NASA CR-135291



# IMPROVED REACTION SINTERED SILICON NITRIDE

BY H. R. BAUMGARTNER

MARCH 1978

NORTON COMPANY
WORCESTER, MASSACHUSETTS 01606


PREPARED FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA LEWIS RESEARCH CENTER
CONTRACT NAS 3-19723

| 1. Report No. | 2. Government Accession No. | 3. Recipient's Catalog No. |
|---|---|---|
| NASA CR-135291 | | |

| 4. Title and Subtitle | 5. Report Date |
|---|---|
| IMPROVED REACTION SINTERED SILICON NITRIDE | March 1978 |
| | 6. Performing Organization Code |

| 7. Author(s) | 8. Performing Organization Report No. |
|---|---|
| H. R. Baumgartner | |
| | 10. Work Unit No. |
| | YHG-7746 |

| 9. Performing Organization Name and Address | 11. Contract or Grant No. |
|---|---|
| Norton Company<br>One New Bond Street<br>Worcester, Massachusetts 01606 | NAS3-19723 |
| | 13. Type of Report and Period Covered |
| | Contractor Report - Final |

| 12. Sponsoring Agency Name and Address | 14. Sponsoring Agency Code |
|---|---|
| National Aeronautics and Space Administration<br>Washington, D.C. 20546 | |

15. Supplementary Notes

NASA Technical Monitor, Thomas P. Herbell, NASA Lewis Research Center, Cleveland, Ohio

16. Abstract

Processing treatments were applied to as-nitrided reaction sintered silicon nitride (RSSN) with the purposes of improving strength after processing to above 350 $MN/m^2$ (50 ksi) and improving strength after oxidation exposure. The experimental approaches are divided into three broad classification: sintering of surface-applied powders, impregnation of solutions followed by further thermal processing and infiltration of molten silicon and subsequent carburization or nitridation of the silicon. Of the three approaches, the solution method was the most successful in achieving program goals, although difficulties were encountered with experimental reproducibility.

The impregnation of RSSN with solutions of aluminum nitrate and zirconyl chloride, followed by heating at 1400-1500°C in a nitrogen atmosphere containing silicon monoxide, improved RSSN strength and oxidation resistance. In the more successful cases, the room temperature bend strength of RSSN was increased nearly fifty percent above the untreated strength with mean absolute strengths up to 420 $MN/m^2$. Likewise, strengths of treated samples that were measured after a 12 hour oxidation exposure in air were up to 90 percent of the original as-nitrided strength, as compared to retained strengths in the range of 35 to 60 percent for untreated RSSN after the same oxidation exposure.

| 17. Key Words (Suggested by Author(s)) | 18. Distribution Statement |
|---|---|
| Reaction Sintered Silicon Nitride<br>Oxidation Resistant Treatments<br>Ceramic Strength | Unclassified - unlimited |

| 19. Security Classif. (of this report) | 20. Security Classif. (of this page) | 21. No. of Pages | 22. Price* |
|---|---|---|---|
| Unclassified | Unclassified | 75 | |

* For sale by the National Technical Information Service, Springfield, Virginia 22161

## ACKNOWLEDGEMENTS

This report covers activities carried out by Norton Company, Worcester, Massachusetts, 01606, under NASA Contract NAS3-19723. The Program Manager for the research was Dr. Thomas P. Herbell, NASA-Lewis Research Center, Cleveland, Ohio. 44135.

The author wishes to thank Dr. Stephen D. Hartline of Norton for his many helpful technical discussions and his contributions to the experimental work on the sintering of powder coatings.

## TABLE OF CONTENTS

TABLE OF CONTENTS
(continued)

## LIST OF FIGURES

## LIST OF TABLES

## LIST OF TABLES
(continued)

# I SUMMARY

The goals of the program were to achieve simultaneously a Reaction Sintered Silicon Nitride (RSSN) with improved room temperature strength and improved oxidation resistance such that the material's strength would not be adversely affected by oxidation exposure. The approach sought to effect these changes was the application of densified coatings to the surface of as-nitrided RSSN. Such coatings are expected to improve RSSN strength by a reduction in the size of critical flaws, which are located on the as-nitrided surface, and to improve oxidation protection by closing the open porosity of the RSSN, thereby reducing the surface area available for oxidation attack. In addition to being dense and continuous, other criteria for successful coatings are that they be mechanically and chemically stable and compatible with the RSSN.

The RSSN materials were fabricated by slip casting techniques and had nitrided densities of 2.2 and 2.6 g/cm$^3$. Bend bars (3.18 x 6.35 x 38 mm) were used as the specimens of the program and coatings were applied to them. Flexural strength after processing, as measured in 4-point bending, was the principal method used to evaluate the effectiveness of a given post-nitridation treatment. Other tools used to characterize the coatings were weight changes during processing, x-ray diffraction methods for crystalline phase identification, optical and scanning electron microscopy and an energy dispersive microprobe.

Coatings which demonstrated an ability to improve the strength of RSSN were evaluated for their ability to provide protection against the effects of oxidation, as measured by retained strength after a standardized oxidation exposure. A twelve hour exposure in air at 1250°C was selected for the evaluation because the 1200°C-1300°C temperature interval was found to produce the greatest strength degradation of as-nitrided RSSN.

A large variety of methods were attempted to form suitable coatings for RSSN. These methods are grouped into the three main classifications: 1) sintering of surface-applied powders, 2) infiltration of silicon followed by the carburization or nitridation of the molten silicon and 3) impregnation of soluble precursors which were decomposed to oxides and then further reacted by appropriate higher temperature processing.

The group of surface-applied coatings included powders of silicon, magnesium silicide, silicon oxynitride, various silicon aluminum oxynitrides, cordierite, spodumene, mullite and zircon plus the use of precursors to form in situ some of the above compounds. The fine powders were applied to the RSSN specimens by either brushing or immersion in suspensions and then processed at elevated temperatures in an attempt to achieve densification.

The furnace atmosphere during the thermal processing was usually nitrogen but air firings were also used in selected cases.

A common characteristic of all approaches in this classification is that the strengths after post-nitridation processing never exceeded the original as-nitrided strength and were much less than the initial RSSN strength in many cases. Aside from processing related strength degradation, other reasons for coating unsuitability were lack of densification and poor adhesion. The poor strengthening prospects for sintered powder coatings caused this approach to be abandoned and oxidation resistance testing was not conducted on these coatings.

The second major approach to produce surface layers on RSSN involved the infiltration of molten silicon and subsequent attempts to form a dense surface of either silicon carbide or silicon nitride. Thin layers of silicon powder were applied to RSSN specimens and then infiltrated into the surface of the RSSN by heating at 1500°C for thirty minutes while under a mechanical pump vacuum. The siliconized surfaces were either carburized by heating at 1450°C in an evacuated furnace with a carbon element and oxide insulation or nitrided at 1450°C under nitrogen.

Successful infiltration of the silicon was found to be highly dependent upon the atmospheric conditions of the siliconizing step. The atmospheres investigated were vacuum, argon, 95 percent argon/5 percent hydrogen and low partial pressures of nitrogen. Of these, only the vacuum processing permitted good wetting and infiltration of the silicon. The conditions for successful siliconizing also produced minor weight losses and major strength losses, of approximately half of the as-nitrided strength, in the samples. Strengths tended to recover somewhat from these very low levels during the carburization or nitridation treatment, but fully processed strengths were still low.

The third major method of coating production involved the use of soluble oxide precursors. Solutions were chosen in order to effect a deeper treatment and to provide more finely divided and reactive powders. The solutions were introduced into the RSSN under hydrostatic pressure and decomposed to the oxide form by a slow thermal treatment in air. The impregnated specimens were processed further at higher temperatures under a nitrogen or a nitrogen and silicon monoxide atmosphere. Organometallics and inorganic salts were used as oxide precursors.

The mixed oxides enstatite, mullite and zircon were investigated with high temperature firings in the range of 1400-1740°C. Specimens tended to lose strength and experience greater weight losses with increasing firing temperature. Minor strengthening of the mixed oxide impregnated samples were occasionally observed after firings at 1400°C-1500°C. However, experimentation with

mixed oxides for strength enhancement purposes was terminated when the use of single oxides produced higher strengths.

Precursor solutions of alumina, zirconia (both unstabilized and stabilized forms), titanium dioxide and yttria were investigated in the single oxide impregnation studies. Bend strengths in excess of 350 $MN/m^2$ were obtained by processing specimens impregnated with either aluminum nitrate or zirconyl chloride solutions. The best strengths were obtained when specimens were fired near 1400°C for a few hours under a nitrogen atmosphere containing silicon monoxide. A study of specimen weight gains in nitrogen and argon atmospheres plus x-ray diffraction patterns of the bar surfaces led to the conclusion that both nitrogen and silicon monoxide are co-reactants with the oxide during the firing treatment. The product of this reaction could not be identified as a crystalline phase by x-ray diffraction methods and is believed to be an amorphous oxynitride.

The treatments involving the oxide impregnations were evaluated for their ability to reduce the adverse effects of oxidation on RSSN. In general, the oxide treatments did provide some oxidation protection in the form of lower weight gains during oxidation and higher strengths after oxidation as compared to untreated samples. In the more successful treatments, up to ninety percent of the as-nitrided strength was retained by treated samples after the oxidation exposure as contrasted to 35-60 percent for untreated samples.

Difficulties in experimental reproducibility were encountered with the use of oxide impregnations for both strengthening and oxidation protection. For ostensibly identical treatments, separate strengthening runs produced material strengths ranging from slightly below to up to 59 percent stronger than the original as-nitrided strengths. Similarly, in the oxidation series, a given treatment would produce marginally to significantly greater strengths after oxidation than those obtainable on untreated specimens. The cause(s) of this variability was not determined.

## II INTRODUCTION

Reaction Sintered Silicon Nitride (RSSN) is a ceramic that is of much interest for its high temperature structural uses. RSSN is made by the nitridation of silicon powder bodies. The absence of appreciable dimensional changes during nitridation is of significant economic advantage. It permits the final shape to be formed in the green, or unnitrided, state by a variety of fabrication methods, such as, cold pressing, slip casting, and injection molding, and thereby eliminates expensive post-nitridation machining operations for all dimensions except those with very critical tolerances. Nitrided densities up to about $2.6 \times 10^{-3}$ $Kg/m^3$, or with approximately 20 percent porosity, may be prepared.

Because of its porosity, the room temperature strength of RSSN is less than that of fully dense, hot-pressed silicon nitride (HPSN). However, because RSSN is made without the additives used to densify HPSN, RSSN has superior high temperature properties, e.g. strength, creep and stress-rupture, as the additives adversely effect these properties.

At the beginning of the program, the mean strength of state of the art RSSN in the as-nitrided surface condition and measured in 4-point bending was approximately 240-275 $MN/m^2$. The strength of the better strength RSSN is controlled by surface flaws which originate in a thin, near-surface layer, of depth approximately 150 micrometers, on the as-nitrided surface. The physical density of this flaw zone is less than that of the interior material and arises during the nitridation process as a result of volatilization from the RSSN. For structural purposes, a higher strength RSSN is desireable, and therefore one of the goals of the program was to improve the room temperature strength of RSSN (as-nitrided surface in 4-point bending) to 350 $MN/m^2$.

Silicon nitride is thermodynamically unstable in a high temperature oxidation environment. However, pure and dense silicon nitride has excellent resistance to oxidation because of the formation of a passivating silica film, as is evidenced by the oxidation of CVD layers of silicon nitride. The oxidation of RSSN is more extensive because of its porosity and high surface area. The extent of oxidation is especially acute with as-nitrided RSSN because of the lower density and increased surface area of the near-surface layer. The results of oxidation in the 1200°C-1300°C temperature range on the strength of as-nitrided RSSN have been found to be especially severe. Up to two-thirds of the original room-temperature strength of as-nitrided material may be lost after a twelve hour oxidation in air at 1250°C. The 1200°C-1300°C temperature interval is within the intended use range of RSSN. Although the detrimental effects of oxidation are less severe for RSSN with machined surfaces, the use of machining after nitridation significantly affects the economics of RSSN. The second goal of the program was to optimize the strength of RSSN after oxidation. It was recognized that the two facets of RSSN strength improvement had to be achieved simultaneously.

Since both the strength and oxidation behaviors are related to the condition of the RSSN surface, post nitridation surface treatments of the RSSN, intended to densify the surface and thereby simultaneously reduce flaw severity and form an oxidation barrier, were chosen as the method of approach to the goals. These surface modifications were applied to the as-nitrided RSSN surface and took three main experimental branches: a) the sintering of powder coatings, b) the impregnation of salt solutions, which were decomposeable to oxides, and subsequent thermal processing and c) the infiltration of molten silicon and its later carburization or nitridation.

## III RSSN MATERIAL PREPARATION AND DESCRIPTION

Specimen preparation began with slip casting silicon powder into 11 x 13 x 0.5 cm open faced plaster molds. The dried plates were given a light sintering treatment at 1100°C under argon to impart green body strength prior to machining specimen bars of dimensions 3.18 x 6.35 x 38 mm. A total of three nitridations, widely spaced in time, were used to produce the approximately 1000 specimens used in the program. The same silicon powder lot was used in all the slip casting. RSSN of nominal density 2600 $kg/m^3$ was produced in all three nitridations. RSSN of nominal density 2200 $kg/m^3$ was produced in the first two nitridations.

Characterization of the as-nitrided RSSN appears in Table 1. Material densities were determined from sample weights and micrometer measurements on the machined as-nitrided bars. Material strengths were measured in 4-point bending with the samples in the as-nitrided surface condition. The successive strength increases in the 2600 $kg/m^3$ densities is attributed to improved nitriding procedures. The reported strength values are for unbevelled bar edges; strength measurements on bars whose edges were bevelled before nitriding showed only small strength differences from bars not bevelled. The alpha to beta silicon nitride phase ratio and the presence of phases other than silicon nitride was determined by x-ray diffraction methods on pulverized samples. Further details on strength testing and x-ray techniques are given in subsequent sections.

The surfaces of the RSSN specimens were covered with a thin layer of alpha silicon nitride fibers after nitriding. These fibers form on the surface and outside the envelope of the original silicon compact and are formed by a vapor phase mechanism believed to be the interaction of silicon monoxide with nitrogen.[1][1] The subsurface of the RSSN, to a depth of 0.05-0.15 mm, is of lower density than the underlying bulk material and is the source of the silicon vapor species for the formation mechanism of the surface fibers.

In the absence of more severe internal flaws, the low density skin is the origin of fracture initiation. Both the surface fibers and the less dense subsurface are susceptible to accelerated oxidation.

It was usual practice to remove the surface fibers by mild rubbing prior to post-nitridation treatments. This removal does not affect the strength of the as-nitrided material. The fibrous surface coat was left intact for a limited number of experiments.

[1]Numbers in brackets refer to references; superscripts refer to footnotes.

TABLE 1 - CHARACTERIZATION OF SLIP CAST RSSN

AS-NITRIDED STRENGTH DATA

| | Density ($kg/m^3$) | Mean Strength; Std. Dev. ($MN/m^2$) | Sample Size | $\alpha/\beta$ $Si_3N_4$ Ratio | Non-$Si_3N_4$ Phases Detected |
|---|---|---|---|---|---|
| SC-I-LD | 2220 | 191; 33 | 3 | 4.0 | None |
| SC-I-HD | 2580 | 231; 24 | 3 | 0.92 | Si ~10-15%<br>$Si_2ON_2$-Trace |
| SC-II-LD | 2170 | 170; 13 | 5 | 4.0 | $Si_2ON_2$-Trace<br>Si-Trace |
| SC-II-HD | 2610 | 290; 28 | 5 | 1.6 | Si ~4%<br>$Si_2ON_2$ ~2% |
| SC-III-HD | 2600 | 353; 47 | 10 | 1.7 | Si ~4%<br>$Si_2ON_2$ ~2% |

Typical Spectrographic Chemical Analysis of Metallic Impurities in RSSN (w/o)

| Al | Ca | Fe | Mg | Ti |
|---|---|---|---|---|
| 0.20 | 0.02 | 0.30 | 0.01 | 0.13 |



REPRODUCIBILITY OF THE ORIGINAL PAGE IS POOR

RSSN material made by the slip casting route was the predominant experimental material. Occasionally, isostatically compacted and nitrided RSSN was used for certain experiments when the supply of slip cast specimens was low. The use of this material is made clear in the text. In no cases are basic conclusions regarding the effectiveness of a given treatment believed to have been applicable only to the alternate RSSN.

## IV EQUIPMENT

### A. STRENGTH TESTING

Material strength as a function of post-nitridation processing was the primary tool used to evaluate the effectiveness of the processing. Specimens were broken in a 4-point, quarter point loading bend fixture of previously described design [2] which minimizes testing errors arising from specimen misalignment. The outer bend span was 2.54 cm. A mechanical testing machine[1] with a crosshead speed of 0.051 cm/min was used to break the specimens. Generally, three fractures were used to establish the mean strength of a given processing procedure. Occasionally, more or fewer breaks were performed, as, for example, when specimens broke in processing or a smaller number of bars were used to survey a procedure.

### B. HIGH TEMPERATURE FURNACING

Three types of furnaces were used to process the treated samples. The type most frequently used was high temperature alumina[2] muffle tubes powered with silicon carbide heating elements. A two inch internal diameter alumina tube furnace, termed the T-furnace, was used for most of the thermal processing and for oxidation experiments in air. This furnace could be operated at temperatures up to 1700°C for short runs. A second furnace, termed the C-furnace, consisted of an internal carbon resistance element and alumina fiber insulation within a water cooled shell. The temperature of both above furnace types was controlled with thermocouples. A third furnace, called the S-furnace, was used whenever temperatures in excess of 1700°C were required. It was a graphite susceptor induction furnace with an alumina crucible internal liner. The temperature of the S-furnace was controlled by the power input and was measured by an optical pyrometer. All furnaces had mechanical roughing pump vacuum capability and inlets for gas atmospheres.

### C. X-RAY DIFFRACTION AND OTHER EQUIPMENT

X-ray diffraction patterns were used to characterize the starting RSSN material and to monitor phase changes as a result

[1] Instron Company, Canton MA
[2] McDanel Refractory Porcelain Co., Beaver Falls, PA

of post-nitridation processing. The x-ray equipment[1] consisted of Ni filtered Cu Kα radiation, vertical rotating goniometer, focusing monochromator scintillation detector and strip chart recorder. Two theta angles from 10-80° were scanned at two degrees per minute. Bulk analyses were made by the powder method after crushing specimen bars. Phase changes as a result of postnitridation processing were followed by diffraction patterns obtained from the external surface of specimen bars placed on the goniometer axis. Phase identification studies were run at high intensity (35 KV, 15 mA) and the resulting patterns were indexed according to the ASTM file, standard internal file patterns, or literature values.

The amounts of crystalline phases present are expressed in qualitative form according to the code below. The relative height of major peaks of phase on the x-ray chart (full scale = 100) are used as the guide to the amounts present.

| Amount Present | Peak Height |
|---|---|
| Major | Greater than 75 |
| Moderate | Between 25 and 75 |
| Minor | Between 10 and 25 |
| Trace | Between background and 10 |
| ND | No peaks or phase detected |

The alpha silicon nitride phase fraction determinations were made at low intensity (30 KV, 10 mA) using the heights above background of the 101 and 201 alpha peaks and the 200 and 101 beta peaks according to the formula [3]:

$$\text{Alpha Fraction} = \frac{\alpha 101 + \alpha 201}{\alpha 101 + \alpha 201 + \beta 200 + \beta 101}$$

The $\alpha/\beta$ ratio may be readily calculated

In addition to conventional optical microscopy, specimens were also examined by scanning electron microscopy[2] and an energy dispersive microprobe[3].

## V DENSIFICATION OF SURFACE-APPLIED POWDER COATINGS

### A. NITRIDABLE POWDERS: SILICON AND DI-MAGNESIUM SILICIDE

Surface layers denser than those on as-nitrided RSSN were sought by applying coatings of silicon and di-magnesium silicide [4] powders to RSSN bars and performing a second nitridation. Preliminary experiments indicated poor adhesion between the

[1] Philips Electronic Instruments, Mount Vernon, NY
[2] AMR, Model 1000, Burlington, MA
[3] Nuclear Diodes, Model 707, Prairie View, IL

freshly nitrided layer and the underlying RSSN. Attempts were made to improve the adhesion by preconditioning the RSSN samples prior to powder coating by either etching the RSSN or immersion in solutions of iron or magnesium ions. The preconditioning steps are listed in Table 2.

