mean particle size or change the surface area, but broadens the particle size distribution significantly. This indicates that the addition of larger amounts of seed particles serves only to create large agglomerates. Also shown in Figure 7.31 is the particle size distribution for the UBE SN-E-10 seed material. This clearly illustrates how much finer the seed powder is than the powders produced by carbothermal reduction.



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Figure 7.31: Cumulative particle size distribution of silicon nitride powders.

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Figures 7.32(a) to (c) are a series of micrographs of the powders discussed above. The unseeded reactants produced a good equiaxed morphology, but with a grain size of between 2 to 4 μ m, which is in good agreement with the Sedigraph results. The micrograph also shows a number of larger agglomerates, as well as particles, which would account for the wide size distribution seen. By seeding with 5% seed, the individual particles became much smaller, 0.5 to 1 μ m, which is smaller than the sedigraph results indicate, which is due to aggiomeration. The agglomeration problem is more noticeable when the seed content is increased to 50%: Figure 7.33 bhows an agglomerate commonly encountered in this powder. The individual particles making up the agglomerate are similar in size to those seen in the powder originally seeded with 5% silicon nitride.

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The agglomerates produced from the 5% seed material can be broken down quite easily by grinding the powder in a pestle and mortar. Figure 7.34 shows how, after a short period of grinding, the median particle size was reduced from 2.5 μ m down to 1.9 μ m.

The previous work by Inoue et al.¹²⁹ showed that, at the lower temperature of 1350°C, the reaction kinetics were enhanced, leading to a greater yield of silicon nitride by the addition of seed material. However, good particle morphology did not become apparent until large amounts of seed material were used (Si₃N₄:SiO₂ = 50%). Such a large percentage of seed material is impractical since, assuming the complete conversion of silica to silicon nitride, the proportion of seed silicon nitride remaining in the final product would be at least 64% by weight.

This statement is made assuming that the original seed material does not take part in the reaction, no reference has ever been made as to whether the seed material takes part in the reaction or does in fact remain simply as a

10 µm

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Figure 7.32 (a): silicon nitride powder. Original seed content = 0%



Figure 7 32 (b): silicon nitride powder. Original seed content = 5%



Figure 7.32 (c): silicon nitride powder. Original seed content = 50%



Figure 7.33: An example of an agglomerate found in powders seen in Figure 7 32 (c).



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Figure 7.34: Cumulative particle size distribution of unground and ground silicon nitride powders.

source of nucleation, since there is also a possibility that the back reaction (Reaction 7.5) can occur:

$$3S_{l}O_{2x} + S_{l}N_{4x} = 6S_{l}O_{2l} + 2N_{2(2)}$$
(7.5)

This could act as a preliminary step to the renucleation of silicon nitride on the carbon via Reaction 7.6.

$$S_{20} = \frac{1}{2} + \frac{3C_{31}}{3} + \frac{N_{2(2)}}{3} = \frac{S_{13}N_{4(2)}}{3} - \frac{3CO_{31}}{3}$$
(7.6)

This has proved difficult to verify since it is impossible to distinguish unequivocally between the seed material and the reaction products. If the back reaction (Reaction 7.5) were to occur, then, since larger quantities of SiO gas would be produced (6 moles of SiO gas to 1 mole of Si₃N₄), the overall weight loss during carbothermal reduction should also increase through loss of the gas from the reaction bed – Table 7.3 is the calculated loss of silica as SiO gas (See Appendix III for calculations) for increasing contents of seed material – The results show a trend towards greater evolution of SiO gas as

Table 7.3. SiO₂ loss as SiO with increasing seed content

Seed Content (%)	Weight' SiO ₂ lost as SiO
()	× 9
5	12-45
25	9.29
33	1616
50	16 58

the seed ratio increases, but the scatter of results renders this inconclusive. In trying to shed light on this possible reaction step, silica (EH5) and silicon Reaction 7.5 (in the absence of carbon), and heated to 1500° C in nitrogen, with the result that only 13% weight loss occurred. It was expected that a great deal more weight loss would have occurred, and that the reactants would almost disappear XRD analysis revealed that the major components in the residue were a-silicon nitride, cristobalite, and the amorphous band characteristic of silica. Therefore, at high seed contents, the presence of carbon appears to aid the evolution of SiO gas for reasons which remain somewhat unclear.

782 Observation of Nucleation

The complexities of the formation of silicon nitride by carbothermal reduction make the task of determining reaction stages and nucleation mechanisms extremely difficult. The fact that the reaction is carried out at high temperatures makes direct observation impossible. In order to follow the nucleation and growth processes in such a case as seeding, the nucleating particles/agents must be clearly distinguishable in the final product from the material formed during the reaction From the micrographs shown in Figures 7.32(b) and (c), this cannot be done However, if the morphology of the seed material were to be significantly different to that of the product, then identification would be made simpler.

To investigate the nucleation processes, fine a-silicon nitride whiskers were used as the seed material, instead of silicon nitride particles, with a weight fraction of $5^{\circ}c$. Figures 7.35(a) and (b) show the whiskers prior to mixing and their condition after reaction, respectively

If the back reaction 7.5 were to occur, then the size of the whiskers might be expected to diminish Instead, quite the reverse happens: the whiskers grow and are no longer smooth, but encrusted with particles. The product is



Figure 7.35 (a): A micrograph of the silicon nitride whiskers.



Figure 7.35 (b): A micrograph of the product of whisker seeded material.

entirely a-silicon nitride, with no trace of any other phase, either crystalline or amorphous.

Since the whiskers grow instead of shrink some other process is involved. Two methods of forming silicon nitride have been previously detailed in Chapter 3 1, where SiO gas can react with carbon as:

$$3SiO_{(g)} + 3C_{(s)} + 2N_{2(g)} \rightarrow Si_3N_{4(s)} + 3CO_{(g)}$$
 (4.1)

(77)

or by the gas phase reaction:

$$3SiO_{(g)} + 3CO_{(g)} + 2N_{2(g)} \rightarrow Si_3N_{4(s)} + 3CO_{2(g)}$$
 (7.8)

and it is the latter reaction that will be considered here.

Section 7.9 2.1 on thermochemistry will show that both of these two reactions are possible under the conditions for carbothermal reduction. However, for the gas phase reaction to proceed ordinarily to form silicon nitride, either homogeneous nucleation must take place in the gas phase, or nucleation must take place on a suitable surface (Section 3.2.8.2).

Freund and Bauer¹⁰⁵ found that homogeneous nucleation of iron from $Fe(CO)_5$ in the gas phase was prevented by the lack of sufficient transfer of the heat of condensation by the gas away from the nuclei, thus maintaining its instability. This meant that very large nuclei had to form, which requires a large activation energy. This was accomplished by subjecting the gas phase to shock waves to promote nucleation. The only other way that the activation energy for this process can be lowered is to provide a "wettable" surface in which the lattice planes with high d spacings have less than 15% disregistry with the phase that forms (Section 3.2.8.2).

Even if the nucleating surface were to have perfect registry with the nucleating phase, growth is not likely to occur on a perfect defect-free surface. Hull¹⁶⁵ states that the supersaturation (P/P_e) required for growth to occur would have to be in the region of 50% whereas in reality, the supersaturation is closer to 1%. The required supersaturation is greatly lowered by irregularities or defects in the surface where atoms or molecules can become readily attached. The activation energy for the addition of atoms or molecules to a perfectly flat surface is high, and is lowered greatly by the presence of defects, such as screw dislocations that terminate at the crystal surface¹⁶⁷. These characteristically produce a step which winds itself into a spiral around the point at which the dislocation meets the surface. The step so formed is a site where atoms or molecules become added to the crystal, and is the widely accepted mechanism of crystal growth. In addition to this, atoms or molecules can also be added singly to a rough, irregular surface in the same way^{168} . This does not mean that the activation energy for the addition of atoms to a surface at a discontinuity is zero, but is some finite value. This would also mean that the contact angle θ , between the nucleus and nucleation site for self-deposition (homoepitaxial growth) is greater than zero¹⁶⁹. This has been borne out by self-deposition studies of silicon on silicon¹⁷⁰ However. despite this activation energy barrier to growth, it is likely to be much less than the activation energy required for nucleation (estimated by Mori et al.¹⁰² for silicon nitride as 682 kJ/mol) on a heterogeneous nucleation site. Brice¹⁶⁷ discusses this in terms of an energy barrier, ΔG_1 (Figure 7.36) that is greater than the difference in free energy between the atoms in the growth phase and crystal. These generalized concepts are valid regardless of the system, whether it be growth from a molten phase or from the vapour phase



Figure 7.36: Activation energy barriers to the movement of atoms close to the crystal/gas interface.

Thus, growth of silicon nitride particles during carbothermal reduction can be considered as a CVD process, involving the self-deposition of silicon nitride on silicon nitride particles. Kijima et al 171 have also used carbothermal reduction of carbon and silica mixtures as a CVD technique to coat silicon wafers with a layer of silicon nitride. This form of growth is also seen as being the process by which the whiskers in the whisker seeded material grew (section 7.8.2). Originally, the whiskers were smooth but, after heat treatment, became very rough and irregular. It is suggested that during the powder mixing and processing stage, the whiskers become scratched and damaged, thus creating more discontinuities to act as sites for nucleation on the whisker surface. In relating this to seeding with fine particles, it is not clear whether the powder particles that form during nitridation are due to the growth of the seed particles alone, or nucleation and growth of more particles on the seeds.

