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Investigation of the Rate-Controlling Mechanism(s) for High Temperature Creep and the Relationship Between Creep and Melting by Using High Pressure as a Variable

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I Introduction

Silicon nitride is a high strength-to weight ratio, insulative material of great interest in the manufacture of high thermal efficiency heat engine parts such as in the automotive industry. A comparison of silicon nitride with other structural materials is presented in Table I. Silicon nitride offers the advantages of high strength, high thermal shock resistance and a low coefficient of thermal expansion. Although Y-TZP offers higher room temperature strength and toughness, the thermal shock resistance properties are poor. SiC is a high hardness material with excellent heat resistance, but the toughness and shock resistance are poor.

The resulting high strength and fracture toughness of silicon nitride is attributed to the cross-linked, lathe-like structure of the β phase which is found to transform during the lengthy sintering process from the initial equiaxed α phase starting powders. However, it is this very high strength that makes machining to form complex parts extremely time consuming and therefore costly. An alternative to the labor intensive machining process would be the use of a superplastic deformation process in which complex parts are virtually stamped out of flat sheets. For the mechanisms of this forming process to operate in a ceramic system, a very small equiaxed grain structure of less than 0.5 microns in size is required [Ref. 1]. Thus, to investigate the mechanisms of superplastic deformation in the silicon nitride system, a consolidation process is required in which the equiaxed α phase of the starting powders are retained along with a submicron grain size. After deformation of the components, heat treatments could be used to transform the α to β phase and regain the high strength and fracture toughness of the silicon nitride.

II) Sintering Processes

a) Conventional Sintering

Silicon nitride is typically consolidated by either hot press sintering (HPSN) or by reaction bonded, pressureless sintering (RBSN). In both processes, the ceramic is heated in a radiation furnace to 1750 °C and held for 3 hours. The starting powders used are composed of >95% equiaxed α phase. Powders prepared for the RBSN process are coated with a polymer based lubricant to optimize the viscosity for complete filling of the molds used for the desired shapes. To remove the polymer lubricant, the RBSN process includes an initial bakeout process at 600 to 700°C.

External pressure assists in the high temperature densification by increasing the localized loads applied at the contact points. In addition, a closed system is maintained which limits the sublimation and volatilization processes at high temperature. Thus HPSN components typically achieve higher densification rates than RBSN, i.e., 100 % vs 75% Theoretical Density (TD), with a corresponding difference in strength. Although the RBSN process produces lower density parts, complex net shape parts can be produced without extensive machining. Whereas, the fully dense HPSN components can only be produced in simple geometric shapes which require subsequent machining to form complex parts. HIP processing is often included after the RBSN processing to increase densification, and has also been shown to be an effective consolidation method by itself [A].

In all of the conventional processing methods, the specimen is heated externally. Therefore in those with very low thermal conductivities, long heating times are required to heat the part to the required temperature of 1750°C which also results in transformation of the starting α phase to the β

phase. Since these processing methods are very lengthy, other novel processing methods were pursued for this project. However, the final consolidation of Si_3N_4 will still rely on combining the known mechanisms with establishing the parameters for the new process.

1) Mechanisms of Consolidation in Conventional Sintering

Although the consolidation processes differ in the applied load, the mechanisms responsible for sintering in both HPSN and RBSN are considered to be the same. Self diffusivity in covalently bonded solids such as nitride ceramics is poor. The surface and grain boundary diffusion rates are slow, and at temperatures which enhance atomic mobility, the nitrides tend to dissociate. An additional barrier to diffusion is the presence of a thin SiO_2 layer around the powders which further inhibits the already slow diffusional rates. This layer is generally a result of oxidation during the synthesis process. Thus achieving full consolidation of pure silicon nitride is considered to be difficult, if not impossible.

Both of the conventional sintering processes use additives which react with the SiO_2 on the powder particle surface to form an eutectic phase at the grain boundaries. SiO_2 melts at 1750°C and reacts with the oxide additives to form the eutectic second phase. Subsequent rate of densification is related to liquid viscosity and wetting characteristics of the liquid which can change with time and temperature. Many liquid phase sintering models have been applied to densification of nitride ceramics [Ref. 2, 3, 4, 5, 6]. Although the models differ in the details of the rate controlling mechanisms, which are strongly influenced by the chemical nature of the impurities and additives, all models require stages of particle rearrangement by grain boundary sliding and of solution-precipitation of solid phases in a liquid to promote densification. Use of the modified version of Coble's grain boundary diffusional creep model [Ref. 6] listed in Table II, for consolidation in ceramics indicates the rate controlling mechanisms will only be effective in the silicon nitride

system for a maximum particle size of 0.5 μm .

