

Hot-pressed β - Si_3N_4 containing small amounts of Be and O in solid solution

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Single phase, hot-pressed Si_3N_4 ceramics with relative densities $> 95\%$ and equiaxed grain structures have been prepared from high purity Si_3N_4 powders having specific surface areas of 8 to 20 $\text{m}^2 \text{g}^{-1}$ and oxygen contents $\geq 2 \text{ wt } \%$ using a small amount of Be_3N_2 or BeSiN_2 as a densification aid. Densification depended sensitively on the concentration of Be and O in a given Si_3N_4 powder and on the usual hot-pressing parameters of pressure, temperature and time. A close association was found between densification and the conversion of α - to β - Si_3N_4 during hot-pressing. Based on the data presented, chemical reactions that occur during hot-pressing involve: (1) reaction of the densification aid with SiO_2 on the Si_3N_4 particle surfaces to form BeO and $\text{Si}_2\text{N}_2\text{O}$; (2) the further reaction of these two reaction products to give probable formation of a transient liquid phase (TLP); and (3) the reaction between TLP and α - Si_3N_4 particles to cause densification, probably by a solution-reprecipitation process, and conversion of α - Si_3N_4 into a β - Si_3N_4 solid solution. The chemical composition of a single phase β - Si_3N_4 solid solution prepared in this study by hot-pressing was approximately $\text{Si}_{2.9}\text{Be}_{0.1}\text{N}_{3.8}\text{O}_{0.2}$.

1. Introduction

There is a growing interest in the fabrication of dense, single-phase Si_3N_4 ceramics for load bearing applications at elevated temperatures near 1400°C . This stems primarily from the well-known marked degradation in strength of hot pressed Si_3N_4 at temperatures above 1000°C associated with the presence of a glassy, second phase(s) on Si_3N_4 grain boundaries [1, 2]. In addition, high temperature creep [2] and oxidation [3] behaviour of commercially-available, hot pressed Si_3N_4 are also controlled at least partly by this intergranular glassy phase, which has been identified primarily as magnesium silicate containing Ca, Al, Na and K cations [2] and N [4]. This glassy phase is believed to originate from chemical reaction between the hot-pressing additive, usually MgO, with SiO_2 on the Si_3N_4 particle surfaces and impurities (Ca, Al, etc.) present in the starting Si_3N_4 powders [1]. Similarly, a more refractory secondary phase(s) forms

in hot pressed Si_3N_4 containing various amounts of Y_2O_3 as a densification aid and also controls the thermomechanical properties of the bulk material [5]. It is apparent, then, that improved properties of Si_3N_4 might be realized by the preparation of dense, single-phase material.

The formation of dense, single-phase Si_3N_4 is simple in theory but quite difficult in practice. Pure, ultrafine Si_3N_4 powder is extremely difficult to densify by conventional methods and requires diamond-forming conditions ($P \sim 5 \text{ GN m}^{-2}$, $T \sim 1550^\circ\text{C}$) to cause sufficient matter transport for good grain-to-grain bonding [6]. In order to enhance matter transport in a typically covalent solid such as Si_3N_4 , chemical additives or impurities are usually required so that conventional hot pressing or sintering methods can be practised. Under these conditions careful control of chemical composition is required to prepare single-phase, β - Si_3N_4 * solid solutions. For example, SiALON ceramics, composed of β - Si_3N_4 solid

* β - Si_3N_4 is the stable high temperature form of Si_3N_4 formed by hot pressing or sintering α - Si_3N_4 powders plus additives at temperature near and above 1700°C .

solution of theoretical compositions $\text{Si}_{3-x}\text{Al}_x\text{N}_{4-x}\text{O}_x$, have a narrow stoichiometric range and are difficult to prepare in single-phase form because of variable oxygen content of starting Si_3N_4 powders, impurity pick-up during ceramic processing and volatilization of components during firing [1, 7]. Even when chemical compositions approach the single-phase solid described above, densification does not occur [7]. Extensive experimentation shows, however, that compacts of SiAlON densify best when the composition is off stoichiometry so that a "nearly" transient liquid phase (TLP) exists during sintering. Unfortunately, this method leaves residual glass on grain boundaries and, consequently, poor mechanical properties of the SiAlON product [7].

The present work describes the formation of dense, single-phase $\beta\text{-Si}_3\text{N}_4$ solid solutions of the chemical formula $\text{Si}_{3-x}\text{Be}_x\text{N}_{4-2x}\text{O}_{2x}$ by a TLP densification process during hot pressing. Phase

equilibria studies [8] in the system $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-BeO-Be}_3\text{N}_2$ (Fig. 1) at 1780°C in N_2 show that the $\beta\text{-Si}_3\text{N}_4$ solid solution extends in the direction of phenacite, Be_2SiO_4 , which is unstable towards BeO and an SiO_2 -rich liquid above about 1560°C . The solid solubility of Be_2SiO_4 in $\beta\text{-Si}_3\text{N}_4$ extends up to about 18 mol% (6.4 eq.% Be and 12.8 eq.% O) and results in the formation of nearly stoichiometric solid solutions with a constant ratio of cations-to-anions of 3:4. However, an advantage of working in this solid solution system is that the data [8] show a small range of nonstoichiometry or "width" to the solid solution "field". Thus, this information led to investigating the effect of small additions of non-oxides, BeSiN_2 and Be_3N_2 , on the densification behaviour and chemical reactions occurring during the hot pressing of high purity Si_3N_4 powders containing various oxygen contents. It was of particular interest to determine if the mechanism of densi-

