

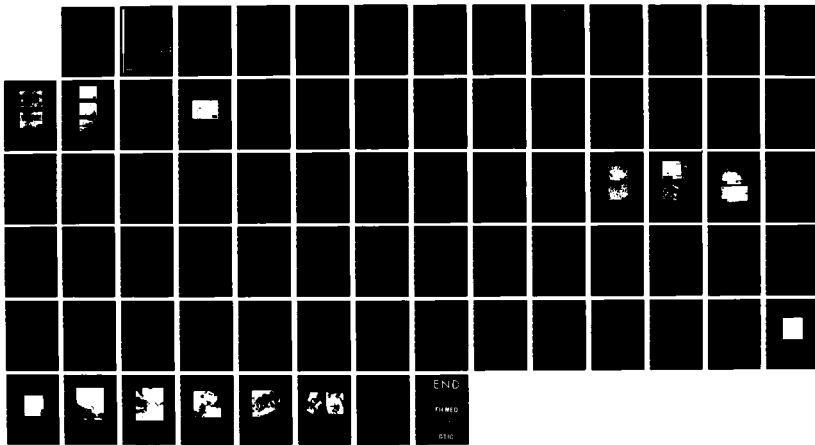
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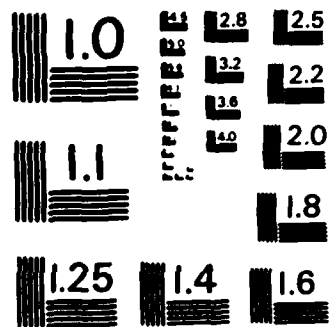
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SILICON NITRIDE JOINING

AD-A162 337

Final Report

October, 1985

By Sylvia M. Johnson and David J. Rowcliffe

Prepared for:

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
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Bolling Air Force Base, DC 20322

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Program Manager
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The results obtained during the investigation of a method of joining silicon nitride with an oxide glass are described. Joining methods for silicon nitride to ceramics and metals are reviewed in Appendix A. Chemical interactions between Si ³ N ⁴ and glass are described in Appendix B. Both hot-pressed and a hot-isostatically pressed Si ³ N ⁴ were used for joining experiments. The vaporization behavior of the materials as determined by mass spectrometry is described. A new method of joining Si ³ N ⁴ which uses very little glass and which has potential for producing joined pieces which retain their strength to high temperatures was developed and preliminary results are presented.			
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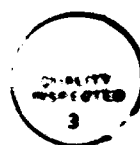
The project leader was David J. Rowcliffe. Sylvia M. Johnson performed the evaluation of the mechanical behavior and high temperature behavior of joined samples. Mass spectrometry experiments were conducted by Robert D. Brittain, and thermodynamic calculations were performed by Robert H. Lamoreaux. The project leader for the early part of this program was Ronald E. Loehman, now of Sandia National Laboratories, Albuquerque, New Mexico. Transmission electron microscopy was performed by Martha L. Mecartney under the supervision of Robert Sinclair at Stanford University.

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Norton Company kindly supplied the experimental grade of hot isostatically pressed Si_3N_4 (3I-004).

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SUMMARY

A method for joining Si_3N_4 which uses an oxide glass has been studied and the results of the program are summarized in this report. The method is simple, requires no applied pressure, and is based on the reaction between Si_3N_4 and the glass. The mechanical behavior of joined samples has been described, as has the vaporization behavior of the joints and materials. The maximum strength at room temperature achieved with the joining method is 460 MPa. At high temperatures, $> 1000^\circ\text{C}$, the joints degrade due to continuing interactions between the glass and the Si_3N_4 . The vaporization and mass transport effects observed in the materials and joints have implications for processing and material behavior in both oxidizing and reducing conditions at high temperatures. A new method of joining which uses little or no glass phase is also described.

INTRODUCTION

The wide variety of uses of structural ceramics ranges from low temperature, wear resistant parts, through high temperature moderate stress components for heat exchangers to high stress, high temperature components in advanced heat engines. Joining technology, whether for mechanical attachment or permanent chemical joints, is required for most applications. However, the technology is not well developed for both ceramic/ceramic and ceramic/metal joints suitable for use in high stress, high temperature and possibly corrosive environments. In particular, few methods are available for joining Si_3N_4 , a material that is under consideration for many of the most demanding applications. Joining methods for Si_3N_4 are reviewed in Appendix A.¹

Under AFOSR sponsorship, SRI has been developing and investigating a method of joining Si_3N_4 for the last four years. The method involves the reaction of an oxide glass layer with Si_3N_4 to form a strong joint. One of the major advantages of this method is its simplicity in that only two steps and no applied pressure are required.

Work performed in the first three years of this program was described in previous annual reports.²⁻⁴ The present report focuses on the work performed during the fourth year and also summarizes the main findings of the whole program.

TECHNICAL PROGRESS

Dense silicon nitride materials made by sintering, hot-pressing, or hot isostatic pressing contain a glassy phase at the grain boundaries that is formed from sintering aids such as MgO, Y₂O₃, Al₂O₃, and SiO₂ necessary for densification and from dissolution of Si₃N₄ in the glass. The joining method described here is based on the reaction between Si₃N₄ and an oxide glass similar to the grain boundary phase.

A number of hot pressed silicon nitrides were used in this study, although most experiments were performed on NC132,* which contains MgO as a densification aid. Other silicon nitrides tested included an Y₂O₃-doped hot pressed material (NCX34)* and an Y₂O₃-doped HIPped Si₃N₄(3X-004), 4% Y₂O₃.* The glass compositions are given in Table 1.

The development of the steps to form a strong joint have been described previously.²⁻⁴ The method consists of polishing the ends of two 2.5 by 1.25 by 0.3 cm slabs of Si₃N₄, glazing one piece with a thin layer of the desired glass, and then placing the glazed piece above the unglazed piece and heating for times of 30 to 60 minutes at temperatures

Table 1
NOMINAL COMPOSITION OF JOINING GLASSES

	<u>Nominal Composition (wt%)</u>			
	<u>MgO</u>	<u>SiO₂</u>	<u>AlO₃</u>	<u>Y₂O₃</u>
MgO glass (HN-9M)	35	55	10	
Y ₂ O ₃ glass (SG-14-0)		34	20	46

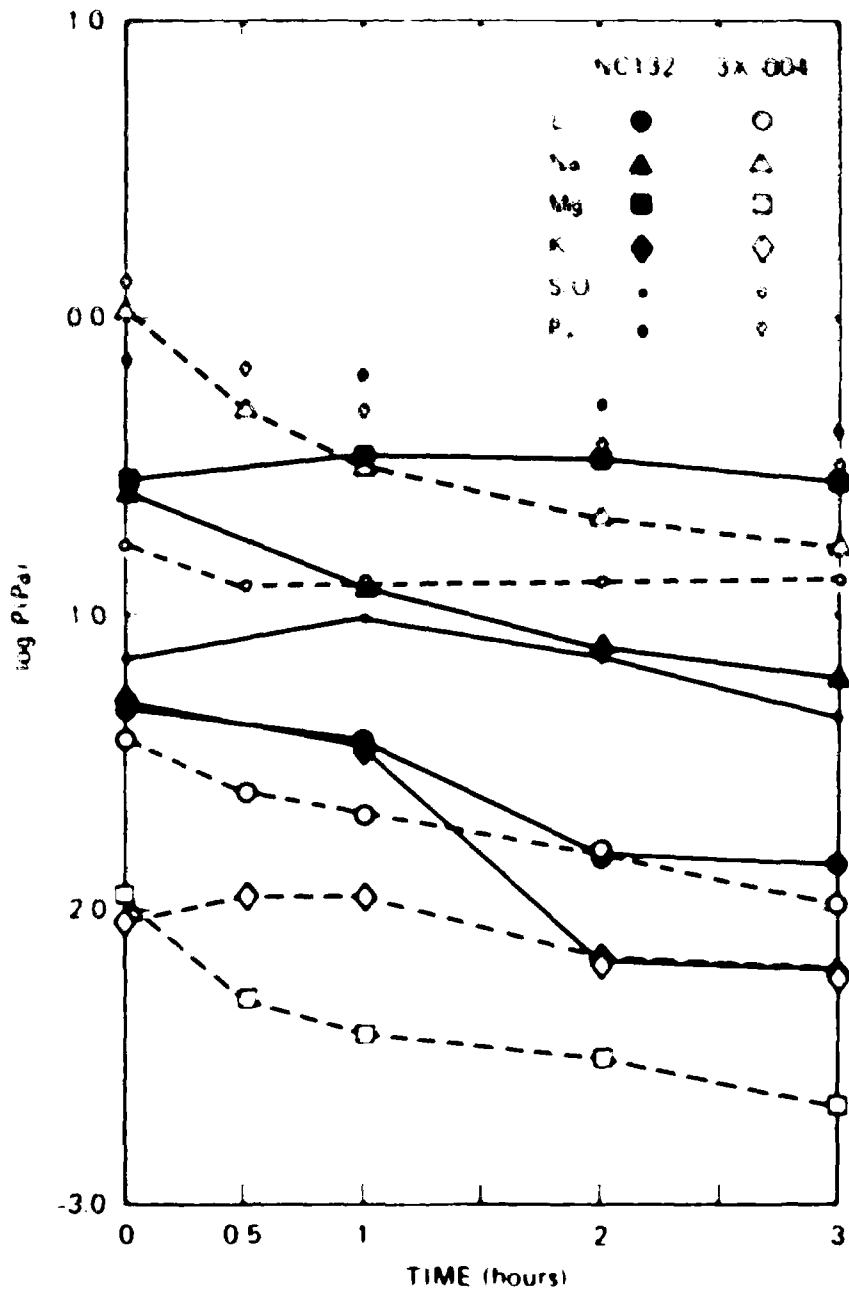
*Norton Company, Worcester, MA.

between 1575°C and 1650°C in ~2 atm of N₂. The strength of the joints appears to be independent of the exact time and temperature within this range.³

The strength at room temperature of the joined bars was found to be dependent on the thickness of the joint formed,³⁻⁵ with a maximum strength of ~460 MPa for joints of 20-30 μm. Thinner joints were often incomplete because of bubble formation during glazing or vaporization during joining. Vaporization of species such as SiO and Mg from both the glass and the material occurs during joining, during crystallization heat treatments, and while the samples are being tested at elevated temperatures. The vaporization behavior of Si₃N₄/glass combinations has been described previously.⁴⁻⁶

The strength at high temperatures of joined bars is adversely affected by vaporization and mass transport of impurity species from the Si₃N₄ to the joint. Mass transport causes expansion of the joint, and vaporization of the volatile species results in the formation of a porous joint. The vaporization behavior of all the materials used in this study was determined by mass spectrometry. The partial pressures of the major vapor species as a function of time are compared for a hot-pressed and a HIPped material in Figure 1. The major species are Mg, Na, K, and Li, all present as metallic species, and SiO. (P_T represents the total pressure.) Note that the HIP material is an experimental material that has not been developed as far as other commercial grades. Thus, it is still high in alkali impurities such as Na, Li, and K. The total vapor pressures of the two materials are approximately equal, although NCl32 contains MgO, which is present at a much higher level in the vapor above NCl32 than in the vapor above 3X-004.

A number of the materials were also heat-treated at 1100°C in 6.7 atm of N₂ for 2.75 and 10 hours. The surfaces of the materials were diamond-polished to 1 μm before the heat treatment. The results of similar heat treatments on some silicon nitrides have been previously described.⁴ The effects of the short-term heat treatments on the HIPped



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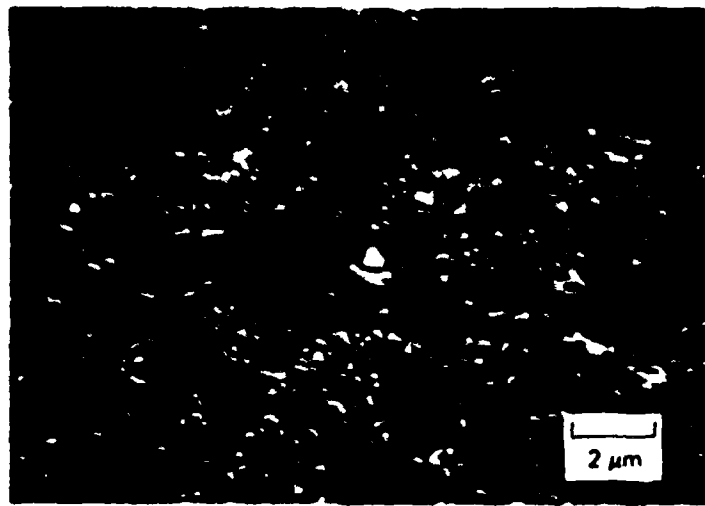
FIGURE 1 PARTIAL PRESSURE OF VAPORIZING SPECIES AS A FUNCTION OF TIME

and hot-pressed material are compared in Figure 2. The effects of the long-term heat treatments on NCl32, NCX34, and 3X-004 are shown in Figure 3. The small surface features on NCl32 contain Mg and Si, as determined by EDAX, whereas the larger features contain W, Fe, Si, and some Co. These large particles result from milling and were observed on the surfaces of all samples, including the HIP material. In general, there is much less mass transport from the HIP material, although after 10 hours there is evidence of a glassy phase on the surface and some roughening of the surface. Clusters of small particles that contain Si and Y are apparent at the grain boundaries and three grain junctions in NCX34. The surface features on NCl32 are larger and contain Mg and Si (as determined by EDAX).

