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CLEVELAND STATE UNIVERSITY
Cleveland, Ohio 44115

# CONSOLIDATION OF $Si_3N_4$ WITHOUT ADDITIVES
(BY HOT ISOSTATIC PRESSING)

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Final Technical Report
to
NASA Lewis Research Center

HUN C. YEH

Department of Chemical Engineering
Cleveland State University
Cleveland, Ohio

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# CONSOLIDATION OF $SI_3N_4$ WITHOUT ADDITIVES

## (By Hot Isostatic Pressing)

## PREFACE

The principal investigator (P.I.) regrets to report that this project has not been carried out completely as planned.

A bright graduate student, Jerry Blimbaum, was recruited to work on the project using the facilities at NASA-Lewis in accordance with the grant proposal. The initial progress was on or exceeding schedule. However, after working on the project for 6 months due to personal reasons, he left CSU for a full time industrial position. Since then, the P.I. could not attract a graduate student to work on the project on a graduate assistantship arrangement. This was mainly because the nature of the project could not stimulate the interest of graduate students in the department of chemical engineering, with which the P.I. is associated as a result of a program reorganization at CSU after the grant was awarded. Nevertheless, the P.I., made every effort to continue the project using five occasional or transient graduate and/or undergraduate students to conduct the project. Most of them were non materials majors, thus requiring considerable training time.

Another unusual situation with this project was that the major experiments in the grant, Hot Isotatic Pressing (HIP'ing), were done off-campus at three different sites: Battelle - Columbus Lab., NASA-Lewis, and TRW. Most processing and testing work were also to be carried out off-campus. Consequently an unusual amount of communication and coordination effort was required.

Despite the above difficulties, some interesting and useful results have been generated in the areas of powder processing, HIP'ing, densification, phase transformation and mechanical properties of $Si_3N_4$ - based materials

The P.I. would like to apoligize for the unusual delay in submitting this report, and express deep appreciation for the cooperation and patience of the NASA Lewis admistrative and technical personnel associated with this grant.

# INTRODUCTION

Silicon nitride ($Si_3N_4$) materials are leading candidates for components in high temperature heat engines. It has been well documented that dense $Si_3N_4$ materials fabricated by either hot pressing (HPSN), pressureless sintering or high nitrogen pressure sintering (HNPS) exhibit high room temperature strengths but the strength deteriorates significantly at elevated temperatures [1]. The degradation in high temperature strength in these materials was attributed to the presence of a grain boundary glassy phase as a result of the required oxide densification aids at 5 w/o or higher[2]. These additives form a lower melting point grain boundary phase which becomes viscous at temperatures above about 1200°C, the temperature range in which the material is intended to be used in heat engines[3]. Consequently these materials do not meet the requirements of their intended applications. The main objective of this project is therefore to investigate the potential of using hot isostatic pressing (HIP'ing) technique to produce dense silicon nitride materials without or with a reduced amount of additives (much less than 5 w/o). Hot isostatic pressing technique can provide higher pressure and temperature than hot pressing can, thus has the potential of requirng less densification aids to consolidate $Si_3N_4$ materials. It was anticipated that if such dense materials could be fabricated, the high temperature strength of the material should be improved significantly.

Three different commerical $Si_3N_4$ powders were chosen for comparison at the initial stage of this study. In one of the earlier experiments of this project it became clear that none of the $Si_3N_4$ powders chosen for study could be densified to near full density without additives under the HIP'ing conditions employed in this investigation. Consequently the bulk of the work in this project was devoted to hot isostatic pressing with low additives (3 w/o or less).

Canning of the $Si_3N_4$ powder sample and HIP'ing behaviors of the (cans with the sample encapsulated in them) were the major experimental problems of this project. A substantial amount of effort was devoted to overcoming these problems. Observations on the phase transformation, densification behavior, and microstructures of the samples are also documented. Density, microhardness, four point bend strength (room temperature and 1370°C) were measured on selected densified materials.

# EXPERIMENTAL PROCEDURES

## 1. Materials

The main characteristics of the three starting $Si_3N_4$ powders are listed in Table I. The three powders are designated by their respective trade or manufacturer's name, KBI, SN502 and Plessey*, respectively. Table II shows the impurity contents of each $Si_3N_4$ powder. The major impurity contents of the additives, $Y_2O_3$, MgO and $Z_rO_2$ are listed in Table III. The powder mixture compositions studied are compiled in Table IV.

## 2. Powder Processing

A small attritor mill[4] was initially used to mix the powders. Due to high impurity pick-up (see results section) this technique was replaced by a procedure using $Al_2O_3$ ball≠ mill as described in the following. One hundred (100) gm of $Si_3N_4$ powder plus the appropriate additive was used in each batch; the weighed powder was put in a 3-1/2 in. dia x 6 in long plastic jar with 370 gm high purity alumina balls (1/2" dia.) as the mixing media. The jar was filled with heptane to 3/4 height of the jar. The filled jar was sealed with a

---

*KBI: High purity CP85, Lot 523-63-1 manufactured by Advanced Materials Engieering Inc. Dukesway Team Valley, Cateshead Co., England.
SN502: Trade name of a product of GTE Sylvania, Towanda, Pa., USA
Plessey: Plessey Co., Ltd., French Town, England.

≠ No good quality $Si_3N_4$ balls were available when this project was conceived.

## TABLE I

## STARTING $Si_3N_4$ POWDERS

| $Si_3N_4$ | Morphology* | Partilce Size* | Phases, wt% $\alpha/\beta$ | Specific Surface area, $m^2/gm$ |
|---|---|---|---|---|
| SN 502 | Fibrous | 0.03-5μm long | 93/7[≠] | 4.57 |
| KBI | Flake-like | 0.03-2μm dia. | 85/15 | 4.83 |
| Plessey | Flake-like | 0.03-3μm | 94/6 | ---- |

*Based on TEM Micrographs

[≠] The crystalline portion of the material. The material consists of 27 w/o amorphous $Si_3N_4$.

# TABLE II

## SPECTROGRAPHIC ANALYSIS OF AS RECEIVED $Si_3N_4$ POWDERS, PPM OR %

| IMPURITY | KBI | SN-502 | PLESSY |
|---|---|---|---|
| Al | 0.3% | 40 | 130 |
| B | <100 | -- | --- |
| Ca | 0.2% | 110 | 250 |
| Co | --- | --- | --- |
| Cr | 290 | 20 | 100 |
| Cu | 110 | 50 | 40 |
| Fe | 0.4% | 30 | 350 |
| Mg | 400 | 90 | 1200 |
| Mn | 260 | --- | 80 |
| Mo | 500 | 70 | --- |
| Na | 270 | --- | <.4% |
| Ni | 370 | 10 | --- |
| Ti | 410 | --- | 750 |
| W | 400 | --- | 40 |
| Zr | 130 | 60 | 8 |

# TABLE III

## SPECTROGRAPHIC ANALYSIS OF ADDITIVE POWDERS, PPM

| IMPURITY | $ZrO_2$ | MgO | $Y_2O_3$ |
|---|---|---|---|
| Al | 50 | --- | 30 |
| Ca | 90 | 110 | 20 |
| Cr | --- | --- | 30 |
| Cu | 80 | 60 | 70 |
| Fe | 40 | 30 | 70 |
| Mg | 90 | Major | 40 |
| Ni | --- | --- | 420 |
| Si | 210 | 150 | 20 |
| Ti | --- | --- | 60 |
| Y | --- | --- | Major |

## TABLE IV

## POWDER MIXTURE COMPOSITIONS

| $Si_3N_4$ Base | Additives (w/o) |
|---|---|
| SN502 | 0 |
| | 0.5 MgO |
| | 1 MgO |
| | 3 MgO |
| | 0.5 $Y_2O_3$ |
| | 1 $Y_2O_3$ |
| | 3 $Y_2O_3$ |
| | 0.5 $ZrO_2$ |
| | 1 $ZrO_2$ |
| | 3 $ZrO_2$ |
| KBI | 0 |
| | 0.5 MgO |
| | 1 MgO |
| | 3 MgO |
| | 0.5 $Y_2O_3$ |
| | 1 $Y_2O_3$ |
| | 3 $Y_2O_3$ |
| | 0.5 $ZrO_2$ |
| | 1 $ZrO_2$ |
| | 3 $ZrO_2$ |
| Plessey | 0 |
| | 0.5 MgO |
| | 1 MgO |
| | 3 MgO |
| | 0.5 $Y_2O_3$ |
| | 1 $Y_2O_3$ |
| | 3 $Y_2O_3$ |

cap and was then placed on a ball mill rotated at 180 rpm for 24hr. After milling, the content of the jar was emptied onto a pan and was let dry at room temperature in air for two days. The powder was then further dried in an argon furnace at 100°C until no further weight loss was observed. The dried powder was sieved through a 70 mesh screen and subsequently isostatically pressed in latex tubing at 60 Ksi. The density of the compacts was determined by their measured weight and volume after they were machined into simple shapes such as cylinders.

### 3. Canning Procedure

Both molybdenum and Tantalum sheets, both 10 mil thick, were used to fabricate the cans. Rectangular and cylindrical can geometries were tried. The rectangular design was discontinued for reasons to be discussed in the results section. Figure 1 shows the cylindrical can design. A flow chart showing the canning procedure for encapsulating a powder compact in a cylindrical can is shown in Fig. 2 and is explained below:

The cold isostatically pressed powder compacts were machined to fit into the cans as closely as possible. A BN coating was used to prevent direct contact, thus reactions between the can wall and $Si_3N_4$. Also, a two-step welding procedure was necessary to facilitate the final seal of the can in vacuum by electron beam welding (EBW). The outgasing step was to remove the undesirable low temperature substances retained in the powder.

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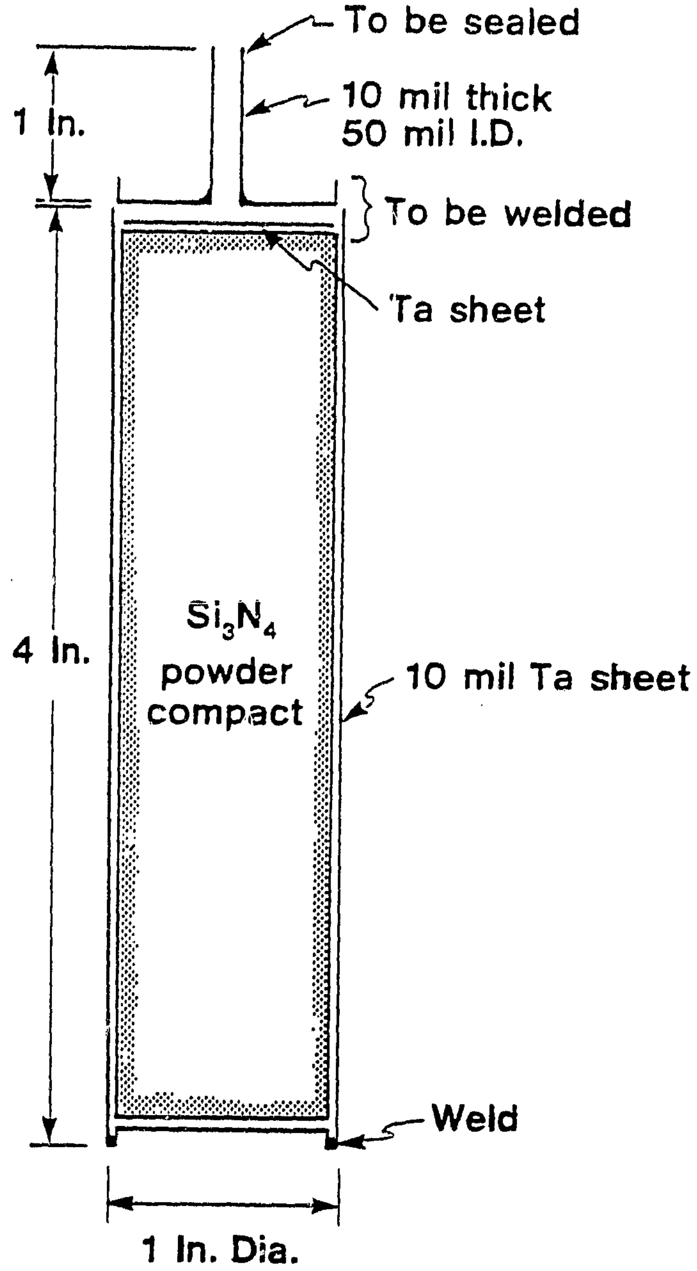

