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# HIGH TEMPERATURE CHEMISTRY OF FIBERS AND COMPOSITES

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CERAMICS RESEARCH BRANCH

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**ABSTRACT**

High temperature chemical reactions can decisively affect the preparation and performance of glass and ceramic fibers and composites. Fiber tensile strength can be limited by critical defects resulting from process chemistry and processing of ceramic composites made difficult, if not impossible, by unwanted high temperature reactions. In some cases, however, advantage can be taken of high temperature reactions to form in situ composites. The foregoing points are discussed and illustrated with examples from the author's research and from the literature.

## FOREWORD

This report is the text of the James I. Mueller Memorial Lecture presented at the invitation of the Engineering Ceramics Division of the American Ceramic Society at the Sixteenth Conference on Composites and Advanced Ceramics in Cocoa Beach, FL on 8 January 1992. The lecture is dedicated to the memory of our late colleague and mentor, Dr. James I. Mueller. Some of his important contributions to what has become an outstanding annual meeting are summarized below.

The first "Cocoa Beach Meeting" attended by the author was the Fourth Conference on Composites and Advanced Ceramics in 1980. At that time, what now comprises two meetings, totaling six days of concurrent sessions over two weeks, was one meeting with single sessions. The 1980 conference program totaled 47 papers including one session of four papers on ceramic matrix composites. Dr. Mueller chaired the plenary session which at the fourth meeting consisted of only three papers. At that time, meetings of the Steering Committee, presided by Dr. Mueller, were held in his hotel room as they had been since the meeting's inception. In addition to these activities, Dr. Mueller also arranged for the speaker and presided at the banquet. The foregoing are just a few examples of Dr. Mueller's contributions, both big and small, to the origins of this conference, and it is no exaggeration to say that without the efforts of Dr. James I. Mueller there would be no Cocoa Beach Meeting.

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## INTRODUCTION

The fabrication and properties of ceramic fibers and composites, as well as oxynitride glasses, are often crucially affected by high temperature chemistry. For example, the high temperature performance of carbide and nitride fibers is limited by vapor phase and crystallization processes, and oxynitride glass and glass fiber properties are critically dependent upon decomposition reactions that occur during glass melting. On the plus side, advantage can be taken of high temperature chemistry to make in situ whisker/fiber composites and to produce materials with oriented microstructures. Whatever the case, improvement of process control invariably requires better understanding of process chemistry.

This report deals with three principal topics, all more or less related to silicon nitride, a long-standing interest of the author. The topics also represent areas in which the understanding and control of high temperature chemistry is critical. The first section of the paper, on carbide fibers and whiskers with high temperature properties suitable for ceramic-matrix composites (CMCs), draws from the author's experience on the Steering Committee of the DARPA-Dow Corning program on the development of advanced SiC fibers<sup>1</sup> and from a recently completed technology assessment trip to Japan.<sup>2</sup> The second part of the paper, which discusses in situ Si<sub>3</sub>N<sub>4</sub>-based composites, ties the author's earlier work on reaction bonded Si<sub>3</sub>N<sub>4</sub> and on the kinetics of the  $\alpha/\beta$  Si<sub>3</sub>N<sub>4</sub> phase transformation to recent developments in this emerging technological area. The final part of the paper considers oxynitride glasses (the grain boundary phase in sintered Si<sub>3</sub>N<sub>4</sub>) and recent progress in improving the properties of oxynitride glass fibers, the topic of the author's current research.

## FIBERS AND WHISKERS

As indicated in the Introduction, the discussion in this section is limited to fibers and whiskers of the type that could be considered for use as reinforcements in high performance CMCs. The discussion is further limited to materials comprised principally of SiC and Si<sub>3</sub>N<sub>4</sub>, the fiber and whisker compositions of greatest current interest for CMCs. With one exception, the fibers considered herein are derived from pyrolysis of fibers spun from organic precursors. The whiskers, on the other hand, are synthesized directly from high temperature reactions involving vapor phases.

### Carbide and Nitride Fibers

Table 1 lists commercially available polymer-derived nitride and carbide fibers. The list is limited to small diameter (10  $\mu\text{m}$  to 20  $\mu\text{m}$ ), uncoated continuous fibers of the type likely to be used in CMCs. Large diameter (100  $\mu\text{m}$  or greater) filaments are unlikely to find extensive use in such composites and are, therefore, not included in this discussion. The fibers listed in Table 1 are all amorphous (or microcrystalline), nonstoichiometric, and contain significant amounts of oxygen (up to 10 wt% or more). All of the fibers are pyrolyzed to their final compositions at temperatures (1400°C or less) below which they are likely to be exposed to during ceramic processing. While glass-ceramic matrix composites have admittedly been successfully fabricated with "Nicalon" silicon carbide fibers by minimizing processing time at high temperatures,<sup>3</sup> the types of fibers listed in Table 1 are thermally unstable and generally of limited utility for the fabrication of CMCs; processing of the latter more typically requires long hold times at high temperatures.

Table 1. COMMERCIALY AVAILABLE POLYMER-DERIVED CARBIDE AND NITRIDE CERAMIC FIBERS

Fiber	Precursor	Source	Remarks
Si-C-O	"Nicaion"	PCS	Nippon Carbon Co. Contains free C, high in O, unstable above 1200°C.
Si-N-C-O	"HPZ"	HPZ	Dow Corning Corp. Amorphous, improved high temperature behavior compared to earlier fibers.
Si-N-O	"SNF"	PSZ	Tonen Corp. Amorphous, crystallizes above 1400°C.
Si-Ti-C-O	"Tyranno"	PTC	Ube Corp. Amorphous, crystallizes above 1400°C.

The high temperature instabilities of polymer-derived ceramic fibers result from several processes. The free carbon contained in carbide fibers generates thermal decomposition reactions such as the following:



Undesirable effects of such decomposition include reduction of fiber strength by formation of pores and channels, and also by formation of voids in the matrix if the latter contains a significant amount of glass.

When heated to temperatures above 1200°C, nitride fibers of the type in Table 1 are susceptible to oxygen uptake that results in substantial strength loss.

Furthermore, since all of the fibers under consideration are amorphous or poorly crystalline, heat treatment for significant times at above 1300°C or so induces crystallization. Formation of coarse crystalline grains also greatly reduces fiber strength.

In view of the above, it is evident that further development is needed to produce a continuous, polymer-derived, carbide or nitride ceramic fiber capable of retaining its properties under the rigorous fabrication conditions required for most CMCs. Ideally, the improved fiber would still be small in diameter (10 μm to 20 μm) but have enhanced high temperature stability. Required for improved fiber thermal stability are lower oxygen contents, stoichiometric chemical compositions (no excess C or O), and uniform, fine-grained crystalline microstructures.

Table 2 summarizes current activity along the guidelines suggested above on the development of carbide and nitride fibers with improved thermal stability. It is clear from Table 2 that the thermal stability problem is well recognized and receiving considerable attention as is indeed essential to progress in the development of viable fiber-reinforced CMCs.

Table 2. CARBIDE AND NITRIDE CERAMIC FIBERS UNDER DEVELOPMENT

Fiber	Precursor	Reference	Remarks
Si-C	PCS	4	Radiation cured, low O fiber. Retains strength at 1500°C.
Si-C	PCS, BSZ	5	Crystalline SiC. Excellent strength retention to 1600°C.
Si-B-N	PBSZ	6	Good high temperature strength and thermal stability.
Si-C	SiC	7	Sintered SiC. Good high temperature stability.
B-N	MAB	8	BN fiber with excellent high temperature properties.

NOTE: Glossary of Abbreviations in Tables 1 and 2; BSZ = Borosilazane; HPZ = Hydridopolysilazane; MAB = Methylaminoborazine; PBSZ = Polyborosilazane; PCS = Polycarbosilane; PSZ = Polysilazane; PTC = Polytitanocarbosilane; and SiC = Silicon carbide.

The high oxygen contents of many polymer-derived fibers stem from the air cure required to polymerize the precursor fibers. Approaches to the production of low oxygen polymer-derived fibers include changing to a radiation cure instead of an air cure,<sup>4</sup> and using precursors that pyrolyze to low oxygen compositions.<sup>5,6,8</sup> An alternative approach is to make fibers by sintering fibrous precursors of particulate, crystalline SiC.<sup>7</sup> Strength loss from fiber crystallization can be minimized by making fibers that are crystalline and stoichiometric to begin with,<sup>5,7</sup> or by the selection of compositions that resist crystallization when heated to high temperatures.<sup>6,8</sup>

While it is encouraging that the problem of high temperature instability is well recognized and the subject of active research, fiber availability is a critical consideration to fabricators of CMCs. It is unlikely that any of the fibers listed in Table 2 will be commercially available in the next several years and, in any event, the extent of application of the fibers depends upon their being readily obtainable and affordable. A key to the latter considerations is the size of the market that develops for the fibers; something difficult to estimate at present. Therefore, while it is recognized that continuous fibers will always be needed for certain applications in which highly directional properties are required, it seems worthwhile to consider alternative composite systems, and the following discusses some of those alternative concepts.