Taking the latter point first, in the case where high seed contents were used (50% seed) and, assuming that two or more particles can be nucleated by a seed, it would be expected that the particle size distribution that evolves would be bimodal. Instead, the distribution that is seen is not bimodal, but wide, consisting of agglomerates and particles. All of the particles that are seen are much larger than the original seed material, suggesting that the seed particles must also grow.

If the seed particles themselves grow, then, rather than nucleating other particles, the number of particles that form should be similar to the number of particles introduced as seeds. An approximation of this can be made from the experimental data

Appendix IV details the calculation of the approximate number of particles of silicon nitride formed per gram in unseeded and 5% seeded

carbon/silica mixtures (molar ration 7.1), as well as in the seed powder (Table 7.4). As would be expected, the number of particles produced in the seeded material is almost two orders of magnitude greater than the number produced from unseeded material. If the seed particles were to grow rather than nucleate other particles (assuming silicon nitride forms preferentially on the seed rather than carbon), then the number of seed particles added should be of similar magnitude to that of the number of particles formed in the seeded material, which appears to be the case. Thus, if the particle size of the seed powder were to be decreased, the number of particles per gram of material added would be increased. Since there would be more growing particles, the ultimate silicon nitride particle size produced should decrease.

	# Particles pei gram
Unseeded	64 x109
Seeded	1 73 ×1011
Seed Powder	40 x10 '

Table 7.4 The number of particles/gram of silicon nitride

To test this hypothesis, an experiment was devised using Starck LC12 silicon nitride as the seed powder – This powder has a high surface area of $\sim 24 \text{m}^2$.g (UBE SN-E-10, $\sim 9 \text{m}^2$ /g), which is due to a large proportion of fine particles, a direct result of the grinding that is done during processing. Figures 7-37 and 7-38 are the particle size distributions and micrographs, respectively, of silicon nitride powders that were derived from UBE and Starck seeded material – It is quite clear from these figures that the particle size produced has been reduced by using the Starck seed powder. Therefore, it



Figure 7.37: Cumulative particle size distribution of silicon nitride produced from mixtures seeded with 5% Ube SN-E-10 or Starck LC-12.



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Figure 7.38 (a): silicon nitride produced from 5% Ube seed material.



Figure 7.38 (b): silicon nitride produced from 5% Starck seed material.
is postulated that the development of a fine-particle size in the final powder is dependent upon the number of seed particles that are available for growth, as opposed to nucleation of more particles on the seeds and their subsequent growth. However, it is likely that both processes are taking place, since the whiskers seen in Figure 7.35 definitly show that particles do nucleate on them. From these observations it may be concluded that the growth of preexisting particles predominates over the nucleation of new particles

7.8.3 Whisker growth

Section 7.7 showed the growth of silicon nitride whiskers on the surface of a carbon substrate by deposition from the gas phase. Exactly what deposition mechanism was responsible for the whisker growth could not be determined since there was no sign of a globule at the tip of the whiskers that would indicate a VSL reaction. From the observations of seeding, however, it appears that particle growth takes place by self-deposition, and it is assumed that whisker growth occurs in the same way. TEM studies¹⁰⁴ of these whiskers shown that the class of the silicon nitride unit cell is parallel to the whisker axis. Therefore, it might be expected that growth is occurring by addition to a screw dislocation whose Burgers vector lies parallel to the whisker axis. As for the preferential formation of whiskers instead of powders, it appears likely that this is due to a difference in supersatoration conditions

The number of favourable nucleation sites, in the form of steps on the surface of a growing crystal, is dependent upon the supersaturation of the gas or liquid phase from which it is growing^{1/2}. Increasing the supersaturation increases the number of available nucleation sites. At very low supersaturations, screw dislocations that emerge at the surface of a crystal

are likely to be the only sources of nucleation and, therefore, growth of the crystal occurs preferentially in the direction of the Burger's vector of the dislocation

7.8.4 Seeding of low surface area carbon precursors

It was shown in Section 7.4 that the surface area of the carbon has a significant effect on the yield of silicon nitride: Low surface area carbons resulted in a large percentage of residual amorphous silica, whereas high surface area carbons produced only a silicon nitride. Seeding experiments using a low surface area carbon (M800), high surface area silica (EH5) and a seed content of 5 wt % silicon nitride (by weight of silica, UBE SN-E-10), were conducted in order to discover more about the importance of carbon in unseeded carbothermal reduction.

Figure 7 39(a) and (b) shows the comparison between the XRD patterns obtained from the powders resulting from the seeded mixture and from the same unseeded mixture. Figure 7 39(c) shows the particle size and morphology produced. The immediate difference between the two is the presence of the amorphous silica peak in the unseeded powder, which is nonexistent in the seeded powder \cdot the seeded powder is entirely a silicon nitride. This suggests that there is enough SiO gas evolved by Reactions 7.9 and 7 10:



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Figure 7.39: XRD of silicon nitride produced from: (a) unseeded and (b) seeded low surface area carbon.



Figure 7 39 (c) Silicon nitride powder produced from a mixture of a low surface area carbon (M-800) and a high suface area silica (EH-5) with 5% seed (UBE SN-E-10)

$$SiO_{2(y)} + C_{(y)} = SiO_{(y)} + CO_{(y)}$$
 (7.9)

$$SiO_{2(s)} + CO_{(g)} = SiO_{(g)} + CO_{2(g)}$$
 (7.10)

which, in the seeded material, reacts to form silicon nitride on the seed particles by the gas phase reaction. On the other hand, for the unseeded material, the rate-controlling step is the nucleation of silicon nitride on the carbon.

Another observation that can be made from this is that the residual amorphous silica that was seen in many of the experiments with low surface area carbons could well have been a result of the reprecipitation of silica from the SiO gas.

7.8.5 Seeding of low carbon silica ratios

Since the nucleation of silicon nitride on carbon by the gas/solid reaction has been identified as being the rate determining step, and not the evolution of SiO gas, it was thought that seeding could be used to help reduce the carbon silica ratio.

In order to demonstrate this, high surface area carbon and silica (M1300, EH-5) were mixed via the sol-gel processing route in a molar ratio of 3.1, with 5wt.% UBE seed powder. The powder that was produced was entirely a silicon nitride but, as Figure 7.40 shows, the powder produced was extremely agglomerated. This means that an excess of carbon is still required in order to adequately disperse the silica and seed material such that the impingement of growing particles on one another is kept to a minimum. For these types of



Figure 7 40. An agglomerate of silicon nitride formed from a low carbon.silica ratio of 3.1.

silicas and carbons, high ratios, much greater than the stoichiometric requirement, will always be needed.

7.9 THERMODYNAMIC MODELLING OF CARBOTHERMAL REDUCTION

7.9.1 Estimation of thermodynamic data

In order to model or perform any systematic study of the carbothermal reduction of silica using the F*A*C*T system, the thermochemical data for a and β silicon nitride had to be estimated from the existing data. The review of the thermochemistry of silicon nitride in Section 4.1 showed that most of the data of ΔG as a function of temperature obtained from experimentation were based upon measurements taken from β silicon nitride. The most recent data are the evaluation of the heat capacity and the entropy at 298K by Koshchenko and Grinberg^{141–142}, the latter of which is close to the values that can be derived from Colquboun et al. The re-evaluation of this data by Hendry¹³¹ meant that the entropy value for β is negative, suggesting too great a dependency on the temperature. The entropy at 298K for this work was therefore taken as being 64.2 kJ/mol, after Koshchenko and Grinberg. The entropy at 298K for a was then evaluated by making three assumptions:

- 1) that the transition temperature of a to β is approximately 1550°C, since no direct formation of β is seen below this temperature during carbothermal reduction.
- 2) the heat capacity (C_p) data for a is that found by Satoh¹³⁴, and for β is after Koshchenko and Grinberg. The heat capacity data for the two phases are very similar, but this is also true of both the a and β phases of scheon carbide.

3) the enthalpy of transformation is probably close to 1.2 to 1.3 kJ/mol. These values are estimated from the heat of transformation of a to β quartz, a to β tridimite, and a to β cristobalite. The transformation of low temperature β silicon carbide to high temperature a is also undetermined. Stull and Prophet^{1.37} adopted the view that the β phase was the most stable at all temperatures, and therefore, the heat of transformation of β to a SiC over a temperature range of 1400°C to 2100°C is between -1.62 to -1.89 kJ/mol (calculated by F*A*C*T) However, since β SiC is observed transforming to a SiC during sintering¹⁷³, the previous statement is thought to be untrue, and therefore estimates of the heat of transformation are unreliable

Having estimated the entropy data, it was then possible to estimate the enthalpy of formation at $298K(\Delta H^{\circ}_{f298})$ for a silicon nitride, by using the Equilib program. This was done by specifying the reactants' side of the equation as:

$$S_{i}O_2 + 7C + 200N_2$$
 (7.11)

to simulate the conditions during carbothermal reduction where silicon nitride is formed. An excess quantity of nitrogen was used to simulate flowing gas. The value of ΔH°_{f298} for a silicon nitride could then be entered and varied on the F*A*C*T system in order to produce the same phase assemblage at a temperature of 1500°C, as was observed in the experimental work. The complete data set found in this manner is shown in Table 7.5.