The resulting second phase formed during consolidation is typically some type of an oxynitride glass which remains at the grain boundaries. Because these glasses soften at temperatures in the range of 1000 to 1200°C, detrimental effects are noted on the resulting high temperature mechanical properties. Thus, additives systems are continually being pursued which would form either a solid solution with the Si_3N_4 , increase the refractory nature of the second phase, or those that can be devitrified by heat treatment. Our studies will rely on the research of others to best match the additive system with the required microstructure sought for this project.

Densification in Si_3N_4 ceramics is historically accompanied by an α to β phase transition, marked by a change in grain morphology. While some studies of the Si_3N_4 system with additives suggest that the transition is primarily temperature dependent and occurs around $1550 \pm 50^\circ\text{C}$ [Ref. 3], other researchers suggest that the phase change occurs in conjunction with the liquid enhanced sintering mechanisms in which the α phase is dissolved in the liquid grain boundary phase and reprecipitated out as the more temperature stable β phase [Ref. 4]. This phase change has been theorized as necessary to complete consolidation by some researchers [Ref. 4]. Still others, such as Bowen, et. al. [Ref. 6] do not consider the phase change to be necessary for consolidation. Since silicon nitride is a very effective insulator, long sintering times are required to heat the component in radiation furnaces. It has therefore been very difficult for researchers to sort out the time versus temperature dependency of the phase transformation from α to β .

Successful consolidation of pure Si_3N_4 has only been achieved in HIP (hot isostatic pressing). The processing parameters are in the range of 1-5 GPa where 99% TD was cited for temperatures above 1900°C with 2-4 hour hold times [A]. Although no oxide additives were used, anywhere

from 1 to 2 wt% can be present in the starting powders which can still be responsible for formation of a liquid phase at the sintering temperatures. The use of very large pressures may indicate deformation processing which are occurring resulting in the high densification. Additionally, at these high temperatures, dissociation of the silicon nitride may also be occurring. Final phase composition and free silicon presence of the specimens were not reported, however for these hold times a large content of β phase would be expected. [Ref. A-Okada, et. al., "Fabrication of Dense Si_3N_4 by Hot Isostatic Pressing", Science of Sintering, Vol. 20, No. 2/3, pp 127-134, 1988].

Our studies have agreed with the liquid phase sintering models. Near full density components have been produced at 1750°C in less than 5 minutes. Our results have shown that if the consolidation temperatures are reached very quickly, the α phase is retained in the near theoretical density specimens. Our results also agree with the solution-reprecipitation mechanisms for the phase transformation. The < 5 wt% β phase present in the starting powders, which is thermally stable, provides the nucleation sites for the reprecipitation of the solutionized α phase from the second phase. Dependent on the chemical composition, the second phase typically melts over a range from 1543 to 1660°C . Therefore heat treatments to produce the phase change can be done at temperatures lower than the 1750°C consolidation temperature.

b) Electrical Resistance Sintering

Electrical resistance sintering is a very rapid process in which powders are consolidated by the direct Joule heating effects of a high electrical current in conjunction with hot pressing. This process is very effective in the case of metals or high electrically conducting powders. However, difficulties in achieving full consolidation are experienced in those highly conductive metal powders which form tenacious oxide films. Thus to augment the resistance heating process,

various schemes have been tried since the 60's to enhance the resistance heating effects. These methods have been referred to as spark sintering or electric-discharge sintering [Ref. 7, 8, 9, 10] and target breaking down the oxide layer to activate the surface for interparticle material diffusion. Most recently Sodick Co. of Japan has produced a prototype of an plasma-activated-sintering (PAS) device.

c) Plasma Assisted Sintering (PAS)

The PAS process incorporates two stages to assist in the consolidation of powdered material. These stages are configured in series with individual controls as illustrated schematically in Figure 1. During the first stage the powder is lightly prepressed and subjected to a RF pulsed (0.5 to 500 Hz) DC current. If the powders are heavily oxidized, the dielectric nature enables electrical power to be stored in the oxide layer. Provided the time of each pulse is sufficiently long, the electrical power will be released when the material experiences a dielectric breakdown. If sufficient energy is discharged, intense heating can locally result in the contact zones of the powder particles and in some cases can create a plasma in the surrounding gas. Both of these phenomena result in the destruction of surface oxide films on the particles.

