NASA Technical Memorandum 101365

Slurry-Pressing Consolidation of Silicon Nitride

William A. Sanders, James D. Kiser, and Marc R. Freedman
Lewis Research Center
Cleveland, Ohio

November 1988

NASA

SLURRY-PRESSING CONSOLIDATION OF SILICON NITRIDE

William A. Sanders, James D. Kiser, and Marc R. Freedman
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

ABSTRACT

This study determined a baseline slurry-pressing method for a silicon nitride material. The Si_3N_4 composition contained 5.8 wt % SiO_2 and 6.4 wt % Y_2O_3. Slurry-pressing variables included volume percent solids, application of ultrasonic energy, and pH. Twenty volume percent slurry-pressed material was approximately 11 percent stronger than both 30 vol % slurry-pressed and dry-pressed materials. The Student's t-test showed the difference to be significant at the 99 percent confidence level. Twenty volume percent (300 h) slurry-pressed test bars exhibited strengths as high as 980 MPa. Large, columnar β-Si_3N_4 grains caused failure in the highest strength specimens. The improved strength correlated with better structural uniformity as determined by radiography, optical microscopy, and image analysis.

INTRODUCTION

Recent work at NASA Lewis Research Center[1,2] demonstrated the benefits of slurry pressing α-SiC powder dispersions. Control of slurry pH reduced viscosity and improved dispersion. SiC strength improved because of more homogeneous and dense microstructures, smaller and more uniformly distributed pores, and smaller critical flaws.

This study compared the slurry-pressing and dry-pressing characteristics of a Si_3N_4 powder. The powder was a high-purity, commercial Si_3N_4 powder made by the nitridation of silicon method. Slurry variables were volume percent solids loading, application of ultrasonic energy, and pH. The objective was to establish a baseline method for slurry pressing Si_3N_4 to produce a

stronger, more reliable monolithic material. Also, slurry-pressing is a possible way to compact tough, reliable, homogeneous Si_3N_4 composites with whisker and/or particulate additions. We require such materials for demanding applications in hot section components of advanced automotive gas turbine engines and for limited application in aerospace systems.[3,4]

EXPERIMENTAL PROCEDURE

Materials and Processing

Table I and Fig. 1 show the material characteristics and the processing flow chart, respectively. A 20-μm screen* removed agglomerates from an ethanolic slurry of Si_3N_4 powder before vacuum drying. Nine 100-g batches of the screened Si_3N_4, plus SiO_2 and Y_2O_3 powder, were milled for 100 h in pure ethanol. Milling hardware consisted of 1-liter, sintered, reaction-bonded silicon nitride (SRBSN) mills[†] and hot-pressed silicon nitride (HPSN) media.[‡] After milling, a 10-μm screen* removed agglomerates and milling debris from a combined master slurry of the nine batches. Controlled drying of five equal portions of master slurry produced two 20 vol % solids and two 30 vol % solids portions and one completely dry portion. Two additional 100-g batches were milled for 300 h before combining and sieving. Controlled drying of the 300-h ground slurry raised the volume percent solids to 20.

Table I shows the sieved slurry characteristics. The powders had surface areas of 25.1 and 22.6 m^2/g for the 100- and 300-h slurries, respectively. The greater surface area of the 100-h ground powder is due to more SiO_2 (166 m^2/g) added to those batches. The powder composition included Si_3N_4 pickup from wear of the milling hardware and SiO_2 from Si_3N_4 oxidation during milling. By weight percent the composition was 87.8 Si_3N_4, 5.8 SiO_2, and

---

2

6.4 Y_2O_3. By mole percent the composition was 83.4 Si_3N_4, 12.8 SiO_2, and 3.8 Y_2O_3. This is essentially the NASA 6Y composition used in previous studies.[5-7]

Addition of NH_4OH to one of each of the 20 and 30 vol % master slurry portions and the 300-h ground slurry raised the pH from 8.3 to 10. Previous work[8] showed that pH 10 dispersed the Si_3N_4 well. Figure 2 shows that good sediment packing occurs in the acid pH range from 1 to 6. Such packing behavior has been correlated[9] with good relative powder dispersion. However, acids react with metallic die components, and well-dispersed "fines" in the acidic slurries "disappear" during pressing. Therefore, we chose pH 10 as an appropriate alkaline dispersion. Figure 2 shows that we should not expect a significant difference in behavior between the pH 10 and pH 8.3 slurries.

