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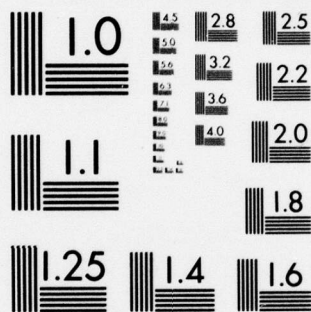
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# GRAIN BOUNDARY ENGINEERING IN NONOXIDE CERAMICS

R. NATHAN KATZ and GEORGE E. GAZZA  
CERAMICS RESEARCH DIVISION

September 1978

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ABSTRACT

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The deliberate selection and control of composition, structure, and processes occurring in the grain boundary, both during and after fabrication, with the aim of specific property modification may properly be defined as grain boundary engineering. We will review various strategies for doing grain boundary engineering and give examples of the use of these strategies in the development of hot-pressed silicon nitride. Research needs for further development of grain boundary engineering (GBE) in nonoxide systems are discussed.

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## INTRODUCTION

The deliberate selection and control of composition, structure, and processes occurring in the grain boundary (or the grain boundary affected region) during or after fabrication, aimed at specific property modification, may properly be termed grain boundary engineering (GBE). It is frequently the case that the nature of the grain boundary controls critical optical and/or mechanical properties. In these instances GBE as a strategy is often more fruitful than the more conventional microstructure development or compositional control approaches. Indeed, in past papers the authors have discussed examples of GBE as applied to improving the optical properties of ionic ceramics.<sup>1,2</sup> A summary of GBE techniques, in the broadest sense, is presented in Table 1.

Table 1. SUMMARY OF GRAIN BOUNDARY ENGINEERING TECHNIQUES

| Techniques                                           | Examples                                                                                                                  | Mechanisms                                                                                                      | References |
|------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|------------|
| <u>Liquid Phase Sintering</u>                        |                                                                                                                           |                                                                                                                 |            |
| Fugitive                                             | MgO + LiF                                                                                                                 | Solution-Precipitation?                                                                                         | 3, 4       |
| Non-Fugitive                                         | $\text{Si}_3\text{N}_4 + \text{MgO}$                                                                                      | Liquid Phase Sintering                                                                                          | 5, 6       |
|                                                      | $\text{Mg Al}_2\text{O}_4 + \text{Li}_2\text{O} \text{ \& \; } \text{SiO}_2$                                              | Liquid Phase Sintering                                                                                          | 7          |
| <u>Compound Formation in Grain Boundary</u>          |                                                                                                                           |                                                                                                                 |            |
| Via Liquid Phase<br>(With Possible Further Reaction) | $\text{Si}_3\text{N}_4 + \text{Y}_2\text{O}_3$                                                                            | Crystallization of Grain Boundary Liquid                                                                        | 8, 9, 10   |
| Without Liquid Phase                                 | Lucalox ( $\text{Al}_2\text{O}_3 + \text{MgO}$ )                                                                          | Spinel at Grain Boundary                                                                                        | 11         |
| <u>Promotion of Volume Diffusion</u>                 | SiC                                                                                                                       | $\left\{ \begin{array}{l} \text{C to Remove SiO}_2 \\ \text{B Changes } \gamma_{\text{SV}} \end{array} \right.$ | 12         |
| <u>Press Forge Single Crystals</u>                   | $\text{CaF}_2$ , KCl                                                                                                      | Dislocation Generation and Organization                                                                         | 13, 14     |
| <u>Impurity Control</u>                              | $\left\{ \begin{array}{l} \text{Si}_3\text{N}_4 + \text{MgO} \\ \text{Si}_3\text{N}_4 \text{ (RBSN)} \end{array} \right.$ | Reduce Ca                                                                                                       | 15, 16     |
| <u>Second Phase Particle Additions</u>               |                                                                                                                           |                                                                                                                 |            |
| Mechanically Added                                   | $\text{BeO} + \text{ZrO}_2$                                                                                               |                                                                                                                 |            |
| <u>Precipitation at Grain Boundary</u>               |                                                                                                                           |                                                                                                                 |            |

As discussed below, the production of fully dense silicon nitride (either hot-pressed or sintered) requires the use of densification aids which form a liquid phase during processing, resulting in a grain boundary phase, which in turn controls the high-temperature mechanical properties of the material. During the past six years an extensive amount of research and development effort has been focused on manipulating this grain boundary phase, primarily to improve the high-temperature properties of hot-pressed silicon nitride (HPSN). Thus, the development of fully dense, high-temperature HPSN provides an excellent ongoing case history in GBE. This case history will be reviewed, highlighting several of the

1. KATZ, R. N. *Recent Developments in High Performance Ceramics*. Materials Technology - 1976, AIP Conf. Proc. No. 32, Am. Inst. Phys., New York, 1976.
2. KATZ, R. N., and GAZZA, G. E. *Grain Boundary Engineering and Control in Nitrogen Ceramics*. Proc. of the Conf. on Nitrogen Ceramics, Canterbury, England, 1977, Noordhoff International Publishing, Leyden, p. 417-431.

GBE techniques (strategies) listed in Table 1.<sup>3-16</sup> This review also emphasizes that the GBE strategies used to develop improved HPSN relied on inferential evidence as to the nature of the grain boundary phase(s) present. While much was accomplished using such inferential evidence as described below, direct, quantitative information relative to the grain boundary would have considerably accelerated these developments. Therefore, the second portion of this paper deals with recent progress in several key areas of materials science relevant to GBE in nonoxide ceramics. Needs for additional capabilities or information critical to the future development of GBE will also be discussed.

