

Hot-Pressing of Silicon Nitride Containing Low Amounts of Y_2O_3 and AlN

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$Y_2O_3 \cdot AlN$ 미량첨가 질화규소의 열간가압소결

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ABSTRACT

Partially stabilized alpha-sialon composition ($X=0.1$) powder was hot-pressed at 1800~2000°C for 0~90 min with 30 MPa. Sintering behavior, phase changes and mechanical properties for the specimens were studied. As sintering temperature was raised from 1800 to 1900°C, the relative density tended to increase and reached 99% of theoretical at 1900°C. However the amount of alpha-sialon decreased because alpha-sialon transformed to beta- Si_3N_4 and yttrium rich silicate glass. In the case of hot-pressing at 1900°C for various times, densification increased with sintering time and full densification above 99% of theoretical was attained by 30 min. The amount of alpha-sialon decreased with sintering time. The maximum strength of 825 MPa was obtained by hot-pressing at 1900°C for 60 min.

요 약

부분 안정화 α -Sialon 조성($X=0.1$)의 분체를 1800~2000°C의 온도범위에서 30 MPa의 압력으로 소결시간을 0분에서 90분까지 변화시키면서 열간가압소결을 하여 소결시의 소결거동 및 상의 변화를 관찰하고 제조되어진 소결체의 기계적 성질을 조사하여 연구하였다. 소결온도를 1800에서 1900°C로 승온시킴에 따라 상대밀도가 증가하여 1900°C에서 99%의 상대밀도를 가지는 소결체가 얻어졌다. 그러나, 1900°C는 α -Sialon이 불안정한 영역이므로 α -Sialon상이 β - Si_3N_4 와 Y-rich 실리케이트로 전이하여 α -sialon의 함량은 감소하였다. 1900°C에서 소결시간을 변화시키면서 열간가압소결을 한 결과 소결시간이 증가함에 따라 소결체의 밀도가 증가하여 30분 이내에 99%이상의 상대밀도에 도달하였다. 소결시간이 증가함에 따라서는 역시 α -Sialon의 양은 감소하였다. 1900°C에서 60분간 열간가압 소결을 하였을 때 825 MPa의 최대강도값을 가지는 소결체가 제조되었다.

1. Introduction

Silicon nitride has been well known for high-temperature applications because of its excellent thermal and mechanical properties at high temperatures. While the covalent nature of the silicon-nitrogen bond provides silicon nitride with the attractive material properties such as chemical inertness, high hardness and strength, it also limits densification of powder compacts without the addition of oxide sintering agents¹⁾. Together with the SiO_2 surface layer on the silicon nitride

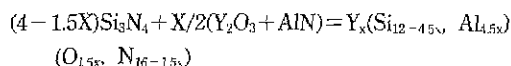
particles, these additives form liquid phases at sintering temperatures which solidify into glass phases below 1500°C, on cooling. However, this glassy grain-boundary phase degrades mechanical properties, particularly at elevated temperature²⁾.

Four approaches for reducing the glass phase content have been considered; (1) the development of densification processes which require less liquid phase³⁾, (2) postsintering treatments to alter the glass composition⁴⁾, (3) postsintering treatments to crystallize the glassy compounds in grain boundary⁵⁾, and (4) transient

liquid-phase sintering where constituents of the glass phase are incorporated into the silicon nitride grains by solid solution⁶⁾.

A transient liquid phase sintering method was used for the fabrication of beta-sialon ceramics by reaction sintering in the Si-Al-O-N system. Alpha-sialon ceramics have received considerable interest in recent years. The general composition for alpha-sialon is $M_x(Si, Al)_{12}(N, O)_{16}$, where $X < 2$ and M is a modifying cation: $M = Li^+, Mg^{2+}, Ca^{2+}, Y^{3+}$, or lanthanide ion other than La^{3+} and Ce^{3+} ⁷⁾. It is guessed from the composition that alpha-sialon is also silicon nitride based material prepared by the transient liquid phase sintering method.

Y- α -Sialon is formed in the Y-Si-Al-O-N system according to the following reaction:



where, $0 < X < 0.8$.

Alpha-sialons are divided into two kinds according to the solubility of yttrium: One is the fully-stabilized alpha-sialon within $0.3 < X < 0.8$, the other is the partially-stabilized alpha-sialon within $0 < X < 0.3$ ⁸⁾.