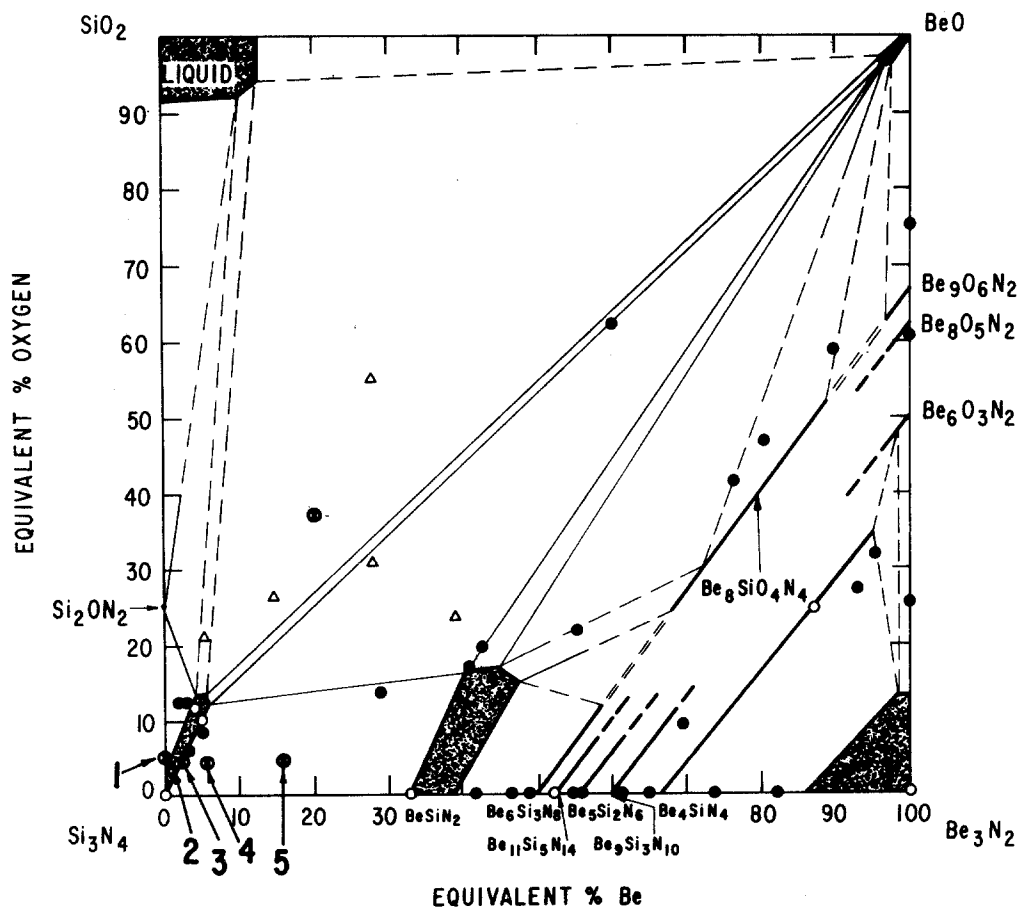


Figure 1 Isothermal section at 1780°C of the system $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-BeO-Be}_3\text{N}_2$. [8]. \circ = 1 phase, \bullet = 2 phases, \triangle = 3 phases. Compositions marked "x" are those investigated in present study.

fication was via a TLP process and if the resulting hot-pressed ceramics were single-phase solid solutions. At 1450°C, the oxidation rate and the creep rate at 70 MN m⁻² stress for single-phase β-Si₃N₄ solid solutions of composition, Si_{2.9}Be_{0.1}N_{3.8}O_{0.2}, are very low and have been measured as 3 × 10⁻¹² kg² m⁻⁴ sec⁻¹ and 5 × 10⁻⁹ sec⁻¹, respectively [9].

2. Experimental procedure

2.1. Powder preparation and processing

The Si₃N₄ powder was derived from the reaction between silane* (SiH₄) and dry ammonia (NH₃). A detailed description of this powder making process has been documented previously [10]. Briefly, SiH₄ and NH₃ in Ar (carrier gas) were reacted in a fused silica reaction tube between 650 and 850°C using gas flow rates of 16, 1.6 and 8 cm³ sec⁻¹, respectively. For example, at 650°C approximately 40 g of a light, yellowish-tan smoke (powder) was accumulated by an electrostatic separator in about 6 h. These powders were amorphous to X-rays, had powder densities ~2.5 g cm⁻³, specific surface areas between 7 and 20 m² g⁻¹ (equivalent particle diameters between 0.27 and 0.09 μm), and contained about 2 to 3 wt% oxygen impurity and a cation purity greater than 99.99%. In addition, these powders contained less than 1 wt% free Si. The amorphous powders were usually calcined at 1460°C in N₂, H₂ or N₂/H₂ mixtures to form finely crystallized α-Si₃N₄ powders which contain a small amount (5 to 8 wt%) of β-Si₃N₄.

Powder compositions containing Be₃N₂[†] or BeSiN₂[‡] additions were prepared by mixing the desired weighed proportions for about 20 min in a ball-mill, using Si₃N₄ grinding media or by mixing in a SiC mortar and pestle. Benzene was used as a liquid vehicle in all experiments. When hygroscopic Be₃N₂ was used, all powder processing was carried out in a dry nitrogen glove box. Non-hygroscopic BeSiN₂ powder could be handled in a ventilated hood area. Understandably, limited chemical homogeneity was expected when mixing was done with a mortar and pestle. The mixed compositions containing Be₃N₂ were then dried and collected under dry N₂ gas.

2.2. Hot pressing conditions

Small hot-pressed samples were fabricated by loading ~0.5g of the desired composition into a graphite die fitted with a 1 cm i.d. BN insert. The faces of the graphite plungers were coated with a thin layer of BN to prevent SiC formation from reaction between Si₃N₄ and C. The loaded die with plungers was inserted into an r.f. heated hot press and a pressure of 3.5 MN m⁻² applied. Full pressure, usually 70 MN m⁻², was applied at ~1100°C. The time to reach 1750°C in N₂, for example, was ~15 min. After the desired soak time at temperature, the power to the induction coils was turned off. An LVDT located along the pressure axis sensed the movement of the graphite plungers during pressing; hence the density of the compact during pressing could be calculated from the plunger displacement and the final density of the pressed sample, provided that corrections are made for thermal expansion of the entire system. Temperature was controlled to within ~20°C and monitored by optical pyrometry. Before sample characterization, a thin layer of BN adhering to the sample faces was removed by surface grinding.

2.3. Measurements and microscopic examination

The final density of hot pressed samples was routinely assessed by Archimedes' (H₂O displacement) method, when samples exhibited densities greater than 90% of the theoretical value (3.18 g cm⁻³), and by mass and geometrical volume measurements for cylindrical samples of relative density ≤90%. Oxygen and beryllium contents were frequently measured on hot-pressed and powder samples by neutron activation analysis and atomic absorption, respectively.

The specific surface area of powders and fired, porous compacts was measured by the single-point BET method using a continuous flow of 30% N₂ in He. X-ray diffractometry provided both qualitative and quantitative analysis of phases present. The amounts of α- and β-Si₃N₄ present were determined by measuring the integrated intensities of (201) and the (101) reflections of α-Si₃N₄ and β-Si₃N₄, respectively, and comparing this intensity ratio to a

*Electronic grade, Union Carbide, Corp., New Jersey, USA.

†Purchased from Ventron-Alpha, Maine, USA.

‡Prepared in-house by reacting an equimolar mixture of Be₃N₂ and Si₃N₄.

TABLE I Results for hot pressing various Si_3N_4 powders with BeSiN_2 or Be_3N_2 additive. Samples hot pressed at 1780°C for 20 min at 70 MN m^{-2} (10 000 p.s.i.).

