The Korean Journal of Ceramics, **6**[3] 193-200 (2000)

Wear Behavior of Silicon Nitride Depending on Gas Pressure Sintering Conditions

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(Received February 29, 2000)

Si_3N_4 powder with 2 wt% Al_2O_3 and 6 wt% Y_2O_3 additives was sintered by the gas pressure sintering (GPS) technique. The unlubricated wear behavior depending on sintering conditions such as sintering temperature, pressure, and sintering time was investigated. When the sintering temperature and time increased, the larger elongated grains were formed and the microstructural heterogeneity increased. When sintering pressure increased, grain growth, however, was impeded. Also, the wear properties depended on microstructure and friction coefficient were related to grain size. Based on the experimental results, the wear properties were associated with initial friction coefficients as well as mechanical properties including fracture toughness and flexural strength.

Key words: Silicon nitride, Gas pressure sintering (GPS), Microstructure, Mechanical properties, Wear properties

I. Introduction

Because of its outstanding mechanical, chemical and thermal properties, silicon nitride ceramics have been considered as a good candidate for automotive components as well as cutting tools.[1-5] Generally, wear mechanisms of rigid materials were classified into ultra mild wear, mild wear, severe wear and ultra severe wear.[6] If wear occurs, the degree of precision of components decreases and reliability and durability of the parts are degraded immediately. Wear behaviors are affected by factors such as mechanical, thermal and chemical properties. Also, they are influenced by composition, microstructure (such as grain size, grain boundary and others) and test conditions (such as normal load, sliding velocity, temperature, sliding distance, and lubricant).[7]

Wear of the two brittle solids sliding over each other occurs by a number of mechanisms. These include brittle fracture caused by the contact force alone and that induced by a combination of contact and thermal stresses. Brittle fracture of ceramics is caused by microcracks and crack propagation. When tensile and shear stresses on the weak bonded grain boundary reached, crack propagated and wear proceeded as a result of grain pull-out and chipping.

This paper introduced microstructure, mechanical properties as well as tribological characterization of silicon nitride with variations of gas pressure sintering conditions such as sintering temperature, time and pressure.

II. Experimental Process

Si_3N_4 (E-10 grade, Ube Industries Ltd., Tokyo, Japan) powder of higher a-fraction and average particle size of 0.2 μm was used. Sintering additives were 2 wt% Al_2O_3 (HP-DBN grade, Leynold Co., Philadelphia, U.S.A.) and 6 wt% Y_2O_3 (fine grade, H.C. Starks, Berlin, Germany). These powders were weighed and mixed in isopropyl alcohol. The slurry was milled with silicon nitride pot for 24 h. The slurry was dried in a dry oven. The powder mixtures were compacted by a uniaxial press under 20 MPa, and cold isostatically pressed (CIP) under 245 MPa. The green body was sintered by gas pressure sintering (GPS). Sintering conditions are shown in Table 1.

Bulk density of the gas pressure sintered samples was measured by the Archimedes technique in toluene. Theoretical density was calculated by a rule of mixture of the starting powders and the relative density was determined with respect to it. The samples were polished with 0.3 μm alumina paste. Hardness and fracture toughness of the sintered samples were measured by indentation method with a load of 196 N. Flexural strength was determined with rect-

Table 1. List of Composition and Sintering Conditions

Sample	Conditions (Si_3N_4+2 wt% Al_2O_3+6 wt% Y_2O_3)		
	Temperature (°C)	Pressure (MPa)	Time (min)
GPS 1	1800	3	120
GPS 2	1900	3	60
GPS 3	1900	3	120
GPS 4	1900	3	180
GPS 5	1900	3	240
GPS 6	1900	8	120
GPS 7	2000	3	120
GPS 8	1900	5	120

angular bar specimens (3×4×36 mm). For the measurement of the flexural strength, three point bending test was applied at room temperature under the conditions of cross-head speed of 0.3 mm/min and span was 25 mm.

Cameron Plint Tribometer (TE77, Cameron Plint Co., Oaklands Park, U.K.) was used for the wear tests. Friction and wear tests were performed on a reciprocating ball-on-plate tester. The surface was finished by 0.3 μm alumina paste. The finished sections were cleaned with acetone and ethanol. The upper ball was commercially available silicon nitride ball (NBD100). The test conditions were fixed at a load of 10 N, speed of 0.122 m/s and testing time of 1 h at room temperature in air. After the wear test, wear volume was measured with a profilometer (Rank Taylor Hobson Company, London, U.K.). The profilometer was utilized to measure a wear track depth, and planemeter was used to calculate wear area. Scanning Electron Microscopy (SEM) was employed to examine the worn area.

