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PRESSURELESS SINTERED β'-Si₃N₄ SOLID SOLUTION: FABRICATION, MICROSTRUCTURE, AND STRENGTH

Sunil Dutta
Lewis Research Center
Cleveland, Ohio

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PRESSURELESS SINTERED $\beta$-Si$_3$N$_4$ SOLID SOLUTION:
FABRICATION, MICROSTRUCTURE, AND STRENGTH

by Sunil Dutta

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

Pressureless sintering of $\beta$'-Si$_3$N$_4$ solid solution was studied as a function of temperature using Si$_3$N$_4$, AlN, and Al$_2$O$_3$ as basic constituents. Y$_2$O$_3$-SiO$_2$ additions were used to promote liquid-phase sintering. The sintered specimens were characterized with respect to density, microstructure, strength, oxidation, and thermal shock resistance. Density greater than 98 percent of theoretical was achieved by pressureless sintering at 1750 °C. The microstructure consisted essentially of fine-grained $\beta$'-Si$_3$N$_4$ solid solution as the major phase. Modulus of rupture strengths up to 483 MPa were achieved at moderate temperature (1000 °C), but decreased to 228 MPa at 1380 °C. This substantial strength loss was attributed to a "glassy" grain boundary phase formed during cooling from the sintering temperature. The best oxidation resistance was exhibited by a composition containing 3 mol % Y$_2$O$_3$-SiO$_2$ additives. Water quench thermal shock resistance was equivalent to that of reaction sintered silicon nitride but lower than hot-pressed silicon nitride.

While work in pressureless sintering is still in the early stages, the results of strength, oxidation, and thermal shock tests are extremely encouraging and suggest that with further development, it will be possible by pressureless sintering to produce dense, high strength $\beta$'-Si$_3$N$_4$ solid solution bodies for high-temperature structural applications.

INTRODUCTION

The existence of $\beta$'-Si$_3$N$_4$ solid solution in the system Si$_3$N$_4$-Al$_2$O$_3$ was first reported by Oyama and Kamigaito$^1$ in Japan and by Jack and Wilson$^2$ in England. Subsequent studies$^3,4$ found that Si$_3$N$_4$-Al$_2$O$_3$ mixtures do not form a single
phase $\beta$-$\text{Si}_3\text{N}_4$ solid solution for any composition. Instead, $\beta$-$\text{Si}_3\text{N}_4$ forms along the join $\text{Si}_3\text{N}_4$ and $\text{AlN}$-$\text{Al}_2\text{O}_3$ in the system $\text{Si}_3\text{N}_4$-$\text{AlN}$-$\text{Al}_2\text{O}_3$-$\text{SiO}_2$ with a metal:nonmetal ratio of 3/4. The extent of the $\beta$-$\text{Si}_3\text{N}_4$ solid solution is indicated in the behavior diagram as shown in Fig. 1. The solid solution can be described by the formula $\text{Si}_{6-x}\text{Al}_x\text{O}_x\text{N}_{8-x}$, where $x = 0 - 4.2$.

Considerable work on stoichiometry, structure, and properties of hot pressed $\beta$-$\text{Si}_3\text{N}_4$ solid solution has been reported in the literature indicating that these ceramics have a combination of mechanical, thermal, and chemical properties, which might make them candidates for high-temperature structural applications in heat engines. These refractory ceramics are difficult to densify without hot pressing. However, hot pressing is a batch process and has limited shape capability. Therefore, it is usually not considered to be a cost effective process. As a result, effort is now being concentrated on the development of pressureless sintering methods to densify these ceramics. Recently, Lumby et al. reported on the fabrication and properties of $\beta$-$\text{Si}_3\text{N}_4$ solid solution but the compositions and additives were not reported. Wills produced high density reaction sintered $\beta$-$\text{Si}_3\text{N}_4$ solid solution of composition 50 mol % $\text{Si}_3\text{N}_4$-25 mol % $\text{AlN}$-25 mol % $\text{Al}_2\text{O}_3$. In order to obtain high final density by pressureless sintering, additives are commonly used to promote sintering. However, the additives also limit the high-temperature strength by forming a viscous grain boundary phase.