These values can be verified using the React program to calculate the temperature at which silicon nitride decomposes to silicon and nitrogen at 1 atmosphere total pressure. This was calculated as being 1920°C for the data

Phase	∆Н`©98 (кЈ mol)	$\Delta H_{1,ars}$ (kJ)	S'298 (J Kmol)	С _р (J К)			
				А	В	C	D
a-Si3N4	-870.0	1.23	61 5	74.5	112 769	-6 046	28 662
β -Si $_3N_4$	-865 8		64.43	103.902	65.429	-26.039	11 571

Table 7.5: α and β silicon nitride estimated thermochemical data.

in Table 7.5, and is in good agreement with the generally accepted temperature of $1900^{\circ}C^{53}$

These data were then used to evaluate:

- the free energy of reaction for the gas/solid and gas phase reactions, processes, which experimentation suggests are directly related to nucleation and growth.
- 2) the effects of varying the amount of nitrogen feed gas and its effects on the deviation away from equilibrium.

7 9.2 Reactions in the Si-O-N-C System

7.9.2.1 The formation of silicon nitride

Earlier sections concerning the deposition of silicon nitride on substrates (Section 7.7) and the effects of seeding (Section 7.8) have indicated that there are two possible reactions for the formation of silicon nitride. The first is the gas/solid reaction:

$$3StO_{(0)} + 3C_{(1)} + 2N_{(0)} = 5t_{1}N_{4t_{1}} + CO_{(1)}$$
(7.12)

and the second is the gas phase reaction (7.12), which involves the deposition of silicon nitride on pre-existing silicon nitride surfaces,

$$3S_{iO} \frac{1}{g} + 3CO_{ig} + 2N_{2(g)} = Si_{3}N_{4(5)} + CO_{2(g)}$$
(7.13)

The React program on the $F^*A^*C^*T$ system was used to calculate the equilibrium reaction temperature and the free energy (ΔG_T) at 1500°C, in order to determine whether either one was valid under the conditions stated. The partial pressures of each of the gases (CO, CO₂, N₂ and SiO) were those determined by the Equilib program at 200 moles of N₂ for Reaction 7.11.

The calculation (Appendix I) shows that the equilbrium ($\Delta G_T=0$) temperature for both the gas/solid and gas phase reactions is 1500°C for the conditions stated above, so that both reactions may theoretically proceed. In reality, the reaction route that is taken would depend on the activation energy barriers to each that must be overcome. From the series of substrate experiments, the carbon surface is the preferred nucleation site for silicon nitride over an inect material like alumina; therefore the activation energy must be lower for the gas/solid reaction. This is not surprising since, in the absence of a suitable surface for nucleation, the gas phase reaction would require homogeneous nucleation to take place; a process requiring a greater activation energy than heterogeneous nucleation (Section 3.2.8.1).

7.9.2.2 The back reaction between silica and silicon nitride

The back reaction between silica and silicon nitride was investigated in Section 7.8.2 as a possible means of reaction between the silicon nitride seed particles and the silica. It was not known if the original seed particles were consumed during carbothermal reduction as per Reaction 7.5, or whether they did not participate in the process, acting instead as a surface for nucleation. Increasing the seed content of a C:SiO₂ mixture appeared to increase the amount of silica lost as SiO gas, but results were inconclusive. Similarly, the reaction between a mixture of silica and silicon nitride in a 3:1 molar ratio at 1500°C did not show very much reaction. By entering the same reactants (SiO₂ and Si₃N₄) plus an excess of nitrogen (to simulate the nitrogen atmosphere used) into the Equilib program, it was found that the resulting products (Appendix I) would be residual silica and silicon oxynitride. Silicon oxynitride is not apparent in the reaction products in the ventilated crucible, however it is well known that in reality the formation of silicon oxynitride is sluggish^{1/4} and can only be made to proceed via the presence of a liquid phase. Therefore, since any reaction is prevented by kinetic considerations, it would appear that this back reaction would not take place under the circumstances encountered during carbothermal reduction.

7.9.3 Modelling of carbothermal reduction of silica

In Reaction 7.14 the stoichiometric ratio of nitrogen:silica is 1:1.5; however, using the Equilib program, it was possible to show how the reaction products are affected by altering the amount of nitrogen feed gas.

$$3S_{i}O_{2(g)} + 6C_{(g)} + 2N_{2(g)} = S_{i}N_{4(f)} + 6CO_{(g)}$$
(7.14)

Figure 7.41 is the partial pressures of oxygen, carbon monoxide and silicon monoxide obtained from the program for a 7:1 carbon silica ratio at equilibrium against the nitrogen content in the system at 1500° C. Also shown on the figure is the amount of nitrogen that marks the boundary between the stability of silicon oxynitride and silicon nitride. This point corresponds to a partial pressure of oxygen of 7 2x10 20 atm, which is the same order of magnitude as the value calculated from experimental work by Blegan³⁶ for the formation of silicon nitride. From an experimental point of view, this data can represent two situations either as a variation in the amount of feed gas introduced into the system, or the amount of gas reaching



Figure 7.41: Partial pressures of SiO, O₂, CO vs. initial nitrogen feed content

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the reactants, as in the use of the closed-end alumina crucibles. The experiments conducted in these crucibles at various carbon:silica ratios frequently resulted in the formation of small quantities of silicon oxynitride (Appendix II) but this was never the only phase present for exactly the same reasons given in the previous section.

The effect of nitrogen is to dilute the amount of oxygen and carbon monoxide to levels that allow the formation of silicon nitride. This situation can be represented with the aid of a predominance diagram, with the abscissa and ordinate axes being the partial pressures of carbon monoxide and oxygen, respectively. Figure 7.42 is the predominance diagram calculated by the Predom program for the SI-O-N-C system at a constant nitrogen partial pressure of 0.98 atm (calculated by Equilib for Reaction 711). These boundaries do not change significantly between nitrogen partial pressures of 0.75 to 1 atm., which in Figure 7.42 corresponds to a range of 5 to 1200 moles of nitrogen feed gas, respectively. Line A-B on the diagram represents the equilibrium partial pressures of oxygen and carbon monoxide for increasing amounts of nitrogen feed gas seen in Figure 7.41. This line defines the equilibrium conditions for the carbothermal reduction reaction. At low partial pressures of nitrogen (A), the equilibrium conditions are well within the silicon oxynitride phase stability region. At higher partial pressures of nitrogen (B), the equilibrium conditions are well into the silicon nitride phase region, lying parallel and very close to the Si₃N₄/SiC boundary Since this line ideally represents equilibrium conditions, slight increases in the carbon monoxide partial pressure (i.e. non-equilibrium conditions) could alter the position of the equilibrium so as to stabilize silicon carbide. Therefore, the is thought to be the reason why silicon carbide is seen in trace amounts in reactions carried out in the closed-end alumina crucible; carbon monorale is



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Figure 7.42: Si-O-N-C predominance diagram at 1773 K p_{O2} vs p_{C0}

not flushed out, with localized build-up promoting silicon carbide formation. When using the ventilated graphite crucible, the action of the gas passing through the reactants greatly reduces the carbon monoxide partial pressure, such that the reaction conditions are well within the silicon nitride stability region.

An alternative means of viewing the system is shown in the predominance diagram seen in Figure 7.43, where the ordinate axis is now the activity of carbon. Once again, the line AB represents the equilibrium conditions for the carbon monoxide partial pressure and the amount of nitrogen feed gas seen in Figure 7.41. This line is consistent with what was shown in Figure 7.42: at low partial pressures, the equilibrium conditions are well within the silicon oxynitride phase stability region, but as the amount of nitrogen feed gas increases, so the equilibrium enters the silicon nitride phase stability region. The equilibrium still runs parallel and close to the silicon nitride/silicon carbide boundary (a carbon activity of 1.409), which is slightly greater than the carbon activity of unity obtained by Equilib. This substantiates the suggestion made by Hendry and Jack¹⁰⁰ that silicon carbide formation from rice hulls was promoted by carbon with activities greater than unity produced by the pyrolysis of organic hydrocarbons. This modelling of the equilibrium conditions of carbothermal reduction shows that there is a very delicate balance which, if upset, leads to the formation of undesirable phases such as silicon carbide and silicon oxynitride. In reality, the reaction must be carried out under favourable conditions that are well away from the equilibrium state. This was achieved by using a ventilated graphite crucible. The flow of nitrogen gas through the reactants (as opposed to being in excess in the system, as in the F*A*C*T modeling) would tend to lower the partial pressure of all the gaseous species in the reactants much more than the excess



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Figure 7.43: Si-O-N-C predominance diagram at 1773 K. $a_c vs. p_{CO}$

of nitrogen used for the calculations which assumes a large volume of gas. On the p_{02}/p_{CO} predominance diagram, this would probably move the reaction equilibrium position to well within the silicon nitride phase stability region.

The idea of non-equilibrium conditions brings the estimation of the ΔH°_{f298} for a-silicon nitride into doubt, since this was based upon t⁽¹⁾e optimum reaction temperature of 1500°C, determined from experimentation. However, two things would indicate that the assumption of a lower value would be incorrect: The first is that if the ΔH°_{f298} for a silicon nitride were reduced to the value obtained by Colquboun et al.¹³⁸ (820 kJ/mol), the equilibrium decomposition temperature is reduced to 1800°C; and second'y, the measurements of ΔH°_{f298} for β (Table 4.1) are much higher than the values estimated here. Thus, the estimation of the thermodynamic propervies of silicon nitride are valid and in accordance with the existing data for other species like silicon carbide, silicon oxynitride and for experimental observations.