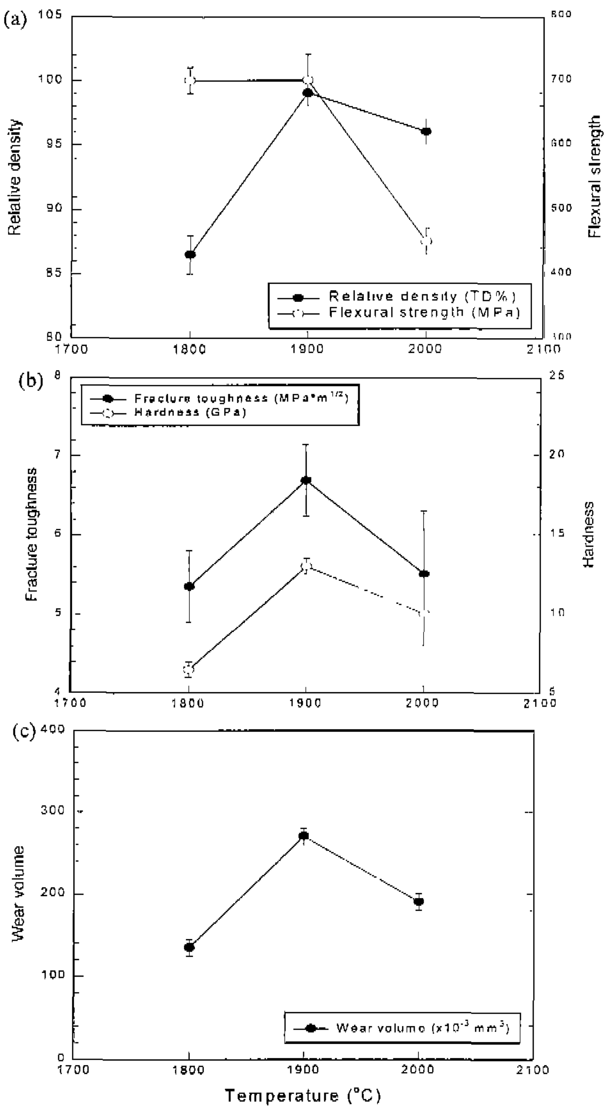

Fig. 1. Variation of mechanical properties and tribological properties with the sintering temperatue at 3 MPa, 120 min.

III. Results and Discussion

3.1. Effect of sintering temperature

Fig. 1(a)-(c) show the variation of mechanical and tribological properties of silicon nitride as a function of the GPS sintering temperature at a fixed nitrogen pressure (3 MPa) and sintering time (120 min). Relative density of the sample sintered at 1800°C and 1900°C were 86.4% and close to 100%, respectively. At 2000°C, the relative density was reduced to 95.8%. Therefore, it was noted the sample sintered at 1900°C revealed the best density. Fig. 2 shows the comparisons of SEM microstructures of the etched specimens. In the specimen sintered at 1800°C in Fig. 2(a), many poor linked with small rod were observed. The sample sintered at

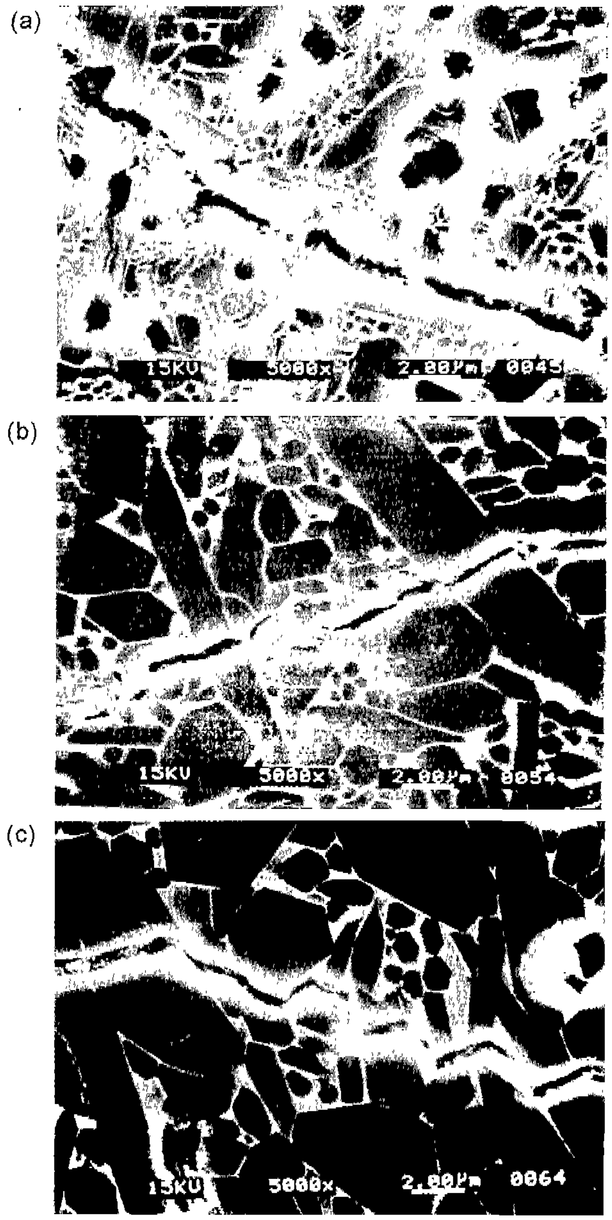

Fig. 2. SEM micrographs of the etched surface with the sintering temperature at 3 MPa, 120 min; (a) 1800°C, (b) 1900°C and (c) 2000°C.

1900°C in Fig. 2(b) showed a microstructure with a bigger grain size and few pores. However, coarse grains and pores were observed at 2000°C in Fig. 2(c).