#### Carbide and Nitride Whiskers

In contrast to the situation regarding continuous fibers, crystalline, stoichiometric, SiC, and Si<sub>3</sub>N<sub>4</sub> whiskers are readily available commercially.<sup>9-11</sup> The whiskers are formed via inorganic vapor phase reactions similar to the following example for SiC:



Whiskers are typically 0.1 μm to 1.5 μm in diameter with aspect ratios (length/diameter) from 20 to 200. Additionally, the whiskers are stoichiometric and crystalline, giving them good high temperature stability. Significant problems, however, are difficulties in handling and incorporating whiskers into composites and, possibly even more important, the potential health hazards from dealing with such fine, sometimes dendritic materials. Discussed in the following section are some alternative approaches to obtaining materials with the advantages of whisker-reinforced structures but without the handling problems and health hazards associated with whiskers.

#### Si<sub>3</sub>N<sub>4</sub>-BASED IN SITU COMPOSITES

In the past few years interest has increased in alternative approaches to obtaining the benefits of composite-type microstructures without the problems of incorporation and achieving a uniform distribution of a second phase. Considered in this section are the formation of whiskers in situ in sintered or reaction bonded Si<sub>3</sub>N<sub>4</sub>, and the fabrication of sintered Si<sub>3</sub>N<sub>4</sub> with oriented microstructures. Both of these approaches have been employed successfully to produce silicon nitride materials with fracture toughnesses and strengths comparable to those of composites fabricated from physical mixtures of components.

## Whisker-Reinforced $\text{Si}_3\text{N}_4$ Materials

Figures 1 through 3, from an early study of the  $\alpha/\beta$   $\text{Si}_3\text{N}_4$  transformation,<sup>12,13</sup> illustrate an interesting phenomenon that has more recently been taken advantage of to fabricate sintered  $\text{Si}_3\text{N}_4$  materials reinforced with SiC whiskers formed in situ.<sup>14-16</sup> The SiC whiskers shown in the figures resulted from merely heating  $\text{Si}_3\text{N}_4$  powder at  $1600^\circ\text{C}$  in a graphite crucible in oxygen-contaminated  $\text{N}_2$ . As shown in Figure 3, no such whiskers appeared in  $\text{Si}_3\text{N}_4$  powder heated for 10 hours at the same temperature in oxygen-free  $\text{N}_2$ . A mechanism for the formation of SiC in  $\text{Si}_3\text{N}_4$  (without reference to whiskers) had been proposed earlier by Colquhoun, et al.,<sup>17</sup> and the chemistry of the process is illustrated in Figure 4. As shown in the figure, SiC whiskers form *via* the reaction of CO gas with the  $\text{Si}_3\text{N}_4$  powder. One likely source of CO is reaction of residual  $\text{O}_2$  in the system with the graphite crucible. Also, as suggested by Colquhoun et al., the SiO gas produced by the SiC-forming reaction can combine with C (from the crucible) to form additional CO. Considering that in the example shown the graphite crucible represents essentially an infinite sink for carbon, the reaction is self-sustaining as long as the  $\text{Si}_3\text{N}_4$  remains at temperature.

As indicated above, several laboratories<sup>14-16</sup> have reported success in forming in situ  $\text{Si}_3\text{N}_4$ -matrix composites reinforced with SiC whiskers. In the references cited, the carbon source is C powder which is mixed with  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  to form the starting material. The powder mixtures are subsequently hot pressed to obtain dense composites. Whisker contents as high as 25 wt% have been realized by heat treatment for two hours at  $1700^\circ\text{C}$ .<sup>15</sup> Song and Liu<sup>16</sup> reported a modulus of rupture of 649 MPa and fracture toughness of  $8.0 \text{ MPa}\cdot\text{m}^{1/2}$  for a hot-pressed composite containing 15 vol% SiC whiskers, both impressively high whatever the preparation method and indicative of the considerable potential of this family of materials.

Another possible but as yet unexploited approach to the fabrication of  $\text{Si}_3\text{N}_4$  composites is illustrated in Figure 5.<sup>18</sup>  $\alpha$ - $\text{Si}_3\text{N}_4$  whiskers, such as the ones evident in the figure, are often observed in the nitridation of Si powder compacts to form reaction bonded  $\text{Si}_3\text{N}_4$  (RBSN). The drops at the tips of the whiskers suggest that they formed via the VLS (Vapor-Liquid-Solid) mechanism first proposed by Wagner and Ellis<sup>19</sup> for the growth of Si whiskers.

The likely VLS mechanism that applies to  $\text{Si}_3\text{N}_4$  is illustrated in Figure 6. Scanning electron microscopy (SEM) analysis indicates that the liquid drop at the tip of the whisker is an iron silicide (Fe being a common contaminant in commercial Si powder),<sup>18</sup> and the likely source of Si in the vapor phase is SiO gas. As illustrated in Figure 6, the gaseous reactants dissolve in the liquid to precipitate  $\text{Si}_3\text{N}_4$  at the solid-liquid interface, thus providing a means of growing the extremely elongated crystals in Figure 5 and, potentially, an in situ composite type of microstructure. Figure 7 is a SEM photomicrograph of a RBSN specimen containing visible quantities of a fibrous phase and illustrating the possibility of forming a duplex  $\text{Si}_3\text{N}_4$  microstructure.<sup>20</sup> While intriguing, no evidence exists to show that such microstructures provide significant toughening, and whether or not these duplex structures can be exploited to fabricate tough composites is an open question.

## Sintered $\text{Si}_3\text{N}_4$ with Oriented Microstructures

Another interesting approach to the formation of composite-like  $\text{Si}_3\text{N}_4$  bodies is to take advantage of the propensity of  $\text{Si}_3\text{N}_4$  to form high aspect ratio grains under certain conditions. An example of the growth of high aspect ratio grains of  $\beta$ - $\text{Si}_3\text{N}_4$  from the liquid phase

is shown in Figure 8 from a study of the  $\alpha/\beta$   $\text{Si}_3\text{N}_4$  phase transformation.<sup>13</sup> That figure shows the development of elongated grains in  $\text{Si}_3\text{N}_4$  powder heated with MgO for various lengths of time at 1600°C. Figure 9 illustrates, schematically, the process through which the columnar grains formed.

While clearly different from the VLS mechanism discussed above, the solid-liquid process shown in Figure 9 produces a similar result; i.e., high aspect ratio crystals. Moreover, it is well documented in the literature on crystal growth that the aspect ratio of such crystals depends upon the chemistry of the liquid from which they are grown,<sup>21</sup> and full advantage of this behavior has been taken by Pyzik and coworkers to produce "self-reinforced  $\text{Si}_3\text{N}_4$ " with impressive properties.<sup>22-24</sup> That group has already reported the fabrication of pressure sintered  $\text{Si}_3\text{N}_4$  bodies with bend strengths of 1200 MPa and fracture toughness,  $K_{IC}$ , values of 10  $\text{MPa}\cdot\text{m}^{1/2}$  (as compared to around 5  $\text{MPa}\cdot\text{m}^{1/2}$  for material without preferred orientation). Clearly, this approach has great potential for the production of composite-like microstructures without the need for mixing separate components, and this research area is deservedly one of considerable current interest.

### OXYNITRIDE GLASSES AND GLASS FIBERS

The author's current research on oxynitride glasses<sup>25</sup> originated from interest in examining in detail the properties of the glassy grain boundary phase in sintered  $\text{Si}_3\text{N}_4$ . In view of the outstanding properties of the latter material, and considering that fracture was known to be intergranular in sintered  $\text{Si}_3\text{N}_4$ , it was felt that the grain boundary glass would be an interesting material in its own right. Furthermore, the properties and high temperature chemistry of the glass are relevant to  $\text{Si}_3\text{N}_4$  technology and, thus, a logical subject for inclusion in this paper.

#### Oxynitride Glasses

Figure 10, after Risbud,<sup>26</sup> schematically shows the structure of an oxynitride glass and illustrates why the properties of the glass are enhanced by the substitution of N for O in the glass structure. While the details require further investigation, this undoubtedly oversimplified picture shows that the substituted N is bonded to three Si atoms rather than two as is the case for O. The result is tighter structure and a glass that is harder and has an increased elastic modulus; also, the melting temperature and density increase although the increase in modulus is considerably more than would be expected from the density increase. Additional advantages of oxynitride glasses are considered elsewhere,<sup>27</sup> and it is now well established that such glasses have the potential for providing properties superior to any known oxide glasses. In accordance with the theme of this paper, however, the realization of that potential requires a better understanding and control of the high temperature chemistry of oxynitride glass systems.

