

Silicon nitride ceramics – review of structure, processing and properties

S. Hampshire*

Materials and Surface Science Institute, University of Limerick, Limerick, Ireland

* Corresponding author: E-mail address: stuart.hampshire@ul.ie

Received 30.03.2007; published in revised form 01.09.2007

Materials

ABSTRACT

Purpose: The purpose of this review is to examine the development of silicon nitride and the related sialons and their processing into a range of high-grade structural ceramic materials.

Design/methodology/approach: Silicon nitride is one of the major structural ceramics that possesses high flexural strength, good fracture resistance, good creep resistance and high hardness. These properties arise because of the processing route which involves liquid phase sintering and the development of microstructures in which high aspect ratio grains and intergranular glass phase lead to excellent fracture toughness and high strength

Findings: This review has examined the development of silicon nitride and the related sialons and their processing into a “family” of structural ceramic materials with high hardness, strength, fracture toughness, creep resistance and wear resistance.

Practical implications: The development of knowledge of microstructure–property relationships in silicon nitride materials is outlined, particularly recent advances in understanding of the effects of grain boundary chemistry and structure on mechanical properties.

Originality/value: This review should be of interest to scientists and engineers concerned with the processing and use of ceramics for engineering applications.

Keywords: Ceramics and glasses; Silicon nitride; Sintering; Fracture toughness

1. Introduction

Silicon nitride has been the subject of major programmes of research for the last four decades, principally in response to the challenge to develop a suitable ceramic for high temperature structural applications in gas turbine engines [1]. It was first developed in the 1950's for use as thermocouple tubes, crucibles for molten metals and also rocket nozzles [2]. This type of material was formed by nitriding silicon powder compacts in the temperature range 1100-1450°C and was later termed reaction-bonded silicon nitride (RBSN) [3]. One advantage was that little or no shrinkage occurred during the nitriding process and therefore, these ceramics could be machined to final size and shape using conventional tooling after an initial nitridation to impart strength. Interest began to grow for potential use in gas turbines but a major obstacle to the use of RBSN for engine applications was its limited mechanical strength (~200-250 MPa) as a result of the presence of 20-30% microporosity.

For an intrinsically high strength, high hardness material such as silicon nitride, the high energy covalent chemical bonds giving rise to these mechanical properties are a disadvantage in sintering processes. Self-diffusivity in silicon nitride is quite low and atomic species only become sufficiently mobile for densification at temperatures where the decomposition of silicon nitride commences (>1850°C). Thus, alternative approaches were developed and, during the 1960's, increased densities resulted from hot-pressing previously formed silicon nitride powder with various sintering additives [4]. With magnesium oxide, full density material was produced by hot-pressing at 1850°C under 23 MPa and strength was substantially improved over that of RBSN. Magnesia was also used as the densification additive in the first commercial hot-pressed silicon nitride (HPSN) [5].

In the 1970's, a full-scale effort to produce the ceramic gas turbine was initiated in the USA. It was realised early in the programme that, since hot-pressing is limited to simple shapes,

the objectives would not be achieved unless sintering without pressure could be achieved where shaping of components could be carried out by more conventional ceramic fabrication processes.

Since the 1970s, the search for improved materials has led to a better understanding of the role of sintering additives in the densification and microstructural development of silicon nitride-based ceramics and the consequences for final properties [6]. Improvements in powder manufacture and ceramic forming techniques and the development of alternative firing processes has led to a complete “family” of silicon nitride materials including RBSN, HPSN, sintered silicon nitrides (SSN), sintered reaction-bonded silicon nitride (SRBSN), hot isostatically pressed silicon nitride (HIPSN) and solid solutions known as SiAlONs, after their major elemental components.

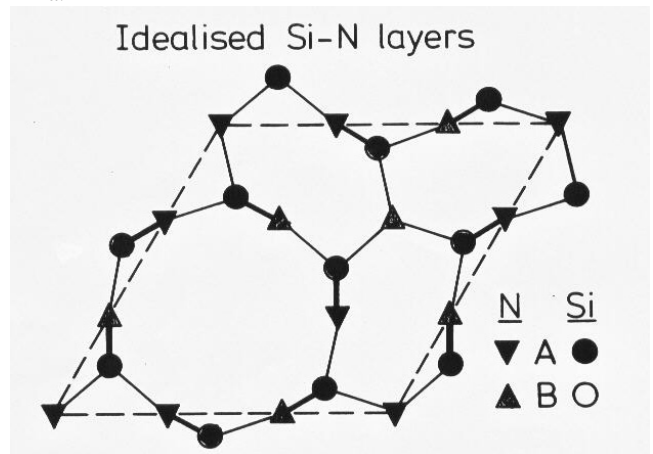
2. Crystal structure and transformations

Silicon nitride exists in two major crystallographic modifications, α and β , both hexagonal [7], with the c dimension of α approximately twice that of β . A complete structure determination assigned β silicon nitride to space group $P6_3/m$. The structure is based on the phenacite type, Be_2SiO_4 , in which the oxygen atoms are replaced by nitrogen and the beryllium atoms by silicon. The bonding leads to a framework of SiN_4 tetrahedra (slightly distorted) joined by sharing nitrogen corners so that each nitrogen is common to three tetrahedra. The β structure is composed of puckered rings of alternating Si and N atoms as shown in Fig. 1(a) [8]; these rings can be considered as layers with a stacking sequence ABAB and forming long continuous channels in the c direction.