The hardness was minimum (7.14 GPa) at 1800°C due to the low sintered density. The hardness was maximum (13.62 GPa) at 1900°C and decreased at 2000°C. It can be suggested that hardness decreases as increasing the sintering temperature because grain growth is promoted by increasing the sintering temperature. Fracture toughness was maximum (6.64 $MPa \cdot m^{1/2}$) at 1900°C. It reveals that flexural strength at 1800°C was similar to that at 1900°C; strength was 699.39 MPa and 696.33 MPa, respectively. The flexural strength was decreased with increasing grain size because of Hall-Petch type effects.[8]

Wear volume of the sintered body at high temperature was increased by the heterogeneity and glassy phases at the grain boundary according to Ferver and Hue.[9] Fig. 3 and 4 show SEM micrographs of wear track and friction graph for various sintering temperatures. Fig. 3 shows that wear debris were fine. Poor sinterability of the specimen at 1800 °C in Fig. 3(a) decreased wear volume, because small size particle acted as solid lubricants. According to the previous works by Rice[10] and Cho *et al.*,[11] wear resistance of ceramics increases with decreasing grain size. Fig. 4(b) shows that friction coefficient of the sample sintered at 1900°C was higher than that of the samples sintered at 1800°C (Fig. 4(a)) and 2000°C (Fig. 4(c)). In this experimental condition, the initial friction was influenced by the wear behavior of silicon nitride. Low wear volume of the sample sintered at 1800 °C was caused by low initial friction.

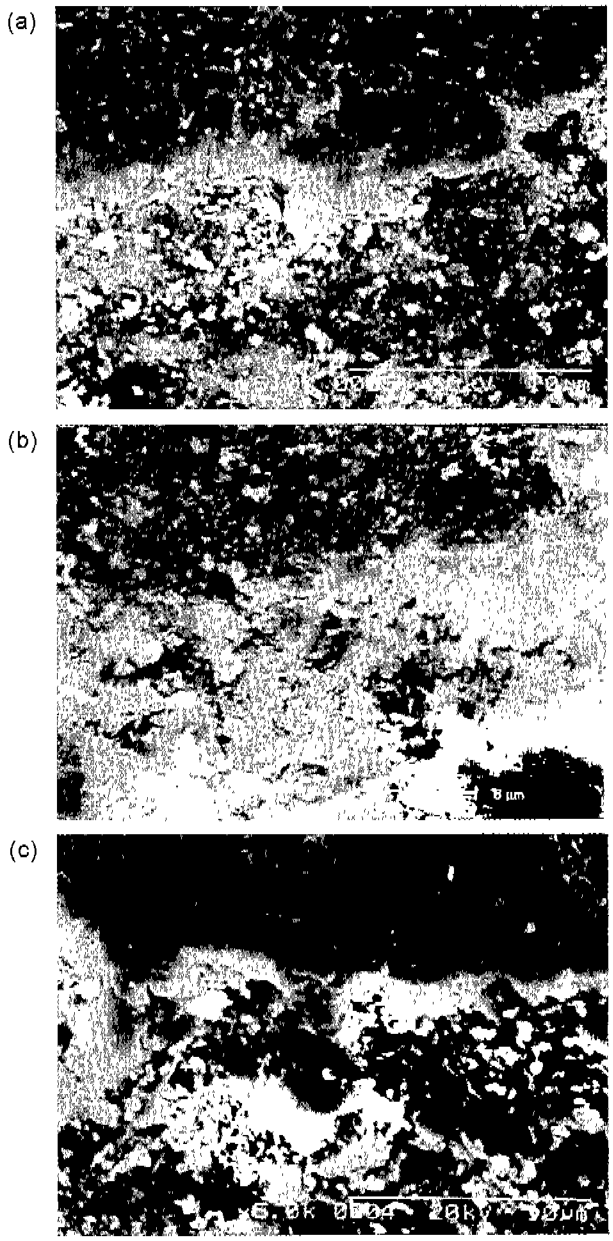

Fig. 3. SEM micrographs of the worn surface of specimen as a function of the sintering temperature at 3 MPa, 120 min; (a) 1800°C, (b) 1900°C and (c) 2000°C.