A major problem with oxynitride glasses of any composition is illustrated by Figure 11 showing two large disks of Y-Si-Al-O-N glass. The glass from which both specimens originated was made in a hot isostatic press under high  $\text{N}_2$  pressure.<sup>28</sup> While one disk is obviously very clear and transparent, the other exhibits black cloudy areas. Extensive optical microscopy on various oxynitride glasses has shown that the black clouds consist of metallic inclusions similar to those apparent in the photomicrographs in Figure 12. The inclusions have been shown by SEM to be Si-rich often containing Fe when the latter is present as an impurity in the glass.<sup>29</sup> In more recent glasses with improved purity and homogeneity, the

inclusions are finer and more uniformly distributed giving the glass a uniform grey color. In addition to reducing transparency, the metallic inclusions represent strength limiting defects in the glass; the latter being particularly significant in the oxynitride glass fibers discussed below.

These colloidal, Si-rich metallic defects, while a key problem in oxynitride glasses, and possibly of significant influence in the glassy, grain boundary phase in sintered  $\text{Si}_3\text{N}_4$  as well, have received scant attention in the literature. The most significant observations on the subject were made by Kelen and Mulfinger<sup>30</sup> who, based upon their studies of the solution of N in glass, and also on earlier work by Zintl,<sup>31</sup> and by Geld and Esin,<sup>32</sup> proposed the mechanism illustrated in Figure 13 for the formation of colloidal Si precipitates in glass. Interestingly, this phenomenon has little if anything to do with the presence of N in the glass. It merely reflects the fact that the glass is produced in a highly reducing atmosphere. Under such conditions, oxygen loss from the melt results in the formation of divalent Si which appears to be stable in solution at high temperatures. As shown in Figure 13, however, when the glass is cooled the divalent Si disproportionates into tetravalent Si and elemental Si; the latter condensing as colloidal precipitate particles.

### Oxynitride Glass Fibers

The potential advantages of oxynitride glasses over conventional oxide glasses have led to interest by the U.S. Army in the possible use of oxynitride glass fibers in high performance composites. A potential application of such composites, a hull for an infantry fighting vehicle, is illustrated in Figure 14. An oxide glass fiber/resin matrix composite has already been successfully tested for that application, and oxynitride glass fibers could provide some of the additional advantages indicated in the figure. While impressively high elastic modulus values have been achieved for oxynitride glass fibers,<sup>25</sup> tensile strengths thus far obtained are unacceptably low for the type of composite shown in Figure 14. The key to improvement in fiber tensile strength is better understanding and control of the high temperature chemistry of glass, and fiber processing and recent progress along those lines is summarized below.

The apparatus employed for making oxynitride glass fibers at the U.S. Army Materials Technology Laboratory (MTL) is shown in Figure 15.<sup>33</sup> Recent efforts have been concentrated on making fibers from glasses in the system Mg-Si-Al-O-N. Glass compositions are similar to "S" glass (an Al-Mg-Si oxide) with 3 atomic % to 4 atomic % N substituted for some of the oxygen. Fibers are drawn from premelted glass contained in the molybdenum crucibles. The crucibles are inductively heated in  $\text{N}_2$  to the drawing temperature of around  $1550^\circ\text{C}$ ; the exact temperature depending upon glass composition. Fibers as small as  $8\ \mu\text{m}$  to  $10\ \mu\text{m}$  in diameter have been drawn at rates as high as 1500 m/min. The elastic moduli of the fibers range from 105 GPa to 110 GPa as compared to 85 GPa for "S" glass which is the highest performance commercially available oxide glass fiber.<sup>34</sup>

As mentioned above, progress in improving the tensile strength of our oxynitride glass fibers has come mainly through understanding of process chemistry. Before process improvements, the fibers often failed from internal defects, one of which is shown in Figure 16. This fiber failed from a  $\mu\text{m}$ -sized inclusion identified by SEM as iron silicide. This type of defect, similar to the inclusions seen in Figure 12 and worsened by the presence of Fe impurities, was eliminated, and tensile strength consequently improved, by eliminating Fe contamination in the glass batch.

Although some earlier evidence indicated that glass quality was improved by batching with AlN rather than Si<sub>3</sub>N<sub>4</sub>, Figure 17 shows a fiber failure from an inclusion rich in Al. The latter probably came from unreacted Al in the AlN powder used to formulate the glass batch. This example, as well as the foregoing one about Fe, illustrates another consequence of melting the glass in a reducing atmosphere; the impurities remain metallic rather than being oxidized to metal ions as would be the case for melting in air.

Increases in oxynitride glass fiber strength from research on improved glass and fiber processing are summarized in Figure 18.<sup>33</sup> The data shown are for work over a period of about two years on fibers of the same Mg-Si-Al-O-N glass composition. The tensile strength increases are mostly attributable to improved process chemistry. Steps found to be particularly important include: (1) The elimination of undesirable impurities, specifically Fe and metallic Al, (2) Premelting of the oxide part of the glass in air before adding Si<sub>3</sub>N<sub>4</sub> and melting in N<sub>2</sub>, and (3) Double melting of the glass to improve homogeneity. The results shown in Figure 18 were admittedly obtained only for the purpose of improving our oxynitride glass fibers. It is not unreasonable, however, to speculate that similar considerations apply to the glassy grain boundary phase in sintered Si<sub>3</sub>N<sub>4</sub>. Along the same lines, it could be further argued that the properties of sintered Si<sub>3</sub>N<sub>4</sub> could benefit from better control of the high temperature chemistry of the glass phase.

### CONCLUSIONS

High temperature chemistry plays a crucial role in the processing and performance of Si<sub>3</sub>N<sub>4</sub> and related materials. While high temperature reactions can produce problems such as critical defects in oxynitride glasses and fibers, they can also provide opportunities such as in the formation of Si<sub>3</sub>N<sub>4</sub> composites containing in situ SiC whisker reinforcements. In any event, understanding and control of high temperature chemistry is essential to the fabrication of high performance composites and engineering ceramics.

### ACKNOWLEDGMENTS

This report would have been impossible without the help of my coworkers over the years, most of whom are cited in the references, and to all of whom I am deeply grateful. A special thanks is due to the Engineering Ceramics Division of the American Ceramic Society for inviting me to present the Mueller Lecture, and with whom I have had a long and rewarding association.

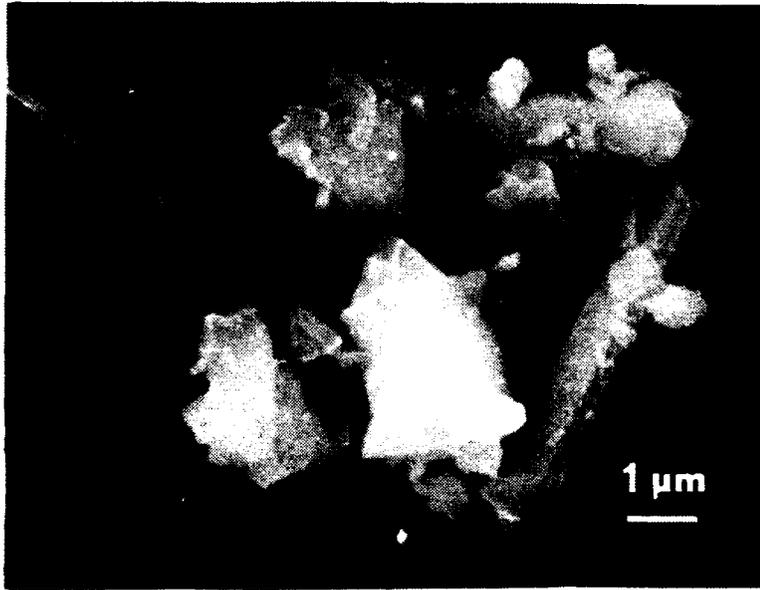


Figure 1. 99% pure  $\alpha$ -silicon nitride powder as-received, scanning electron photomicrograph, Ref. 13.

