Variations in pore structure of reaction-bonded silicon nitride (RBSN) *

It is widely agreed that the strength of brittle ceramic materials (e.g. RBSN) is controlled by the stress necessary to propagate the largest surface or internal flaws as described by the Griffith theory [1]. Consequently, the strength of such materials can be increased by controlling the size and shape of failure-initiating flaws [2]. It is, therefore, very important to understand the large variations in pore structure that are often found in reaction-bonded Si_3N_4. A discussion is presented relating the observed pore structures (size) to the reaction mechanisms for α- and β-Si_3N_4.

Ceramics (except those of theoretical density) which are formed by compacting powders, have a certain post-compaction porosity. The pore size and volume fraction of porosity may vary over a wide range depending on the powder size and compaction techniques employed. One can reduce both the pore content and pore size† by increased compacting pressures, decreased particle size, and improved void filling techniques (by use of particle packing theory [3]). In relation to reaction-bonded Si_3N_4, this macro-porosity may vary in volume fraction [4, 5] from 0.27 to 0.44 and in size from 10 to several hundred microns. Clearly to improve strength both the volume fraction and size of this green macro-porosity must be reduced [2, 6].

While the techniques for reducing the residual macro-porosity are quite well-developed for reaction-bonded Si_3N_4, it is important to be aware of three other orders of magnitude of porosity present in reaction-bonded Si_3N_4 as a result of the nitriding process itself, and how these types of nitridation induced porosity [7, 8] can be controlled.

For ease of description we have called these types of nitridation-induced porosity micro-pores, nano-pores, and pico-pores in order of their decreasing size‡. Micro-pores are associated with the melting of the Si particles [4, 5–9] (either due to local impurity segregation or as a result of a large reaction exotherm) and (depending on the size of the silicon powder) may range up to a hundred microns in size. The largest of the micro-pores form in materials with large starting powders and low α/β ratios [2]. This is not to say [10] that the β-formation mechanism requires melting of the Si, (for Jennings *et al.* [8] suggest a diffusion controlled mechanism based on the kinetics and the structure of the β-phase), but rather that this melting is often associated with the formation of the largest of the micro-pores.

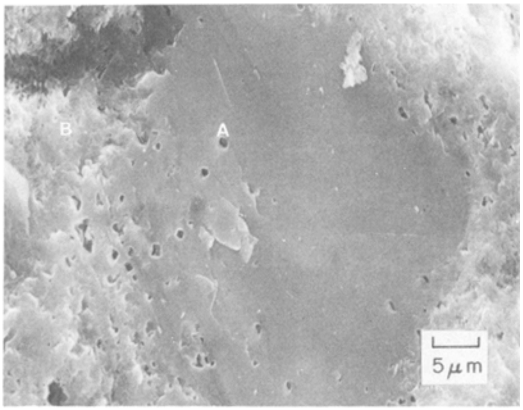

Figure 1 Scanning electron micrograph showing nano-pores (marked A) isolated in the unreacted Si and pico-pores (marked B) in the α-matte Si_3N_4.

When Si grains are reacted to form α-matte Si_3N_4, two additional types of porosity result. It can be seen in Fig. 1 that medium sized or nano-pores are present in the unreacted Si ahead of the $Si-Si_3N_4$ interface, while the finest pores, pico-pores, are seen in the α-matte just after the transformation interface has passed. A schematic representation of these pore size categories, macro-, micro-, pico-, and nano-pores, appears in Fig. 2.

The earlier mechanism for α-matte growth set forth by Atkinson *et al.* [11] proposes that after an initial layer of Si_3N_4 forms on the Si surface, Si migrates out through this layer providing Si to form Si_3N_4 on the exterior. The Si migration leaves vacancies in the bulk Si which can then condense to form internal nano-porosity ahead of the transformation interface. The diffusion of nitrogen across the interface and its reaction with Si vapour present in the internal nano-porosity causes the partial filling of the nano-pores, thus creating the finer pico-pores behind the $Si-Si_3N_4$

---

*Supported by the National Aeronautics and Space Administration, Lewis Research Center, NSF-3118.

†Without the addition of densification aids (such as MgO and Ca), which lower the creep resistance of the final product.

‡Macro-porosity has been used to describe the green or post-compaction level of porosity.