The α silicon nitride structure has a space group of $P31c$ [7]. Where the layers of atoms in β are linked along the [001] direction in the sequence ABAB, the α structure has the sequence ABCDABCD. The CD layer, shown in Fig. 1(b) [8], is similar to the AB layer except that it is rotated by 180° on the c -axis. The long continuous channels seen in the β (ABAB) form are thus closed off into two large interstices.

The $\alpha \rightarrow \beta$ transformation in silicon nitride requires a lattice reconstruction. This type of process occurs usually only when the transforming material is in contact with a solvent. The greater solubility of the more unstable form drives it into solution after which it precipitates as the less soluble, more stable form. The predominantly α silicon nitride powder used to produce dense silicon nitride ceramics was observed to transform to the β modification during the sintering process at temperatures in excess of 1400°C when the original α phase is in contact with a metal-silicon-oxynitride liquid phase.

a.



b.

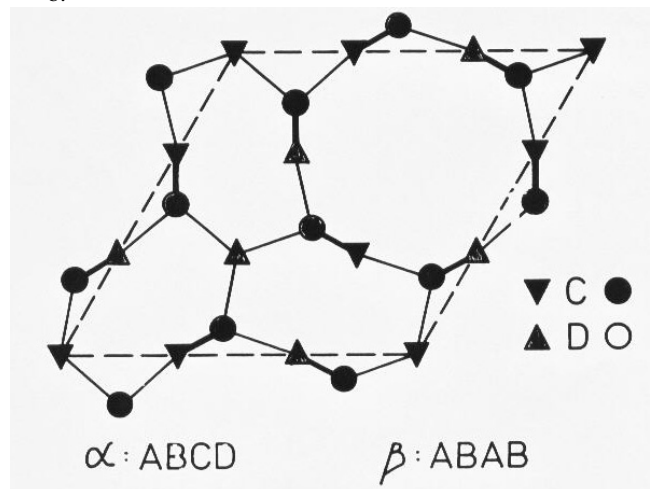
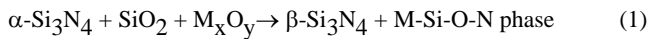


Fig. 1(a) AB layers of Si and N atoms in β - Si_3N_4 (b) CD layers of Si and N atoms in α - Si_3N_4

3. Liquid phase sintering and microstructural development in silicon nitride

Every powder particle of silicon nitride is surrounded by a surface layer of silica. Oxide additives to silicon nitride react with this silica and some of the nitride itself at sintering temperatures to form an oxynitride liquid which promotes densification by solution-precipitation. The α - Si_3N_4 dissolves in the liquid and is precipitated as β - Si_3N_4 which grows in the longitudinal direction as prismatic hexagonal rod-like crystals that eventually impinge on each other forming an interlocked microstructure. The liquid cools as an intergranular phase, usually a glass, according to:



Initially, additives such as MgO or Y₂O₃ were used to sinter silicon nitride [9, 10] and, subsequently, mixed oxide additives such as Y₂O₃ + Al₂O₃ [11] and various rare earth oxides [12] were explored to develop specific microstructures by modifying the nature of the grain boundary phase. Figure 2 is a scanning electron micrograph of silicon nitride densified with Y₂O₃ + Al₂O₃ and shows the elongated rod-like β-silicon nitride grains surrounded by a Y-Si-Al-O-N glass phase.

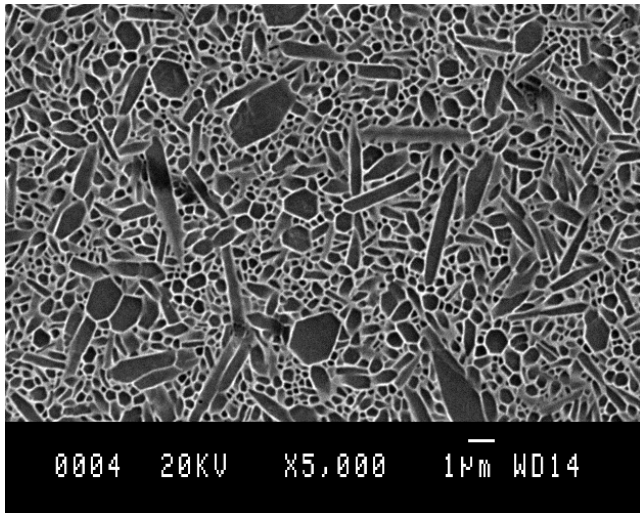


Fig. 2. Scanning electron micrograph of silicon nitride sintered with Y₂O₃ + Al₂O₃