TABLE 2. - STRENGTH RESULTS FOR SC-I-HD RSSN WITH NITRIDED COATINGS.

| Powder Coating | Preconditioning Treatment | Mean Strength ($MN/m^2$) | (Std.Dev.) |
|---|---|---|---|
| Si | None, as-nitrided | 176 | (39) |
| Si | Etched in HF, washed, dried | 103 | (3) |
| Si | Immersed in conc. aq. soln. of $Fe(NO_3)_3$, dried | 95 | (19) |
| Si | Etched in HF, immersed in conc. aq. soln. of $MgF_2$, dried | 143 | (27) |
| Si | Immersed in conc. aq. soln. of $MgF_2$, dried | 84 | (20) |
| Si | Vacuum assisted infiltration of strong aq. soln. of $Mg(C_2H_2O_2)_2 \cdot 4H_2O$, dried | 119 | (12) |
| Si | Same as above last plus air decomposition of acetate at 650°C | 137 | (29) |
| None | Controls cycled with Si coating nitridation | 238 | (21) |
| $Mg_2Si$ | None, as-nitrided | 128 | (4) |
| $Mg_2Si$ | Etched in HF, washed, dried | 142 | (45) |

Approximately 0.010-0.015 cm thick coatings of three micron silicon[1] particles were applied to bars by dipping in a water based slip. Approximately 0.005 cm thick layers of di-magnesium silicide[2], ball milled to an average particle size of less than five microns, were brushed onto bars from an acetone slurry. Three bars per variation were prepared.

[1]Union Carbide Corp, NY, NY
[2]Gallard Schlesinger Chemical Mfg. Corp., Carle Place, NY

The coated specimens were nitrided in the C-furnace within an inverted high purity alumina crucible placed directly over the flowing nitrogen gas inlet. The silicon coatings were nitrided in a series of steps: six hours at 1150°C, eight hours at 1250°C, fifteen hours at 1350°C and finally five hours at 1400°C. The $Mg_2Si$ coatings were nitrided according to the schedule: eight hours at 650°C, twelve hours at 900°C and eight hours at 1200°C. The nitrided coatings on the bars with the $Mg_2Si$ powder were extensively covered with cracks and tended to delaminate from the RSSN. The appearance of the silicon bars was visually unremarkable. X-ray diffraction patterns from the bars' surfaces showed complete nitridation; the silicon converted to a mixture of the alpha and beta $Si_3N_4$ phases, while the $Mg_2Si$ converted to $MgSiN_2$ and a mixture of alpha and beta $Si_3N_4$.

The strengths results for the nitrided coatings are shown in Table 2. As may be seen by the control comparison, all treatments resulted in a strength reduction; all individual treated bar strengths were less than the mean as-nitrided or mean cycled control strength. The weakness of the interfacial bond between the RSSN bars and the freshly nitrided coatings was manifested by a tendency, more pronounced with the $Mg_2Si$ bars, to delaminate during fracture testing. The preconditioning treatments did not improve strength and were detrimental in some cases.

Scanning electron microscopy of the nitrided silicon layers (see Figure 1) showed a granular RSSN as contrasted to the well developed alpha matte in the original RSSN bar. This granular structure has been associated with reduced RSSN strength. In addition, trapped air bubbles from the slip dipping process sometimes caused pore formation at the old/new RSSN interface which also contributed to strength reductions. The grain size in the nitrided $Mg_2Si$ layers were finer but little densified.

The granular RSSN arises from the conditions of nitriding. Additional silicon slip coated specimens were renitrided in another nitriding furnace during the preparation of the second batch slip cast specimens. Although a somewhat better interfacial bond and the alpha matte structure were established, these bars exhibited essentially the same strength as the original RSSN material. Work on nitrided coatings was terminated because of the inability to achieve strength improvements or a significantly denser surface.

## B. COATINGS CONTAINING SILICON OXYNITRIDE

Silicon oxynitride is of interest as a coating material for RSSN because it is in phase equilibrium with silicon nitride in the Si-Al-O-N quaternary system [5] and is the equilibrium adjacent phase to silicon nitride under oxidizing conditions. The silicon oxynitride powder[1] had a three micron average particle

[1]Norton Company, Worcester, MA 01606

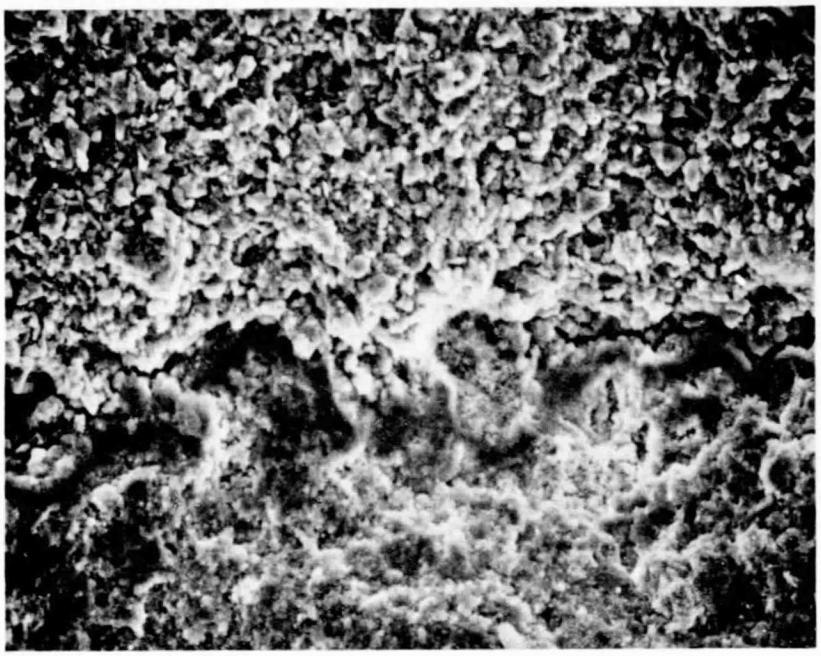


Figure 1. - Interface of substrate (bottom) and fresh RSSN. SEM, 500X. Note interfacial separation.

size and was of 95 percent purity. The remaining five percent consisted mainly of silica and alpha and beta silicon nitride. Approaches using silicon oxynitride powder included attempted sinterings of coatings with sintering aids and the manufacture of powders of beta prime silicon nitride solid solutions which were then used in surface coatings.

1) Sintering of $Si_2ON_2$ with Additives - Silicon oxynitride has reportedly been sintered to nearly theoretical density by the use of oxide additives [6]. Silicon oxynitride powder was mixed and ground in acetone with five weight percent of the following additives: MgO, $CaF_2$, $CeO_2$, B, $Y_2O_3$ and $Al_2O_3$. Thin surface powder coatings were applied to non-slip cast RSSN by dipping bars into the suspensions. The samples were fired in the S-furnace, after the furnace was evacuated and back-filled with 0.7 atm of nitrogen gas, for either 30 minutes at 1600°C or one hour at 1700°C. A mixture of silicon and silica powders was placed at the bottom of the container crucible to generate silicon monoxide, which, together with the nitrogen, tends to suppress decomposition of the oxynitride.[7]

The bend strengths of these samples after firing are shown in Table 3. The processed strengths were generally less than the

TABLE 3. - FIRED BEND STRENGTHS ($MN/m^2$) OF RSSN WITH $Si_2ON_2$ CONTAINING COATINGS

| Sample | Strength After 1/2 hr at 1600°C | Strength After 1 hr at 1700°C |
|---|---|---|
| A. Sintering Aids | | |
| $Si_2ON_2$ + 5% MgO | 164, 212, 250 | 194, 210 |
| $Si_2ON_2$ + 5% MgO (water suspension) | 155, 186 | - |
| $Si_2ON_2$ + 5% $CaF_2$ | 196, 230 | - |
| $Si_2ON_2$ + 5% $CeO_2$ | 209, 210 | 197, 217 |
| $Si_2ON_2$ + 5% B | 224, 250 | 153, 218 |
| $Si_2ON_2$ + 5% $Y_2O_3$ | - | 249, 256 |
| $Si_2ON_2$ + 5% $Al_2O_3$ | - | 196, 204 |
| B. Silicon Aluminum Oxynitride | | |
| Stoichiometric mix + 5% MgO | 128, 250 | 163, 182 |
| Stoichiometric mix + 5% $CeO_2$ | 188, 235 | 154, 187 |
| Al deficient mix + 5% MgO | 197, 246 | - |
| Al excess mix + 5% MgO | 105, 214 | |
| C. Untreated Control Strength = 259 ± 26 $MN/m^2$ | | |

untreated strength of 259 $MN/m^2$. The best strengths resulted from the yttria additive samples, which did not have a reduced strength. Very little sintering or densification occurred for any of the coatings; all coatings could be scraped off with a sharp tool.

Since the densification obtained was significantly less than that reported in Reference 6, subsidiary experiments were conducted to investigate the effect upon densification of a higher green density and better suppression of the silicon oxynitride decomposition, both of which were used in the referenced study. Cylindrical pellets, of 2.5 cm diameter, containing silicon oxynitride and five weight percent magnesium oxide were die pressed at three pressures. Two pellet stacks of three pellets each were placed within a crucible and covered with silicon oxynitride powder.

The samples were fired for one-half hour under nitrogen in the S-furnace. Initial and fired pellet densities are shown in Table 4.

TABLE 4. - INITIAL AND FIRED DENSITIES FOR $Si_2ON_2$ + 5 w/o MgO PELLETS

| Pressing Pressure ($MN/m^2$) | Green Density (g/cc) | Fired Density (g/cc) | Density Change (%) |
|---|---|---|---|
| 8.3 | 1.09 | 1.58 | 45 |
| 8.3 | 1.09 | 1.62 | 49 |
| 34 | 1.25 | 1.89 | 51 |
| 34 | 1.25 | 1.92 | 54 |
| 62 | 1.32 | 1.87 | 42 |
| 62 | 1.32 | 1.90 | 44 |

Significant amounts of sintering did occur, but the sintered densities are far less than those achieved in Reference 6 under similar conditions. Possible reasons for this discrepancy are silicon oxynitride powder purity differences, the use, in the current study, of a packing powder of different composition (without sintering aid) from the powder to be densified, or lower green densities.

In a final attempt to densify the oxynitride powder with an oxide additive, a powder coating containing ten weight percent magnesium oxide was applied. The coated bars were encased in a wax jacket to hold the coating in place while it was compacted under isostatic pressure of 138 $MN/m^2$. Wax removal was accomplished by a low temperature burn-off in air. The coated bars were embedded in a powder of the same composition as the coating material and fired for one hour under slightly flowing nitrogen at 1650°C in the alumina tube furnace.

This thermal treatment did cause more coating densification than what had been previously observed and the greater degree of sintering is attributed to either a greater amount of liquid phase formation as a result of using more additive or a higher green density. The coating did not adhere well to the RSSN substrate, partially because the coating tended to delaminate during the wax burn off.

Strengths after treatment were 109 and 117 $MN/m^2$, well below the as-nitrided strength of 170 $MN/m^2$ for the starting RSSN. Most importantly, the bars were found to be noticeably warped upon removal from their packing powder. This distortion is attributed to a high vapor pressure species containing magnesium. Since the deformation occurred under minimal stress, the attainment of improved RSSN may not be achieved by this method, as interior creep-stress rupture properties would result.

2) Coatings of Silicon Nitride Solid Solutions from Silicon Oxynitride - In another approach to produce coatings with the use of silicon oxynitride, silicon nitride solid solutions were formed by the reaction [8]:

Eqn 1

$$Si_2ON_2 + Al + 1/2\ N_2 \rightarrow Si_2AlON_3$$

Acetone suspensions were prepared by grinding together powders of silicon oxynitride, atomized aluminum and five weight percent of a sintering aid, either magnezium or cerium oxide. The ratio of silicon oxynitride to aluminum in the powder mixtures was varied from stoichiometric (as defined by Equation 1) to either an aluminum excess of deficiency on the order of five percent in order to investigate its potential effect upon sintering. Coatings were applied to the RSSN by dipping in the suspensions.

Firing conditions were identical to those used to fire the previously described coatings of oxynitride powders with sintering aids. Post firing strength results are presented in Table 3. Again, processed strengths were generally lower than the as-nitrided, untreated material and the coatings showed little tendency to adhere or densify

In another experiment, coatings of pre-reacted powders of silicon nitride solid solutions were used to form coatings. The powders had been previously prepared by the idealized reaction.[8] $(4-x)Si_2ON_2 + (x-2)SiO_2 + XAl + (x/2)N_2 \rightarrow Si_{6-x}Al_xO_xN_{8-x}$, where $Si_{6-x}Al_xO_xN_{8-x}$ defines the stoichiometric solid solution[9]. The analytically determined compositions of these powders are shown in Table 5. Composition A corresponds to the pure solution $Si_2AlON_3$. While all powders gave essentially pure x-ray diffraction patterns of the solution series, minor amounts of the "J" phase[1] of equivalent composition $Si_3N_4 \cdot 5\text{-}6Al_2O_3 \cdot 3SiO_2$ [10] and another unidentified phase were detected in the patterns for Composition B and C. Furthermore the chemistry of these latter powders puts them outside the single phase region defined by $Si_{6-x}Al_xO_xN_{8-x}$.

A smooth coating of the powders was painted onto higher density RSSN bars from an acetone and powder slurry. No sintering additives were used. The samples were then fired in an alumina tube furnace at 1700°C for two hours in nitrogen.

[1]This phase has also been referred to as the $X_1$ phase (Ref 5) or as the X phase by K. H. Jack [17].

TABLE 5 - CHEMICAL COMPOSITIONS OF $Si_3N_4$ SOLID SOLUTION POWDERS

| Composition | Chemical Analysis (wt%) Si | Al | O | N |
|---|---|---|---|---|
| A | 37.2 | 22.5 | 13.7 | 26.3 |
| B | 35.2 | 22.7 | 18.6 | 27.2 |
| C | 31.2 | 26.0 | 21.4 | 23.8 |

The fired powders showed no tendency to densify or adhere to the RSSN and could be easily rubbed off. The resultant strengths for the bars were 191,232 and 270 $MN/m^2$ for Compositions A, B and C, respectively, as compared to a mean as-nitrided strength of 290 $MN/m^2$.

C. OTHER POWDER DERIVED COATINGS

1) Nitrogen Atmosphere Firings - This section describes attempts to form acceptable coatings from a) mixed oxide powders (zircon, mullite, spodumene, cordierite), b) various precursors intend to form in-situ oxides (alumina, zircon, mullite) during firings and c) "J" phase powder. All firings were done under nitrogen. The following processing details are keyed with letters which correspond to the letters used in Table 6, which presents processed strengths and firing details.

a) Spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$) - After ball milling the initial 200 mesh spodumene[1], coatings of the material were applied to RSSN by dipping in an acetone suspension. Firings were conducted for six hours at 1250°C and two hours at 1500°C. The fired coatings densified and adhered well to the RSSN, however, the resultant strengths were poor, especially for the higher temperature firing.

b) Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) - The cordierite frit[2] was ball milled, with and without eight weight percent of titanium dioxide, and acetone suspensions were prepared. Coatings were applied either by dipping or brushing; those prepared by the former method were about 0.006 cm thick while those prepared by the latter were about 0.03 cm thick. Firings were conducted for an additional twelve hours at 1300°C. All coatings were visually well reacted and had good adherence. However, no indications existed for RSSN strength enhancement. The thicker coatings exhibited a significantly lower strength which may have been caused by differential thermal expansion stresses.

[1] Foot Mineral Company, Exton, PA
[2] Ferro Corp., Cleveland, OH

TABLE 6 - STRENGTHS AND NITROGEN FIRING CONDITIONS FOR POWDER DERIVED COATINGS.

| Coating Material | | Time; Temperature of Nitrogen Firing (Hrs; °C) | Furnace Type | Mean As-Nitrided Strength ($MN/m^2$) | Individual Processed Strengths ($MN/m^2$) |
|---|---|---|---|---|---|
| a) Spodumene | | 6; 1250 | T | 231 | 150, 153 |
| " | | 2; 1500 | T | 290 | 79, 73 |
| b) Cordierite (thin layer) | 1) | 2; 1500 | T | 290 | 152, 267 |
| with 8% $TiO_2$ (thin layer) | 2) | 2; 1500 plus 12; 1300 | T | 290 | 222, 265 |
| with 8% $TiO_2$ (thick layer | 3) | 2; 1500 plus 12; 1300 | T | 290 | 56, 111 |
| c) Zircon | | 2; 1500 | T | 290 | 203, 250 |
| d) Zircon Precursors A | | 2; 1500 | T | 290 | 142, 154 |
| e) Zircon Precursors B | | 2; 1500 | T | 290 | 153, 164 |
| f) Alumina Precursor A | | 2; 1500 | T | 290 | 213, 218 |
| g) Alumina Precursor B | | 2; 1500 | T | 290 | 188, 225 |
| h) Mullite | | 2; 1500 | T | 290 | 201, 287 |
| i) Mullite Precursor A | | 2; 1500 | T | 290 | 203, 238 |
| j) Mullite Precursor B | | 2; 1500 | T | 170 | 71, 88 |
| k) "J" Phase | 1) | 2; 1650 | S | 290 | 204 |
| " | 2) | 2; 1740 | S | 290 | 166, 185 |
| " | 3) | 2; 1675 | T | 353 | 21, 26 |

c) Zircon ($ZrSiO_4$) - A fine zircon[1] powder was used to prepare layers by dipping in an acetone suspension. Firing was done at 1500°C for two hours.

d) Zircon Precursors A - A zirconia containing solution[2] was mixed with a silicone[3] source for silica and applied to RSSN bars with the intent of forming zircon during firing at 1500°C.

e) Zircon Precursors B - A stoichiometric mixture for zircon was made from fine zirconia powder[4] and ortho-ammonium silicate (OAS)[5], which was brushed onto RSSN specimens. Firings were made at 1500°C.

f) Alumina Precursor A - Alumina gel flakes[6] ($Al_2(OH)_5Cl \cdot 3H_2O$) were dissolved in water in order to form coatings by solution dipping. Firings were made at 1500°C.

g) Alumina Precursor B - An aluminum sulphate[7] suspension was created by grinding in acetone and was brushed onto bars for firing at 1500°C.

h) Mullite ($3Al_2O_3 \cdot 2SiO_2$) - A suspension of fine mullite powder[8] in acetone was brushed onto RSSN for firing at 1500°C.

i) Mullite Precursor A - A mullite forming suspension was prepared from alumina gel flake and colloidal silica[9] from which coatings were prepared by slip dipping to be fired at 1500°C.

j) Mullite Precursor B - An acetone suspension intended to form mullite was prepared from OAS and alumina powder and brushed onto bars for firing at 1500°C.

k) "J" Phase - A billet of the "J" phase, of equivalent composition $Si_3N_4 \cdot 6Al_2O_3 \cdot 3SiO_2$ [10] was hot pressed from a powder mixture of silicon oxynitride, alumina and fumed silica. The billet was crushed and ball milled to produce a fine powder. Preliminary experiments with coatings of this material indicated that although the powder showed a tendency to sinter at 1600°C, adhesion to the RSSN was minimal.

---

[1]NL Industries, ICD, Hightstown, NJ
[2]Zirbind A Solution, NL Industries, ICD
[3]Silicone SR 324, General Electric Company, Schenectady, NY
[4]Zircon, Solon, OH
[5]Philadelphia Quartz, Lock Haven, PA
[6]Hostachem Corp., Mountainside, NJ
[7]Fisher Scientific Co. Fair Lawn, NJ
[8]Carborundum Co. Niagara Falls, NY
[9]Ludox 130M, DuPont Co., Inc, Wilmington, DE

Further efforts with this material were directed at improving the adhesion by using an alumina rich layer between the RSSN and the applied "J" phase. The alumina layer was introduced by impregnating RSSN specimens with aluminum nitrate solutions. The following variations of the basic approach differ in the degree of thermal processing given to impregnated bars prior to the application of the "J" phase coating and in the final firing. In the first variation, dried impregnated bars were coated and fired in nitrogen at 1650°C. In the second variation, impregnated bars were dried in air to 600°C, coated, and then fired at 1740°C while buried in silicon nitride powder. In the third variation, impregnated bars were dried in air to 600°C, fired under nitrogen at 1400°C for three hours, coated, and finally fired at 1675°C under a nitrogen and a silicon monoxide containing atmosphere. The silicon monoxide was produced by an equimolar mixture of silicon and silica powder placed within the furnace. The degree of adherence increased in the sequence of the variations. In the final variation, the coatings tended to infiltrate the RSSN and produced a glassy interior. Resultant strengths were inferior in all cases.