7.10 SUMMARY OF RESULTS

The process for the carbothermal reduction of carbon and silica mixtures to form a silicon nitride powders has been shown to be optimized by the following conditions:

- 1. Sol-gel processing particularly for intimate mixing.
- 2. Carbon silica ratio of 7:1.
- **3**. Temperature of 1500°C to 1550°C.
- 4. High surface area carbon, and high surface area silica.
- 5. Nitridation of loose powders rather than compacted pellets.
- 6. Nitrogen feed gas scrubbed of O_2 .

7. Ventilated graphite crucible to allow the feed gas to pass through the reactants.

Despite these conditions, the a-silicon nitride particle size derived under these conditions, being approximately 3-4 μ m, is still too large to be considered as a high-quality sinterable powder. The large particle size was seen as relating to the amount of nucleation occurring during nitridation. So seed material, in the form of ultra-fine silicon nitride, was used as a nucleating agent, which resulted in a greatly reduced particle size. From the observation of the nucleation behaviour, it is proposed that the seed material did not act as sites for the nucleation of more particles but, instead, grew larger by self-deposition. The particles obtained in this manner are much smaller than those seen in the unseeded material because it is suggested that there are more seed particles than there were original nucleation sites in the unseeded material. Therefore, in the seeded material, growth takes place preferentially on the seed particles, rather than nucleation on the carbon surface.

In Section 7.6.2 on unseeded nucleation and growth mechanisms, it was observed that clumps of silicon nitride particles developed on the free surfaces within pellets of carbon and silica. The fact that they were in the form of clumps suggested that they perhaps originated from a single particle of silicon nitride that happened to form. Subsequent particles were then nucleated on this one and they, in turn, would have nucleated more in an ever-increasing cluster. However, it would be expected that there would be a range of particle sizes seen in the clumps from the recently nucleated up to those that had been growing, which is generally not the case. Instead, it is suggested that the development of the clumps occurs along the lines of the schematic seen in Figure 7.44, based upon the observations on nucleation and growth made in



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Figure 7.44: Suggested development of clumps of particles seen on surfaces within capping fractures of carbon/silica pellets.

section 7.8.3.

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Initially, a cluster of nuclei form in a very localized area of the pellet subsurface the carbon/silica compact (a). The individual particles then grow (b & c) and in so doing, the clump expands outwards from the surface until the growth ceases (d). The nucleation in loose powder is presumed to take place in much the same way.

7.10.1 Bulk Powder Production

The amount of powder produced from any of the experiments discussed in this study has been no more than a few grams. The greatest hurdle to overcome is the scale-up of the process to make larger quantities, especially of a high-quality and reproducible nature A larger graphite crucible was made (15 cm diameter by 23 cm high) with a series of equally spaced trays, each with holes in (See Figure 7.15). Holes were placed around the base of the crucible so that gas could flow in through the base and out through a hole in the top. The gas, flowing at at 1.9 L/min, was introduced into the furnace heating chamber, the only way out to the atmosphere being through the base of the crucible, through the levels of trays, and out through the top. The highest area carbon and silica (M1300 and EH-5) were mixed, using the solgel preparation technique, in a molar ratio of 7 1, with 5 wt % (by weight of silica) of UBE seed silicon nitride. The gel was not crushed up into a loose powder in this instance, since the high flow-rate used tended to blow the fine particles out of the crucible. Instead, the gel was used in the state that it was formed, with some of the larger lumps being broken down

A carbon element resistance furnace was used to heat the crucible Prior to heating, the furnace was evacuated and then flushed with nitrogen. After



Figure 7.45: Graphite element resistance furnace with graphite crucible, trays and powder in position.

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flushing, the gas flow was started. The crucible was then heated up to a temperature of 1500°C, which was maintained for a period of five hours.

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Once the crucible was cool, the powders from each tray were removed and kept separate, the carbon was then removed by heating the powders at 700°C for two hours. No immediate difference between the trays could be seen with the naked eye, except for the top tray which had many clusters of whiskers The space between the top of the crucible and the top tray was much larger than for any of the other levels. The occurrence of whiskers was thought to be due to the turbulent nature of the gas flow in the upper level.

The lower trays all produced fine particles similar to those seen in Figure 7.46 which were in the region of 1 μ m in diameter, with no sign of any whiskers. The cumulative size distribution of the powder is seen in Figure 7.47 with a median partical size of approximately 2.4 μ m, which is larger than the micrograph might suggest. Also seen in the figure is the distribution for a commercially produced silicon nitide powder (Toshiba A-200), which has a median particle size of almost half that produced in this work

The major disappointment with this powder was the relatively high silica content detected as cristobalite by XRD, and confirmed by a high oxygen content of 2.77 wt%.

From the modelling of the process with the F*A*C*T system, The occurrence of silica was associated with reduced partial pressure of nitrogen, and higher partial pressures of oxygen. This was probably associated with the design of the crucible; since, under the present condition, the partial pressures of the gaseous species would be greater at the top than at the base of the crucible, i.e. as the gas flows up through the crucible, so the gases like SiO and CO will be picked up and passed on from tray to tray, becoming more concentrated with increasing tray level. One way to remedy this would be to



Figure 7.46: Bulk powder particles.

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Figure 7.47: Cumulative particle size distribution of silicon nitride produced in bulk and experimentally, compared with a commercial Toshiba powder (A-200).

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have the gas flow "in parallel" through the trays, rather than "in series", as was used before. Figure 7.48 is a suggested design where gas enters the crucible through holes in the circumference of each tray, and passes out of the crucible through a graphite pipe up the center, thereby eliminating severe concentration build up of waste gases.

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Figure 7.48: Suggested improvements in crucible design.

CHAPTER 8

CONCLUSIONS AND FUTURE WORK

8.1 CONCLUSIONS

The research work into the formation of silicon nitride by the carbothermal reduction of silica has been carried out in order to determine the optimum conditions under which high-quality powders will form. In so doing, the manner in which silicon nitride forms during carbothermal reduction has also been clearly determined.

A) The Influence of Carbon Black and Silica

The carbon black has a two-fold effect on the conversion of silica to silicon nitride:

- (1) The amount of carbon black used must be in excess of the stoichiometric requirement in order to satisfactorily disperse the silica and prevent sintering. In this work, the minimum carbon:silica molar ratio that gave complete conversion was 7:1.
- (2) The specific surface area of the carbon black must be as high as possible (in this instance 560 m²/g) in order to provide sufficient nucleation sites for the formation of silicon nitride.
- (3) The particle size of the silica has no direct bearing on the degree of conversion to silicon nitride for ultra-fine powders with surface areas between 130m²/g and 380 m²/g.

B) Mixing

The advantages to using sol-gel processing of silica and carbon mixtures with iso-propanol as the dispersing liquid were:

- Improved dispersion of silica and carbon than for dry mixing of powders.
- (2) Full conversion of silica to silicon nitride could be achieved, whereas dry mixing could never approach complete conversion even when using large excesses of carbon.
- (3) The particle morphology of silicon nitride obtained from sol-gel processed mixtures, when using high surface area carbons, was always more uniform and equiaxed than powders derived from drymixed powders; the latter were invariably tape or ribbon morphologies.

C) Particle Characteristics of Silicon Nitride

- (1) Silicon nitride powders with uniform equiaxed morphologies had qualitatively much higher nitrogen and significantly lower oxygen contents than those with tape or ribbon morphologies. The existence of a high oxygen content is indicative of either residual silica or oxynitride.
- (2) The minimum particle size that could be produced in unseeded mixtures was between 2-3 µm with a broad particle size distribution due to agglomeration.
- (3) The particle size of unseeded mixtures is affected by the condition of the powder mixture used. This particle size is achieved when using sol-gel mixtures that were broken into very light powders (blended as opposed to crushed) providing more free surface for nucleation

D) Ideal Reaction Conditions and Thermoynamic Modelling

- (1) The temperature range over which the maximum conversion takes place after a five-hour period is between 1500°C and 1550°C. Below 1500°C, the reaction is incomplete with large amounts of residual silica remaining, whereas exceeding 1550°C results in the formation of silicon carbide.
- (2) Nitrogen gas flowing through the reactants by means of a ventilated crucible leads to the production of silicon nitride with no additional phases present. Thermodynamic modelling showed that an excess of nitrogen of at least 100 moles per mole of silica was required to prevent the stabilization of silicon oxynitride, and furthermore showed that silicon carbide was a non-equilibrium phase. The action of the nitrogen gas flowing through the reactants reduces the partial pressures of oxygen and carbon monoxide gas and therefore stabilizes a-silicon nitride.
- (3) Flowing nitrogen gas alone was not sufficient to prevent the formation of silicon oxynitride, but had to be gettered with titanium sponge to eliminate oxygen
- (4) Thermodynamic modelling provided a means by which a working set of data for both a and β silicon nitride could be estimated based upon data existing in the literature.