In the range of partially stabilized alpha-sialon, strength is improved as the content of alpha-sialon decreases. An alpha-sialon composition powder with $X < 0.2$, however, shows poor sinterability at temperatures lower than 1800°C because the solution-precipitation proceeds not much due to the little material transport. In general, more than 5 wt% of oxide additive was required for densification by hot-pressing. In sintering of Si_3N_4 at high temperature above 1800°C, there is weight loss due to thermal decomposition which prevents the densification of Si_3N_4 -based materials. Therefore, there is a maximum applicable sintering temperature in hot-pressing of Si_3N_4 . Previous work has been performed below 1850°C, and few cases were reported that Si_3N_4 was hot-pressed at 1900°C. The present paper reports the sintering behavior, changes of product phases and mechanical properties of a partially stabilized alpha-sialon ceramics ($X = 0.1$) hot pressed at 1800~2000°C for 0~90 min with 30 MPa.

2. Experimental Procedure

2.1. Starting Materials

Table 1. Composition of Specimen

Component	Si_3N_4	AlN	Y_2O_3
wt(%)	94.781	3.237	1.982

The commercial powders of Si_3N_4 (H.C. Starks, H1 Grade), Y_2O_3 (Aldrich Chemical Co., 99.999% pure) and AlN (H.C. Starks, A Grade) were used as starting materials. The mixture of the starting composition powders (Table 1) was obtained by milling in a polyethylene vessel with Si_3N_4 media and anhydrous ethanol. The mixture was dried at 110°C, and granulated by passing through a 100 mesh Tyler standard screen.

2.2. Fabrication of Silicon Nitride Specimens and their Examination

The mixtures were hot-pressed in a BN-coated graphite die (34 by 34 mm) for 0 to 90 min in flowing nitrogen gas, in the temperature range of 1800~2000°C. A pressure of 30 MPa was applied uniaxially through the graphite punches to the compact.

The amount of weight loss was calculated from weights measured before and after hot-pressing. After the surfaces of the hot-pressed specimens were ground using diamond wheels of 140, 400 and 600 grit, the displacement density in water was measured. Rectangular bars (approximation dimension 4 by 3 by 34 mm) were cut in a plane perpendicular to the hot-pressing direction. The edges of the sectioned bars were chamfered (lengthwise) to prevent edge effects. Flexural strength was measured by 3-point loading with a 30-mm span and a cross head speed of 0.5 mm/min in air. More than five specimens were subjected to flexural strength tests for each sintering condition. Vickers microhardness was measured using a diamond Vickers indenter. The load and loading time were 200 g and 5 sec, respectively. The fracture toughness, K_{IC} , was measured using the indentation method proposed by Evans and Charles⁹⁾. An indenter load of 10 Kg was applied to the specimen for 5 sec.

The phases of hot-pressed specimens were determined by X-ray powder diffraction using Ni-filtered, $CuK\alpha$ radiation. The phase content of alpha- and beta- Si_3N_4 were analyzed quantitatively according to Gazzara and Messier method¹⁰⁾. Microstructures of the polished surfaces of the hot-pressed specimens were observed by scanning electron microscopy after etching for 25

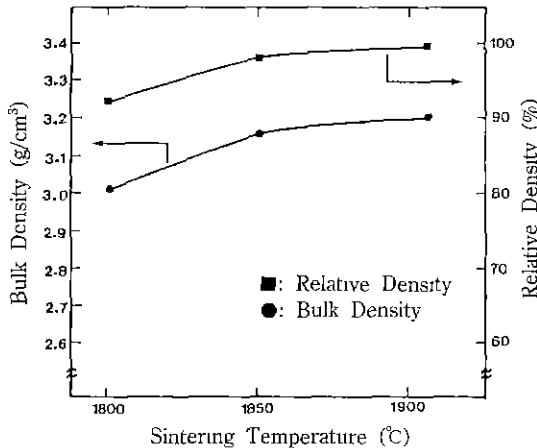


Fig. 1. Density of specimen sintered at various temperature for 1 h.

to 60 sec in a molten NaOH.