After the slurry was separated into two equal portions, the die shown in figure 3 slurry-pressed samples under 9 MPa. An ultrasonic probe* dispersed samples from one of each of those two equal portions just before slurry pressing. The probe operated for 1 min at 165 W. In the slurry-pressing process, the slurry charge was compacted between filter-paper disks, which trapped the solids. Porous stainless steel disks assured uniform pressure application and expulsion of liquid. Preformed bulk filter-paper pads swelled during pressing and prevented leakage up the die wall. A porous Teflon pad separated the top die plunger surface from the upper preformed filter-paper pad. The eight slurry types (SP designations 1 to 8 in Fig. 1) yielded four to six 5.1-cm-diameter disks. After careful drying to avoid cracking, the disks were sealed with evacuated thin-wall plastic tubing. Cold isostatic pressing under 414 MPa increased the green density.

Remaining portions of the four original solids-adjusted slurries were air dried. HPSN hardware crushed the soft agglomerates in the dried portions, and

---

*Model W-370 with standard 3/4-in. horn with sapphire tip, Heat Systems Ultrasonics Inc., Farmingdale, NY.

a 149-µm screen* removed large, hard agglomerates. A double-acting, tungsten-carbide-lined die pressed these powders into bars under 21 MPa (DP designations in Fig. 1). These bars measured 3.81 by 0.79 by 0.45 cm. Evacuated surgical tubing sealed the bars, and cold isostatic pressing under 414 MPa increased the green density.

Slurry pressing of a 20 vol % solids, 300-h ground slurry (hereafter referred to as 20 vol % (300 h) slurry pressed) followed adjustment to pH 10.

Determination of green densities for all bars and disks was from weights and linear measurements. Viewing conventional radiographs with variable-intensity backlighting showed relative uniformity of green bars and disks. Inspection of black-and-white prints of the radiographs aided the interpretation.

Densification and Material Characterization

Sintering was in a tungsten mesh element, all refractory metal, water-cooled, double-wall furnace. Sintering was at 2140 °C for 3 h under 5 MPa N_2. The bars were sintered in groups of up to 15 in a tungsten cup with a loose-fitting lid. Disks were sintered in groups of four to six. High-purity boron nitride setters separated bars and disks from each other and from the tungsten cup.

Radiography of all bars and disks followed sintering. A 400-grit diamond wheel longitudinally ground specimens from the sintered bars and disks. Sintered bars and disks had final machined dimensions of 3.0 by 0.56 by 0.18 cm. The four long edges had a 0.12-mm bevel. Surface finish measured 0.15 and 0.38 µm in the longitudinal and transverse directions, respectively. Radiography and the determination of density by an immersion method followed machining.

---

*100-mesh stainless steel frame and cloth, all welded construction, Newark Wire Cloth Company, Newark, NJ.

Optical microscopy of polished cross sections of sintered specimens supplemented radiographic analysis. An image analyzer* characterized microstructural porosity. The analyzer scanned about a fixed reference point for efficient evaluation of several randomly selected areas on a polished cross section. The analyzer scanned 25 regions in a 5 by 5 matrix (0.003 cm^2) at each of five randomly selected points. The total scanned area was 0.015 cm^2 for each specimen. The number of features recognized for each specimen examined averaged over 2600. The analyzer determined average pore areas and lengths and listed the largest pore areas and lengths.

Polished cross sections of test bars were etched by immersion in fused KOH for approximately 45 sec. Transmission electron microscopy (TEM) of two-stage carbon replicas of the etched material enabled examination of grain morphology and size, and porosity.

Four-point flexural strength tests at room temperature and at 1370 °C used a crosshead speed of 0.51 mm/min. Inner and outer fixture spans were 9.53 and 19.05 mm, respectively. Room-temperature tests used steel fixtures. Elevated-temperature tests used SiC fixtures in a SiC muffle furnace mounted on a universal testing machine. All tests were in air. Fractography was by scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Sintering

Table II shows the average densities for the 14 different dry-pressing and slurry-pressing conditions. Green densities ranged from 1.81 to 1.89 g/cm^3 and were similar for all groups of materials. Sintered densities of dry-pressed bars ranged from 3.25 to 3.31 g/cm^3. Bars cut from 20 and 30 vol % slurry-pressed disks had densities which ranged from 3.25 to 3.29 g/cm^3. Thus,

---

*Quantimet 900, Cambridge Instruments Inc., Monsey, NJ.

slurry pressing did not improve the green or the sintered density of this Si_3N_4 composition relative to dry pressing. The sintering shrinkages were also similar for slurry-pressed disks and dry-pressed bars. They were 16.5 percent diametral and 17.1 percent bar width, respectively. Average sintering weight losses were 2.5 percent for disks and 3.3 percent for bars. The 20 vol % (300 h) slurry-pressed material had the highest sintered density (3.3 g/cm^3). This is a result of the 300-h milling, which imparts fineness and homogeneity for good sintering.