The second stage of the process is the application of resistance heating to the graphite punches and powders by Joule heating effects. Studies of resistance heating have indicated that the electric current does provide an activating effect and diffusional processes during electrical heating are accelerated [Ref. 11]. Very high heating rates can be obtained in this stage of up to 100°C/sec.

Thus the two mechanisms operating in the PAS equipment for consolidation of powders are the use of a cycled current to create a electric-discharge that promotes locally high temperatures for the melting and/or ionization of surface oxide films and the subsequent creep deformation and

enhanced diffusional processes of the newly activated powder surface under load.

1) Mechanisms of Consolidation in PAS

The benefits of this PAS stage apply to heavily oxidized metals and also ceramic systems. In oxidized powders, the oxide film is advantageously used to form a dielectric gap between the adjacent particles. Electrical energy can be stored in this dielectric layer over a period of time to be made available intermittently by discharging the capacitor in a short period of time. It is this high energy discharge that results in locally high temperatures which are sufficient to break down the oxide layers. A further homogeneity of the ionization of the surface oxide is achieved by control of the environmental conditions (ie, pressure, temperature, and composition) to form a gas plasma. The electrical discharge would breakdown the oxide layers at points of contact between the particles while the plasma would attack the oxide layers on the non-contacting areas of the particles. Pulsing of the current homogenizes the distribution of electric discharges in the material and can also help sustain a gas plasma once created. Once local areas of surface oxides have been broken down, an electrical path becomes established between adjacent particles. These additional paths are then effective at charging the remaining oxide dielectric layers.

With electrically insulative ceramic materials, sufficient electrical energy must be stored within the powders. That is, a critical value and strength of the dielectric properties must be present. Establishment of a current path is dependent on the time required to store enough energy to result in the dielectric breakdown of the insulating ceramic. As the dielectric field breaks down, the current path is established between adjacent particles. Thus the activation of the powder surfaces by causing a dielectric breakdown of the insulator also sets up the current path required for subsequent resistance heating of the powders. This mechanism can be especially beneficial in powders which rely on liquid phase sintering where the additives and the processing parameters

can be chose on the basis of the dielectric properties rather than the material being sintered.

To maximize the charging capabilities of the PAS equipment the electrical power can be focused through the powders by insulating the outside die from the center punches and powder as illustrated in Figure 2. Spraying of BN powder on the internal diameter of the outside die serves as an effective insulating layer. Ceramic liners can also be used to insulate the punch from the die. Graphite is used for the die material to permit operation at high temperatures ($>2000^{\circ}\text{C}$). However, the maximum load that can be applied is 700 kgf/cm^2 . Metal dies have been used for higher loading conditions for sintering of metals at lower temperatures ($< 1000^{\circ}\text{C}$).

III PAS Consolidation Experiments with Si_3N_4

All experiments were conducted in PAS equipment with a 4000 amp capacity. During sintering the temperature of the outer surface of the graphite die was monitored with an IR optical pyrometer which has an expected accuracy of $\pm 100^{\circ}\text{C}$. The inside powder temperature was not measured at this time. Based on the high heat conductivity properties of the graphite, a high thermal gradient is not expected between the outside and inside of the graphite die. Type C thermocouples (2000°C capability) have been ordered and will be used to measure the inside temperature of the powders in future consolidation experiments.

Approximate density measurements were made for all pressed samples by measurements of the dry weight and geometrical dimensions. Those that indicated densities greater than 90% TD were measured using the Archimedes method for greater accuracy. A Scintag X-Ray Diffraction (XRD) unit with Cu $k\text{-}\alpha$ radiation source was used to identify phases based on the lattice parameter spacings in the initial powder and consolidated specimens. Relative compositions of α and β phases were calculated using the methods of Gazzara [Ref. 12] and Babini [Ref. 13].

a) Pure Si_3N_4

A series of experiments was performed to determine the benefits of the PAS process for pure silicon nitride. Effectiveness of the electrical discharge pulses between the powders during the PAS cycle in activating the particle surfaces was evaluated. The dielectric constant for pure silicon nitride is approximately 6 and is not noted to increase with temperature or frequency [Ref. 14]. This corresponds to a low capacitance for the Si_3N_4 material which may not be able to store sufficient energy to locally ionize surface oxides or surrounding gases. Attempts to maximize the electrical energy supplied to the powder by isolating the die from the center punches resulted in cracked dies. This suggests a possible limit to the current carrying capability of the graphite.