### GBE AND THE OPTIMIZATION OF HOT-PRESSED $\text{Si}_3\text{N}_4$

Since the late 1950's, considerable interest has grown in the development of  $\text{Si}_3\text{N}_4$  and SiC materials which have high potential as component materials in various propulsion and power generation systems.<sup>1</sup> State-of-the-art high-strength, hot-pressed  $\text{Si}_3\text{N}_4$  has resulted from a series of developments involving: empirical selection of densification aids, control of high-temperature strength limiting reaction products in the grain boundary via a variety of strategies, and selection of new families of densification aids specifically chosen to yield grain boundary phases with improved properties. In contrast to materials improvements in many other ceramic systems, essentially all improvements in hot-pressed  $\text{Si}_3\text{N}_4$  as an engineering ceramic have resulted from grain boundary phase manipulations. These developments will now be reviewed.

#### MgO: Its Role and Importance

Since  $\text{Si}_3\text{N}_4$  dissociates before significant sintering can occur, an additive was required which would permit densification at temperatures below those at which significant dissociation occurs. Early attempts to obtain a densification aid which would produce fully dense, high-strength, hot-pressed  $\text{Si}_3\text{N}_4$  were successfully carried out by Deely et al.<sup>5</sup> who demonstrated that MgO additions gave results superior to the many other additives considered. Although X-ray diffraction analysis

3. RICE, R. W. *Production of Transparent MgO at Moderate Temperatures and Pressures*. Am. Ceram. Soc. Bull., v. 41, 1962, p. 271.
4. ATLAS, L. M. *Effect of Some Lithium Compounds on Sintering of MgO*. J. Am. Ceram. Soc., v. 40, 1957, p. 196.
5. DEELEY, G. G., HERBERT, J. M., and MOORE, N. C. *Powder Met.*, v. 8, 1961, p. 145.
6. LUMBY, R. J., and COE, R. F. *The Influence of Some Process Variables on the Mechanical Properties of Hot-Pressed Silicon Nitride*. Proc. Brit. Ceram. Soc., v. 15, 1970, p. 91.
7. GATTI, A., MEHAN, R. L., and NOONE, M. J. Naval Air Systems Comm. Report, Contract N00019-71-C-0126, December 1971.
8. GAZZA, G. E. *Hot-Pressed  $\text{Si}_3\text{N}_4$* . J. Am. Ceram. Soc., v. 56, no. 12, 1973, p. 662.
9. GAZZA, G. E. *Effect of Yttria Additions on Hot-Pressed  $\text{Si}_3\text{N}_4$* . Am. Ceram. Soc. Bull., v. 54, no. 9, 1975, p. 778.
10. TSUGE, A., KUDO, H., and KOMEYA, K. *Reaction of  $\text{Si}_3\text{N}_4$  and  $\text{Y}_2\text{O}_3$  in Hot-Pressing*. J. Am. Ceram. Soc., v. 57, no. 6, 1974, p. 269.
11. COBLE, R. L. *Sintering Crystalline Solids: I. Intermediate and Final State Diffusion Models*. J. Appl. Phys., v. 32, no. 5, 1961, p. 787-799.
12. PROCHAZKA, S. *Sintering of Silicon Carbide in Ceramics for High Performance Applications*, Chapter 12, J. J. Burke, A. E. Gorum, and R. N. Katz, ed., Brook Hill Publishing Co., Chestnut Hill, Massachusetts, 1974.
13. RICE, R. W. in *Ultrafine Grain Ceramics*. Syracuse University Press, New York, 1970, p. 203.
14. HARRISON, W. B. AFML-TR-75-109, July 1975, p. 210.
15. RICHESON, D. W. *Effect of Impurities on the High Temperature Properties of Hot-Pressed Silicon Nitride*. Am. Ceram. Soc. Bull., v. 52, no. 7, 1973, p. 560.
16. MANGALS, J. *Development of a Creep-Resistant Reaction-Sintered  $\text{Si}_3\text{N}_4$  in Ceramics for High Performance Applications*, Chapter 9, J. J. Burke, A. E. Gorum, and R. N. Katz, ed., Brook Hill Publishing Co., Chestnut Hill, Massachusetts, 1974.

of the hot-pressed samples indicated only  $\text{Si}_3\text{N}_4$  present, primarily beta phase, it was assumed that the MgO additive reacted with the surface silica on the  $\text{Si}_3\text{N}_4$  particles to form a vitreous glass which produced a continuous bonding boundary phase. Further optimization of the system was carried out by Lumby and Coe,<sup>6</sup> who showed the significance of using high alpha phase  $\text{Si}_3\text{N}_4$  powder as starting material and the strength dependence on hot-pressing time. This work implied the importance of the  $\alpha \rightarrow \beta$  transformation in developing high-strength material, as later rationalized by Lang.<sup>17</sup> Further attempts to define the role of MgO during densification were carried out by Evans and Sharp<sup>18</sup> who confirmed the existence of a glass phase at triple points by transmission electron microscopy. However, a similar uniformly distributed grain boundary phase was only inferred. Indirect evidence for a non-crystalline grain boundary phase of  $\text{MgSiO}_3$  composition was obtained by Wild et al.<sup>19</sup> from annealing experiments on hot-pressed  $\text{Si}_3\text{N}_4$  containing 10% MgO. Visual evidence for glassy phases existing in high MgO content, hot-pressed  $\text{Si}_3\text{N}_4$  by a transmission electron microscopy (TEM) study were subsequently obtained by Drew and Lewis.<sup>20</sup> This study also confirmed the role of the glassy phase in the  $\alpha \rightarrow \beta$  transformation, thought necessary for the attainment of high-strength  $\text{Si}_3\text{N}_4$ .