Flexural Strength

Table II lists the room-temperature flexural strengths for the 14 different pressing conditions. There was no consistent effect of ultrasonic energy as applied in this study. As expected, there was also no apparent effect of pH control on material strength. The 20 vol % slurry-pressed material was stronger than the 30 vol % slurry-pressed material in three of four direct comparisons. Those comparisons were SP2 versus SP1, SP3 versus SP5, and SP4 versus SP7. The strengths were the same in the SP6 versus SP8 case. Figure 4 compares the room-temperature strengths for the four material groups. The four groups are dry pressed, 20 and 30 vol % slurry pressed, and 20 vol % (300 h) slurry pressed. The 20 vol % slurry-pressed group was approximately 11 percent stronger than both the 30 vol % slurry-pressed and dry-pressed groups. The Student's t-test showed the difference to be significant at the 99 percent confidence level. The 20 vol % (300 h) slurry-pressed material was the strongest in this study. The room-temperature strength of that material was 826 MPa. It approaches the highest strength NASA 6Y material produced in a previous study.[7] The 20 vol % (300 h) slurry-pressed material was approximately 21 percent stronger than the 20 vol % slurry-pressed material. The Student's t-test showed the difference to be significant at the 99 percent confidence level.

6

Table II also lists the 1370 °C flexural strengths for 20 vol %, 30 vol %, and 20 vol % (300 h) slurry-pressed bars. There is no statistically significant difference between these materials. This similarity probably results from the strong influence of grain-boundary glass softening on 1370 °C strength.

Fractography

Table III summarizes the fractography of dry-pressed, 20 vol % slurry-pressed, and 30 vol % slurry-pressed materials tested at room temperature. For all three groups, the most common critical flaw was a surface or subsurface pore. Figure 5(a) shows this type of flaw. The distribution of critical flaw types was similar for both the 20 vol % and 20 vol % (300 h) slurry-pressed materials.

Slurry-pressed material did not have metallic inclusions as critical flaws. In dry-pressed materials, these inclusions result from dry sieving with metal screens. Direct pressing of the wet slurry avoids this procedure.

Slurry pressing reduced the incidence of seam flaws (lenticular pores). Figure 5(b) shows this type of flaw, which may result from contaminant burnout during sintering. The reduced incidence in the slurry-pressed material may be the result of fewer handling steps. The 20 vol % slurry-pressed material had half as many seam flaws as the 30 vol % slurry-pressed material.

Large β-Si$_3$N$_4$ grains caused failure only in the highest strength 20 vol % and 20 vol % (300 h) slurry-pressed bars. These bars had strengths as high as 980 MPa. Figure 6 shows an example of this type of flaw. A previous study[7] found that elimination of pores as critical flaws resulted in improved strength. Large, columnar β-Si$_3$N$_4$ grains were the critical flaws in that study.

7

Structure

Radiographically, the 20 vol % slurry-pressed material had less density variation than both the dry-pressed and 30 vol % slurry-pressed materials. This was true from the green state through the sintered and machined states. The dry-pressed and 30 vol % slurry-pressed materials were similar. The difference between the three material groups decreased after sintering. The 20 vol % (300 h) slurry-pressed material had no detectable density variation.

Figures 7(a) and (b) show polished cross sections of sintered 20 vol % and 30 vol % slurry-pressed materials, respectively. Porosity clusters, which appear as white patches on the polished cross sections, are fewer and more diffuse in the 20 vol % slurry-pressed material. This may reflect a difference in void removal during pressing due to the lower viscosity of the 20 vol % solids slurry. The 20 vol % (300 h) slurry-pressed material was the most uniform and had no porous regions.

Image analysis showed average pore sizes of 0.5 and 0.8 μm^2 for the 20 vol % and 30 vol % slurry-pressed materials, respectively. However, the largest pore areas and pore lengths were similar for both materials.

The grain size and morphology of all materials were similar as shown by transmission electron microscopy (TEM). Figure 8 shows a typical microstructure. Equiaxed grains ranged from 0.4 to 2.5 μm. Columnar grains, which filled about 20 vol %, were up to 27 μm long with aspect ratios from 2 to 9.

CONCLUSIONS

Pressing of 20 vol % slurries is the preferred green consolidation method for sintered Si_3N_4. This method improved the microstructural uniformity and the strength of the material. Slurry-pressed materials did not have metallic inclusions, and there were fewer lenticular pores. Increasing the milling

8

time from 100 to 300 h further improved the material by increasing the powder blend homogeneity.