The purpose of this study was to develop high density $\beta$-$\text{Si}_3\text{N}_4$ solid solutions by pressureless sintering utilizing two levels of additive, and to determine high-temperature mechanical strength, thermal shock, and oxidation resistance.

**EXPERIMENTAL PROCEDURES**

The compositions investigated correspond more or less to 20 Al:80 Si/10 O:90 N (equivalent percent), as marked in the behavior diagram shown in Fig. 1. "X" phase has a detrimental effect on high-temperature strength, therefore, the target composition was selected purposely below the $\beta$-$\text{Si}_3\text{N}_4$ solid solution homogeneity line (Fig. 1) to prevent its formation during sintering by a shift in com-
position over the $\beta'$-$\text{Si}_3\text{N}_4$ solid solution line. The composition shift was anticipated to be very likely because of the presence of oxygen in the form of SiO$_2$ in the starting materials, and further utilization of oxide additives. The basic constituents were $\text{Si}_3\text{N}_4$, AlN, and Al$_2$O$_3$. To them were added minor amounts of additives Y$_2$O$_3$-$\text{SiO}_2$, to promote sintering. A molar ratio of 1:2 was chosen to form Y$_2$Si$_2$O$_7$ phase, which has been found to be compatible with $\beta'$-$\text{Si}_3\text{N}_4$ solid solution, according to the phase diagram shown in Fig. 2. Further, it was anticipated that the Y$_2$Si$_2$O$_7$ phase might improve the oxidation behavior since both Y$_2$O$_3$ and SiO$_2$ are in the highest state of oxidation, thus acting as a barrier for further diffusion of oxygen in the sintered material. Using the target composition 20 Al: 80 Si/10 O: 90 N (equivalent percent), two different mixtures were made with $\text{Si}_3\text{N}_4$, AlN, Al$_2$O$_3$, Y$_2$O$_3$, and SiO$_2$ powders with two levels in the Y$_2$O$_3$-SiO$_2$ additive system. For simplicity, they are to be referred as composition A and B containing 6 mol % and 3 mol % Y$_2$O$_3$-SiO$_2$. These are listed in Table I. The Y$_2$O$_3$ to SiO$_2$ molar ratio was always constant at 1:2. The purpose of utilizing the additive system (Y$_2$O$_3$-SiO$_2$) was to develop a process capable of yielding fully dense $\beta'$-$\text{Si}_3\text{N}_4$ solid solution by pressureless sintering under a nitrogen pressure of 1 atmosphere.

Commercial grade $\text{Si}_3\text{N}_4$, AlN, Al$_2$O$_3$, Y$_2$O$_3$, and SiO$_2$ powders were used in the fabrication studies. Mixtures for 100 gram batches were wet milled in polyethylene bottles for 17 to 20 hours using high alumina grinding media and ethanol. The starting compositions were adjusted to allow for pick up of alumina from the mills. The pick up varied slightly depending on the milling time and weight of the ball charge but was typically 0.8 wt % for a 200 gram ball charge (in a 100-g powder charge) milled for 17 to 20 hours.

After milling, the slurry was dried on a heated aluminum plate, and sieved through a 60-mesh sieve to break up the agglomerates. Twenty grams of mixed powder was cold formed into rectangular blocks of 7.6 by 2.5 by 0.64 cm, by die pressing followed by cold isostatic pressing of four blocks in one batch (in rubber bags) at a total pressure of 414 MN/m$^2$. 
The compacts were pressureless sintered in a "cold-wall" furnace at temperatures between 1450°C and 1750°C for periods of 1 to 2 hours under nitrogen pressure of 1 atmosphere. After sintering, the compacts were furnace cooled.