3. Results and Discussion

The density change with sintering temperature for 1 h sintering time is given in Fig. 1. The relative density increased as sintering temperature increased from 1800 to 1900°C, and attained 99% of theoretical at 1900°C. It was difficult to measure the density of the specimen hot-pressed at 2000°C due to severe thermal decomposition. Fig. 2 shows that the phases analyzed by XRD are beta-Si₃N₄ and alpha-Si₃N₄ solid solution, indicating that partially-stabilized alpha-sialon was formed. It was found that the amount of alpha-sialon, however, decreased as temperature increased. The alpha-sialon amount was 16.1% at 1800°C and 10.5% at 1850°C, respectively, and alpha-sialon was not observed at all at 1900°C. Suzuki *et al.*¹¹⁾ reported that alpha-sialon was stable below 1700°C and transformed to beta-Si₃N₄ slowly by the solution-reprecipitation process at temperatures higher than 1700°C. Sintering temperatures in this work were in an unstable region (1800~1900°C) for the formation of alpha-sialon, therefore it is thought that with increasing hot-pressing temperature, the amount of alpha-sialon was reduced because the yttrium component of the starting materials formed a glassy phase in grain boundary instead of being incorporated into the alpha-Si₃N₄ lattice. This is in good agreement with the results of SEM observation for the polished surfaces of sintered bodies (Fig. 3). Light colored

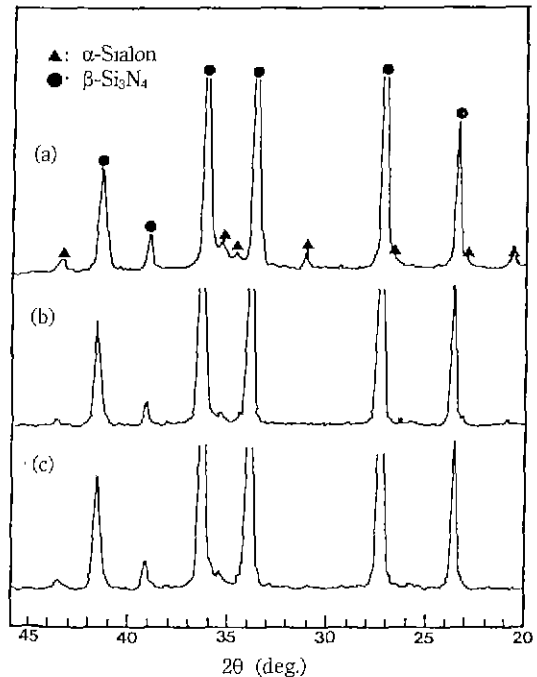
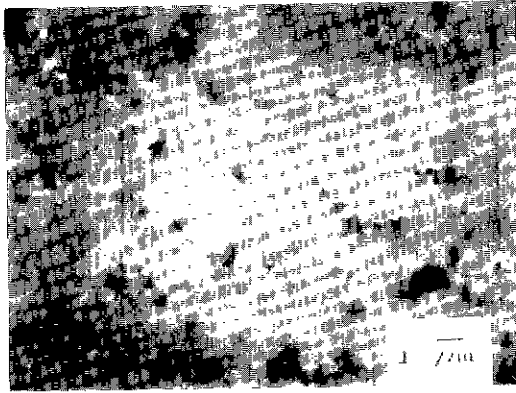


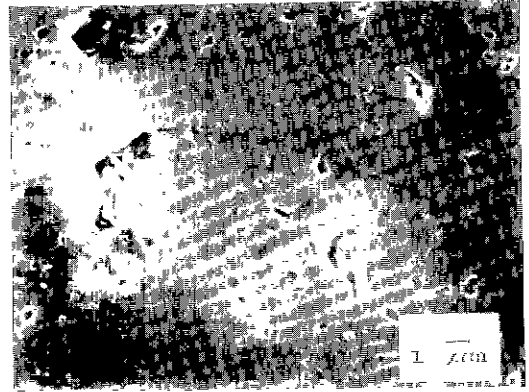
Fig. 2. X-ray diffraction pattern of specimen sintered at various temperature for 1 h.
(a) 1800°C (b) 1850°C (c) 1900°C