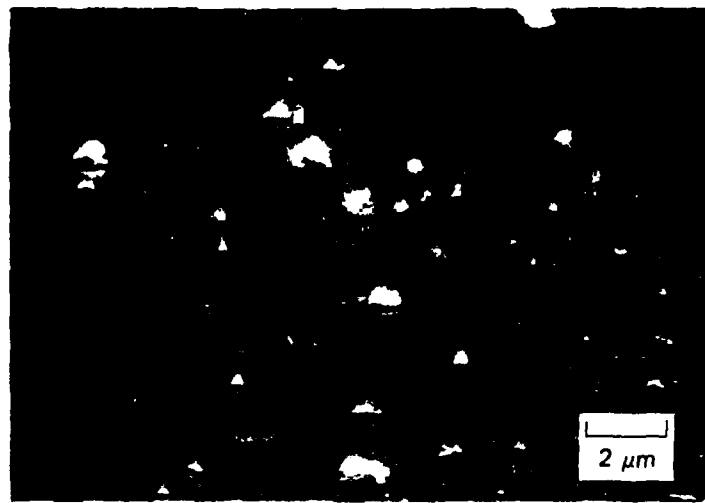
The dependence of strength on joint thickness indicated that a method of reliably controlling the joint thickness was required. Grooves 25 or 50 μm deep were cut into the end of the piece to be glazed. The grooves were cut across the end so as to leave a small raised piece on either end. The glazing on grooved pieces was very even, and it was possible to make joints of a controlled thickness in this way.

A series of bend tests were performed at temperatures up to 1000°C in air. The series of joints tested did not have the optimum thickness and were not made under the optimum conditions. However, the bend tests indicated that the strength was fairly constant up to $\sim 800^\circ\text{C}$. Most samples tested at 1000°C or above broke under small preloads during equilibration of the furnace. Examination of the fracture surfaces indicated that extensive vaporization of the glass from the joint was occurring above 800°C.

A new method of joining to alleviate the problems associated with vaporization and mass transport was investigated. This method uses either no or little added glass, with the expectation that the joints will be more stable at high temperatures. The new concept for joining involves depositing a layer of α or amorphous Si_3N_4 onto an untreated, lightly oxidized or thinly glazed piece of Si_3N_4 and then joining this



(a) Hot Pressed Si_3N_4 (NC132)

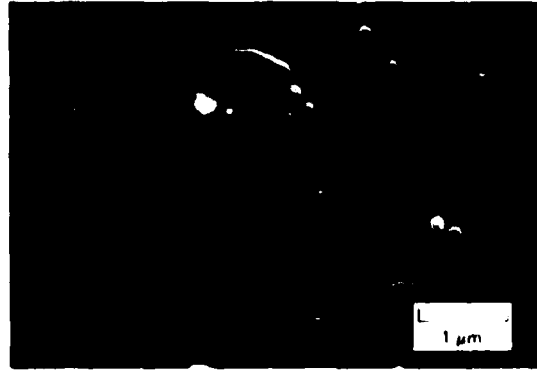


(b) HIPped Si_3N_4 (3X-004)

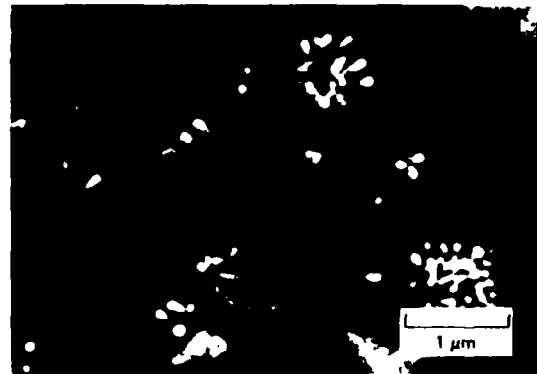
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FIGURE 2 EFFECTS OF HEAT TREATMENT ON HOT PRESSED AND HIPped Si_3N_4

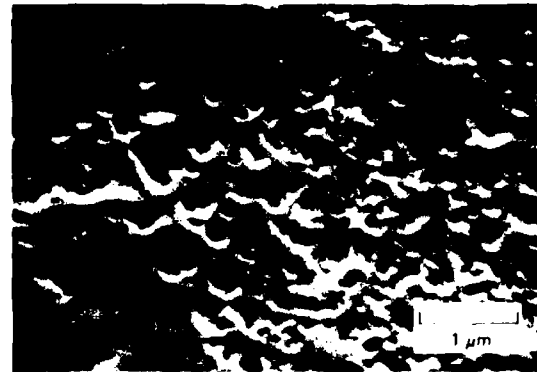
Samples were exposed for 2.8 hours at 1100°C in 6.7 atm of N_2 .



(a) Hot-Pressed Si_3N_4 containing MgO (NC132)



(b) Hot-Pressed Si_3N_4 containing Y_2O_3 and Al_2O_3 (NCX34)



(c) HIPped Si_3N_4 containing Y_2O_3 (3X-004)

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FIGURE 3 EFFECTS OF HEAT TREATMENT ON VARIOUS SILICON NITRIDES

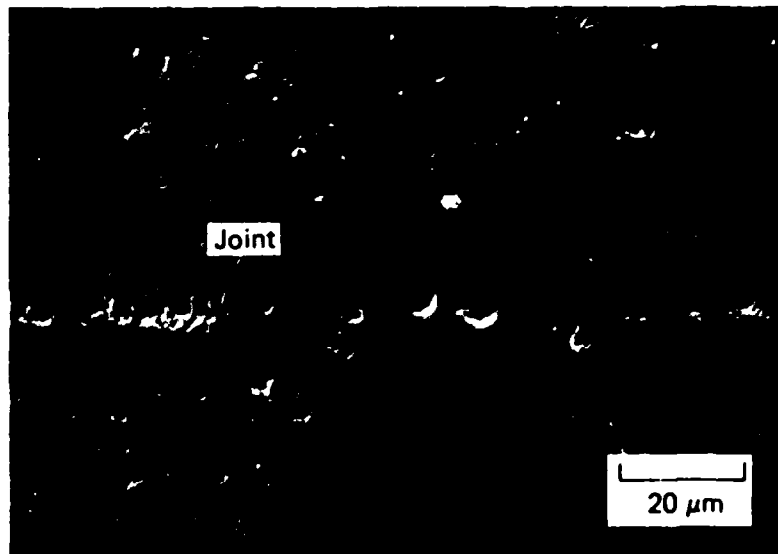
Samples were exposed for 10 hours at 1100°C in 6.7 atm of N_2 .

piece to another which may be untreated or have a thin oxide layer. The method is based on sintering Si_3N_4 , where $\alpha\text{-Si}_3\text{N}_4$ sinters by a process of transforming to the β -phase in the presence of oxide additives. It is important that the deposited Si_3N_4 layer be α or amorphous phase because $\beta\text{-Si}_3\text{N}_4$ will not sinter.

The method has not been fully investigated, and only room temperature strengths have been determined. Various combinations of oxide layers and coatings were used to produce joints. Samples were oxidized for 1 hour and 3 hours at 1395°C in air to produce oxide layers. The calculated thickness of the oxide layer on a sample oxidized for 3 hours is $\sim 10 \mu\text{m}$.⁷ Some samples were glazed with HN-9M glass as in the original method. Most of the glass was ground off in this case to leave only a very thin oxide layer. Silicon nitride was deposited on the samples by chemical vapor deposition.* Silicon nitride layers 8-10 μm thick were deposited on the first samples. Some of these samples partially joined, but none of the samples survived grinding. SEM examination indicated that although there was a reaction between the CVD layer and the oxide, the oxide layer had buckled and peeled.

A second series of samples were coated with a Si_3N_4 layer 2-4 μm thick. The samples were joined at 1650°C for 45 minutes in an overpressure of $\sim 100 \text{ MPa}$ of N_2 . The joint area in one sample is shown in Figure 4. This joint consists of a coated, thinly glazed piece joined to an untreated piece. This sample was proof-tested by applying a stress of 230 MPa in a 4-point bend test. The strength and joint composition of a number of samples are shown in Table 2. Examination of the fracture surfaces of bars joined by this method did not indicate the fracture origins. Fracture was through the CVD layer, and in a number of cases the CVD layer did not appear to be completely dense. The joints are very thin, usually $< 10 \mu\text{m}$, and the individual layers could not be easily distinguished.

*Scientific Coatings, Santa Clara, CA.



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FIGURE 4 JOINT REGION IN SAMPLE JOINED BY COATING TECHNIQUE

Table 2

STRENGTHS AND JOINT COMPOSITIONS FOR VARIOUS SAMPLES

<u>Sample No.</u>	<u>Strength,</u> <u>MPa</u>	<u>Joint Composition</u>	<u>Joint Thickness</u> <u>μm</u>	
1	a	54	Oxidized(10 hr)/coating//	9
	b	40	oxidized (10 hr)	8
	c	124		7
8	a	167	Oxidized (3 hr)//	7
	b	194	coating	9
9	a	19	Thin glaze/coating// thin glaze	31
11	a	70	Thin glaze/coating	5
	b	> 228		4
	c	19 ^r		4

Note: Single slashes (/) indicate layers placed on one piece; double slashes (//) indicate joining surfaces.

Although no testing of this joining method has been performed at elevated temperatures and the joint composition and joining conditions have only been briefly examined, the method appears to have potential. The initial survey of strengths indicates that joints with strengths equivalent to those achieved by the original method could be made.

CONCLUSIONS

The implications of this study extend beyond joining and into processing and the behavior of materials at high temperatures. The presence of impurities (particularly alkalis and alkaline earths), both in the joint and in the Si_3N_4 , is particularly deleterious to joint integrity and surface finish. These species diffuse to the joint, to the surface, and through the joint. Tungsten also moves to the surface, although it was not observed as a vaporizing species in the mass spectrometer. It is clear from the results of this work that improvements in material purity need to be made not only to improve short-term mechanical reliability, but also to prevent degradation of materials with time.

The method of joining with an oxide glass produces joints with strengths in excess of 450 MPa that are suitable for use at temperatures up to $\sim 800^\circ\text{C}$. At higher temperatures, continuing reactions between the glass and the Si_3N_4 and vaporization cause degradation of the joint. The new method of joining using CVD Si_3N_4 avoids the use of large amounts of oxide glass and therefore has potential for use at higher temperatures. Our preliminary studies indicate that joints with strengths at least as high as joints made with glasses can be formed.

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APPENDIX A

INVITED PAPER PRESENTED AT THE SECOND INTERNATIONAL CONFERENCE ON
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BAD NAUHEIM, WEST GERMANY
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JOINING OF SILICON NITRIDE

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Abstract

Methods of joining Si_3N_4 to itself or to metals are reviewed and common problems and deficiencies in these methods are identified. A method of joining Si_3N_4 with an oxide glass that fulfills a number of the criteria for a joining method that gives high strength joints at elevated temperatures is reviewed in more detail.

Introduction

The use of ceramic materials such as Si_3N_4 , SiC , ZrO_2 , and Al_2O_3 for structural purposes requires methods of joining these materials to similar and dissimilar ceramics and to metals. Joining methods include both mechanical attachment methods that rely heavily on design concepts and chemical joining methods that rely on reaction or interdiffusion between the materials to be joined and the joining material. The major difficulty encountered in joining dissimilar materials or in using joining materials is caused by differences in thermal expansion. Complicated joining methods must often be used, therefore, to minimize the resulting stresses, and the strength of the joint is often inadequate. Nonoxide ceramics such as Si_3N_4 and SiC have very low coefficients of thermal expansion and are fairly stable materials, and joining methods for these materials have received less attention than those for oxide ceramics. This paper first reviews methods for joining Si_3N_4 , and then focuses on a joining method that involves the use of an oxide glass as the joining material.