Sintered specimens were machined into test bars and the surfaces were subsequently ground with a 220-grit diamond wheel to a final surface roughness of 10 to 15 microinches rms. The final dimensions of the test bars were 2.54 by 0.64 by 0.32 cm with four edges beveled.

Density was measured on the machined test bars by liquid immersion and pycnometric methods. Microstructural characterization was made by optical microscopy and transmission electron microscopy, while phase identification and elemental analysis were carried out by X-ray diffraction and EDAX techniques.

Modulus of rupture tests were conducted by four point loading with 0.95 cm top and 1.87 cm bottom spans. Testing was done at room temperature, 1000°C, 1200°C, and 1380°C. All testing was conducted in air with a cross head velocity of 0.02 cm/min. Fracture surfaces of selected test specimens were examined in the scanning electron microscope to determine the fracture origins.

For oxidation tests, the machined bars (2.54 by 0.64 by 0.32 cm) were placed in a platinum crucible. The crucible was introduced into a preheated furnace and automatically cycled. Each cycle consisted of 1 hour at 1375°C followed by 20 minutes cooling. After each 15 hours at temperature (20 hr elapsed time) had accumulated, the bars were separately weighed. The cyclic heating was continued for a total of 90 hours at temperature. Characterization of the oxide scales was performed by light microscopy and X-ray diffraction.

Thermal shock tests were conducted by holding the bars in a vertical tube furnace for 15 minutes to reach an equilibrium temperature and dropping them into a container of water at room temperature. The severity of thermal shock was adjusted by varying the temperature of the tube furnace. Strength after thermal shock was measured at room temperature in a four point bend test with a cross head speed of 0.02 cm/min.
RESULTS AND DISCUSSIONS

A. Powder Characterization

Impurity analyses of the "as-received" powders are shown in Table II, indicating that the AlN starting powder contained most of the major impurities found, that is, Fe, Si, Ti, W, Ni, while the starting powder Y₂O₃ had only Al as a major impurity. All other powders Si₃N₄, Al₂O₃, and SiO₂ were relatively free from such impurities. The oxygen content of the starting Si₃N₄ powder was 2.7 wt %, while the specific surface area (BET method) was 11.84 m²/g. The surface areas of other starting powders were 3.40 m²/g for AlN; 14.45 m²/g for Al₂O₃; 5.16 m²/g for Y₂O₃; and 158.46 m²/g for SiO₂.

B. Densification

Densification behavior of compositions A and B as a function of temperature is shown in Fig. 3. Very rapid densification takes place between 1550°C and 1650°C. At 1700°C, maximum density of 3.08 g/cc was obtained in the composition A with 6 mol % Y₂O₃-SiO₂ additives, while with 3 mol % additives in composition B, the density was 2.94 g/cc. These values are approximately 98 percent of theoretical for composition A and 94 percent of theoretical for composition B, on the basis of an assumed density of 3.14 g/cc for the blend of Si₃N₄, AlN, and Al₂O₃, adjusted for the additions of Y₂O₃ and SiO₂. Densification was facilitated by increased Y₂O₃-SiO₂ additives. Further, the densification of these mixtures is consistent with a liquid phase sintering process, and appears to be analogous to that of silicon nitride.

C. Characterization

X-ray diffraction examinations were made for phase identification in the sintered specimens. Figure 4 shows X-ray diffraction results of compositions A and B sintered at 1700°C for 1 hour. The diffraction pattern for both compositions were almost identical in every detail, and only β'-Si₃N₄ solid solution was detected as a major phase. No other phases or additional peaks of significant intensities were observed. Also, no Y₂Si₂O₇ could be detected in either of the
sintered compositions. This observation is consistent with those of Rowcliffe et al.\textsuperscript{19} and Smith,\textsuperscript{20} who also did not find the crystalline $Y_2Si_2O_7$ phase in sintered $Si_3N_4$ specimens utilizing $Y_2O_3$ sintering aid. It is concluded that the additives $Y_2O_3-SiO_2$ most probably formed an yttria-silica glassy phase, which became liquid at the sintering temperature and thus facilitated densification. The presence of such a noncrystalline phase although not identifiable by X-rays was deduced either from the observed deterioration of mechanical properties\textsuperscript{21} at elevated temperatures or from the observation of presumed devitrification products after heat treatment.\textsuperscript{22}