Work on the above approaches was terminated because of the lack of encouraging strength results.

2) Oxidation of RSSN as Silica Source - Most of the coatings discussed in the preceding section contained added silica. In the present section, coatings of mixed oxides containing silica were attempted with the use of intentional oxidation of RSSN to provide the silica source. The non-silica oxides investigated were alumina, zircon, and enstatite, respectively. Salt solutions and powders were used to prepare the coatings.

In one experimental series, RSSN specimens were impregnated with concentrated water solutions of either aluminum nitrate[1] ($Al(NO_3)_3 \cdot 9H_2O$) or zirconyl chloride[1] ($ZrOCl_2 \cdot 8H_2O$). The bars were slowly heated in air to 600°C to dry and decompose the salts. The samples were then air fired for two hours at 1450°C. Resultant strengths for all intentionally oxidized specimens in this section are listed in Table 7.

In a second series, water slurries of alumina, zirconia and magnesia powders were brushed onto RSSN samples, which were then oxidized in air for twelve hours at 1400°C.

In the final series, specimens with powder coatings were prepared and oxidized as above, but were additionally processed to achieve a theoretically more stoichiometric mixed oxide (mullite, zircon, or enstatite, respectively). The specimens of the first two series were silica rich after oxidation. The stoichiometry change was made in the event the excess silica

[1] Fisher Scientific Company, Fair Lawn, NJ

TABLE 7 - STRENGTHS OF MIXED OXIDE COATINGS WITH INTENTIONAL OXIDATION OF RSSN

| Coating Description | Mean As-nitrided Strength ($MN/m^2$) | Processed Strength ($MN/m^2$) |
|---|---|---|
| I. Coatings prepared from salt solutions | | |
| a) $Al(NO_3)_3$ | 290 | 144, 196 |
| b) $Al(NO_3)_3$ | 170 | 31, 48 |
| c) $ZrOCl_2$ | 290 | 172, 212 |
| d) $ZrOCl_2$ | 170 | 22, 43 |
| e) Control oxidized with impregnated samples | 290 | 206 |
| II. Coatings prepared from powders | | |
| a) $Al_2O_3$ | 290 | 109, 143 |
| b) $ZrO_2$ | 290 | 240, 293 |
| c) MgO | 290 | 225, 265 |
| III. Coatings prepared from powders, adjusted stoichiometry | | |
| a) $Al_2O_3$ | 290 | 132, 154 |
| b) $ZrO_2$ | 290 | 126, 156 |
| c) MgO (adjusted for enstatite) | 290 | 199, 203 |

was causing a lower strength than might be expected from a more stoichiometric coating. The adjustment towards stoichiometry was made after the air oxidation. The amount of additional oxide powder necessary to achieve mixed oxide stoichiometry was calculated from the known initial oxide weight and the weight gain from oxidation. The assumption was made that the majority of silica formed was confined to a near-surface layer; a reasonable assumption considering the oxidation temperature. Although the amount of additional oxide added could not be precisely controlled, the amount of silica added by oxidation was generally within five percent of the stoichiometric amount of silica in the pertinent mixed oxide. The specimens were then fired an additional twelve hours at 1400°C under nitrogen.

The reduced strength of the control sample (i.e. in Table 7) illustrates the strength reduction associated with oxidized RSSN. Most treatments involving the oxidation of the RSSN resulted in lower strength than the oxidized control. The best strengths after oxidation were obtained with zirconia and magnesia powders that were unadjusted for stoichiometry. These results were not pursued because the emphasis was on strength improvements at the time these results were obtained and the processed samples did not show this sought improvement.

## D. EFFECT OF ALPHA TO BETA SILICON NITRIDE PHASE TRANSITION UPON RSSN STRENGTH

Alpha phase silicon nitride tends to irreversibly transform to the beta phase upon heating at elevated temperatures [11]. The transformation appears to be purity dependent and the alpha phase may exist even after extended times at high temperatures [12]. The phase transformation in RSSN was studied in order to investigate the hypothesis that the generally low strengths observed after high temperature processing were associated with the phase transformation, such as by the disruption of intergranular cohesion.

Machined bend bars of isostatically pressed RSSN were packed in silicon nitride powder and heated at 1650°C under a nitrogen atmosphere for times up to eight hours. The bars were strength tested and examined for alpha phase content by x-ray diffraction after the thermal treatment.

The results are summarized in Table 8. Significant transformation occurred sometime between four and eight hours under these conditions. No strength drop was associated with decreasing alpha content. Instead, there appears to be a mild strengthening trend. This behavior is contrary to the microstructural disintegration hypothesis.

TABLE 8 - EFFECT OF ALPHA TO BETA SILICON NITRIDE TRANSFORMATION UPON RSSN STRENGTH

| Treatment | Strength ($MN/m^2$) | % Alpha $Si_3N_4$ |
|---|---|---|
| As Machined | 116[1] | 79 |
| 2 hours at 1650°C | 137; 176 | 78 |
| 4 hours at 1650°C | 192; 191 | 77 |
| 8 hours at 1650°C | 177; 246 | 47 |

[1]Mean of four samples; standard deviation = 10 $MN/m^2$

## E. DISCUSSION OF SURFACE POWDER COATINGS AND RECOMMENDATIONS

Strength after processing was the main criteria used to evaluate the effectiveness of processing with surface powders. In no case was the processed strength greater than the initial unprocessed strengths and in the majority of cases the processed strength was significantly less. The strength reductions imply an adverse interaction between the RSSN and the coating materials as the strength of RSSN, by itself, does not degrade upon exposure to a nitrogen atmosphere. Because the as-nitrided strength of RSSN is high, its strength after post-nitridation treatments is very sensitive to processing interactions. Obviously, for a coating to be well bonded to RSSN, some interaction between the RSSN and the coating must exist. In addition to strength reasons, coatings were also found to be unacceptable because of poor densification and adhesion.

A variety of factors are believed to contribute to the poor densification of many of the powder coatings. Firstly, the physical densities of the coatings are relatively low as they are applied, a condition that is not conducive to a high final sintered density. Secondly, vapor pressures of many of the coating systems, for example the oxynitride approaches, are relatively high. Material losses from gases escaping from the system are expected to be more severe for thin layer, as opposed to bulk, densification. Some of the coating materials, i.e. the oxynitrides, are difficult to sinter and appear to require a liquid phase for appreciable densification [13]. Although densification aids were tried with limited success, the work on silicon oxynitride suggests that relatively more liquid phase formation is required for effective densification of thin or low density layers. The use of oxides introduces another complication in the form of oxide-nitride interactions which produce volative species of silicon monoxide and nitrogen, such as has been observed in heated mixtures of silicon nitride and alumina [14]. This interaction can result in significant weight losses which begin at relatively low temperatures and become larger with increasing temperatures. Since this type of reaction occurs at particle contact points, poor oxide adhesion to RSSN or powder sinterability may result from such an interaction.

As has been mentioned, work with supra-micron sized powders was terminated because the treatments did not show promise for strength enhancements. If this criterion were dropped, it is conceivable that some of the approaches would be useful in decreasing the susceptability of RSSN to strength reductions after oxidation. Of the methods investigated, the most promising approaches for improving oxidation resistance are expected to be those which produced minimal strength reductions. It is suggested that further research in the following areas may be beneficial:

1) Use of yttria as a sintering aid for silicon oxynitride coatings (Table 3).

2) Use of increased amounts (greater than 5%) of sintering aids for oxynitride coatings (Section IIIb1).

3) Higher strength processes of Table 6.

## VI COATINGS DERIVED FROM SOLUTIONS

### A. INTRODUCTION

In an effort that began in parallel with the use of surface powders, coatings were also generated from precursor solutions. The injection of liquids into the porosity of RSSN permits material modifications to a greater depth and utilizes more finely divided and reactive precursors. Solutions were used which, if heated by themselves in air, would form the single oxides of alumina, zirconia, titania or yttria or the mixed oxides of mullite, enstatite or zircon. Although the coatings are named after these theoretical reaction products for reasons of convenience, the nomenclature is not meant to imply that the names were the actual chemical species in the processed specimens. In many cases, because of the actual conditions of the high temperature firings, the final products were different from their names because of additional or incomplete reactions.

The solutions used in this study are listed in Table 9. Oxides were derived from both organometallic (O) and inorganic (I) precursors. Historically, the work began with mixed oxides from organometallic precursors and later shifted to the use of single oxides from inorganics.

Treated specimen preparation generally consisted of (a) the impregnation of the solutions into the RSSN, (b) the drying and decomposition of the impregnated samples in air, and (c) the high temperature firing of the samples, usually under a nitrogen atmosphere. Impregnation was effected by sealing RSSN specimens within plastic bags containing the solution and isostatically pressing at 140 $MN/m^2$ for about 45 minutes. Decomposition of the precursor chemicals to the oxides was accomplished by slowly heating to 600-700°C. It was demonstrated by thermogravimetric means that these temperatures were required to produce the decomposition. The rate of thermal decomposition of zirconyl chloride and magnesium acetate solutions was especially critical and required processing times on the order of days to prevent specimen damage arising from internal pressurization.

TABLE 9 - FORMULATIONS OF IMPREGNATION SOLUTIONS[a]

| Coating Type | Precursor Solution |
|---|---|
| Alumina | 0.9g $Al(NO_3)\cdot 9H_2O$[b]: 1 ml ethyl alcohol |
| Titania | Triethanolamine titanate[c] |
| Yttria | 1.33 g $Y(NO_3)_3\cdot 5H_2O$[d]: 1 ml ethyl alcohol |
| Zirconia (O) | Zirconium resinate[e] |
| Zirconia (I) | 2 g $ZrOCl_2\cdot 8H_2O$[b]: 1 ml water |
| Mullite | 5.8 ml alumina solution: 1 ml ethyl silicate[f] |
| Spinel | 1g Mg $(C_2H_3O_2)_2\cdot 4H_2O$[b]; 1.86 g Al $(NO_3)_3\cdot 9H_2O$[b]: 3.2 ml water |
| Enstatite (O) | 1.68 g magnesium resinate[g]: 1 g silicon resinate[h] |
| Enstatite (I) | 1 ml ethyl silicate[f]: 0.667 g $Mg(C_2H_3O_2)_2\cdot 4H_2O$[b]: 1.46 ml ethyl alcohol: 0.364 ml water |
| Zircon (O) | 2.04 g zirconium resinate[e]: 1 g silicon resinate[h] |
| Zircon (I) | 1 g $ZrOCl_2\cdot 8H_2O$[b]: 1 ml ethyl silicate[f]: 1.41 ml ethyl alcohol: 0.353 ml water |

NOTES:

a) Concentrations are approximate maximum room temperature solubilities
b) Fisher Scientific Co., Fair Lawn, NJ
c) ICN Pharmaceuticals Inc., Plainview, NY
d) Ventron Corp., Beverly, MA
e) Resinate #5437, Engelhard Industries, East Newark, NJ
f) Silbond ® H-5, Stauffer Chemical Co., NY, NY
g) Resinate #9236, Engelhard Industries
h) Resinate #28-FC, Englehard Industries

Roughly comparable amounts of oxide could be introduced into 2.2 g/cc RSSN on the first impregnation cycle (~40mg) by either the organometallic or inorganic salt precursors. For subsequent impregnations of the 2.2 g/cc material, the amount of oxide introduced per successive cycle slowly decreased. Much less oxide (~10-20 mg) could be introduced into the 2.6 g/cc RSSN on the first impregnation cycle and the amount of additional oxide added by impregnations after the first was always less than 5 mg. Multiple impregnations were often used to increase the oxide content of the specimens. The effect of solution viscosity on the amount of oxide that could be readily introduced into the RSSN was most pronounced on the higher density material; for example, approximately twice the weight of "zircon" could be introduced into the 2.6 g/cc RSSN with the more fluid inorganic zircon precursor solution than with the organometallic solution.

In addition to the universal strength testing after processing, specimen weight changes were frequently used to monitor changes during processing. Treatments which improved the RSSN strength were evaluated for their oxidation resistance properties.

## B. MIXED OXIDES

Material of both RSSN densities was impregnated with solutions described in Table 9 and fired under nitrogen at temperatures ranging from 1400° to 1740°C. The primary mixed oxides investigated were enstatite and zircon, each prepared from the organometallic and inorganic precursors, and mullite, prepared from the inorganic precursors.

Strength results for specimens impregnated two or three times with organometallic precursors are shown in Table 10. The strengths are the mean values of three individual fractures. These samples were fired for three hours under 0.7 atmosphere of nitrogen in the S-furnace at either 1500°C or 1600°C.

In all cases, the strengths of the treated specimens were less than the as-nitrided RSSN. The 1600°C firing strengths were less than the 1500°C firing strengths. A control sample which was thermally cycled in the 1500°C firing was unaffected.

Higher firing temperatures were investigated with RSSN impregnated with inorganic precursor solutions. Firings were conducted in the S-furnace for two hours under nitrogen at 1550°, 1650°, and 1740°C. In an attempt to suppress specimen decomposition, the samples were packed in silicon nitride powder. Those samples containing magnesium in their impregnation solutions were fired in a separate packed crucible.

The fired strengths of this group of samples are reported In Table 11 and are similar to the organometallic impregnations

TABLE 10 - STRENGTHS OF ZIRCON AND ENSTATITE (ORGANOMETALLIC) IMPREGNATED RSSN AFTER FIRING IN NITROGEN AT 1500°C and 1600°C

| Impregnation Solution | Oxide Wt/ Specimen (mg) | Mean Strength; Std. Dev. ($MN/m^2$) 3 hrs, 1500°C | 3 hrs, 1600°C |
|---|---|---|---|
| I 2.22 g/cc RSSN of as-nitrided strength of 191 $MN/m^2$ | | | |
| A. Enstatite | 45* | 109;33 | - |
| B. Enstatite | 55** | 154;24 | 43;1 |
| C. Zircon | 27* | 160;19 | - |
| D. Zircon | 38** | 183;15 | 145;28 |
| II 2.58 g/cc RSSN of as-nitrided strength of 231 $MN/m^2$ | | | |
| A. Enstatite | 6* | 178;31 | - |
| B. Zircon | 9* | 193;20 | |
| C. Unimpregnated, Cycled Control | 0 | 232 | |

* Two impregnation cycles; maximum precursor decomposition temperature = 480°C

**Three impregnation cycles; Maximum percursor decomposition temperature = 700°C

of Table 10 in that the higher strengths tend to be correlated with the lower firing temperatures and the processed strengths were less than the as-nitrided strengths. Despite the use of the silicon nitride packing powder, two untreated control samples fired in a run 1650°C run did experience a 0.28 percent weight loss and significant strength reductions. The strength losses may have been accentuated by carbon vapor contamination from the graphite susceptor. In any event, the use of the S-furnace for high temperature firings was avoided thereafter.

Selected specimens from Tables 10 and 11 were examined by x-ray diffraction methods to determine which phases were present and the alpha to beta silicon nitride ratio. For phase identification, specimens that were impregnated with the organometallic precursors (Table 9) were crushed to powder for x-ray analysis, whereas the specimens that were impregnated with the inorganic precursors were examined with x-rays on their external surfaces.

TABLE 11 - STRENGTHS OF RSSN IMPREGNATED WITH INORGANIC PRECURSORS AND FIRED IN NITROGEN AT 1550°, 1650° and 1740°C FOR TWO HOURS. SPECIMENS WERE PACKED IN $Si_3N_4$ POWDER.

| Impregnation System | Individual Strengths ($MN/m^2$) 1550°C | 1650°C | 1740°C |
|---|---|---|---|
| A. Zircon | 229,248 | 234,250 | 168,194 |
| B. Mullite | 165,228 | 207,231 | 163,197 |
| C. Mullite + 5 w/o MgO | 275,290 | 148,225 | 183,235 |
| D. Spinel | 221,240 | 137,208 | 181,200 |
| E. Alumina | 231,294 | 142,210 | 216,225 |
| F. Zirconia | 175,188 | 228,255 | 165,170 |
| G. Unimpregnated, Cycled Controls (Separate Run) | - | 101,109 | |

As-nitrided strength of RSSN that was impregnated = 290 $MN/m^2$
As-nitrided strength of RSSN used as cycled control = 170 $MN/m^2$

Silicon nitride phase ratios were determined from powdered samples in both cases. The detected phases are reported in Table 12.

The inability to detect any of the introduced oxides in the samples impregnated with the organometallic solutions is most likely due to the small concentration from the small amount of oxide diluted by the bulk of the sample. The possibility of the detection of oxides introduced with inorganic precursors is greater because of the oxide concentration tends to be largest at the surface and a surface XRD examination method was used. While residual zirconia was readily detected on the fired zirconia and zircon specimens, there was no trace of either alumina or mullite crystals.

With the exception of the 1500° and 1600°C firings of the zircon (organometallic) specimens, minor amounts of silicon oxynitride formation were formed in all samples investigated. Subsequent XRD studies have confirmed that oxynitride formation usually occurs when oxide impregnated samples are fired at about 1500°C. Oxynitride formation is believed to result from the oxidation of silicon nitride [14, 15] under the low partial pressures of oxygen in the system. According to Blegen [11], at 1800°K and one atmosphere nitrogen pressure, silicon oxynitride is stable at oxygen partial pressures between about $5 \times 10^{-15}$ to $10^{-19}$ atmospheres.

TABLE 12 - XRD PHASE ANALYSES OF SAMPLES IN TABLES 10 and 11

| | Sample Identification (Table 10 or 11) | Firing Temperature (°C) | Percent $\alpha$-$Si_3N_4$ | Phases Present Other Than $Si_3N_4$ and Relative Intensities |
|---|---|---|---|---|
| I | **Organometallic Precursors** | | | |
| | RSSN, as-nitrided | - | 80 | None |
| | IB-Enstatite | 1500 | 58 | $Si_2ON_2$:minor |
| | IB-Enstatite | 1600 | 17 | $Si_2ON_2$:minor |
| | ID-Zircon | 1500 | 80 | None |
| | ID-Zircon | 1600 | 73 | None |
| II | **Inorganic Precursors** | | | |
| | RSSN, As-nitrided | - | 61 | Si:minor; $Si_2ON_2$:trace |
| | RSSN, Not impregnated, but thermally cycled | 1740 | 36 | N.M. |
| | E- Alumina | 1550 | N.M. | $Si_2ON_2$:minor to moderate |
| | B- Mullite | 1550 | 64 | $Si_2ON_2$:minor to moderate |
| | B- Mullite | 1740 | 31 | N.M. |
| | F- Zirconia | 1550 | N.M. | Tetragonal $ZrO_2$:major; Monoclinic $ZrO_2$:moderate; $Si_2ON_2$: minor to moderate |
| | A- Zircon | 1550 | 66 | Tetragonal $ZrO_2$:moderate $Si_2ON_2$:minor to moderate |
| | A- Zircon | 1740 | 0 | N.M. |

N.M. = Not Measured

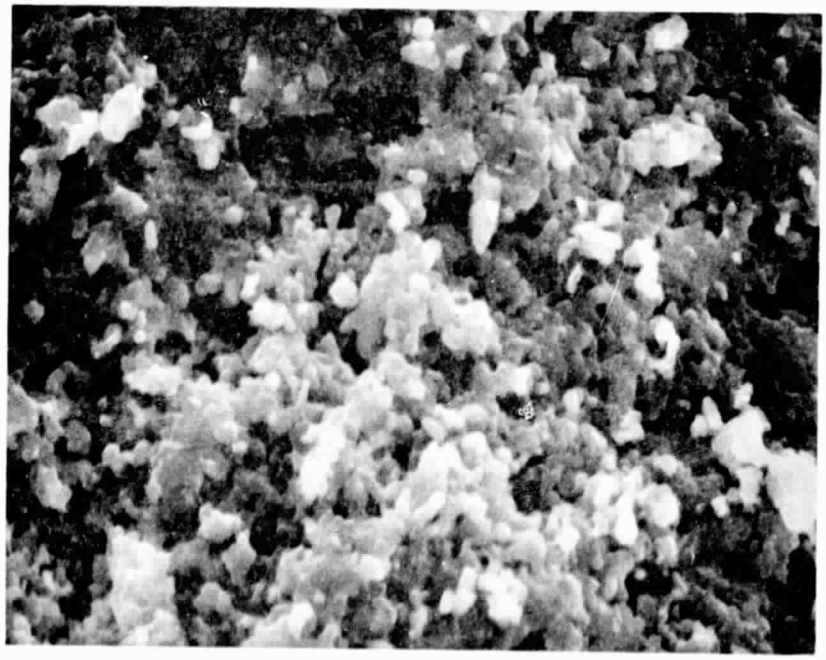
Table 12 also shows how the various impregnants influence the rate of the alpha to beta silicon nitride transformation. At 1500°C, enstatite specimens have substantially converted; at 1550°C, the zircon specimens are essentially unchanged but are fully converted by 1740°C; the mullite specimens show a conversion at 1740°C that is comparable to the purer specimens that were not impregnated.