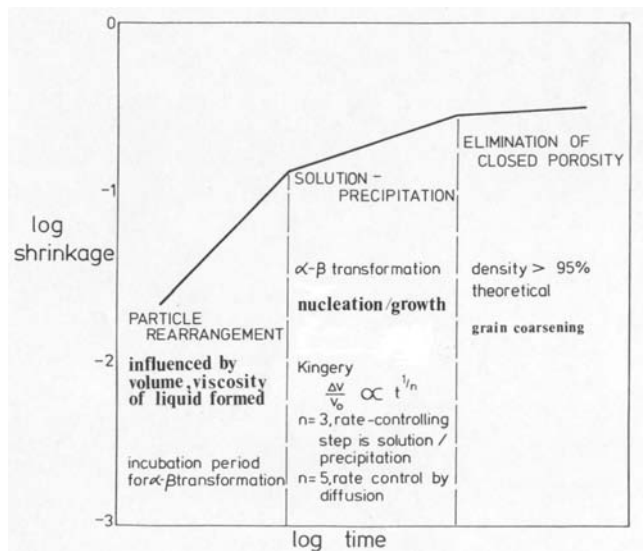


Fig. 3. Schematic plot of three stages of liquid phase sintering of silicon nitride [9]

The only systematic study [9] of pressureless sintering kinetics applies the Kingery liquid-phase sintering model [13] in

which three stages are identified, as summarized by the log-shrinkage/log-time plot of Figure 3. The stages are:

1. particle rearrangement within the initial liquid, where the rate and the extent of shrinkage depend on the volume and viscosity of the liquid; this is the incubation period for the $\alpha \rightarrow \beta$ transformation;
2. solution-diffusion-precipitation, where shrinkage can be expressed as:

$$\Delta V/V_0 \propto t^{1/n} \quad (2)$$

where t is time. $n = 3$ if solution into or precipitation from the liquid is rate controlling and this was found to be the case for MgO additive. $n = 5$ if diffusion through the liquid is rate-controlling as is the case for the Y₂O₃ additive, where diffusion through a more viscous oxynitride liquid is much slower; the $\alpha \rightarrow \beta$ transformation begins during this stage and is more rapid for Y₂O₃;

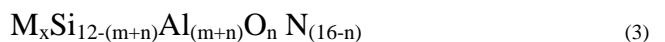
3. final elimination of closed porosity during which the liquid acts to form a more rounded grain morphology; final density is greater than 95% of the theoretical value.

The type and amount of additive used for sintering, not only aids densification but also determines the nature and quantity of the resulting grain boundary phase as indicated in Eq. (1). The concept of "grain boundary engineering" [10] sought to control the structure of, and reactions occurring at, the grain boundaries in silicon nitride based materials and significant advances in materials properties were realized as a result of this approach. One breakthrough was the discovery of the "sialons".

4. Sialons

Sialons are solid solutions based on the silicon nitride structure [14]. β -sialons (β') are formed when oxygen replaces nitrogen in the $\beta\text{-Si}_6\text{N}_8$ structure while, at the same time, silicon is replaced by aluminium to maintain charge neutrality [15]. The phase composition is: $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$, retaining the 3:4 metal:nonmetal ratio, with z values in the range 0–4.2 [16, 17]. Figure 4 shows the Si-Al-O-N behaviour diagram at 1750°C. The diagram shows that, by using silicon nitride powder with its surface silica plus one of the AlN polytypoids (8H, 15R, etc.) [18], a single phase $\beta\text{-SiAlON}$ is formed with $z = 1$. The single-phase form still requires a sintering additive such as Y₂O₃ in order to densify the ceramic but less glass remains as Al and O are taken into solid solution.

α -sialons (α') are based on the $\alpha\text{-Si}_{12}\text{N}_{16}$ unit cell with general composition [8]:



where x (< 2) is determined by the valence of the M ion ($M = \text{Li}, \text{Ca}, \text{Mg}, \text{Y}$ and various lanthanide ions). Again, Y₂O₃ is often used to provide the $\text{M}^{3+} = \text{Y}^{3+}$ for stabilization of α' and as a densification aid.