Experiment no.	Powder condition	Specific surface area ($\text{m}^2\text{ g}^{-1}$)	Oxygen content (wt %)	Additive (wt %)	Relative density (%)
1	$\alpha\text{-Si}_3\text{N}_4$	12.3	1.8	—	50
2	Amorphous	17.0	2.1	0.5 BeSiN_2	70
3	Amorphous	15.5	3.1	0.5 BeSiN_2	80
4	Amorphous	15.5	3.1	2% Be_3N_2 + 2% C	62
5	$\alpha\text{-Si}_3\text{N}_4$	12.1	1.7	2% Be_3N_2 + 2% C	52
6	$\alpha\text{-Si}_3\text{N}_4$	15.5	3.1	2% Be_3N_2	98
7	$\alpha\text{-Si}_3\text{N}_4$	15.5	3.1	2% Be_3N_2 + 5% $\beta\text{-SiC}$	99 +

standard calibration curve. Precise lattice parameters of the $\beta\text{-Si}_3\text{N}_4$ phase was measured by the Debye-Scherrer method.

Phase identification was also determined by optical microscopy, whereby polished sections of hot pressed specimens were observed in reflected and polarized light at magnifications up to $\sim 1200\times$. Silicon nitride compositions slightly rich in beryllium usually resulted in microstructures containing microcracked particles of BeSiN_2 , which exhibit light scattering and can be detected conveniently by polarized light. Microcracking usually occurred in larger BeSiN_2 particles ($> 5\ \mu\text{m}$), and was probably due to thermal expansion mismatch between the BeSiN_2 particles and the $\beta\text{-Si}_3\text{N}_4$ solid solution matrix.

Compositions slightly rich in oxygen gave rise to a dark grey phase, $\text{Si}_2\text{N}_2\text{O}$, which is distinguishable in the microstructure. Bright particles of silicon were observed in all microstructures of hot-pressed samples, partly due to a small amount of thermal decomposition of Si_3N_4 into Si and N_2 during hot pressing. Chemical etching experiments were conducted on well-polished specimens to reveal grain boundaries; an excellent etch was a solution of $\text{KOH}:\text{NaOH}:\text{LiOH}$ (4:4:1 by weight) at a temperature of $\sim 200^\circ\text{C}$ for 20 min.

SEM was used to determine grain size and fracture mode. TEM was used to determine if thin intergranular phase(s) could be observed on $\beta\text{-Si}_3\text{N}_4$ grain boundaries.

3. Results

3.1. Parameters controlling densification during hot pressing

3.1.1. Si_3N_4 powder characteristics

In general, Si_3N_4 powders with higher specific surface areas (15 to $20\text{ m}^2\text{ g}^{-1}$) densified more

rapidly during hot pressing than powders with lower specific surface areas (8 to $10\text{ m}^2\text{ g}^{-1}$) when Be_3N_2 or BeSiN_2 densification aid was used. However, under certain hot-pressing conditions all Si_3N_4 powders containing optimum amounts of Be_3N_2 or BeSiN_2 could be hot pressed to relative densities $> 95\%$ of the theoretical value ($\sim 3.18\text{ g cm}^{-3}$), provided that the oxygen content of the starting composition was greater than 2 wt%. Another interesting finding was that the final density of hot-pressed Si_3N_4 containing beryllium was independent of whether the Si_3N_4 starting powder was amorphous or crystalline ($\alpha\text{-Si}_3\text{N}_4$), as long as the specific surface areas and oxygen contents were similar. Finally, Si_3N_4 powders having various colours (light yellow-to-tan) and containing excess silicon have been successfully hot pressed to full density when beryllium compounds are used as densification aid, suggesting that free silicon in the starting Si_3N_4 powder has no adverse effect on densification.

3.1.2. Oxygen content of Si_3N_4 powders

Table I shows data from a number of hot pressing experiments made with both amorphous and crystalline (α) Si_3N_4 powders. Experiment 1 illustrates that pure submicron ($0.15\ \mu\text{m}$) Si_3N_4 powder does not densify beyond 50% relative density under extreme hot-pressing conditions of 70 MN m^{-2} (10 000 p.s.i.) and 1800°C . This result is unchanged for Si_3N_4 powders with oxygen contents ranging between 1 and 3.5 wt%. Comparison of experiments 2 and 3 shows that, for Si_3N_4 powders of similar specific surface areas and identical BeSiN_2 concentration, the relative density of the hot-pressed material is higher for the starting Si_3N_4 powder having a higher oxygen content. This trend is further supported by the results of

Experiments 4 and 5 in which 2 wt% Be_3N_2 and 2 wt% C are added to two different Si_3N_4 powders having different oxygen contents.

Carbon* addition to Si_3N_4 powders containing Be_3N_2 was explored to determine the possibility of controlling oxygen content, or composition, during hot pressing. It was believed that if oxygen exists in the form of SiO_2 particles or as a thin SiO_2 layer on the Si_3N_4 particle surfaces, then addition of carbon would result in carbothermic reduction of SiO_2 and oxygen loss. The effect of various C additions on the relative density of hot-pressed Si_3N_4 containing 2 wt% Be_3N_2 is illustrated in Fig. 2. Clearly, the addition of a few tenths of a per cent carbon inhibits densification appreciably and results in hot-pressed samples with high residual porosity. For example, the relative density drops from $\sim 98\%$ to 73% by the addition of 1 wt% C. To determine if oxygen loss occurred during hot pressing of carbon-containing compositions, samples from Experiments 4 and 6 (Table I) were analysed for oxygen by neutron activation analysis and found to contain 2.0 and 2.9 wt% oxygen, respectively. These data show that in the absence of carbon the oxygen loss is small, only 0.2 wt%, whereas when 2 wt% C is added to the otherwise same composition, the oxygen loss is much higher, 1.2 wt%. This result further confirmed results obtained from other hot-pressing experiments which showed that unless the oxygen content of the starting composition was ≥ 2 wt%, relative densities $>95\%$ could not be achieved when

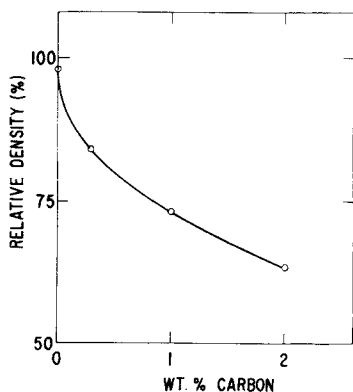


Figure 2 The effect of density on carbon concentration for high purity Si_3N_4 powder containing 3.1 wt% O and 7 wt% BeSiN_2 , hot pressed at 70 MN m^{-2} for 15 min at 1750°C .