The enstatite samples exhibit a marked strength decrease upon heating above 1500°C (Table 10). This strength loss is associated with the melting (1557°C) of the enstatite phase. Liquid phase formation in the 1600°C enstatite firing was indicated by spot staining of the setter plate beneath the samples. The strength drop, decrease in alpha silicon nitride content and enstatite melting are accompanied by gross microstructural changes in the RSSN. Figure 2 shows that the alpha silicon nitride matte structure has been destroyed after heating enstatite impregnated samples to 1600°C. Although happening concurrently, the decreasing $\alpha/\beta$ ratio, per se, is not responsible for the strength loss, as has been shown earlier.

Weight changes of samples fired at elevated temperatures were monitored and found to be dependent upon the temperature of firing, the use of protective powders and the nature of the introduced oxides. For the zircon and enstatite specimens of Table 10 fired at 1500°C without a surrounding powder, weight losses approximated the weight of introduced oxide, which amounted to approximately 45 and 27 mg for groups 1A and 1C, respectively. These losses are large compared to weight changes associated with the samples of Table 13 which were embedded in silicon nitride powder. Most of the weight changes in the 1550° and 1650°C firings of Table 13 are minor. All are less then the changes for the unprotected samples that were fired at a lower temperature. This observation suggests that the blanketing powder was at least partially successful in suppressing weight losses. At the highest temperature of Table 13, 1740°C, weight changes are mostly losses and are relatively large.

Although the weight changes in these firings tend to be weight losses, the measured net changes are believed to reflect the balance of simultaneous gains and losses with the losses predominating. The zircon samples of the 1650°C firing are on example of net weight gains. (As will be shown in the next section, weight gains are commonly observed in oxide impregnated samples under certain nitrogen firing conditions). Among the potential causes of weight losses are silicon nitride decomposition, silica or silicon oxynitride film evaporation and oxide-nitride interactions. Regardless of the actual mechanism responsible for weight loss, the effectiveness of the silicon nitride blanketing powder in suppressing losses can be explained on a kinetic basis as the result of a lower escape rate of the product gases. Of the three

A) SEM, 5000X



B) SEM, 5000X

Figure 2 - A) Typical $\alpha$-$Si_3N_4$ matte microstructure in RSSN
B) Absence of $\alpha$-$Si_3N_4$ matte in enstatite impregnated RSSN after firing at 1600°C.

TABLE 13 - WEIGHT CHANGES OF OXIDE IMPREGNATED RSSN AS FUNCTION OF TEMPERATURE. SPECIMENS WERE PACKED IN $Si_3N_4$ POWDER

| Impregnation System* | Oxide Introduced per Specimen Mean Wt;Std.Dev. (mg) | Individual Specimen Weight Changes During Firings (mg) | | |
|---|---|---|---|---|
| | | 1550°C | 1650°C | 1740°C |
| Zircon | 15.2;3.9 | -1.9, 0.6 | 4.7, 6.2 | -14.9, 21.2 |
| Mullite | 12.5;1.1 | -0.7, 1.1 | 0.2, 1.4 | -5.3,-17.2 |
| Mullite + 5% MgO | 15.2;2.0 | -0.7,-3.0 | 0.6, 4.1 | -4.7,-10.7 |
| Spinel | 8.3;0.4 | -0.8,-0.5 | -1.8,-0.7 | -4.0,-2.1 |
| Alumina | 11.5;0.5 | 0, 0 | 1.9 | -14.9,-12.0 |
| Zirconia | 43.8;1.9 | -2.6,-4.3 | -5.4,-5.6 | -32.6,-33.4 |
| Unimpregnated Controls (separate run) | 0;0 | - | -3.9,-5.6 | |

*See Table 11

loss mechanisms,,the decomposition of silicon nitride,

$$Si_3N_4 \rightarrow Si\ (\ell) + 2N_2\ (g),$$

is not expected to make a major contribution to the losses, at least at the 1500°-1600°C temperatures, because the nitrogen overpressure (0.7 atmosphere) is far in excess of the dissociation pressure. In addition, no free silicon was detected by XRD (Table 12) on surfaces of samples which were fired up to 1600°C and which did experience large weight losses. With respect to the evaporation of oxygen containing films, the oxygen content of the RSSN material used as the unimpregnated control (Tables 11 and 16) contained 1.7 weight percent oxygen, as determined by neutron activation analysis. Assuming a comparable oxygen content in the other RSSN materia, an oxygen loss from the nominally two gram samples by either of the reactions,

$$3SiO_2 + Si_3N_4 \rightarrow 6SiO(g) + 2N_2(g)$$

or

$$6Si_2ON_2 \rightarrow 2Si_3N_4 + 2N_2(g) + 6SiO(g)$$

could account for the observed weight losses. Another reaction which is believed to be capable of producing the weight losses is

the interaction of the impregnated oxide with the RSSN to evolve silicon monoxide and nitrogen. Such interactions have been observed in silicon nitride-alumina mixtures[14]. If this type of reaction was operable in the current experiments, the nitride-zirconia reaction appears to be especially active as the zirconia specimens of Table 13 consistently experienced the largest weight losses for that experimental series.

The usefulness of the preceding experiments and their analysis lay primarily in the insight they provided of potential reactions and problems with oxide impregnations. In no case was specimen strength enhanced by the above processing treatments. A greater appreciation of volatilization losses led to the investigation of lower firing temperatures and the intentional use of silicon monoxide in the firing atmosphere. Coincident with the trend to lower firing temperatures was the increased use of the alumina tube furnace. This furnacing shift permitted greater atmospheric control and eliminated the potentially detrimental, but incompletely evaluated, effect of carbon vapor species from the graphite susceptor in the S-furnace. It is known that silicon nitride tends to convert to silicon carbide in graphite furnaces, especially if trace amounts of oxygen are also present.

Firing runs of other oxide impregnated samples were conducted in the T-furnace with maximum firing temperatures of 1400° and 1500°C, respectively. Both firing series employed runs with and without silicon monoxide vapor in the furnace atmosphere. The predominant furnace atmosphere was stagnant nitrogen at atmospheric pressure. The silicon monoxide was generated from a mixture of fine silicon and silica powders which was placed within the furnace hot zone. Equilibrium silicon monoxide at 1400° and 1500°C are approximately $6.8 \times 10^{-3}$ and $2.7 \times 10^{-2}$ atmospheres, respectively [17]. Minor procedural differences existed among the runs. For the 1400°C runs, the samples were held at 1200°C for twelve hours prior to raising the temperature to 1400°C for a final three hour soak; for the 1500°C runs, samples were held at 1300°C for one hour prior to raising the temperatures to 1500°C for a final two hour soak. In addition, the rate of furnace cooling after processing was lengthened to a mean rate of 130°C/hr (between 1500°C to 1100°C) for the 1500°C firings as compared to the mean rate of 800°C/hr for the 1400°C firings.

The resultant strength values for these firings are presented in Table 14. The strengths for the 1400°C and 1500°C firings are similar, indicating no adverse affect of the faster cooling rate. The strengths of the mixed impregnations are little affected by the presence of silicon monoxide; in some cases, the absence of silicon monoxide appears to yield marginally higher strengths. In general, these strengths are greater than the strengths of specimens fired in the S-furnace at 1500°C

TABLE 14 - STRENGTHS OF OXIDE IMPREGNATED RSSN FIRED AT 1400° and 1500°C T-FURNACE ATMOSPHERE OF NITROGEN, WITH AND WITHOUT SILICON MONOXIDE

| | Impregnation System | Individual Bend Strengths ($MN/m^2$) 1400°C Firings With SiO | 1400°C Firings Without SiO | 1500°C Firings With SiO | 1500°C Firings Without SiO |
|---|---|---|---|---|---|
| I | Mean As-nitrided RSSN Strength = 170 $MN/m^2$ | | | | |
| | Mullite (I)* | 151, 184 | 156, 190 | 100, 142 | 76, 145 |
| | Zircon (I) | 171 | 165, 192 | 198, 206 | 197, 257 |
| | Zircon (O)** | 194, 223 | 216, 217 | - | - |
| | Enstatite (I) | - | 172, 199 | - | - |
| | Enstatite (I) | - | 50, 97 | - | - |
| II | Mean As-nitrided RSSN Strength = 290 $MN/m^2$ | | | | |
| | Mullite (I) | 256 | 276, 378 | 191, 221 | 272, 310 |
| | Zircon (I) | 264, 284 | 294, 330 | 204, 266 | 184, 363 |
| | Zircon (O) | - | - | 300, 334 | 300, 315 |
| | Enstatite (I) | - | 256, 257 | 199, 301 | 297, 318 |
| | Repeated Dippings in solution of $Al(NO_3)_3$ | 360, 369 | - | - | - |

*I = Inorganic precursor
**O = Organic Precursor

(Table 10) or 1550°C (Table 11). Most importantly, for the first time, treated RSSN strengths significantly exceeded the mean as-nitrided strength of the untreated RSSN. This strengthening occurred with enstatite, mullite and zircon specimens. However, because enstatite impregnated samples are susceptible to large strength losses at 1400°C, no further work was done with the enstatite approach.

Specimens that were fired in the absence of silicon monoxide experienced minor weight losses on the order of one to five milligrams, whereas those fired in the monoxide containing atmosphere consistently gained approximately one milligram. The exact role of the silicon monoxide is unclear, although its presence appears to suppress an unidentified decomposition reaction within the samples, possibly involving the introduced silica.

Another run at 1550°C, similar to the preceding T-furnace firings except for the use of a slightly flowing atmosphere, was marred by the formation of a crack in the tube while the run was in progress. Specimen weight changes as a result of the firing were highly erratic. It is known that tube leaks can cause RSSN weight losses by active oxidation, and, of course, the passive oxidation of RSSN results in weight gains. Therefore, one explanation for the variable weight change behavior is based upon the locally variable oxygen partial pressure within the tube and the positioning of the samples within the concentration gradient. Under this explanation, samples located in a relatively low (but necessarily higher than the uncracked tube conditions) partial pressure of oxygen area underwent active oxidation:

$$2Si_3N_4 + 3O_2 \rightarrow 5SiO + 4N_2$$

whereas, samples in an oxygen rich area underwent passive oxidation:

$$Si_3N_4 + 3O_2 \rightarrow 3SiO_2 + 2N_2$$

Strength and weight change data for this run are compiled in Table 15. The lower density mullite sample lost considerable weight, suggesting active oxidation, and greatly increased in strength. The higher density mullite sample gained considerable weight, suggesting passive oxidation, and apparently decreased in strength. An apparently reversed weight change - strength correlation was observed for the zircon samples; those that gained weight gained strength and vice versa. These results are presented to show the complexity and importance of the furnace atmosphere on material behavior. Although other interpretations for the weight changes are possible, net weight change measurements alone cannot separate the various possibilities.

The last entry of Table 14, the firing of samples dipped in aluminum nitrate, represented the best strengthening effect to

TABLE 15 - FIRED STRENGTHS AND WEIGHT CHANGES OF OXIDE IMPREGNATED BARS IN OXYGEN CONTAMINATED (CRACKED TUBE) RUN.

| Impregnation System | As-Nitrided Strength ($MN/m^2$) | Fired Strength ($MN/m^2$) | Mean Specimen Wt. Change (mg) | Percent Strength Change |
|---|---|---|---|---|
| Mullite (I) | 170 | 240 | -96 | +41 |
| Mullite (I) | 290 | 252 | +50 | -13 |
| Zircon (O) | 170 | 193, 193 | +32 | +14 |
| Zircon (O) | 290 | 232, 250 | -4 | -17 |
| Zircon (I) | 170 | 171, 181 | +34 | +4 |
| Zircon (I) | 290 | 257 | -3 | -11 |

that time. Because of the magnitude of the strengthening, efforts were concentrated on the use of single oxide impregnations. The strengthening of RSSN by alumina surface coatings has also been reported by Skrovanek and Bradt [18].

## C. SINGLE OXIDES

Firings of specimens impregnated with a single oxide were conducted to determine optimum processing conditions. Table 16 presents strengths which resulted from some of these processing variations for zirconyl chloride and aluminum nitrate impregnations. All firing treatments were conducted in the T-furnace with a nitrogen flow of one CFPH.

The purpose of Runs A and B was to evaluate the effect of silicon monoxide in the furnace atmosphere on strength after firing. The zirconia samples benefited from the presence of the monoxide (Run B), whereas the alumina specimens were relatively unaffected. However, subsequent runs (Run D, among others) showed that alumina samples could be strengthened in the presence of monoxide. Although limited in number, runs in which the monoxide was not present during alumina specimen firings did not result in strength enhancements as large as those observed when the monoxide was present. The use of the monoxide with alumina specimen firings was, therefore, continued.

In Run C, an unsuccessful attempt was made to reproduce the strength enhancements, reported in Table 14, with specimens that had been dipped in an aluminum nitrate solution. In the repeat test, the isostatic pressure method of solution introduction was found to be superior to the dipping method on the basis of strength after firing and was continued thereafter.

TABLE 16 - PROCESS STRENGTHS FOR $ZrO_2$ and $Al_2O_3$ (INORGANIC PRECURSOR) IMPREGNATIONS

| Firing Run Designation | Inorganic Salt Impregnation System | Processing Conditions | Individual Strengths ($MN/m^2$) | Mean Strength ($MN/m^2$) |
|---|---|---|---|---|
| A | $Al_2O_3$ | 1200°C for 2 hrs + 1400°C for 2 hrs No SiO | 295, 305 | 300 |
| A | $ZrO_2$ | 1200°C for 2 hrs + 1400°C for 2 hrs No SiO | 228, 270 | 249 |
| B | $Al_2O_3$ | 1200°C for 2 hrs + 1400°C for 2 hrs With SiO | 260, 278 | 269 |
| B | $ZrO_2$ | 1200°C for 2 hrs + 1400°C for 2 hrs With SiO | 399, 420 | 410 |
| C | $Al_2O_3$* | 1400°C for 2 hrs With SiO | 224, 285 | 255 |
| C | $ZrO_2$* | 1400°C for 2 hrs With SiO | 286, 351 | 319 |
| C | $Al_2O_3$ | 1400°C for 2 hrs With SiO | 305, 390 | 348 |
| C | $ZrO_2$ | 1400°C for 2 hrs | 381, 422 | 402 |
| C | None, Cycled Controls | 1400°C for 2 hrs | 249, 285 | 267 |
| D | $Al_2O_3$ | 1400°C for 3 hrs With SiO | 410, 419, 435 | 421 |
| D | $ZrO_2(H_2O)$** | 1400°C for 3 hrs With SiO | 171, 304, 318 | 264 |
| D | $ZrO_2$(EtOH)*** | 1400°C for 3 hrs With SiO | 299, 371, 372 | 347 |

*Coating applied by dipping in impregnation solution; all others introduced by isostatic impregnation.

**80 mg $ZrO_2$/specimen

***13 mg $ZrO_2$/specimen

As-nitrided Strength: Runs A, B, C = 290 $MN/m^2$
Run D = 302 $MN/m^2$

In Run B, the hold at 1200°C was intended to increase the partial pressure of silicon monoxide within the tube; however, the results of Runs C and D indicate that the 1200°C hold is unnecessary.

The non-impregnated but thermally cycled controls of Run C, as well as larger numbers of controls in firing runs not reported in Table 16, show that the strength of as-nitrided RSSN specimens are not materially affected by the 1400°C firing cycle.

In Run D, the zirconia content in the specimens was varied by using concentrated solutions of zirconyl chloride in either water or ethyl alcohol. The aqueous solutions introduced over five times the weight of oxide than did the alcohol solutions. A comparison of the strengths for these two impregnations shows that higher strengths are not obtained necessarily with a greater amount of oxide. Run D also demonstrated that alumina and zirconia specimens may be strengthened in the same firing, i.e., under identical conditions.

The strengths of Table 16 clearly demonstrate the strengthening potential of alumina and zirconia impregnations. Both treatments are capable of producing RSSN strengths greater than 350 $MN/m^2$, one of the goals of the program. On the other hand, the inability to reproduce the dipped coating results and some of the impregnation results foreshadowed serious reproducibility difficulties that lay in the future.

Another firing series was conducted to determine an optimum firing time and temperature. The RSSN bars were impregnated once with the pertinent inorganic salt solution, dried and given a salt thermal decomposition cycle in air. After decomposition, the mean oxide content of the bars were 13 and 59 milligrams for the alumina and zirconia specimens, respectively. The samples were fired two and eight hours at each of the temperatures of 1200°, 1350° and 1500°C. The atmosphere in the T-furnace consisted of slowly flowing nitrogen with silicon monoxide generation. The post-treatment strengths and the mean weight gains during firing are presented in Table 17.

For both oxide impregnations, strength after firing passed through a minimum as the firing temperature and time increases. For alumina, the minimum occured after eight hours at 1200°C, and, for zirconia, after two hours at 1350°C. After passing through a maximum with increasing temperature, a slight strength downturn occured at 1500°C. At 1200°C, firing weight changes were small and small weight losses were sometimes observed. With increasing firing temperature or time at temperature, weight gains increased. The strength-weight gain data suggest the onset of a chemical reaction about 1200°-1350°C which becomes more active as the firing temperature is raised. The start of this interaction

TABLE 17 - PROCESSED STRENGTH AND FIRING WEIGHT GAINS OF ALUMINA AND ZIRCONIA INORGANIC SALT IMPREGNATIONS AS FUNCTION OF FIRING CYCLE

| Impregnation System | Firing Cycle (Hrs;Temp°C) | Individual Strengths ($MN/m^2$) | Mean Strength ($MN/m^2$) | Mean Specimen Wt. Gain In Firing (mg) |
|---|---|---|---|---|
| As-nitrided RSSN | - | - | 290 | - |
| $Al_2O_3$ | 2:1200 | 248, 314, 360 | 307 | 0.5 |
| $Al_2O_3$ | 8;1200 | 193, 272, 346 | 270 | 2.1 |
| $Al_2O_3$ | 2;1350 | 335, 339, 343 | 339 | 6.6 |
| $Al_2O_3$ | 8;1350 | 276, 344, 353 | 324 | 8.8 |
| $Al_2O_3$ | 2;1500 | 191, 335, 338 | 288 | 14.1 |
| $Al_2O_3$ | 8;1500 | 224, 267, 316 | 269 | 23.4 |
| $ZrO_2$ | 2;1200 | 356, 399, 402, 426 | 396 | -1.5 |
| $ZrO_2$ | 8;1200 | 94, 100, 309, 359 | 216 | 0.5 |
| $ZrO_2$ | 2;1350 | 89, 184, 195, 261 | 182 | 4.7 |
| $ZrO_2$ | 8,1350 | 313, 355, 401, 404 | 368 | 6.4 |
| $ZrO_2$ | 2;1500 | 312, 352, 386, 432, 439 | 384 | 8.6 |
| $ZrO_2$ | 8;1500 | 263, 264, 354 | 294 | 15.5 |

appears to be accompanied by a strength decrease. From these data, a firing temperature near 1400°C for a few hours optimizes the strength of treated specimens.

When solution impregnated samples are thermally dried and decomposed, the solution tends to migrate to the surface of the sample, which leaves a higher surface and near-surface concentration of the oxide solute. Vacuum freeze drying was investigated as a potential means of modifying the oxide distribution within the RSSN. This experimental series also investigated the effect of variations in the amount of salt introduced, the method of sample drying and firing atmosphere. Groups of three RSSN specimens of the lower density were given one or three impregnations with saturated solutions of either aluminum nitrate in alcohol or zirconyl chloride in water. The prefiring process variations are described in Table 18A.