Joining Methods for Silicon Nitride

Most methods of joining Si_3N_4 to itself or to a metal are solid-state methods that often require the application of a pressure to the parts. These methods may involve the use of a joining material such as Si_3N_4 powder with various additives,¹⁻³ ZrO_2 or ZrSiO_4 powder,⁴ or metals.⁵⁻⁷ Silicon nitride can also be hot-pressed together with a thin layer of Si_3N_4 powder between the pieces.⁸ Other methods do not involve joining materials but rely on direct hot-pressing,⁹ pressureless direct bonding,⁹ or on a reaction between oxidation products and a metal.¹⁰ Exceptions to solid-state methods include brazing of Si_3N_4 with alloys that contain Si¹¹ and the method of joining Si_3N_4 with an oxide glass.¹²⁻¹⁵

One of the earliest patents for joining Si_3N_4 ¹ involved hot-pressing Si_3N_4 pieces together with an intermediate layer of Si_3N_4 powder containing 5 wt% MgO. A more recent paper by Kaba et al.³ describes joining of hot-pressed Si_3N_4 both to itself and to Al_2O_3 using Si_3N_4 powder either without additives or doped with 4 wt% Y_2O_3 . The strength of pieces joined with MgO-containing powder was reported as ~ 550 MPa; no strength measurements were reported by Kaba et al., whose method required both a higher temperature (1800°C cf. 1650°C) and a higher pressure (3 GPa cf. 450-700 MPa) than that of Coe.¹ Kaba et al. observed Y diffusion from the joint into the bulk that was accompanied by a change in hardness. The presence of Y_2O_3 in the joining material also caused the hardness to decrease rapidly at temperatures above 1000°C.

Another early method of joining Si_3N_4 , reported by Wilks,² involved bonding two pieces together with a Si powder/adhesive mixture, burning out the binder, and nitridding the Si. This method is not suitable for applications requiring high strength because the joint formed will be porous.

Becher and Halen⁴ used a low-pressure (< 1.5 MPa) method involving the use of ZrO_2 or ZrSiO_4 powder to join both hot-pressed and reaction-bonded Si_3N_4 . The best strengths obtained were 175 MPa for hot-pressed

Si_3N_4 bonded with ZrO_2 under vacuum, and for hot-pressed Si_3N_4 joined to reaction-bonded Si_3N_4 under oxidizing conditions. The joints formed by this method were not tested at elevated temperatures. The fracture toughness of the joints ranged from $1.3 \text{ MPa m}^{1/2}$ for joints involving reaction-bonded Si_3N_4 to $5.0 \text{ MPa m}^{1/2}$ for the highest-strength joints between hot-pressed Si_3N_4 . Zircon was not useful as a joining material because of low reactivity between Si_3N_4 and ZrSiO_4 .

Reaction-bonded Si_3N_4 and hot-pressed Si_3N_4 have been successfully joined by hot-pressing to form what is termed a "duodensity" rotor; the resulting components have been spin-tested under severe conditions (1100°C and $50,000 \text{ rpm}$).⁸ Sintered Si_3N_4 has also been hot-pressed together by Tabata et al.⁹ Materials containing MgO as a sintering aid formed stronger joints than materials containing Y_2O_3 ; the MgO -containing materials could be joined satisfactorily with the application of only a nominal pressure. The materials used in this study contained substantial amounts of additives (11-15 wt%), and although the high temperature properties of the joined pieces were not examined, the materials themselves will not have superior high temperature performance because of the large amount of second phase. The grain boundary phase in the materials is responsible for joining, and this method is related to one using a glass similar to the grain boundary phase as a joining material.^{12,13}

Metals that have been bonded to Si_3N_4 either as a joining material or to form a ceramic-metal couple include Zr, Al, Cu, Si and Si-containing alloys, and Mo. Wicker et al.⁵ used an Al ring as an intermediate layer to join Si_3N_4 to a superalloy. The Al ring could be bonded to Si_3N_4 by hot-pressing under either vacuum or reducing conditions. However, the tensile strength of the joints was low, with the maximum strength being 15 MPa. The strength of joints formed in a similar way with a sialon was much higher and more consistent (300-550 MPa).

Although Mo-Mn alloys are used to metallize oxide ceramics, Mo does not bond well to Si_3N_4 .⁶ Suganuma et al.⁶ have investigated a method

termed "composite interlayer bonding" to overcome the problems of thermal expansion mismatches between ceramics and metals. The joining material that forms the composite interlayer is a powdered mixture of the ceramic and metal constituents. A high pressure is applied at an elevated temperature to form the bond. Silicon nitride can be joined to Mo by this method if the temperature is controlled so that reaction between Mo and Si_3N_4 to form molybdenum silicides does not occur extensively. The small pieces joined by this method are strong enough to survive quenching from the joining temperature ($\sim 1400^\circ\text{C}$), but no other strength data has been reported.

Elssner et al.⁷ studied bonding of Si_3N_4 to Zr and to Nb through a Zr layer. The bonding between hot-pressed Si_3N_4 and Zr is dependent on temperature, purity, and additive content of the Si_3N_4 ; higher purity Si_3N_4 forms the strongest bonds at high temperatures ($\sim 1400^\circ\text{C}$), while the maximum bond strength in lower purity Si_3N_4 occurs at lower temperatures. Here the rate of formation of a SiO_2 surface layer on the Si_3N_4 is slower. Fracture toughness measurements were performed on joined pieces that incorporated Nb in the joint. The fracture toughness and fracture site are both dependent on the thickness of the Nb layer. Samples joined with thick layers of Nb (1 mm) fractured in the Si_3N_4 , whereas the fracture initiated in the Zr layer in samples joined with thinner layers of Nb.

Copper has been bonded to the oxidized surface of sintered Si_3N_4 containing Y_2O_3 and Al_2O_3 .¹⁰ Bonding occurs by reaction between the oxide layer and the metal, although the exact mechanism has not been reported. The shear strength of the bonded pieces is dependent on the oxidation temperature and therefore on the amount and composition of the glassy and other phases formed on the surface. Shear strength is maximum when a maximum amount of glass is present, and decreases when large amounts of $\text{Y}_2\text{O}_3 \cdot 2\text{SiO}_2$ are present on the surface.

Si_3N_4 can be brazed together with Si-containing alloys that have thermal expansion coefficients similar to Si_3N_4 .¹¹ Mizuhara¹⁷ has also demonstrated that Si_3N_4 can be joined to itself or to oxide ceramics

with an active element braze. Si shapes that have not been nitrided can be joined with a Si slip that is subsequently nitrided with the entire assembly.⁸ Goodyear and Ezis⁸ found that the bonding between Si and reaction-bonded Si_3N_4 was poor and that good joints could not be made in that way.

A number of the methods for joining Si_3N_4 described above are useful for applications near ambient temperatures, and others are usable to moderate temperatures. However, for high-temperature applications, the only proven one is the duodensity or hot-pressing method. Only components joined by the duodensity method have been tested at high temperatures or under service conditions. However, this method requires hot-pressing, as do a number of the other methods. Hot-pressing is time-consuming and is limited to joints that have a fairly simple shape. An ideal method of joining Si_3N_4 would be one that requires only nominal, if any, applied pressure, is not restricted to simple interfaces, and which employs a joining material chemically and physically compatible with Si_3N_4 so that joints have adequate strength over a wide temperature range. A method of joining Si_3N_4 with an oxide glass fulfills several of these criteria, as described in more detail in the remainder of this paper.

Method of Oxide Glass Joining

The method of oxide glass joining of Si_3N_4 , developed at SRI International, is described in detail elsewhere,^{12,13,15} but will be outlined briefly here. An oxide glass with a composition similar to the grain boundary phase in hot-pressed Si_3N_4 ^{*} is applied to the polished end of a ~ 2.5 cm x 1.25 cm x 0.3 cm slab followed by a glazing heat treatment. Glazed layers are ground down and the glazed piece is placed on top of an unglazed piece in a BN jig (Figure 1). Samples are joined under ~ 200 kPa of N_2 for ~ 45 minutes at 1580°C. Joined pieces are subsequently ground, polished, and cut into bars for testing. Three glasses have been used for joining with compositions as follows:

^{*}NC132, Norton Co., Worcester, MA.

Table 1
 SAMPLES INVESTIGATED BY MASS SPECTROMETRY

Sample	Designation	Nominal composition (wt%)				
		MgO	SiO ₂	Al ₂ O ₃	Y ₂ O ₃	N
MgO glass	HN-9M	35	55	10		
Y ₂ O ₃ glass	SG-14-0		34	20	46	
Y ₂ O ₃ oxynitride glass	SG-14		32	19	43	6

An extensive study of the reactions between the glass and Si₃N₄ during joining has been performed by Mecartney et al.¹⁵ and will only be outlined here. Silicon nitride dissolves in the oxide glass and Si₂N₂O precipitates. Acicular crystals of Si₂N₂O grow out into the joint from Si₃N₄ grains. The glass also penetrates into the bulk Si₃N₄ via the grain boundaries.

Properties of Joined Si₃N₄

The strength of joined pieces has been tested by performing 4-point bend tests on bars ~ 3 mm x 50 mm at temperatures up to ~ 1100°C in air. Fracture surfaces have been examined by SEM. The strength of joined bars is independent of joining time and temperature for times and temperatures between 30 and 60 minutes and 1575 and 1650°C. The strength is, however, dependent on joint thickness, as is shown in Figure 2. The strongest joints, ~ 450 MPa, are those with joint thicknesses in the range of 20-30 um. Thinner joints tend to be porous or incomplete for two reasons: (1) there is a volume change associated with the precipitation of Si₂N₂O from the glass, and (2) there is a vaporization problem associated with the glass-Si₃N₄ system. Also, the strength of very thick joints approaches that of the glass. The strongest joints are those that have a network of cracks normal to the joint, as shown in Figure 3. These cracks are caused by differences in thermal expansion between the glass and the Si₃N₄. Although fractures

initiate in one or more of the "squares," the thermal expansion cracks stop or divert these cracks in to the Si_3N_4 . This pattern of cracks and multiple fracture origins on a fracture surface is shown in Figure 4.

The strength of joined pieces has been tested at temperatures up to $\sim 1100^\circ\text{C}$. Above 1000°C joints cannot be tested satisfactorily because the joints expand and fail under very low loads. Heat treatment in N_2 of the joints to promote crystallization resulted in weaker joints and an apparent loss of glass.

The strength of joints in the range of 25 - 1000°C was also measured. The strength is constant up to $\sim 800^\circ\text{C}$, peaks at 900°C , and decreases near zero at 1000°C . Within this temperature range, the strength of the joints is dependent on the joint thickness in a similar manner to the room temperature behavior. The fracture surface reveals a loss of glass that increases with increasing temperature. The appearance of samples tested at ambient temperature indicated that there were some incompletely joined areas, and the strengths of this series of samples were also low. The chemistry of the system is complex, and it is difficult to determine the exact reactions that occur, but it is probable that oxygen contamination in the furnace atmosphere causes oxidation of the Si_3N_4 and alters the reaction that normally occurs at the interface, lowering the strength.

The results of the strength measurements at elevated temperatures indicated that vaporization was occurring. This vaporization behavior of the joining system was studied by mass spectrometry¹² at temperatures up to 1200°C . Vaporization is insignificant until the temperature exceeds 1000°C , at which point the major species that vaporize are SiO , Mg , and Na . Sodium is present as an impurity and Mg is present either as an impurity or in the form of MgO as a sintering aid. Magnesium migrates from within the bulk Si_3N_4 where conditions are reducing to the Si_3N_4 surface or to the glass where conditions are less reducing. This mass transport, which is based on differences in chemical potential between the ceramic, the surface, and the glass, is responsible for the "bloating" and loss of joint integrity observed. An X-ray scan of Mg

showing its diffusion from Mg-containing Si_3N_4 into a glass that contains no Mg is shown in Figure 5. The appearance of glazed layers before and after heat treatment is shown in Figure 6; porosity develops in the glass as a result of the mass transport and vaporization losses.

Discussion

The results of this study have several implications for both joining and processing of Si_3N_4 . The presence of impurities, particularly alkali and alkaline earth species, is detrimental to the high temperature behavior of Si_3N_4 . It should be particularly noted that the vaporization effects were observed under neutral atmospheric conditions and that the mass transport of Mg to the surface and to the joint is observed in high (~ 700 kPa) overpressures of N_2 . Materials will degrade at high temperatures irrespective of the atmosphere.

The method of joining Si_3N_4 with an oxide glass is suitable for applications where the maximum use temperature will be below $\sim 800^\circ\text{C}$. This maximum use temperature may be increased by improving the purity of the Si_3N_4 and using more refractory glasses based on the Y_2O_3 - Al_2O_3 - SiO_2 system. The strength of joints is also deleteriously affected by the presence of oxygen in the furnace atmosphere. Oxygen-contaminated Si_3N_4 powders, i.e., powders where the particles have surface oxide layers, are not as readily sintered as higher-purity powders. These observations imply that oxide surface layers will slow down the reaction between the Si_3N_4 and the glassy phase, whether the reaction is the partial dissolution and crystallographic structure change associated with sintering or the dissolution/precipitation reaction associated with the oxide glass joining method.