heterogeneities which were different from the matrix were observed in micrographs of unetched polished surface. The amount of light phase was found to increase with the sintering temperature, as shown in Fig. 3-1. However, after etching the light phase almost disappeared, suggesting that these light phases were yttrium rich silicate glass phase which could be removed by etching, as can be seen in Fig. 3-2. Flexural strength at room temperature improved with increasing sintering temperature due to the increased density, with the maximum flexural strength (825 MPa) was obtained at 1900°C of sintering temperature (Fig. 4). Fig. 5 shows the variation of fracture toughness and hardness with sintering temperature. As sintering temperature increased from 1800 to 1850°C, fracture toughness increased from 4.9 to 5.5 MN/m^{3/2} and the value at 1900°C was almost same with that of 1850°C. On the other hand, hardness increased as a sequence of 15.4, 17.2 and 17.6 GPa at 1800, 1850 and 1900°C, respectively and the changes in hardness well agrees with that of density.

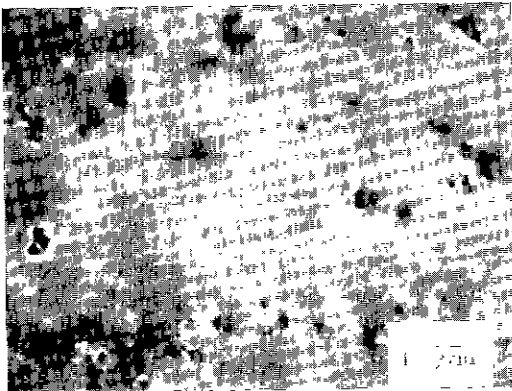
The densification curve at 1900°C as a function of



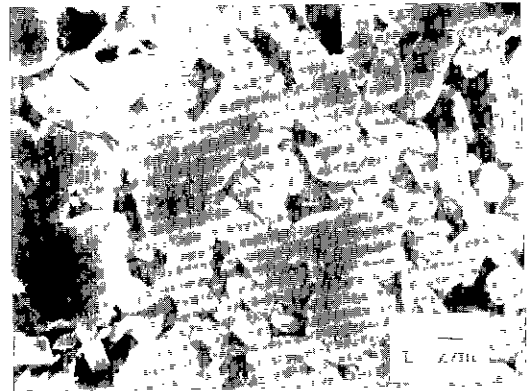
(a)



(a)



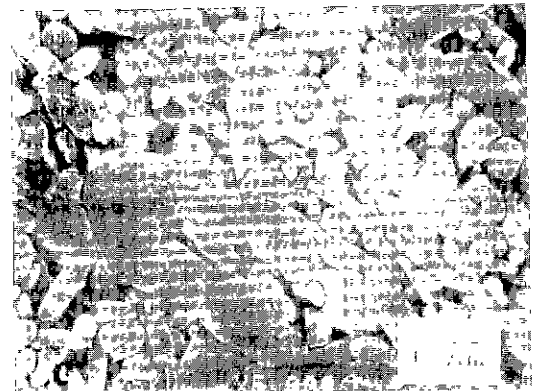
(b)



(b)



(c)



(c)

Fig. 3-1. SEM micrographs of polished specimen surface sintered at various temperature for 1 h (before etching).

(a) 1800°C (b) 1850°C (c) 1900°C

Fig. 3-2. SEM micrographs of polished specimen surface sintered at various temperature for 1 h (before etching).

(a) 1800°C (b) 1850°C (c) 1900°C

sintering time is given in Fig. 6. A relative density of 89% was obtained for specimens heated to 1900°C then immediately cooled. Densification proceeded, as can be

seen in Fig. 6, with the increase of hot-pressing time and a large increase in density was observed in the early part of sintering time, that is, within 15 min. Full

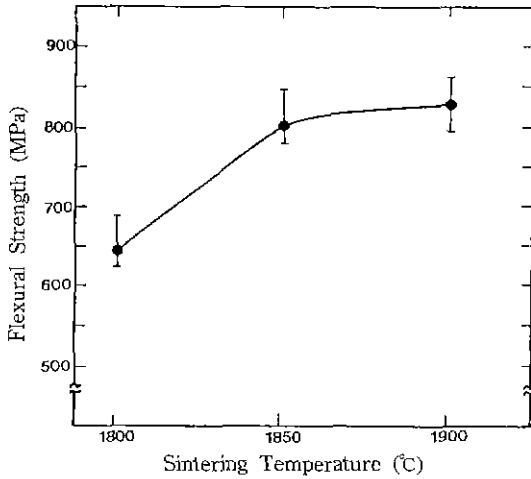


Fig. 4. Flexural strength of specimen sintered at various temperature for 1 h.