Microstructure characterization was made by optical microscope, transmission microscope and energy dispersive X-ray analysis (EDAX) techniques. Figure 5 shows typical microstructures developed in the sintered compositions A and B. The microstructures consist of an essentially single phase $\beta$-$Si_3N_4$ solid solution (light gray) phase with isolated porosity (dark gray) combined with some pull outs from polishing.

The porosity was typically associated with the lower density of the sintered specimens from composition B. Several "white" particles were also identified in very limited areas and were examined in the SEM using X-ray energy dispersive spectrometer. Spectra were taken from several of these particles and the matrix. Si and Al were detected only in the matrix. Elements detected in the white metallic particles were Fe, W, Ti, Cr, and Mo, which can be attributed to the impurities present in the "as-received" AlN powder as indicated in Table II.

Further microstructural characterization was conducted on electron transparent specimens. Figures 6 and 7 show typical transmission micrographs of sintered material. Composition A with $6 \text{ mol } % Y_2O_3-SiO_2$ additives had a mixture of equiaxed grains ranging between 0.15 to 1.2 $\mu$m, and columnar grains of size range 0.15 $\mu$m wide by 2.0 $\mu$m long to 1.3 $\mu$m wide by 5.0 $\mu$m long (Fig 6). By contrast, composition B containing $3 \text{ mol } %$ additives had predominantly
equiaxed grains of size range 0.25 to 2.0 μm (Fig. 7). Indications of a non-
crystalline phase, which however, could not be identified, were present in the 
microstructures at the triple grain intersections. The grain morphology, in all 
instances, is typical of liquid phase sintering and solution reprecipitation mecha-
nisms, that is, the silicate liquid forms the reactive transport medium in the 
form of a thin layer between transforming crystals. The liquid phase is re-
tained in intercrystalline spaces, and grain boundaries, during cooling from 
the sintering temperature.

D. Modulus of Rupture Test

Modulus of rupture tests were conducted to evaluate the strength of the sintered β-Si₃N₄ solid solution at both room and elevated temperatures. Machined 
bend bars from both compositions (A and B) having density values 3.08 and 2.94 
g/cc were evaluated. The variation in M. O. R. strength as a function of temperature to 1380°C is plotted in Fig. 8. Each point on the curve is the average of 
four tests. Average strengths for composition A (6 mol % Y₂O₃-SiO₂) were 
483 MPa up to a temperature of 1000°C, 345 MPa at 1200°C, and 220 MPa at 
1380°C. For composition B (3 mol % Y₂O₃-SiO₂), the average M. O. R. strength 
was 428 MPa at room temperature, 400 MPa at 1000°C, 324 MPa at 1200°C, 
and 220 MPa at 1380°C. The lower strength value for composition B at room 
temperature can be attributed to higher porosity than that in composition A. On 
the other hand, the lower strength values at 1200°C and 1380°C for both com-
positions A and B can be attributed to the effect of additives (Y₂O₃-SiO₂), which 
formed a grain boundary amorphous phase(s) which, in turn, became viscous at 
the test temperatures. This behavior is analogous to that of both sintered and 
hot pressed Si₃N₄ containing MgO, Y₂O₃, CeO₂, ZrO₂, etc. It was 
anticipated, however, that a lower amount of additives or liquid phase(s) might 
result in greater high-temperature strength in the sintered materials. However, 
the present results indicated that the strength values at 1380°C are almost 
equivalent for composition A containing 6 mol % additives as compared to com-
position B containing 3 mol % additives. The exact effect of the amount of additives
on the high temperature strength cannot be explained in the present study due to
the fact that composition B, although containing less additives, also has lower
density than that of composition A, which could counterbalance any effect of addi-
tives on improvement in strength.