E) <u>Reaction Stages</u>

(1) Substrate deposition experiments demonstrated two ways in which silicon nitride can form: The first is by deposition on a carbon surface, and secondly by growth or accretion on pre-existing silicon nitride by the gas phase reaction. (2) It was shown that SiO formation occurred quite readily, but the nucleation of silicon nitride on carbon by the gas-solid reaction is the rate-limiting step Once silicon nitride has nucleated, growth takes place by the gas phase reaction.

F) The Effect of Seeding

- (1) By using 5 wt.% of very fine particle seed material, the particle size of silicon nitride after carbothermal reduction could be reduced by a factor of two. The ultimate particle size achieved was dependent upon the particle size of the seed material. The finer the seed particle size, the finer the silicon nitride powder that was formed.
- (2) A large excess of seed powder in the reactants resulted in a heavily agglomerated powder.
- (3) From the seeding experiments it was found that the seed particles grow by self-deposition rather than act as nucleation sites for more particles. Since this was the case, nucleation of particles in unseeded reactants was envisaged as taking place on the carbon by the gas-solid reaction which, once formed, continued to grow via the gas phase reaction.

G) Bulk Powder Production

Larger quantities (~80g) of silicon nitride were produced in conditions that took advantage of the conditions optimized in the preceding conclusions. A reasonably fine powder was produced, but the mean particle size did not come close to that achieved in a commercial powder The oxygen content (2.7 wt.%) of the powder was high, suggesting that the reaction was incomplete, and it was assumed that this could be overcome by a better reactor design.

8.2 SUGGESTED FUTURE WORK

- A) This work has shown that production of fine particle (1µm) silicon nitride by carbothermal reduction starting with the precursors that were used is not possible without seeding. Therefore it is suggested that other carbon sources, such as those derived from organic compounds, be investigated to try to determine the factors involved in nucleation on carbon.
- B) If seeding proves to be the only way to achieve sub-micron powders, further work should be conducted to ascertain the influence that the initial seed powder has on the product particle size. It would be of interest to try seeding with ultra-fine silicon nitride powders, such as those produced by the plasma technique, since these are the finest available. However, problems may arise if the seed powder is amorphous and may have to undergo a crystallization heat treatment.
- C) The bulk powders produced in this study had a relatively high oxygen content, the cause being attributed to the unsatisfactory design of the reactor. It was not known whether this was a result of insufficient nitrogen gas, or poor temperature distribution in the reactor. Further work should be carried out to:
 - (a) model the flow of gas through the reactor and reactants and change the design of the reactor such that gas flow conditions are as uniform as possible.
 - (b) study and optimize the furnace temperature and the temperature distribution within the reactor.
- D) Finally, the sintering behaviour of the powders should be studied and compared with commercial powders. However, rather than using addit.ve compositions that have proved successful for other powders,

new compositions must be tried that make allowance for, or take advantage of the silica and carbon content of the powder.

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CHAPTER 9

STATEMENT OF ORIGINALITY

This Ph.D. thesis is the first complete study of the critical process parameters and reaction mechanisms involved in the carbothermal reduction of silica to form silicon nitride powder.

This work has been the first to demonstrate the following:

- (1) The viability of a sol-gel processing stage, using iso-propanol as the dispersing liquid, in order to intimately mix ultrafine carbon and silica powders. Nitridation of carbon and silica mixtures prepared by the sol-gel method was shown to be more effective than with mixtures prepared by dry mixing.
- (2) The optimum carbon to silica ratio was found to be 7:1. An excess of carbon was necessary in order to: (a) adequately disperse the silica and prevent it from sintering, and (b) to provide a large surface area for nucleation of silicon nitride.
- (3) The requirement for nitrogen gas to flow through the reactants in order to prevent the formation of silicon oxynitride and silicon carbide.
- (4) All possible sources of oxygen must be kept to a minimum in order to prevent the formation of silicon oxynitride. This meant using a graphite crucible and the removal of the oxygen from the nitrogen feed gas.
- (5) That silicon nitride, formed by unseeded carbothermal reduction, which had a ribbon morphology, was high in oxygen as opposed to equiaxed particles, which had a low oxygen content.
- (6) A working set of thermodynamic data for a and β silicon nitride were established.

- (7) Thermodynamic modelling to show the effect of gaseous and solid species on the outcome of carbothermal reduction. The partial pressures of oxygen and carbon monoxide, the activity of carbon, and the volume of nitrogen feed gas were found to be the critical parameters controlling the formation of silicon nitride With the aid of predominance diagrams, these parameters were effectively able to show the complete Si-O-N-C system.
- (8) The reaction mechanism for the nucleation and growth of silicon nitride: first by the nucleation of silicon nitride by the gas-solid reaction (SiO, N₂ gas and C) and then growth of the nucleated particles via the gas phase reaction (SiO, N₂ and CO).
- (9) The small addition of sub-micron sized silicon nitride particles as seed material, was sufficient to reduce the final particle size to below one micron. The final particle size was dependent upon the initial particle size of the seed material the smaller the seed particles, the smaller the silicon nitride produced.
- (10) The seed material does not provide additional sites for the nucleation of new particles but, rather, grew by the gas phase reaction.

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APPENDIX I

EQUILIB PROGRAM

1 SiO	G ₁ gas	298.0 K - 2000.0 K
$2 \operatorname{Si}_2 \mathrm{N}$	G ₁ gas	298.0 K - 6000 0 K
3 SIN	G_1 gas	298.0 K - 6000.0 K
$4 \operatorname{Si}_2 \mathrm{C}$	G ₁ gas	298.0 K - 6000.0 K
$5 \operatorname{SiC}_{2}$	G ₁ gas	298.0 K - 6000.0 K
6 SIC	G ₁ gas	1400.0K - 6000.0 K
7 Si 3	G ₁ gas	298.0 K - 3000.0 K
8 Si ₂	G ₁ gas	298.0 K - 6000.0 K
9 Si $[+]$	G ₁ gas	298 0 K - 6000.0 K
10 Si	G_1 gas	298.0 K - 3000.0 K
11 CNO	Gigas	298.0 K - 6000.0 K
$12 N_2O_5$	G ₁ gas	298.0 K - 2000.0 K
13 N_2O_4	G ₁ gas	298.0 K - 6000.0 K
$14 N_2 O_3$	G ₁ gas	298.0 K - 6000.0 K
$15 NO_3$	G ₁ gas	298.0 K - 6000.0 K
$16 NO_{2}[-]$	G ₁ gas	298.0 K - 6000.0 K
17 NO_2	G ₁ gas	298.0 K - 3000.0 K
18 N ₂ $O[+]$	G ₁ gas	298 0 K - 6000.0 K
19 N_2O	G ₁ gas	298.0 K - 6000.0 K
20 NO[+]	G ₁ gas	298.0 K - 6000.0 K
21 NO	G ₁ gas	298.0 K - 3000.0 K
22 $C_{3}O_{2}$	G ₁ gas	298.0 K - 6000.0 K
23 CO ₂ [-]	G ₁ gas	298.0 K - 6000.0 K
24 CO_2	G ₁ gas	298.0 K - 2500 0 K
25 CO	G ₁ gas	298.0 K - 2500 0 K
26 O ₃	G ₁ gas	298.0 K - 2000 0 K
$27 O_2[-]$	G ₁ gas	298 0 K - 6000.0 K
$28 O_2$	G ₁ gas	298 0 K - 3000 0 K
29 O[+]	G_1 gas	298.1 K - 6000 0 K
30 O[-]	G ₁ gas	298.0 K - 6000 0 K
31 O	G_1 gas	298.0 K - 3000.0 K
$32 C_4 N_2$	G ₁ gas	298.0 K - 6000.0 K
$33 C_2 N_2$	G ₁ gas	298 0 K - 2000.0 K
34 CN_2	G ₁ gas	298.0 K - 6000.0 K
$35 C_2 N$	G ₁ gas	298.0 K - 6000 0 K
36 CN[+]	G ₁ gas	298.0 K - 6000.0 K
37 CN[-]	G ₁ gas	298.0 K - 6000.0 K
38 CN	G ₁ gas	298.0 K - 2000 0 K
39 N ₃	G ₁ gas	298.0 K - 6000.0 K
40 N ₂	G ₁ gas	298.0 K - 2500 0 K
41 N[+]	G ₁ gas	298.0 K - 6000.0 K
42 N	G ₁ gas	298.0 K - 2500 0 K
43 C ₅	G ₁ gas	298.0 K - 6000.0 K
44 C ₄	G ₁ gas	298.0 K - 6000.0 K
45 C ₃	G ₁ gas	298.0 K - 6000.0 K