TABLE 18A - PROCESSING VARIATIONS OF VACUUM FREEZE DRIED SPECIMENS

| Variation # | Processing Procedure |
|---|---|
| 1 | Single impregnation, Vacuum Freeze Dried (VFD) |
| 2 | Three impregnations, VFD after first two only, thermally dried only after last impregnation. |
| 3 | Three impregnations, VFD after each. Bar ends prior to decomposition. |
| 4 | Three impregnations, VFD after each. |
| 5 | Three impregnations, VFD after each. Fired in argon with SiO |

The samples were cooled to -70°C and then dried in a vacuum glove box after each impregnation, with the exception of the third impregnation of Variation #2 for which the freeze drying was omitted. Only the water solvent solutions freeze at -70°C. Samples were air dried at 80° and 150°C between impregnations to remove excess solvent and some of the water of hydration. After the last impregnation and freeze dry (if in schedule), all samples were thermally dried and decomposed in air. This procedure consisted of three to four hour isothermal holds at the successively higher temperatures of 80°, 150°, 250°, 350°, 450° and 650°C.

The differentiation between Variations #3 and #4 consisted of the removal of the surface layers by grinding of the bar ends in Variation #3. This was done to facilitate the venting of water and decomposition vapors through the interconnected porosity in the event the salt completely filled the near surface porosity. In Variation #5, nitrogen was omitted from the furnace atmosphere and replaced with argon.

All specimens were fired at 1400°C for three hours in the presence of silicon monoxide generated from a silicon-silica powder mixture. Nitrogen and argon flows were one CFPH. Strength and weight changes after firing are reported in Table 18B. It is seen that a single impregnation introduced approximately half the weight of oxide as three impregnations. The oxide weights and the firing weight gains for Variations #2, #3 and #4 were essentially the same, suggesting no significant difference among these methods of oxide introduction.

TABLE 18B - WEIGHT AND STRENGTH CHANGES AFTER FIRING OF VACUUM FREEZE DRIED SPECIMENS

| Variation Number | Mean Specimen Oxide Weight (g) | Mean Specimen Firing Weight Gain (g) | Mean Strength ($MN/m^2$) | Strength Standard Deviation ($MN/m^2$) | Firing Atmosphere |
|---|---|---|---|---|---|
| I. $Al_2O_3$ | | | | | |
| 1 | 0.022 | 0.015 | 218 | 15.7 | $N_2$/SiO |
| 2 | 0.056 | 0.012 | 194 | 10.3 | $N_2$/SiO |
| 3 | 0.056 | 0.012 | 198 | 1.1 | $N_2$/SiO |
| 4 | 0.055 | 0.013 | 151 | 24.2 | $N_2$/SiO |
| 5 | 0.056 | 0.003 | 185 | 12.4 | A/SiO |
| II. $ZrO_2$ | | | | | |
| 1 | 0.085 | 0.010 | 261 | 15.7 | $N_2$/SiO |
| 2 | 0.169 | 0.008 | 214 | 14.2 | $N_2$/SiO |
| 3 | 0.146 | 0.007 | 270 | 21.3 | $N_2$/SiO |
| 4 | 0.156 | 0.007 | 246 | 13.8 | $N_2$/SiO |
| 5 | 0.138 | 0.001 | 218 | 14.4 | A/SiO |
| III. Controls cycled in Argon/SiO | | | | | |
| | 0 | 0.003 | 177 | 21.0 | A/SiO |
| IV. As-nitrided reference | | | | | |
| | - | - | 170 | - | - |

Specimen weight gains during firing are very instructive. Impregnated specimens fired in a nitrogen atmosphere gained considerably more weight than those fired in the argon atmosphere. The latter gained the same as the unimpregnated controls present in the firings. This weight behavior proves that nitrogen chemically interacted with the impregnated samples. The extent of nitrogen reactivity was greater for the samples which received just one impregnation, even though these samples contained less oxide. This greater reactivity is explained on the basis of sample permeability; because the singly impregnated samples contained less oxide, their pores were less filled and this permitted greater admittance of the gaseous reactant species. In the following section, silicon monoxide is shown also to be a reactant species.

Significant strength gains were observed for most of the impregnated samples fired under nitrogen. Samples fired under argon showed a slight strength increase over the as-nitrided RSSN value or the thermally cycle control value. This slight strengthening with minimal weight gain is reminiscent of the behavior of impregnated bars fired at 1200°C in nitrogen (Table 17). In both cases, the minor strengthening is believed to have been caused by the presence of unreacted oxide. In the current argon firing case, the oxide is believed to be unreacted because of the absence of nitrogen, in the former case because of the low reaction temperature.

## D. CHARACTERIZATION BY X-RAY DIFFRACTION AND SCANNING ELECTRON MICROSCOPY

Surfaces of selected samples, whose strengths have been reported in Tables 17 and 18 and whose firing temperatures ranged between 1200° and 1500°C, were examined with x-rays to determine the phases present. The phases found for alumina and zirconia impregnations are shown in Table 19.

It is a characteristic of the alumina impregnations that only traces of alumina were detectable after firings. Crystalline aluminum containing phases were rare even though an appreciable amount of alumina was introduced. Despite the very low weight gain when samples were fired in argon, relatively much more mullite formation was observed in that case than when specimens were fired in nitrogen. Mullite formation itself proves that the silicon monoxide was a reactant in coating formation. When nitrogen was present during firings at 1400°C and above, traces of 'J' phase, $Si_3Al_6O_{12}N_2$, were formed. Identification of the 'J' phase was made from a literature [19] diffraction pattern. However, despite the much greater weight gains of nitrogen firings, aluminum containing crystals were still infrequent, which suggests that the aluminum and incorporated nitrogen and silicon monoxide were present in an amorphorous phase, possible uncrystallized 'J' phase or a composition near to this phase [20]. The presence of uncrystallized 'J' phase in fired alumina coatings on RSSN has also been inferred in another study [18] of this system. Additional evidence for amorphous phase formation was the glass reflectance of some fired surfaces; however, no diffuse diffraction halos have been observed in the XRD patterns.

In contrast to the alumina specimens, zirconia samples exhibited substantial amounts of unreacted oxide after firing. Both the tetragonal and monoclinic forms of zirconia were present. For the 1400° and 1500°C firings, the polymorphs were present in roughly equal amounts, whereas the tetragonal phase predominated after the 1200°C firing. The highest intensity zirconia reflections occurred after the argon atmosphere firing. Despite the

TABLE 19 - XRD SURFACE PHASES FOUND ON FIRED SPECIMENS, ALUMINA AND ZIRCONIA IMPREGNATIONS.

Alumina Impregnations

| Firing Temperature, Time | Firing Atmosphere | XRD Phases Present* | | |
|---|---|---|---|---|
| | | $3Al_2O_3 2SiO_2$ | $Si_3Al_6O_{12}N_2$ | $Si_2ON_2$ |
| 1200°C, 2 hrs (Table 17) | $N_2$+SiO | Trace | N.D. | Trace |
| 1400°C, 3 hrs (Table 18, I3) | $N_2$+SiO | Trace | Trace | Trace |
| 1400°C, 3 hrs (Table 18, I5) | Argon + SiO | Minor | N.D. | Trace |
| 1500°C, 2 hrs (Table 17) | $N_2$+SiO | Trace | Trace | Trace + |

*Present on all surfaces: $\alpha$-$Si_3N_4$, major; $\beta$-$Si_3N_4$, moderate; $\alpha$-$Al_2O_3$, trace

Zirconia Impregnations

| Firing Temperature, Time | Firing Atmosphere | XRD Phases Present** | | | |
|---|---|---|---|---|---|
| | | $ZrO_2$ Tetragonal | $ZrO_2$ Monoclinic | $ZrSiO_4$ | $Si_2ON_2$ |
| 1200°C, 2 hrs (Table 17) | $N_2$+SiO | Moderate | Minor | N.D. | Trace |
| 1400°C, 3 hrs (Table 18, II3) | $N_2$+SiO | Moderate | Moderate | Trace | Trace |
| 1400°C, 3 hrs (Table 18, I15) | Argon + SiO | Major | Major | N.D. | Trace |
| 1500°C, 2 hrs (Table 17) | $N_2$+SiO | Moderate | Moderate | Trace | Trace + |

**Present on all surfaces: $\alpha$-$Si_3N_4$, major; $\beta$-$Si_3N_4$, moderate

greater weight gains of the nitrogen firings, traces of zircon represented the extent of other zirconium containing crystalline phases. For these reasons, an amorphous phase is believed to form also during the nitrogen firings of zirconia samples. It is unknown whether a 'J' phase analog exists in the Zr-O-N-Si system; zirconium oxynitrides are known to exist [21]. For both of the 1500°C firings, the trace level of silicon oxynitride approximately doubled. This is in accord with diffraction data presented in the section on mixed oxides.

In no case could the nature of the phases present be correlated with strength levels. The presence of the monoclinic zirconia phase did not produce low strengths as the monoclinic form was present in high strength samples. Moreover, in later work, eight mole percent of yttria was added to the zirconia impregnation in order to stabilize all of the zirconia in the tetragonal form. Despite the full stabilization, there was no significant strengthening that could be attributed to the phase stabilization.

The appearance of surfaces before and after impregnation and firing are shown in Figures 3-7. Particulate material, arising from the impregnations, is seen on all fired surfaces. The energy dispersive microprobe easily detected the presence of aluminum and zirconium on the appropriate external surfaces. Samples fired in nitrogen were covered with larger and more complex particles than those fired in argon; the comparison for the zirconia samples being especially striking.

Figures 8 and 9 show exposed fracture faces near and at the original external surface. As in Figures 4-7, these micrographs are of the 2.2 g/cc RSSN material which has been significantly strengthened by the impregnation treatments. With the exception of a faint trace of a near-surface affected zone in the alumina containing sample, there is little evidence for surface densification. Examination of the near-surface edges at higher magnification showed little change in pore size in the RSSN. The concentration of aluminum or zirconium atoms decreases very rapidly inward from the external surface. Beyond a depth of ten microns, the probe could not detect aluminum. These observations demonstrate that the strengthening is affected by relatively small concentrations of either aluminum or zirconium atoms.

## E. OTHER OXIDE IMPREGNATIONS

The increase in RSSN strength after processing with alumina and zirconia salts suggested that other oxides, such as titania, ceria and yttria, might also be suitable for strengthening purposes. Each of these oxides form oxynitrides, and, with the exception of titanium dioxide, binary silicates. Titanium dioxide and yttria were briefly investigated for their strengthening potential; the former oxide was selected because of the chemical

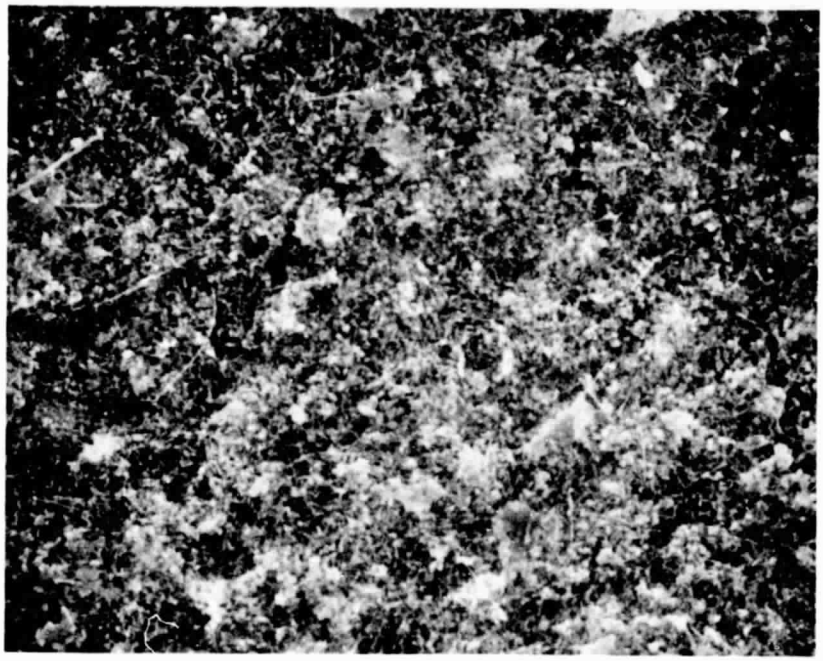


Figure 3 - Pre-impregnated RSSN surface, SEM, 2000X.

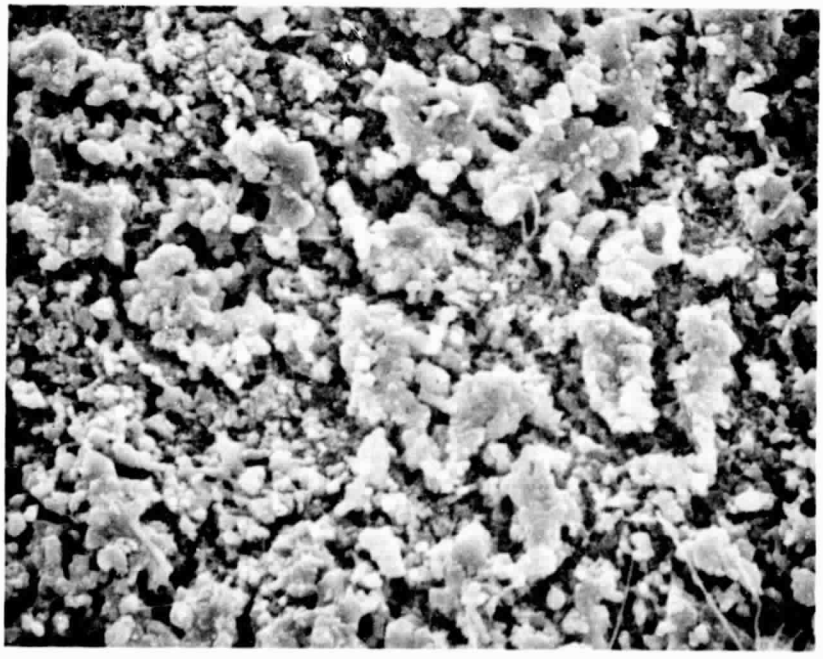


Figure 4 - Alumina impregnated RSSN surface after firing in $N_2$ + SiO atmosphere for three hours at 1400°C, SEM, 2000X.

Figure 5 - Alumina impregnated RSSN surface after firing in A + SiO atmosphere for three hours at 1400°C, SEM, 2000X.

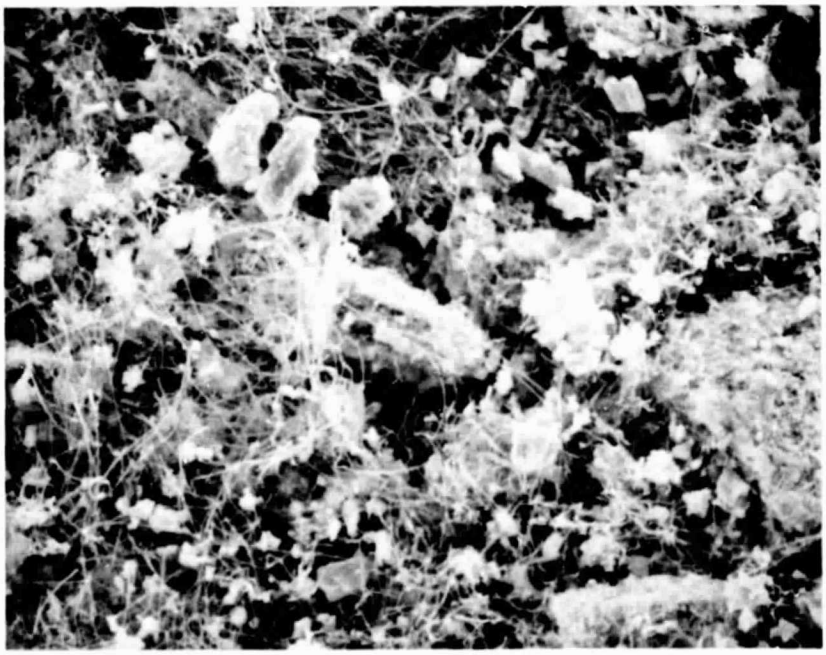


Figure 6 - Zirconia impregnated RSSN surface after firing in $N_2$ + SiO atmosphere for three hours at 1400°C, SEM, 2000X.

Figure 7 - Zirconia impregnated RSSN surface after firing in A + SiO atmosphere for three hours at 1400°C, SEM, 2000X.

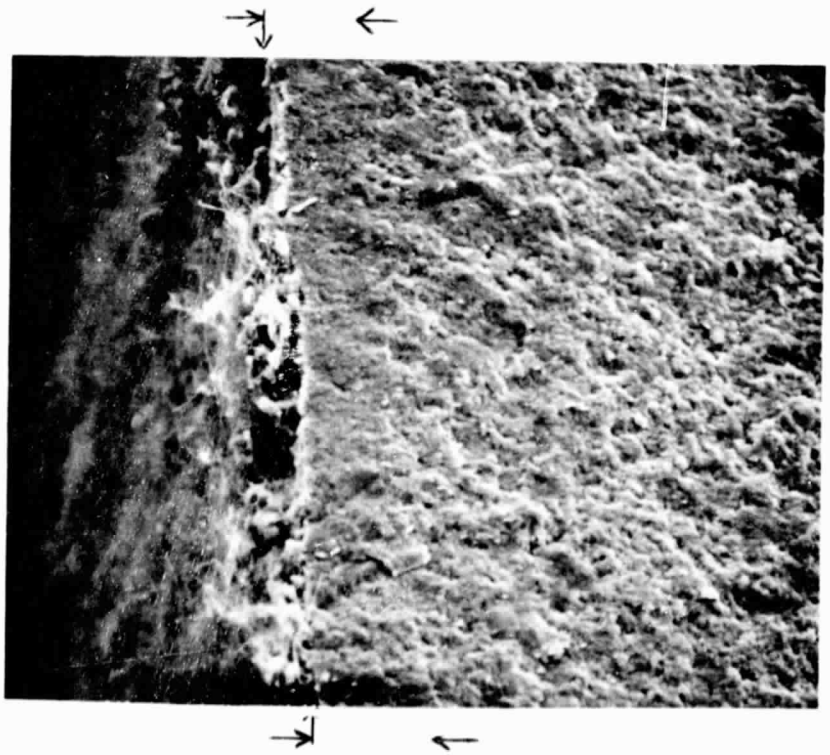


Figure 8 - Exposed fracture surface of alumina treatment sample. Original surface to left of vertical arrows. Width of near-surface treatment affected zone shown by horizontal arrows, SEM, 500X.

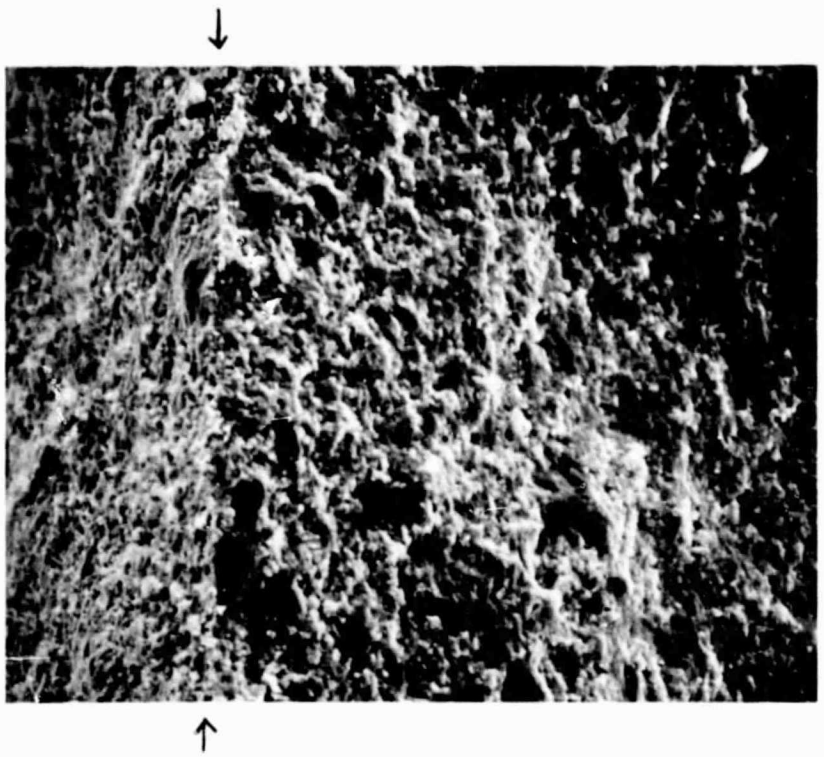


Figure 9 - Exposed fracture surface of zirconia treatment sample. Original surface to left of vertical arrows. SEM, 500X

similarity of titanium to zirconium, the latter because yttria is an effective hot-pressing aid for silicon nitride [22]. Triethanolamine titanate was used as the source of titanium dioxide[1] and a concentrated solution of hydrated yttrium nitrate[2] in ethyl alcohol was the yttria precursor. RSSN bars were isostatically impregnated and given the same slow drying and decomposition procedure used for alumina and zirconia impregnations. The bars were fired, in separate runs, at 1400°C for three hours in a nitrogen and silicon monoxide atmosphere. Strength and weight change behavior for these samples appear in Table 20.