*Monarch carbon black, Cabot Corp., Mass, USA.

Be_3N_2 or BeSiN_2 additives and applied pressures up to 70 MN m^{-2} ($10\,000 \text{ p.s.i.}$) were used.

The addition of C to Si_3N_4 usually results in the formation of $\beta\text{-SiC}$ particles in samples hot pressed at 1700 to 1800°C . In order to elucidate if the presence of $\beta\text{-SiC}$ is responsible for the reduction in final density observed in Fig. 2, Experiment 7 (Table I) was performed and showed that 5 wt% $\beta\text{-SiC}$ added to the otherwise identical powder composition used to generate data presented in Fig. 2, has no adverse effect on the relative density of the resulting hot-pressed sample.

3.1.3. Beryllium content

Generally, Be_3N_2 or BeSiN_2 additives give rise to identical densification behaviour, provided the percentage of beryllium is the same and the powder batches are mixed equally. Results presented in Table I demonstrate that Be_3N_2 or BeSiN_2 additions (Experiments 1 to 3 and 6) act as densification aids during hot pressing of Si_3N_4 powders. Optimization of the beryllium concentration for a given Si_3N_4 powder is necessary for producing hot-pressed Si_3N_4 with relative densities $>95\%$. For example, Table II shows a strong dependence of relative density on Be_3N_2 concentration for a series of samples prepared from the same $\alpha\text{-Si}_3\text{N}_4$ powder, having a specific surface area of $15.5 \text{ m}^2 \text{ g}^{-1}$ and oxygen content of 3.1 wt%, and hot pressed under identical conditions. The relative density increases markedly from 50 to 80% by adding only 0.5 wt% Be_3N_2 . Hot-pressed material attains a maximum relative density of 98% for a 2 wt% Be_3N_2 addition, and further increases of 5 and 15 wt% Be_3N_2 result in lower final densities of 75 and 62% respectively. The shape and magnitude of the curve obtained by plotting relative density versus wt% Be_3N_2 will depend generally on the oxygen and other impurity contents of the starting Si_3N_4 powder and the hot-pressing conditions (pressure, temperature, time, atmosphere). An explanation of the effect of Be_3N_2 concentration on density of hot pressed material is offered in Section 3.2.

3.1.4. Effect of applied pressure

The effect of pressure on relative density was studied only under one set of heat treatment conditions – 1780°C for 15 min – which are found to

TABLE II Relative density and X-ray results for hot-pressed Si_3N_4 containing various amounts of Be_3N_2 . The starting composition contained 3.1% O and was hot pressed at 1750°C for 20 min at 70 MN m^{-2} .

Composition	Be_3N_2 addition (wt %)	Relative density (%)	Phases present (X-ray diffraction)	Lattice parameters of $\beta\text{-Si}_3\text{N}_4$ phase	
				a (Å)	c (Å)
1	0	50	$\alpha\text{-Si}_3\text{N}_4 + \text{Si}_2\text{N}_2\text{O}(\text{tr})$ + $\beta\text{-Si}_3\text{N}_4(\text{tr})$		
2	0.5	80	$\beta\text{-Si}_3\text{N}_4^*(\text{ss}) + \text{Si}_2\text{N}_2\text{O}(\text{tr})$ + $\alpha\text{-Si}_3\text{N}_4(\text{tr})$	7.593(2) [†]	2.902(1)
3	2.0	98	$\beta\text{-Si}_3\text{N}_4(\text{ss}) + \text{BeSiN}_2(\text{tr})$	7.587(1)	2.902(1)
4	5.0	75	$\beta\text{-Si}_3\text{N}_4(\text{ss}) + \text{BeSiN}_2(\text{tr})$	7.589(1)	2.902(1)
5	15	62	$\beta\text{-Si}_3\text{N}_4(\text{ss}) + \text{BeSiN}_2(\text{minor})$	7.588(1)	2.902(1)
6	0	Loose powder [‡]	$\beta\text{-Si}_3\text{N}_4$	7.596(2)	2.904(1)

* $\beta\text{-Si}_3\text{N}_4(\text{ss})$ refers to $\beta\text{-Si}_3\text{N}_4$ solid solution.

[†] The number in parenthesis signifies the standard deviation in the third decimal place.

[‡] $\beta\text{-Si}_3\text{N}_4$ prepared by firing high purity $\alpha\text{-Si}_3\text{N}_4$ at 1800°C in an Al_2O_3 furnace.

be nearly optimum for obtaining maximum density without serious decomposition of Si_3N_4 . Different Si_3N_4 powders of high cation purity ($\sim 99.99\%$) usually exhibited different hot-pressing behaviour even though the average particle size, ceramic processing and concentration of BeSiN_2 or Be_3N_2 densification aids were identical. In particular, the applied pressure required to achieve full density appeared to depend sensitively on the chemical nature, especially the oxygen content, of the starting Si_3N_4 powder. This is illustrated in Fig. 3 for four different Si_3N_4 powders, two (powders 1 and 2) of which were from different commercial lots.* Processed powder 1, which had an unusually high oxygen content of 4.6 wt%, was the easiest one to densify to nearly theoretical density. The relative density of this powder composition increased sharply from 62 to 99% with increasing pressure between 14 MN m^{-2} (2000 p.s.i.) and 25 MN m^{-2} (3700 p.s.i.). Nearly theoretical density was achieved at pressures near and above 25 MN m^{-2} at 1780°C for 15 min. In contrast, the densification behaviour of powder 2, having a lower oxygen content of 3%, is similar to powder 1 for pressures below 18 MN m^{-2} but quite different at higher pressures where the rise in relative density with increasing pressure occurs much more slowly. In fact, full density can be achieved for powder 2 only if the applied pressure is raised to about 70 MN m^{-2} (10000 p.s.i.) at 1780°C . Powder 3, although prepared

differently from powder 2, had nearly the same oxygen content and densified similarly. Powder 4 could not be densified beyond 90% relative density at the maximum pressure of 70 MN m^{-2} because of its low (2.0 wt %) oxygen content.

