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GAS PRESSURE SINTERING OF SILICON NITRIDE TO OPTIMIZE FRACTURE TOUGHNESS

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INTRODUCTION

Silicon nitride materials are the leading ceramics for structural applications at elevated temperatures. To increase the Weibull modulus and improve their reliability, high toughness materials are being developed using gas-pressure sintering (GPS) techniques [1,2]. During gas pressure sintering at elevated temperatures, silicon nitride materials exhibit elongated grain growth which leads to materials with high fracture toughness.

A study was initiated to examine the effects of GPS processing parameters on the densification and mechanical properties of silicon nitride materials to maximize the fracture toughness. Important parameters affecting the microstructural development include the densification temperature, densification time, grain growth temperature, grain growth time and heating rates. Because of the number of variables to be studied, a Taguchi experimental array was formulated to assess the impact of each of the variables on a two-step gas-pressure sintering process. In addition, two compositions of silicon nitride with different intergranular phases were tested. These compositions were Si_3N_4-6% Y_2O_3-2% Al_2O_3 , and Si_3N_4-$Sr_2La_4Yb_4(SiO_4)_6O_2$ (at 8 equivalent % oxygen).

EXPERIMENTAL PROCEDURES

Five GPS parameters were examined in the experimental array as shown in Table 1. The starting materials consisted of appropriate amounts of Si_3N_4, Al_2O_3, La_2O_3, Y_2O_3, Yb_2O_3, or SrO to form the desired intergranular phase.[a] The oxygen content of the silicon nitride powders was taken into account in the calculation of the silica addition and milling was done in isopropanol to minimize

[a] Si_3N_4- Ube, Japan, E10; Al_2O_3- Reynolds, Malakoff, TX, RC-HP DBM; La_2O_3, Y_2O_3, Yb_2O_3- Molycorp, White Plains, NY; >99.9%; SrO as $SrCO_3$; Mallinckrodt, St. Louis, MO; Reagent Grade

any oxygen pickup during processing. The powders were turbomilled for ~2 h (1.3 wt.% PVP[b] and 1 wt.% Darvan[c] were added as dispersants) to fully deagglomerate and mix the various constituents. The mixtures were dried, screened to -200 mesh and isopressed at 207 MPa into discs approximately 7 cm in diameter and 2 cm thick. Binder burnout consisted of a heat-treatment to 600°C in air prior to sintering. Sintering was performed in a graphite element furnace with gas overpressure capability.

Densities were determined by the Archimedes' method. Selected samples of high density were machined into bend bar specimens with nominal dimensions of 3 mm x 4 mm x 50 mm. Flexural strength testing was done in four point bending with inner and outer spans of 20 mm and 40 mm, respectively. Fracture toughness was determined by an indentation and fracture method.

RESULTS AND DISCUSSION

The test results on densification, flexural strength and fracture toughness are given in Table 1. As shown, high densities were achieved for all of the samples in the Taguchi array. Consequently, no significant effects on the densification were due to the processing conditions chosen. The conditions had been selected to obtain high densities so the effects on the flexural strength and fracture toughness could be better determined.

Analysis of the results for optimizing the processing conditions to maximize the flexural strength and fracture toughness are shown in Tables 2 and 3. For the Si_3N_4-6% Y_2O_3-2% Al_2O_3 samples, only moderate effects were observed for the processing conditions in the experimental array. For the strength, the most important conditions appeared to be the grain growth temperature and the densification time as illustrated in Figs. 1 and 2, respectively. The fracture toughness for the Si_3N_4-6% Y_2O_3-2% Al_2O_3 samples was most affected by the densification temperature as shown in Fig. 3.

The Si_3N_4-$Sr_2La_4Yb_4(SiO_4)_6O_2$ samples showed significantly more deviation in the flexural strength and fracture toughness results depending on the processing conditions. The most significant factor affecting the flexural strength was the grain growth temperature as shown in Fig. 4. The analysis indicated that temperatures ≥1900°C were required to achieve high strength values. The fracture toughness was significantly dependent on several factors including densification and grain growth temperature plus the heating rate to the densification temperature. These effects are shown in Figs. 5, 6, and 7, respectively. Microstructural analysis revealed that the lower densification temperature results in generally larger grains with higher aspect ratios, and this probably related to the nucleation and growth of the ß-Si_3N_4 grains during the initial densification stages. At the lower densification temperature, there are generally fewer ß-nuclei which can grow into larger grains before impingement

[b] GAF Chemicals, Wayne, NJ: Polyvinylpyrrolidone K-15 [c] R. T. Vanderbilt, Norwalk, CT, 821A,

into another grain. On the other hand, at the higher densification temperature, the ß-nuclei concentration is higher and as grain growth occurs impingement into an adjacent grain occurs sooner. This results in a finer overall grain size with lower aspect ratios. The grain growth temperature results indicate that the higher temperatures result in larger grain sizes and increased fracture toughness. As with the densification temperature, the improved fracture toughness with the slower initial heating rate is probably related to the early ß-Si_3N_4 nucleation and growth during sintering.