Figure 1 - Skematic Showing the Cylindrical Ta Can Design

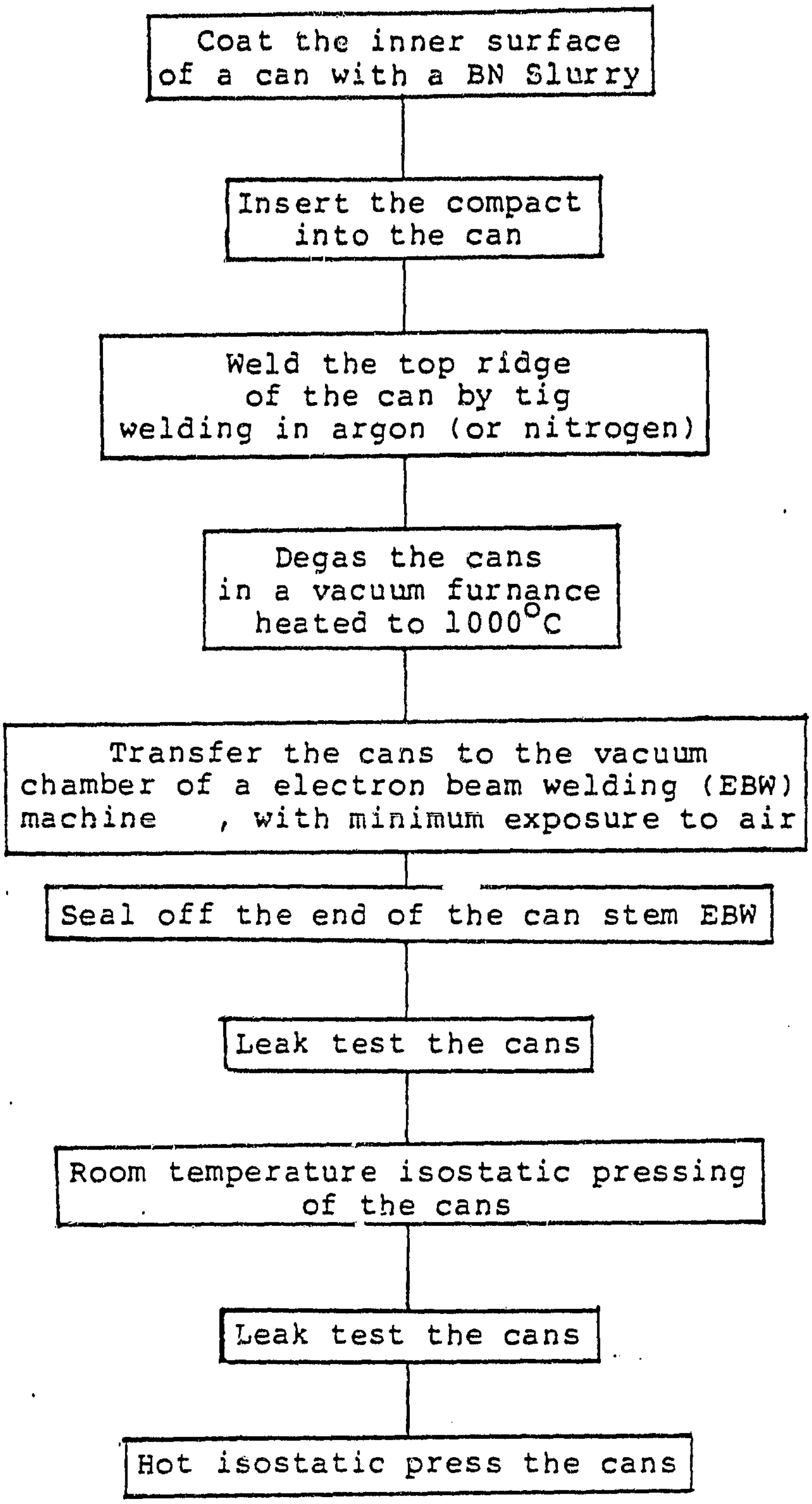

Figure 2 - FLOW CHART SHOWING CANNING AND HIP'ING PROCEDURES

Degassing of the semi-sealed cans (before the stems were sealed) was done using a vacuum furnace. The furnace containing the cans was evacuated to $10^{-6}$ torr. It was then heated up slowly, over a period of 4.25 hrs., to 1000°C. such that the vacuum reading of the furnace did not exceed $10^{-6}$ torr. After a two hour hold at temperature, the furnace was cooled to room temperature, then refilled by Argon. The argon filled cans were then quickly transferred to a vacuum desiccator to keep it dry during transport to an electron beam welding machine (EBW) which sealed off the stems of the cans under vacuum.

Cold isostatic pressing of the sealed cans was to reduce the void space between the can and the sample, thus minimizing the subsequent deformation of the can when the powder compact is being densified during HIP'ing. This would minimize the probability of cracking and/or leak development of the can during HIP'ing.

It was necessary to insure that the sealed cans were free of leaks shortly before they were placed into the HIP unit. This was accomplished by placing the sealed cans in a chamber filled with helium at 100 psi. After removal from the pressured chamber, the cans were immediately immersed into an alcohal bath. Bubbling from a can would indicate leakage.

The leak tested cans (if free of leaks) were wrapped with a Ta foil in a bundle and then were loaded into the HIP unit. HIP'ing runs were performed at Battelle Memorial

Institute (Columbus), NASA-Lewis and TRW-Cleveland. A description of a typical HIP unit can be found in reference 5. The maximum temperature and pressure capabilities of the above three HIP'ing units are 1750°C - 30Ksi, 2200°C - 20 Ksi and 2000° - 30 Ksi, respectively. A typical heating and pressurizing cycle of HIP'ing runs is shown in Figure 3.

## 4. Decanning and Characterization

After HIP'ing the cans (Ta) were striped from the samples by heating to 1100°C for 2 hrs in air to oxidize the Ta metal can. The oxidized Ta became fragile and was then removed by simple mechanical means. Molybdenum cans were stripped by HCl acid leaching. The HIP'ed samples, usually not perfect cylinders, were cleaned before density measurement by water immersion technique. The samples large enough for test bars were then sent to Bomas Machine Specilities, (334 Washington St., Somerville, Mass.) to be machined to standard 4-point bend strength test bars, (1/8" x 1/4" x 2") in accordance with NASA specifications (No. 193167). Specimen densities were measured again by water-immersion as well as weight and volume. Bend tests both at room temperature and 1370°C were performed at the mechanical testing laboratory at NASA-Lewis. Microhardness was measured on selected HIP'ed samples following a procedure described in Appendix 1.

Standard x-ray phase analyses were performed on most HIP'ed samples, and TEM on selected samples. TEM samples

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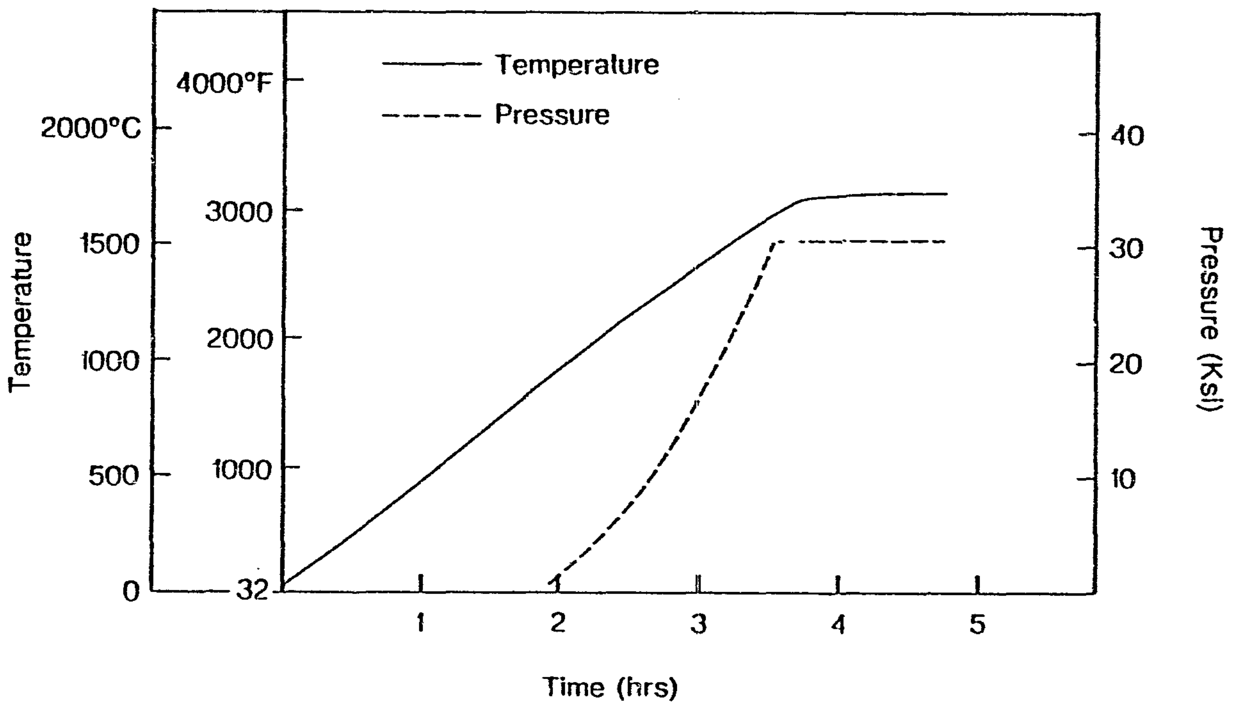


Figure 3 - Typical Temperature and Pressure Cycle of a Hot Isostatic Pressing Run

were prepared by standard ion thinning procedures. Both light and scanning microscopy were carried out on the fracture surfaces. Gold sputter coating was made on the fracture surface for the SEM work.

# RESULTS AND DISCUSSION

## 1. Mixing

It is important to have the additive powder particles evenly distributed in the base $Si_3N_4$ material. Milling was chosen as the method in mixing additives to the base $Si_3N_4$ materials. However, milling introduces impurities from the mixing media and the milling jar materials due to the abrasive nature of the $Si_3N_4$ powders. High quality $Si_3N_4$ balls would minimize the impurity pick-up problem, but they were not commercially available when this project was conceived. Some low quality reaction-bonded $Si_3N_4$ balls were tried. The balls chipped extensively and therefore were used only for a few batches.