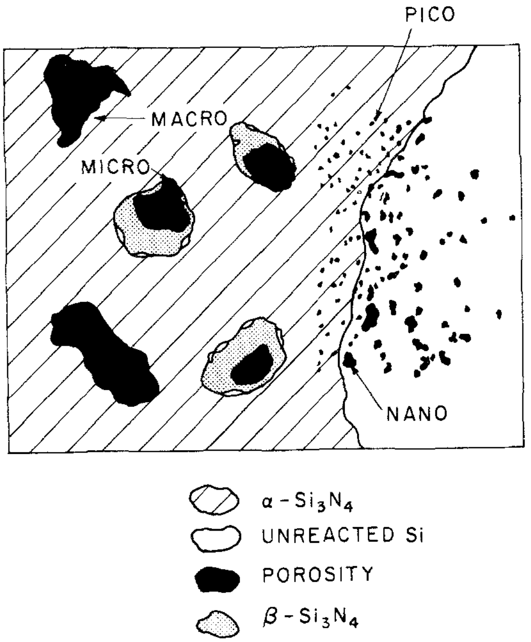

Figure 2 Schematic of macro-, micro-, pico-, and nano-porosity in RBSN.

interface. The presence of Fe in the Si powder may promote these vacancy-condensed nano-pores as a result of the increased lattice diffusion of Fe-doped Si (noted by Lin [12]).

A more recently proposed mechanism [13] states that the vacancy-condensation process is highly unlikely. The new mechanism suggests that nuclei of silicon nitride are formed as N_2 is chemisorbed onto the heated Si surface. The nitrogen around these nuclei is depleted as the nuclei grow resulting in a nitrogen depleted region (which ultimately determines the nuclei spacing and grain size). Si is supplied by surface diffusion and/or evaporation–condensation, thus depressing the adjacent regions. As growth continues, the nitride layer can seal off the depressed regions resulting in nano-pores at the Si–Si_3N_4 interface which can then be partially filled as mentioned above. Thus, while the new mechanism [13] is capable of explaining both nano- and pico-porosity, it does not account for the isolated nano-pores observed in unreacted Si head of the Si–Si_3N_4 interface. The assumption that both proposed α-matte growth mechanisms are active explains the production of the observed isolated nano-pores and their partial filling with α-Si_3N_4, leaving behind very fine-grained α-matte and pico-pores.

It is clear that the 22% volume increase on nitridation is advantageous in filling in the residual pore structure. If this is done so as to avoid the micro-pores often associated with the formation of β, a great deal of the pore structure (size and distribution) can be minimized at constant density (volume fraction porosity). The success of porosity control at all levels to date [2] points to its importance for future development of reaction-bonded Si_3N_4.

References

1. R. W. DAVIDGE and A. G. EVANS, *Mater. Sci. Eng.* 6 (1970) 281.
2. S. C. DANFORTH, H. M. JENNINGS and M. H. RICHMAN, to be published.
3. H. E. WHITE and S. F. WALTON, *Bull. Amer. Ceram. Soc.* 16 (1937) 7.
4. S. C. DANFORTH, M. S. Thesis, Brown University, June, 1975.
5. A. EZIS, "Ceramics for High Performance Applications", edited by J. J. Burke, A. E. Gorum and R. N. Katz (Brook Hill Inc. Chesnut Hill, 1974) pp. 207–222.
6. B. F. JONES, K. C. PITMAN and M. W. LINDLEY, *J. Mater. Sci.* 12 (1977) 563.
7. H. M. JENNINGS, S. C. DANFORTH and M. H. RICHMAN, *Metallography* 9 (1976) 427.
8. H. M. JENNINGS, J. O. EDWARDS and M. H. RICHMAN, *Inorg. Chim. Acta.* 20 (1976) 167.
9. P. ARUNDALE and A. J. MOULSON, *J. Mater. Sci.* 12 (1977) 2139.
10. D. P. ELIAS, B. F. JONES and M. W. LINDLEY, *Powder Met. Int.* 8 (1976) 162.
11. A. ATKINSON, P. J. LEATT, A. J. MOULSON and E. W. ROBERTS, *J. Mater. Sci.* 9 (1974) 981.
12. S. S. LIN, *J. Amer. Ceram. Soc.* (1977) 78.
13. A. ATKINSON, A. J. MOULSON and E. W. ROBERTS, *J. Amer. Ceram. Soc.* 59 (1976) 285.

Received 21 April
and accepted 25 May 1978.

S. C. DANFORTH[*]
M. H. RICHMAN
Brown University,
Providence, RI 02912, USA

---

[*] Currently at the Massachusetts Institute of Technology, Cambridge, Mass, USA.