CONCLUSIONS

Gas-pressure sintering (GPS) can be used to densify silicon nitride containing a wide variety of sintering additives. Parameters affecting the sintering behavior include densification temperature, densification time, grain growth temperature, grain growth time and heating rates. The Si_3N_4-6% Y_2O_3-2% Al_2O_3 samples sintered to high densities at all conditions used in the present study, whereas the Si_3N_4-$Sr_2La_4Yb_4(SiO_4)_6O_2$ samples required the highest temperatures and longest times to achieve densities ≥98 % T. D. The main effect on the fracture toughness for Si_3N_4-6% Y_2O_3-2% Al_2O_3 samples was the use of a lower densification temperature, which was 1900°C in the present study. For the Si_3N_4-$Sr_2La_4Yb_4(SiO_4)_6O_2$ composition, fracture toughness was sensitive to and improved by a slower heating rate (10°C/min), a lower densification temperature (1900°C), a higher grain growth temperature (2000°C), and a longer grain growth time (2 h).

ACKNOWLEDGMENTS

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Table 1. Taguchi experimental design array for optimization of densification parameters to obtain silicon nitride ceramics with improved mechanical properties. Compositions are Si_3N_4-6% Y_2O_3-2% Al_2O_3 and Si_3N_4-$Sr_2La_4Yb_4(SiO_4)_6O_2$ (at 8 equivalent % oxygen). The design is a L_8 ($4^1 \times 2^4$).

						Si_3N_4-6% Y_2O_3-2% Al_2O_3.			Si_3N_4-$Sr_2La_4Yb_4(SiO_4)_6O_2$		
Test No.	Final Sinter. Temp. (°C)	Initial Sinter. Temp. (°C)	Initial Sinter. Time (h)[a]	Final Sinter. Time (h)	Heating Rate to Initial Sinter. Temp. (°C/min)	Sintered Density (g/cm^3, % T.D.)	Flexural Strength (MPa)	Fracture Toughness (MPa$\sqrt{m}$)	Sintered Density (g/cm^3, % T.D.)	Flexural Strength (MPa)	Fracture Toughness (MPa$\sqrt{m}$)
1	2000	1900	2 (Min)	2	25	3.24 99.4	679±41	8.4±0.3	3.51 100	607±160	7.0±0.3
2	2000	1950	2.5 (Min+1)	1	10	3.24 99.4	749±49	8.0±0.1	3.50 100.0	574±47	5.7±0.5
3	1950	1900	2 (Min)	1	10	3.24 99.3	542±37	8.3±0.1	3.30 94.2	---	6.1
4	1950	1950	2.5 (Min+1)	2	25	3.21 98.6	817±62	8.0±0.2	3.48 99.2	503±43	5.0±0.5
5	1900	1900	3 (Min+1)	2	10	3.25 99.6	627±52	8.2±0.2	3.50 100.0	550±42	7.5±0.7
6	1900	1950	1.5 (Min)	1	25	3.24 99.5	651±87	7.5±0.3	3.46 98.8	---	4.7
7	1850	1900	3 (Min+1)	1	25	3.23 99.1	662±37	8.2±0.1	3.47 99.1	396±52	4.3±0.2
8	1850	1950	1.5 (Min)	2	10	3.22 98.9	653±65	8.0±0.6	3.42 97.7	362±38	4.6±0.1

[a] Minimum time to obtain closed porosity (1900°C - 2h, 1950°C - 1.5h) with either no further hold time or a 1h additional hold time. Times defined as minimum (min) or minimum plus 1h (min + 1).

Table 2. Optimum sintering conditions to maximize flexural strength and fracture toughness of Si_3N_4-6% Y_2O_3-2% Al_2O_3 during gas pressure sintering.

Sintering Condition Variable	Optimum Condition to Maximize Strength	Variable Significance	Optimum Condition to Maximize Toughness	Variable Significance	Combined Optimum Conditions
Grain Growth Temp. (°C)	2000°C	Moderate	2000°C	Very Low	2000°C
Densification Temp. (°C)	1950°C	Moderate	1900°C	Moderate	1900°C
Densification Time (h)[a]	3 (Min+1)	Moderate	Either	None	3 (Min+1)
Grain Growth Time (h)	2	Low	2	Very Low	2
Heating Rate (°C/min)	25 °C/min	Moderate	10°C/min	Very Low	25°C/min

[a] Minimum time to obtain closed porosity (1900°C - 2h, 1950°C - 1.5h) with either no further hold time or a 1h additional hold time. Times defined as minimum (min) or minimum plus 1h (min + 1).