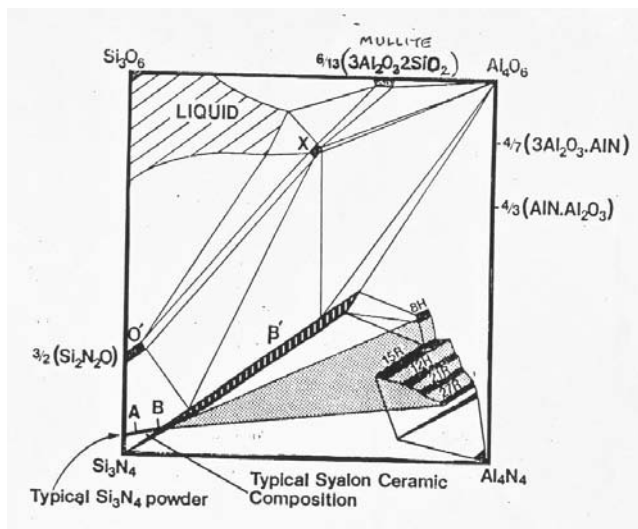


Fig. 4. The Si-Al-O-N behaviour diagram at 1750°C

Unlike the situation in silicon nitride ceramics, the $\alpha' \leftrightarrow \beta'$ transformation is fully reversible, and the two phases have different morphologies. The β' phase morphology consists of elongated prismatic grains similar to those formed in β - Si_3N_4 , whereas the α' grains tend to be small and equiaxed. The mechanical and thermal properties of these materials, therefore, can be controlled by the α -SiAlON: β -SiAlON ratio which depends on the M cation used. The phase composition can be controlled by heat-treatment procedures when rare earth oxides are used as sintering aids [19, 20]. Because the α' -phase can accommodate rare earth metal ions but the β' -sialon only Al, the rare earth ions are rejected into the intergranular regions during the $\alpha' \leftrightarrow \beta'$ transformation, according to the following process:



Because of the formation of more glass on conversion of α' to β' , the creep resistance and high temperature strength of the β' -SiAlONs decreases. However, the transformation provides a mechanism for optimizing the microstructure and, hence, properties by appropriate heat treatments.

5. Microstructure-Property-Relationships

In both silicon nitride and sialons, the microstructure consists of prismatic β - Si_3N_4 grains with an intergranular glass phase. The amount of additive initially introduced determines the quantity and chemistry of the glass phase and this affects properties such as fracture toughness, ambient and high temperature strengths, creep resistance and oxidation resistance [21, 22]. Thus it is important to understand the phase equilibria in M-Si-O-N and related M-Si-Al-O-N systems and then apply this knowledge to processing in order to develop beneficial

microstructures [23]. In addition to controlling the nature of the intergranular phase, the morphology of the β - Si_3N_4 grains is important in determining strength and fracture toughness. For silicon nitrides sintered with different amounts and ratios of $\text{Y}_2\text{O}_3:\text{Al}_2\text{O}_3$, to produce ceramics with the same level of porosity and the same grain size, fracture toughness and aspect ratio (length/diameter) of the β grains both vary with composition in the same way [24] showing that more elongated rod-like crystals have better resistance to crack propagation. As the grain boundary composition changes, the aspect ratios of β grains vary and grain coarsening also occurs as sintering time or temperature is increased.

High resolution transmission electron microscopy (HRTEM) gave valuable insights into the nature of the grain boundaries in silicon nitride in which nanoscale films of glass are present at almost all β - Si_3N_4 grain faces [25] as shown in Figure 5.

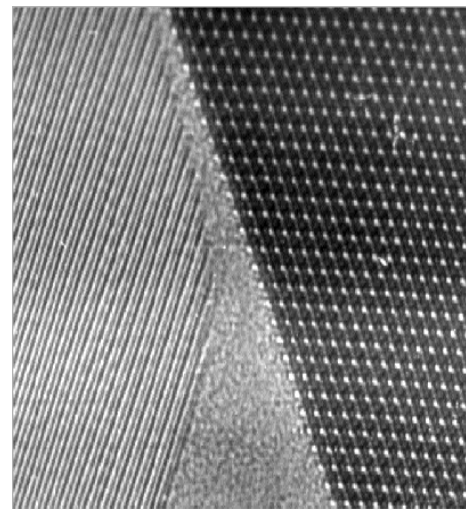


Fig. 5. TEM image of grain boundary glass film and triple point between two silicon nitride grains

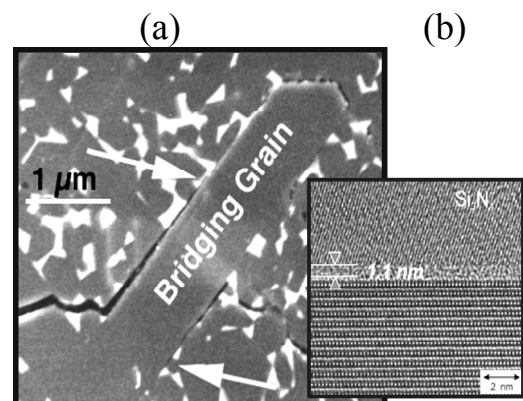


Fig. 6. (a) SEM image of large bridging grain in smaller grain size matrix, (b) TEM image of oxynitride glass film between two β - Si_3N_4 grains [25]

Grain-boundary thicknesses and compositions are characteristic of the metal oxide additive system, and film thickness (in the range 0.5–1.5 nm) depends strongly on chemical composition [26].