Two milling methods were used: stainless steel attritor mill and $Al_2O_3$ ball mill using a plastic bottle as the jar. The major impurity pick-up after attritor milling were carbon and Fe. The increase in C and Fe were in the ranges of (0.2 - 0.4) and (3.0 - 7.3) wt%, respectively. The Fe pick-up was a strong function of the type of base $Si_3N_4$ materials. If Fe pick-up is used as a reference, Plessey is the least while SN502 being the most abrasive powder. The iron and C contents in the mixed powder were considered to be too high and no further results from the attritor milled materials are to be reported. Typical results of $Al_2O_3$ ball milled $Si_3N_4$ powders are listed in Tables V a - c. It is

## TABLE V - a

## MAJOR IMPURITIES IN SN 502 $Si_3N_4$ Mixtures

## MILLING WITH $Al_2O_3$ MEDIA*, WT.%

| ADDITIVES (WT.%) | C | O | Al | Mg | Y |
|---|---|---|---|---|---|
| 0.5 $Y_2O_3$ | 0.81 | 3.25 | 1.62 | 0.05 | 0.37 |
| 1.0 $Y_2O_3$ | 1.00 | 3.21 | 1.50 | 0.05 | 0.72 |
| 0.5 MgO | 0.48 | 2.64 | 0.34 | 0.30 | ---- |
| 1.0 MgO | 0.51 | 2.97 | 0.29 | 0.58 | ---- |

*After 24 hr Milling

## TABLE V - b

## MAJOR IMPURITIES IN KBI $Si_3N_4$ MIXTURES AFTER MILLING WITH $Al_2O_3$ MEDIA*, WT.%

| ADDITIVES (WT.%) | C | O | Al | Mg | Y |
|---|---|---|---|---|---|
| 0.5 $Y_2O_3$ | 1.15 | 3.00 | 1.56 | 0.08 | 0.38 |
| 1.0 $Y_2O_3$ | 1.17 | 2.99 | 1.52 | 0.06 | 0.77 |
| 0.5 MgO | 1.14 | 3.97 | 0.63 | 0.33 | ---- |
| 1.0 MgO | 0.92 | 4.10 | 0.64 | 0.58 | ---- |

*After 24 hr Milling

## TABLE V - c

## MAJOR IMPURITIES IN PLESSEY $Si_3N_4$ MIXTURES AFTER MILLING WITH $Al_2O_3$ Media*, WT%

| ADDITIVES (WT.%) | C | O | Al | Mg | Y |
|---|---|---|---|---|---|
| 0.5 $Y_2O_3$ | 1.21 | 2.01 | 0.72 | 0.028 | 0.37 |
| 1.0 $Y_2O_3$ | 1.24 | 2.00 | 0.64 | 0.03 | 0.76 |
| 0.5 MgO | 1.19 | 2.32 | 0.17 | 0.29 | ---- |
| 1.0 MgO | 1.23 | 2.30 | 0.27 | 0.53 | ---- |

*After 24 hr Milling

interesting to note that in all three $Si_3N_4$ mixtures the Al contents, which were obviously primarily from the milling media, consistently showed a higher level when $Y_2O_3$ was the additive than when MgO was the additive. More detailed investigaion is needed before a good explanation can be given. The level of Y and Mg contents is consistent with the amounts of the respective oxides added in all three types of $Si_3N_4$ chosen for study, reflecting the high accuracy of the weighing, mixing and chemical analysis results.

## 2. Powder Compaction

The higher the green compact density of a powder, the less is the necessary bulk volume contraction to reach full densification, thus less possible dimensional distortion during densification. This is particularly important in HIP'ing using a metallic can, because metal cans have a limited degree of plasticity even at high temperature. Larger extent of volume and shape changes of a metal can would result in higher cracking possibility during HIP'ing. Representative green densities of the three $Si_3N_4$ materials after being cold pressed at 60 KSI are listed in Table VI. The densities range from 46%, SN 502 $Si_3N_4$ group, to 62% theoretical for KBI $Si_3N_4$ group. Throughout this report, 3.18 g/cc, density of $\beta$-$Si_3N_4$, is used as the theoretical density for the purpose of comparison. The type and amount of addditives do not affect the powder density to a detectable amount. Fig. 4 shows the typical microstructures

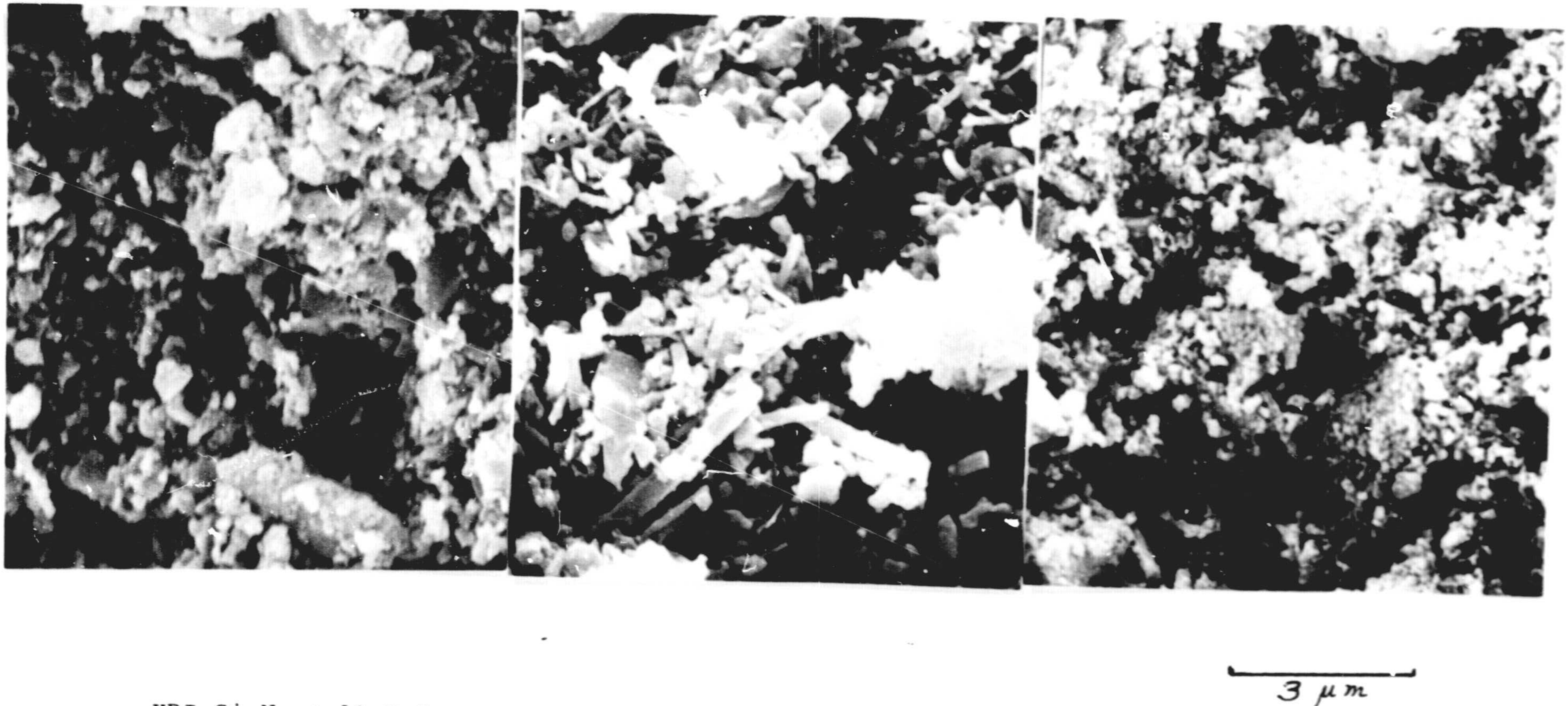
## TABLE VI

## GREEN COMPACT DENSITIES ‡

| $Si_3N_4$ Mixture Group | Densities % Theoretical* |
|---|---|
| SN502 | 43 ± 2 |
| Plessey | 55 ± 2 |
| KBI | 62 ± 2 |

‡ Isostatically pressed at 60 Ksi at room temperature

* The theoretical density of $\beta$-$Si_3N_4$, 3.18 g/cc, is used as a reference.



KBI $Si_3N_4$ + 1% $Y_2O_3$

SN502 $Si_3N_4$ + 1% $Y_2O_3$

Plessey $Si_3N_4$ + 1% $Y_2O_3$

Figure 4 - Scanning Electron Micrographs Showing the Typical Microstructures of the Powder Compacts After Cold Isostaically Pressed at 60 Ksi.

of the compacts made from the three $Si_3N_4$ powder chosen for study. Aggolmeration in the compact is apparent and the macropores between the agglomerates are in the order of 2-4 μm.

## 3. Canning

### a) Can materials

Selection of the can material is a very crucial step in HIP'ing studies. The can material first has to be able to withstand the temperatures at which HIP'ing is performed (1750°C in this investigation). Second it must be ductile and strong enough to transmit the high pressure of HIP'ing to the powder compact inside of the can. Only Mo and Ta metals meet these mechanical property requirements and also are economical enough to be fabricated into cans. Ideally a high temperature glass having a wide softening temperature range (1100°C - 1800°C) would be better. Among the major advantages of a glass can are that it can retain the shape of the powder compact pre-form better and it can be removed easier after HIP'ing. An ARPA contract conducted at Battelle - Columbus Laboratories was aiming at making such a glass.[6] Yet, a reliable glass composition does not seem to have been developed.

Even with Mo and Ta, cracking prior to or during HIP'ing was still occurring frequently. Between these two metals, Ta seemed to perform better. In addition, after

HIPing, the Ta-can can be stripped by a simple oxidation step, while Mo-can requires a messy HCl acid leaching procedure. These are the reasons for using Ta cans for the bulk of the experiments in this project.

### b) Degassing and Cold Isostatic Pressing

Gases or low vapor pressure substances trapped in the powder compact may expand during the heat up period counteracting with the external pressure on the can. These trapped gases may also cause the formation of macro-pores in the HIP'ed sample. Evidences indicated that without the degassing step the success rate of a HIP'ing run was very low.

Ta sheet which was used to construct the can was ductile enough to be deformed plastically to reduce the gap between the can and the sample, although care was taken to make the sample fit tightly into the can. Figure 5 shows the cold isostatically pressed cans. This step was to minimize the cracking problem of the can during HIP'ing.