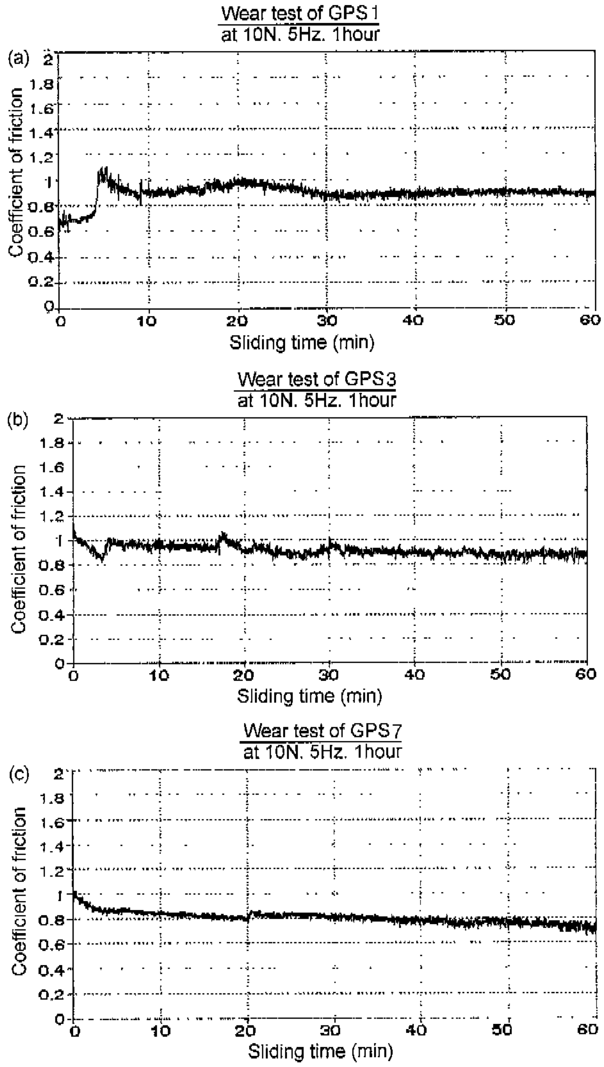

Fig. 4. Variation of friction coefficient with the sintering temperature at 3 MPa, 120 min; (a) 1800°C, (b) 1900°C and (c) 2000°C.

3.2. Effect of sintering time

Fig. 5 shows the variation of mechanical and tribological properties of silicon nitride as a function of the GPS sintering time at the fixed sintering temperature (1900°C) and pressure (3 MPa). Fig. 6 shows microstructures of the etched surfaces of samples with different sintering times at 1900°C. When sintering duration time increased, the density, however, decreased. A rapidly decrease of the relative density was caused by existence of pores around large grains after sintering for 180 min.

The hardness was maximum (13.62 GPa) after sintering for 60 min and it decreased with increasing sintering time. Rice *et al.*[10] had reported that the hardness increased as grain size decreased. On the contrary, Armstrong *et al.*[12-14] reported that hardness decreased as grain size (mainly at larger grain size). For this reason, the hardness was increased again after sintering for 240 min. The fracture toughness was decreased with increasing sintering time. When sintering temperature increased, the toughness was reduced because of the decreased aspect ratio. The fracture toughness of the sample sintered for 60 min was the highest (7.8 MPa·m$^{1/2}$) and it was gradually reduced futher sintering time. The flexural strength was affected by average grain size. As increased sintering time increased, it was decreased because of coarse grain size. Also, fine-grained sample exhibited higher strength than coarse-grain ones.

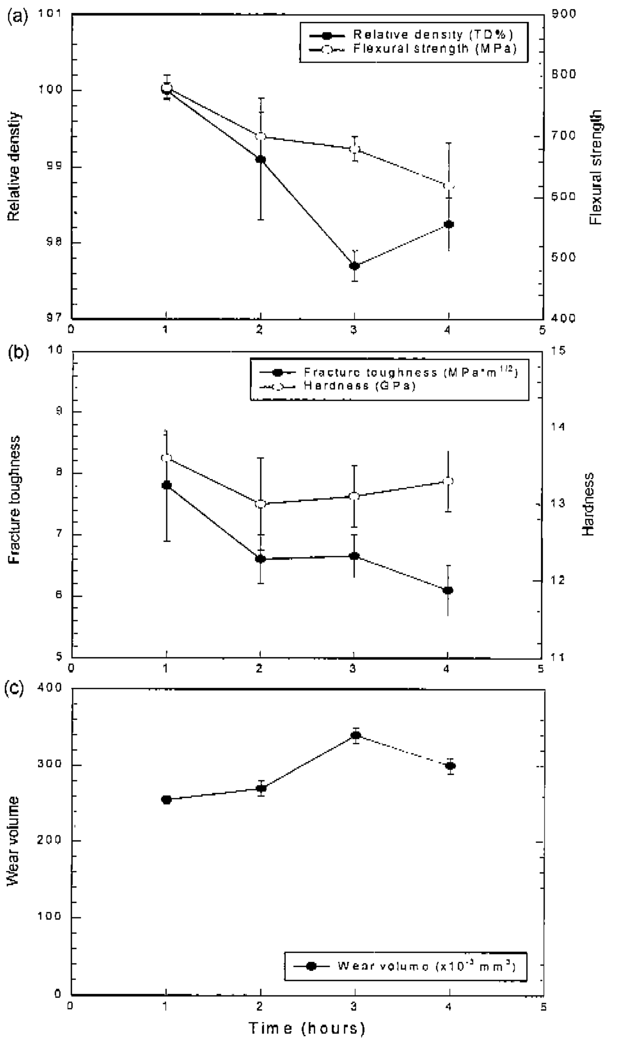

Fig. 5. Variation of mechanical properties and tribological properties with the sintering duration time at 1900°C under 3 MPa.