In attempting to define the composition of the observed glassy phase, studies with Auger spectroscopy and electron probe microanalysis were performed<sup>21,22</sup> and results suggested the existence of various grain boundary glass compositions, i.e.,  $x\text{SiO}_2 \cdot y\text{CaO} \cdot z\text{MgO}$ . These analyses also indicated that a proportion of the smaller cations, (i.e., Mg, Al) have diffused into the  $\text{Si}_3\text{N}_4$  structure during hot pressing.

While hot-pressed  $\text{Si}_3\text{N}_4$  produced in this way had properties which were encouraging for use in high-temperature applications (e.g., gas turbines), in-depth studies of creep and high temperature modulus of rupture (MOR) at  $\sim 1200^\circ\text{C}$  indicated that, in contrast to reaction-bonded  $\text{Si}_3\text{N}_4$ , hot-pressed material exhibited a significant fall off in properties. Much inferential evidence from the results of Auger spectroscopy, TEM, creep behavior, etc., pointed to the glassy grain boundary phase being responsible for this behavior.

Studies<sup>21,15</sup> initiated to determine the influence of residual impurities in the starting materials on the high-temperature properties of the boundary phase have shown that the apparent viscosity of the boundary phase is purity-dependent. In particular, the Ca cation was found to be detrimental to high-temperature properties of  $\text{Si}_3\text{N}_4$  which exhibited increased subcritical crack growth<sup>23</sup> and decreased creep resistance.<sup>21</sup> Evidence to date suggests that this is due to the presence of the boundary phase which becomes viscous at high temperature, allowing grain boundary sliding and associated slow crack growth.

17. LANGE, F. F. *Relation Between Strength, Fracture Energy, and Microstructure of Hot-Pressed  $\text{Si}_3\text{N}_4$* . J. Am. Ceram. Soc., v. 56, no. 10, 1973, p. 518.
18. EVANS, A. G., and SHARP, J. V. *Microstructural Studies on Silicon Nitride*. J. Mat. Sci., v. 6, 1971, p. 1292.
19. WILD, S., GRIEVESON, P., JACK, K. H., and LATIMER, M. in *Special Ceramics 5*, P. Popper, ed., Brit. Ceram. Res. Assoc., 1972, p. 377.
20. DREW, P., and LEWIS, M. H. *The microstructures of Silicon Nitride Ceramics During Hot-Pressing Transformations*. J. Mat. Sci., v. 9, 1974, p. 261.
21. KOSSOWSKY, R. *The Microstructure of Hot-Pressed Silicon-Nitride*. J. Mat. Sci., v. 8, 1973, p. 1603.
22. POWELL, B. D., and DREW, P. *The Identification of a Grain-Boundary Phase in Hot-Pressed Silicon Nitride by Auger Electron Spectroscopy*. J. Mat. Sci., v. 9, 1974, p. 1867.
23. LANGE, F. F., and ISKOE, J. L. *High Temperature Strength Behavior of Hot-Pressed  $\text{Si}_3\text{N}_4$  and SiC: Effect of Impurities in Ceramics for High Performance Applications*, Chapter 11, J. J. Burke, A. E. Gorum, and R. N. Katz, ed., Brook Hill Publishing Co., Chestnut Hill, Massachusetts, 1974.

To summarize the above, the importance of MgO as an additive to hot-pressed  $\text{Si}_3\text{N}_4$  was that it permitted the attainment of full density and possibly provided the medium through which an  $\alpha \rightarrow \beta$  solution-reprecipitation transformation could occur, with concomitant high RT strength. The principal drawback of the conventional use of MgO as an additive was the limitation it imposed on high-temperature strength and creep behavior.

At this point the central problem faced by researchers was to find a way to create a more refractory grain boundary phase (GBP) or to eliminate it. In spite of the experimental difficulties in direct characterization of this grain boundary phase (namely that the small volume percent of this "amorphous" phase in a crystalline matrix is not amenable to X-ray diffraction methods and its small dimension rules out conventional microprobe and similar direct techniques) and having to rely on inferential results, significant improvements in hot-pressed  $\text{Si}_3\text{N}_4$  have been made by applying the GBE strategies shown in Figure 1.

STRATEGIES TO INCREASE THE HIGH-TEMPERATURE  
BEHAVIOR OF HOT-PRESSED  $\text{Si}_3\text{N}_4$

1. Reduce Ca, Na, etc., impurities to make the grain boundary  $\text{MgSiO}_3$  glass more refractory.
2. Develop a densification aid to yield a more refractory glass than  $\text{MgSiO}_3$ .
3. Develop a nonglass grain boundary.
4. Eliminate the grain boundary phase by promoting sintering via volume diffusion.

Figure 1.