### c) Can Geometry

Bend strength is one of the important properties to be measured. The standard test bar is rectangular in shape. Therefore it would be more desirable to HIP the sample into rectangular stock from which individual test bar can be machined with minimum material waste. It was thought that a rectangular can with a rectangular powder compact pre-form sealed in it could produce a rectangular sample. However,

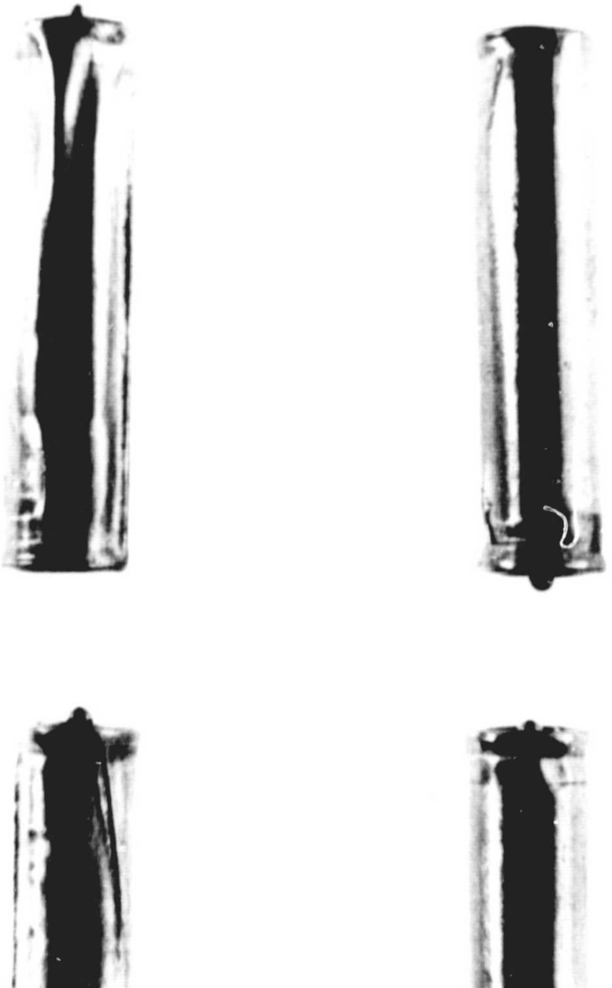


Figure 5 - Typical Cold Isostatically Pressed (60Ksi) Sealed Ta Cans with Powder Compacts Encapsulated in Them.

due to the tendency of the can to deform nonsymmetrically and the limited plasticity of the metal can at HIP'ing temperature, the deformation took place at the weakest spot of the can (center of the larger can surface), and wrinkling occurred at the can edges, as shown in Fig. 6. The cylindrical geometry provided a more uniform deformation and the contraction tended to result in the formation of wrinkles along the length of each can as shown in Fig. 7. One of the cans (marked HY8) in the figure was leaked, as evidenced by the pin hole at the end of the stem, and thus did not show much contraction. It is obvious that the cylindrical shape of the powder compact pre-form was retained in all other five cans. The bottoms of two cans separated, apparently during the cooling cycle after densification had already occurred.

## 4. Hot Isostatic Pressing

The HIP'ing runs were initially conducted at Battelle-Columbus Laboratory (contact: Roger Wills), then at NASA-Lewis (contact: G. Waston) and TRW-materials lab (contact: Jim Fleck). Table VII summarizes all the HIP'ing runs attempted in this investigation. The number of samples in each run varied from 6 to 20. Figure 8 shows samples of a more successful run (Run No.5, Table VII) after the cans were stripped. The number under each pair of samples represents a composition code to be defined later. The darker colored samples (Fig. 8) indicated that they were successfully HIP'ed to full (or near full) density, while

Figure 6 - Deformation of Rectangular Ta cans after HIP'ing

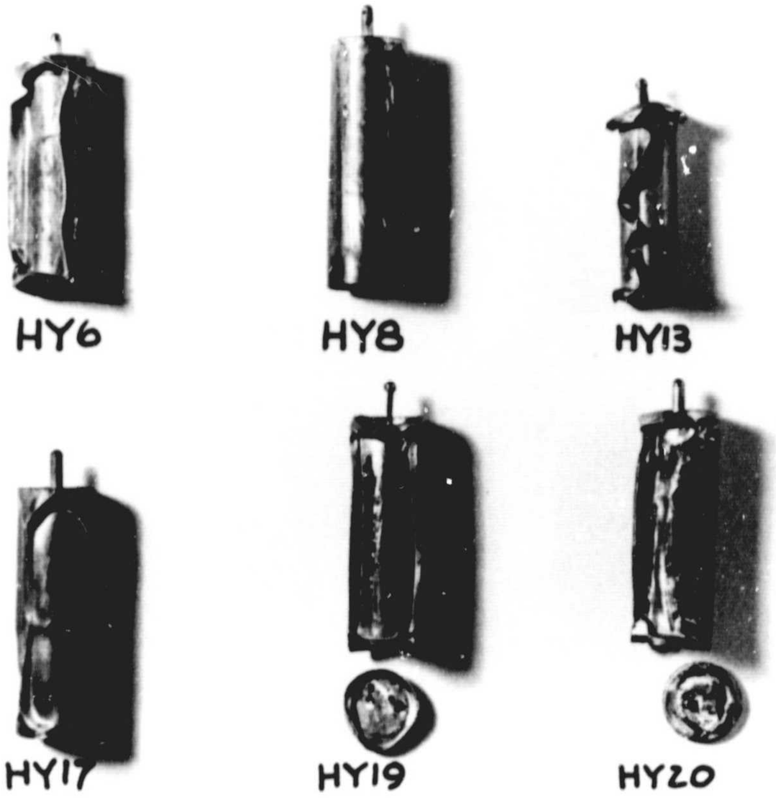


Figure 7 - Deformation of Cyclindrical Ta Cans After HIP'ing

## TABLE VII

## SUMMARY OF HIP'ING RUNS

| Run No. | Facility | HIP'ing Conditions ($^{o}$C Ksi - Min) | Remarks |
|---|---|---|---|
| 1 | Battelle - Columbus | 1550 - 9 - 0 | Failure run |
| 2 | " " | 1750 - 30 - 60 | Success run |
| 3 | " " | 1750 - 30 - 10 | Failure Run |
| 4 | " " | 1750 - 30 - 60 | Success Run |
| 5 | TRW - Cleveland | 1750$^{o}$C-30 Ksi - 120 | Success Run |
| 6 - 10 | NASA - Lewis | (see Appendix 2 ) | undesigned runs* |

*It was piggy-back with the runs designed for another project conducted by Tom Moore and G. Watson

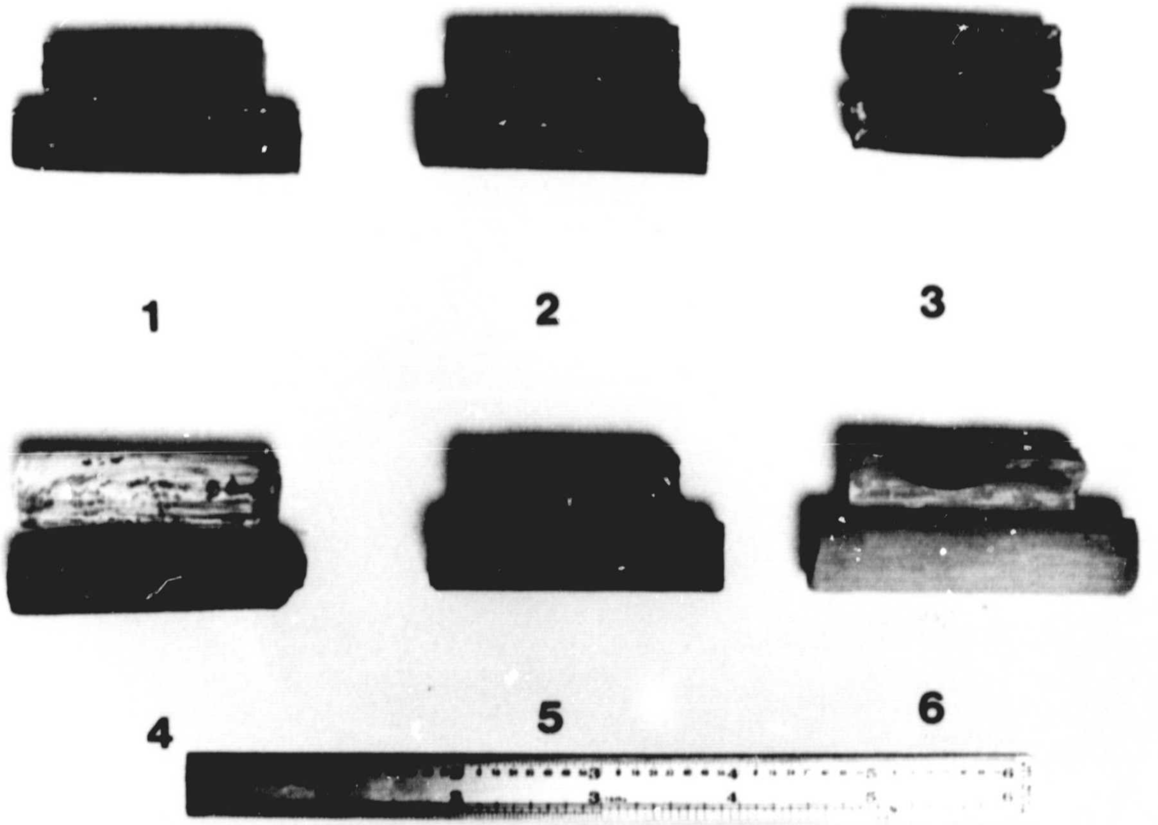


Figure 8 - HIP'ed Samples of a More Successful Run (Run No. 5 in Table VII), 1750°C - 30 Ksi - 2 hr. The Darker Colored Samples are Fully Dense While the Lighter Ones Are Not.

the gray or lighter colored ones indicated that they are not densified and a leak in the can was developed before HIP'ing was effected on the sample. Leakage could occur during the heating and pressurizing period or at the isothermal period when can deformation was still in progress. There is no reliable method to detect and/or prevent them from happening, and this is why there were always a few un-HIP'ed (leaked) cans in each run. In addition, failure of the HIP unit components could happen during a run.

## 5. Densities and Phases of HIP'ed Samples

Tables VIII a-d list the measured densities along with the HIP'ing conditions and sample compositions. For convenience of comparison, full (or theoretical) density is defined as the density of Beta $Si_3N_4$ phase, 3.18 gm/cc. The data in Table VIII show that in most cases as low as 0.5% additive is necessary to obtain near full density (>95% theoretical).

The data in Table VIII-a are plotted in Figure 9 to show the increase in density of each sample from its green density (dot in the graph) as the amount of additive is increased. The exception to this trend (SN502 + 1% $Y_2O_3$ sample) probably was due to possible leakage developed in the can during HIP'ing. ($ZrO_2$ containing samples did not consolidate well and therefore are not included in the graph.) Note, in Table VIII-a that KBI + 0.0 mixture milled with $Si_3N_4$ balls has a much lower density than that of its

# TABLE VIII - a

## DENSITIES AND PHASES OF HIP'ED SAMPLES

Facility: Battelle

Condition: 1750°C - 30 Ksi - 60 Min.

| Composition ($Si_3N_4$ + additive) | Can Leaked Yes | Can Leaked No | Density (% $\rho_{th}$) | Phase, Wt% α/β/ other |
|---|---|---|---|---|
| KBI + 0.0 | | X | 96.2(85.4)* | Not available |
| $0.5\%Y_2O_3$ | | X | 97.2 | " " |
| $3\%Y_2O_3$ | | X | 98.4 | " " |
| 0.5%MgO | | X | 96.3 | " " |
| 1%MgO | | X | 99.3 | " " |
| $0.5ZrO_2$ | | ? | 89.7 | " " |
| $1\%ZrO_2$ | | ? | 92.6 | " " |
| SN-502 + 0.0 | | X | 88.6 (88.6)* | " " |
| $0.5\%Y_2O_3$ | | X | 96.1 | " " |
| $1\%Y_2O_3$ | | X | 93.9 | " " |
| 0.5%MgO | | X | 95.0 | " " |
| 1%MgO | | X | 99.8 | " " |
| $0.5\%ZrO_2$ | ? | | 76.0 | " " |
| $1\%ZrO_2$ | ? | | 82.0 | " " |
| $3\%ZrO_2$ | ? | | ---- | " " |
| Plessey + 0 | | X | 88.9 | " " |
| $0.5\%Y_2O_3$ | | X | 96.5 | " " |
| $1\%Y_2O_3$ | | X | 96.4 | " " |
| 0.5%MgO | ? | | 91.8 | " " |
| 1%MgO | | X | 99.3 | " " |
| $1\%ZrO_2$ | ? | | ---- | " " |
| $3\%ZrO_2$ | ? | | ---- | " " |

*Note: The density value in ( ) was measured on samples prepared using poor quality $Si_3N_4$ balls as the mixing media.