The silicon nitride powders used in this study are commercially available from UBE Industries. Powder specifications are listed in Table III. Table IV summarizes the PAS operational parameters with the results of the pure silicon nitride consolidation experiments.

1) Discussion of Pure Si_3N_4 Results

Consolidation experiments were conducted in a non-pressurized gaseous nitrogen (GN_2) environment. Only one experiment produced a consolidated specimen (#05109402) which was extremely thin (~ 1 mm) and brittle. Free silicon resolidified at the base of the graphite die indicating some decomposition had occurred. XRD analysis of specimen #05109402 in Figure 3 corresponds to a 100% β phase with the presence of one unknown peak at 28.53° (d spacing = 3.126 Å). The unidentified peak is suspected to be a contaminant, possibly carbon diffusion from the graphite dies.

No consolidation was noted in the remaining specimens with XRD analysis of the cold pressed powder indicating 100% pure α phase. Lattice distortion of the α phase was noted in specimen #05239401 by a slight shift in the peak locations of the XRD analysis in Figure 4. This specimen was subjected to a slightly higher temperature (2090° C) than the other unconsolidated specimens. This uniform shift of the lattice parameters is presumed to be due again to solid state diffusion of carbon into the silicon nitride matrix. To verify the XRD operation, a calibration check of the quartz standard was performed with no peak shifts noted.

Consolidation temperature for the final specimen #05239402 was 2200 °C which resulted in complete sublimation of the specimen. As silicon nitride sublimates the nitrogen is liberated and the remaining silicon becomes a liquid (melting temperature silicon = 1200 °C). The crystals coating the inside of the cavernous graphite die were determined to be a SiC phase by the XRD analysis shown in Figure 5. Again the SiC peaks were noted to be shifted slightly.

These experiments suggest that silicon nitride is a very effective electrical insulator which does not undergo dielectric breakdown at the powder levels generated in this PAS equipment. Results of the pure silicon nitride consolidation experiments in which consolidation was only achieved in a very thin specimens with carbon diffusion, indicated a critical level of conductivity was required for completing the current path necessary for consolidation. The following experiments utilized conductive additives to establish a conductive path through the Si_3N_4 powders.

b) Doped Si_3N_4

To verify the role of additives in consolidation of silicon nitride, prepared powders with additives known to assist in the conventional consolidation processes were investigated. Two series of experiments were conducted with silicon nitride powders and oxide additives of Mg, Y, and Al as

summarized in Table V. This powder had been prepared by Toyota Co. of Japan and consisted of powder granules formed by spray drying of a polybinder coated slurry [Ref. 15]. The average granule size was 70 μm and consisted of 0.3 μm Si_3N_4 and spinel particles and 1 μm yttria particles as shown in Figure 6. The range of spherical shapes, summarized in Figure 7, resulted in very efficient packing. The presence of the polybinder acts as a lubricant and prevents agglomeration of the powder particles.

Cold press densities in the range of 52-56% TD were obtained for all specimens. Cold press density was also measured following the PAS cycle and indicated a slight increase of 1-2 % TD, which was not considered significant.

1) Discussion of Doped Si_3N_4 Results

The conditions for the first set of experiments consolidated in air from 1395 to 1632 $^{\circ}\text{C}$ are summarized in Table VI. Full consolidation was achieved while retaining 68 to 82 % α phase. SEM photographs in Figure 8 indicate essentially no particle growth from the initial starting powder sizes. However, Figure 9 shows photomicrographs of the sintered surface at low magnification (100X) which indicates preservation of the initial granule geometry. Apparently at this temperature the polybinder and additives were able to redistribute and fill in the pores forming a second phase around the granules as illustrated in Figure 10. Limited diffusion may have been obtained among the smaller particles. Hardness measurements were in the low range of 50-60 HRA.

Table VII summarizes the second set of experiments conducted in a variety of environments in the temperature range of 1650 to 1820 $^{\circ}\text{C}$. Densities of 80% of TD were obtained with a 30 ms (17 Hz) current pulse during the PAS stage. Higher densities of 98+% TD were obtained by going to

a lower frequency pulse 160 ms (3 Hz). Retention of the α phase was approximately 88%.

Hardness measurements of these samples were in the range of 79-110 HRA.