Compositional Control of the Magnesium-Silicate Grain Boundary Glass Phase

The first approach to compositional control of the magnesium-silicate grain boundary glass phase was to reduce the amounts of impurities which would lower the softening temperature of this phase. This approach was initially pursued by Kossowsky<sup>21</sup> and Lange<sup>23</sup> at Westinghouse and Richerson<sup>15</sup> at the Norton Company. These investigators elucidated the detrimental role of Ca, as well as other alkali and alkaline earth elements, on the high-temperature strength and creep resistance of the magnesium silicate grain boundary phase.

Efforts were then made to produce higher purity  $\text{Si}_3\text{N}_4$  starting powder in order to reduce detrimental impurity levels. Lange also demonstrated that control of the  $\text{MgO}/\text{SiO}_2$  ratio\* could beneficially influence the high-temperature properties of HPSN.<sup>24</sup> Strength values at 25 C and 1400 C were measured for molar ratios from 1 to 10. It was shown that maximum values were obtained at 1400 C for

\*Some  $\text{SiO}_2$  is always present on the surface of  $\text{Si}_3\text{N}_4$  powder. Hence it is essential to account for the precise amount of  $\text{SiO}_2$  in any given powder when doing GBE, in spite of the difficulties in doing so.

24. ANDERSSON, C. A., LANGE, F. F., and ISKOE, J. L. *Effect of the  $\text{MgO}/\text{SiO}_2$  Ratio on the Strength of Hot-Pressed  $\text{Si}_3\text{N}_4$* . Westinghouse Electric Corp., R&D Center, Contract N00014-74-C-0284, Tech. Rpt. 3, October 15, 1975.

MgO/SiO<sub>2</sub> ratios of 3 to 4. This was attributed to either a change in refractoriness or volume content of the grain boundary phase. The change in refractoriness may be the result of increasing nitrogen solubility in the phase or shifting away from glass-forming regions in the MgO-SiO<sub>2</sub>-impurity system.

Efforts to produce higher purity Si<sub>3</sub>N<sub>4</sub> powders were pursued in attempting to minimize the residual detrimental impurity content. This produced significant improvement in high-temperature properties but the properties of the specific MgO-Si<sub>3</sub>N<sub>4</sub> reaction products formed, i.e., MgSiO<sub>3</sub> or Mg-Si-O-N, then became limiting on strength and creep resistance. It thus became apparent that significant increases in the high-temperature properties of hot-pressed Si<sub>3</sub>N<sub>4</sub> would require other approaches.

#### Densification Aids Other Than MgO

Another approach for increasing high-temperature properties would be to induce the formation of more refractory reaction products between the additive and the SiO<sub>2</sub> layer on the Si<sub>3</sub>N<sub>4</sub>, to form the boundary phase. Gazza<sup>8,9</sup> explored this approach and found that yttria was an effective additive for this purpose (Figure 2). It was reasoned that the probable formation of xY<sub>2</sub>O<sub>3</sub>·ySiO<sub>2</sub> glasses and compounds would be more refractory than xMgO·ySiO<sub>2</sub> glasses; further, that the large ionic radius of the Y cation would tend to keep it in the boundary vicinity rather than diffusing away into the Si<sub>3</sub>N<sub>4</sub> grains. Also, it might be possible to crystallize these "glassy" phases. At low Y<sub>2</sub>O<sub>3</sub> additive levels, <5 w/o, these glasses appear to form and some improvements in high-temperature properties were observed. However, it was found that maximum strengths were obtained with 10 to 15 w/o Y<sub>2</sub>O<sub>3</sub>, which is more than required to completely react with the surface silica on Si<sub>3</sub>N<sub>4</sub> powder, and a more complex role of Y<sub>2</sub>O<sub>3</sub> additions to Si<sub>3</sub>N<sub>4</sub> was explained by work at Newcastle.<sup>25</sup> These studies have shown that the refractory nature of the Si<sub>3</sub>N<sub>4</sub>-Y<sub>2</sub>O<sub>3</sub> reaction products are due to the formation of xSi<sub>3</sub>N<sub>4</sub>·yY<sub>2</sub>O<sub>3</sub>·zSiO<sub>2</sub> compounds

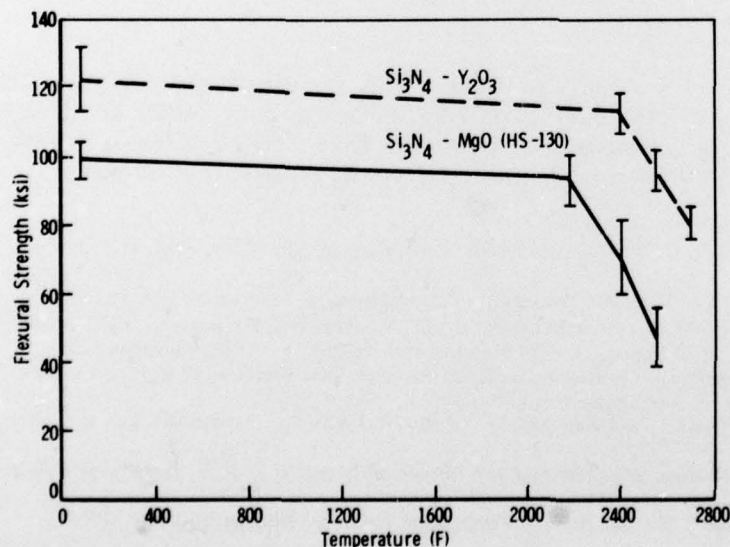


Figure 2. Strength versus temperature for Si<sub>3</sub>N<sub>4</sub> + Y<sub>2</sub>O<sub>3</sub> versus Si<sub>3</sub>N<sub>4</sub> + MgO.