## TABLE VIII - b

## DENSITIES AND PHASES OF HIP'ED SAMPLES

Facility: Battelle
Condition: 1750°C - 30 Ksi - 10 Min. (Intended to be 60 Min.)

| Composition | Can Leaked | | Density*g/cc | Phase, Wt% |
|---|---|---|---|---|
| ($SI_3N_4$ + additives) | Yes | No | (% $\rho_{th}$.) | $\alpha/\beta/Si_2ON_2$ |
| SN-502 + 0.5%$Y_2O_3$ | X | | 2.913<br>(91.3) | 45/48/7 |
| SN-502 + 1%$Y_2O_3$ | | X | 3.136<br>(98.6) | 46/46/8 |
| KBI + 0.5%$Y_2O_3$ | | X | 3.156<br>(99.3) | 43/54/3 |
| KBI + 1.0%$Y_2O_3$ | | X | 3.170<br>(99.7) | 45/52/3 |
| Plessey + 0.5%$Y_2O_3$ | | X | 3.172<br>(99.8) | 29/67/4 |
| Plessey + 1.0%$Y_2O_3$ | | X | 3.170<br>(99.7) | 16/81/3 |

*Mo and Ta cans were used for each composition.

Only the higher density value between the two samples was listed, assuming the lower value was due to can leakage.

## TABLE VIII - c

## DENSITIES AND PHASES OF HIP'ED SAMPLES

Facility: Battelle
Condition: 1750°C - 30 Ksi - 60 Min.

| Composition ($Si_3N_4$ + Additive) | Can Leaked | | Density, g/cc (% $\rho_{th}$) | Phases, Wt% $\alpha/\beta/Si_2ON_2$ |
|---|---|---|---|---|
| | Yes | No | | |
| SN-502 + 0.0≠ | | X | 2.828<br>(88.9) | 90/10/0 |
| + 0.5%MgO | | X | 3.154<br>(99.2) | 18/77/5 |
| + 1.0%MgO | | X | 3.159<br>(99.3) | 22/66/12 |
| KBI + 0.0≠ | | X | 2.874<br>(90.4) | 86/9/15 |
| + 0.5%MgO | | X | 3.144<br>(98.9) | 20/73/7 |
| + 1.0%MgO | | X | 3.145<br>(98.9) | 21/75/4 |
| Plessey + 0.5%MgO | | X | 3.158<br>(99.3) | 15/81/4 |
| + 1.0%MgO | | X | 3.166<br>(99.6) | 22/78/0 |

≠ mixed with $Si_3N_4$ balls

## TABLE VIII - d

## DENSITIES AND PHASES OF HIP'ED SAMPLES

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Facility: TRW - Cleveland

Condition: 1750°C - 30 Ksi - 120 min.

| Composition ($Si_3N_4$ + additive) | Can Leaked Yes | No | Density, g/cc (% $\rho_{th}$) | Phase* $\alpha/\beta/Si_2ON_2$ |
|---|---|---|---|---|
| SN502 + 1%$Y_2O_3$ | | X | 3.18<br>(100) | 2/96/2 |
| SN502 + 3%$Y_2O_3$ | | X | 3.20<br>(101) | 1/97/1 |
| KBI + 1%$Y_2O_3$ | | X | 3.21<br>(101) | 2/98/0 |
| 3%$Y_2O_3$ | | X | 3.23<br>(102) | 2/97/1 |
| 0.5%MgO | | X | 3.20<br>(101) | 2/98/0 |
| 1%MgO | X | | 2.85<br>( 92) | 1/99/0 |

*Use 3.18 $g/cm^3$ as the theorectical density for the purpose of comparison.

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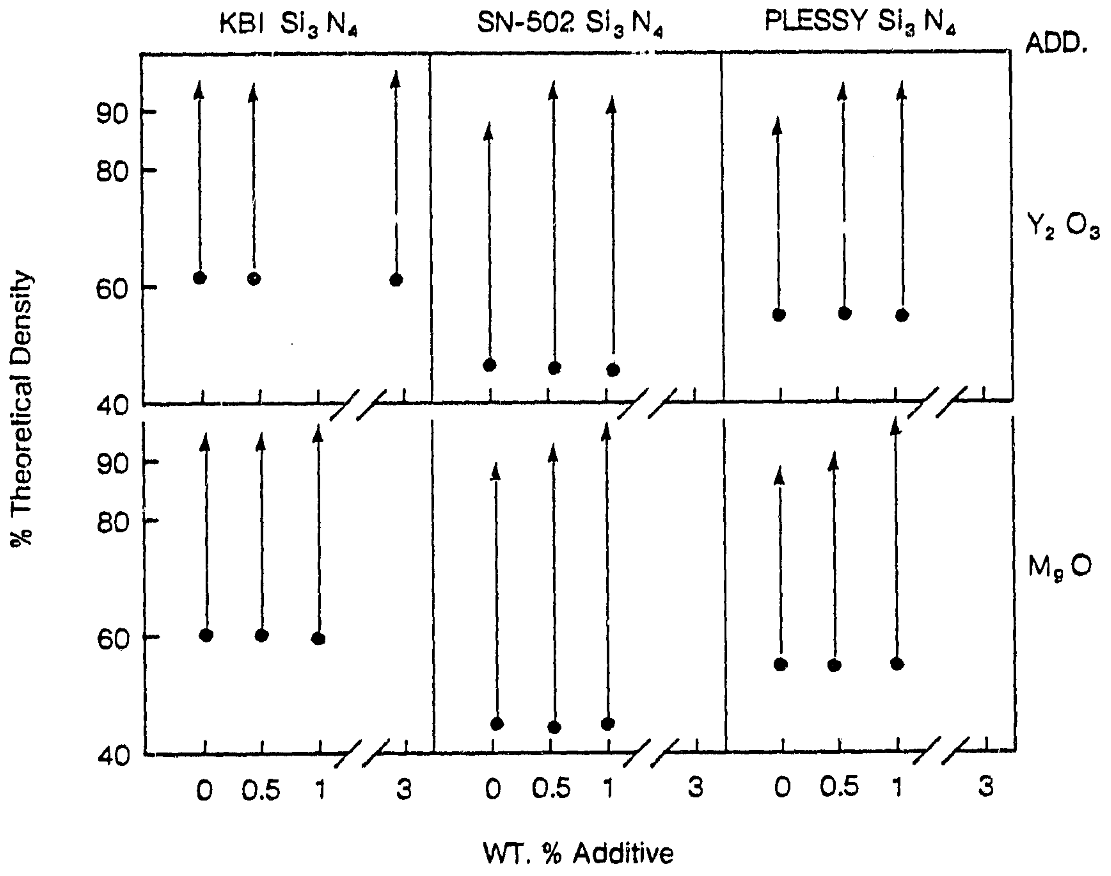


Figure 9 The increase in density of each powder mixture from its green density (dot in the graph) as a function of additives. Data taken from Table VIII-a

counterpart milled with $Al_2O_3$ balls. This illustrates the effect of $Al_2O_3$ pick up on densification from the milling media. However, SN502 + 0.0 mixtures milled by both $Al_2O_3$ balls and $Si_3N_4$ balls have the same density (Table VIII-a). Obviously the high impurity content in the starting KBI powder combined with the $Al_2O_3$ was the reason for the difference in KBI + 0.0 samples.

Dense $Si_3N_4$ materials consolidated by sintering or hot-pressing usually undergoes a full conversion of $\alpha$-$Si_3N_4$ to $\beta$-$Si_3N_4$ in the final product. It is interesting to note in Table VIII-b that most of the high density samples only have above 50% beta $Si_3N_4$. In Table VIII-c, the beta phase contents increase to about 75% and finally in Table VIII-d the beta content increases to about 95%. This observation illustrates that fully dense $Si_3N_4$ materials can be made without a full conversion of alpha to beta phase transformation. The increase in beta phase contents in the above samples (Tables VIII-a to VIII-c) was related to the longer holding time at 1750°C - 30 Ksi from 10 min to 120 min. when the sample densities were already near full density. Note, also that the two powder mixtures in Table VIII-c ball milled with $Si_3N_4$ balls (SN502 + 0.0 and KBI + 0.0) retain their respective starting. Alpha phase contents, within the error of the x-ray technique, although the samples had already been densified to as high as 90% theoretical.

6. Microhardness

A set of samples (Coded M-1 through M-6 in Table IX) with varying mixture compositions, was HIP'ed in the same run (run No. 5) and were subsequently mounted, polished and tested (microhardness) following the procedures described in a paper by Greshovich and Yeh (Appendix 1). The density and microhardness results are listed in Table IX. The highest hardness value is comparable to the highest value in Appendix 1. It is interesting to note that the density of the HIP'ed sample increases with the impurity level (KBI has a higher impurity level than SN502) when the additive level is identical. Also it increases with the additive level when the type of $Si_3N_4$ is the same. The data suggest that the microhardness of a dense $Si_3N_4$ is very sensitive to its impurity level in addition to it's density (or percentage of pores). Comparing samples M-1 with M-3, the only difference between the two samples is the starting silicon nitride; the higher purity SN502 exhibits a higher hardness. The same trend also exists between M-2 and M-4. Samples M-1 and M-2 were made of the same starting $Si_3N_4$ (SN502) but with different additive levels, 1% and 3% $Y_2O_3$ respectively. Although the density of M-2 is slightly higher than that of M-1, the microhardness is significantly lower. This fact can only be attributed to the increased level of $Y_2O_3$ in M-2. Furthermore, among the three dense samples (M-3, M-4 and M-5) made of KBI $Si_3N_4$, the sample with the lowest additive (M-5), again exhibits the highest hardness, even though the additives are different (MgO or $Y_2O_3$). The above

## TABLE IX

## MICROHARDNESS OF HIP'ED SAMPLES ≠

| CODE | MIXTURE COMPOSITION $Si_3N_4$ + ADDITIVE | DENSITY g/cc | MICROHARDNESS, $kg/mm^2$ MEASURED | AVERAGE |
|---|---|---|---|---|
| M-1 | SN502 + 1% $Y_2O_3$ | 3.16 | 1970 | |
| | | | 1920 | |
| | | | 1970 | 1924 |
| | | | 1790 | |
| | | | 1970 | |
| M-2 | SN502 + 3% $Y_2O_3$ | 3.20 | 1880 | |
| | | | 1750 | |
| | | | 1790 | 1800 |
| | | | 1750 | |
| | | | 1830 | |
| M-3 | KBI + 1% $Y_2O_3$ | 3.18 | 1640 | |
| | | | 1830 | |
| | | | 1750 | 1778 |
| | | | 1880 | |
| | | | 1790 | |
| M-4 | KBI + 3% $Y_2O_3$ | 3.22 | 1790 | |
| | | | 1790 | |
| | | | 1790 | 1760 |
| | | | 1680 | |
| | | | 1750 | |
| M-5 | KBI + 0.5% MgO | 3.18 | 1920 | |
| | | | 1750 | |
| | | | 1880 | 1812 |
| | | | 1790 | |
| | | | 1720 | |
| M-6* | KBI + 1% MgO | 2.85 | 1070 | |
| | | | 1040 | |
| | | | 1150 | 1108 |
| | | | 1110 | |
| | | | 1170 | |

*Can leaked, sample not densified.