Current work on this joining method is concentrated on joining in atmospheres with minimized partial pressure of O_2 , the use of glasses and Si_3N_4 with lower impurity contents, and the use of more refractory glasses.

Conclusions

A number of the methods available for joining Si_3N_4 to itself or to metals have been described above, but those that are available are generally unsuitable for use at elevated temperatures or have not been evaluated above ambient temperature. Methods that involve metals are limited by the temperature capability of the metal or oxidation/corrosion resistance of the metal. Methods that involve glasses or glassy phases are limited by currently available materials and by degradation over time caused by ongoing reactions between Si_3N_4 and glasses. Hot-pressing methods are limited by component shape and equipment requirements. Joining of Si_3N_4 by hot isostatic pressing clearly needs further investigation, as less joining material is required and complex shapes can be joined. Material behavior is clearly dependent on the chemical behavior of the Si_3N_4 and joining phases.

Of all the methods described, only two types have potential for high temperature use. The duodensity method has been proven by tests on components. The oxide glass method can be used up to $\sim 800^\circ\text{C}$, and has potential for improvement past this temperature. However, the success of this and all other methods is dependent on material properties. Improved materials, particularly in terms of levels of impurities and additives, are required before adequate joining techniques can be developed.

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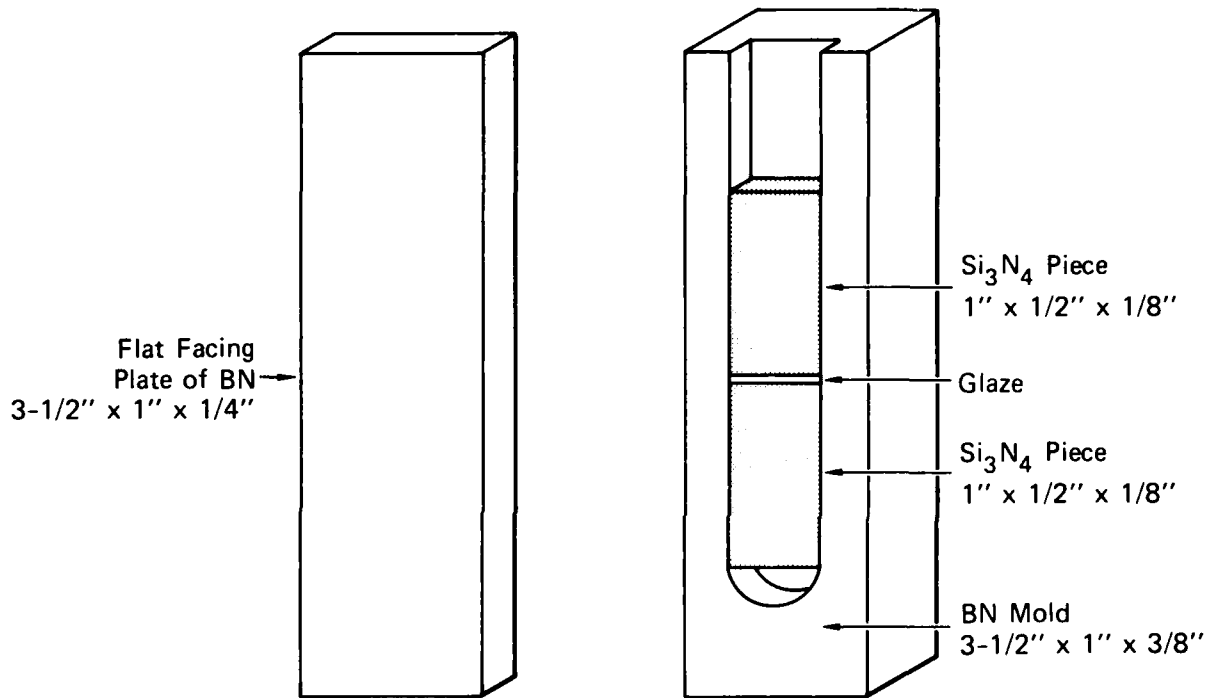
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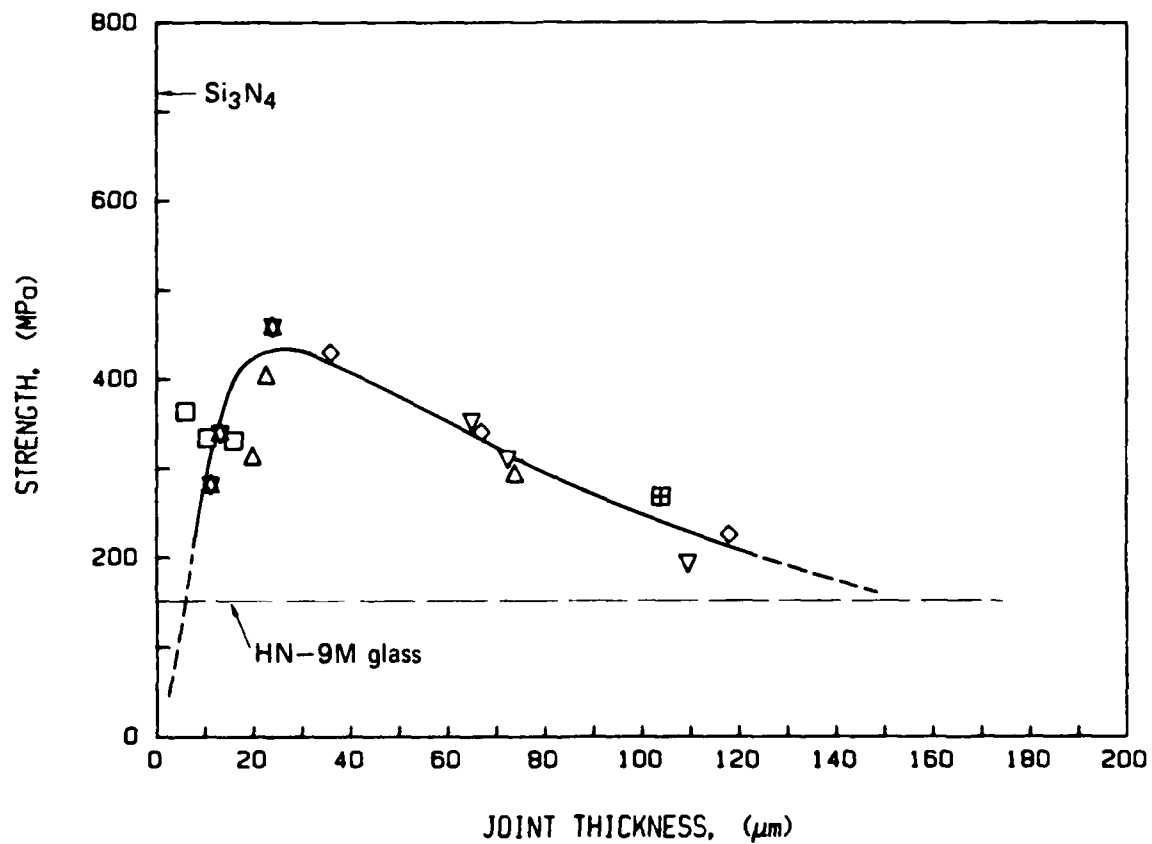
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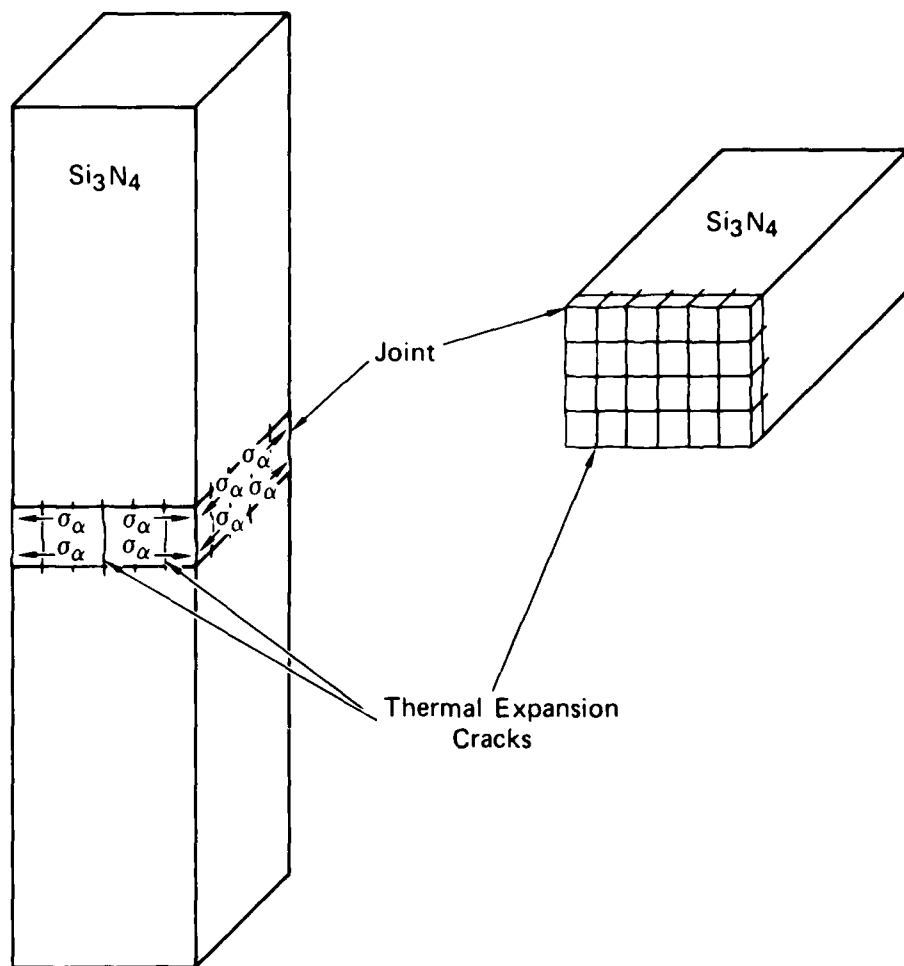
FIGURE 1 BORON NITRIDE JIG USED IN JOINING TWO PIECES OF Si₃N₄
The upper piece is glazed before being joined to the lower piece.



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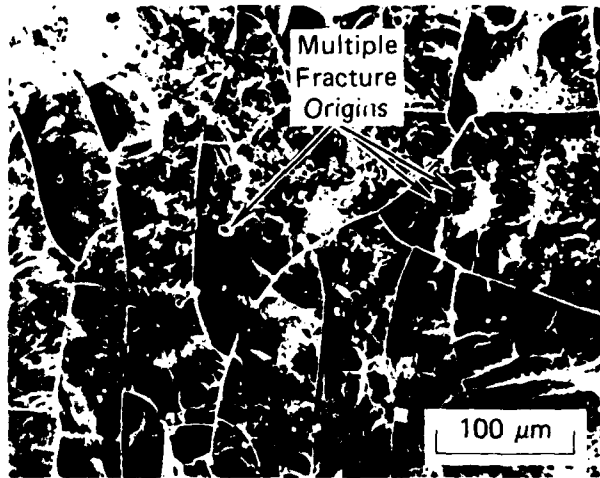
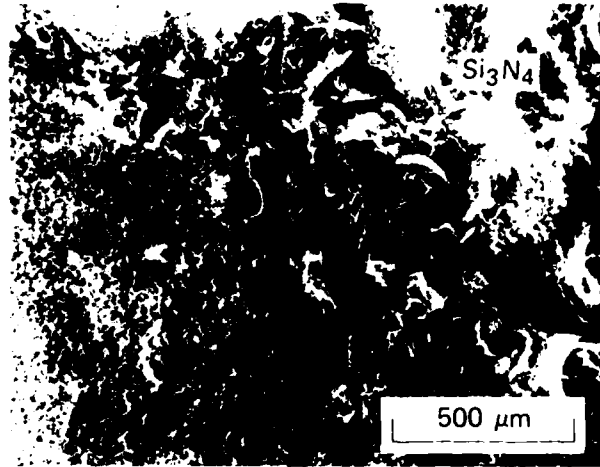
FIGURE 2 STRENGTH VERSUS JOINT THICKNESS

Joining conditions were 1580°C for 45 minutes under 2 atm N₂.
 Like symbols indicate test bars cut from a single joined specimen.