The processing of the titanate impregnated bars left the material strength unchanged. The titanium dioxide was at least partially reduced to the sequioxide during firing, as evidenced by a deep blue sample coloration. An x-ray diffraction examination of a fired surface detected only silicon nitride phases.

The strength of the yttria impregnated samples was greatly reduced after firing. This decrease was greater than any observed with similarly processed bars with alumina or zirconia

[1] ICN Pharmaceuticals, Inc., Plainview, NY
[2] Ventron Corp., Beverly, MA

TABLE 20 - WEIGHT AND STRENGTH DATA FOR TITANIUM DIOXIDE AND YTTRIA IMPREGNATIONS

| Impregnation System | Mean Oxide Weight per Specimen (mg) | Mean Firing Weight Gain per Specimen (mg) | Mean As-Nitrided Strength ($MN/m^2$) | Individual Processed Strengths ($MN/m^2$) | Mean Processed Strength ($MN/m^2$) |
|---|---|---|---|---|---|
| $TiO_2$ | 37 | 6.5 | 170 | 139, 148, 163, 179, 201, 210 | 173 |
| $Y_2O_3$ | 40 | 1.1 | 353 | 233, 234, 291 | 253 |

impregnations and is believed to result from a more extensive interaction between the nitride and the oxide. Work with these oxides was discontinued because of the unpromising strength results.

## F. DIFFICULTIES WITH OXIDE IMPREGNATIONS

Two major difficulties with the oxide impregnation method were sample breakage during processing and an inability to attain consistently high processed strengths. Some of the impregnated bars would break with explosive force during the drying/decomposition procedure or during the high temperature firing. Breakage was encountered only with the use of certain salts and only with the higher density RSSN. Breakage was encountered with impregnations of the hydrated salts of zirconyl chloride, zirconium sulphate, aluminum sulphate and magnesium acetate. The breakage was found to be associated with an excessively rapid drying/decomposition procedure and could be virtually eliminated by an extended procedure. Rapid drying leads to the formation of pores clogged with salt which hinders the venting of the vapors of the water of hydration and other decomposition products. Large internal stresses arise from internal gas pressurization and/or the swelling of the salt during the loss of water of hydration. In the worst case, the breaking specimen shatters; in a less severe case, a small conical spall may separate from the bar. The entrapment of decomposition gases can postpone complete decomposition until the firing step which is then reflected in unusual weight losses during firing. For zirconyl chloride solutions, drying at 150°C, where the first water of hydration losses occur, and below are especially critical. Other factors found to influence the incidence of sample breakage during processing were

solution strength, where a less concentrated solution tended to cause less fractures, and sample oxidation before impregnation, which increased the incidence of breakage.

The second difficulty involved the lack of reproducibility of processing related strength enhancement. Ostensibly identical treatments, separated in time, gave widely different strength results. If a significant strengthening did not occur, the processed strengths were usually near to, or slightly less than, the mean as-nitrided strength; large processed strength reductions were infrequent.

This behavior is an indication that a subtle but critical processing variable(s) was not under control. Efforts to identify the elusive parameter were unsuccessful and were hampered by the lack of an indicator which could be correlated with the higher strengths. The amount of oxide introduced into the sample, firing weight gains, detectable crystalline phases, and microstructural observations were not helpful in this regard. In an effort to identify a processing variable responsible for the non-reproducible strength behavior, the following areas were investigated as potential causes of the variable strength behavior, but were not identified as causative: a) introduced mechanical damage through handling, b) age of impregnation solution, c) nature of salt solvent, d) extent of alpha-silicon nitride fibers on surface, e) placement and amount of silicon monoxide generating powder within furnace and f) furnace gas flow conditions. Although the reproducibility problem was not resolved, one incompletely explored area, which may shed light on the strength behavior, is the state of the oxide as a function of the drying/decomposition schedule. It is hypothesized that the reactivity, and possibly the nature of the reaction product after firing, is influenced by the state of the oxide and that this condition may influence strength. The availability of an RSSN with an as-nitrided strength in excess of 350 $MN/m^2$ shifted the emphasis of the work from strength enhancement to strength retention after oxidation.

## VII OXIDATION OF RSSN

### A. PASSIVE OXIDATION OF UNTREATED RSSN

At high oxygen pressures, an overall reaction equation for the oxidation of silicon nitride may be written as [23]:

$$Si_3N_4(s) + 3O_2(g) \rightarrow 3SiO_2(s) + 2N_2(g)$$

Mass spectrometric evidence [24] suggests that nitrous oxide may be an intermediate stage reaction product, which then dissociates:

$$Si_3N_4(s) + 5O_2(g) \rightarrow 3SiO_2(s) = 4NO(g)$$
$$2NO(g) \rightarrow N_2(g) + O_2(g)$$

At somewhat lower oxygen pressures, silicon oxynitride may form [15, 16]:

$$Si_3N_4(s) + O_2(g) \rightarrow Si_2ON_2(s) + SiO(g) + N_2(g)$$

The oxidation of porous RSSN is rapid at elevated temperatures, but the extent of oxidation is dependent upon the oxidation temperature [25]. At approximately 1000°C and below, oxidation occurs throughout the porous body. Above about 1300°C, rapid oxidation forms a silica film over the RSSN body which drastically slows the rate of oxidation. Thus, after equal times of oxidation, RSSN material oxidized at a relatively low temperature, where the initial rate of oxidation is less, may actually exhibit larger weight gains than material oxidized in the regime where continuous surface films form.

In addition to the oxidation temperature, the condition of the RSSN surface also influences the amount of oxide formation. As-nitrided surfaces which are covered with alpha silicon nitride whiskers oxidize very rapidly because of the high surfaces area per mass and ease of oxygen accessibility. Such surfaces tend to form a thicker silica coating than machined surfaces. Forms of silica that have been observed as the oxidation product of silicon nitride are amorphous silica [23], tridymite [23, 26] and cristobalite [24, 26]. Oxidation in laboratory air favors cristobalite formation because the presence of water vapor assists in the nucleation of cristobalite crystals [27].

The room-temperature strength of oxidized RSSN is dependent upon the pre-oxidized surface condition [26]. RSSN with an as-nitrided surface can be severely weakened by air oxidation. The strength reduction is especially marked after oxidation in the temperature range of 1200°-1300°C, which is why the temperature of 1250°C was selected as the oxidation temperature for this study. The strength degradation of as-nitrided surfaces is much greater than that for machined surfaces, which may be slightly strengthened by an oxidation treatment. The removal of the oxidized surface layer, as by grinding, reverts the strength after oxidation to at least the initial, unoxidized value.

An explanation for the large drop-off in room-temperature strength after oxidation has been given by Davidge et.al. [25] who showed that oxidized RSSN suffers the strength loss upon cooling through the beta to alpha cristobalite transformation temperature of approximately 250°C. This transformation involves a large volumetric contraction which generates tensile stresses and cracks in the cristobalite. An example of cracks in the oxidized surface layer of RSSN is shown in Figure 10.

An oxidation test series was conducted to evaluate the effects of initial RSSN surface condition and oxidation procedure upon post-oxidized strength. Isostatically pressed RSSN samples

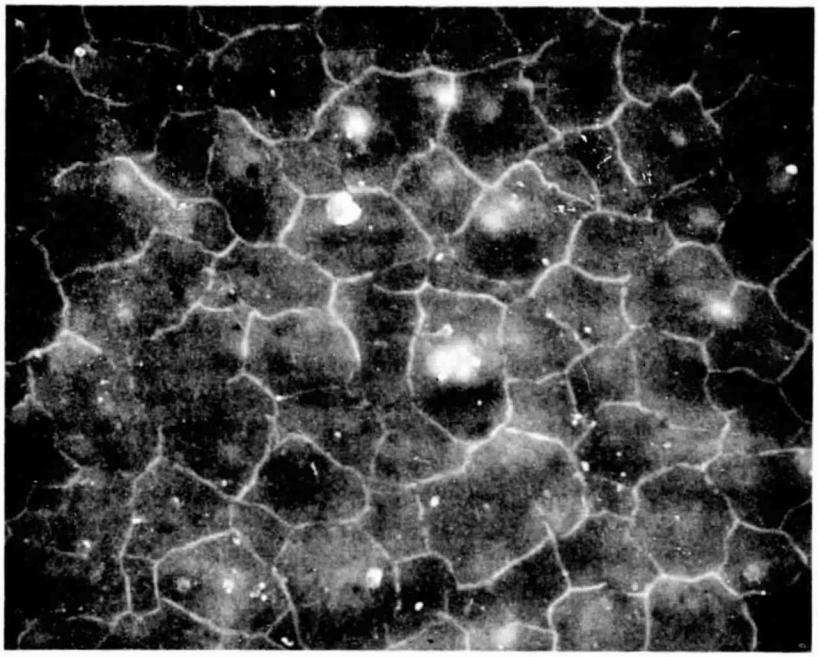


Figure 10 - Cracks in an α-Cristobalite oxidation layer on RSSN, SEM, 2000X.

in three surface conditions were used: a) machined, b) as-nitrided with all surface alpha fibers present, and c) as-nitrided with the loose surface fibers removed by rubbing with a cloth. Bars were oxidized under three oxidation exposures in air: a) at 1250°C for 12 hours, b) at 1450°C for one hour after plunging the bars into the pre-heated furnace, and c) a 12 hour oxidation at 1250°C after the bars had been given the 1450°C treatment and cycled to room temperature. Mean oxidation weight gains and resultant strengths for the oxidations are reported in Table 21. The strength data were generated from a usual sample size of three bars while the weight gains were obtained from usually four or eight bars. Initial strengths for all surface conditions were identical.

The table illustrates many of the points discussed above. The 64 percent decrease in strength of the as-nitrided surfaces after the 1250°C oxidation dramatically illustrates the oxidation problem of as-nitrided RSSN. In contrast to this strength decrease, the strengths of the machined samples increased after the identical oxidation exposure. The effectiveness of a high temperature oxidation in sealing surface porosity is seen by comparing the weight gains of the two oxidations at 1250°C; the weight gains are much less if the RSSN is first conditioned by an oxidation at 1450°C.

TABLE 21 - EFFECT OF RSSN SURFACE CONDITION AND OXIDATION PROCEDURE ON STRENGTH AND OXIDATION WEIGHT GAINS

| Surface Condition | Initial Strength ($\sigma$) ($MN/m^2$) | 1250°C Oxidation(1) Strength ($\sigma$) ($MN/m^2$) | 1250°C Oxidation(1) Wt. gain/ bar (4) ($mg/cm^2$) | 1450°C Oxidation(2) Strength ($\sigma$) ($MN/m^2$) | 1450°C Oxidation(2) Wt.gain/ bar (4) ($mg/cm^2$) | 1450°C + 1250°C Oxidation (3) Strength ($\sigma$) ($MN/m^2$) | 1450°C + 1250°C Oxidation (3) Wt. gain/ bar (4,5) ($mg/cm^2$) |
|---|---|---|---|---|---|---|---|
| Machined | 228 (36) | 256 (40) | 1.65 | 262 (41) | N.M. | 253 (33) | 0.24 |
| As Nitrided With Surface Fibers | 228 (16) | 82 (21) | 3.56 | 207 (8) | 0.93 | 192 (13) | 0.10 |
| As Nitrided Without Surface Fibers | 228 | N.M. | N.M. | 172 (13) | 1.35 | 200 (29) | 0.31 |

(1) Oxidized in air at 1250°C for 12 hours.
(2) Upquenched to 1450°C in air and held for 1 hour.
(3) Oxidation (2), returned to 25°C, followed by oxidation (1).
(4) Sample dimensions (mm): 3.18 x 6.35 x 50.8; Surface Area = 10.1 $cm^2$
(5) Weight gain for 1250°C part of oxidation exposure only.

N.M. = Not Measured

$\sigma$ = Standard Deviation

Oxidized surfaces were examined by x-ray diffraction to determine the nature of the oxidation product and, in each case, the sole detectable silica polymorph was α-cristobalite. The relative cristobalite diffraction intensities of the machined and as-nitrided surfaces were compared for each of the three oxidation conditions: at 1250°C for 12 hours, at 1450°C for one hour, and at 1450°C for one hour followed by 12 hours at 1250°C. For the first two conditions, the amount of cristobalite detected was much more and the amount of residual silicon nitride much less on the originally as-nitrided surface as compared to the machined surface. For the last condition, the amount of cristobalite was classified as major on both surface types, but the initially machined surface had more residual silicon nitride. Microscopy showed the oxide surface layer to be severely cracked in all cases. These observations show that the cristobalite transformation, with its attendant cracking, is not a sufficient condition for observing strength reductions after oxidation exposure. In addition, the amount of silica formed, as determined by weight gains, is not a good indicator of oxidized strength: the two types of as-nitrided surfaces that were oxidized at 1450°C had both lower weight gains and lower strengths than the machined surfaces that were oxidized at 1250°C. Apparently the distribution of silica in the surface and near-surface volume influences the ease of the propagation of the cracks in the cristobalite layer into the underlying RSSN and this propagation is easier for the initially as-nitrided surfaces.

## B. OXIDATION OF OXIDE IMPREGNATED RSSN

Oxidation studies were conducted on RSSN that was impregnated with oxides derived from the inorganic precursors. The oxides investigated were stabilized and unstabilized zirconia, zircon, alumina and mullite. Oxidations were performed in the open-ended T-furnace in laboratory air for 12 hours at 1250°C. Specimens were weighed before and after oxidation for weight gains during the exposure and strengths were measured after oxidation.

Table 22 presents oxidation data for specimens initially fired at 1400°C for three to sixteen hours under a nitrogen and silicon monoxide atmosphere. Due to the inconsistency of strengths after firing, it was not always possible to generate the oxidation data on specimens which had been appreciably strengthened as a result of the firing procedure. Results are presented for RSSN of two as-nitrided strength levels but of the same ($2.6 \times 10^{-3}$ Kg/m$^3$) density. For the 290 MN/m$^2$ material, Group I, all treated sub-groups show a higher strength after oxidation and a lower weight gain during oxidation relative to the strength and weight change of the untreated and oxidized controls. Within a given sub-group, a tendency towards lower individual strengths with greater oxidation weight gains was observed. This observation is a generalization, not always

TABLE 22 - OXIDATION DATA FOR UNTREATED AND OXIDE TREATED RSSN
(1400°C Firing Temperature)

| Impregnation System | Firing* Time (hrs) | Mean Fired Strength; (Std. Dev.) ($MN/m^2$) | Mean Oxidation Weight Gain ($mg/cm^2$) | Mean Post 1250°C Oxidation Strength; (Std. Dev.) ($MN/m^2$) | Fraction of As-Nitrided Strength After Oxidation (%) |
|---|---|---|---|---|---|
| I As-Nitrided Strength = 290 $MN/m^2$ | | | | | |
| a) Untreated | - | 290 | 1.02 | 117; (7) | 40 |
| b) $Al_2O_3$ | 3 | 318; (31) | 0.42 | 166; (11) | 57 |
| c) $Al_2O_3$ | 3 | 302; (6) | 0.44 | 166; (14) | 57 |
| d) $ZrO_2$ | 3 | 324; (87) | 0.04 | 180; (28) | 62 |
| e) $Al_2O_3$ | 16 | N.M. | 0.11 | 250; (33) | 86 |
| f) $ZrO_2$ | 16 | N.M. | 0.16 | 160; (17) | 55 |
| II As-Nitrided Strength = 353 $MN/m^2$ | | | | | |
| a) Untreated | - | 353 | N.M. | 203; (50) | 58 |
| b) $Al_2O_3$ | 3 | 320; (32) | 0.71 | 149; (47) | 42 |
| c) Mullite | 3 | 358; (47) | 0.71 | 174; (34) | 49 |
| d) $ZrO_2$ | 3 | 414; (25) | N.M. | 215; (33) | 61 |
| e) Zircon | 3 | 322; (36) | 0.57 | 223; (31) | 63 |

*All treated specimens fired at 1400°C in $N_2$/SiO

N.M. - Not Measured

obeyed. The specimens of Group Id show the lowest net weight gain during oxidation, but this low value resulted from unique weight losses during oxidation in two of the three samples. In the sample groups with the higher as-nitrided strength, Group II, the strengths after oxidation of untreated bars are not consistently higher than the oxidized control samples. The weight gains during oxidation of the treated Group II material were higher than that of the Group I material.

The last column of Table 22 expresses the oxidized RSSN strength as a percentage of the initial, as-nitrided strength, and is less than 100 percent in all cases. The highest percentage of strength retention was found for the group of alumina impregnated bars which were fired for 16 hours. Since firing weight gains are larger for the extended firing times, an hypothesis was formed that large firing gains are desirable for oxidation resistance in order to close off porosity and form a physical barrier to the ingress of oxygen. To promote larger weight gains, two series of firings were performed at 1500°C. For these runs, the impregnated specimens were buried in a mixture of silicon, silica and silicon oxynitride powders whose purpose was to supply a source of nitrogen and silicon monoxide. The bars and powder were contained in a RSSN boat and covered with another loosely fitting boat. A slight flow of nitrogen was used for the firings which were done in the T-furnace.

The first series of firings contained bars which were impregnated with either alumina, zirconia, or zirconia with eight mole percent of yttria. The purpose of the yttria addition was to prevent the formation of the monoclinic phase upon cooling after firing [28] and was added to the impregnation solution as yttrium nitrate. The second series of firings contained samples which were impregnated with either zirconia, stabilized zirconia or zircon and untreated controls. Data for both series appear in Tables 23 and 24; the first table contains information that was obtained preceding, and the second obtained after, oxidation.

The promising high retained strength of the alumina impregnated samples in Table 22 was not repeated in Series 1 (Table 25). On the other hand, the zirconia specimens of Table 25 have a higher percentage of retained strength than their counterparts of Table 22. This variable behavior is reminiscent of the strength behavior of impregnated bars after firing.

The strength behavior of the yttria stabilized zirconia specimens of Series 1 is of interest. The strength of the material fired for eight hours is considerably less than that for the material fired for only two hours. The lower strength for the longer firing may be caused by a more severe attack of the yttria on the RSSN (See Section IV D). However, during oxidation, the strength of the material fired for the shorter time decreased,

TABLE 23 - FIRING DATA FOR OXIDE IMPREGNATED SPECIMENS FIRED AT 1500°C AND SUBSEQUENTLY OXIDIZED.

| | Oxide System | Mean Oxide Wt./Bar (mg) | Firing Time (hrs) | Mean Firing Wt. Change/Bar (mg) | Mean Fired Strength; Std.Dev. ($MN/m^2$) |
|---|---|---|---|---|---|
| SERIES 1 | | | | | |
| A. | $Al_2O_3$ | 7.8 | 2 | 2.3 | 327; 59 |
| B. | $Al_2O_3$ | 7.2 | 8 | 4.3 | 308; 41 |
| C. | $ZrO_2$ | 21.1 | 2 | 7.4 | 326; 43 |
| D. | $ZrO_2$+8 m/o $Y_2O_3$ | 21.3 | 2 | 6.8 | 311; 64 |
| E. | $ZrO_2$+8 m/o $Y_2O_3$ | 22.6 | 8 | 12.4 | 249; 18 |
| SERIES 2 | | | | | |
| F. | $ZrO_2$ | 24.1 | 8 | 7.0 | N.M. |
| G. | $ZrO_2$+8 m/o $Y_2O_3$ | 22.1 | 8 | 9.2 | N.M. |
| H. | Zircon | 14.2 | 8 | 5.2 | 351; 37 |
| I. | Untreated; Thermally Cycled | 0 | 8 | 1.1 | 377; 8 |

As-nitrided strength = 353 $MN/m^2$

N.M. = Not Measured

TABLE 24 - OXIDATION DATA AND 1370°C STRENGTH FOR OXIDE IMPREGNATED SPECIMENS FIRED AT 1500°C

| Oxide System | Mean Post Oxidation* Strength;Std.Dev. ($MN/m^2$) | Oxidized Strength As Fraction of As-nitrided Strength (%) | Mean Oxidation Wt.Gain/Bar** ($mg/cm^2$) | 1370°C Strength;Std.Dev. After Oxidation ($MN/m^2$) |
|---|---|---|---|---|
| **SERIES 1** | | | | |
| A. $Al_2O_3$ | 234; 70 | 66 | 0.99 | N.M. |
| B. $Al_2O_3$ | 230; 26 | 65 | 0.50 | N.M. |
| C. $ZrO_2$ | 293; 47 | 83 | 0.26 | N.M. |
| D. $ZrO_2$+8 m/o $Y_2O_3$ | 255; 9 | 72 | 0.35 | N.M. |
| E. $ZrO_2$+8 m/o $Y_2O_3$ | 318; 19 | 90 | 0.48 | N.M. |
| **SERIES 2** | | | | |
| F. $ZrO_2$ | 267; 21 | 76 | 0.46 | 347; 53 |
| G. $ZrO_2$+8 m/o $Y_2O_3$ | 279; 21 | 79 | 0.71 | 352; 5 |
| H. Zircon | 264; 60 | 75 | 0.80 | 382; 24 |
| I. Untreated; Thermally Cycled | 267; 43 | 76 | 1.41 | N.M. |
| As-Nitrided | - | - | - | 367; 13*** |

N.M. = Not Measured

*Oxidation Conditions: 12 hours at 1250°C in air
**Bar Dimensions (mm): 3.18 x 6.35 x 36.5
***Not Oxidized prior to testing

while the longer fired material strongly increased in strength. Ninety percent of the as-nitrided strength was recoverd after oxidation. This level is the highest that has been observed for initially as-nitrided material - exclusive of machined material - after the particular oxidation treatment.