≠ 1750°C - 30 Ksi - 2 hr.

observations would suggest the possibility that the hardness of a Beta-$Si_3N_4$ solid solution decreases as the amount of solute increases. As will be presented later, the grain sizes of the HIP'ed samples are below 1 μm, which is significantly below the size of the microhardness indentation (21.7 to 23.5 μm). Therefore, the microhardness values should also reflect the nature and amount of the grain boundary phase present in the sample. The relative degree of contribution between the property of the grain and the property of the grain boundary to the bulk hardness would require a more systematic investigation beyond the scope of this investigation. However, the above observation has clearly demonstrated that the hardness of a fine grained $Si_3N_4$ alloy is strongly dependant on its impurity (or alloying element level), not just its density.

## 7. Bend Strength Test

Bend test bars were machined from samples HIP'ed at 1750°C - 30 Ksi - 2hr in the same HIP'ing run (Run No. 5), thus being processed under identical conditions. Only up to six bend bars could be machined from each sample code (composition). In view of the facts that the number of test bars was limited, only one bend test per sample code was made at room temperature, the remaining test bars were all tested at 1370°C. The emphasis on hot strength is because the main objective of this project is to determine whether the high temperature strength of HIP'ed samples is higher than that of hot-pressed $Si_3N_4$ (HPSN) and sintered $SI_3N_4$. The four-point bend strength results are listed in Table X. The highest room temperature strength obtained was 132 Ksi (914 MPa), which is about the same as that of the best hot-pressed $Si_3N_4$ (Ref. 1). The lower measured room temperature values (in Table X) could be attributed to defects, subsurface or internal. The average of all the room temperature bend strength values measured is 94 Ksi (649 MPa), which is higher than the dense sintered $Si_3N_4$ alloys (550 MPa)[1]. Although not enough samples were tested, the dense HIP'ed $Si_3N_4$ samples probably have the same room temperature strength as that of the hot pressed silicon nitride. The hot pressed silicon nitride has a higher amount of additives than that of the HIP'ed samples. This would mean that the amount of grain boundary phase does not affect the room temperature strength of dense $Si_3N_4$ materials. As a comparison the room temperature bend strength data reported by Roger Wills ranged from 326 to 846 MPa[6], lower than those obtained in this investigation.

It is dissappointing to find that the high temperature bend strength values obtained range only from 17.4 to 35.5 Ksi (120-245) MPa), and the highest average among all five sample compositions tested is only 33 Ksi (227 MPa), which is not as good as the HPSN containing 8% $Y_2O_3$ (59Ksi/400MPa)[1]. Even the highest value obtained, 35.5 Ksi/245 MPa, is not as good as that of HPSN. The limited number of bend strength values measured on samples HIP'ed at

## TABLE X

## BEND STRENGTH OF HIP'ED SAMPLES ≠

| CODE | MIXTURE COMPOSITION $Si_3N_4$ + ADDITIVE | ROOM TEMPERATURE STRENGTH, Ksi (MPa) | | 1370°C STRENGTH Ksi (MPA) |
|---|---|---|---|---|
| M-1 | SN502 + 1% $Y_2O_3$ | 70 (483) | | 25.4(175) |
| | | | | 28.3(195) |
| | | | | 29.7(205) |
| | | | | 19.6(135) |
| | | | | 31.2(215) |
| | | | Average = | 27.2(187) |
| M-2 | SN502 + 3% $Y_2O_3$ | 81 (556) | | 26.8(185) |
| | | | | 26.8(185) |
| | | | | 29.7(205) |
| | | | | 32.6(225) |
| | | | Average = | 29.0(200) |
| M-3 | KBI + 1% $Y_2O_3$ | 132 (914) | | 34.8(240) |
| | | | | 28.2(194) |
| | | | | 26.1(180) |
| | | | Average = | 29.7(205) |
| M-4 | KBI + 3% $Y_2O_3$ | 79 (543) | | 35.5(245) |
| | | 80 (550) | | 30.5(210) |
| | | | Average = | 33.0(227) |
| M-5 | KBI + 0.5 MgO | 122 (841) | | 29.0(200) |
| | | | | 23.2(160) |
| | | | | 18.9(130) |
| | | | | 34.8(240) |
| | | | | 17.4(120) |
| | | | Average = | 24.7(170) |
| M-6* | | --- | | --- |

*Can leaked, sample not densified.

≠ 1750°C - 30 Ksi - 2 hr.

1750°C-20Ksi-2hr are even lower (Appendix 2). These results lead to the unexpected conclusion that the HIP'ed $Si_3N_4$ prepared in this investigation does not have a hot strength higher than that of the HPSN.

Note also that the average hot bend strength (Table X) has a narrow scattering band of 24.7 - 29.7 Ksi (170.4 - 205 MPa), reflecting the reliability of the measured values. If one accepts the low hot strength value being valid, than one possible explanation for these low values is that the property of the grain boundary phase, which becomes viscous at high temperatures, is the controlling factor, rather than the amount.

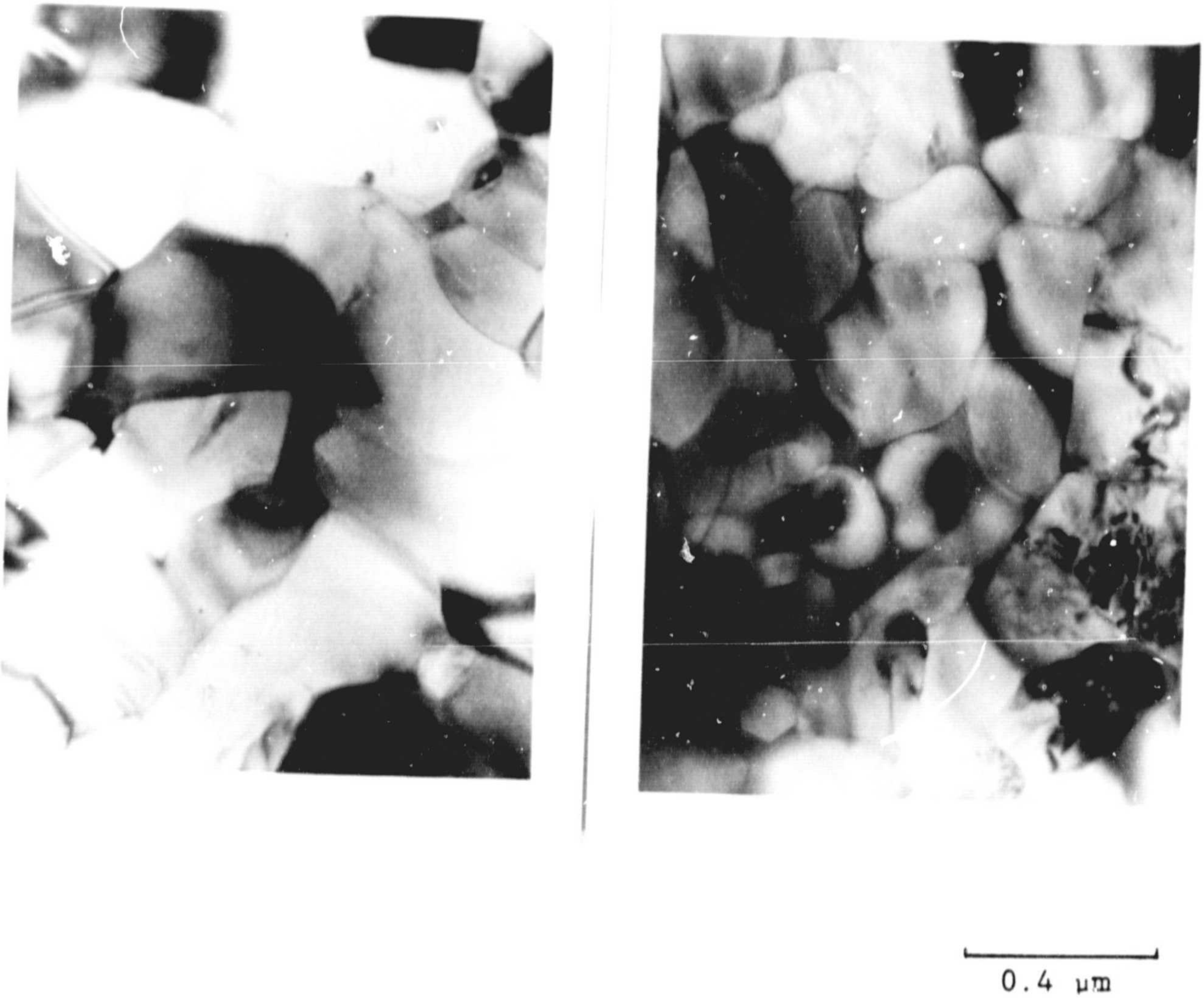
Smith and Quackenbush[7] reported that the $Al_2O_3$ had the effect of decreasing the high temperature strength of a $Si_3N_4$ + 6% $Y_2O_3$ material. The low 1370°C strength observed on the HIP'ed samples in this investigaton could be caused by the $Al_2O_3$ pick up from the milling media. However, the measured 1370°C strength does not seem to vary with the amount of $Al_2O_3$ pick up. Among the samples tested, sample code M-1 has the highest $Al_2O_3$ pickup, while M-5 the lowest.

Although, the number of test bars were not sufficient, some trends are noticeable. The hot strength of samples made of KBI $Si_3N_4$ (M-3 and M-4) are higher than the counterparts of the samples made of SN502 $Si_3N_4$ (M-1 and M-2 respectively). The higher amount of additives in a given type of $Si_3N_4$ also yield a high strength (M-3 compared with M-1; M-4 compared with M-2). These trends are consistent with the density trends (Table IX) mentioned previously. It is also interesting to note that the microhardness (Table IX) behaves opposite to hot strength in relation to density. The lowest average hot strength obtained is from M-5, which contains the lowest amount of additives (0.5% MgO).

## 8. Microstructures

A selected number of samples were examined under a transmission electron microscope. The grain size of the samples ranges from 0.06 to 0.6 μm. No grain boundary phase was detected in samples made of Plessey $Si_3N_4$ up to 1%MgO or 1% $Y_2O_3$ as the additive. A small amount of a grain boundary phase was found at the triple-point of a sample made of SN502 with 1% $Y_2O_3$. Samples made of KBI $Si_3N_4$ with 1.0% $Y_2O_3$ and higher additives show an amorphous grain boundary phase. Figure 10 compares the microstructures of a high purity $Si_3N_4$ (Plessey) sample and a low purity $Si_3N_4$ (KBI) sample, both with an 1% $Y_2O_3$ additive, which were HIP'ed in the same run. Clearly it is shown that the KBI sample has a grain boundary phase. One fully developed hexagonal crystal can be seen at lower left quarter of the KBI sample micrograph, suggesting that the solutioning - precipitation phenomenon was operative during HIP'ing. Most grains in the KBI sample are rounded apparently due to the solutioning phenomenon; while most grains in the Plessey sample retain the plate-like morphology of the original $Si_3N_4$ particles.

A detailed energy dispersive X-ray chemical analysis



Plessey $Si_3N_4$ + 1% $Y_2O_3$

KBI $Si_3N_4$ + 1% $Y_2O_3$

Figure 10 - Transmission Electron Micrographs of Samples HIP'ed at 1750°C - 30 Ksi - 1 hr.

(EDAX) was done on M-1 and M-3 samples (Table IX) to compare the grain boundary compositions. It was found that the M-2 sample (KBI $Si_3N_4$) contains higher concentrations of Mo and Fe than that of M-1 sample. The yittrium content is higher in the grain than in the grain boundary phase in both samples.