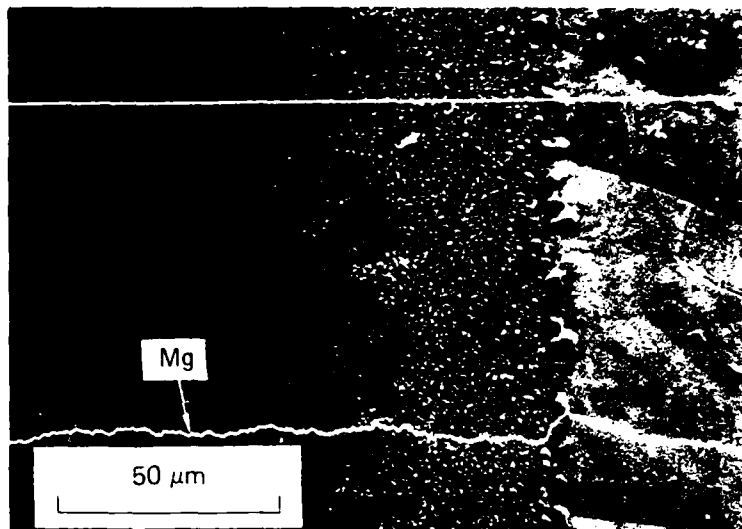
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FIGURE 3 SCHEMATIC DRAWING SHOWING DEVELOPMENT OF THERMAL EXPANSION MISMATCH CRACKS IN THE JOINT

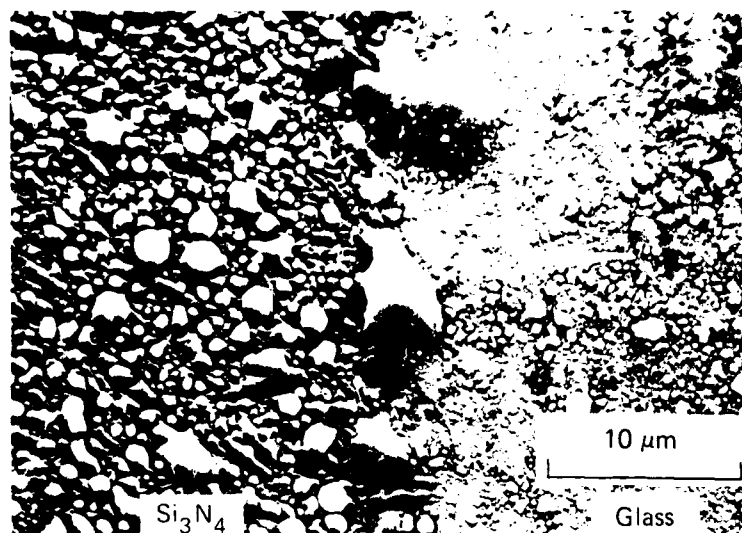


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FIGURE 4 THERMAL EXPANSION CRACKS AND MULTIPLE FRACTURE ORIGINS ON A FRACTURE SURFACE



(a) Mg Scan



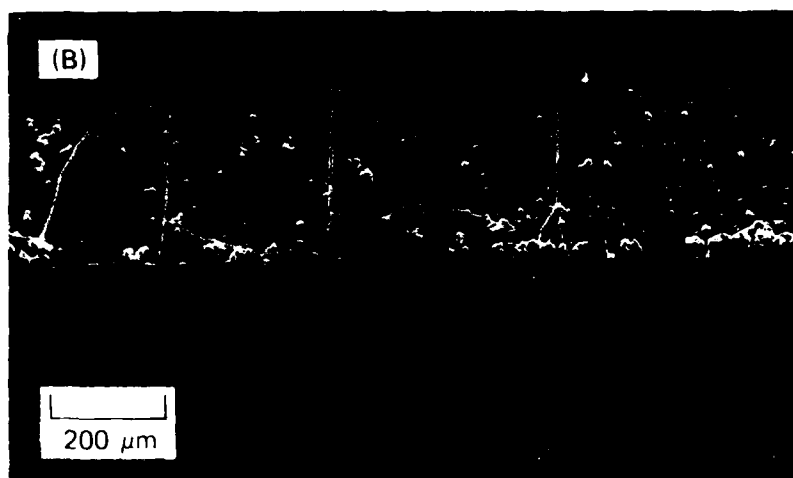
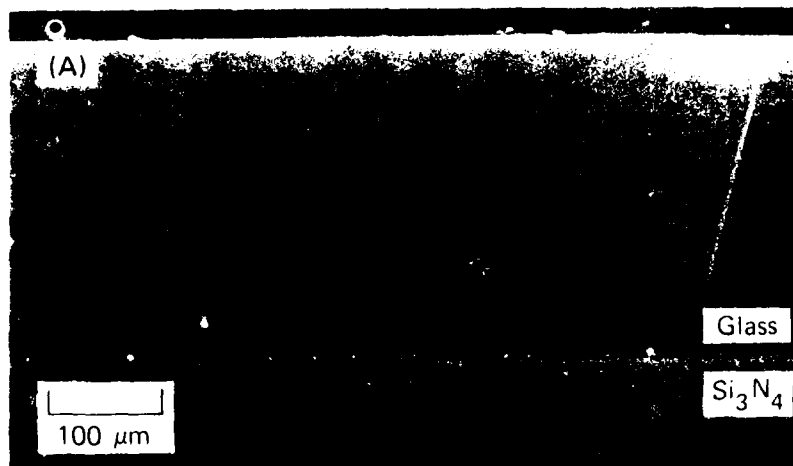
(b) Interfacial Region

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FIGURE 5 EDAX SCANS OF Mg-DOPED Si_3N_4 (NC132) GLAZED WITH $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ GLASS (SG-14-0) AFTER HEAT TREATMENT IN 6.7 atm N_2

(a) Mg scan across NC132

(b) Interface between NC132 and SG-14-0



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FIGURE 6 NC-132 (MgO) Si₃N₄ GLAZED WITH MAGNESIA (HN-9M) GLASS

(A) As glazed.

(B) After heating to 1480 K in mass spectrometer.

APPENDIX B

SILICON NITRIDE JOINING[±]

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ABSTRACT

Hot pressed Si_3N_4 has been joined using a $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ glass composition that was chosen to approximate the oxide portion of the grain boundary phase in the ceramic. After heating at 1550°-1650°C, the interface of the joined ceramic is an interlocking mixture of $\text{Si}_2\text{N}_2\text{O}$, $\beta\text{-Si}_3\text{N}_4$, and a residual oxynitride glass. The kinetics of reactions between Si_3N_4 and the molten joining composition were studied by x-ray diffraction analysis of the phases present in Si_3N_4 powder-glass mixtures quenched after heating for different times and temperatures. Analytical transmission electron microscopic analysis of the composition and microstructure of the reaction zone in joined specimens, together with the x-ray diffraction results, suggests the driving force for joining is the lowering of the Si_3N_4 interfacial energy when it is wet by the molten silicate, augmented by the negative Gibbs energy for the reaction $\text{SiO}_2(\ell) + \text{Si}_3\text{N}_4 = 2\text{Si}_2\text{N}_2\text{O}$.

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Silicon nitride ceramics can be joined to give room temperature bond strengths in excess of 450 MPa (65,000 psi)[1-5]. The technique consists of heating a thin layer of glass between the parts to be joined at a temperature sufficient to react the molten glass with the ceramic and thus create the bond. The idea motivating this approach is that the most advantageous joining composition for a particular type of Si_3N_4 should be one that duplicates the composition of its intergranular phase. When Si_3N_4 is sintered or hot-pressed, the individual amorphous or α - Si_3N_4 grains are joined together by reaction with a liquid created by melting of the additives and impurities present in the compact. Bulk Si_3N_4 can be joined in an analogous fashion using small amounts of reactive, high-temperature liquids if they promote dissolution and precipitation of the β - Si_3N_4 at the interface. Alternately, bonding could result from reaction between the ceramic and the liquid to form new phases (e.g. $\text{Si}_2\text{N}_2\text{O}$) at the interface. Ideally, in the former case, the interface between the joined pieces will resemble a Si_3N_4 grain boundary and the joint should be as strong and as durable as the individual grain boundaries in the bulk ceramic. In the latter case, the interface will differ from the ceramic grain boundaries, and the properties of the bond will depend on the composition and microstructure of the interface.

The present research was undertaken to study the joining of Si_3N_4 in greater detail, to establish the validity of the hypothesized joining mechanism, and to learn enough about the process so that it can be improved and optimized on a rational basis. The work was divided into several phases: (1) selection and synthesis of joining compositions; (2)

experiments to model the solution-precipitation process that is believed to occur at the ceramic-liquid interface; and (3) studies of interfacial compositions and microstructures using analytical transmission electron microscopy (AEM). The results of an extensive investigation of the mechanical properties of joined Si_3N_4 will be published separately.[6]

Experimental

A single type of Si_3N_4 ceramic and one main joining composition were used in this study. NC132* hot-pressed Si_3N_4 was chosen because it is readily available and because its wide use in other experiments allows ready comparison of data. How we selected the joining composition is described below. The analogy between joining and solution-precipitation in hot-pressing or sintering is imprecise because densification involves solution of amorphous or α - Si_3N_4 , whereas joining already densified Si_3N_4 requires dissolution of material in the β -form. Consequently, reactions between the molten glass and all three forms of Si_3N_4 powders (amorphous, α -, and β -) were studied, as described below, to assess whether differences in crystallographic form significantly alter the reaction mechanism.

Joining Compositions Hot-pressed NC132 Si_3N_4 contains MgO as a densification aid. Table I lists the impurities present in the material we studied, as determined by emission spectrographic and neutron activation analyses, together with data provided by the manufacturer for two different lots of hot-pressed Si_3N_4 .

Average compositions of intergranular phases in the hot-pressed Si_3N_4 were calculated using the data listed in Table I. The oxygen present was

assumed to be partitioned between the major cation impurities (Al^{3+} and Mg^{2+}) with any remainder assigned to Si as SiO_2 . The Ca was ignored, as a first approximation and, based on previous observations[7], the Fe and W were assumed to form carbides or silicides that are not part of the continuous oxide intergranular phase.

The range of impurity concentrations reported for NC132 Si_3N_4 suggests the composition of the grain boundary phase varies among different Si_3N_4 billets that are nominally the same. Local differences in the composition of intergranular phases also can be expected as a result of failure to reach equilibrium during processing. Such variations in the intergranular phase have been reported by Clarke, et al.[8], who studied hot-pressed Si_3N_4 by AEM techniques. The observation that the grain boundary composition in silicon nitride ceramics is not unique implies that there is a range of joining compositions compatible with Si_3N_4 . Thus, additional criteria can be considered to optimize the joining material. The HN-9M composition listed in Table I falls within the range calculated for Si_3N_4 grain boundaries. After preliminary experiments on several other materials, HN-9M was selected for further study because it melts around 1500°C , and because it has a lower Si content than some other compositions calculated from the analyses. A low Si content is desirable because the solubility of Si_3N_4 in oxide melts increases with decreasing SiO_2 content[9], and Si_3N_4 dissolution is an essential feature of the present joining model. A 1550°C maximum for the melting point was selected for convenience in processing.

Because the HN-9M glass contains the same ingredients as the NC132 grain boundary phase, its penetration into the bulk Si_3N_4 during joining

cannot be detected by AEM. Thus, one other glass composition was prepared, Sc-HN-9M, in which Sc replaced about 20 at% of the Mg. The Sc in that glass served as a tracer that allowed AEM measurement of the penetration depth of the joining composition into the bulk Si_3N_4 .

The glasses were prepared by melting suitable mixtures of oxides and carbonates for 4-16 hr in air at 1600°-1650°C in Pt crucibles with occasional stirring. At the end of that period some of the melt was cast into bars, which were then annealed for 2 hr at 775°C, while the remainder was fritted by pouring into water. The frit was ball-milled in plastic jars using Al_2O_3 balls and the resulting powder was sieved to separate the -100 mesh fraction for further experiments.

The glasses were characterized by a variety of properties measurement techniques. Thermal expansion was measured to the softening point on a double pushrod dilatometer using fused SiO_2 as a standard. The glass transition temperature (T_g) and the temperature of the onset of the first crystallization exotherm (T_c) were measured in a DTA apparatus with Al_2O_3 as the reference. Young's modulus was determined on rods of the bulk glass using an acoustic resonance technique. The sessile drop technique was used to survey the compatibility of joining compositions with Si_3N_4 . Glass cubes were placed on Si_3N_4 plates ground to a 600 grit finish, and they were heated for various times at 1500° or 1600°C in a W-element furnace under N_2 .

Modelling Reactions Between Si_3N_4 and the Joining Composition

Conceptually, the joining reaction can be divided into several stages. Initially there is an excess of silicate liquid localized at the interface

and the oxygen activity there is high. With continued heating, Si_3N_4 dissolves in the liquid, liquid penetrates the ceramic, and, as equilibrium is approached, the oxygen activity at the interface decreases. We modelled the initial and later stages of that process by reacting two glass/ Si_3N_4 ratios for a series of increasing times at 1650°C, followed by quenching to room temperature and recovery for analysis. Mixtures of Si_3N_4 powder and HN-9M glass were used so that the concentrations of reaction products were high enough for analysis by x-ray diffraction. The approach is similar to the study of Tsai and Raj[10], but with several modifications. Our glass composition is different from that used by Tsai and Raj[10], we chose two extreme glass/ Si_3N_4 ratios rather than a middle value, and our reactions were run several hundred degrees higher in temperature, in the range appropriate for joining.