25. RAE, A. W. J. M., THOMPSON, D. P., PIPKIN, N. J., and JACK, K. H. in *Special Ceramics 6*, P. Popper, ed., Brit. Ceram. Res. Assoc., 1976.

which may further react with  $\text{Si}_3\text{N}_4$  to produce  $\text{Si}_3\text{N}_4 \cdot \text{Y}_2\text{O}_3$  composition. In addition to producing high melting point refractory phases, residual impurities such as Ca, Al, and Mg are accommodated into solid solution by these compounds thus limiting their detrimental effect. Similar reaction products were reported by Tsuge et al.<sup>10</sup> in concurrent work. Although enhanced properties have been demonstrated for the  $\text{Si}_3\text{N}_4$ - $\text{Y}_2\text{O}_3$  additive system, a problem with anomalous strength degradation at approximately 1000 C has been reported and further studied by several investigators.<sup>26-28</sup> Lange<sup>26</sup> found that this behavior is related to the lack of oxidation resistance of certain  $\text{Si}_3\text{N}_4$ - $\text{Y}_2\text{O}_3$  reaction phases at 1000 C and severe cracking of specimens containing these phases occurs. More recent work of Lange's also indicates that if one remains within the  $\text{Si}_2\text{ON}_2 \cdot \text{Y}_2\text{Si}_2\text{O}_7 \cdot \text{Si}_3\text{N}_4$  compatibility triangle in the  $\text{SiO}_2 \cdot \text{Y}_2\text{O}_3 \cdot \text{Si}_3\text{N}_4$  phase diagram, one obviates the intermediate temperature stability problem.<sup>27</sup> High yttria additions (>10 w/o) to  $\text{Si}_3\text{N}_4$  were reported to form phases which had poor oxidation resistance and exhibited linear-type kinetics rather than parabolic.  $\text{Si}_3\text{N}_4$ - $\text{Y}_2\text{O}_3$  compositions containing these phases cracked severely during oxidation at 1000 C but not at higher temperatures. It was found that by altering the composition so that phases formed were within the  $\text{Si}_3\text{N}_4 \cdot \text{Si}_2\text{N}_2\text{O} \cdot \text{Y}_2\text{Si}_2\text{O}_7$  compatibility triangle, excellent oxidation resistance is observed. It was suggested that this was due to the formation of  $\text{Y}_2\text{Si}_2\text{O}_7$  which exists in equilibrium with  $\text{SiO}_2$  and preserves a protective surface coating. Brennan<sup>28</sup> is investigating  $\text{Si}_3\text{N}_4$ -15 w/o  $\text{Y}_2\text{O}_3$  materials using high and low purity  $\text{Si}_3\text{N}_4$  starting powders, and thus far, finds the anomalous 1000 C behavior to be purity-dependent. Tsuge, Nishida, and Komatsu<sup>29</sup> found that for their particular  $\text{Si}_3\text{N}_4$ - $\text{Y}_2\text{O}_3$  additive (~5%) system, strength problems at intermediate temperatures could be overcome by crystallizing the glass phase formed by the additive reaction with  $\text{Si}_3\text{N}_4$ .

Other additives such as  $\text{CeO}_2$ ,<sup>30,31</sup> other rare earth oxides,<sup>32</sup> and  $\text{ZrO}_2$ ,<sup>33,34</sup> have also been studied to determine their effect on pressure sintering of  $\text{Si}_3\text{N}_4$  and potential for enhancing high-temperature properties of  $\text{Si}_3\text{N}_4$ .

#### Crystallization of Grain Boundary Phases

The Mg-silicate liquid acts as a densification aid in hot pressing  $\text{Si}_3\text{N}_4$  with MgO additions. The resultant grain boundary phase is vitreous and tends to creep at high temperature, thus limiting its usefulness above this temperature. A glassy phase has also been inferred in yttria-doped (~5 w/o)  $\text{Si}_3\text{N}_4$  resulting in some

26. LANGE, F. F., SINGHAL, S. C., and KUZNICKI, R. C. Westinghouse Electric Corp., Contract N0014-74-C-0284, Tech. Rpt. 6, April 1976.
27. BRATTON, R. J., ANDERSSON, C. A., and LANGE, F. F. *Hot-Pressed  $\text{Si}_3\text{N}_4$  Developments in Ceramics for High Performance Applications II*, J. J. Burke, E. Lenoe, and R. N. Katz, ed., Brook Hill Publishing Co., Chestnut Hill, Massachusetts, 1978, p. 805.
28. BRENNAN, J. J. United Tech. Research Center Tech. Report R75-912081-2, Contract N62269-75-C-0137, September 1975.
29. TSUGE, A., NISHIDA, K., and KOMATSU, M. *Effect of Crystallizing the Grain-Boundary Glass Phase on the High-Temperature Strength of Hot-Pressed  $\text{Si}_3\text{N}_4$  Containing  $\text{Y}_2\text{O}_3$* . J. Am. Ceram. Soc., v. 58, no. 7-8, 1975, p. 323.
30. HUSEBY, I. C., and PETZOW, G. *Influence of Various Densifying Additives on Hot-Pressed  $\text{Si}_3\text{N}_4$* . Powder Met. Int., v. 6, no. 1, 1974, p. 17.
31. MAZDIYASNI, K. S., and COOKE, C. M. *Consolidation, Microstructure, and Mechanical Properties of  $\text{Si}_3\text{N}_4$  Doped with Rare-Earth Oxides*. J. Am. Ceram. Soc., v. 57, no. 12, December 1974, p. 536.
32. ANDERSSON, C. A., and BRATTON, R. J. *Ceramic Materials for High Temperature Turbines*. Final Report under ERDA Contract E (40-1) 5210, August 1977.
33. RICE, R. W., and McDONOUGH, W. J. Am. Ceram. Soc. Bull., v. 54, no. 8, 1975, p. 753.
34. VASILOS, T. AVCO Corp., Lowell, Massachusetts, personal communications.