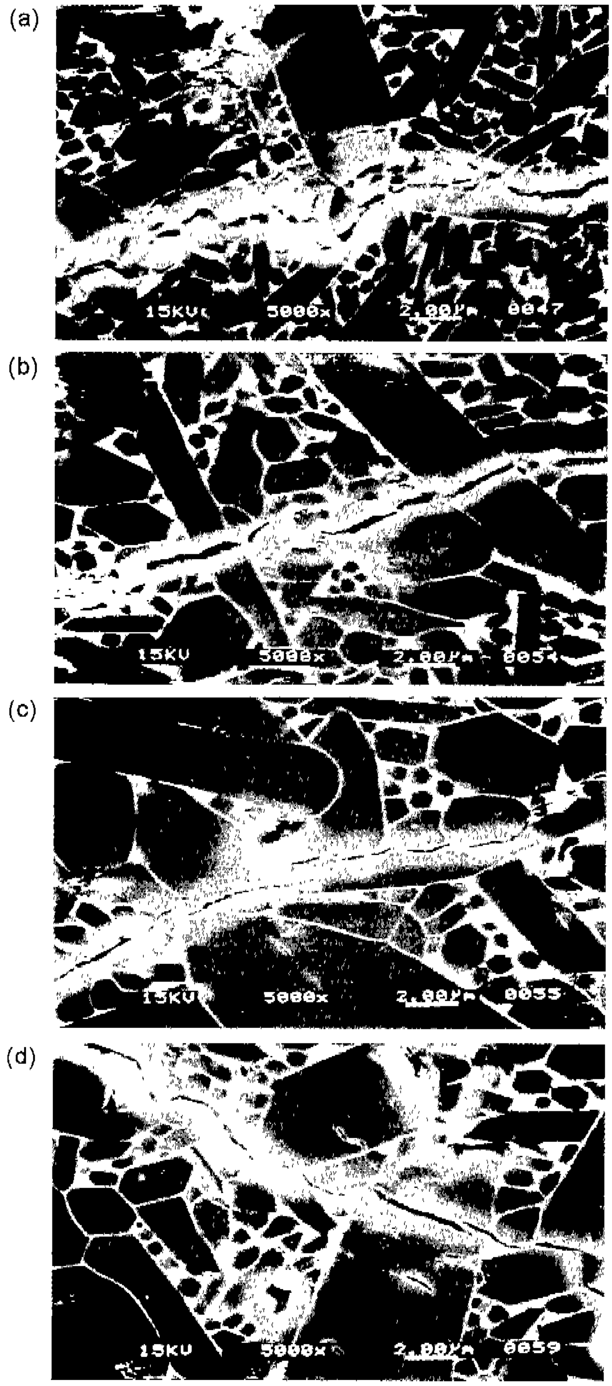

Fig. 6. SEM micrographs of the etched surface with the sintering duration time at 1900°C under 3 MPa; (a) 60 min, (b) 120 min, (c) 180 min and (d) 240 min.

Fig. 7 shows SEM micrographs of wear track of samples according to sintering time. Wear volume increased with sintering time but it was decreased after 240 min. Wear resistance of samples sintered for longer time was reduced by degradation of mechanical properties. Morphology of wear track changed according to the sintering time. For polycrystalline ceramics, grain boundaries are the sites for crack propagation, and intergranular fracture leads to "grain pull-out." Once cavities were produced on the surface, "edge-spalling" account for continued formation of wear debris, which is a typical wear behavior in the brittle regime. In this case, wear was mainly associated with microcracking, grain pull-out, and chipping. Wear debris came off the wear track and agglomeration of the debris formed platelets that were physically attached to the groove surface. Attached debris decreasing the friction coefficient. Also, wear volume was reduced because of the lower friction coefficient due to formation of attached debris. As shown in Fig. 8, the initial friction coefficient was high but it was constant after 20 min. The variation of wear volume was similar to that of initial friction coefficient. Initial wear behavior