Grain boundary chemistry also affects interfacial bond strengths. Weak interfaces favour high toughness, but the debonding of very large β grains can lead to loss of strength [27]. Other practical advantages of high toughness values ($K_{Ic} = 7\text{--}10 \text{ MPa}\cdot\text{m}^{1/2}$) include resistance to machining damage and improved fatigue behavior, K_{Ic} increasing with the volume fraction of elongated grains and proportional to $(\text{grain size})^{1/2}$, an effect due to “crack wake mechanisms”, such as crack bridging, grain rotation and grain pullout. High fracture resistance ($>10 \text{ MPa}\cdot\text{m}^{1/2}$) combined with a steeply rising R -curve and high fracture strength ($>1 \text{ GPa}$) can be developed in self-reinforced silicon nitrides by careful control of the size and amount of well-dispersed large elongated grains in a fine-grained matrix [27]. If not regulated, a microstructure with a broad grain diameter distribution tends to form. If large elongated grains are present, increased fracture resistance can be achieved but is less than that achieved when techniques such as seeding are used to develop a reinforced microstructure with a distinct bimodal grain diameter distribution.

Significant improvement in the R -curve behaviour and the steady-state fracture toughness values were observed in seeded silicon nitride processed with a high Y:Al ratio in the sintering additives [28]. Compared to silicon nitrides with low Y:Al ratios, the high Y:Al ratio materials exhibited more extensive debonding at grain boundary interfaces, resulting in increased intergranular fracture. Microstructural and chemistry characterization revealed that the Y:Al ratios in the additives influence the atomic bonding structure across the $\beta\text{-Si}_3\text{N}_4$ /intergranular glass interface by altering the composition of the glassy phase and inducing different Al and O contents in the growth region of the elongated grains. The overall trend is shown in Figure 6 and it was concluded that reducing the Al concentration in silicon nitride ceramics could result in a more abrupt structural/chemical interface and ultimately achieve improved fracture resistance by activation of toughening mechanisms such as crack-deflection and crack-bridging via interfacial debonding.

In order to gain further understanding of the influence of intergranular glass on the fracture toughness of silicon nitride, the debonding behaviour of the interface between the prismatic faces of $\beta\text{-Si}_3\text{N}_4$ whiskers and oxynitride glasses was investigated in model systems based on various Si-(Al)-Y(Ln)-O-N (Ln = rare-earth) oxynitride glasses [29]. It was found that while the interfacial debonding strength increased when an epitaxial $\beta\text{-SiAlON}$ layer grew on the $\beta\text{-Si}_3\text{N}_4$ whiskers, the critical angle for debonding was lowered with increasing Al and O concentrations in the SiAlON layer showing that by tailoring the densification additives and hence the chemistry of the intergranular glass, it is possible to improve the fracture resistance of silicon nitride.

The $\beta\text{-Si}_3\text{N}_4$ grain morphology is known to be very sensitive to the particular additive used, especially in the case of the oxides of the rare earths (RE). A first-principles model, the differential binding energy, has been developed [30] to characterize the competition between RE and Si for migrating to the $\beta\text{-Si}_3\text{N}_4$ grain surfaces. The theory predicts that, of the RE, La should have

the strongest and Lu the weakest preferential segregation to the grain surfaces. Figure 7 shows that the degree of anisotropic grain growth, represented by the increase in grain aspect ratio, follows the increasing preference of the additive element to segregate to the Si_3N_4 grain surface as represented by the differential binding energy (DBE).

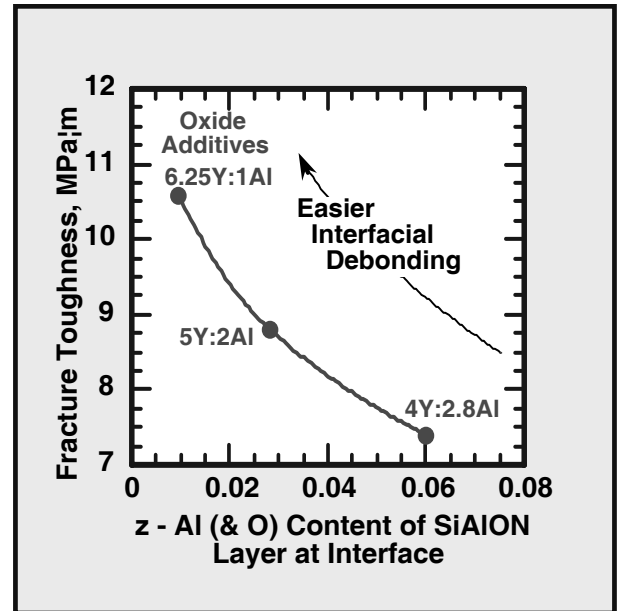


Fig. 6. Fracture toughness v. intergranular glass composition (lower Al results in easier debonding and higher fracture toughness) [26]