REFERENCES

1. M.R. Freedman and M.L. Millard, "Improved Consolidation of Silicon Carbide," Ceram. Eng. Sci. Proc., 7[7-8] 884-892 (1986).

2. J.B. Hurst and S. Dutta, "Simple Processing Method for High-Strength Silicon Carbide," Am. Ceram. Soc. J. Commun., 70[11] C303-C308 (1987).

3. H.E. Helms, P.J. Haley, and L.E. Groseclose, "AGT 100 Advanced Gas Turbine Technology Development Project," pp. 137-148 in Proceedings of the Twenty-Fourth Automotive Technology Development Contractors' Coordination Meeting, SAE P-197, Society of Automotive Engineers, Warrendale, PA, 1986.

4. G.L. Boyd, J.R. Kidwell, and D.M. Kreiner, "A Technology Development Summary for the AGT101 Advanced Gas Turbine Program," pp. 115-136 in Proceedings of the Twenty-Fourth Automotive Technology Development Contractors' Coordination Meeting, SAE P-197, Society of Automotive Engineers, Warrendale, PA, 1986.

5. D.M. Mieskowski, W.A. Sanders, and L.A. Pierce, "Reliability of Two Sintered Silicon Nitride Materials," NASA TM-87092, 1985.

6. L.A. Pierce, D.M. Mieskowski, and W.A. Sanders, "Effect of Grain-Boundary Crystallization on the High-Temperature Strength of Silicon Nitride," J. Mater. Sci., 21[4] 1345-1348 (1986).

7. W.A. Sanders and G.Y. Baaklini, "Correlation of Processing and Sintering Variables with the Strength and Radiography of Silicon Nitride," Adv. Ceram. Mater., 3[1] 88-94 (1988).

8. M.R. Freedman, J.D. Kiser, and T.P. Herbell, "Factors Influencing the Ball Milling of Si3N4 in Water," Ceram. Eng. Sci. Proc., 6[7-8] 1124-1134 (1985). (NASA TM-86932.)

9. R.O. James, "Characterization of Colloids in Aqueous Systems" pp. 349-410 in Advances in Ceramics, Vol. 21 - Ceramic Powder Science. Edited by G.L. Messing, K.S. Mazdiyasni, J.W. McCauley, and R.A. Haber, The American Ceramic Society, Westerville, OH, 1987.

TABLE I. – CHARACTERIZATION OF SILICON NITRIDE, OXIDE, AND SLURRY POWDERS

Material	Source	Manufacturer's designation	Purity, percent	Specific surface area, m²/g	X-ray diffraction analysis, percent			Chemical analysis		
					α	β	Free Si	Oxygen, wt %	Carbon, wt %	Spectrographic analysis, ppm
Si_3N_4	AME	High purity	99.5	3.72	82.9	16.4	0.7	0.71	0.08	930 Al, 110 Ca, 1900 Fe, 500 Mo, 220 Ni, 210 Pb, 170 Ti, 470 V
SiO_2	Apache Chemicals	6846	99.99	166	---	---	---	---	.16	220 Al, 150 Ca, 30 Cr, 50 Cu, 50 Fe, 130 Mg, 90 Mn, 340 Na, 40 Ti
Y_2O_3	Molycorp	5600	99.9	7.5	---	---	---	---	.11	60 Cu, 60 Mg, 40 rare earth oxides
Slurry* (100-h grind)	---	---	---	25.1	---	---	---	4.76	.11	1240 Al, 90 Ca, 1970 Fe, 510 Mo, 450 Ni, 120 Ti, 290 V, 5.5 wt % Y
Slurry* (300-h grind)	---	---	---	22.6	---	---	---	---	---	---

*Ground slurry composition, 87.8 Si_3N_4 – 5.8 SiO_2 – 6.4 Y_2O_3, by weight percent; 83.4 Si_3N_4 – 12.8 SiO_2 – 3.8 Y_2O_3, by mole percent.