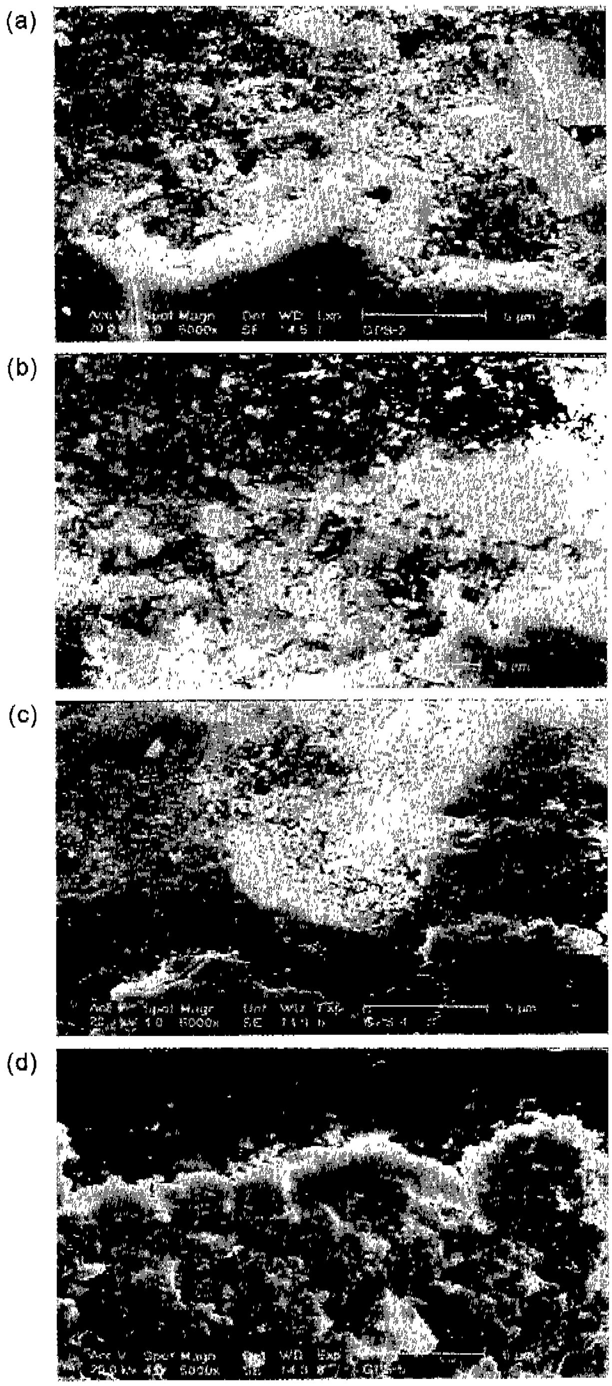

Fig. 7. SEM micrographs of the worn surface of specimen as a function of the sintering duration time at 1900°C under 3 MPa; (a) 60 min, (b) 120 min, (c) 180 min and (d) 240 min.

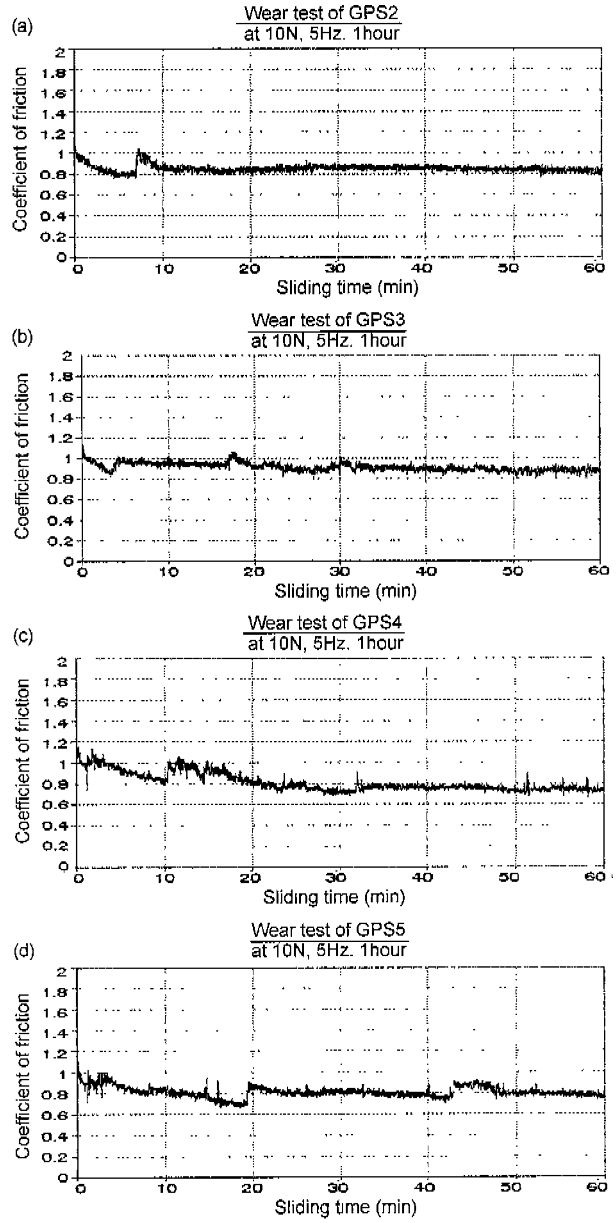

Fig. 8. Variation of friction coefficient with the sintering duration time at 1900°C under 3 MPa; (a) 60 min, (b) 120 min, (c) 180 min and (d) 240 min.

was severe and it became mild after 20 min. Also, total wear rates were affected by initial wear rates. Constant friction coefficient after initial wear was caused by the contact behavior on wear debris. When sintering time increased, the initial friction coefficient was relatively high and the final wear rate was increased. In addition, fracture toughness, flexural strength and wear resistances were degraded because of coarsening of grains and poor densification as sintering time increased.

3.3. Effect of sintering pressure

Fig. 9 shows the variation of mechanical and tribological properties of silicon nitride as a function of the nitrogen pressure at GPS with the fixed temperature (1900°C) and sintering time (120 min). Fig. 10 shows the comparisons of micrographs of the etched specimens according to the nitrogen pressure. As the nitrogen pressure increased, the grain size as well as the aspect ratio decreased. Mechanical properties were related to the microstructure. As nitrogen pressure increased, flexural strength was increased. High flexural strength was obtained from the specimen with fin grains. When the nitrogen pressure increased, flexural strength and wear volume increased.

Fig. 11 shows SEM micrographs of wear track according to the nitrogen pressures. Wear volume was minimum at 5 MPa, and was maximum at 8 MPa. Wear volume at 3 MPa was higher than that at 5 MPa because wear resistance of ceramics increases with decreasing grain size as mentioned above. However, high wear volume at 8 MPa was caused by lower fracture toughness. In this case, wear occurred by chipping caused by the lateral crack at edge of wear track.