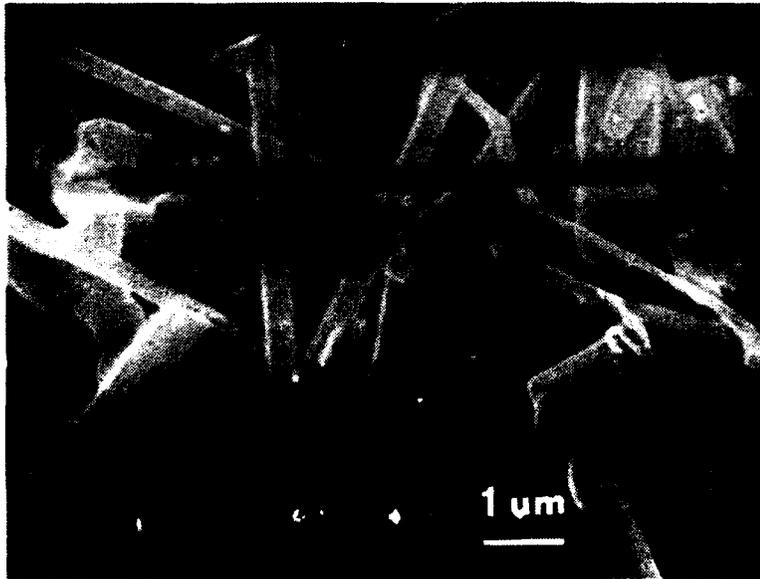
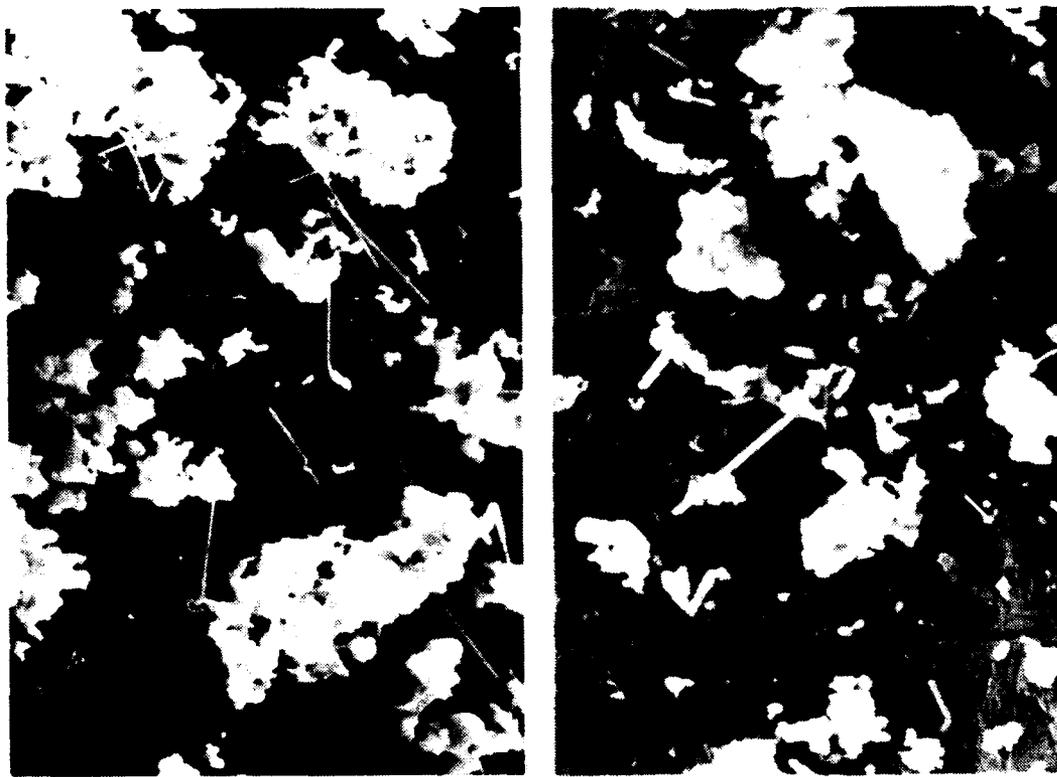


Figure 2. Silicon carbide whiskers in silicon nitride powder after heat treatment at 1600°C in nitrogen contaminated with oxygen, scanning electron photomicrograph, Ref. 13.

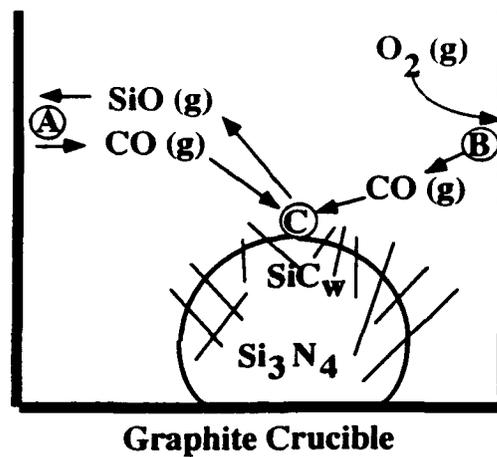


(a)

5  $\mu$ m

(b)

Figure 3. (a) Silicon carbide whiskers in silicon nitride powder heated for four hours at 1600°C in nitrogen contaminated with oxygen, and (b) silicon nitride powder heated without additives for 10 hours at 1600°C in pure nitrogen, scanning electron photomicrographs, Ref. 12.



- Ⓐ  $\text{SiO (g)} + 2 \text{C (s)} = \text{CO (g)} + \text{SiC (g)}$
- Ⓑ  $\text{O}_2 \text{(g)} + 2 \text{C (s)} = 2 \text{CO (g)}$
- Ⓒ  $3 \text{CO (g)} + \text{Si}_3\text{N}_4 \text{(s)} = 2 \text{SiC}_w \text{(s)} + 2 \text{N}_2 \text{(g)} + \text{CO}_2 \text{(g)} + \text{SiO (g)}$

Figure 4. Mechanism for silicon carbide formation in a silicon nitride powder compact.



Figure 5.  $\alpha$ -silicon nitride whiskers formed during reaction bonding of a silicon powder compact. The drops at the tips of the whiskers suggest that growth occurred by a VLS mechanism, optical photomicrograph, transmitted light, Ref. 18.

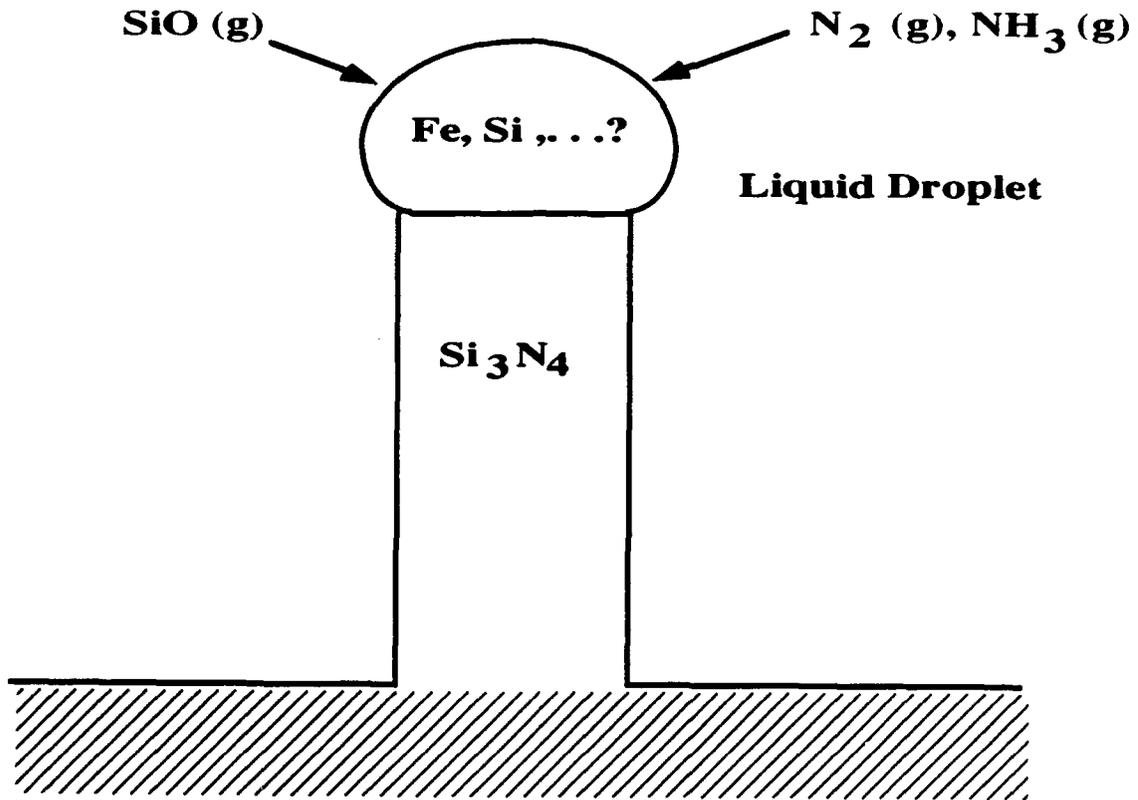


Figure 6. Growth of  $\alpha$ -silicon nitride whiskers by the VLS mechanism.