Resulting grain morphology of the specimens with greater than 99% TD were examined using SEM of the fracture surfaces. Figure 11 notes the appearance of equiaxed particles in the range of 0.5 to 1 μm . This equiaxed particle morphology and XRD analysis of a high α phase content should provide a suitable microstructure for investigation of superplasticity mechanisms. A glassy phase is noted surrounding the grain boundaries when the oxide additives are increased to levels containing >10 wt% oxygen

IV Summary

Various types of materials can be produced by changing the starting powders, additive content and concentration, and manufacturing processes. It is readily conceivable that the resulting properties of Si_3N_4 could ultimately be tailored by control of the chemistry and microstructure. The initial experiments show promise for the use of the PAS equipment in consolidation of Si_3N_4 . The residual glassy phase which appears to be present could be minimized by controlling the amount of oxygen in the additive system. Figure 13 shows the microstructure of Si_3N_4 with 5 wt% Y_2O_3 (6 wt% oxygen), added in which the grain boundaries appear to be very clean. However, only 94% TD was achieved due to the low amount of oxygen in the additives introduced.

The two step process of the PAS equipment has been found to have benefits for heavily oxidized metal powders as well as ceramic powders. For metal powders, the degree of electrical conductivity is sufficient to route the current density through the powders. When insulating oxide films are encountered, a capacitor effect is noted in which the electrical energy is stored until a

dielectric breakdown is experienced. The release of this energy is sufficient to locally heat and ionize the surface oxides. There may be an additional gas plasma created by this release of energy to the surrounding gases. Ionization of the surface oxides and contaminants activates the surface for the subsequent resistance heating phase. The conductivity of the metal powders ensures the current density is focused directly and efficiently through the powders.

Applicability of the PAS process to ceramic materials can be characterized by their electrical and thermal conductivity. Mechanisms of sintering for ceramic materials that exhibit electrical conductivity properties are similar to metal powders. If the electrical conductivity properties are temperature dependent, benefits of the initial PAS process would be limited. Although the temperature of the powder components does increase during the PAS stage, the temperature is typically between 100 to 300 °C. The extremely fast consolidation would be dependent on the nature of resistance heating. The diffusional nature of grain growth predicts a time dependency, thus very fast heating can eliminate or minimize grain growth.

For purely electrical and thermally insulative powders, the equipment can still be used. The current path through the graphite die becomes a furnace which can radiate heat inward to the powders. This unfortunately takes time and much of the benefits of this fast sintering method are not realized. Therefore, to efficiently use the PAS equipment with non-electrically conducting powders, the use of additives is recommended to establish an electrically conductive path within the interior of the powders.

V PAS Equipment Control

To select optimal parameters for the PAS operation, the dielectric, electrical and thermal conductivity properties should be characterized for the powders of interest. For purely conductive

powders in which oxide films do not form a barrier to diffusion, the PAS stage does not offer any benefit. The powders will be rapidly consolidated by the resistance heating stage.

For difficult to sinter materials due to stable oxide formations, the PAS stage offers the most benefit. The dielectric constant and strength of the material will determine the charge capabilities. To determine the effectiveness of the PAS process in activation of the powder surface, the required energy to breakdown oxide films will need to be calculated based on the thermodynamic properties of the compound. The most effective system will be one in which the charge capabilities of the dielectric material is greater than the energy needed to breakdown the oxide layer.

Once the required electrical charge is known to activate the surfaces, this will be directly related to the PAS frequency. Those materials that charge slowly (low dielectric constants) will require slow frequencies, whereas high frequencies can be applied to rapidly charged materials (high dielectric constants).

Dielectric properties can be introduced or enhanced by use of additives in the starting powders. Additional experiments are planned to determine the critical levels required for consolidation using the PAS equipment.