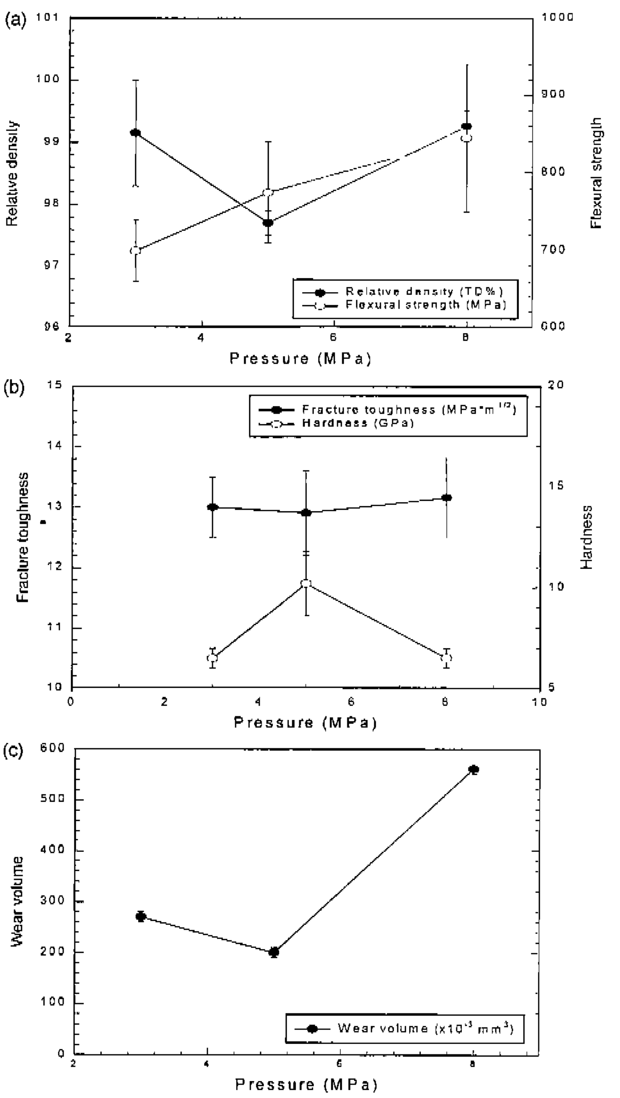

Fig. 9. Variation of mechanical properties and tribological properties with the gas pressure of sintering at 1900°C,120 min.

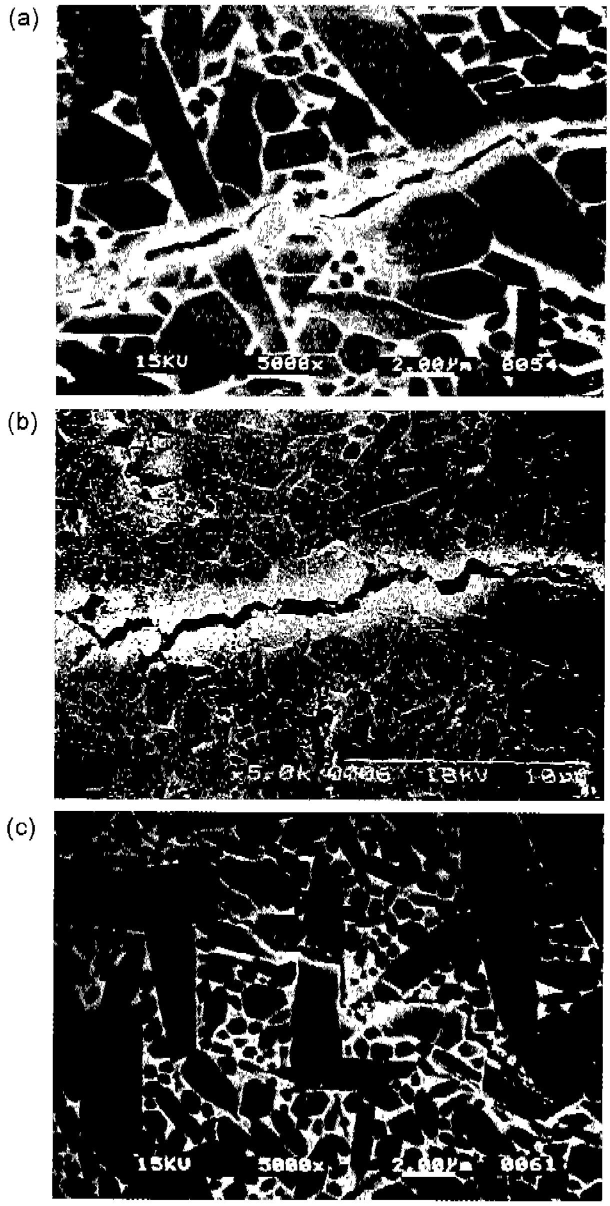

Fig. 10. SEM micrographs of the etched surface with the gas pressure of sintering at 1900°C, 120 min; (a) 3 MPa, (b) 5 MPa and (c) 8 MPa.