strength reduction at high temperature. High-temperature strength behavior was improved by crystallizing the glass phase. Further development of high-temperature strength by grain boundary crystallization (GBC) was accomplished by using  $Y_2O_3$  and  $Al_2O_3$  as additives to promote densification. Thermal shock resistance measurements by quenching into water indicated  $\Delta T_C$  values  $> 1000$  C could be obtained. Strength retention of 140 ksi at 1000 C was also achieved.<sup>29,35</sup>

#### Promotion of Volume Diffusion

Thus far, additions used for enhancing the sinterability of  $Si_3N_4$  have resulted in the formation of separate boundary phases which have controlled properties. A further approach to sintering, successfully used by Prochazka<sup>12</sup> with SiC, would be to use additions which promote greater degrees of volume diffusion, remove inhibiting species from the system by volatilization, form solid solutions, and produce "clean" grain boundaries. While various teams are pursuing research on  $Si_3N_4$  using this concept, no one has yet achieved the goal. The achievement, however, may result in differences in microstructural morphology and fracture mode of  $Si_3N_4$  which may benefit some properties and be detrimental to others.

#### GBE RESEARCH TOOLS - PROGRESS AND NEEDS

At present GBE in nonoxide ceramics is more of an art than a science. The further development of several areas of research is critical to future progress on GBE. These areas include:

- Grain Boundary Characterization Techniques
- Phase Equilibria Data
- Diffusion Data
- Improved Processing Technology

While much progress has been made in improving silicon nitride and silicon carbide materials based on inferential models of the grain boundary, the need for direct observational techniques is clearly evident. In the past two years lattice-imaging transmission electron microscopy has emerged as a powerful tool for obtaining such information.<sup>36</sup> Figure 3 shows the grain boundary phase in HPSN with a MgO additive. By coupling lattice-imaging TEM with microanalysis and microdiffraction techniques,<sup>37</sup> direct evidence has been obtained to support liquid phase sintering via solution-reprecipitation mechanism models for HPSN with  $Y_2O_3$  additions. This work has also confirmed that Y does not migrate into the grains, but remains in the grain boundary as initially hypothesized by Gazza.<sup>9</sup>

Phase equilibria studies, particularly in the  $MgO-Si_3N_4-SiO_2$  and  $Y_2O_3-Si_3N_4-SiO_2$  systems, are contributing to improved strategies for compositional optimization in silicon nitride systems. However, detailed diagrams for other systems,

35. KOMEYA, K., TSUGE, A., HASHIMOTO, H., KUBO, T., and OCHIALI, T. *Silicon Nitride Ceramics for Gas Turbine Engines*. Gas Turbine Society of Japan, Paper 65, Tokyo Joint Gas Turbine Congress, Tokyo, Japan, May 1977.
36. CLARKE, D. R., and THOMAS, G. *Grain Boundary Phases in a Hot-Pressed MgO Silicon Nitride*. ERDA Contract W-7405-ENG-48, Report LBL-6004, January 1977. In press with J. Am. Ceram. Society.
37. CLARKE, D. R., and THOMAS, G. *Microstructure of  $Y_2O_3$  Fluxed Hot-Pressed Silicon Nitride*. Lawrence Berkeley Laboratory, Report 6272. Submitted for publication with J. Am. Ceram. Society.