TABLE II. - DRY-PRESSED AND SLURRY-PRESSED Si₃N₄ SPECIMEN PROPERTIES

TABLE II. - DRY-PRESSED AND SLURRY-PRESSED Si_3N_4 SPECIMEN PROPERTIES

Treatment*	Volume percent solids	Adjusted pH	Ultra-sonics applied	Number of pressed shapes	Pressed density, g/cm³	Sintered + machined density, g/cm³	Room-temperature flexural strength/ standard deviation, MPa
DP Slurry base	--	--	--	41 Bars	1.89	3.27	647/39 (10 Bars)
DP "2/6"	--	--	--	16 Bars	1.89	3.28	617/99 (10 Bars)
DP "3/4"	--	--	--	23 Bars	1.87	3.31	649/89 (10 Bars)
DP "1/8"	--	--	--	12 Bars	1.89	3.29	606/64 (10 Bars)
DP "5/7"	--	--	--	20 Bars	1.81	3.25	567/71 (10 Bars)
SP 2	20	10	✓	6 Disks	1.84	3.29 (18 Bars)	715/129 (10 Bars)
SP 6	↓	10	--	5 Disks	1.85	3.26 (15 Bars)	585/102 (10 Bars)
SP 3		--	✓	4 Disks	1.89	3.26 (12 Bars)	640/99 (10 Bars)
SP 4	↓	--	--	5 Disks	1.85	3.26 (15 Bars)	780/104 (10 Bars)
SP 1	30	10	✓	4 Disks	1.83	3.28 (12 Bars)	592/63 (10 Bars)
SP 8	↓	10	--	5 Disks	1.83	3.27 (15 Bars)	587/93 (10 Bars)
SP 5		--	✓	5 Disks	1.87	3.25 (15 Bars)	589/72 (10 Bars)
SP 7	↓	--	--	5 Disks	1.86	3.27 (15 Bars)	650/68 (10 Bars)
SP 2, 3, 4, 6	20	--	--	-------	----	--------------	428/50 (17 Bars)†
SP 1, 5, 7, 8	30	--	--	-------	----	--------------	416/43 (15 Bars)†
SP (300 hr)	20	10	--	8 Disks	1.82	3.33 (24 Bars)	826/141 (10 Bars) 465/96 (10 Bars)†

*DP denotes dry pressed, SP denotes slurry pressed.
†1370 °C.

TABLE III. - FRACTOGRAPHY SUMMARY FOR DRY-PRESSED AND SLURRY-PRESSED SINTERED Si_3N_4

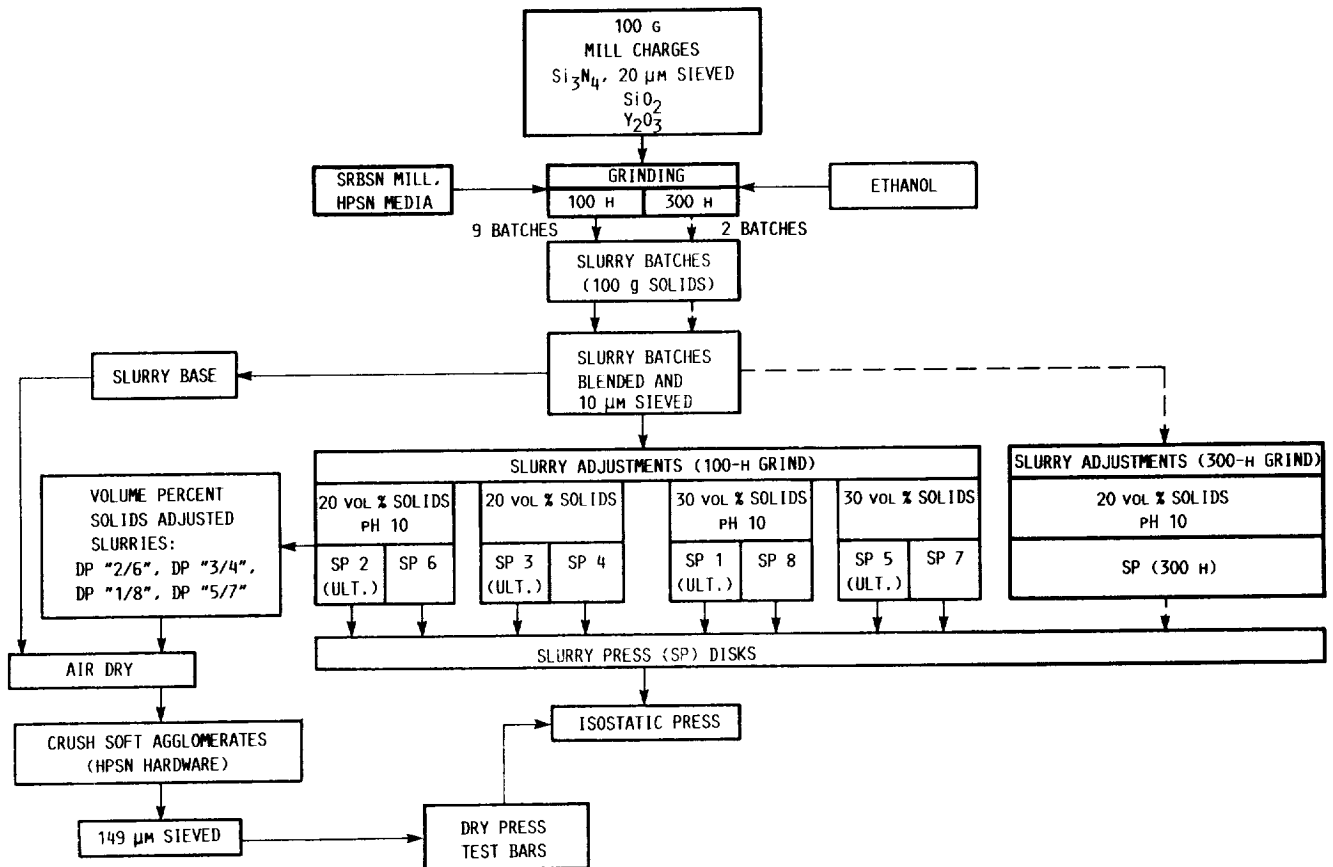| Treatment	Number of test bars	Incidence of undetermined region or flaw, percent	Flaw occurence, percent			
			Subsurface or surface pore	Seam	Large grain	Metallic inclusion
Dry pressed	50	24	55	34	0	11
20 vol % slurry pressed	40	22	68	16	16	0
30 vol % slurry pressed	40	15	71	29	0	0