Table 3. Optimum sintering conditions to maximize flexural strength and fracture toughness of Si_3N_4-$Sr_2La_4Yb_4(SiO_4)_6O_2$ (at 8 equivalent % oxygen). during gas pressure sintering.

Sintering Condition Variable	Optimum Condition to Maximize Strength	Variable Significance	Optimum Condition to Maximize Toughness	Variable Significance	Combined Optimum Conditions
Grain Growth Temp. (°C)	2000°C	High	2000°C	Moderate	2000°C
Densification Temp. (°C)	1900°C	Moderate	1900°C	High	1900°C
Densification Time (h)[a]	3 (Min+1)	Low	2 (Min)	Moderate	2 (Min)
Grain Growth Time (h)	2	Low	2	Moderate	2
Heating Rate (°C/min)	25 °C/min	Very Low	10°C/min	High	10°C/min

[a] Minimum time to obtain closed porosity (1900°C - 2h, 1950°C - 1.5h) with either no further hold time or a 1h additional hold time. Times defined as minimum (min) or minimum plus 1h (min + 1).

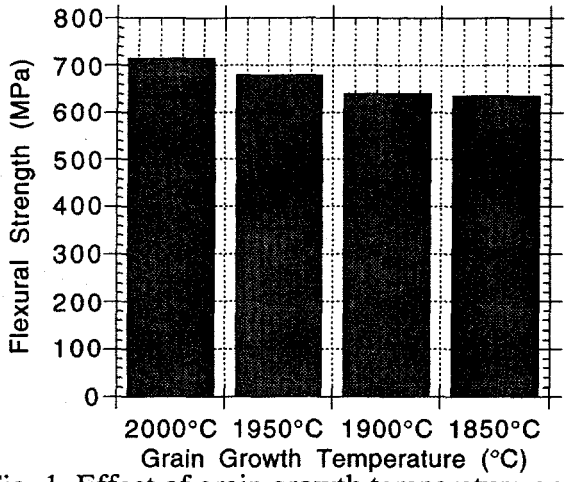

Fig. 1. Effect of grain growth temperature on the average flexural strength of gas pressure sintered Si_3N_4-6% Y_2O_3-2% Al_2O_3.

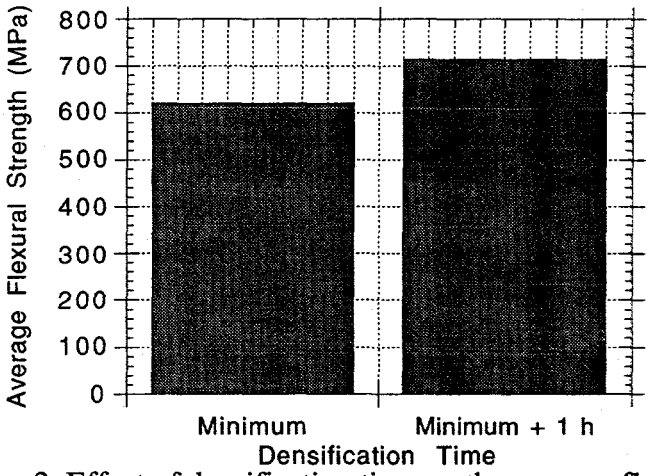

Fig. 2. Effect of densification time on the average flexural strength of gas pressure sintered Si_3N_4-6% Y_2O_3-2% Al_2O_3.

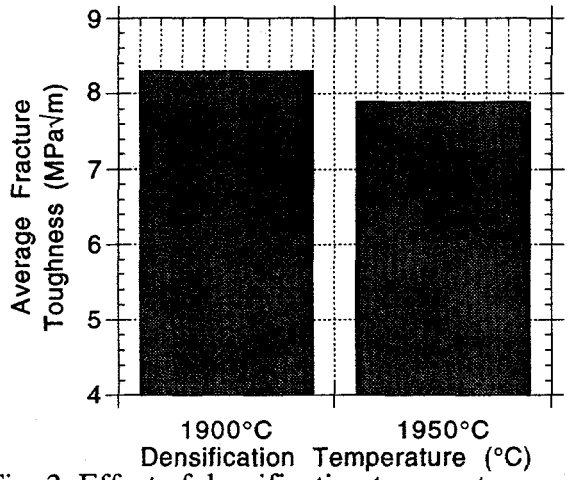

Fig. 3. Effect of densification temperature on the average fracture toughness of gas pressure sintered Si_3N_4-6% Y_2O_3-2% Al_2O_3.