Once a powder has achieved an acceptable level of consolidation, the effective current density (E) can be calculated per Eqn. (1) [Ref. 10]. This provides a method of scaling the selected parameters to different size specimens.

$$E = \frac{(I^2) (t) (l_m)}{(g) (s)}$$

Eqn. (1)

where:

E = Effective Current Density (A/m^2)

I = Current (A)

t = Sintering Time (sec)

l_m = Mean Specimen Length (m)

g = Specimen Weight (kgs)

s = Cross Sectional Area (m^2)

VI Recommended Studies

a) Dopant Introduction Schemes

A homogeneous dispersion of sintering additives is beneficial to accelerate the consolidation process and produce the best microstructure for mechanical property testing. Since Si_3N_4 is consolidated by liquid phase sintering where the liquid phase is produced as a eutectic reaction between the SiO_2 layer surrounding the powder and the oxide additives, the resulting second phase is assured of uniformity due to capillary action. However, even with this method best results are expected when the additives are uniformly dispersed. Additives used have had particles as large as $1.6 \mu m$ which resulted in a very homogeneous chemical distribution after consolidation as determined by WDS microprobe analysis.

b) Final Heat Treatments

Once the parts have been densified and deformed, it may be possible to lock in the shape by completing the alpha to beta phase transformation. Since the studies so far indicate a time and temperature dependent nature for complete phase transformation, a conventional furnace can be

used to hold the final specimen at 1550 to 1750 °C for the required time. The hot press furnace at UCD has GN₂ capabilities and would accommodate continued studies of the phase transformation in the Si₃N₄ system.

In addition to locking in the microstructure, possibly by the β particles, any residual glassy interface could possibly limit the high temperature strength of the material. Review of the literature is being used to provide guidelines as to the types of oxynitride glasses that have been successfully de-vitrified or have refractory nature. Improvements have been noted in the mechanical properties of the silicon nitride system when mixtures of oxides are added rather than a single oxide. This will be balanced with the PAS consolidation which requires the oxygen content to be 10 wt% to achieve 99%TD.

VII Conclusion

The ability to consolidate Si₃N₄ with additives to 99% TD while retaining > 88% alpha phase has been demonstrated with the PAS equipment. The process is controlled by second phase sintering. Because of the mechanisms for formation of the second phase, temperatures of 1750°C are required. Near theoretical density consolidation can be achieved in air or vacuum within 5 minutes with no discernible dissociation. The process is independent of stress, although 12 Mpa is required for operation of the PAS equipment.

Preliminary heat treatments of the consolidated specimens in conventional furnaces will further the understanding of the phase transformations in the Si₃N₄ system. The β transformation may well prove to be time and temperature dependent. Although the solution-reprecipitation processes predicted in the presence of an intergranular second phase may indicate that the level of β transformation achieved during sintering is directly related to the weight percent of the additives.

Therefore the recommended path to minimize additive content will not only minimize resulting high temperature mechanical property degradation, but should also limit the phase transformation during the consolidation process.

Specimens are now available to begin mechanical property testing. Initial compression tests will be used to understand the strain rate sensitivity of the Si_3N_4 system.

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Figure 1
PAS Sintering Schematic

Figure 2

Focusing of Electrical Power Through Powder

Figure 3

β silicon nitride crystalline structure

Figure 4

α silicon nitride crystalline structure

Figure 5

SiC crystalline structure

Figure 6
Electron Microprobe
WDS Particle Size Identification in Granules

Figure 7
Initial Granule Size Distribution

SN 1119-2
Temperature = 1395°C
Density = 92 % TD
Alpha Phase = 90 %

SN 1119-3
Temperature = 1632°C
Density = 100 % TD
Alpha Phase = 42 %

Figure 8
SEM of Fracture Surface of Granule Specimen
Consolidated at Low Temperature in Air

Figure 9
Photomicrograph of the Surface of the Consolidated Granule Specimens

Figure 10
Details of Low Temperature Consolidated Granule Specimens

Figure 11
SEM of Fracture Surface of SN 721-2 Consolidated Granules

SN 06289403

Temperature = 1760°C

Density = 98 % TD

Alpha Phase = 88.5 %

SN 06289404

Temperature = 1700°C

Density = 98 % TD

Alpha Phase = 88.0 %

Figure 12
Convention Temperature Range
in PAS Consolidation of Granules

Figure 13
SEM of Fracture Surface of SN NGK-4
(Si₃N₄ w/ Y₂O₃)

Table I
Comparison of Ceramic Materials for Structural Application

Material	Melting Point (°C)	Density (g/cc)	CTE (10 ⁻⁶ /°C)	Youngs Modulus (GPa)	Fracture Toughness (MPa m ^{1/2})	Tensile Strength (MPa)	Vickers Hardness (kg/mm ²)	Thermal Conductivity (W/m °K)	Electrical Resistivity (ohm-cm)	Dielectric Constant (@ 1 MHz)
HPS (1) Si ₃ N ₄ (2)	1900 (3)	3.29	3.3	300	6-7 (4)	375	1400-1700	20-24	10 ¹³	6
HPS SiC	2200 (3)	3.23	4.55	440	3.9	200	2400	50-170	< 10 ¹³	40
Y-TZP	2700	6.0	10.1	200	5-6		1200-1300	1.7-3.3		
Al ₂ O ₃	2050	3.89	6.5		2.5		1500	20	> 10 ¹⁴	9/ >20