3.1.5. Effect of temperature on changes in microstructure

The starting compositions listed in Table II were converted into equivalent concentrations of Be and O and plotted in the lower left-hand corner of the isothermal section at 1780°C of the system

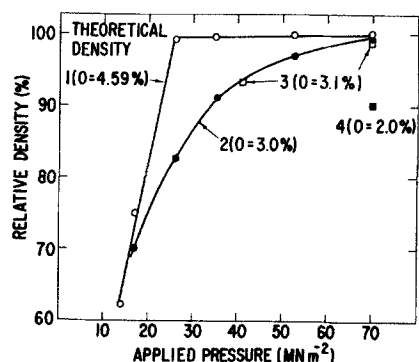


Figure 3 Relative density as a function of applied pressure for Si_3N_4 powders of about the same specific surface area (11 to $13\text{ m}^2\text{ g}^{-1}$) and containing 7 wt % BeSiN_2 but different amounts of oxygen. Powders 1 and 2 are processed Sylvania Si_3N_4 powders initially prepared by reaction with SiCl_4 and NH_3 ; Si_3N_4 powders 3 and 4 were prepared by reacting SiH_4 and NH_3 and processing in-house. Samples were hot pressed at 1780°C for 15 min in N_2 .

*SN 502 silicon nitride powder, GTE Sylvania, Towanda, PA, USA.

[8] $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-BeO-Be}_3\text{N}_2$ illustrated in Fig. 1. The phases present in material hot pressed at 1750°C are identified in Table II and agree well with those predicted by the phase diagram. Silicon nitride compositions containing less than about 2 wt% Be_3N_2 (2.52 eq.% Be and 4.47 eq.% O) result in a second phase of $\text{Si}_2\text{N}_2\text{O}$ whereas compositions having greater than about 2 wt% Be_3N_2 lead to the formation of BeSiN_2 as a second phase in hot-pressed material. The β -form of Si_3N_4 is the dominant phase present in these beryllium-containing hot-pressed materials, but in the absence of beryllium (composition 1) $\alpha\text{-Si}_3\text{N}_4$ is the major phase at 1750°C . The measured values of the a and c lattice parameters for the hexagonal $\beta\text{-Si}_3\text{N}_4$ phase are smaller than those for pure $\beta\text{-Si}_3\text{N}_4$ powder (composition 6), with the a -parameter decreasing more than the c -parameter. These results agree well with X-ray findings of Jack [11] and Huseby *et al.* [8] who showed that Be and O can substitute for Si and N, respectively, in $\beta\text{-Si}_3\text{N}_4$ with a resulting decrease in lattice parameters.

The effect of temperature and time on relative density and conversion of α - to $\beta\text{-Si}_3\text{N}_4$ during the hot pressing of pure $\alpha\text{-Si}_3\text{N}_4$ and $\alpha\text{-Si}_3\text{N}_4$ containing 7 wt% BeSiN_2 , are illustrated in Figs. 4 and 5. The $\alpha\text{-Si}_3\text{N}_4$ powder used in obtaining these data (and data in Fig. 6) contained 2.0 wt% oxygen and about 8 wt% $\beta\text{-Si}_3\text{N}_4$, and had a specific surface area of $10.8\text{ m}^2\text{ g}^{-1}$. Again, this high purity Si_3N_4 powder undergoes only a slight amount of densification and conversion of α - to $\beta\text{-Si}_3\text{N}_4$ at temperatures up to $\sim 1800^\circ\text{C}$ with a constant applied pressure of 70 MN m^{-2} and time of 15 min at temperature. These findings agree with recent hot-pressing experiments on high purity (99.9%) powder of submicron ($0.15\ \mu\text{m}$) $\alpha\text{-Si}_3\text{N}_4$ by Bowen *et al.* [12]. In contrast, the addition of 7 wt% BeSiN_2 or 2 wt% Be_3N_2 (2.5 eq.% Be) resulted in considerable densification and conversion of α - to $\beta\text{-Si}_3\text{N}_4$ at temperatures above 1500°C . Relative density increases rapidly with rising temperature between 1500 and 1700°C , and reaches nearly a terminal density of about 90% at 1800°C . The rate of conversion of α - to $\beta\text{-Si}_3\text{N}_4$ also increases rapidly with rising temperature between 1500 and 1700°C , with nearly full conversion to $\beta\text{-Si}_3\text{N}_4$ after hot pressing for 15 min at 1700°C . This transformation occurs during most of the early and inter-

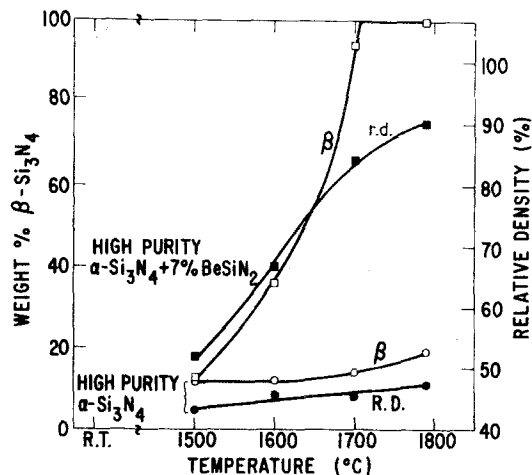


Figure 4 Dependence of relative density and weight per cent $\beta\text{-Si}_3\text{N}_4$ on temperature for pure $\alpha\text{-Si}_3\text{N}_4$ and for $\alpha\text{-Si}_3\text{N}_4$ containing 7 wt% BeSiN_2 , both hot pressed at constant pressure (70 MN m^{-2}) and time (15 min).

mediate stages of densification and is complete when the relative density reaches about 85%.

Additional evidence confirming this close association between densification and α - to $\beta\text{-Si}_3\text{N}_4$ conversion is obtained from the kinetic data at 1675°C shown in Fig. 5. During hot pressing the shapes of the densification and conversion curves are very similar, indicating high initial rates that decrease rapidly during about the first 10 min. The decrease in densification rate with time is apparently due to decreasing driving force caused by grain growth and densification which is predicted by intermediate stage, hot-pressing theory [13]. Furthermore, there is a linear fit of the densification data

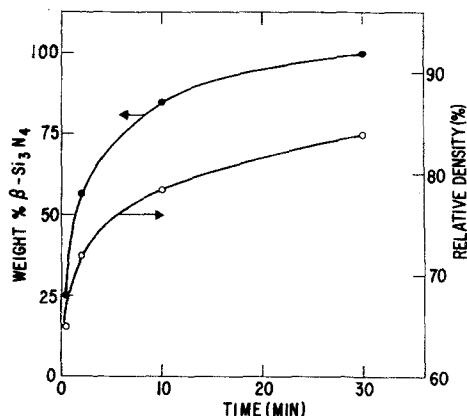


Figure 5 Kinetics of densification and conversion of α - to $\beta\text{-Si}_3\text{N}_4$ at 1675°C for $\alpha\text{-Si}_3\text{N}_4$ powder containing 7 wt% BeSiN_2 . Applied pressure = 70 MN m^{-2} .

on a plot of relative density versus log time, suggesting that a diffusional process controls densification kinetics. Consequently, the similarity in time and temperature behaviour for densification and conversion data suggests that both processes may be controlled by mass transport via diffusion. This deduction is supported by measurement of specific surface area as a function of temperature, shown in Fig. 6, for the same hot-pressed compacts used to generate the data in Fig. 4. At any given temperature between 1500 and 1780°C, the specific surface area is higher for compacts of pure α - Si_3N_4 than for α - Si_3N_4 containing 7 wt % BeSiN_2 . This means that the total driving force (effective stress + surface energy) for densification is higher for compacts of undoped Si_3N_4 because the high specific surface area observed is a consequence of a porous, fine pore structure. Because of the absence of densification in pure α - Si_3N_4 (containing oxygen) and the rapid densification observed for BeSiN_2 -containing powder, the role of the BeSiN_2 addition is to enhance matter transport by increasing the mobility of the major diffusional species, Si and N.