46 C ₂ [-] 47 C ₂ 48 C		$egin{array}{c} G_1 & { m gas} \ G_1 & { m gas} \ G_1 & { m gas} \end{array}$	298.0 K - 6000 0 K 298.0 K - 4000.0 K 298.0 K - 4500 0 K
49 SiO ₂ 50 SiO ₂ 51 SiO ₂ 52 Si 53 N ₂ O ₄	<	L ₁ liquid L ₁ liquid 1 L ₂ Liq-trid L ₁ liquid L ₁ liquid	298 0 K = 1700 0 K 996.0 K - 3000 0 K 295.0 K - 300.0 K 1685.0 K - 3492 0 K 295.0 K - 300 0 K
54 Si ₃ N ₄ 55 Si ₃ N ₄ 56 SiO ₂ 57 SiO ₂ 58 SiO ₂ 59 SiO ₂ 60 SiO ₂ 61 SiO ₂ 62 Si ₂ N ₂ O 63 SiO ₂ 64 SiO ₂ 65 SiO ₂ 66 SiO ₂ 66 SiO ₂ 68 Si ₃ N ₄ 69 SiC 70 SiC	< < < < < <	S_1 alpha S_2 beta S_1 quartz(A) S_2 quartz(B) S_3 trid(A) S_4 trid(B) S_5 crist(A) S_6 crist(B) S_1 solid S_1 quartz(L) S_2 quartz(H) S_3 crist(L) S_4 crist(H) S_5 trid S_1 solid S_1 solid S_1 solid S_1 alpha S_2 beta S_2 beta	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
$\begin{array}{c} 72 \ N_2O_5 \\ 73 \ C \\ 74 \ C \end{array}$		S_1 solid S_1 graphite S_2 diamond	295.0 K - 1005 0 K 295.0 K - 300 0 K 298 0 K - 4073 0 K 298.0 K - 1200 0 K

Code numbers of seleted species:

/1-48/54556162697073

 $\begin{array}{l} SiO_2 + \ 7\ C \ + \ 200\ N_2 \\ (1773,1,S6) \ (1773,1,S1) \ (1773,1,G) \end{array}$

201.34		+ 0.99007	N_2
	+	0.98983e ¹⁾²	CŌ
	+	$0.35178e^{-0.4}$	SiO
	+	$0.14242e^{-0.6}$	C_2N_2
	+	$0.29184e^{-07}$	Si
	+	0.14797e ⁻⁰⁷	SiN
	+	0.85052e ⁻¹⁾⁸	CO_2
	+	0.38278e-08	CN
	+	0.38494e ⁻⁰⁹	${ m SiC}_2$
	+	0.36161 e ⁻⁰⁹	$\rm Si_2N$

$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	
$\begin{array}{cccc} + & 5.0070 & C \\ (& 1773.0, 1.00 & , S_1, 1.0000 &) \end{array}$	
+ 0.33097 Si ₃ N ₄ (1773.0, 1.00 , S ₁ , 1.0000)	<
+ $0.00000E + 00$ Si ₃ N ₄ (1773 0, 1.00 ,S ₂ , 0.99756)	<
+ $0.00000E + 00$ SiC (1773.0, 1.00, S ₂ , 0.69231)	
+ $0.00000E + 00$ SiC (1773.0, 1.00 ,S ₁ , 0.60436)	
+ $0.00000E + 00$ Si ₂ N ₂ O (1773.0, 1.00 ,S ₁ , 0.44750)	<
+ 0 00000E + 00 SiO ₂ (1773.0, 1.00 S_6 . 0.9 $\overline{6}$ 092E-04)	<

Gaseous ionic species are suppressed below 3000 K

The cutoff concentration has been specified to 0.100e-48

Data on 4 product species identified with '<---' have been drawn from your private data collection

******	*******	*****	*****	*****	*****	*** * * * * * * * * * *
ЧL	ΔG	ΔV	2 S	۵U	ΔA	V
(J)	(J)	(L)	(J)	(J K)	(J)	(J)
******	******	*****	*****	****	******	****
257498	8.6 -59101.5	0.145e + 0.3	178.567	242760.4	-73839 8	$0.291e \cdot 03$

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Thermodynamic calculation with EQUILIB relating to the reaction between silica and silicon nitride.

1 SiO 2 Si $_2$ N 3 SiN 4 Si $_3$ 5 Si $_2$ 6 Si[+] 7 Si 8 N $_2$ O $_5$ 9 N $_2$ O $_4$ 10 N $_2$ O $_3$ 11 NO $_3$ 12 NO $_2$ [-] 13 NO $_2$ 14 N $_2$ O[+] 15 N $_2$ O 16 NO[+] 17 NO 18 O $_3$ 19 O $_2$ [-] 20 O $_2$ 21 O[+] 22 O[-] 23 O 24 N $_3$ 25 N $_2$ 26 N[+] 27 N		G1 Gas G1 G	$\begin{array}{c} 298.0 \ \mathrm{K} - 2000 \ 0 \ \mathrm{K} \ 1 \\ 298 \ 0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 2 \\ 298 \ 0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 2 \\ 298.0 \ \mathrm{K} - 3000 \ 0 \ \mathrm{K} \ 1 \\ 298.0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 2 \\ 298.0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 2 \\ 298.0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 2 \\ 298.0 \ \mathrm{K} - 3000 \ 0 \ \mathrm{K} \ 1 \\ 298.0 \ \mathrm{K} - 2000 \ 0 \ \mathrm{K} \ 1 \\ 298.0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 2 \\ 298.0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 2 \\ 298.0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 2 \\ 298.0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 2 \\ 298.0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 2 \\ 298.0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 2 \\ 298.0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 2 \\ 298.0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 2 \\ 298.0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 2 \\ 298.0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 1 \\ 298.0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 1 \\ 298.0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 1 \\ 298.0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 1 \\ 298.0 \ \mathrm{K} - 6000 \ 0 \ \mathrm{K} \ 2 \\ 298.0 \ \mathrm{K} - 3000 \ 0 \ \mathrm{K} \ 1 \\ 298.0 \ \mathrm{K} - 3000 \ 0 \ \mathrm{K} \ 1 \\ 298.0 \ \mathrm{K} - 3000 \ 0 \ \mathrm{K} \ 1 \\ 298.0 \ \mathrm{K} - 3000 \ 0 \ \mathrm{K} \ 1 \\ 298.0 \ \mathrm{K} - 3000 \ 0 \ \mathrm{K} \ 1 \\ 298.0 \ \mathrm{K} - 3000 \ 0 \ \mathrm{K} \ 1 \\ 298.0 \ \mathrm{K} - 3000 \ 0 \ \mathrm{K} \ 2 \ 298.0 \ \mathrm{K} \ 2 \ 298.0 \ \mathrm{K} - 3000 \ 0 \ \mathrm{K} \ 2 \ 298.0 \ \mathrm{K} \ 2 \$
28 SiO ₂ 29 SiO ₂ 30 SiO ₂ 31 Si 32 N ₂ O ₄	<	L ₁ Liquid L ₁ Liquid L ₂ Liq-Tridy. L ₁ Liquid L ₁ Liquid	298.0 K - 1700.0 K 2 1996.0 K - 3000 0 K 1 295 0 K - 300.0 K 1 1685.0 K - 3492 0 K 1 295.0 K - 300.0 K 1
$\begin{array}{cccc} 33 & {\rm Si}_{3}{\rm N}_{4} \\ 34 & {\rm Si}_{3}{\rm N}_{4} \\ 35 & {\rm SiO}_{2} \\ 36 & {\rm SiO}_{2} \\ 37 & {\rm SiO}_{2} \end{array}$	< < < <	S_1 alpha S_2 beta S_1 quartz(a) S_2 quartz(b) S_3 trid(a)	298.0 K - 2000.0 K 1 298.0 K - 2000 0 K 1 298.0 K - 848 0 K 1 848.0 K - 2000.0 K 1 298.0 K - 390.0 K 1

-38 Si	iO2 ·	< S4	trid(b)	390.0 K -	2000.0 K 1
39 Si	iO_2^{-}	< S5	crist(a)	298 0 K -	543.0 K 1
40 Si	iO2 ·	< S ₆	crist(b)	543 0 K -	3000.0 K 2
41 Si	i_2N_2O	< S1	solid	298 0 K -	2100.0 K 1
42 S	ıÕ2	S_1	quartz(1)	298.0 K -	847.0 K 1
43 Si	iO_2	S2	quartz(h)	847 0 K -	1696.0 K 1
44 Si	iO_2^-	−−−S}	erist.(1)	298.0 K -	543.0 K 1
45 Si	iO_2	S4	crist.(h)	543.0 K -	1996.0 K 1
46 Si	iO_2^-	S5	tridymite	295.0 K -	300.0 K 1
47 Si	$i_3 N_4$	S_1	solid	298.0 K -	2151.0 K 1
48 Si	i	S_1	solid	298 0 K -	1685.0 K 1
49 N	205	S_1	solid	295.0 K -	300.0 K 1

Code numbers of selected species:

/1-27/28,33-41,48 $3 \operatorname{SiO}_2 + \operatorname{Si}_3 \operatorname{N}_4 + 1200 \operatorname{N}_2$ ${
m N}_2
m SiO$ 1201.6 (0.99900) + 0.10011E-02+ 0.22711E-08 Si + 0.11567E-08 SiN + 0.50031E-09NO + 0.22144E-10 N + 0.46180E-11 0 + 0.21998E-11 Si_2N + 0.29040E-13 N_2O + 0.15599E-13 Si_2) (17730, 1.00).G) SiO₂ <---+ 15990(1773 0, 1 00 ,S₆, 1.0000) + 1.5990 Si_2N_2O <--- $(17730, 100, S_1, 1.0000)$ <--- X + 0.00000E + 00 SiO_2 (1773.0, 1 00 ,S₃, 8.5138) $+ 0.00000E + 00 SiO_2$ <--- X $(17730, 1.00, S_1, 1.2517)$ <--- X + 0.00000E + 00 SiO_2 $(17730, 1.00, S_5, 1.0958)$

Gaseous ionic species are suppressed below 3000 K

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Data on 10 product species identified with '<---' have been drawn from private data collection