## CONCLUDING REMARKS

1. Commercial $Si_3N_4$ without additives can not be densified by HIP'ing at 1750°C - 30 Ksi - 2 hr.
2. The minimum amount of additives needed to densify $Si_3N_4$ (with $Al_2O_3$ pickup from the mixing media) by HIP'ing can be as low as 0.5% MgO or 0.5% $Y_2O_3$.
3. The highest room temperature bend strength obtained is 132 Ksi (914Mpa), measured on a KBI - 1% $Y_2O_3$ test bar.
4. The high temperature (1370°C) bend strength values range from 17 to 35.5 Ksi (117.1 - 244.6 MPa) with most of the data centered around 29.0 Ksi. (199.8 MPa), lower than the reported strength of HPSN at 1370°C. These low values could be caused by $Al_2O_3$ pick up from the milling media used.
5. Samples made from KBI silicon nitride seemed to exhibit higher hot strength than those made from SN502 silicon nitride having the same amount of additives. This suggests that the higher amount of impurities in KBI silicon is beneficial to high temperature strength.
6. Microhardness (room-temperature) as high as 1970 $Kg/mm^2$ was obtained. The average hardness values for fully densified samples range from 1760 to 1924 $Kg/mm^2$.
7. The microhardness value measured on samples made

from SN502 $Si_3N_4$ are consistently higher than those made from KBI $Si_3N_4$ having the same amount of additives. Also samples made from the same $Si_3N_4$ material show a consistent decreasing trend in hardness with amount of additive. Microhardness is a sensitive and reliable tool to detect impurities (or presence of glassy phase) in dense $Si_3N_4$ materials.

8. The alpha to beta phase tranformation in a dense $Si_3N_4$ material at 1750°C - 30 Ksi is a function of time. $Si_3N_4$ without additive milled with $Si_3N_4$ balls could retain high alpha phase concentration after HIP'ing.
9. Tantalum is a good envelope material for HIP'ing $Si_3N_4$ at 1750°C - 30 Ksi. A sample preparation and canning procedure has been developed.

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# ACKNOWLEDGEMENTS

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# APPENDIX 1

## Hardness of Dense $Si_3N_4$

A paper submitted to J. of Materials Science Letter for publication.

# Hardness of Dense $\beta$-$Si_3N_4$

C. GRESKOVICH
General Electric Corporate Research & Development
Schenectady, New York 12301 USA

H. C. YEH
Cleveland State University
Cleveland, Ohio 44115 USA

Hardness is an important property of silicon nitride ceramics considered for use in cutting tool and other applications. Previous investigations (1-3) and our own show that the microhardness of $Si_3N_4$ decreases with increasing load as expected for hard, brittle ceramics. Furthermore, the hardness of $Si_3N_4$ varies with the fabrication techniques of reaction sintering (4), hot pressing (1,5) and CVD (2,3), and may be related to differences in microhardness testing methods, phase and chemical composition, and microstructure (porosity, grain size and orientation, second phase(s), etc.).

There is little hardness data on high density $Si_3N_4$ produced by powder consolidation methods. Coe et al. (1) reported an inverse relationship exists between hardness and maximum strength of hot pressed $Si_3N_4$ containing 1% MgO as a densifying aid. They also presented evidence indicating that an inverse relationship exists between hardness and grain size. Tsuge and Nishida (5) studied Vickers microhardness values of hot pressed $Si_3N_4$ with $Y_2O_3$ and $Al_2O_3$ additions and found large decreases in hardness with increasing $Y_2O_3$ and/or $Al_2O_3$ additions. For example, under a 500g load the room temperature Vickers hardness number was 2040 $kg/mm^2$ for dense $Si_3N_4$ containing 5 wt% $Al_2O_3$ whereas a value of 1460 $kg/mm^2$ was measured for samples containing 5 wt% $Al_2O_3$ and 10 wt% $Y_2O_3$. Although an explanation was not offered for the drop in hardness with increasing concentration of $Y_2O_3$ and/or $Al_2O_3$, Tsuge and Nishida (5) presented X-ray diffraction and crystallization results that strongly suggested the presence of a greater amount of residual glassy phase in hot pressed $Si_3N_4$ containing greater concentrations of additives. In all cases, $\beta$-$Si_3N_4$ solid solution was the only crystalline phase detected in the "as-pressed" material.

Recently, Tsukuma et al. (6) studied the high temperature Vickers microhardness of $Si_3N_4$ with and without additives prepared by high pressure (3.0 GPa) hot pressing. A drastic decrease in microhardness was measured at 750°C for dense $\beta$-$Si_3N_4$ containing 4 wt% MgO and at ≈ 950°C for dense $\beta$-$Si_3N_4$ containing 4 wt% $Al_2O_3$ or $Y_2O_3$. Since the hardness of $Si_3N_4$ without additive only gradually decreased with increasing temperature up to 1200°C, they concluded the drop in high temperature microhardness for $Si_3N_4$ with additives is apparently due to softening of the residual glassy phase at the $\beta$-$Si_3N_4$ grain boundaries.

The present work represents a study of the effect of small changes in concentration of a densification aid (oxygen content) on the room temperature microhardness of $\beta$-$Si_3N_4$ ceramics fabricated by sintering and hot isostatic pressing methods. The compositions studied were $Si_3N_4$ containing 7 wt% $BeSiN_2$, a fixed nonoxide densification aid, and 1.9 to

3.7 wt% oxygen, the other variable densification aid. The difficulty in sintering compositions with low oxygen contents required that hot isostatic pressing be used for the consolidation step. The compositional range of oxygen content was selected to (1) investigate the changes in microhardness for $\beta$-$Si_3N_4$ ceramics prepared with single-phase and polyphase (glass-containing) microstructures and (2) minimize the concentration of densification aids necessary for making dense $Si_3N_4$ so that a large degree of covalent bonding would be maintained within the $\beta$-$Si_3N_4$ crystal structure.

The ceramic processing of the as-received, high purity $Si_3N_4$ powder* has been reported previously (7, 8). The processed powder contained 7 wt% $BeSiN_2$ as a densification aid and had a specific surface area of 10.7 $m^2g^{-1}$, an oxygen content of 1.86 wt% and an Fe impurity level of 50 ppm. Green bars with dimensions 6 cm x 1 cm x 1 cm were formed from the processed powder by die-pressing to shape at 35 MPa then isostatic pressing at 200 MPa. The oxygen content of each green compact was then carefully controlled by an oxidation method (9) and measured accurately by neutron activation analysis. The oxidation treatment provided compacts with oxygen contents of 1.86 (unoxidized), 2.50, 3.12 and 3.65 wt%.

Previous hot pressing (10) and sintering (8) studies pointed out the difficulty of achieving full density ($\gtrsim$99% of theoretical density) when $Si_3N_4$ compositions, having 7 wt% $BeSiN_2$, contain $<$3.5 wt% O.

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* SN-502 grade, GTE Sylvania, Towanda, PA

Consequently, compacts with the lower oxygen levels of 1.86, 2.50 and 3.12 wt% were hot isostatically pressed in Ta-cans at 1750°C for 120 minutes using Ar gas at a pressure of 138 MPa (20,000 psi). The resulting samples were recovered by mechanical removal of the Ta-can. The compact having an oxygen content of 3.65 wt% was sintered in a BN crucible at about 2000°C for 30 minutes in 20 to 70 atm of $N_2$ gas.

The fired samples were characterized by the measurement of bulk density by the water immersion method and identification of phases by X-ray diffraction and optical microscopy. Vickers microhardness values were measured at room temperature on ceramographic sections having a final polish with 0.25 micron diamond paste. The hardness numbers reported were the average values for 5 indentations in each specimen under a 500g load. A loading rate of 0.05 mm/sec for a duration of 10 seconds was used for each impression. In every case the size of the diamond indenter impression was substantially larger (by more than a factor of 10) than the average grain size of the $\beta$-$Si_3N_4$ phase.

The preparative conditions, characterization and microhardness values for samples of $\beta$-$Si_3N_4$ containing 7 wt% $BeSiN_2$ and various (initial) oxygen contents are listed in Table I. The proportional relationship between high density and high oxygen content, regardless of the type of heat treatment, is illustrated by samples 1-4. X-ray diffraction analysis of these samples showed that they were composed primarily of $\beta$-$Si_3N_4$ containing small amounts of Be and O in solid solution. Sample 1, with an initial O-content of 3.65 wt%, contained 1 to 2% of residual glass located primarily at the edges and corners of the $\beta$-$Si_3N_4$ grains which were elongated and of average size $\approx 5\ \mu m$. This glass-containing sample had a low microhardness of 1650 kg/mm$^2$. Samples 2 and 3, containing lower oxygen contents of 3.12 and 2.50 wt%, respectively, exhibited lower densities and finer grain sizes but still gave rise to substantially higher microhardness values of 1950 and 1840 kg/mm$^2$. No glassy phase could be observed in these high hardness samples by examining polished sections under the optical microscope up to 1000 X magnification. Although it was difficult to measure grain size in HIP samples 2 and 3, SEM observations on fractured surfaces showed the presence of submicron, equiaxed $\beta$-$Si_3N_4$ grains typical of that found previously for single-phase hot pressed $Si_3N_4$ of the same composition (10, 11). The small amount of free Si present in all samples may be attributed to the partial dissociation of $Si_3N_4$ during firing. Sample 4 contained the lowest oxygen content and had the lowest density (only 83% of the theoretical value) and microhardness. Clearly the kinetics of densification were too slow for this powder composition consolidated under the hot isostatic conditions employed. All samples contained a uniform distribution of fine (micron to submicron) pores throughout the microstructure.

The Vickers microhardness of pure $\beta$-$Si_3N_4$ single crystals has been measured to be nearly 2000 kg/mm$^2$ under a 500g load (3) and is included in Table I for comparison. When the hardness data in Table I ware plotted as a function of density in Figure 1, a linear relationship exists among all samples except sample 1 which contains glassy phase. The significant drop in hardness for sample 1 suggests that the presence of a small amount of glassy phase has a large effect on the final hardness of $\beta$-

$Si_3N_4$ ceramics. The estimated volume fraction glass of 1 to 2% in sample 1 is equivalent to single-phase $\beta$-$Si_3N_4$ having a density of $\approx$2.92 g/cm$^3$ or a residual porosity of $\approx$8% (based on a theoretical density of 3.18 g/cm$^3$). The above linear relationship also suggests that the microhardness of pure $\beta$-$Si_3N_4$ single crystal (basal planes) is the upper limit of the polycrystalline, full density, single-phase $\beta$-$Si_3N_4$. (This suggestion assumes that their is little hardness anisotropy with crystal orientation for $\beta$-$Si_3N_4$ at relatively high loads of 500g). Although $\beta$-$Si_3N_4$ ceramics with relatively high hardness (1800 kg/mm$^2$) are useful as cutting tools (12), there is reason to believe that $\alpha$-$Si_3N_4$ ceramics may be even harder because it has been reported (3) that the basal planes of $\alpha$-$Si_3N_4$ are $\approx$28% harder than those of $\beta$-$Si_3N_4$ single crystals under identical microhardness testing conditions.

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## FIGURE CAPTIONS

Fig. 1 Vickers microhardness at 500g load vs. density of β-$Si_3N_4$. Only the sintered sample showed a small amount of grain boundary, glassy phase under a light microscope at 1000X. Data for β - $Si_3N_4$ single crystal taken from Ref. (3).