- (1) HPS - Hot Pressed Sinter
 (2) 100 % TD with additives
 (3) sublimation/decomposition
 (4) 4.8 at RT, increases with temperature

[Ref. Ceramic Source, Vol. 7, 1991]

Table II

Consolidation Model for Silicon Nitride

Modified form of Coble's grain-boundary diffusional creep model

$$\frac{dp}{dt} = \frac{47.5 P D_b a^3 W}{G^3 k T}$$

where:	$\frac{dp}{dt}$	= densification rate
	D_b	= second phase grain boundary diffusion coefficient (m ² /sec)
	P	= applied pressure (MN/m ²)
	a^3	= volume of Si ₃ N ₄ transported by each atom of rate controlling species (Si or N)
	W	= second phase boundary thickness (m)
	G	= grain size (m)
	k	= Boltzmann Constant (J/K)

[Ref. L.J. Bowen, et.al., J. Mat. Sc., Vol. 13, pp. 341-350, 1978]

Table III

Silicon Nitride Starting Powder Characteristics

Supplier: Ube Industries
Preparation: Thermal Decomposition of $\text{Si}(\text{NH})_2$

Grade:	SN-E-10
Grain Morphology:	Equiaxed
Grain Size:	≈ 550 nm
Specific Surface Area (BET):	9-13 m^2/g
Phase Composition:	> 95% Alpha Phase
Chemical Analysis:	$\text{O} < 1.5 \text{ wt\%}$ $\text{C} < 0.1 \text{ wt\%}$ $\text{Cl} < 100 \text{ ppm}$ $\text{Fe} < 100 \text{ ppm}$

Table IV
PAS Parameters for
Pure Silicon Nitride (Ube SN-10E)

Specimen	Wt. (gms)	Load kg/cm2	PAS Para meters			Sintering Para meters			Density (% TD)	Phase	Atm			
			Pulse (msec)	Time (sec)	Current (amps)	Volts	Sinter Time (sec)	Current (amps)				Volts	Final Temp. (°C)	Temp Ramp (°/sec)
SN														
5/10/94 #1	5	306	30	90	750	75	2028	1000/2400	5	1700	slow	No	100% α	GN ₂ (2)
5/10/94 #2	4.75	306	30	90	750	75	792	2300/2700 (7)	6	1900	12.5	86.5	100% β	GN ₂ (2)
5/17/94 #1	8.9	287	30	90	750	99	528+	1000/3800	6	? (1)	(6)	No	100% α	GN ₂
5/17/94#2	8	287	30	90	750	99		2700	6	1943		No	100% α	GN ₂
5/23/94 #1	5.5	293	30	90	750	99	270	2500/3400	6	2090	14.68	No	100% α	GN ₂
5/23/94 #2	8.6	293	30	90	750		426	3400/3500	6	2360(s)	8.1	Sublim	100% α	GN ₂ SiC

Comments:
for all GN₂ environments: GN₂ supply = 60 psig, chamber pressure = 0 Kgf/cm².

- (1) Pyrometer not focused
- (2) Air leak in chamber, probably did not achieve a GN₂ environment
- (3) graphite die cracked
- (4) Shrinkage noted to start
- (5) Sublimated
- (6) Delayed Recorder Start

Table V

**UC Davis Study
Silicon Nitride Starting Powder Characteristics**

SN	Supplier	Composition	Reported Powder Size	Preparation
B-1	Toyota Lab. (Aishin)	5 wt% Y₂O₃ 5 wt% MgAl₂O₄ balance Si₃N₄ poly binder	1.6 μm 300 nm 300 nm	Spray Drying to form granules of slurry prepared with poly binder