REACT PROGRAM

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The data for the partial pressures used in the REACT program were obtained from the output of EQUILIB above

The gas solid reaction:

 $3 \operatorname{SiO} + 3 \operatorname{C} + 2 \operatorname{N2} = \operatorname{Si3N4} + 3 \operatorname{CO}$ (T,.3517E-4.G) (T,1,S1) (T,99007.G) (T,1,S1) (T,9898E-2,G)

Calculations are based on the indicated number of gram moles

******	*****	******	*****	*****	* * * * * * * * * * * *	*****
(T) (K)	ΔH (J)	ΔG (J)	∆V (L)	ΔS (J/K)	<u> Ц</u> Ц	ΔA
******	*******	******	*****	*****	*****	*****
1773.0	-868717.4	12.3 -	0.124e + 08	-489.976	-839235.6	29493.8
<u>The gas</u>	phase reacti	<u>on</u>				
3SiO + (T,.3517	3 C1O + 2 N 7E-4,G) (T,.9	2 = Si3 898E-2,	N4 + 3102 G) (T99007,	G)(T,1,S1)	(T,.8505E-8	, G)
Cal	culations are	e based o	on the indica	ted number	of gram mo	les
******	****	** *****	*****	*****	****	*****
(T) (K)	(J)	∆G (J)	ΔV (L)	ΔS (J K)	∆U (J)	ΔA (J)
1773.0	-1355302.0	*******	**************************************	-764 418	-1281602.0	**************************************

 SiO_2

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FORMULA: SiO₂

NAME. Silica CSIRO DATA

FORMULA WEIGHT: 60 085

PHASE NAME CPRANGE(K)

S_1	quartz(A)	298.0 - 848.0	$\Delta H TRANS (848.00 \text{ K}) =$	= 1.213 (K J)
S_2	quartz(B)	848.0 - 2000 0		
S_3	trid(A)	298 0 - 390.0	$\Delta H TRANS (390.00 \text{ K}) =$	0.167 (KJ)
S_{4}	trid(B)	390.0 - 2000 0		
S_5	erist(A)	298.0 - 543.0	$\Delta H TRANS (543.00 \text{ K}) =$	1.343 (KJ)
S_6	crist(B)	543 0 - 2000 0		
S_6	crist(B)	2000.0 - 3000 0		
L	liquid	298.0 - 1500.0		
Ll	lıquıd	1500.0 - 1700 0		

Cp = A + 1.0E - 3*B*T(K) + 1.0E5*CT(K)**-2 + 1.0E - 6*D*T(K)**2

******	* * * * * * * * * * *	*****	* * * * * * * * * * * * *	<*******	<*****	********	*******
PHASE	$\Delta H(298)$	S(298)	DENSITY	А	В	С	D
	(KJ)	(J /K)	(g/cm-3)		(,	J /K)	
* * * * * * * * * *	* * * * * * * * * * *	*****	********	******	****	******	******
S_1	-910.857	$41 \ 463$		46.944	34.309	-11.297	0.0
S_2	-911.186	$37\ 776$		60.291	8.117	0 0	0.0
S_3^-	-907.489	43.932		13.682	103.763	0.0	0.0
S_4	-908.377	$41\ 225$		57.070	11.046	0.0	0.0
S_5	-908.346	$43 \ 396$		43.126	41.927	-8.901	-7.427
S_6	-905.493	50.049		72.762	1.304	-41 378	-0.053
S_6	$-907\ 183$	46.376		72.012	1.631	-33.095	-0.057
L	-902.656	47.928		49.950	32.152	-13.053	-10.416
L_1	-872.185	96.880		-9.339	55.898	0.0	0.0

FORMULA: Si₃N₄

NAME. Silicon nitride

FORMULA WEIGHT: 140.285

PHASE NAME CPRANGE(K)

 $C_P = A + 1.0E - 3*B*T(K) + 1.0E5*CT(K)**-2 + 1.0E - 6*D*T(K)**2$

******	*****	******	*****	*****	*****	*****	****
PHASE	$\Delta H(298)$	S(298)	DENSITY	' A	В	С	D
	(KJ)	(JK)	(g/cm-3)		(J K)	
<* ~ *****	*****	*****	*****	*****	*****	****	******
S_1	-870.000	61.500		74.500	112.767	-6.046	-28.660
S_2	-865.800	64.429		103.901	65.429	-26.037	-11.573

FORMULA: Si₂N₂O

NAME: Silicon oxynitride (FEGLEY DATA)

Formula weight: 100.185

PHASE NAME CPRANGE(K)

S1 SOLID 298.0 - 2100.0

CP = A + 1.0E - 3*B*T(K) + 1.0E5*CT(K)**-2 + 1.0E - 6*D*T(K)**2

FORMULA: SiC

NAME: Silicon carbide

Formula weight: 40.097

PHASE NAME CPRANGE(K)

S_1	alpha	298.0 - 662 0
Si	Joha	662.0 - 3200.0
S_2	beta	298.0 - 678.0
S_2^-	beta	678.0 - 3200.0
$\tilde{G_1}$	gas	1400.0 - 6000.0

 $CP = A + 1.0E \cdot 3^*B^*T(K) + 1.0E5^*CT(K)^{**} \cdot 2 + 1.0E \cdot 6^*D^*T(K)^{**} \cdot 2$

******	******	*******	******	*******	******	******	*******	****
PHASE	$\Delta H(298$) S(298)	DENSI	TY A	В	С		D
	(KJ)	(JK)	(g/cm 3)		(J'K)		
*******	*****		*******	< <i>**</i> ******	** ****	******	******	****
S_1	-71 546	$16 \ 485$	3 217	36.489	14.652	-13 037	0.0	
S_1	70.057	20.520	3.217	49.597	2.636	-35.606	0.0	
S_2	$73\ 220$	16.610	3.217	35.648	15.954	-12.523	0.0	
\mathbf{S}_2	-71583	21.044	3.217	50.576	1.992	-37 639	0.0	
\mathbf{G}_1	719.648	$212\ 97$	ideal	39.392	0.393	7058	0.0	

REFERENCE

"JANAF THERMOCHEMICAL TABLES", D.R. STULL AND H. PROPHET, U.S. DEPARTMENT OF COMMERCE, WASHINGTON, 1977.

Formula: Al₂O₃

Name: aluminum oxide

Formula weight: 101.961

PHASE NAME CPRANGE(K)

S_1	corundum	298.0 - 800.0
S_1	corundum	$800.0 - 2327.0 \Delta H \text{ TRANS} (2327.00 \text{ K}) = 118.407 \text{ (KJ)}$
L_1	liquid	2327.0 - 3500.0

CP = A + 1.0E - 3*B*T(K) + 1.0E5*CT(K)**-2 + 1.0E - 6*D*T(K)**2

********** PHASE $\Delta H(298)$ S(298) DENSITY С А В D $(KJ) = (J/K) = (g/cm^{-3}) = \dots = (J/K)$ S_1 $-1675\ 274$ 50 936 3.970 103 851 26.267 -29.091 0.0 S_1 -1674.876 $52\ 392$ 3.970 120 516 9.192 -48.367 0.0L -1595.529 - 45.1443 970 144.863 0.00.00.0

REFERENCE

"THERMOCHEMICAL PROPERTIES OF INORGANIC SUBSTANCES", I. BARIN, O. KNACKE, AND O. KUBASCHEWSKI, SPRINGER-VERLAG, BERLIN, 1977.

APPENDIX II

SEMI-QUANTITATIVE XRD MEASUREMENT

Tables II.1 and II.2 show the % integrated peak heights (i.e. % peak areas) of a-silicon nitride, silicon carbide, amorphous silica, silicon oxynitride and cristobalite for Figures 7.1, 7.2, 7.7 and 7.8. β -silicon nitride was never observed in any carbothermally produced powders, and was assumed to be below the limit of detection (~5%) by XRD.

	Carbon: Silica Ratio	a- Si ₃ N4 ~~	${\mathop{\mathrm{SiO}}_2_{c_{\mathcal{O}}}}$	${{ m Si}_2 { m N}_2 { m O}}_{{}^{m_{ m N}}}{ m O}$	$\operatorname{Crist}_{c_{\mathcal{V}_{o}}}$	$\operatorname{SiC}_{\gamma_0}$
Alumina crucible						
Loose	1:1	7.9	48.5	-	37.8	5.8
	2:1	16.5	76.1	7.4	-	-
	4:1	15.1	68.7	16.2	-	-
	7:1	34 9	-	18.2	-39.4	7.6
	10.1	100	-	-		
Graphite Crucible				-	-	-
Loose	1:1	3.0	95.7	-	~	-
	2:1	16.0	87.1	25.5	-	-
	4:1	88.5	-	-	19.9	
	7:1	100	-	-	-	-
	10:1	100	-	-	-	-

Table II.1: Data for Figures 7.1& 7.2

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Silica	Carbon	a- S13N4 'ć	SiO_2	$\mathrm{Si}_{2}\mathrm{N}_{2}\mathrm{O}_{\mathcal{T}_{0}}$
Loose				
EH5	M-800	35.6	87.2	-
	M-880	38.2	80.7	-
	M-1000	45.6	80.9	-
	M-1300	100	-	-
		-		
M-5	M-800	36.8	86.8	-
	M-880	37.6	84.0	-
	M-1300	100	-	-
LM-130	M-800	22.4	94.0	-
	M-880	34.7	86.5	-
	M-1300	100	-	-
Pellet				
EH5	M-800	22.9	94.6	-
	M-880	12.8	97.6	-
	M-1000	22.0	95.2	-
	M-1300	93.6	-	99
M-5	M-800	12.1	97.7	-
	M-880	12	97.2	-
	M-1300	94.4	-	97
LM-130	M-800	19.2	96 2	-
	M-880	22.4	93.8	-
	M-1300	94 3	0	9.6

Table II.2: Data for Figures 7.7& 7.8

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Errors

The principal errors or uncertainty were:

- 1. The measurement of the peak area using the Zeiss IBAS image analyzer.
- 2. The minimum peak detectable above the background noise.
- 3. The bandwidth of the background noise.