3.2. Chemical reactions occurring during densification

The foregoing information shows that Be-doped submicron Si_3N_4 powder can be densified near and above 1500°C by hot pressing at pressures above 15 MN m^{-2} if the concentrations of both Be and O are sufficient. Furthermore a single-phase β - Si_3N_4 solid solution can be formed at high temperatures (1700 to 1800°C) by using α - Si_3N_4 powders having 3.1 wt % O and adding 7 wt % BeSiN_2 (or 2 wt % Be_3N_2).

Besides the transformation of α - to β - Si_3N_4 that occurs during densification, other chemical reactions take place between the Be-additive and the oxygen-bearing phase present in the Si_3N_4 starting powder. Since it is generally accepted that oxygen impurity in Si_3N_4 powders exists primarily as a surface layer of SiO_2 on the Si_3N_4 particles, an important reaction to understand is that between SiO_2 and BeSiN_2 . (BeSiN_2 was chosen as a reactant over Be_3N_2 because of its nonhygroscopicity). An understanding of the reaction sequence between SiO_2 and BeSiN_2 at temperatures above 1500°C could lead to identification of

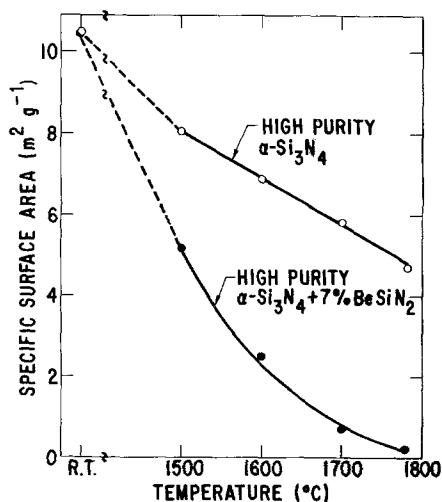


Figure 6 Specific surface area reduction as a function of temperature for pure α - Si_3N_4 and α - Si_3N_4 containing 7 wt % BeSiN_2 . Both compositions were hot pressed at 70 MN m^{-2} for 15 min in N_2 .

the mechanism(s) of densification during hot pressing.

Chemical reaction between SiO_2^* and BeSiN_2 was explored by using homogeneous powder mixtures and reaction couples consisting of powder compacts. Only one chemical composition was examined, 56 wt % BeSiN_2 + 44 % SiO_2 , which is the approximate corresponding composition of these constituents in a densifiable Si_3N_4 powder that results in a single-phase β - Si_3N_4 solid solution after hot pressing at 1750°C. This composition point (21.3 eq. % Be and 36.2 eq. % O) is designated as a circled "X" in Fig. 1. The results of the reaction between SiO_2 and BeSiN_2 are presented in Table III. Below 1500°C the reaction rate is very low. Experiments 1 and 2 show that at 1500°C two new crystalline phases start to form, BeO and $\text{Si}_2\text{N}_2\text{O}$. In the powder mixture the SiO_2 -rich phase is incompletely reacted at 1500°C and is present primarily in the form of glass. Heat treatment at 1640°C (Experiments 3 and 4) results in major amounts of BeO and $\text{Si}_2\text{N}_2\text{O}$ and, for the powder mixture, a large weight loss and significant amount of β - Si_3N_4 formation. Although the reaction products BeO and $\text{Si}_2\text{N}_2\text{O}$ occur in a porous reaction medium in Experiments 1 to 4, these same phases are found to form in a dense, hot-pressed sample of composition 56 wt %

*Cabosil silica, Cabot Corp., New Jersey, USA.

TABLE III Results of chemical reaction between BeSiN₂ and SiO₂ in N₂ gas.

Experiment no.	Reactants	Heat treatment	Weight loss (%)	Phases present*
1	Compact of mixture of 56 wt % BeSiN ₂ + 44% SiO ₂	1500° C–30 min–N ₂	5	Major BeSiN ₂ , glass Minor Si ₂ N ₂ O, BeO, α-SiO ₂ (tr)
2	BeSiN ₂ /SiO ₂ couple	1500° C–30 min–N ₂	–	Si ₂ N ₂ O + BeO
3	Compact of mixture of 56 wt % BeSiN ₂ + 44% SiO ₂	1640° C–10 min–N ₂	15	Major BeO, Si ₂ N ₂ O Minor BeSiN ₂ , β-Si ₃ N ₄
4	BeSiN ₂ /SiO ₂ couple	1640° C–10 min–N ₂	–	Si ₂ N ₂ O + BeO + α-SiO ₂ (tr)
5	56 wt % BeSiN ₂ + 44% SiO ₂ mixture	Hot-pressed at 1625° C–1 min– 70 MN m ⁻² –N ₂	–	Major BeSiN ₂ , glass Minor BeO, Si ₂ N ₂ O
6	56 wt % BeSiN ₂ + 44% SiO ₂ mixture	Hot-pressed sample from Experiment 5 annealed at 1640° C– 15 min–N ₂	18	Major BeO, Si ₂ N ₂ O Minor β-Si ₃ N ₄

* Phases identified by X-ray diffraction.

BeSiN₂ + 44% SiO₂ (Experiments 5 and 6). Hot-pressing temperatures above 1640° C could not be used because this composition was so fluid that under a pressure of 70 MN m⁻² it flowed out of the die cavity.