The samples were reacted in Mo crucibles under 2 atm N_2 in a graphite-element furnace. When the power was shut off, the furnace cooled at 44°C/min from 1600° to 800°C and at about 16°C/min from 800° to 300°C. A slice of each specimen was powdered and analyzed by x-ray diffraction under conditions that allowed us to make a semiquantitative estimate of the relative proportions of the crystalline phases present. A 90% β -, 10% α -phase powder[±] (for convenience referred to as β from here on) was used to model the joining reaction. Two other Si_3N_4 powders were included in the experiments to assess the effect of crystal structure on reactivity: SN402⁺, a mostly amorphous powder; and SN502⁺, a powder that is approximately 55% α -phase, 5% β -phase, and 40% amorphous. We determined the BET surface areas of the β , SN402, and SN502 Si_3N_4 powders to be 1.39, 10.36, and 7.01 m²/g, respectively. A 85 w% glass - 15 w% Si_3N_4 ratio was

used to simulate the early stage reaction, whereas a 20 w% glass - 80 w% Si_3N_4 ratio was used to study the later stage.

Microstructural Analysis

Small bars of Si_3N_4 were joined with HN-9M in an end-seal configuration using procedures that gave high mechanical strengths [1,2,6]. Some joint cross-sections were metallographically polished for scanning electron microscopic examination. Slices of other joint cross-sections were ground, polished, and then Ar-ion thinned to prepare electron-transparent samples for TEM study. Slices of reacted glass - Si_3N_4 powder mixtures were prepared in a similar manner. The transmission electron microscopy was performed on a 120KV STEM* equipped with an energy dispersive spectrometer sensitive to elements with atomic number greater than 11. Compositions of the glassy pockets at the three-grain junctions in both the as-received and the joined ceramics were analyzed using energy dispersive spectroscopy (EDS). The spot size we used was small enough so that the x-rays were generated only from the specific amorphous region being analyzed. The diffuse-ring diffraction pattern was monitored during the collection period to ensure that the beam remained on the amorphous pocket. Relative concentrations were calculated using the standardless K values provided by the EDAX 411 system. The compositions thus determined have a relative accuracy of $\pm 10\%$.

Results and Discussion

Compositions and Properties of the Ceramic Grain Boundary Phase

In this section we wish to compare the calculated Si_3N_4 grain boundary composition with that measured by EDS analysis and to present physical properties data on the joining material.

The composition of the HN-9M glass (Table I) used as a joining agent was calculated from bulk impurity analyses under the assumptions already discussed. Analyses of the impurity cation** and oxygen** concentrations in the specific hot-pressed Si_3N_4 billet used in the present study yield a grain boundary composition of 3 wt% Al_2O_3 -27% MgO -70% SiO_2 if any nitrogen solubility is neglected.

EDS analysis of amorphous material at three grain junctions in the hot-pressed Si_3N_4 provided estimates of cation concentrations equivalent to a glass composition of 1.3 wt% Al_2O_3 -24.3% MgO -74.3% SiO_2 , assuming only oxides are present. The composition calculated from the bulk impurity analysis is different from that measured by EDS because some of the Si is in the grain boundaries as an oxynitride glass. If about 10 wt% Si_3N_4 is dissolved in the glassy regions, which is reasonable based on extensive oxynitride glasses research[9], the two analytical results are consistent. Such an oxynitride glass would give the 3wt% Al_2O_3 -27wt% MgO -70wt% SiO_2 composition calculated by the trace-element analysis, but the EDS analysis would show it to be 2.6 wt% Al_2O_3 -23.6% MgO -73.5% SiO_2 , or very nearly what was actually found. Thus, in accord with previous observations on Si_3N_4 [8,14] and on oxynitride glasses[9,15] the grain boundary phase very likely is an oxynitride glass and the composition calculated from the bulk impurity analysis is close to the oxide component of that oxynitride glass.

Properties measured on bulk glasses are presented in Table II. The thermal expansion coefficient of the HN-9M glass is almost double that of

hot-pressed Si_3N_4 ($35 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$)[27]. The significance of thermal expansion mismatch to the strength of Si_3N_4 joints is discussed by Johnson and Rowcliffe[6]. Substitution of Sc for 20 at% of the Mg in HN-9M raises the expansion coefficient, the T_g , and the crystallization temperature by small-to-moderate amounts. The sessile drop experiments showed that when the joining composition melts it wets the Si_3N_4 and spreads very rapidly. A zero contact angle was observed for 2 min. at 1500°C for HN-9M. Longer times, higher temperatures, or substitution of nitrogen for oxygen or scandium for magnesium in HN-9M also gave a zero contact angle.

Microstructure of Joined Si_3N_4

As described earlier[1-5], and in the recent work of Johnson and Rowcliffe[6], joints made by the present technique have the highest room temperature strengths of any ambient pressure method yet reported for Si_3N_4 . In practical terms, the method works. Our objective here is to describe the high temperature reactions that take place and to analyze the joining process.

Figure 1 presents a pair of optical micrographs of the joint region in bonded Si_3N_4 . Because of small irregularities in the surface finish of the Si_3N_4 parts, the joint thickness varies from point to point over the area of the bond. Figure 1a shows a thin region in which crystallization during joining has proceeded through the entire interfacial volume. Figure 1b, which is more typical of the process, shows there is about a $50 \mu\text{m}$ thick glassy region in the center of the joint, with an array of interlocking, needle-like crystals that appear to have grown into the glass from each of

the bulk Si_3N_4 surfaces. The bright particles are impurities, present initially in the hot-pressed Si_3N_4 .

Examination of the reaction interface using transmission electron microscopy reveals a complex microstructure of well-formed crystallites, glassy regions, and scattered, 50-1000 nm diameter, electron-dense particles. Those dense particles were found to contain W and Fe. We believe that the particles are a W-Fe silicide similar to those reported in hot-pressed Si_3N_4 by other workers[7]. The W-Fe particles are ubiquitous in as-received NC132 Si_3N_4 . They probably result from reaction of WC impurities (from ball milling) with Fe impurities in the Si_3N_4 powder and Si_3N_4 or SiO_2 during hot pressing. Because the particles are not present in any of the glass joining compositions, their location in the joined specimens marks the position of the original glass- Si_3N_4 interface at the start of the bonding reaction. Thus, the location of the particles can be used to determine the direction of mass transport across the interface during joining.

The interface between the remnant glass and the ceramic is marked by an interlocking network of lath-like crystals that were identified as $\text{Si}_2\text{N}_2\text{O}$ by electron diffraction. $\text{Si}_2\text{N}_2\text{O}$ is orthorhombic with $a_0 = 8.843\text{\AA}$, $b_0 = 5.43\text{\AA}$, and $c_0 = 4.835\text{\AA}$ [27]. Figure 2 shows a $\text{Si}_2\text{N}_2\text{O}$ crystal at the interface surrounded by glass, with an electron diffraction pattern from the crystal included in the inset. Figure 3 is a micrograph of an assemblage of $\text{Si}_2\text{N}_2\text{O}$ crystallites in another part of the interface. The arrows in the figure mark several of the W-Fe particles described above. The presence of the particles indicates that the region was originally bulk ceramic and that the molten HN-9M composition dissolves the interface and

penetrates the ceramic, followed by crystallization of $\text{Si}_2\text{N}_2\text{O}$ from the silicon oxynitride liquid that forms. Although the W-Fe particles may move slightly from their original positions their high density and the high viscosity of the molten glass argue against any wholesale mixing. Thus, the $\text{Si}_2\text{N}_2\text{O}$ crystallizes in the interfacial volume that was originally occupied by Si_3N_4 . The alternate possibility, that Si_3N_4 dissolves and diffuses into the molten glass, can be ruled out because the W-Fe particles that mark the position of the original ceramic are distributed throughout the volume in which the $\text{Si}_2\text{N}_2\text{O}$ crystals are found, whereas they are never seen in the glass away from the joint.

Further evidence for penetration of the molten glass into the Si_3N_4 is obtained from TEM observation of how the composition and microstructure of the ceramic vary with distance from the original glass- Si_3N_4 interface. Figure 4 presents a typical microstructure for NC132 Si_3N_4 . The microstructure is characteristic of both the as-received Si_3N_4 and ceramic that has been through the joining process but is some distance from the interface. As has been well-documented in previous studies[11] the bulk material consists of 0.1 - 1 μm β - Si_3N_4 grains with small glassy pockets at the grain triple junctions. By contrast, the glassy regions in the ceramic nearer the interface are much larger. For example, Figure 5 illustrates that they are larger by a factor of four or more at a distance of 50-100 μm from the original interface. Figure 6 is a bright-field/dark-field pair taken at a distance of 25 μm from the original interface showing still larger glassy regions at the grain triple junctions. The small, dark particles, seen in Figures 4-6, are the W-Fe impurities described above,

which demonstrate that the regions photographed were a part of the original ceramic.

The observation, illustrated in Figures 2, 3, 5, and 6, that many of the Si_3N_4 grains exhibit a rounded morphology, whereas the $\text{Si}_2\text{N}_2\text{O}$ crystallites are sharply faceted, suggests that the reaction sequence is initial dissolution of the Si_3N_4 by the molten oxide followed by precipitation of $\text{Si}_2\text{N}_2\text{O}$ when the nitrogen content of the liquid reaches saturation. That sequence is consistent with the observations of Tsai and Raj[10] on the dissolution of $\beta\text{-Si}_3\text{N}_4$ in a Mg-Si-O-N glass. The enlarged glassy regions in the ceramic indicate that diffusion of the joining composition into the glassy second phase material on the Si_3N_4 grain boundaries is relatively easy.

The experiments in which the Sc-doped glass was used for joining confirm the ready diffusion of liquid into the Si_3N_4 ceramic. A specimen was heated for 1 hr at 1600°C using Sc-HN-9M in the end-seal arrangement described above. EDS analysis revealed a roughly parabolic decrease in Sc concentration with distance from the interface and a maximum penetration depth of 700 μm . An estimate of the diffusion coefficient of Sc^{+3} in the grain boundary liquid can be obtained by setting the maximum penetration distance equal to $(Dt)^{1/2}$. Using the value from the EDS measurements gives $D = 1.4 \times 10^{-6} \text{ cm}^2/\text{sec}$ for Sc at 1600°C. This compares favorably with values of $D = 3.4 \times 10^{-6} \text{ cm}^2/\text{sec}$ at 1540°C for Ca self-diffusion in a 38.5w% CaO-20.9w% Al_2O_3 -40.5w% SiO_2 melt [12], and $D = 2.0 \times 10^{-6} \text{ cm}^2/\text{sec}$ at 1520°C for Al diffusion in a 47w% CaO-6w% Al_2O_3 -47w% SiO_2 melt[13].

The driving force for diffusion is the chemical potential difference that results from the variation in composition between the grain boundary

phase and the joining composition, both of which are liquid during joining. Diffusion of the joining liquid into the ceramic grain boundaries raises the local oxygen concentration so that they no longer are saturated in nitrogen. This lowering of the relative nitrogen concentration at the grain boundaries promotes dissolution of the surrounding β - Si_3N_4 grains until the liquid is once again nitrogen saturated. Because only a small amount of liquid phase is present in the interior of the hot-pressed Si_3N_4 at 1600°C, in the bulk ceramic there is no large-scale conversion of Si_3N_4 to $\text{Si}_2\text{N}_2\text{O}$ as occurs at the joint interface.

Modelling Si_3N_4 Joining Reactions

Identification of the phases in the reaction zone at the glass- Si_3N_4 interface and determination of their evolution with time at temperature are essential for complete understanding of the present joining process. The x-ray diffraction experiments on mixtures of glass and Si_3N_4 powder allowed us to sample a larger volume of reaction zone than was practical with the TEM and the two techniques thus are complimentary. As mentioned previously, three types of Si_3N_4 powder were included in the x-ray study to assess differences in reactivity due to the particular crystallographic form of the Si_3N_4 .

The general results from analysis of the glass- Si_3N_4 reaction experiments at 1650°C may be summarized as follows. The only crystalline species identified by XRD for any of the reaction conditions are α - Si_3N_4 , β - Si_3N_4 , and $\text{Si}_2\text{N}_2\text{O}$. For mixtures containing 85 w% glass+15 w% Si_3N_4 there is a tendency to form $\text{Si}_2\text{N}_2\text{O}$ initially, but for longer times the $\text{Si}_2\text{N}_2\text{O}$ dissolves into the liquid phase and the specimen cools to a glass. For

mixtures containing 20 wt% glass+80% Si_3N_4 , $\alpha\text{-Si}_3\text{N}_4$, $\beta\text{-Si}_3\text{N}_4$, and $\text{Si}_2\text{N}_2\text{O}$ all are present initially at 1650°C and with longer heating times only their relative proportions change.