Series 2, which was expected to reproduce the high retained strength of the stabilized zirconia treatment, did not. All Series 2 samples had essentially the same percentage of retained strength (75-79 percent) after oxidation. This includes the untreated RSSN bars which were fired along with other bars in the series. The minor weight gain during firing is typical for untreated RSSN fired in the presence of silicon monoxide and nitrogen and is much less than is observed for treated specimens. The smaller weight gains during oxidation of the treated samples relative to the gains of the untreated bars suggests a lessened accessibility of the treated RSSN to oxygen. However, as already mentioned, this lower weight gain was not reflected in the percent of retained strength.

Treated bars of Series 2 were bend tested at 1370°C after they had been given the standard oxidation exposure and cycled through room temperature. The high temperature bend testing was done in air on a three-point fixture whose span was 2.30 cm. Specimens were held in the furnace hot-zone for 15-20 minutes. before breaking to allow temperature equilibration. The 1370°C strength is much greater than the strength of identical samples tested at room temperature and is equal, to within five percent, to the strength of as-nitrided material at 1370°C. The recovery in strength can be attributed in large part to the healing or blunting of cracks in the cristobalite layer during the temperature hold prior to bend testing.

Table 25 contains the results of an X-ray diffraction study on the surfaces of specimens described in Tables 23 and 24. The study was conducted with the intent of correlating crystalline phase information with strength differences. Two cases, one after firing and the other after oxidation, are available for comparing stabilized and unstabilized zirconia. For the as-fired case, samples of C and D show similar amounts of the all phases, with the exception that monoclinic zirconia is absent in the yttria stabilized zirconia. After oxidation (F versus G), the phases are also similar. Strengths in the two comparisons are also similar. The oxidized strength of the stabilized zirconia samples fired for eight hours in Series 1 (E) were higher than corresponding samples in Series 2 (G). Again, no significant phase differences existed.

In Series 1, the stabilized zirconia samples fired for two hours (D) had a higher after-firing strength than samples fired for eight hours (E). However, after oxidation, the relative

TABLE 25 - SURFACE XRD PHASES OF SPECIMENS LISTED IN TABLES 23 and 24

| Identification* | α $Si_3N_4$ | β $Si_3N_4$ | $Si_2ON_2$ | α Cristobalite | Tetragonal $ZrO_2$ | Monoclinic $ZrO_2$ | $ZrSiO_4$ |
|---|---|---|---|---|---|---|---|
| I after firing | Major(+) | Mod. | Trace | ND | ND | ND | ND |
| I after oxidation | Major | Mod.(-) | Trace | Major(+) | ND | ND | ND |
| B after firing | Major | Mod. | Trace | ND | ND | ND | ND |
| B after oxidation | Mod. | Mod. | Trace | Major | ND | ND | ND |
| H after firing | Mod.(+) | Mod. | Minor(+) | ND | Mod.(-) | Minor | Mod.(-) |
| H after oxidation | Mod. | Mod. | Mod. | Major | Mod. | ND | Major |
| E after firing | Major(-) | Mod. | Mod.(-) | ND | Mod.(+) | ND | Minor(+) |
| E after oxidation | Mod. | Mod. | Mod. | Major | Major | ND | ND |
| D after firing | Major | Mod. | Minor | ND | Major | ND | ND |
| D after oxidation | Mod. | Minor | Trace | Major(+) | Major | ND | Mod. |
| G after oxidation | Mod. | Mod. | Minor | Major(+) | Major | ND | Trace(?) |
| F after oxidation | Major | Mod. | Minor | Major | Mod. | ND | ND |
| C after firing | Major | Minor | ND | ND | Mod. | Minor | ND |

*Letter designations correspond to those in Tables 23 and 24

strengths of the samples were reversed. The D specimens decreased in strength with oxidation, but the E samples increased in strength. This divergent strength behavior was paralleled by divergent behavior with respect to the zircon phase; the samples which increased in strength during oxidation (E) lost the zircon which was present after firing, whereas the oxidation weakened samples increased in zircon content. It is not known whether this phase behavior is causatively related to the strength behavior, as the behavior is unique.

## VIII RSSN SURFACE INFILTRATION WITH SILICON AND SUBSEQUENT PROCESSING TO NITRIDE OR CARBURIZE SURFACE

### A. INTRODUCTION

A third approach to densifying the surface of RSSN involved the infiltration into the RSSN surface of molten silicon which was then either carburized or nitrided. The wetting of silicon nitride by silicon appears to require the removal of surface films of oxynitride or silica and has been studied in the literature [29, 30, 31]. RSSN has been given some oxidation resistance by CVD coatings of silicon carbide [16] and infiltrated silicon layers [31], but corresponding strength measurements have not been reported. Although CVD coatings of silicon nitride on RSSN have been widely mentioned as an oxidation barrier, the author is unaware of any reported oxidation studies with these coatings on RSSN.

In preliminary studies, it was found possible to carburize silicon layers by heating at about 1450°C in the presence of a carbon vapor species, such as in a carbon heating element furnace. The presence of a small amount of oxygen in the furnace atmosphere is believed to promote the carbon transfer in the form of carbon monoxide. It was also known that continuous beta-silicon nitride films form on molten silicon. The thickness of silicon that can be successfully nitrided is not known although it is recognized that the thickness of the nitrided layer may be kinetically limited by diffusion through the covering film.

### B. INITIAL INFILTRATION AND CARBURIZATION/NITRIDATION STUDIES

Acetone slurries were prepared with powders of a) silicon, b) silicon plus two atomic percent aluminum, c) silicon plus two atomic percent titanium, and d) silicon plus two atomic percent boron. All powders were initially equal to or less than -325 mesh and were mixed and further comminuted by grinding in a boron carbide mortar and pestle. RSSN specimens were painted with the slurries and fired in the tube furnace for thirty minutes at 1450°-1500°C under a mechanical pump vacuum.

The silicon coatings bonded well to the RSSN with the exception of the boron containing coating. This coating separated from the RSSN and the use of boron containing coatings was discontinued. The use of either aluminum or titanium additions promoted more uniformly thick coatings than unalloyed silicon which did not infiltrate as well and tended to form large molten drops on the undersides of the end-supported RSSN bars.

The photomicrograph of Figure 11 shows the infiltration of a silicon layer containing two atomic percent aluminum. The infiltration of the titanium containing coatings was similar.

With the development of an apparently satisfactory infiltration technique, specimens were prepared for carburization and nitridation. Powder coatings of Si, Si+2 a/o Al and Si+2 a/o Ti were applied to RSSN by either aerosol spraying or brushing. Approximately 40 mg of powder per bend bar was deposited with the spray method and at least twice that amount by brushing. The coated RSSN specimens were surface siliconized by heating in vacuum for 30 minutes at 1500°C.

After siliconizing, some coated and uncoated bars were strength tested, while others were given either a carburizing or nitriding treatment. The carburization process consisted of

Figure 11 - Fracture face of RSSN infiltrated with Si+2 a/o Al. Coating on left. 2000X

heating specimens to 1450°C for two hours in a carbon element furnace under a mechanical pump vacuum. The nitriding process consisted of heating bars to 1460°C for 12 hours under slowly flowing nitrogen. During these additional processing steps, the carburized bars lost weight (~15 mg/bar).

Bend strengths of completely processed bars are shown in Table 26. Final processed strengths were much less than the as-nitrided RSSN strength, primarily as the result of sample decomposition during the vacuum conditions of the siliconizing step, as may be seen by the strength measurements taken at that stage of the processing. In addition to the strength losses, the decomposition was evidenced by weight losses (~20 mg/bar) in thermally cycled control bars, condensation deposits of alpha silicon nitride within the furnace tube and beta silicon nitride formation on the melted silicon surfaces. A fraction of the strength reduction after siliconizing was due to the silicon itself as strengths of coated bars (spray application) were less than the strength of the uncoated controls.

TABLE 26 - STRENGTHS OF SILICONIZED, SILICONIZED PLUS CARBURIZED AND SILICONIZED PLUS NITRIDED BARS OF EARLY EXPERIMENTS

| Group # | Treatment | Silicon Coating Description (2 a/o additive, application) | Strength (Std.Dev.) (MN/m ) | Group Size # |
|---|---|---|---|---|
| 1 | As-nitrided | No coating | 353 (47) | 10 |
| 2 | Siliconizing Cycle | No coating | 151 (36) | 3 |
| 3 | Siliconized | Al, Spray | 125 (38) | 3 |
| 4 | Siliconized | Ti, Spray | 102 (11) | 3 |
| 5 | Carburized | Al, Brush | 24 (-) | 1 |
| 6 | Carburized | Ti, Brush | 23 (-) | 1 |
| 7 | Carburized | Al, Spray | 183 (23) | 3 |
| 8 | Carburized | Ti, Spray | 195 (32) | 3 |
| 9 | Nitrided | No additive, Brush | 41 (5) | 2 |
| 10 | Nitrided | Al, Brush | 78 (-) | 1 |
| 11 | Nitrided | Ti, Brush | 71 (-) | 1 |
| 12 | Nitrided | Al, Spray | 139 (20) | 3 |
| 13 | Nitrided | Ti, Spray | 119 (49) | 3 |

The strength of brush-coated specimens immediately after siliconizing was not measured and, therefore, a strength comparison of brushed versus sprayed coatings after siliconizing cannot be made. However, when sprayed versus brushed coating strengths are compared after either carburizing or nitriding treatments, the strengths of the sprayed coatings are always stronger. This result suggests that the thinner silicon coating is more desirable, possibly because of a greater tendency of the thicker silicon coatings to crack during cooling from the siliconizing temperature.

The effects of the carburizing and nitriding treatments upon strength are best seen by studying the sprayed coatings where a baseline, as-siliconized strength is available. Despite the weight loss that occurred during the carburizing process, the carburized bars slightly increased in strength. On the other hand, the bars which were subsequently nitrided gained weight from the nitridation but showed only a minimal strength improvement. The absence of a greater strength recovery (from the as-siliconized value) was not considered serious, provided the treatment would provide oxidation resistance. The loss in strength during the siliconizing process was considered to be critical for the success of this approach and, therefore, was investigated.

## C. WEIGHT AND STRENGTH LOSSES OF THERMAL CYCLED RSSN

A series of experiments were conducted to determine RSSN strength losses during simulated siliconizing conditions. Lower density (2.2 g/cc) RSSN bars of as-nitrided strength of 170 $MN/m^2$ were used in the uncoated condition. The bars were of uniform size and weighed about two grams. Experiments were performed in the T-furnace under a variety of heating and atmospheric conditions. Processing related weight changes and post-heating strengths were used to follow effects of the experimental conditions.

The simulated siliconizing conditions are listed in Table 27 in chronological sequence. The procedure basically consisted of heating RSSN bars in a RSSN boat to 1200° or 1250°C at a constant rate of 400°C per hour. At this temperature, changes in tube atmosphere were instituted or an isothermal hold was used. The original intent of the hold was to provide time for oxide films on the RSSN to be volatilized. The furnace was then rapidly heated above the melting point of silicon to either 1450° or 1500°C for a final hold, usually of 30 minutes duration. The final rate of temperature rise was controlled by varying the power input to the furnace. Atmospheric variations included the use of mechanical pump vacuum, control of the nitrogen partial pressure, introduction of silicon monoxide vapor (internally generated from silicon-silica mixtures) and the use of an argon

atmosphere. In those runs where the tube was evacuated to a pressure of 2000 microns of nitrogen, the pressure of 2000 microns was chosen because it is the approximate equilibrium vapor pressure of nitrogen over silicon nitride at 1450°C [17]. Usually two or three, although occasionally as few as one, RSSN samples were contained in a given run.

The weight losses per sample for a given run were very consistent, differing by usually no more than a couple tenths of milligrams. A very strong correlation was found to exist between the strength after thermal exposure and sample weight loss. This relationship is shown in Figure 12 for runs in which both weights and strengths were measured. The strong effect of temperature upon RSSN strength or weight loss under vacuum conditions is seen by comparing Run 1 (1250°C peak temperature) with Runs 2 or 10 (1450°C peak temperature). This correlation between weight loss and temperature is what might be expected from a thermally activated decomposition process.

The effect of a prolonged vacuum exposure at high temperature on the interior microstructure of RSSN is shown in Figure 13. The sample was a bar of the RSSN material used in the current experimental series and was exposed to a mechanical pump vacuum for five hours at 1400°C. From a comparison with other RSSN micrographs, it is visually apparent that substantial material loss has occurred and, in fact, the sample experienced a 115 mg weight loss. Although the above is an extreme case, it clearly demonstrates the adverse effects of vacuum exposure on RSSN.

However, there are difficulties in attributing the weight losses of the short runs listed in Figure 12 solely to the decomposition of pure silicon nitride. For example, the use of a 2000 micron nitrogen pressure did not eliminate weight losses in Runs 4, 5 or 6. In addition, the weight losses in these runs exceeded those in Runs 7 and 8 wherein the nitrogen pressure was further reduced by tube evacuation.

Runs 1-9 were conducted without measurements of the tube's leak rate under vacuum. To obviate the possibility that the large weight losses were caused by active oxidation of the RSSN as the result of an air leak in the tube, leak testing was instituted and conducted before and after each subsequent run to ensure tube integrity. The weight losses sustained in the runs for which the tube was known to be leak-tight were not much different from previous runs, thereby disproving the active oxidation hypothesis.

If one assumes the sample weight loss to be due to the nitrogen evolved from the decomposition of silicon nitride, the released gas volume can be calculated from the weight loss, mean tube temperature, tube volume, equilibrium partial pressure of nitrogen

TABLE 27 - RSSN DECOMPOSITION UNDER SIMULATED SILICONIZING CONDITIONS

| Run # | Run Description | Mean Sample Wt. Loss (mg) |
|---|---|---|
| 0 | As-nitrided reference | --- |
| 1 | 1/2 hour at 1250°C with continual vacuum pumping | 1.7 |
| 2 | 1/2 hour at 1250°C, 15 minutes to reach 1450°C, 1/2 hour hold at 1450°C with continual vacuum pumping | 12.8 |
| 3 | Same as Run 2 except rise time to 1450°C was 8 minutes and silicon nitride powder was placed in flanking boats | 8.5 |
| 4 | 1/4 hour at 1250°C under vacuum, tube backfilled with nitrogen and evacuated to 2000 micron pressure, tube isolated from pump, 3 minutes to 1450°C, 1/2 hour at 1450°C | 11.8 |
| 5 | Same as Run 4 except silicon nitride powder present in flanking boats | 10.9 |
| 6 | Nitrogen pressure adjusted to about 5000 microns at 800°C, tube closed off and heated to 1250°C and held there for one hour, tube evacuated to 2000 microns and then isolated from pump, heated to 1450°C in 3 minutes, held at 1450°C for one hour | 13.8 |
| 7 | Bars in RSSN boat clamshell, silicon nitride powder in flanking boats, 1/2 hour at 1250°C under vacuum pumping, tube isolated from pump, 3 minute rise to 1450°C, 1/2 hour at 1450°C | 7.7 |
| 8 | Same as Run 7 except hold at 1250°C was for 45 minutes and hold at 1450°C was for 15 minutes | 7.1 |
| 9 | Repeat of Run 1 | 3.1 |
| 10 | Vacuum pumped, no hold at 1200°C, 9 minutes to reach 1450°C, 1/2 hour hold at 1450°C | 13.5 |
| 11 | To 1200°C under slightly flowing nitrogen. At 1200°C, tube evacuated to 2000 microns and then isolated from pump. Heated to 1450°C in 8 minutes, held there for 1/2 hour. | 5.8 |

TABLE 27 - RSSN DECOMPOSITION UNDER SIMULATED SILICONIZING CONDITIONS (continued)

| Run # | Run Description | Mean Sample Wt. Loss (mg) |
|---|---|---|
| 12 | Same as #11, but with $Si_3N_4$ powder in flanking boats | 9.8 |
| 13 | Same as #11 except tube pressure adjusted to - 5" Hg after 1450°C hold and before cooling | 8.4 |
| 14 | Same as #11 except $Si/SiO_2$ powder placed in flanking $Si_3N_4$ boats | 7.8 |
| 15 | Si powder getter placed outside furnace hot zone. Slight nitrogen flow to 1000°C, where pressure adjusted to 2000 microns. Temperature increased to 1200°C at 400°C/hr and then to 1450°C in 5 minutes for a 1/2 hour hold. Pressure adjusted to - 5" Hg after hold and before cooling | 11.3 |
| 16 | Repeat of #11 | 11.0 |
| 17 | Si getter in place, slightly flowing argon until 1200°C at which tube closed off and heated rapidly to 1450°C for a 30 minute hold. $Si/SiO_2$ powder placed in flanking boats | 4.7 |
| 18 | Tube condensates removed by mechanical and thermal means before run. Other conditions identical to Run 17 except no SiO generator used | 4.1 |

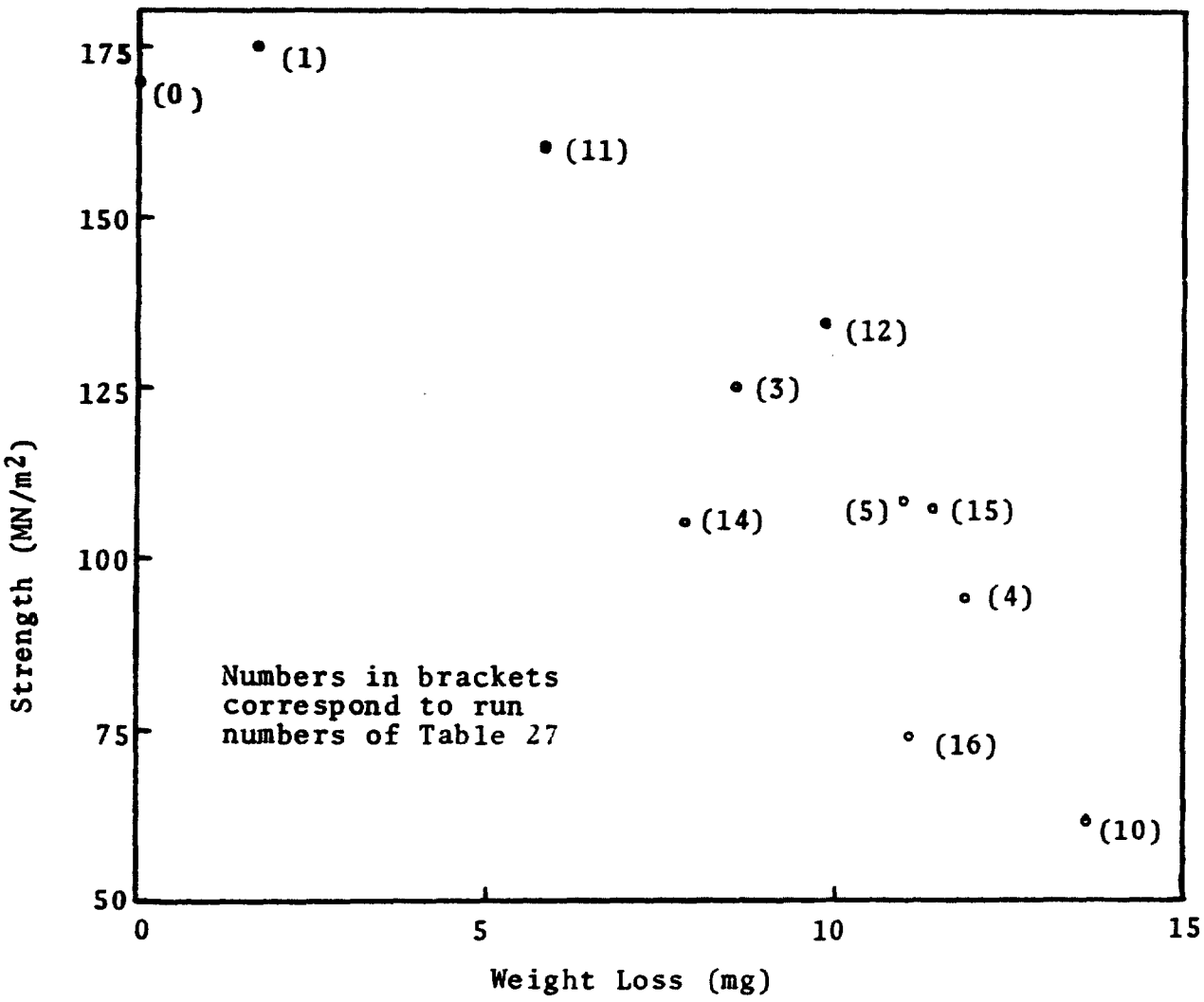



Figure 12 - Mean specimen weight losses during simulated siliconizing runs versus mean bend strengths after runs.