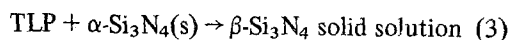
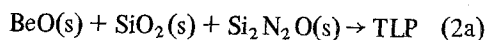
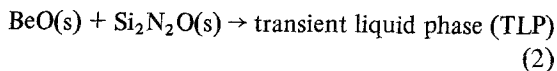
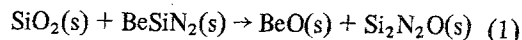
The reaction products, BeO and Si₂N₂O, are also observed in hot-pressed Si₃N₄, derived from a powder composition containing 4.6 wt % O (8.6 wt % SiO₂) and 10 wt % BeSiN₂, and hot pressed at 1675° C for 2 min at 70 MN m⁻². This hot-pressed sample was about 85% dense and contained ~90% β-Si₃N₄, 10% α-Si₃N₄ and trace amounts of BeO and Si₂N₂O. Even though a rapid heating rate of ~200° C min⁻¹ was used in this case to suppress dissolution of the BeO and Si₂N₂O phases into the β-Si₃N₄ phase, precise lattice parameter measurements of the α-Si₃N₄ phase showed that the value of the *a*-parameter (7.589 ± 0.003 Å) is significantly smaller than that (7.596 ± 0.002 Å) of pure β-Si₃N₄, indicating that dissolution of Be and O in β-Si₃N₄ occurs during densification.

Additional experimental information about the mode of densification occurring during hot pressing can be obtained by careful examination of the microstructure by TEM techniques. Typical photomicrographs are presented in Fig. 7 for a hot-pressed specimen of single-phase β-Si₃N₄ solid solution, according to X-ray diffraction, having a relative density of 99.5% and a chemical composition of approximately Si_{2.9}Be_{0.1}N_{3.8}O_{0.2}. In Fig. 7a the grain boundaries and triple points (three grain intersections) between the equiaxed β-Si₃N₄ grains of average size ~1 μm appear free of any second phases. However, closer inspection

of grain boundary regions at higher magnification using the lattice fringe technique (Fig. 7b) reveals that some grain boundaries and triple points have a thin (~15 Å) continuous second phase. From its distribution, and using surface tension arguments, the second phase observed is most likely to be a liquid film that wets the β-Si₃N₄ grains. This evidence suggests that densification during hot pressing proceeds via a liquid phase.

4. Discussion

A complete phase diagram, i.e. phases present as a function of composition and temperature, is not available for the Si₃N₄–Be₃N₂–SiO₂–BeO system. However, based on the above observations the following chemical reactions are proposed to occur during hot pressing of α-Si₃N₄ powders containing small amounts of SiO₂ and BeSiN₂.



At temperatures near and above 1500° C in N₂, SiO₂ on the Si₃N₄ particle surfaces reacts at the contact regions with the BeSiN₂ particles (densification aid) according to Equation 1 to form BeO and Si₂N₂O. No Be₂SiO₄ (phenacite) forms, probably because of its high energy for nucleation, as found during reaction between pure SiO₂ and BeO powders [14]. It is speculated, then, that the

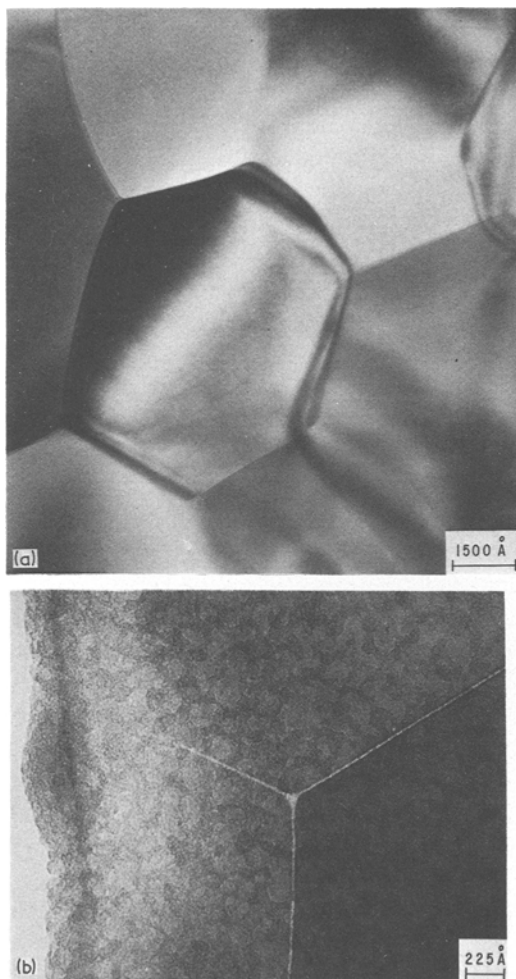
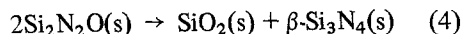


Figure 7 TEM photomicrographs of grain structure in hot pressed β - Si_3N_4 solid solution of composition $\text{Si}_{2.9}\text{Be}_{0.1}\text{N}_{3.8}\text{O}_{0.2}$. (a) Typical grain structure and (b) intergranular phase, and lattice fringes in lower left grain. The mottled structure is due to surface contamination.

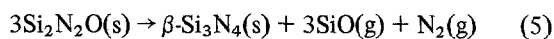
BeO formed continues to react with $\text{Si}_2\text{N}_2\text{O}$ (Equation 2) or with unreacted SiO_2 and $\text{Si}_2\text{N}_2\text{O}$ (Equation 2a) to form a metastable (transient) liquid phase containing Be, Si, N and O. An analogous situation prevails in the Al_2O_3 - SiO_2 system in which $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (mullite) is difficult to nucleate, resulting in the formation of a metastable SiO_2 -rich liquid phase at temperatures 200 to 300°C below the eutectic temperature [15, 16]. The transient liquid phase, if sufficient in volume fraction, can dissolve and wet the α - Si_3N_4 grains, thereby causing macroscopic densification by a solution-reprecipitation process. It is believed that the reason for the strong dependence of densification on oxygen (SiO_2) and beryllium (BeSiN_2 or Be_3N_2) contents observed during hot

pressing α - Si_3N_4 powders is related to the amount of transient liquid phase formed. For example, under appropriate hot-pressing conditions the data in Tables I and II demonstrate that if a sufficient amount (1 to 2 wt %) of Be_3N_2 or BeSiN_2 (3.5 to 7 wt %) is available, high purity α - Si_3N_4 powders densify to relative densities >95% only if the oxygen content is greater than ~ 2 wt % (≈ 3.8 wt % SiO_2). This is rationalized in terms of Reactions 2 and 2a, where increasing amounts of SiO_2 result in formation of greater amounts of transient liquid phase. On the other hand, carbon addition was shown to reduce the SiO_2 content by carbothermic reduction during hot pressing and most likely decreases the amount of transient liquid phase. It is difficult to explain, however, the observation in Table II that when sufficient (5.6 wt %) SiO_2 exists in the otherwise high purity Si_3N_4 powder, large amounts (≥ 5 wt %) of Be_3N_2 drastically reduce the final density of the hot-pressed body. For these compositions BeSiN_2 is detected as a second phase at 1750°C, as predicted by the phase diagram in Fig. 1. Perhaps the presence of a second phase (BeSiN_2) inhibits densification by reducing the vacancy annihilation rate at the Si_3N_4 grain boundaries, but such an effect appears unimportant for the case when 5 wt % β - SiC is intentionally added to a densifiable form of Si_3N_4 (Experiment 7, Table I). In view of the fact that BeSiN_2 can dissolve BeO (see Fig. 1), a more likely explanation is that the "unreacted" BeSiN_2 second phase dissolves a significant portion of the BeO phase before it reacts to form a transient liquid phase.