Fracture surfaces of selected broken bend bars were examined to identify
the origin of fractures. In most cases, the room-temperature fractures ap-
peared to initiate from surface or edge flaws, indicating that better surface
preparation might lead to improved strengths. On the other hand, high-
temperature fractures were due to slow crack growth regions, where the crack
front advanced along the grain boundaries resulting in an intergranular failure
which is typical of Si₃N₄ based ceramics. These are shown in Figs. 9 (compo-
sition A) and 10 (composition B). While Fig. 9(a) shows room-temperature
brittle fracture, Figs. 9(b) and (c) are fracture surfaces at 1200°C and 1380°C,
respectively, showing the fracture initiation site (V-shaped area when the two
halves joined together), which is typical of slow crack growth at high tempera-
tures. Similar behavior was observed in the fracture surfaces of composition B,
which are shown in Figs. 10(a), (b), and (c).

E. Oxidation

Oxidation tests were carried out under identical conditions for both compo-
sition A and composition B. The oxidation cycle consisted of 1 hour at tempera-
ture (1375°C) followed by 20 minutes cooling. After each 15 hours at tempera-
ture (20 hr elapsed time) had accumulated, weight gain for each bar was measured
separately. Weight gain versus time for compositions A and B is linearly plotted
in Fig. 11, while the parabolic plot is in Fig. 12. Composition A with 6 mol %
Y₂O₃-SiO₂ additives exhibited a higher weight gain than composition B with
3 mol % Y₂O₃-SiO₂, that is, less oxidation resistance than composition B, al-
though it had been anticipated initially that composition A would exhibit better
oxidation resistance than composition B due to its higher Y₂O₃-SiO₂ content.
Both compositions A and B exhibited more or less parabolic rate behavior which
is shown in Fig. 12. However, in composition A, a change in the slope of the parabolic plot was observed after approximately 30 hours of oxidation time and parabolic behavior continued at the new slope for the duration of the test. Whether this change in parabolic behavior was due to different types of reaction occurring during oxidation, for example, reaction with the impurities, phase transformation or spalling was not determined.

The oxide scale in composition A was identified by X-ray to contain cristobalite as the major phase with minor amounts of mullite, while in composition B, mullite was the major phase with minor amounts of cristobalite. Further, composition A produced thick oxide scales whitish in color with a rough surface, while composition B exhibited thinner scales with smooth surface. These differences were attributed to the different nature of the oxidation products from composition B.

F. Thermal Shock

The water quench thermal shock test was performed on a total of 20 test bars of composition A only. After quenching from various temperatures into water at room temperature, the test bars were dried, and 4-point modulus of rupture strength was measured at room temperature on each thermally shocked bar to determine the residual strength. These values are plotted as a function of quenching temperature difference as shown in Fig. 13. Each point on the curve is the average of four tests. No strength loss was observed up to a temperature difference of 300°C, followed by a gradual strength loss in a "quasi-static" manner up to 460°C, after which the strength drop was catastrophic.

The ΔT°C was determined to be between 460°C to 480°C (Fig. 13). The value was found to be higher than that of various silicon carbide ceramics, equivalent to that of reaction sintered silicon nitride but lower than hot pressed silicon nitride which are shown in Fig. 13. The result suggests that the pressureless sintered β′-Si₃N₄ solid solution possesses thermal shock resistance comparable to that of materials which are currently being considered for high-temperature applications.
CONCLUDING REMARKS