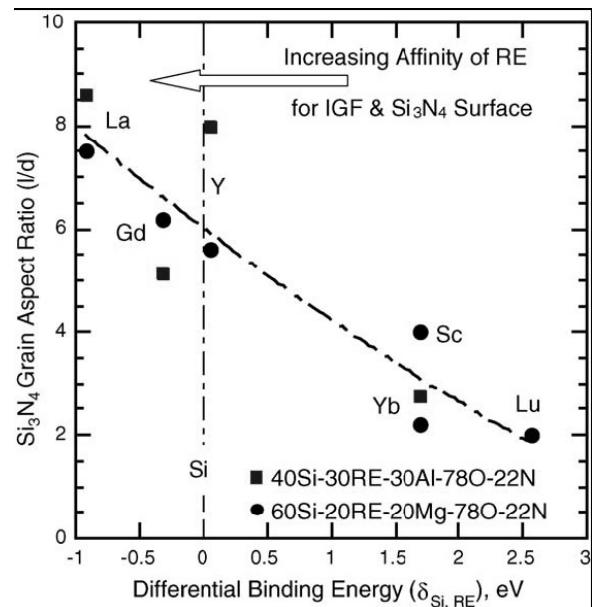


Fig. 7. Si_3N_4 grain aspect ratio as a function of RE additive used for sintering [30]

Elements with larger positive DBE values than Si prefer to reside in regions containing oxygen while those with negative values have a preference for the nitrogen-terminated Si_3N_4 grain surfaces, even more so than Si.

Additional calculations define the adsorption sites and their binding strengths for each of the REs on the prismatic plane of the $\beta\text{-Si}_3\text{N}_4$ grains. These predictions are confirmed by unique atomic-resolution images obtained by aberration-corrected Z-contrast scanning transmission electron microscopy (STEM). The combined theoretical and STEM studies reveal that the elements that induce the greatest observed grain anisotropy are those with the strongest preferential segregation plus high binding strength to the prismatic grain surface.

The impact of various rare-earth and related doping elements (R = Lu, Sc, Yb, Y, Sm, La) on the grain growth anisotropy and the mechanical properties of polycrystalline silicon nitride ceramics has been studied using model experiments [31], in which Si_3N_4 particles are able to grow freely in an RE-Si-Mg-O-N glass matrix. With increasing ionic radius of the RE, grain anisotropy increases due to non-linear growth kinetics. Toughness and strength are affected by the rare-earth element. Samples of equivalent grain sizes and morphologies yield an increasing toughness with increasing ion size of the RE^{3+} , reflecting an increasingly intergranular crack path. Other work also demonstrates the effect of MgO + CeO₂ additives on strength [32]. The choice of the rare-earth is essential to tailor microstructure, interfacial strength and mechanical properties.

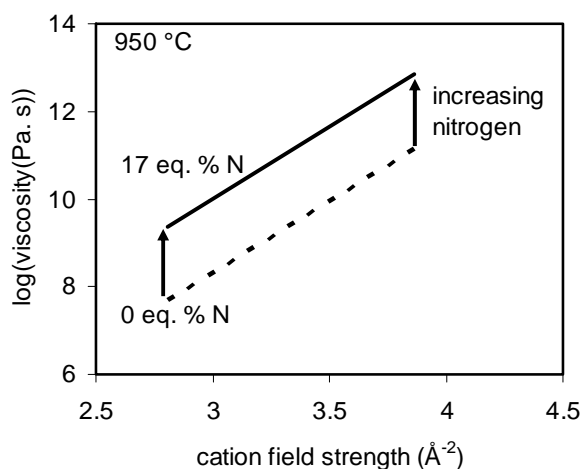


Fig. 8. Schematic showing combined effects of cation field strength of RE ion and nitrogen content on viscosity of RE-Si-Al-O-N glasses [36].

At temperatures exceeding 1000°C, strengths decrease due to the softening of the intergranular glass phase. Grain boundary chemistry, effective viscosity and volume fraction of the intergranular glass phase control creep rate and formation and growth of cavities in the amorphous phase [33]. A number of studies [34-36] have shown that oxynitride glasses have higher glass transition temperatures, elastic moduli, viscosities and microhardness values than the equivalent silicate glasses due to extra cross-linking within the glass network as a result of

substitution of oxygen by nitrogen. For RE-Si-Al-O-N (RE = La, Nd, etc.) glasses with constant O:N and Si:Al ratios, properties increase with increasing rare earth cation field strength (CFS) [36]. Viscosity increases by more than two orders of magnitude as 18 e/o N is substituted for oxygen. Viscosity generally increases as more Si or Y is substituted for Al but this is a smaller effect than that of nitrogen. A further increase in viscosity of three orders of magnitude is achieved by substituting smaller rare earth cations for the larger ones. Figure 8 shows the combined effects of cation field strength and nitrogen content on viscosity of RE-Si-Al-O-N glasses [36]. The implications for silicon nitride and sialon ceramics are that intergranular glasses containing more N and less Al and smaller RE cations will provide enhanced creep resistance.

6. Application

Silicon nitride is now being exploited for turbocharger rotors (figure 9) and in various wear parts for engines (figure 10).