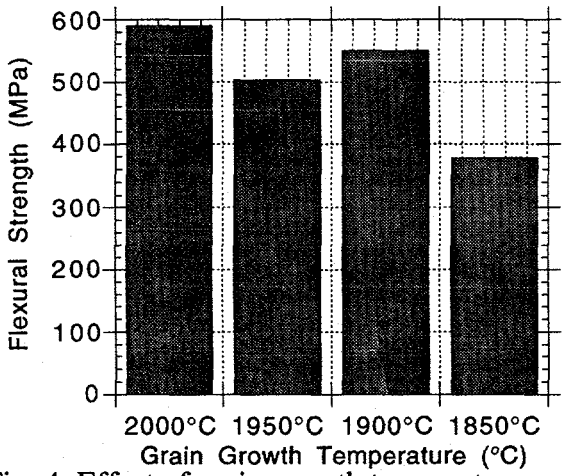

Fig. 4. Effect of grain growth temperature on the average flexural strength of gas pressure sintered Si_3N_4-$Sr_2La_4Yb_4(SiO_4)_6O_2$ (at 8 equivalent % oxygen).

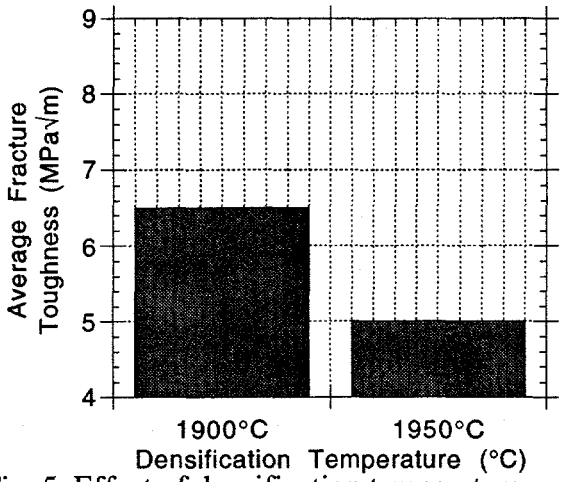

Fig. 5. Effect of densification temperature on the average fracture toughness of gas pressure sintered Si_3N_4-$Sr_2La_4Yb_4(SiO_4)_6O_2$ (at 8 equivalent % oxygen).

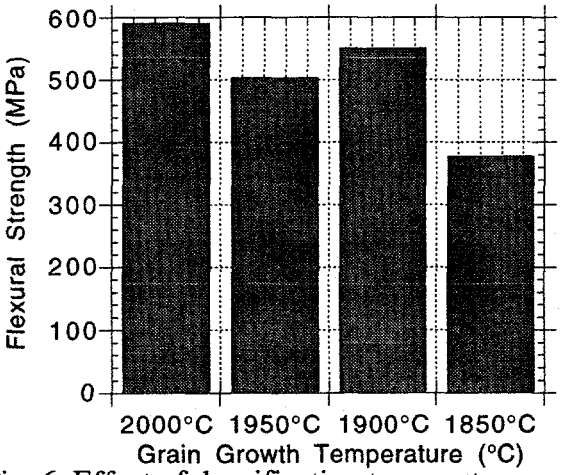

Fig. 6. Effect of densification temperature on the average fracture toughness of gas pressure sintered Si_3N_4-$Sr_2La_4Yb_4(SiO_4)_6O_2$ (at 8 equivalent % oxygen).

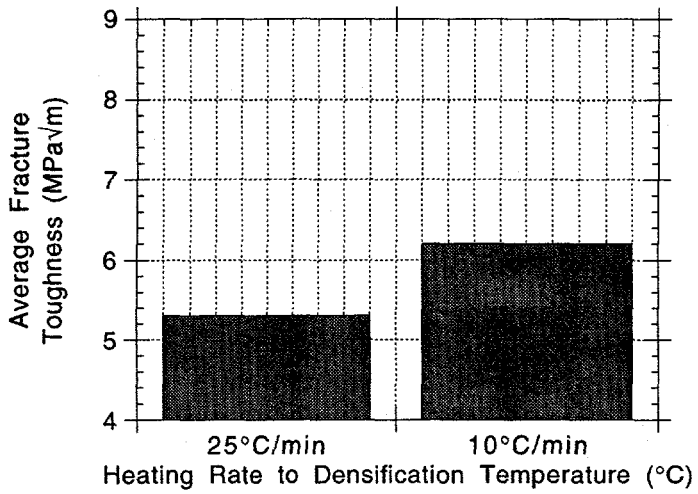

Fig. 7. Effect of heating to densification temperature on the average fracture toughness of gas pressure sintered Si_3N_4-$Sr_2La_4Yb_4(SiO_4)_6O_2$ (at 8 equivalent % oxygen).