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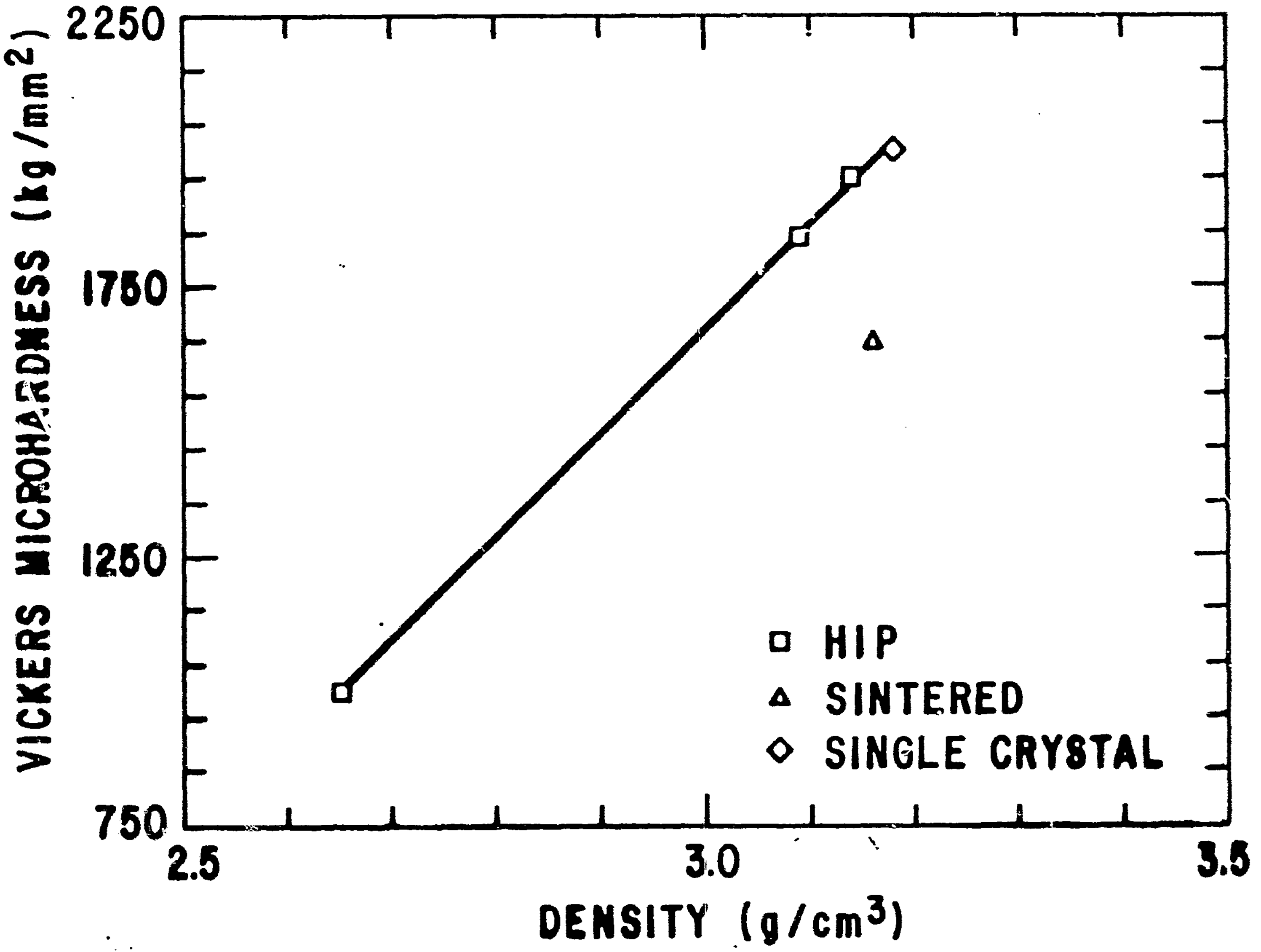

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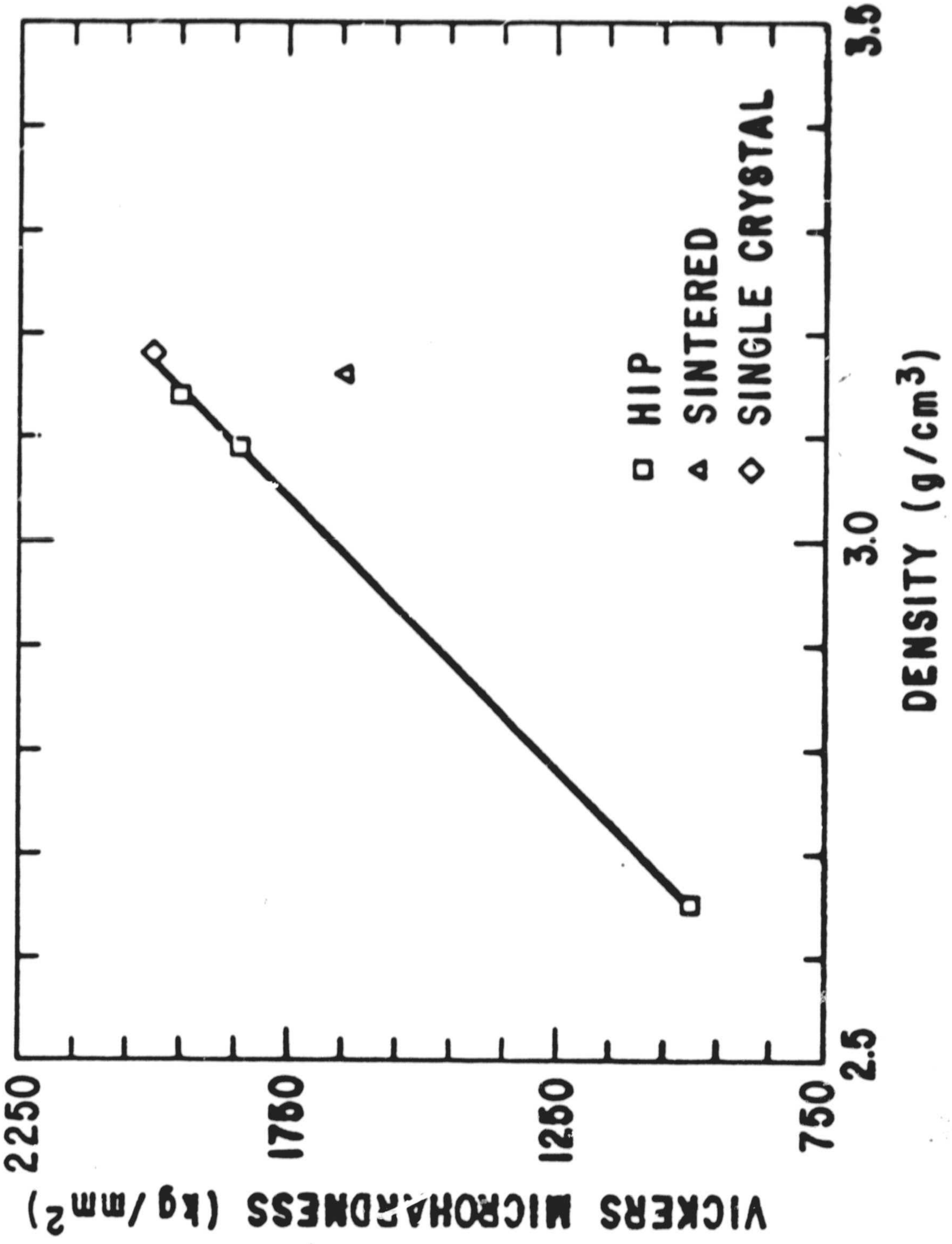

## TABLE I

Preparation, characterization and microhardness of $\beta$-$Si_3N_4$ ceramics containing 7 wt% $BeSiN_2$ and various oxygen contents.

| Sample | Oxygen Content (wt%) | Heat Treatment | Density + (g/cc) | Phases Present | $\beta$-$Si_3N_4$ grain size (μm) | Vickers (500g load) microhardness ($kg/mm^2$) |
|---|---|---|---|---|---|---|
| 1 | 3.65 | Sintered, 2000°C | 3.16 | $\beta$-$Si_3N_4ss$, glass<br>tr(Si, $Si_2N_20$, $Be_2Si0_4$) | 5 | 1650 |
| 2 | 3.12 | HIP, 1750°C | 3.14 | $\beta$-$Si_3N_4ss$<br>tr ($Si_2N_20$, Si) | < 1 | 1950 |
| 3 | 2.50 | HIP, 1750°C | 3.09 | $Si_3N_4ss$<br>tr (Si, ? $Si_2N_20$) | < 1 | 1840 |
| 4 | 1.86 | HIP, 1750°C | 2.65 | $\beta$-$Si_3N_4ss$, minor Si | n.d. | 1000 |
| Single crystals of pure $\beta$-$Si_3N_4$ grown at 1450°C* | | | | | 30-60 | 2000<br>(basal plane) |

+ theoretical density ≈ 3.18 g/cc
SS solid solution
tr trace amount
HIP hot isostatically pressed
n.d. not determined
* data from Ref. 3

# APPENDIX 2

## NASA HIP'ing Runs

## NASA HIP'ing Runs

A number of rectangular canned samples were run at Lewis along with other runs by G. Waston and T. Moore. The sample compositions were not selected systematically, therefore, no meaningful comparison can be recorded. They are listed in the following
Some strength measurements were made and are listed in the tables.

## TABLE A2 - 1

| Run | Composition | Density g/cm$^3$ | |
|---|---|---|---|
| | | Ta can | Mo can |
| HT 1 | KBI, No additive | 3.003 | 3.139 |
| | KBI + 1.0% $ZrO_2$ | 3.167 | 3.148 |
| | Plessey, No additive | 2.822 | 3.162 |
| HT 2 | KBI + 3.0% $ZrO_2$ | 2.719 | 3.190 |
| | 502 + 3.0% $ZrO_2$ | 2.675 | 2.784 |
| | Plessey + 1.0% $ZrO_2$ | 3.173 | - - - |
| HT 3 | Plessey + 3.0 $ZrO_2$ | 2.539 | - - - |
| | 502 + 0.5% $ZrO_2$ | 3.163 | - - - |
| | Plessey + 3.0% $ZrO_2$ | - - - | 3.200 |
| HT 4 | 502 + 0.5% $ZrO_2$ | - - - | 2.857 |
| | Plessey + 0.5% $ZrO_2$ | 2.988 | - - - |
| HT 5 | 502 + 1.0% $ZrO_2$ | 3.182 | - - - |

HIPPING CONDITIONS:

HT 1 --- 1850°C, 20 Ksi, 2 hrs.
HT 2 --- 1750°C, 20 Ksi, 2 hrs.
HT 3 --- 1850°C, 20 Ksi, 2 hrs.
HT 4 --- 1750°C, 20 Ksi, 2 hrs.
HT 5 --- 1950°C, 20 Ksi, 1 hr.

TABLE A2 - 2

HOT ISOSTATICALLY PRESSED $Si_3N_4$

| Composition<br>$Si_3N_4$ + wt.% $Y_2O_3$ | | Density<br>g/cm$^3$ | Bend Strength, Ksi<br>RM | <br>1370°C |
|---|---|---|---|---|
| SN502 | 0.5 | 3.11 | 88.3 | 20.3 |
| SN502 | 1.0 | 3.13 | 76.8 | 21.9 |
| Plessey | 0.5 | 3.14 | 26.9 | 29.0 |
| KBI | 0 | 2.86 | 55.1 | 21.5 |
| KBI | 0.5 | 3.06 | 74.9 | 17.4 |
| KBI | 1.0 | 3.05 | 73.9 | 18.9<br>3 1 |
| KBI | 3.0 | 3.20 | 79.7<br>113.3 | 15.7<br>15.4 |

Note: Samples were HIP'ed at 1750°C - 20 Ksi - 2 hr. at NASA-Lewis.

Phase distributions were obtained by X-Ray diffraction on flat sample surface.