Fig. 9. Silicon nitride turbocharger rotor



Fig. 10. Silicon nitride wear parts for engines

While applications in engines may still be some years away, sintered silicon nitride has very good wear resistance, low friction, high modulus, and low density which has led to the development of high-temperature, unlubricated roller and ball bearings. Other uses include crucibles for molten metal [37] and cutting tools (coated) [38]. As further developments occur through better understanding of grain boundary chemistry and its effects on microstructure and properties, silicon nitride ceramics with improved thermal and mechanical properties will become more reliable and growth in its usage can be envisaged well into the future.

7. Summary

This review has examined the development of silicon nitride and the related sialons and their processing into a “family” of structural ceramic materials with high hardness, strength, fracture toughness, creep resistance and wear resistance. The development of knowledge of microstructure–property relationships in silicon nitride materials has shown the importance of understanding the sintering process and the effects of grain boundary chemistry and structure on mechanical and thermal properties.

References

- [1] F.L. Riley, Silicon Nitride and Related Materials, *Journal of America Ceramic Society*, 83 (2000) 245–265.
- [2] J.F. Collins, R.W. Gerby, New Refractory Uses for Silicon Nitride Reported, *Journals of Met.* 7 (1955) 612–615.
- [3] N.L. Parr, G.F. Martin and E.R.W. May, Preparation, Microstructure, and Mechanical Properties of Silicon Nitride, in *Special Ceramics 1*, ed. P. Popper, Heywood, London, 1960, pp. 102–135.
- [4] G.G. Deeley, J.M. Herbert, N.C. Moore, Dense Silicon Nitride, *Powder Metall.*, 8 (1961) 145–151.
- [5] R.F. Coe, R.J. Lumby, M. F. Pawson, Some Properties and Applications of Hot-Pressed Silicon Nitride, in *Special Ceramics 5*, ed. P. Popper, British Ceramics. Association, Stoke-on-Trent, U.K. (1972) 361–376.
- [6] F.F. Lange, The sophistication of ceramic science through silicon nitride studies, *Journal of Ceramic. Society Japan* 114 (2006) 873–879.
- [7] D. Hardie and K.H. Jack, Crystal Structures of Silicon Nitride, *Nature* 180 (1957) 332–333.
- [8] S. Hampshire, H.K. Park, D.P. Thompson, K.H. Jack, α '-sialons, *Nature* 274 (1978) 880–882.
- [9] S. Hampshire and K.H. Jack, The Kinetics of Densification and Phase Transformation in Nitrogen Ceramics, *Proceedings of . British. Ceramic Society* 31 (1981) 37–49.
- [10] G.E. Gazza, Effect of Yttria Additions on Hot-Pressed Si_3N_4 , *America Ceramic Society Bull.* 54 (1975) 778–781.
- [11] A. Tsuge and K. Nishida, High-Strength Hot-Pressed Si_3N_4 with Concurrent Y_2O_3 and Al_2O_3 Additions, *American Ceramic Society Bull.* 57 (1978) 424–31.
- [12] W.A. Sanders, D.M. Miekowski, Strength and Microstructure of Si_3N_4 Sintered with Rare-Earth Oxide Additions, *America Ceramic Society Bull.*, 64 (1985) 304–309.
- [13] W.D. Kingery, Sintering in the Presence of a Liquid Phase, *Journal of Applied Physic.* 30 (1959) 301–306.
- [14] D.P. Thompson, Materials Science – Cooking up Tougher Ceramics, *Nature* 417 (2002) 237.
- [15] K.H. Jack W.I. Wilson, Ceramics Based on the Si-Al-O-N and Related Systems, *Nature Physic Science* 238 (1972) 28–29.
- [16] K.H. Jack, Review: SiAlONs and Related Nitrogen Ceramics, *Journal of Materials Science* 11 (1976) 1135–1158.
- [17] M.H. Lewis, B.D. Powell, P. Drew, R.J. Lumby, B. North A.J. Taylor, The Formation of Single-Phase Si-Al-O-N Ceramics, *Journal of Materials Science* 12 (1977) 61–74.
- [18] D.P. Thompson, The Crystal Chemistry of Nitrogen Ceramics, in *Preparation and Properties of Silicon Nitride-Based Materials*, ed. D.A. Bonnell and T.Y. Tien, TransTech, Aedermannsdorf, Switzerland, 1989, 21–42
- [19] H. Mandal, T. Ekström, D.P. Thompson, Reversible $\alpha \rightarrow \beta$ -SiAlON Transformation in Heat-Treated SiAlON Ceramics, *Journal of European Ceramic Society*, 12 (1993) 421–429.
- [20] N. Camescu, D.P. Thompson and H. Mandal, Effect of Starting Composition, Type of Rare-Earth Sintering Additive, and Amount of Liquid Phase on $\alpha \rightarrow \beta$ -SiAlON Transformation, *Journal of European Ceramic Society*, 17 (1997) 599–613.
- [21] H. J. Kleebe, G. Pezzotti, G. Ziegler, Microstructure and Fracture Toughness of Si_3N_4 Ceramics: Combined Roles of Grain Morphology and Secondary Phase Chemistry, *Journal of American Ceramic Society*, 82 (1999) 1857–1867.
- [22] S.M. Wiederhorn, R.F. Krause, F. Lofaj, U. Taffner, Creep behavior of improved high temperature silicon nitride, *Key Engineering Materials* 287 (2005) 381–392.
- [23] S. Hampshire, Nitride Ceramics, Chapter 3 in *Structure and Properties of Ceramics*, Ed. M. Swain, VCH Materials Science and Technology - A Comprehensive Treatment 11, VCH Verlagsgesellschaft, Weinheim, pp.121–171.
- [24] G. Ziegler, J. Heinrich, G. Wötting, Review: Relationships between Processing, Microstructure, and Properties of Dense and Reaction-Bonded Silicon Nitride, *Journal of Materials Science* 22 (1987) 3041–3086.
- [25] C.M. Wang, W.Q. Pan, M.J. Hoffmann, R.M. Cannon, M. Rühle, Grain-Boundary Films in Rare-Earth-Glass-Based Silicon-Nitride, *Journal of American Ceramic Society* 79 (1996) 788–792.
- [26] D.R. Clarke, On the Equilibrium Thickness of Intergranular Glass Phases in Ceramic Materials, *Journal of American Ceramic Society*, 70 (1987) 15–22.
- [27] P.F. Becher, E.Y. Sun, K.P. Plucknett, K.B. Alexander, C.H. Hsueh, H.T. Lin, S.B. Waters, C.G. Westmoreland, E.S. Kang, K. Hirao, M. E. Brito, Microstructural Design of Silicon Nitride with Improved Fracture Toughness: I, Effects of Grain Size and Shape, *Journal of American Ceramic Society*, 81 (1998) 2821–2830.
- [28] E. Y. Sun, P. F. Becher, K. P. Plucknett, C.-H. Hsueh, K. B. Alexander, S. B. Waters, K. Hirao, M. E. Brito, Microstructural Design of Silicon Nitride with Improved Fracture Toughness: II, Effects of Yttria and Alumina Additives, *Journal of American Ceramic Society*, 81 (1998) 2831–2840.
- [29] E.Y. Sun, P.F. Becher, C.H. Hsueh, G.S. Painter, S.B. Waters, S.L. Hwang, M.J. Hoffmann, Debonding Behavior