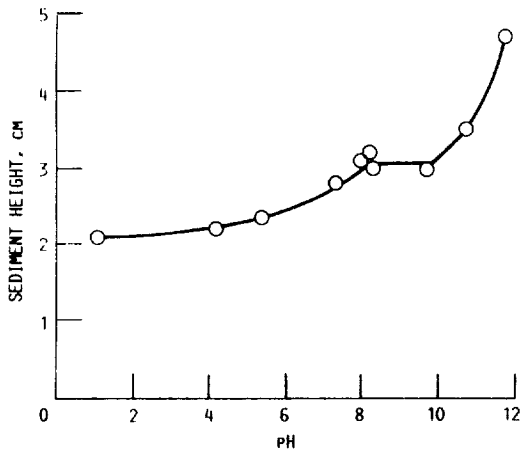FIGURE 1. - PROCESSING OF Si_3N_4-SiO_2-Y_2O_3 SLURRY.

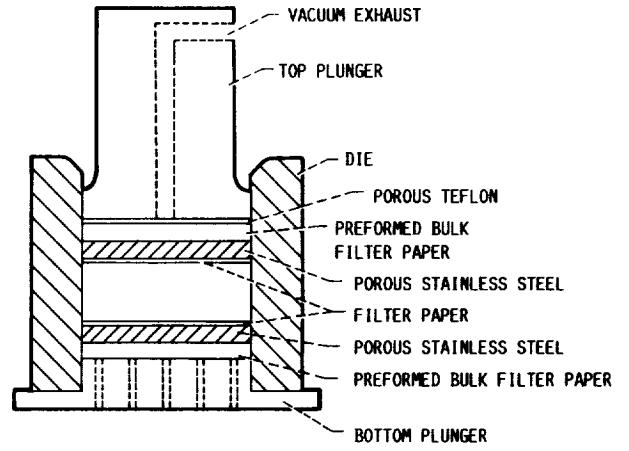FIGURE 2. - EFFECT OF pH ON DISPERSION OF SILICON
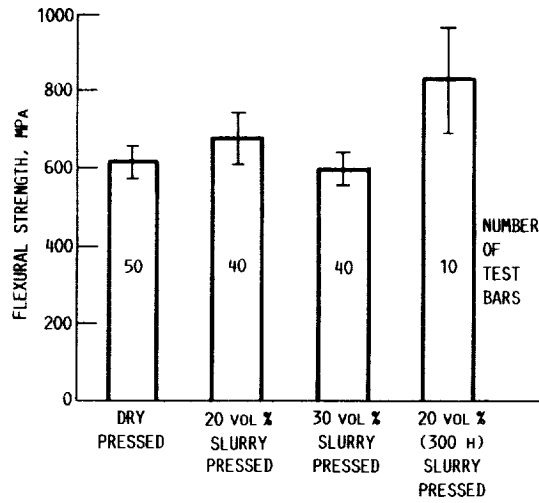NITRIDE IN ETHANOL.

FIGURE 3. - SCHEMATIC OF SLURRY-PRESSING DIE.