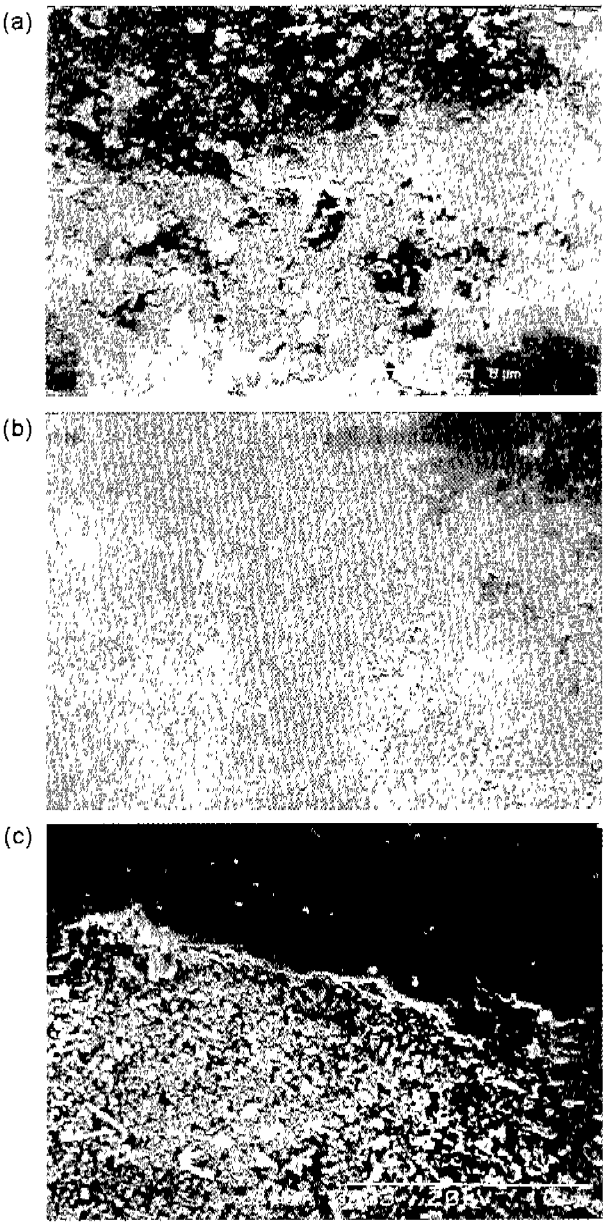

Fig. 11. SEM micrographs of the worn surface of specimen as a function of the gas pressure of sintering at 1900°C, 120 min; (a) 3 MPa, (b) 5 MPa and (c) 8 MPa.

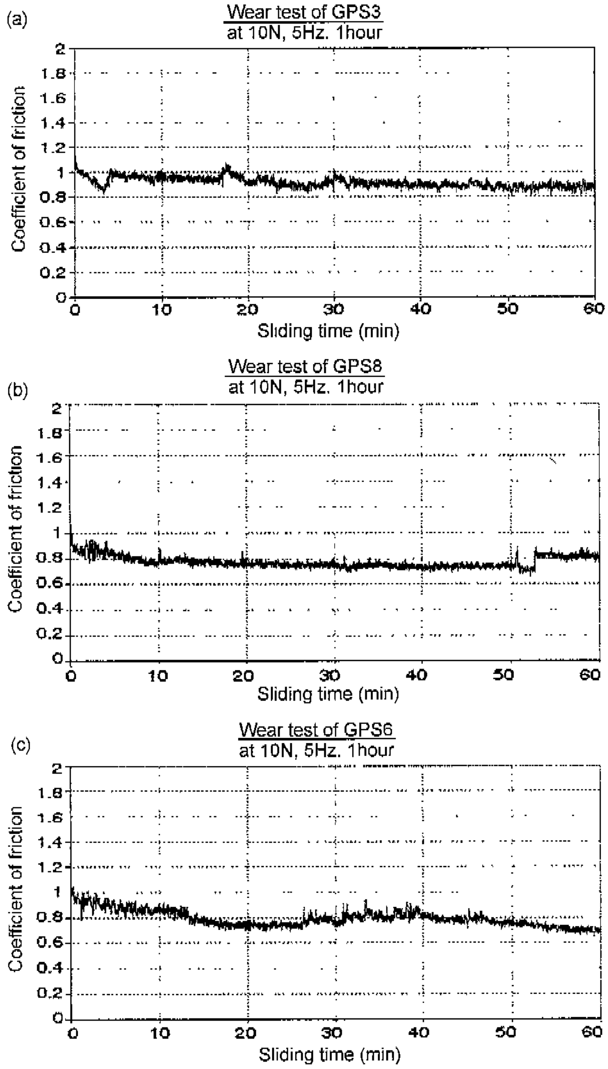

Fig. 12. Variation of friction coefficient with the gas pressure of sintering at 1900°C, 120 min; (a) 3 MPa, (b) 5 MPa and (c) 8 MPa.

Wear behavior was influenced by the fracture toughness. Fig. 12 shows the friction coefficient graphs for different sintering gas pressures. Wear rates were related to initial friction coefficient. Therefore, high wear rates were caused by the high initial friction coefficient.

IV. Conclusions

Variation of mechanical and wear properties according to various sintering conditions were studied. The results were summarized as follows;

1. When increasing sintering temperature, mechanical properties were improved, but wear rate increased. In this case, the wear rate of specimen with the poor sinterability were reduced.
2. When increasing sintering time, abnormal grain growth was enhanced. Wear behavior was associated with grain pull-out or grain fracture.
3. When increasing the nitrogen gas pressure, both flexural strength and wear volume increased.

Achnowlegdement

This study was supported under the KOSEF grant (No. 95-0300-01-10-3).

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