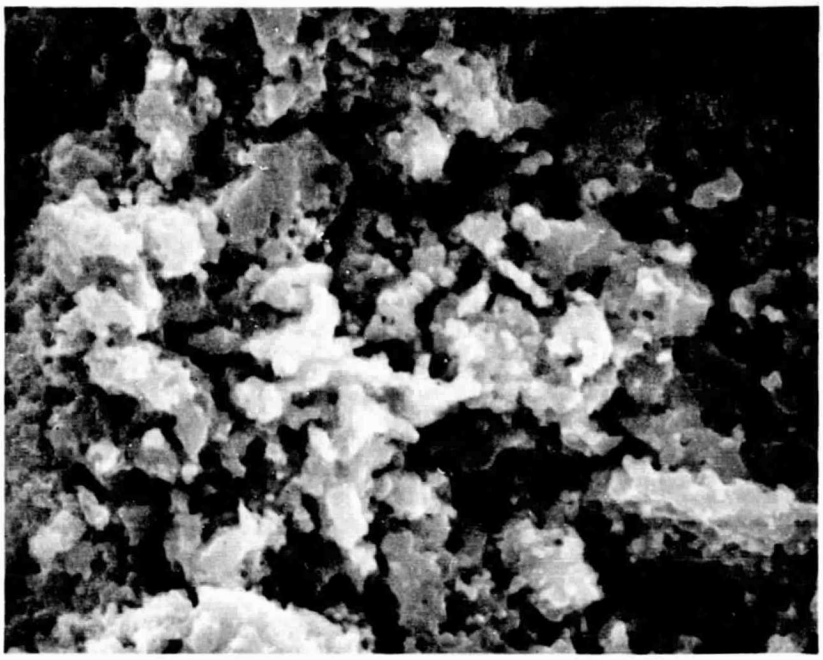


Figure 13 - Microstructure of RSSN exposed to vacuum conditions for five hours at 1400°C. 5000X.

over silicon nitride and the Ideal Gas Law. Such a calculation was carried out and it was found that the volume that would be filled by 10 mg (the approximate weight loss of a single specimen) of nitrogen at the equilibrium decomposition pressure of silicon nitride at 1450°C would be approximately ten times the actual volume of the chamber. This result indicates that an equilibrium decomposition can not account for the weight loss.

The possibilities that either an evaporization-condensation loop existed in the furnace or that the majority of the weight loss was not related to the thermal decomposition of pure silicon nitride were considered. For an evaporation-condensation process to operate, a silicon containing vapor species is required to transport the silicon to the condensate. At the nitrogen dissociation pressure of silicon nitride at 1500°C, the vapor pressures over silicon nitride of two potential carrier species, elemental silicon and silicon mononitride, are both less than $5.5 \times 10^{-7}$ atm [30]. These pressures are believed to be too low to enable the required mass transport in the time of the experiment. Furthermore, the placement of sacrificial silicon nitride powder within the hot zone (Runs #5 and #12) was not effective in significantly suppressing weight losses, which might reasonably have been expected if the losses were controlled by the decomposition of pure silicon nitride.

With regard to a decomposable substance other than pure silicon nitride, it is known that the RSSN contained oxygen; the material in use was found to contain 1.7 percent oxygen by neutron activation analysis. The rapid loss of a substantial fraction of this oxygen could account for the observed weight losses. The vacuum treated sample of Figure 13 preferentially lost oxygen during the vacuum exposure: the total sample weight loss was approximately six percent as compared to an oxygen loss of thirty-one percent. Assuming that oxygen loss does occur during the short test runs, it is almost assuredly removed as silicon monoxide, which is capable of condensing in the cooler furnace parts and potentially effecting an evaporation-condensation loop. However, when silicon monoxide was intentionally introduced into the tube (Run 14) to suppress the rate of monoxide evolution from the RSSN, the magnitude of the change in the weight loss in this run exceeded that of Run 11 which did not use a monoxide generator. This result indicates that silicon monoxide volatilization is not responsible for the weight losses.

The use of an argon atmosphere produced relatively small weight losses (Runs 17 and 18 of Table 27). As a result, silicon infiltrations were attempted at 1500°C using argon and 95 percent argon plus 5 percent hydrogen atmospheres. In both cases, the silicon failed to wet the RSSN, whereas wetting and infiltration readily occurred under vacuum at 1500°C. This dependence of wetting on pressure is similar to that found by Swartz [31] for both RSSN and a CVD silicon nitride. Although the reluctance of silicon to wet silicon nitride under pressure has been observed on a variety of silicon nitride materials, as Swartz points out, this is very unusual behavior and it is doubtful that it is intrinsic to silicon nitride since Inomota [32] has reported wetting and infiltrating RSSN under nitrogen at atmospheric pressure. It is the author's belief that the unusual weight losses and the unusual wetting behavior are related.

After many simulated siliconizing runs, fluffy, white condensates were found near the cooler ends of the furnace tube. These deposits were hydroscopic and bubbled when exposed to laboratory air. When heated in a gas flame, the deposits emitted the characteristic yellow radiation of sodium ions and thus were identified as containing sodium. The two potential sources of this sodium are the alumina furnace tube and the RSSN specimens. Alkali and alkaline earth oxides are frequent impurities in alumina tubes and their presence in the atmosphere during the nitridation process [33]. On the other hand, the RSSN specimens used in this study are known to contain a small amount of sodium as a result of conditions existing during the nitridation process. It is postulated that the specimen weight losses during heating are related to the sodium species by one of two mechanisms depending on the source of the sodium species. The first possibility involves the interaction of a species, originating from the furnace wall, with

the RSSN to produce another volatile species. The second possibility, and the one which is considered more relevent to the current discussion, is the volatilization of a sodium species from the RSSN itself. Weight losses have been monitored as a function of the number of vacuum exposure cycles and it has been found that smaller losses occur on successive cycles. This is strong evidence that the volatile species originates within the RSSN and may be exhausted. The rapid volatilization of such a species from the RSSN can explain the unusual weight losses that have been observed [34] when RSSN, manufactured under similar conditions, was rapidly inserted into a furnace under oxidizing conditions.

Although a sodium species is known to be present in the RSSN, the identity of the species is unknown. However, assuming the volatilization of the species is responsible for the strength losses of RSSN during vacuum heating, it would seem likely that the sodium is present in chemical combination with the silicon nitride, possibly as a grain boundary phase. If the species were not an integral part of the RSSN, it is difficult to understand how the removal of such a small amount of material could so strongly influence the mechanical properties. Jack [20] has discussed the existence of lithium silicon nitrides and noted that they usually contain oxygen with the general formula, $Li_{1-x}Si_2N_{3-x}O_x$, where x is the degree of oxygen substitution for nitrogen. It is suggested that analogous compounds containing sodium, rather than lithium, exist in the current RSSN and whose volatilization is responsible for the RSSN's unusual wetting, weight loss and strength behaviors.

Time considerations did not permit a testing of the above hypotheses regarding sodium contamination and the strength losses associated with the siliconizing step as currently practiced could not be eliminated. Since the complete strength loss of the processing occurs during the siliconizing step and since the later carburizing or nitriding steps are expected to confer substantial oxidation protection to the RSSN, further work with this approach appears warranted using sodium-free RSSN.

## IX CONCLUSIONS

The strength behavior at 25°C of as-nitrided RSSN before and after oxidation is strongly influenced by the properties of the initial as-nitrided surface. In the absence of especially severe internal flaws, the relatively less dense surface layer contains the critical flaws for fracture and promotes more extensive oxidation. Efforts to strengthen and improve the oxidized strength of RSSN must be concerned with modifying the surface layer. (All statements regarding material strength in this section refer to measurements at 25°C.)

Attempts to form coatings on RSSN by the sintering of layers of micrometer sized particles were generally unsuccessful and are not regarded as the most feasible method of producing suitable coatings. The temperatures required to promote sintering are frequently accompanied by other undesireable reactions, such as silicon nitride decomposition or oxide-nitride interactions, which are detrimental to the strength of RSSN. Furthermore, in the presence of an essentially rigid RSSN substrate and without appreciable amounts of a liquid phase during sintering, it is difficult to see how a dense and adherent interface is capable of formation.

The introduction of oxides into the porosity of the RSSN via the impregnation and thermal decomposition of liquid precursor solutions yields finely divided powders of greater reactivity and permits additional thermal processing at temperatures which do not weaken the material. Some improvements in room-temperature bend strengths can be obtained by impregnating with either enstatite, zirconia-silica, or alumina-silica mixtures and firing at 1400°-1500°C under nitrogen. In these cases, the bonding of the oxides to the RSSN is believed to be through a silica phase.

Greater and more consistent strength improvements are possible with impregnations of alumina or zirconia derived from aluminum nitrate or zirconyl chloride solutions. Optimized strengths result from firing specimens in a nitrogen and silicon monoxide atmosphere for a few hours near 1400°C. With respect to the strengthening potential of other oxides, titania, derived from triethanolamine titanate, and yttria, derived from yttrium nitrate, produced unchanged and reduced strengths, respectively, when fired under the same conditions.

The strengthening mechanism of the alumina and zirconia treatments is incompletely understood, but is believed to result from a partial densification of the porous surface layer. Studies of specimen weight gains and surface XRD phases as a function of firing temperature and atmosphere suggest the formation of metastable nitrogen containing glasses. The strength enhancements of oxide impregnation treatments, although observed many times, were not consistently reproducible for unknown reasons. It is speculated that the spatial distribution and state of subdivision of the introduced oxide in the surface of the RSSN prior to the nitrogen firing critically influences the extent and nature of the reaction products and the final mechanical properties.

In the course of the investigations, it was found that various oxides influenced the rate of the alpha to beta phase transformation in the order $MgO > ZrO_2 > Al_2O_3$. The alpha to beta transition, by itself, does not degrade the strength of RSSN but changes occuring simultaneously with the transition may produce large strength decreases. For example, the presence of liquid enstatite within RSSN promotes the transformation and, in this case, the recrystal-

lization is accompanied by a large strength reduction. In addition, the presence of enstatite can produce severe strength loss in RSSN even below its melting point (1543°C) and liquid enstatite induces creep under the stress of gravity. For these reasons, the use of magnesium oxide or enstatite in RSSN should be avoided.

Under oxidation exposure (12 hours in air at 1250°C), oxide impregnated samples generally have lower weight gains per unit area and a higher percentage of retained strength than do untreated samples. These results are believed to be caused primarily by the partial sealing of the surface porosity by the new surface material. The development of RSSN with improved as-nitrided strength has relaxed the requirement that given treatment simultaneously improve strength both before and after oxidation exposure and has increased the relative emphasis on strength after oxidation. Indeed, little correlation was found between strength after firing treatment and strength after oxidation. In the best treatment for oxidation protection, wherein 90 percent of the as-nitrided strength (353 $MN/m^2$) was retained after oxidation, the strength actually increased as a result of the oxidation. Although the above result marks a substantial improvement over untreated material, the strength retention after oxidation also showed poor reproducibility. Until the cause of this variability is understood and controlled, the oxide impregnation approach lacks practical applicability.

The formation of continuous silicon nitride or silicon carbide layers on RSSN are expected to confer substantial oxidation protection because of the non-porous nature of the films. In addition, such coatings are expected to be mechanically and thermally compatible with RSSN if properly applied. Silicon nitride and silicon carbide were formed on RSSN with a two stage process involving first the infiltration of molten silicon and a second operation to either nitride or carburize the silicon. Small amounts of aluminum or titanium in the silicon improve the uniformity of the wetting and infiltration. The infiltration of molten silicon into RSSN is pressure dependent and occurred only under vacuum conditions. This behavior is not believed to be intrisic to pure silicon nitride, but rather to result from the presence of a non-wettable, sodium containing, film on the RSSN. Sublimination of the film under vacuum conditions produces minor weight losses and large strength decreases in the RSSN. Only a part of this strength loss was recoverable by carburizing or nitriding the introduced silicon. It is felt that if the strength losses associated with the siliconizing step could be suppressed, then this approach may produce a strong and oxidation resistant RSSN.

## REFERENCES


1. S. Wild, P. Grieveson and K. H. Jack, "Thermodynamics and Kinetics of Formation of Phases in the Ge-N-O and Si-N-O' Systems", p. 271 in Special Ceramics 5, P. Popper, ed., Brit. Ceram. Res. Assn., Stoke on Trent, 1972.

2. H. R. Baumgartner and D. W. Richerson, "Inclusion Effects on the Strength of Hot Pressed $Si_3N_4$", p. 367 Fracture Mechanics of Ceramics, R. S. Bradt et.al. eds., Plenum Press, 1974.

3. M. E. Washburn, Unpublished Norton Company Internal Report, 1973

4. S. Wild, et.al., "The Crystal Chemistry of New Metal-Silicon-Nitrogen Ceramic Phases", p. 289 in Special Ceramics 5.

5. L. J. Gauckler, H. L. Lukas and G. Petzow, "Contribution to the Phase Diagram $Si_3N_4$-AlN-$Al_2O_3$-$SiO_2$", J. Am. Ceram. Soc. 58 (1975), 346.

6. J. P. Mary, P. Lortholary, P. Goursat and M. Billy, "Procedure of Fabrication of Refractory Pieces Base on Silicon Oxynitride", French Patent #2,221,421, Oct 11, 1974.

7. P. Lortholary and M. Billy, "The Thermal Stability of $Si_2ON_2$ in Inert Atmosphere", C. R. Acad. Sc. Paris, 278, Series C, May 27, 1974, p. 1343.

8. H. R. Baumgartner and G. Q. Weaver, "Preparation of Beta Prime Sialon Using Silicon Oxynitride as a Reactant", paper presented at September 1975 Am. Ceram. Soc. Meeting, Indianapolis IN.

9. R. J. Lumby, B. North and A. J. Taylor, "Chemistry and Creep of Sialons", p. 283 in Special Ceramics 6, P. Popper, ed., Brit. Ceram. Res. Assn., 1975.

10. P. L. Land and J. M. Wimmer, "The product or Quasi-Equilibrium Diagram and the Kinetics for the System Delineated by $Si_3N_4$,$Al_2O_3$, $SiO_2$ and AlN for Temperatures Near 1750°C", Paper 68-B-75, Amer. Ceram. Soc. Meeting, Washington, DC, May, 1975.

11. K. Blegen, "Equilibrium and Kinetics in Systems Si-N and Si-N-O", p. 223 in Special Ceramics 6.

12. H. Priest, F. C. Burns, G. L. Priest and E. C. Skaar, "Oxygen Content of Alpha Silicon Nitride", J. Am. Ceram, Soc., 56, 1974, 395.

13. G. K. Layden, "Pressureless Sintering of Sialon Gas Turbine Components", Final Rept. of Contract N62269-76-C-0108, Naval Air Development Center, Feb. 1977.

14. D. R. Messier and G. E. Gazza, "Thermal Decomposition of $Al_2O_3$-$Si_3N_4$ Mixtures", J. Am. Ceram. Soc., 58, (1975), 538.

15. M. E. Washburn, "Silicon Oxynitride Refractories", Bull. Am. Ceram. Soc., 46 (1967), 667.

16. F. Thummler, F. Porz, G. Grathwohl and W. Engel, "Creep and Oxidation of Reaction Sintered $Si_3N_4$", p. 133 in Science of Ceramics 8, Brit. Ceram. Soc., 1976.

17. D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2nd Ed., U. S. Govt. Printing Office, 1971.

18. S. D. Skrovanek and R. C. Bradt, "Surface Treatment Strengthening of a Reaction-Bonded $Si_3N_4$", Paper 62-B-76, presented at Amer. Ceram. Soc. Meeting, Cincinnati, OH, May 1976.

19. G. K. Layden, "Process Development for Pressureless Sintering of Sialon Ceramic Components", Second Quarterly Report on Navy Contract N00019-75-C-0232.

20. K. H. Jack, "Sialons and Related Nitrogen Ceramics", J. Mater. Sci., 11, (1976), 1135.

21. J. C. Gilles, "Formation of Oxynitrides from Refractory Oxides; A Study of Their Structures and Properties", Rev. Haute Temper. et Refract., 2, 1965, 237.

22. G. E. Gazza, "Hot Pressed $Si_3N_4$", J. Amer. Ceram. Soc., 56 1973, 662.

23. R. M. Horton, "Oxidation Kinetics of Powdered Silicon Nitride", J. Amer. Ceram. Soc., 52, (1969), 121.

24. S. Lin, "Mass Spectrometric Analysis of Vapors in Oxidation of $Si_3N_4$ Compacts", J. Amer. Ceram. Soc., 58, (1975), 160.

25. R. W. Davidge, A. G. Evans, D. Gilling, P. R. Wilyman, "Oxidation of Reaction Sintered Silicon Nitride and Effects on Strength", p. 329 in Special Ceramics 5, P. Popper, Ed., Brit. Ceram. Res. Assn., 1972.

26. M. E. Washburn and H. R. Baumgartner, "High Temperature Properties of Reaction Bonded Silicon Nitride", p. 479 in Ceramics for High Performance Applications, J. J. Burke et.al. eds., Brook Hill Publishing Co., 1974.

27. F. W. Ainger, "Formation and Devitrification of Oxides on Silicon", J. Mater., Sci., 1, (1966), 1.

28. H. E. Otto, Figure 354 in Phase Diagrams for Ceramists, E. M. Levin et. al., eds., Amer. Ceram. Soc., 1964.

29. T. J. Whalen and A. T. Anderson, "Wetting of SiC, $Si_3N_4$ and Carbon by Si and Binary Si Alloys", J. Am. Ceram. Soc. 58, 1975, 396.

30. S. C. Singhal, "Thermodynamic Analysis of High-Temperature Stability of Silicon Nitride and Silicon Carbide", Ceramurgia Intl., 2, 1976, 123.

31. J. C. Swartz, "Atmosphere Effects on Wetting of $Si_3N_4$ by Liquid Si", J. Am. Ceram. Soc., 59, 1976, 272.

32. Y. Inomota, "Oxidation Resistant Si-Impregnated Surface Layer of Reaction Sintered Nitride Articles", Yogyo-Kyokai-Shi, 83, [1], 1975, 9.

33. R. B. Guthrie and F. L. Riley, Effect of Oxide Impurities on the Nitridation of High Purity Silicon", J. of Matls. Sci., 9, 1974, 1363.

34. W. C. Tripp and H. C. Graham, "Internal Structures and Physical Properties of Ceramics at High Temperature", Quarterly Report 6731-2 under Wright Patterson Air Force Base Contract No. F33615-71-1841, Dec., 1971.