FIGURE 4. - ROOM-TEMPERATURE FLEXURAL STRENGTH
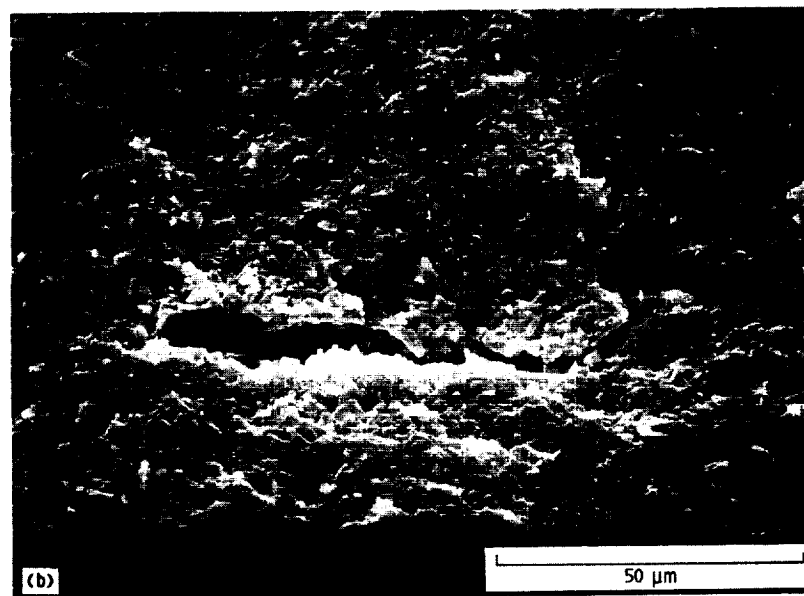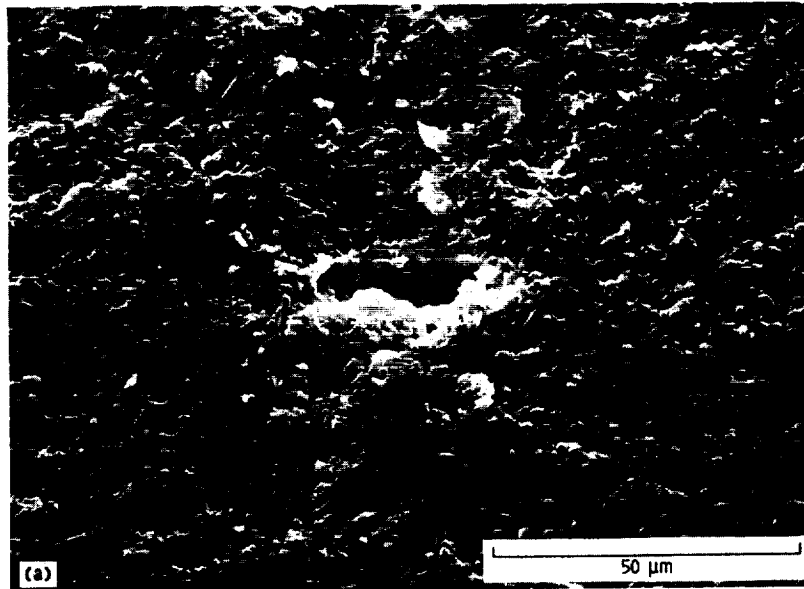(±1 STANDARD DEVIATION) OF DRY-PRESSED AND
SLURRY-PRESSED SILICON NITRIDE.

14

FIGURE 5. - PORE AND SEAM CRITICAL FLAWS IN ROOM-TEMPERATURE FRACTURE OF SLURRY-PRESSED SILICON NITRIDE. (a) PORE (FLEXURAL STRENGTH, 725 MPa), (b) SEAM (FLEXURAL STRENGTH, 561 MPa).

FIGURE 6. - COLUMNAR β-Si₃N₄ GRAIN (a), SHOWN AT GREATER MAGNIFICATION IN (b),
ACTING AS CRITICAL FLAW IN ROOM-TEMPERATURE FRACTURE OF 20 vol % SLURRY-
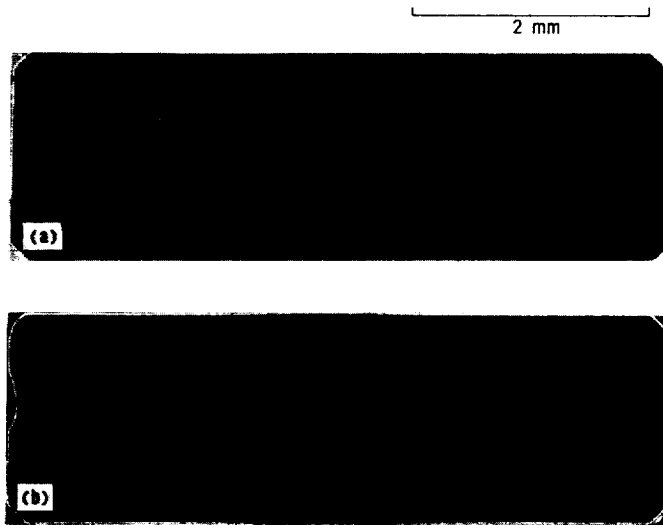PRESSED SILICON NITRIDE (FLEXURAL STRENGTH, 980 MPa).