The stability of $\text{Si}_2\text{N}_2\text{O}$ plays an important role in understanding the formation of the reaction products observed. The decomposition of $\text{Si}_2\text{N}_2\text{O}$ into SiO_2 and Si_3N_4 according to the reaction,



apparently does not occur at temperatures up to $\sim 1750^\circ\text{C}$ because $\text{Si}_2\text{N}_2\text{O}$ is occasionally detected in SiO_2 -rich compositions explored in this hot-pressing study. In addition, based on thermochemical data [17] the free energy change for this reaction is +40 to +65 kcal mol⁻¹ at temperatures between 1600 and 1800°C. In the absence of a confined system, however, $\text{Si}_2\text{N}_2\text{O}$ can decompose rapidly at temperatures above $\sim 1600^\circ\text{C}$ in N_2 according to the reaction,



The high values of 3×10^{-4} and 1.5×10^{-3} atm., respectively, calculated for the partial pressure of SiO at 1600 and 1700° C suggest that Reaction 5 is possible and can explain the large weight loss and significant amounts of β -Si₃N₄ found in Experiments 3 and 6 (Table III).

During densification via a reactive liquid phase, Be and O dissolve into Si₃N₄ to make β -Si₃N₄ solid solutions of approximate compositions Si_{3-x}Be_xN_{4-2x}O_{2x}. This process is accompanied by the conversion of α - to β -Si₃N₄ and designated overall by Equation 3. The mechanism of formation of β -Si₃N₄ may proceed by two possible routes: (1) β -Si₃N₄ forms from the solution of α -Si₃N₄ into the reactive liquid followed by reprecipitation of the β -form, similar to that proposed for hot-pressed Si₃N₄ with an MgO densification aid [12], or (2) β -Si₃N₄ forms as a result of diffusion of Be and O into the α -Si₃N₄ grains, an independent process occurring during liquid-assisted densification. In the case of MgO-doped Si₃N₄ the conversion of α to β takes place primarily after completion of densification, whereas both processes occur simultaneously for Be-doped Si₃N₄. In the present study, however, the proposed transient liquid phase, or possibly the BeO and Si₂N₂O phases, react with α -Si₃N₄ to make essentially single-phase β -Si₃N₄, as indicated by Fig 7a, but a residual glassy phase(s) is detected in hot-pressed forms of Si₃N₄ containing 1 to 5 wt% MgO. The unusual observation of an equiaxed β -Si₃N₄ grain structure, shown clearly in Fig. 8, is believed to be a consequence of grain growth in a single phase material after full density was reached.

It is not yet certain to what extent densification proceeds in the liquid and/or solid state during the hot pressing of Si₃N₄ compositions containing BeSiN₂ or Be₃N₂. If a transient liquid phase is essential for the densification process, then the key to obtaining highly dense material is to prevent significant dissolution of the liquid in the β -Si₃N₄ phase before it completes its role in causing full densification. Since the activation energies for densification and dissolution are expected to be different, an optimum temperature–time cycle during heating could provide a “longer-lasting” liquid to insure attainment of high density during hot pressing. Although a detailed study of this effect has not been made, preliminary results show that higher final densities could be achieved by

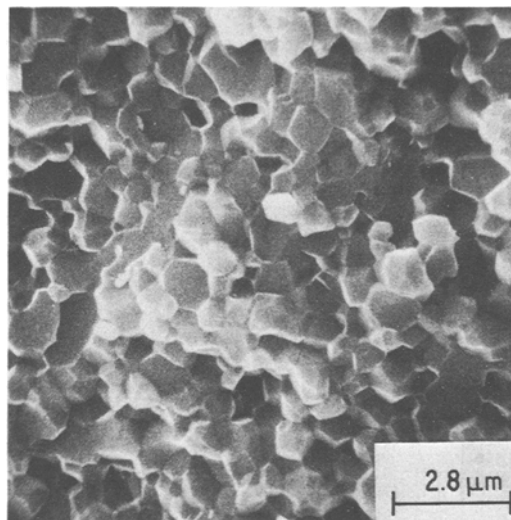


Figure 8 Typical SEM photomicrograph of the grain structure showing the fracture surface developed in hot-pressed Si₃N₄ containing 3.1 wt% O and 7 wt% BeSiN₂.

holding the temperature at 1650° C for 10 to 15 min under pressure before raising the temperature to 1750 to 1780° C.

5. Conclusions

Single phase, hot-pressed Si₃N₄ ceramics with relative densities >95% and equiaxed grain structures can be prepared from high purity Si₃N₄ powders having specific surface areas of 8 to 20 m² g⁻¹ and oxygen contents ≥ 2 wt% using small amounts of Be₃N₂ (1 to 2 wt%) and BeSiN₂ (3.5 to 7 wt%) as a densification aid. Both amorphous and crystalline (α) Si₃N₄ powders can be hot pressed to high densities as long as optimum amounts of Be and O are present. At 1750° C chemical compositions falling in the two-phase field, β -Si₃N₄ solid solution + Si₂N₂O, densify more easily than compositions located in the β -Si₃N₄ solid solution + BeSiN₂ phase field. Interpretation of the densification data (influence of composition, temperature, applied pressure, time), chemical reaction studies and microstructural characterization leads to the postulation that densification, and perhaps conversion of α - to β -Si₃N₄, probably proceed in the presence of a transient liquid phase. By proper control of the chemistry and hot-pressing parameters, single-phase β -Si₃N₄ solid solutions of approximate composition Si_{2.9}Be_{0.1}N_{3.8}O_{0.2} can be prepared with a relative density greater than 98% and average grain size ~ 1 μ m.

Acknowledgements

The author wishes to thank S. Prochazka for many valuable discussions, J. H. Rosolowski for critical reading of the manuscript, C. O'Clair and C. Krystyniak for their skills in ceramic processing and hot pressing, A. Davis for lattice parameter measurements and the Naval Air Systems Command for partial support of this investigation under the Department of the Navy Contract N00019-77-C-0259.

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Received 8 January and accepted 5 March 1979.