The evolution of phases for the 85% glass+15% Si_3N_4 mixtures is represented schematically in Figure 7a. The data are only semiquantitative and are considered accurate to $\pm 20\%$ of the relative amounts presented in the figure. According to the work of Tien, et al.[16] the subsolidus phases present at equilibrium in the 85 wt% glass+15 wt% Si_3N_4 specimens are β -cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), enstatite (MgSiO_3), forsterite (Mg_2SiO_4), and $\text{Si}_2\text{N}_2\text{O}$. The present results indicate that equilibrium is not reached for the cooling rates we used and, instead, there is a strong tendency to form oxynitride glasses that are resistant to devitrification.

Comparison of the data in Figure 7a for the three forms of Si_3N_4 powder allows one to postulate the reaction sequence for joining reactions in which the liquid silicate phase is in excess. The experiments with the $\beta\text{-Si}_3\text{N}_4$ powder suggest that reaction between $\beta\text{-Si}_3\text{N}_4$ and the molten silicate is relatively slow and that diffusion of nitrogen throughout the liquid volume is sluggish. Thus local regions with high nitrogen concentrations are outside the glass-forming region and $\text{Si}_2\text{N}_2\text{O}$ precipitates on cooling.

The SN502 Si_3N_4 -glass mixtures behave similarly, but the reactions are accelerated relative to the $\beta\text{-Si}_3\text{N}_4$ just discussed. Mixtures reacted for 10 min. contain $\text{Si}_2\text{N}_2\text{O}$, $\alpha\text{-Si}_3\text{N}_4$, and $\beta\text{-Si}_3\text{N}_4$, but the Si_3N_4 content decreases with time leaving only $\text{Si}_2\text{N}_2\text{O}$ plus residual glass after 90 min. Reactions between SN402 Si_3N_4 and the silicate liquid appear to be even more rapid than those for SN502 Si_3N_4 . Only $\text{Si}_2\text{N}_2\text{O}$ is observed after 10

min. and 40 min. at 1650°C and the reaction product is entirely amorphous after heating for 90 min. Presumably, if the SN402-liquid silicate mixture had been quenched after a very short time at 1650°C β - Si_3N_4 would have been present, but it formed and redissolved too quickly to have been captured within the heating periods used.

The results from the silicate- Si_3N_4 reaction experiments can be combined to give the following picture of the early stages of joining. Once the silicate joining composition is fluid it wets the ceramic and starts dissolving the β - Si_3N_4 grains at the areas of contact. Silicon oxynitride precipitates in local regions where, because of incomplete mixing, the material is outside the Mg-Si-Al-O-N glass-forming region. (Research on oxynitride glasses[9] has shown that $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ liquids can dissolve 10-20 wt% Si_3N_4 without precipitation of crystalline phases). The driving force for the dissolution-precipitation reaction is the negative Gibbs energy for $\text{SiO}_2(\text{l}) + \beta\text{-Si}_3\text{N}_4 = 2\text{Si}_2\text{N}_2\text{O}$; $\Delta G^\circ(1900\text{K}) = -163.3$ KJ [10,17]. If the silicate joining composition is in sufficient excess, the $\text{Si}_2\text{N}_2\text{O}$ crystals will dissolve once enough time is allowed for diffusion because 1650°C is above the liquidus temperature for that overall MgSiAlON composition. If, however, the concentration of Si_3N_4 is high enough the $\text{Si}_2\text{N}_2\text{O}$ is stable at 1650°C. The order of reactivity of the three forms of Si_3N_4 can be explained by particle size differences and because of increased driving force for reaction in the order $\beta\text{-Si}_3\text{N}_4$ to $\alpha\text{-Si}_3\text{N}_4$ to amorphous Si_3N_4 due to decreased thermodynamic stability of the α - and amorphous Si_3N_4 . The experiments with amorphous and $\alpha\text{-Si}_3\text{N}_4$ are not strictly relevant to joining of hot-pressed ceramics where all the Si_3N_4 is in the β -form. However, the experiments do give information that would be

useful if one were to join Si_3N_4 that is composed of a mixture of crystallographic forms, or if one desired to seed the joining composition with different forms of Si_3N_4 [18] in an attempt to promote specific crystallization. Lange[19] has shown that crystallographic transformations during Si_3N_4 processing can be affected by doping the starting $\alpha\text{-Si}_3\text{N}_4$ with $\beta\text{-Si}_3\text{N}_4$.

Mixtures of 20 wt% glass+80% Si_3N_4 model the latter stage of the present joining method. That liquid-to- Si_3N_4 ratio can be compared with the 7.5 vol% grain boundary phase[15] estimated for the hot-pressed billet from which the present Si_3N_4 joining specimens were machined. The model experiments incorporate a larger volume fraction of liquid than is present at the grain boundaries of the hot pressed Si_3N_4 and, thus, the experiments model the part of the reaction zone where the amount of grain boundary phase has increased, as shown in Figure 5. Figure 7b is a semiquantitative representation of the phases found by x-ray diffraction after various times at 1650°C. The subsolidus phase equilibrium work of Tien et al.[16] predicts that cooled 20% glass+80% Si_3N_4 mixtures should contain forsterite (Mg_2SiO_4), $\beta\text{-Si}_3\text{N}_4$, $\text{Si}_2\text{N}_2\text{O}$, and X* (suggested to be $\text{Mg}_2\text{SiAlO}_4\text{N}$) at equilibrium. Only $\alpha\text{-Si}_3\text{N}_4$, $\beta\text{-Si}_3\text{N}_4$, and $\text{Si}_2\text{N}_2\text{O}$ were observed in the x-ray diffraction spectra for the present experiments. As confirmed by EDS analysis of the reacted mixtures, the MgO and Al_2O_3 , as well as some of the SiO_2 , segregate to a residual glassy phase.

The experiments with $\beta\text{-Si}_3\text{N}_4$ show that a moderate amount of $\text{Si}_2\text{N}_2\text{O}$ is present after 10 min. at 1650°C followed by a decrease in its concentration with heating time. The $\alpha\text{-Si}_3\text{N}_4$ found in the 10 min. experiments probably is unreacted material originally present in the mostly $\beta\text{-Si}_3\text{N}_4$. Within the

precision of the data, the amount of β - Si_3N_4 does not change with time at 1650°C. Those results suggest an initial rapid formation of $\text{Si}_2\text{N}_2\text{O}$, probably from dissolution of the finer particle size fraction of the β - Si_3N_4 . At later times, some of the oxynitride and the β - Si_3N_4 dissolve into the liquid phase to form an oxynitride glass on cooling.

The experiments with SN502 Si_3N_4 show a slow increase in $\text{Si}_2\text{N}_2\text{O}$ concentration and a moderate increase in β - Si_3N_4 concentration with time at 1650°C. The α - Si_3N_4 concentration decreases only slightly over time, implying that crystallization of most of the $\text{Si}_2\text{N}_2\text{O}$ and β - Si_3N_4 is fed by dissolution of the amorphous fraction of the SN502 Si_3N_4 .

Figure 7b shows that for the experiments with the amorphous SN402 Si_3N_4 there is rapid initial formation of α - Si_3N_4 , β - Si_3N_4 , and $\text{Si}_2\text{N}_2\text{O}$, all of which must crystallize by way of a solution-precipitation reaction with the liquid silicate. For heating times of 10 to 85 min. at 1650°C, the concentration of $\text{Si}_2\text{N}_2\text{O}$ is approximately constant, that of α - Si_3N_4 decreases slightly, and that of β - Si_3N_4 increases slightly.

If the specimens heated for longer times are approaching equilibrium, the relative proportions of the three phases in Figure 7b should be tending to a common end point. The particular crystallographic form or particle size of the Si_3N_4 should affect only the kinetics of the reaction. The proportions of the different phases at the longest heating times are obviously very different. If the Al_2O_3 is neglected, we can use Lange's MgO-SiO₂- Si_3N_4 equilibrium diagram[20] to calculate the phases present at equilibrium in the 20% glass+80% Si_3N_4 mixtures as approximately 64 wt% β - Si_3N_4 , 22 wt% $\text{Si}_2\text{N}_2\text{O}$, and 14 wt% forsterite. No forsterite is observed in the x-ray spectra because as discussed previously, the MgO segregates to a

Mg-Si-Al-O-N residual glassy phase. The phase equilibrium diagram[20] predicts a 3:1 β - Si_3N_4 to $\text{Si}_2\text{N}_2\text{O}$ ratio with no α - Si_3N_4 . The experiment with the amorphous SN402 Si_3N_4 is perhaps closest to the predicted phase assemblage, which is in keeping with the observation made earlier that the reaction rates appear greater for that fine particle-size, amorphous Si_3N_4 , than for α - or β - Si_3N_4 . The small amount of liquid phase at 1650°C in the 80% Si_3N_4 +20% glass mixtures probably contributes to the observed slow approach to equilibrium. An increase in Si_3N_4 -liquid silicate reaction rates as the proportion of liquid increases was also found for the Si_3N_4 - Y_2O_3 - Al_2O_3 system[15].

In sum, the Si_3N_4 + HN-9M glass reaction experiments suggest that the driving force for joining is the negative Gibbs energy for the $\text{Si}_3\text{N}_4 + \text{SiO}_2 = 2\text{Si}_2\text{N}_2\text{O}$ reaction but that the phases observed at the end of the process depend on the relative concentrations of Si_3N_4 and the joining liquid. Because of the relatively favorable oxynitride glass formation in the MgSiAlON system a portion of the liquid phase cools to an oxynitride glass that is present on the grain boundaries near the interface in the joined ceramic.

Stability of Joined Si_3N_4

The presence of Si_3N_4 creates a chemically reducing environment, which, in turn, enhances vaporization of some species during joining or subsequent reheating of the joined ceramic[21]. Silicon monoxide, and alkali and alkaline earth elements produced by decomposition of their respective oxides are the prevalent vapor species. The vaporization is from both the Si_3N_4 ceramic, typified by Si_3N_4 hot-pressed with MgO, and

from the joining composition. Joints less susceptible to thermal degradation should be feasible if the alkali and alkaline earth contents of the ceramic and the joining composition are lowered. For example, use of a $Y_2O_3-Al_2O_3-SiO_2$ joining composition with a Si_3N_4 ceramic hot pressed with Y_2O_3 should give a bond with greater thermal stability. Brittain, et al.[21] found that vaporization from the latter compositional system was less than that from HN-9M/NC132 Si_3N_4 .

Complete or nearly complete crystallization of the joint to increase its strength is an objective yet to be achieved. The easy formation of oxynitride glasses by dissolution of Si_3N_4 in $MgO-Al_2O_3-SiO_2$ is an impediment to crystallization in that system. Doping the $MgO-Al_2O_3-SiO_2$ glass with Sc, as was done with the Sc-tracer diffusion experiments, increases its tendency to devitrify[18,22], and such compositional modifications are worth further exploration. Crystallization of amorphous grain boundary phases has been attempted with some success[23] in Si_3N_4 densified with Y_2O_3 and Al_2O_3 additions. Y-Si-Al-O-N glasses have been found to be more refractory, to have higher glass transition temperatures (T_g), and to have a narrower range of glass formation than Mg-Si-Al-O-N glasses[9,24-26]. Joining with $Y_2O_3-Al_2O_3-SiO_2$ compositions thus might show improvements over the present system in three areas: (1) decreased mass loss by vaporization under reducing conditions; (2) increased tendency to crystallize the material in the joint region; and (3) a higher softening point for any residual glass.

Summary and Conclusions

Even though joining Si_3N_4 ceramics with reactive silicates is not optimized in its present state of development the technique produces bonds that are very strong (450 MPa) at room temperature[6]. The bonding reactions are driven thermodynamically by a lowering of the Si_3N_4 interfacial energy when it is wet by the liquid silicate (as evidenced by the zero contact angle of molten HN-9M drops on bulk Si_3N_4) and by chemical reactions between Si_3N_4 and the silicate to give more stable products. The joining composition is miscible with the Si_3N_4 grain boundary phase and readily penetrates the grain boundaries up to several hundred micrometers, which creates a reaction zone where the volume fraction of the intergranular phase is increased relative to the unreacted ceramic. The reaction zone also is characterized by many rounded Si_3N_4 grains, indicating partial dissolution, and by faceted $\text{Si}_2\text{N}_2\text{O}$ crystallites, which form by crystallization from the intergranular phase.