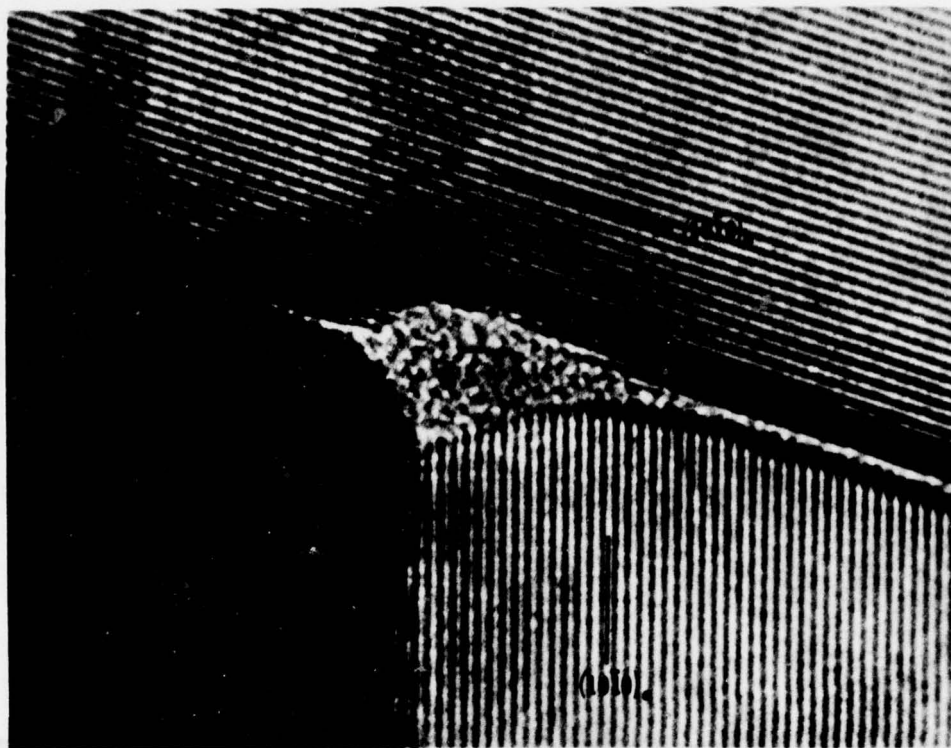


Figure 3. Grain boundary phase (A) in HPSN with MgO addition. (Reference 36)  
19-066-1539/AMC-77

i.e.,  $\text{CeO}_2\text{-Si}_3\text{N}_4\text{-SiO}_2$  or  $\text{ZrO}_2\text{-Si}_3\text{N}_4\text{-SiO}_2$  are required. Also, these systems are in reality not ternaries, but are at least quaternaries (and most probably much more complex). Therefore, there is a great need for multicomponent phase equilibria data, particularly in the  $\text{Si}_3\text{N}_4$  rich portions of the phase diagrams.

Diffusion data is critical if sintering by volume diffusion is to be attained in  $\text{Si}_3\text{N}_4$  and similar nonoxide ceramics. Such data for  $\text{Si}_3\text{N}_4$  is limited to self-diffusion studies carried out by Wuensch and Vasilos.<sup>38</sup> This is clearly an area requiring more emphasis.

The area of improved processing technology is very broad, but can be focused on those issues which would tend to make grain boundary compositional control easier to attain. Better techniques to assure uniform distribution of additives are needed. Similarly, ball milling or other mixing procedures must be designed so the "tramp" impurities are not introduced into the system. For example, when milling  $\text{MgO-Si}_3\text{N}_4$  mixtures in alumina mills one may have to deal with the system  $\text{Al}_2\text{O}_3\text{:MgO:Si}_3\text{N}_4\text{:SiO}_2$  rather than  $\text{MgO:Si}_3\text{N}_4\text{:SiO}_2$ . Similarly, if more than one additive is used, it may be preferable to pre-react or pre-mix the additives to promote homogeneities. Improved processing control will help limit the "unknown" variables.

38. WUENSCH, B. J., and VASILOS, T. *Self Diffusion in Silicon Nitride*. Final Report under ARPA Contract N00014-73-C-0212, March 1975.

### SUMMARY

The above review has demonstrated that GBE provides a useful perspective for the development of useful engineering materials, where the grain boundary properties are performance-limiting. It is also clear that while much progress in grain boundary characterization techniques has been made in the past several years, much remains to be done. It is the authors' view that future developments and materials optimization studies in the development of sintered silicon nitrides, "SiAlONs," and silicon carbides, will be significantly aided by the combination of the GBE perspective, with the "new" characterization techniques.