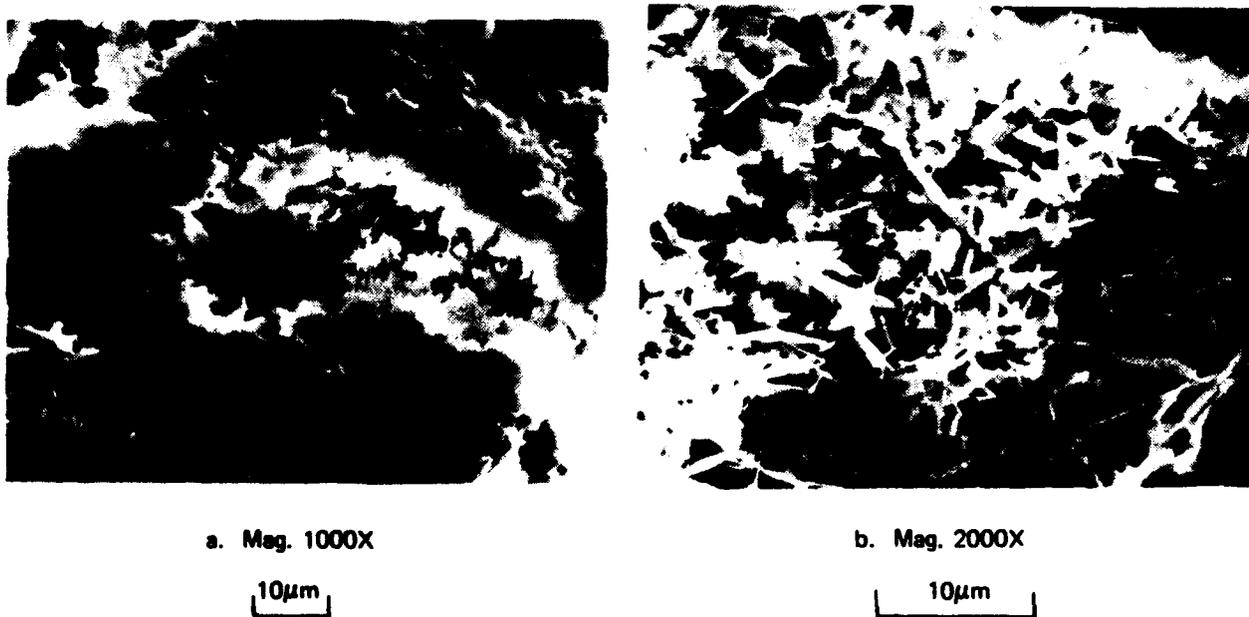


Figure 7. Fracture section of a reaction bonded silicon nitride specimen showing extensive whisker formation in voids, scanning electron photomicrographs, Ref. 20.



Figure 8. Silicon nitride powder containing 10 wt% magnesia at various stages of the  $\alpha$  to  $\beta$  transformation after heat treatment at 1600°C. (a) and (b): 0.5 hour, 47 wt%  $\beta$ . (c) and (d): 1.0 hour, 64 wt%  $\beta$ . (e) and (f): 4.0 hour, 100%  $\beta$ , scanning electron photomicrographs, Ref. 13.

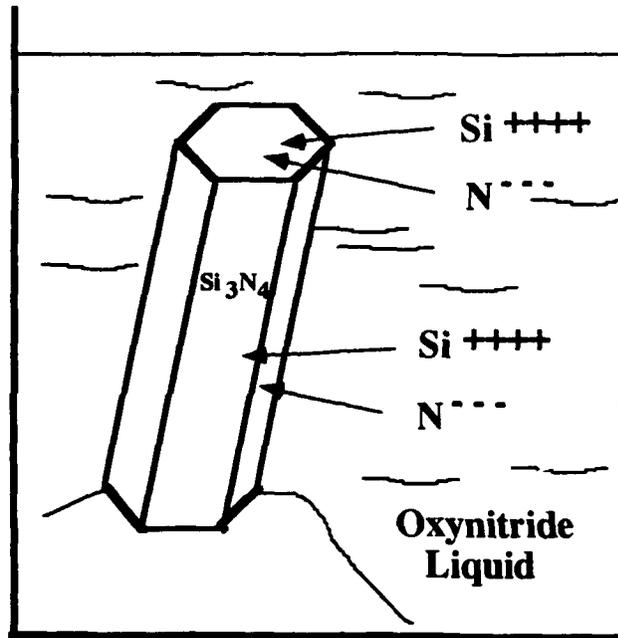


Figure 9. Growth of high aspect ratio  $\beta$  silicon nitride crystals from the liquid. The aspect ratio depends upon the chemistry of the liquid.

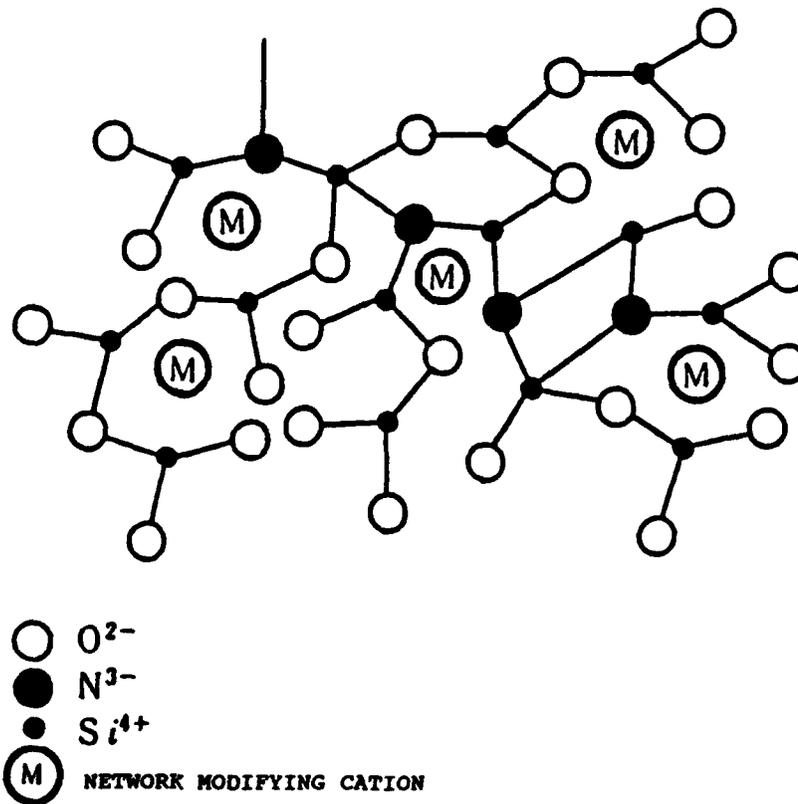
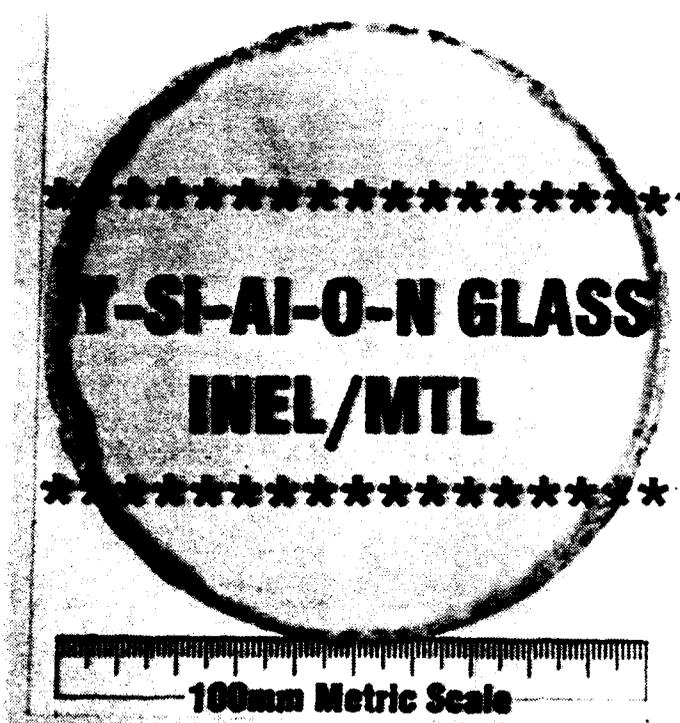


Figure 10. Schematic two-dimensional view of the network structure of oxynitride glasses based on metal-silicon-oxygen systems, Ref. 26.



(a)



(b)

Figure 11. Y-SI-AL-O-N Glass disks, 100 mm diameter x 10 mm thick. The black, cloudy regions in (b) stem from metallic inclusions (the glass was made under high nitrogen pressure by Ref. 28).