- Between β - Si_3N_4 Whiskers and Oxynitride Glasses With or Without an Epitaxial β -Sialon Interfacial Layer, *Acta Materialia*, 47 (1999) 2777-2785.
- [30] P.F. Becher, G.S. Painter, N. Shibata, R.L. Satet, M.J. Hoffmann, S.J. Pennycook, Influence of additives on anisotropic grain growth in silicon nitride ceramics, *Materials Science Engineering 422A* (2006) 85–91.
- [31] R.L. Satet, M.J. Hoffmann, R.M. Cannon, Experimental evidence of the impact of rare-earth elements on particle growth and mechanical behaviour of silicon nitride, *Materials Science Engineering 422A* (2006) 66-76.
- [32] L. Gao, H. Yang, R. Yuan, P. Huang, R. Xu, J.Y. Jung and K.M. Park, Sintering and microstructure of silicon nitride with magnesia and cerium additives, *Journal of Materials Processing Technology*, 115 (2001) 298-301.
- [33] W.E. Luecke, S.M. Widerhorn, B.J. Hockey, R.F. Krause, G.G. Long, Cavitation Contributes Substantially to Tensile Creep in Silicon Nitride, *Journal of American Ceramic Society* 78 (1995) 2085–2096.
- [34] S. Hampshire, RAL. Drew, K.H. Jack, Oxynitride Glasses, *Physical Chemistry, Glasses* 26 (1985) 182-186.
- [35] S. Hampshire, E. Nestor, R. Flynn, J.L. Besson, T. Rouxel, H. Lemerrier, P. Goursat, M. Sabai, D.P. Thompson, K. Liddell, Oxynitride Glasses: Properties and Potential for Crystallisation to Glass Ceramics, *Journal of European Ceramic Society*, 14 (1994) 261-273.
- [36] R. Ramesh, E. Nestor, M.J. Pomeroy, S. Hampshire, Formation of Ln-Si-Al-O-N Glasses and their Properties, *Journal of European Ceramic Society*., 17 (1997) 1933-1939.
- [37] C. Santos, S. Ribeiro, K. Strecker Jr., D. Rodrigues, C.R.M. Silva, Highly dense Si_3N_4 crucibles used for Al casting: An investigation of the aluminum–ceramic interface at high temperatures, *Journal of Materials. Processing and Technology*, 184 (2007) 108-114.
- [38] D. Pakuła, L.A. Dobrzański, K. Gołombek, M. Pancielejko, A. Kříž, Structure and properties of the Si_3N_4 nitride ceramics with hard wear resistant coatings, *Journal of Materials. Processing and Technology* 157-158 (2004) 388-393.