### ACKNOWLEDGMENT

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## LITERATURE CITED

1. KATZ, R. N. *Recent Developments in High Performance Ceramics*. Materials Technology - 1976, AIP Conf. Proc. No. 32, Am. Inst. Phys., New York, 1976.
2. KATZ, R. N., and GAZZA, G. E. *Grain Boundary Engineering and Control in Nitrogen Ceramics*. Proc. of the Conf. on Nitrogen Ceramics, Canterbury, England, 1977, Noordhoff International Publishing, Leyden, p. 417-431.
3. RICE, R. W. *Production of Transparent MgO at Moderate Temperatures and Pressures*. Am. Ceram. Soc. Bull., v. 41, 1962, p. 271.
4. ATLAS, L. M. *Effect of Some Lithium Compounds on Sintering of MgO*. J. Am. Ceram. Soc., v. 40, 1957, p. 196.
5. DEELEY, G. G., HERBERT, J. M., and MOORE, N. C. *Powder Met.*, v. 8, 1961, p. 145.
6. LUMBY, R. J., and COE, R. F. *The Influence of Some Process Variables on the Mechanical Properties of Hot-Pressed Silicon Nitride*. Proc. Brit. Ceram. Soc., v. 15, 1970, p. 91.
7. GATTI, A., MEHAN, R. L., and NOONE, M. J. Naval Air Systems Comm. Report, Contract N00019-71-C-0126, December 1971.
8. GAZZA, G. E. *Hot-Pressed Si<sub>3</sub>N<sub>4</sub>*. J. Am. Ceram. Soc., v. 56, no. 12, 1973, p. 662.
9. GAZZA, G. E. *Effect of Ytria Additions on Hot-Pressed Si<sub>3</sub>N<sub>4</sub>*. Am. Ceram. Soc. Bull., v. 54, no. 9, 1975, p. 778.
10. TSUGE, A., KUDO, H., and KOMEYA, K. *Reaction of Si<sub>3</sub>N<sub>4</sub> and Y<sub>2</sub>O<sub>3</sub> in Hot-Pressing*. J. Am. Ceram. Soc., v. 57, no. 6, 1974, p. 269.
11. COBLE, R. L. *Sintering Crystalline Solids: I. Intermediate and Final State Diffusion Models*. J. Appl. Phys., v. 32, no. 5, 1961, p. 787-799.
12. PROCHAZKA, S. *Sintering of Silicon Carbide in Ceramics for High Performance Applications*, Chapter 12, J. J. Burke, A. E. Gorum, and R. N. Katz, ed., Brook Hill Publishing Co., Chestnut Hill, Massachusetts, 1974.
13. RICE, R. W. in *Ultrafine Grain Ceramics*. Syracuse University Press, New York, 1970, p. 203.
14. HARRISON, W. B. AFML-TR-75-109, July 1975, p. 210.
15. RICHERSON, D. W. *Effect of Impurities on the High Temperature Properties of Hot-Pressed Silicon Nitride*. Am. Ceram. Soc. Bull., v. 52, no. 7, 1973, p. 560.
16. MANGALS, J. *Development of a Creep-Resistant Reaction-Sintered Si<sub>3</sub>N<sub>4</sub> in Ceramics for High Performance Applications*, Chapter 9, J. J. Burke, A. E. Gorum, and R. N. Katz, ed., Brook Hill Publishing Co., Chestnut Hill, Massachusetts, 1974.
17. LANGE, F. F. *Relation Between Strength, Fracture Energy, and Microstructure of Hot-Pressed Si<sub>3</sub>N<sub>4</sub>*. J. Am. Ceram. Soc., v. 56, no. 10, 1973, p. 518.
18. EVANS, A. G., and SHARP, J. V. *Microstructural Studies on Silicon Nitride*. J. Mat. Sci., v. 6, 1971, p. 1292.
19. WILD, S., GRIEVESON, P., JACK, K. H., and LATIMER, M. in *Special Ceramics 5*, P. Popper, ed., Brit. Ceram. Res. Assoc., 1972, p. 377.
20. DREW, P., and LEWIS, M. H. *The microstructures of Silicon Nitride Ceramics During Hot-Pressing Transformations*. J. Mat. Sci., v. 9, 1974, p. 261.
21. KOSSOWSKY, R. *The Microstructure of Hot-Pressed Silicon-Nitride*. J. Mat. Sci., v. 8, 1973, p. 1603.
22. POWELL, B. D., and DREW, P. *The Identification of a Grain-Boundary Phase in Hot-Pressed Silicon Nitride by Auger Electron Spectroscopy*. J. Mat. Sci., v. 9, 1974, p. 1867.
23. LANGE, F. F., and ISKOE, J. L. *High Temperature Strength Behavior of Hot-Pressed Si<sub>3</sub>N<sub>4</sub> and SiC: Effect of Impurities in Ceramics for High Performance Applications*, Chapter 11, J. J. Burke, A. E. Gorum, and R. N. Katz, ed., Brook Hill Publishing Co., Chestnut Hill, Massachusetts, 1974.
24. ANDERSSON, C. A., LANGE, F. F., and ISKOE, J. L. *Effect of the MgO/SiO<sub>2</sub> Ratio on the Strength of Hot-Pressed Si<sub>3</sub>N<sub>4</sub>*. Westinghouse Electric Corp., R&D Center, Contract N00014-74-C-0284, Tech. Rpt. 3, October 15, 1975.
25. RAE, A. W. J. M., THOMPSON, D. P., PIPKIN, N. J., and JACK, K. H. in *Special Ceramics 6*, P. Popper, ed., Brit. Ceram. Res. Assoc., 1976.
26. LANGE, F. F., SINGHAL, S. C., and KUZNICKI, R. C. Westinghouse Electric Corp., Contract N0014-74-C-0284, Tech. Rpt. 6, April 1976.
27. BRATTON, R. J., ANDERSSON, C. A., and LANGE, F. F. *Hot-Pressed Si<sub>3</sub>N<sub>4</sub> Developments in Ceramics for High Performance Applications II*, J. J. Burke, E. Lenoe, and R. N. Katz, ed., Brook Hill Publishing Co., Chestnut Hill, Massachusetts, 1978, p. 805.
28. BRENNAN, J. J. United Tech. Research Center Tech. Report R75-912081-2, Contract N62269-75-C-0137, September 1975.
29. TSUGE, A., NISHIDA, K., and KOMATSU, M. *Effect of Crystallizing the Grain-Boundary Glass Phase on the High-Temperature Strength of Hot-Pressed Si<sub>3</sub>N<sub>4</sub> Containing Y<sub>2</sub>O<sub>3</sub>*. J. Am. Ceram. Soc., v. 58, no. 7-8, 1975, p. 323.
30. HUSEBY, I. C., and PETZOW, G. *Influence of Various Densifying Additives on Hot-Pressed Si<sub>3</sub>N<sub>4</sub>*. Powder Met. Int., v. 6, no. 1, 1974, p. 17.
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33. RICE, R. W., and McDONOUGH, W. J. Am. Ceram. Soc. Bull., v. 54, no. 8, 1975, p. 753.
34. VASILOS, T. AVCO Corp., Lowell, Massachusetts, personal communications.
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37. CLARKE, D. R., and THOMAS, G. *Microstructure of Y<sub>2</sub>O<sub>3</sub> Fluxed Hot-Pressed Silicon Nitride*. Lawrence Berkeley Laboratory, Report 6272. Submitted for publication with J. Am. Ceram. Society.
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