1. Measurement of Peak Area

The peaks all had to be traced by hand using a stylus. Each peak was measured three times, and the variance determined for all the measurements representing one species (e.g. Si_3N_4) using the lumped variance technique.

Integrated peak intensity $(Si_{3}N_{4})$ = y_{11},y_{12},y_{13}

 $\Sigma_{i} = (y_{11} - y_{1})^{2} + (y_{12} - y_{1})^{2} + (y_{12} - y_{1})^{2}$

Since all groups have three replicates, the number of degrees of freedom is 2.

The uncertainty of measuring the peak areas is given in Table II.3.

	% uncertainly in peak area
a-Si3N4	1
SiO ₂ (amor.)	16
$\rm Si_2N_2O$	8
SiC	5
crystobalite	5.2

Table II 3

2. Minimum Detectable Peak

The minimum amount of any species detectable above the background noise was conservatively estimated at 2% and was otherwise neglected since there were much larger errors encountered with area measurement and the background noise signal

3. Bandwidth of Backgroud Noise

The background noise was taken into account by measuring the area of the background under each peak. These values were then added to the original peak heights and the 75 integrated peak height for silicon nitride was recalculated in order to obtain the percentage uncertainty for silicon nitride.

The total uncertainty in each measurement due to area measurement and background noise are given in Tables II.4 and II.5, the total error or uncertainty being:

 $(Total Error)^2 = (Background Error)^2 + (Area error Si_3N_4)^2 + ...$

+(Area error SiC)2

	Si Bekd			ž	Area (۲۷)			Fotal
	SiO2 ratio	(Tr)	$S_{13}N_4$	S_1O_2	$S_{12}N_2O$	Crist	SiC	tainty
Alumina Crucible Fig. 7.1 and 7.2	$1:1 \\ 2:1 \\ 4:1 \\ 7:1 \\ 10:1$	$9.8 \\ 10 \ 4 \\ 13 \ 4 \\ 16.6 \\ 6.5$	1 1 1 1	16 16 16 -	8 8 8	52 - 52	.) .)	$\begin{array}{c} 20 \ 1 \\ 20 \ 7 \\ 22 \ 3 \\ 19 \ 8 \\ 6 \ 6 \end{array}$
Graphite Crucible Fig. 7.2	$ \begin{array}{c c} 1 \cdot 1 \\ 2 \cdot 1 \\ 4 \cdot 1 \\ 7 \cdot 1 \\ 10 \cdot 1 \end{array} $	$\begin{array}{c} 3 \\ 16 \\ 6.3 \\ 4.11 \\ 7 \ 03 \end{array}$	1 1 1 1	$ \begin{array}{c} 16 \\ 16 \\ 0 \\ 0 \\ 0 \\ 0 \end{array} $	0 8 0 0)	52 0 52 -	-	$ \begin{array}{r} 17 \\ 24 \\ 8 \\ 4 \\ 4 \\ 7 \\ 1 \end{array} $

Table II.4

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Table II 5

	Carbon	Bkg	Area (%)					Total
	Туре	$(\mathcal{C}_{\mathcal{C}})$	$S_{13}N_4$	SiO_2	Si ₂ N ₂ O	Crist.	SiC	tainty
Loose Powder Fig. 7.7	M-800 M-880 M-1000 M-1300	$37 \\ 19 \\ 39 \\ 4.1$	1 1 1 1	16 16 16 -	- - -	- -		$ \begin{array}{r} 41 \ 3 \\ 24 \ 9 \\ 42 \ 2 \\ 7 \ 1 \end{array} $
Pellets	M-800 M-880 M-1000 M-1300	$ \begin{array}{r} 10.9 \\ 15 1 \\ 19 8 \\ 9.7 \\ \end{array} $	1 1 1 1	16 16 16 -	- - -	- - -	-	$ \begin{array}{r} 19 \\ 22 \\ 0 \\ 25 \\ 5 \\ 9 \\ 8 \end{array} $

APPENDIX III

CALCULATION OF THE AMOUNT OF SiO₂ LOST AS SIO GAS FOR SEEDED AND UNSEEDED REACTANTS

Starting Material

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Decarburization of starting powder

wt. $\% SiO_2$ in C·SiO_2 mixture = <u>Residue - (Residue × wt. $\% Si_3N_4$ seed)</u> Total wt. of C.SiO_2 before decarburization

Note: wt.% seed Si₃N₄ = $\underline{\text{wt.of Si}_3N_4} \times 100$ wt. of SiO₂

Total weight of seed in C:SiO₂ mixture = $\underline{wt\%.of Si_3N_4 \text{ seed} \times \text{Residue}}$ Total wt. of C:SiO₂

EXPERIMENT

Before Reaction

Initial wt. of seed = initial wt. of C:SiO₂ mixture $\times \frac{\text{wt\%.of Si_3N_4 seed}}{100}$

After Reaction

 $Wt.\% Si_3N_4 \text{ seed in final residue} = \frac{Initial wt. of \text{ seed } Si_3N_4 \times 100}{Total wt. of residue}$

DECARBURIZATION

Wt. of $S_{13}N_4$ seed = Initial wt. before decarb. $\times \underline{\text{wt. of } S_{13}N_4 \text{ seed in residue}}{100}$

Wt. of residue without Si_3N_4 seed = wt. after decarb. - wt. of Si_3N_4 seed

Amount of SiO₂ remaining = (wt. residue w/o seed) × (100- wt% .Si₃N₄estim*) 100

* estimated from XRD measurements.

Amount of SiO₂ converted to Si₃N₄ = $(wt.residue w \circ seed - amount SiO₂ remaining) x 1.297$

 $= 3 \operatorname{SiO}_2 + 6C + 2N_2 = \operatorname{Si}_3N_4 + 6CO$

180g/mol 140g/mol

Therefore, 1 gram Si_3N_4 requires 1.29 g SiO_2 .

 $SiO_2 lost as SiO = [SiO_2]_{init} - [SiO_2]_{Si_3N_4} - [SiO_2]_{remainder}$

[SiO₂]_{init}

ERRORS

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The three principal sources of uncertainty were:

- 1. weight measurement.
- 2. estimation of the wt.% of silicon nitride in the final product from XRD
- 3. Errors in conducting the experimentation (reproducibility).
- Weight measurement was carried out to four decimal places with an estimated uncertainty of ± 0.002 g.
- The uncertainty in estimating the amount of silicon nitride in the final product was taken from Appendix II.
- By repeating experiments five times at carbon to silica ratios of 2:1 and 7-1, the standard deviations were ± 1.958 and ± 0.8897 , respectively.

The total uncertainty for the weight measurement and Si_3N_4 estimation by substituting in the maximum values of the uncertainty in the calculation above, and are shown in Table III.1 for the data seen in Figure 7.4.

C.SiO ₂	Graphite crucible	Alumina crucible		
1 1	9.18 ± 0.13	り±り 39		
2:1	29.28 ± 0.50	12.65 ± 0.66		
4:1	33.23 ± 0.47	12.65 ± 0.66		
71	15.59 ± 1.53	19.03 ± 0.56		
10.1	8.73 ± 0.92	9.41 ± 0.92		

Table III.1. SiO_2 Lost as SiO

APPENDIX IV

CALCULATION OF THE NUMBER OF SILICON NITRIDE PARTICLES, GRAINS PRODUCED FROM UNSEEDED AND SEEDED PRECURSOR MIX FURES

Using Carbon:Silica Ratios of 7.1:

From Experimentation:

(a) unseeded: $4.0214 \text{ g of } \text{C} + \text{SiO}_2 \text{ provides } 1.1530 \text{ g Si}_3\text{N}_4$

Therefore $1 \text{ g of } C + SiO_2 \text{ provides } 0.2867 \text{ g Si}_3N_4$

(b) seeded (5%): $4.0183 \text{ g of } C + SiO_2 \text{ provides } 1.1610 \text{ g Si}_3 N_4$

Therefore $1 \text{ g of } C + SiO_2 \text{ provides } 0.2889 \text{ g Si}_3N_4$

	Unseeded	Seeded	Seed Particle
Particle sıze (µm)	3	1	0.5
Volume of particle (4/3πr ³ , cm ³)	1.41×10 ¹¹	$5\ 24 \times 10^{-13}$	6 55×10 11
Mass of particle (g)	4.51×10^{-11}	1 67 × 10 12	2 09×10 13
Particles/g reactants	6.36×10^{9}	1.73×10^{11}	1.23×10^{11}

Density $Si_3N_4 = 3.19 \text{ g cm}^3$

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