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TABLE I

	Analysis in Wt%					
	Mg	O	W	Al	Fe	Ca
NC132, lot HN-9*	0.7	1.2	1.7	0.14	0.20	0.02
NC132, lot HN-10*	0.8	2.6	1.92	0.21	0.20	0.01
NC132 hot-pressed billet ⁺	0.8	1.5	3.0	0.08	0.23	0.02
HN-9M Glass Joining Composition	55w% SiO ₂ -35w% MgO-10w% Al ₂ O ₃					

*provided by manufacturer

⁺cations analyzed by American Spectrographic, San Francisco, CA,
Oxygen analysis by neutron activation, IRT Corp., San Diego, CA

TABLE II

Glass	$\alpha(23-750^{\circ}\text{C})$	T _g (°C)	T _c (°C)	E(GPa)
HN-9M ¹	$60 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$	755	956	140
Sc-HN-9M ²	62×10^{-7}	782	991	

1. Composition (at.fractions): Mg_{.178}Si_{.188}Al_{.020}O_{.614}

2. Composition (at.fractions): Sc_{.039}Mg_{.140}Si_{.177}Al_{.037}O_{.608}

FOOTNOTES

*Norton Co., Worcester, MA 01606

+G.T.E. Products, Corp., Towanda, PA

±Cerac, Inc. Milwaukee, WI 53201

*+Philips Electronic Instruments Inc., Mahwah, NJ 07430

**American Spectrographic, San Francisco, CA

** IRT Corp., San Diego, CA

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FIGURE 1a OPTICAL MICROGRAPH OF THIN JOINT REGION
Bright region is a W-Fe particle.



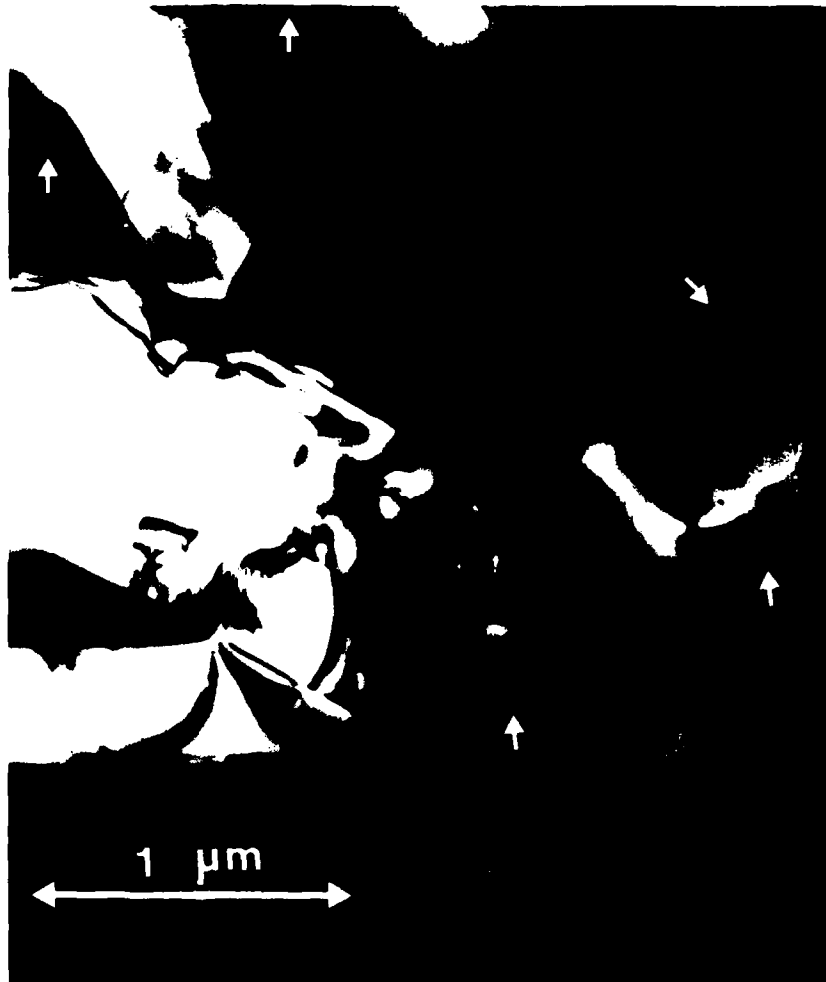
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FIGURE 1b OPTICAL MICROGRAPH OF THICKER JOINT REGION



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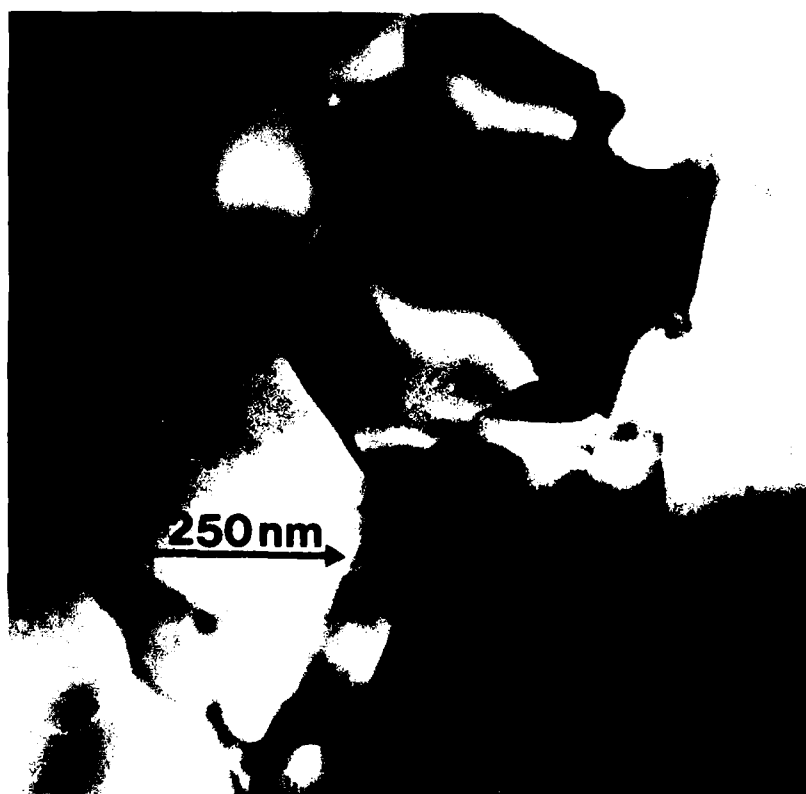
FIGURE 2 TRANSMISSION ELECTRON MICROGRAPH OF $\text{Si}_2\text{N}_2\text{O}$ CRYSTALLITE IN GLASS MATRIX IN JOINT REGION
Inset: electron diffraction pattern from $\text{Si}_2\text{N}_2\text{O}$. Zone axis approximately [012].



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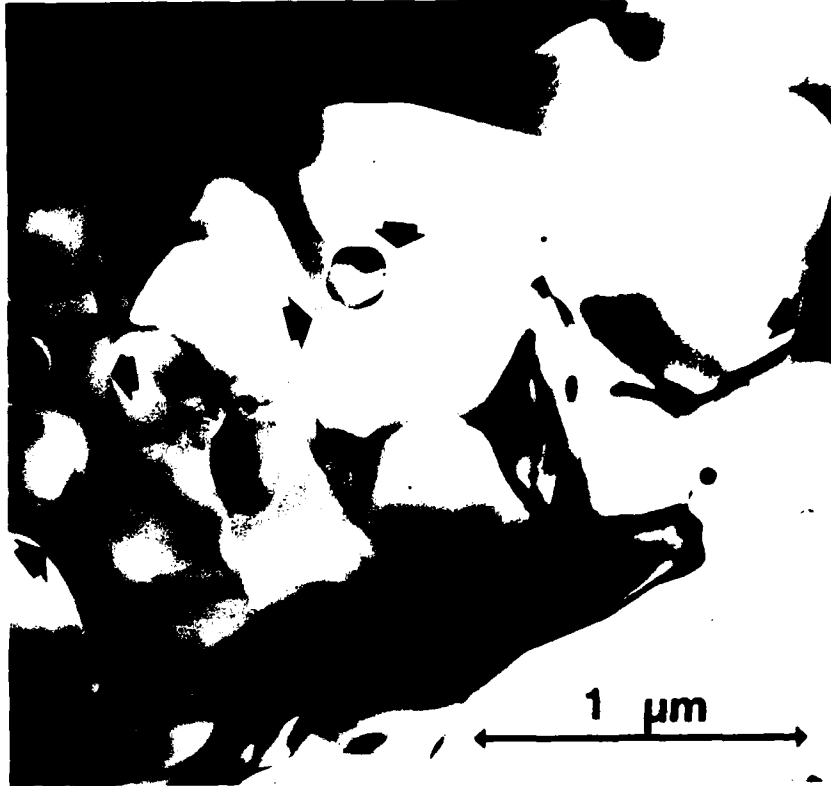
FIGURE 3 $\text{Si}_2\text{N}_2\text{O}$ CRYSTALLITES IN INTERFACIAL REACTION ZONE

Arrows indicate W-rich particles from WC contamination of the Si_3N_4 .



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FIGURE 4 MICROSTRUCTURE OF AS-RECEIVED Si_3N_4 CERAMIC SHOWING IT IS A MIXTURE OF $\beta\text{-Si}_3\text{N}_4$ GRAINS WITH GLASS AT THE 3- AND 4-GRAIN JUNCTIONS



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FIGURE 5 MICROSTRUCTURE OF CERAMIC AFTER JOINING,
ABOUT 100 μm FROM ORIGINAL INTERFACE

Shown are rounded β -Si₃N₄ grains and glass pockets
enlarged by diffusion of the joining composition.



(a)



(b)

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FIGURE 6 BRIGHT FIELD (6a) - DARK FIELD (6b) PAIR OF MICROGRAPHS SHOWING EXTENSIVE GLASSY REGIONS 25 μm INTO THE JOINED CERAMIC

Amorphous regions are in light contrast in the diffuse dark field micrograph.

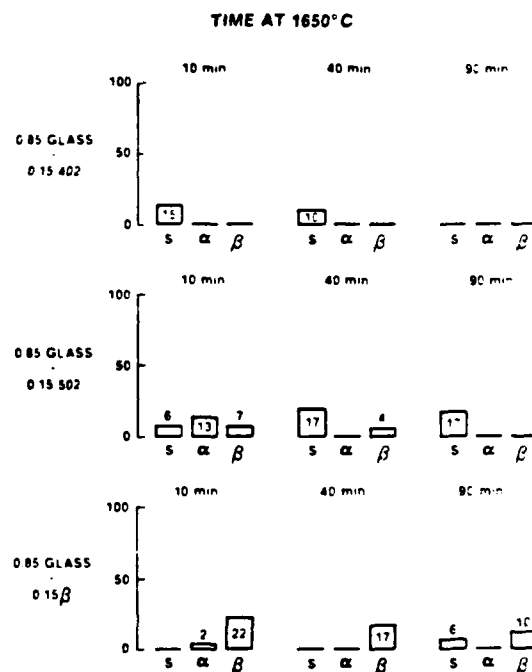


FIGURE 7a PHASES FOUND IN 15 wt% Si_3N_4 POWDER-85 wt% GLASS MIXTURES AFTER REACTION FOR THE INDICATED TIMES AT 1650°C

Glass = HN-9M (Table I) 402 = SN402 Si_3N_4^+ , 502 = SN502 Si_3N_4^+ ,
 $\beta = 90\% \beta$ -, $10\% \alpha$ - Si_3N_4^+ , bar graph labels: S = $\text{Si}_2\text{N}_2\text{O}$, $\alpha = \alpha$ - Si_3N_4 ,
 $\beta = \beta$ - Si_3N_4 .

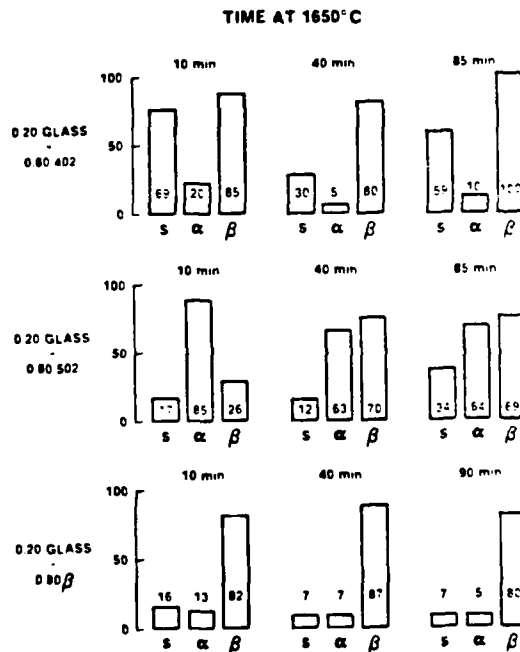


FIGURE 7b PHASES FOUND IN 80 wt% Si_3N_4 POWDER-20 wt% GLASS MIXTURES AFTER REACTION FOR THE INDICATED TIMES AT 1650°C

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