The experimental studies reported here have shown that high density
$\beta'\text{-Si}_3\text{N}_4$ solid solution can be prepared by pressureless sintering ultrafine
$\text{Si}_3\text{N}_4$, AlN, and $\text{Al}_2\text{O}_3$ powders with an $\text{Y}_2\text{O}_3$-$\text{SiO}_2$ additive system, under relatively simple sintering conditions. Densification takes place by a liquid phase
sintering mechanism involving solution of $\alpha\text{-Si}_3\text{N}_4$ and reprecipitation as
$\beta'\text{-Si}_3\text{N}_4$. The sintered product is essentially $\beta'\text{-Si}_3\text{N}_4$ solid solution. No
$\text{Y}_2\text{Si}_2\text{O}_7$ could be detected suggesting the formation of an yttria-
silica glassy phase during sintering. Strengths up to 483 MPa (70 000 psi) are
achieved at moderate temperature ($1000^\circ \text{C}$), while a substantial strength loss
occurs at high temperature ($1350^\circ \text{C}$). It is believed that this problem can be
overcome by better understanding of the grain boundary recrystallization pro-
cess.

The oxidation resistance of a composition containing 3 mol % $\text{Y}_2\text{O}_3$-$\text{SiO}_2$ is
better than the oxidation resistance of a composition containing 6 mol % ($\text{Y}_2\text{O}_3$-
$\text{SiO}_2$). In thermal shock, $\beta'\text{-Si}_3\text{N}_4$ solid solution exhibits higher resistance
than silicon carbide and resistance equivalent to reaction sintered silicon ni-
tride but lower than hot pressed silicon nitride.

The results of strength, oxidation, and thermal shock tests at this stage in
our development of $\beta'\text{-Si}_3\text{N}_4$ solid solution are comparable to many currently
sintered silicon nitride based ceramics and are extremely encouraging; they
suggest that, with further development, it will be possible to make sintered
$\beta'\text{-Si}_3\text{N}_4$ solid solution with properties suitable for high-temperature applica-
tions.
REFERENCES


22. M. E. Milberg and W. M. Miller, "Observation of a Noncrystalline Phase in Sintered Si$_3$N$_4$-Al$_2$O$_3$-Y$_2$O$_3", " submitted to the J. Amer. Ceram. Soc. (To be published).


### TABLE I. - MATERIAL COMPOSITIONS FOR $\beta$-$\text{Si}_3\text{N}_4$ SOLID SOLUTION

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<th>Material</th>
<th>Mol %</th>
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<tr>
<td>SiO$_2$</td>
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### TABLE II. - TRACE IMPURITY ANALYSIS OF RAW POWDERS (ppm)

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<tr>
<th>Element</th>
<th>Si$_3$N$_4$</th>
<th>AlN Shield alloy</th>
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<th>SiO$_2$ Apache</th>
<th>Y$_2$O$_3$ United Mineral</th>
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Figure 1. - The Si$_3$N$_4$-Al$_2$O$_3$-SiO$_2$ system (after Jack).
Figure 5. - Microstructures of β'-Si₃N₄ solid solution compositions sintered for 1 hour at 1700 °C; X250.

Figure 6. - Transmission electron micrograph of β'-Si₃N₄ solid solution showing both equiaxed and elongated grain structures.

Figure 7. - Transmission electron micrograph of β'-Si₃N₄ solid solution showing faceted grain structures.

Figure 8. - Modulus of rupture strength (4-point bend) of β'-Si₃N₄ solid solutions.
Figure 9. - Macrographs of β' - Si₃N₄ solid solution fractured at different temperatures; composition, A=6 mol% Y₂O₃·SiO₂; density, 3.08 g/cc.

Figure 10. - Macrographs of β' - Si₃N₄ solid solution fractured at different temperatures; composition, B=3 mol% Y₂O₃·SiO₂; density, 2.94 g/cc.

Figure 11. - Weight gain in air at 1375°C of β' - Si₃N₄ solid solutions (linear plot).
Figure 12. - Weight gain in air at 1375°C of β'-Si₃N₄ solid solutions (parabolic plot).

Figure 13. - Residual strength at room temperature after water quenching vs quench temperature for β'-Si₃N₄ solid solution (composition A).