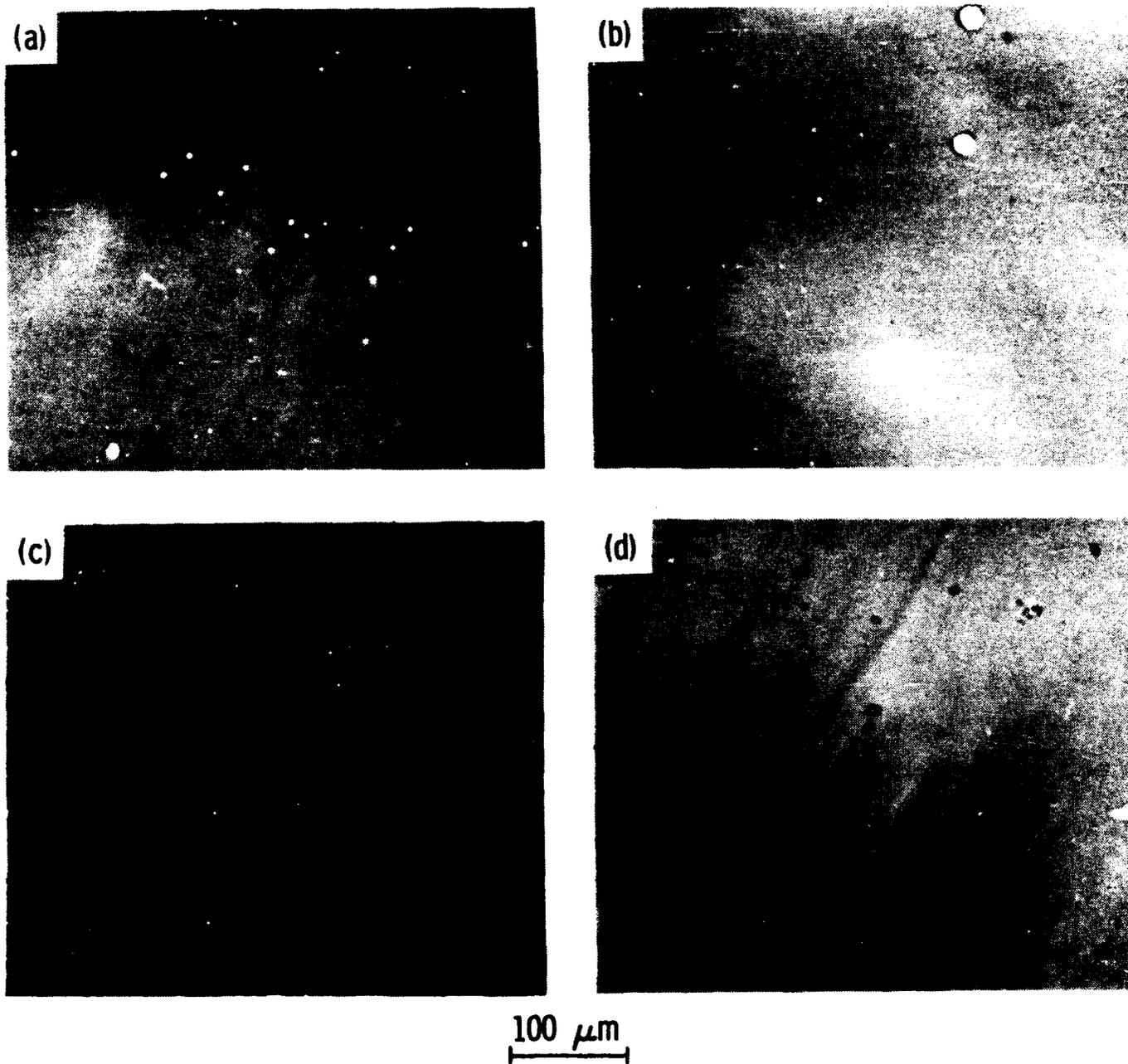
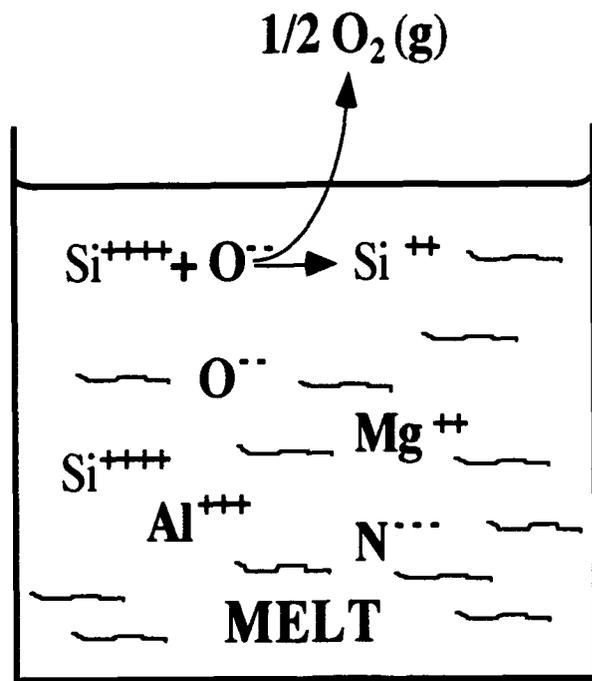
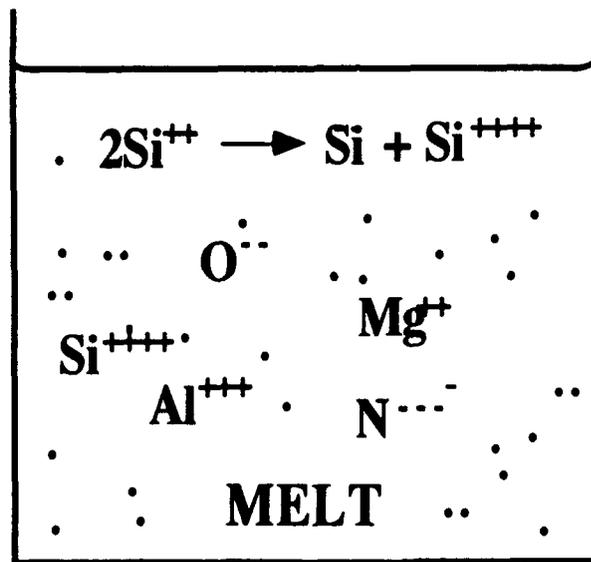


Figure 12. Photomicrographs of polished sections of Y-Si-Al-O-N glass specimens prepared under various conditions: (a) with low purity silicon nitride, (b) with high purity silicon nitride, (c) with low purity silicon nitride at high nitrogen pressure, and (d) with aluminum nitride. The bright spots appearing to some extent or another in all of the specimens represent silicon-rich metallic inclusions, optical photomicrographs, Ref. 29.



(a) Heating



(b) Cooling

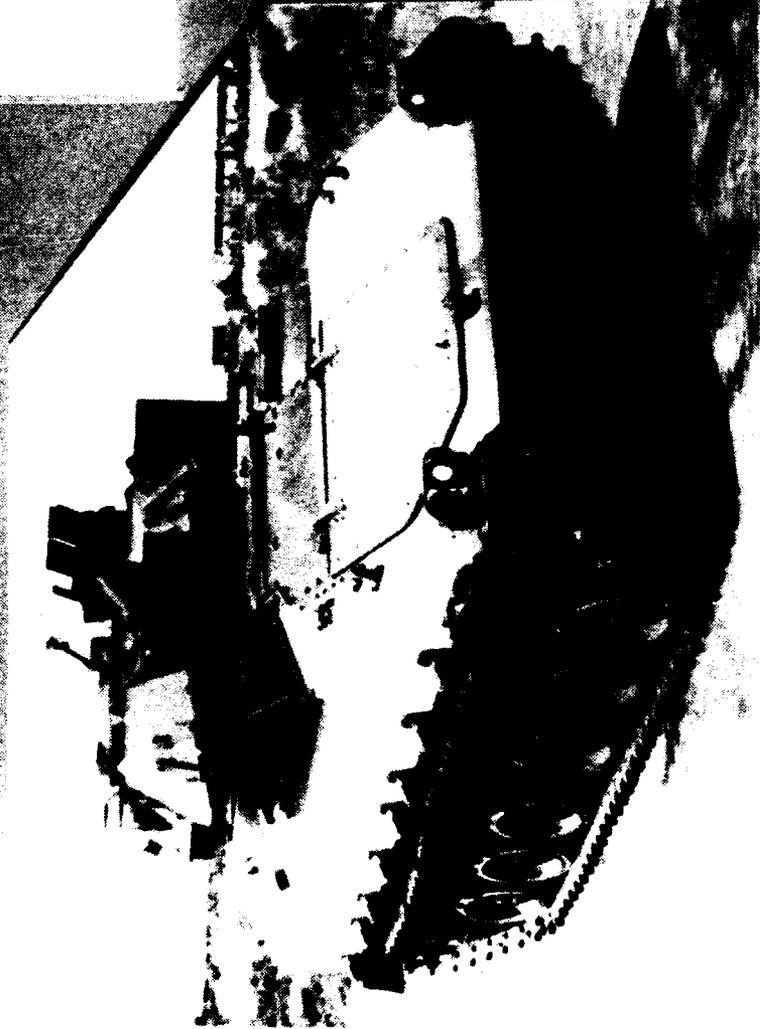
Figure 13. Mechanism for the formation of metallic precipitates in oxynitride glass; after Ref. 30 through Ref. 32.