Table VI

PAS Parameters
for
Silicon Nitride in Air

S / N		PAS Parameters		Sinter Parameters		Parameters						
Load Pressure		Pulse (msec)	Time (sec)	Current (amps)	Current (amps)	Final Temp. (°C)	Time (sec)	Temp. Ramp (°/sec)	Density (% TD)	% Alpha Phase		
B-1	1119-1	(300)	24.9	30	90	750	2000	1395	420	3.7	92	90
	1119-2	(300)	24.9	30	90	750	2000/3000	1549	141	12.9	100	68
	1119-3	(300)	24.9	30	90	750	2000/3200	1632	120	13.6	100	42
	1119-4	(300)	24.9	30	90	750	2000/3200	1582	126	12.6	100	83
	1119-5	(300)	24.9	30	90	750	2000/3000	1570	138	11.4	100 (1)	-

(1) - Reported Density - no specimen

Table VII
PAS Parameters for
Toyota Silicon Nitride Granules*

Specimen	Wt.	Load	PAS Parameters				Sintering Parameters						
		PAS/Sinter	Pulse	Time	Current	Volts	Sinter Time	Current	Final Temp.	Temp Ramp	Density	Phase	Atm
SN	(gms)	kg/cm ²	(msec)	(sec)	(amps)		(sec)	(amps)	(°C)	(°/sec)	(% TD)	(% α)	
6/23/94 #1	9	293/293	30	90	750	25	210	3400/2400	1730	27.7	85	86.6	GN ₂
6/23/94 #3	4	299/299	80	90	750	25	200	(1) 3600/2300	1650	29.58	84	91.6	GN ₂
6/28/94 #1	3	127/296	160	30	750	25	NA	(2)			54	92.6	Air
6/28/94 #2	3	121/ -	160	30	750	25	NA	(3)					Air
6/28/93 #3	3	108/312	160	30	750	25	300	1000/2900	1760	9	98	88.5	0.3 torr
6/28/94 #4	3	143/318	160	30	750	25	230	2000/2900	1700	9.4	98.85	88	GN ₂
6/28/94 #5	3	110/318	160	30	750	25	NA	(4)			52	91.8	GN ₂
6/28/94 #6	3	96/318	160	30	750	25	160	2500/3000	1700	10.5	79	92.6	GN ₂
6/28/94 #7	3	146/315	80	30	750	25	110	3000	1700	15.3	78	90.4	GN ₂
6/28/94 #8	3	146/300	30	90	750	25	90	2000/3000	1775	19.7	71	92.3	GN ₂
6/28/94 #9	3	- /300	NA				72	2000/3000	1820	25.4	74	92.6	GN ₂
6/28/94 #10	3	153/309	160	30	750	25	115	2000/3000	1775	16.4	82	90.5	GN ₂

Comments: for all GN₂ environments: GN₂ supply = 60 psig, chamber pressure = 0 Kgf/cm²

* Granules composed of 5 wt% Y₂O₃, 5 wt% MgAl₂O₄, polybinder, bal. Si₃N₄

- (1) > 90 sec for sintering current to register
- (2) BN sprayed die, no sintering current registered
- (3) Repeat #1 w/o BN, no sintering current displayed, reused powder in #3
- (4) graphite die possibly cracked, no PAS current, no sintering current registered

Table VIII

**Calculated Concentration Levels
for Various Silicon Nitride Systems**

System	Total Weight (gms/mole)	Density (gms/cc)	Si Wt %	Al Wt %	Mg Wt %	Y Wt %	O Wt. %	N Wt %
90% Si ₃ N ₄ + 5% Y ₂ O ₃ + 5% MgAl ₂ O ₄	144.66	3.29	52.42	1.87	0.84	6.15	3.87	34.86
90% Si ₃ N ₄ + 5% Y ₂ O ₃ + 5% AlN	139.59	3.28	54.32	0.97	-	6.37	1.72	36.62
90% Si ₃ N ₄ + 5% Y ₂ O ₃ + 5% Al ₂ O ₃	142.64	3.31	53.16	1.89	-	6.23	3.36	35.35
85% Si ₃ N ₄ + 10% Y ₂ O ₃ + 5% Al ₂ O ₃	146.92	3.41	48.75	1.84	-	12.1	4.9	32.41
85% Si ₃ N ₄ + 5% Y ₂ O ₃ + 10% AlN	134.63	3.29	53.2	0.2	-	6.6	1.78	36.41
90% Si ₃ N ₄ + 2.5% Y ₂ O ₃ + 5% AlN	137.45	3.24	56.61	1.01	-	3.32	0.9	38.17
85% Si ₃ N ₄ + 5% Y ₂ O ₃ + 5% AlN + 5% Al ₂ O ₃	183.56	3.32	39.02	15.43	-	4.84	14.38	26.33