FIGURE 7. - POLISHED CROSS SECTIONS OF SLURRY-PRESSED AND SINTERED
SILICON NITRIDE SHOWING FINE POROSITY CLUSTERS. (a) 20 VOL %
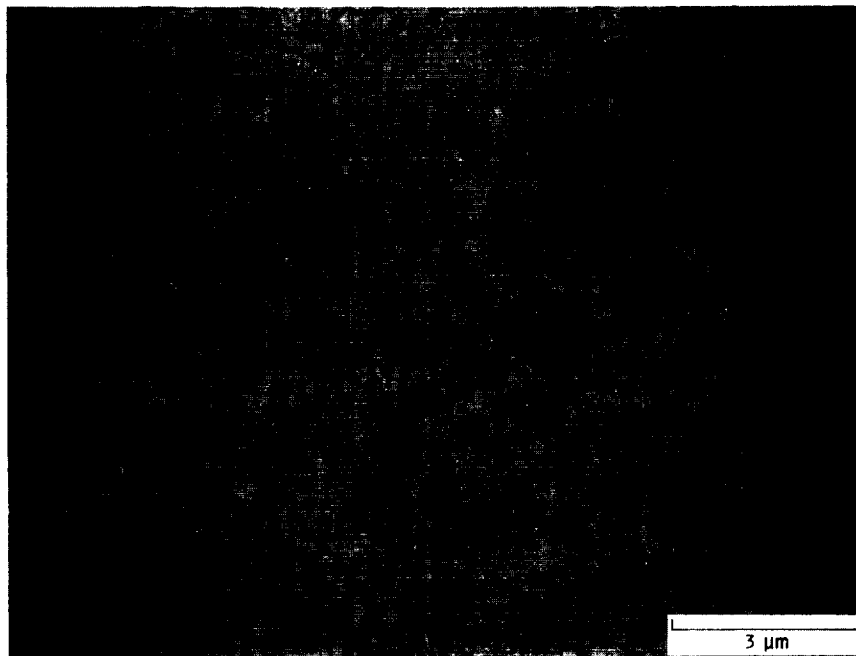SLURRY PRESSED. (b) 30 VOL % SLURRY PRESSED.

FIGURE 8. - TRANSMISSION ELECTRON MICROSCOPE (TEM) MICROSTRUCTURE OF SLURRY-PRESSED
SINTERED SILICON NITRIDE.

NASA
National Aeronautics and
Space Administration

Report Documentation Page

1. Report No. NASA TM-101365	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Slurry-Pressing Consolidation of Silicon Nitride		5. Report Date November 1988
		6. Performing Organization Code
7. Author(s) William A. Sanders, James D. Kiser, and Marc R. Freedman		8. Performing Organization Report No. E-4352
		10. Work Unit No. 505-63-01
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135-3191		11. Contract or Grant No.
		13. Type of Report and Period Covered Technical Memorandum
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546-0001		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

This study determined a baseline slurry-pressing method for a silicon nitride material. The Si_3N_4 composition contained 5.8 wt % SiO_2 and 6.4 wt % Y_2O_3. Slurry-pressing variables included volume percent solids, application of ultrasonic energy, and pH. Twenty volume percent slurry-pressed material was approximately 11 percent stronger than both 30 vol % slurry-pressed and dry-pressed materials. The Student's t-test showed the difference to be significant at the 99 percent confidence level. Twenty volume percent (300 h) slurry-pressed test bars exhibited strengths as high as 980 MPa. Large, columnar β-Si_3N_4 grains caused failure in the highest strength specimens. The improved strength correlated with better structural uniformity as determined by radiography, optical microscopy, and image analysis.

17. Key Words (Suggested by Author(s)) Silicon nitride; Slurry pressing; Flexural strength; Microstructure; Fractography	18. Distribution Statement Unclassified – Unlimited Subject Category 27	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No of pages 18	22. Price* A03

National Aeronautics and
Space Administration

Lewis Research Center
Cleveland, Ohio 44135

Official Business
Penalty for Private Use $300

FOURTH CLASS MAIL

ADDRESS CORRECTION REQUESTED

NASA