# OXYNITRIDE GLASS FIBERS

## ARMY REQUIREMENT:

• IMPROVED COMPOSITE ARMOR  
FOR FIGHTING VEHICLES

- SUPERIOR TO OXIDE GLASSES
- HIGH ELASTIC MODULUS
- HIGH STRENGTH
- EXCELLENT CORROSION RESISTANCE
- INCREASED PERFORMANCE/  
REDUCED WEIGHT



COMPOSITE IFV HULL TECHNOLOGY DEMONSTRATOR

MODULUS/DENSITY FOR SIMILAR GLASSES  
WITH AND WITHOUT NITROGEN

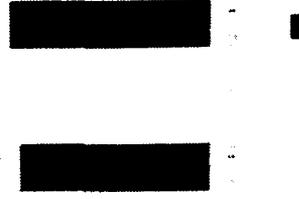


Figure 14. Potential U.S. Army application for oxynitride glass fibers.

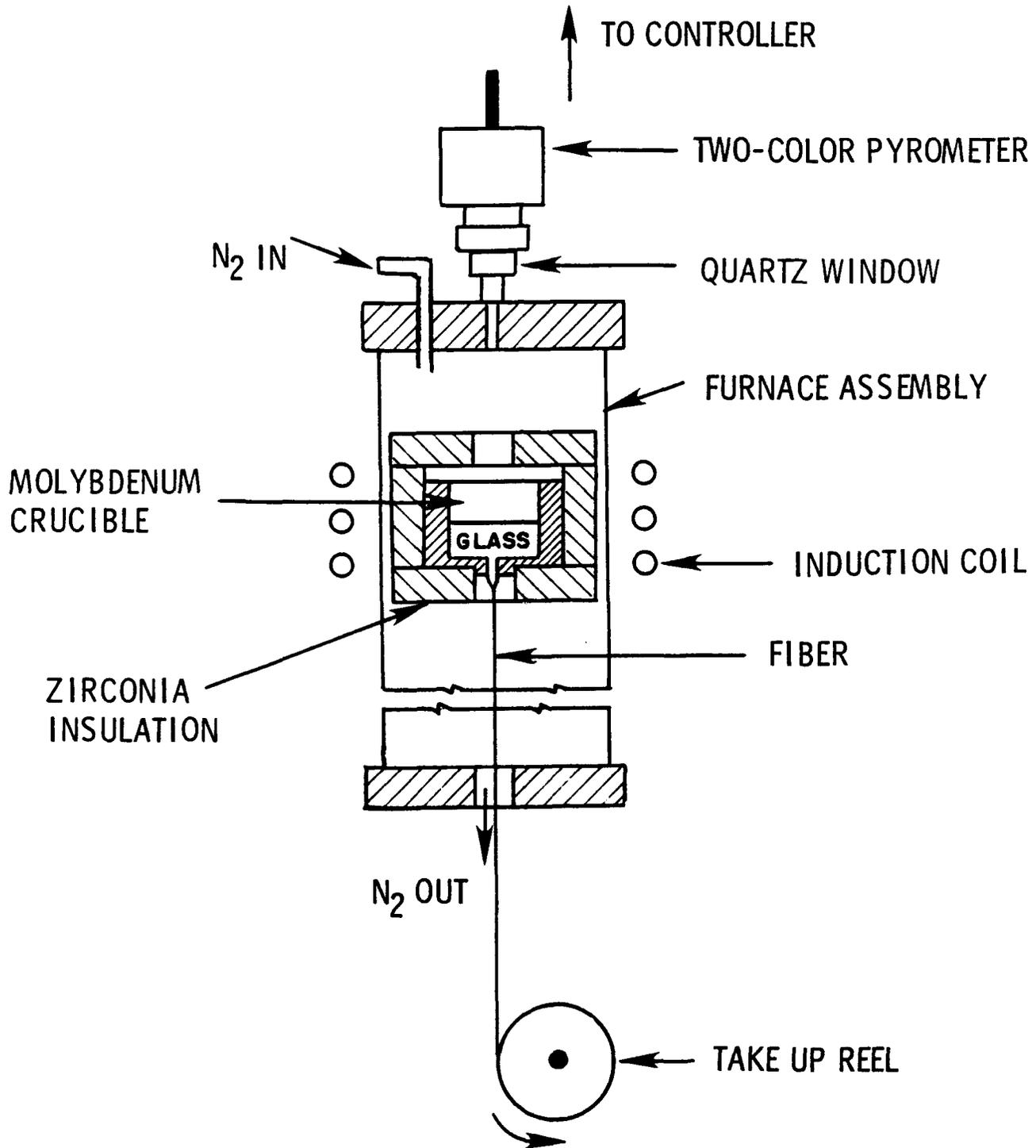


Figure 15. Schematic representation of the system employed for drawing oxynitride glass fibers, Ref. 33.

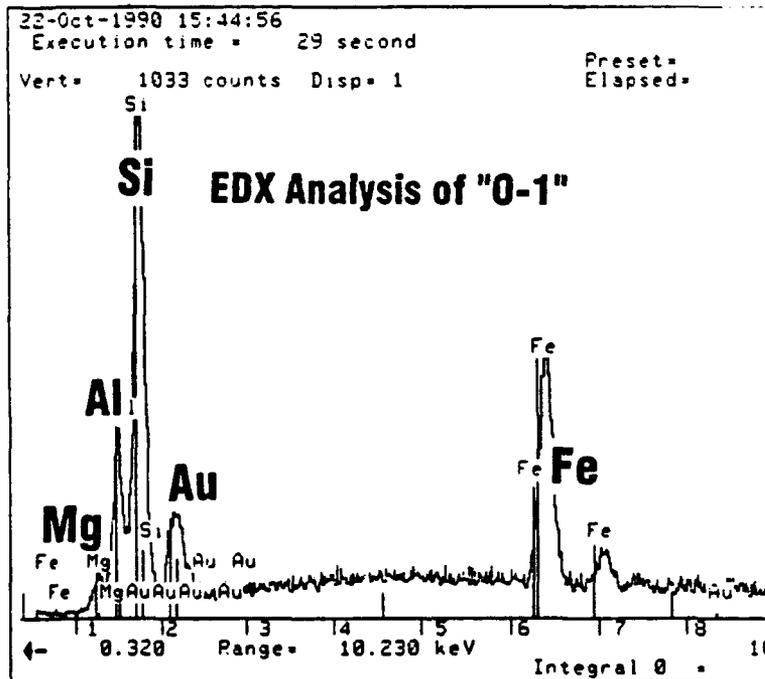
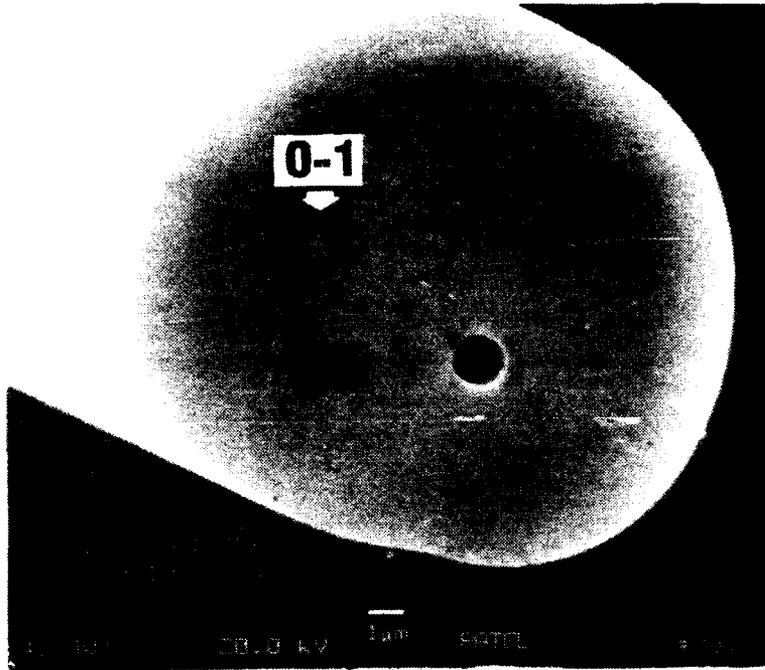


Figure 16. Mg-Si-Al-O-N fiber fracture surface showing a critical defect high in iron. It was later found that this and similar defects came from contamination in the acetone used to wet mix the batch. Axial voids such as the one clearly evident were sometimes observed; the voids are not strength-limiting, scanning electron photomicrograph, Messier and Patel, unpublished work.

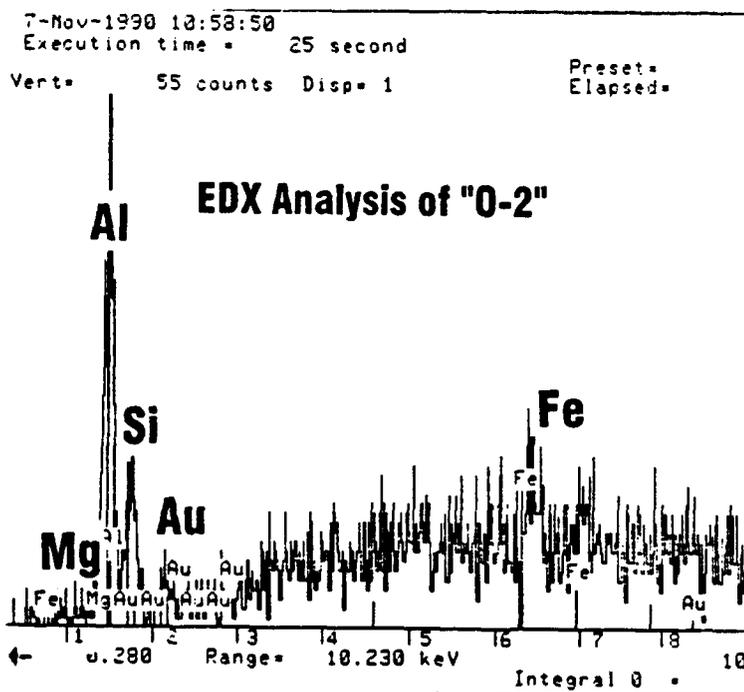
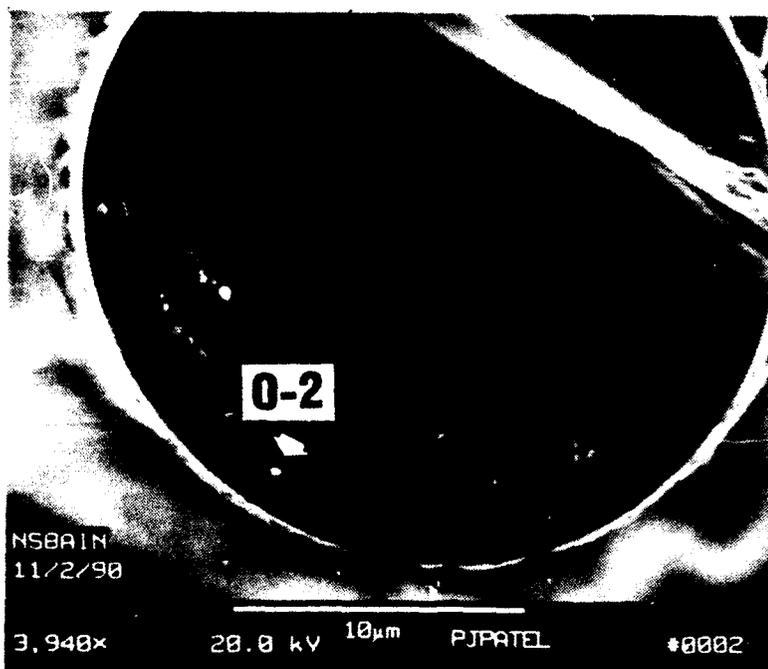


Figure 17. Mg-Si-Al-O-N fiber fracture surface showing a critical defect rich in aluminum believed to be from unreacted metal in the aluminum nitride used as a batch component, scanning electron photomicrograph, Messier and Patel, unpublished work.

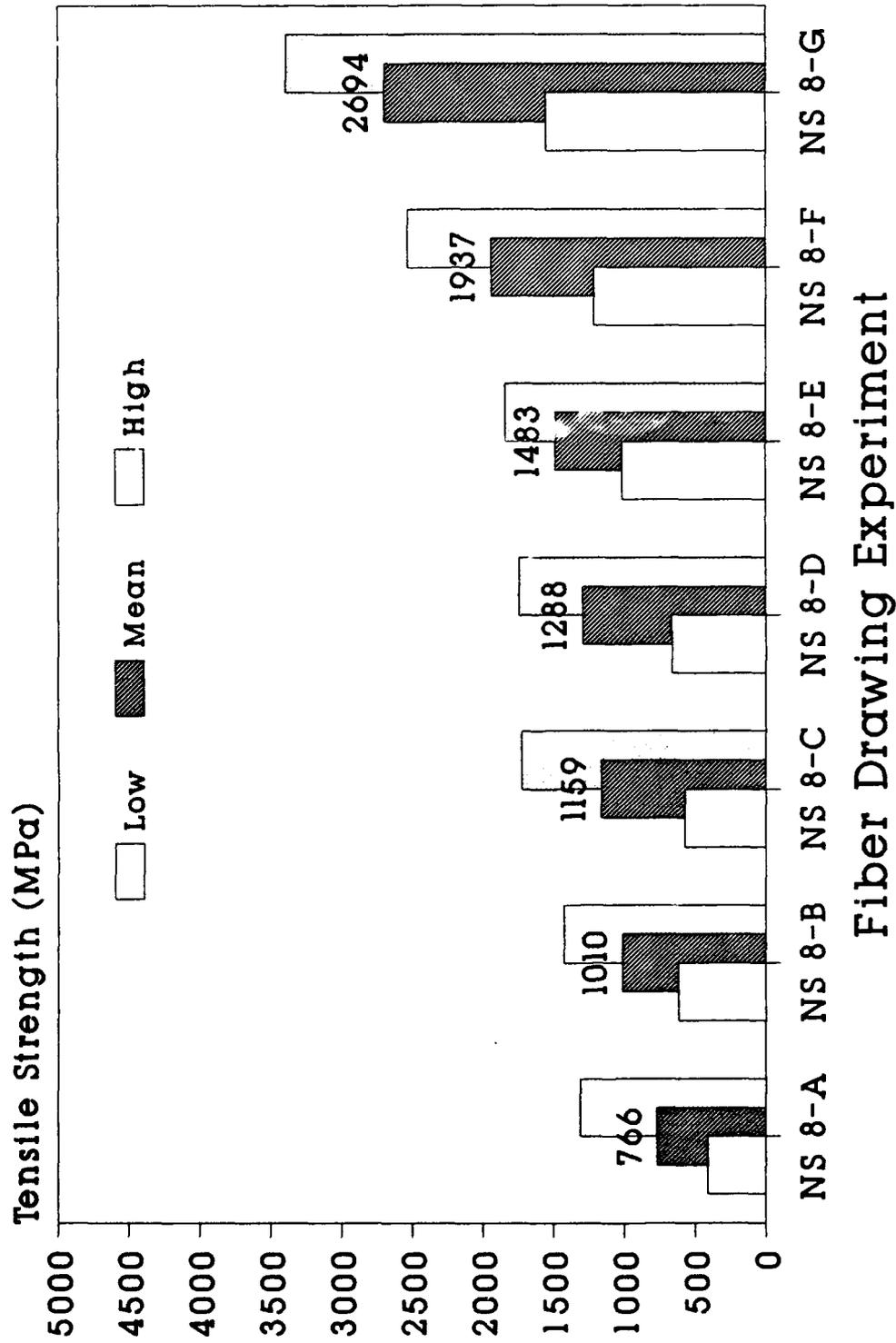


Figure 18. Tensile strength increases resulting from processing improvements. All data are for Mg-Si-Al-O-N fibers of the same nominal composition, Ref. 33.

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HIGH TEMPERATURE CHEMISTRY OF FIBERS  
AND COMPOSITES-  
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High temperature chemical reactions can decisively affect the preparation and performance of glass and ceramic fibers and composites. Fiber tensile strength can be limited by critical defects resulting from process chemistry and processing of ceramic composites made difficult, if not impossible, by unwanted high temperature reactions. In some cases, however, advantage can be taken of high temperature reactions to form *in situ* composites. The foregoing points are discussed and illustrated with examples from the author's research and from the literature.