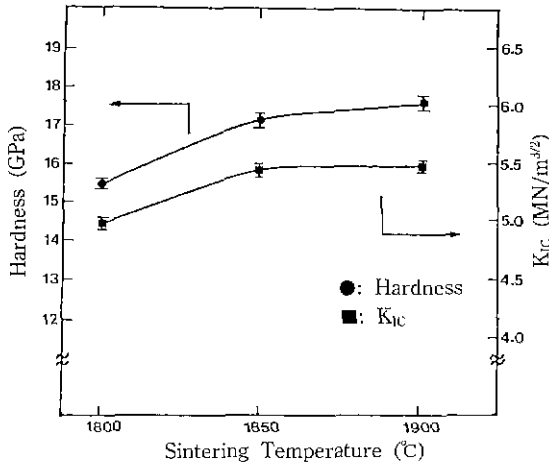


Fig. 5. Hardness and K_{Ic} of specimen sintered at various temperature for 1 h.

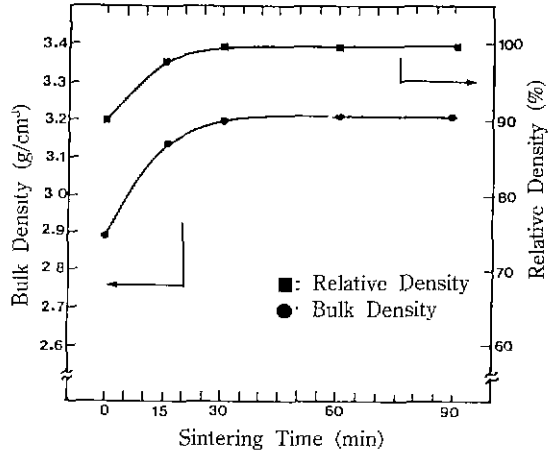


Fig. 6. Density of specimen sintered at $1900^\circ C$ as a function of times.

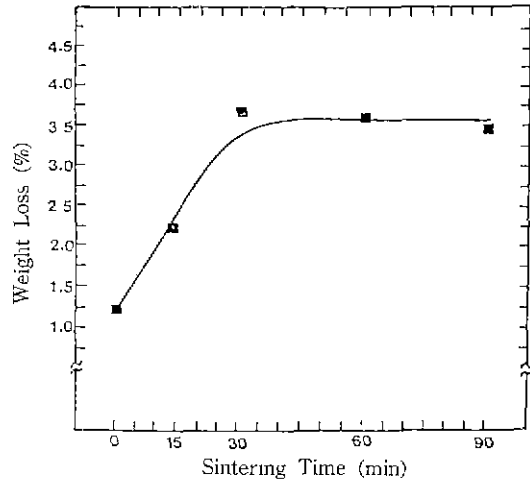


Fig. 7. Weight loss of specimen sintered at $1900^\circ C$ as a function of time.

densification above 99% of theoretical density was attained in about 30 min. Although sintering time was lengthened to more than 30 min, density was not affected by more sintering time. This result is not in agreement with that reported by Ishizawa *et al.*⁹⁾ Where it was found that the relative density of $Y-\alpha$ -Sialon of $X=0.1$ was less than 98% up to $2000^\circ C$.

Little work has been reported for Si_3N_4 hot-pressed as high as $1900^\circ C$. Weight loss, which is attributed to the thermal decomposition of silicon nitride at $1900^\circ C$ (Fig. 7), closely parallels the density change (Fig. 6). The maximum value of weight loss was 3.5 wt%, which

means little effect on densification of silicon nitride. It is, therefore, thought that dense Si_3N_4 ceramics can be fabricated by hot-pressing at $1900^\circ C$ even if for oxide sintering aids as low as 2 wt%. Fig. 8 shows that the phases of specimens change with sintering time. The amount of α -sialon decreased with increasing of hot-pressing time and remained as traces on XRD patterns even after 30 min. This suggests, as can be seen in Fig. 2 and 3, that α -sialon was transformed to β - Si_3N_4 and yttrium rich silicate glass because α -sialon was unstable at $1900^\circ C$. This is supported by EDS analysis of etched surfaces of hot-pressed spe-

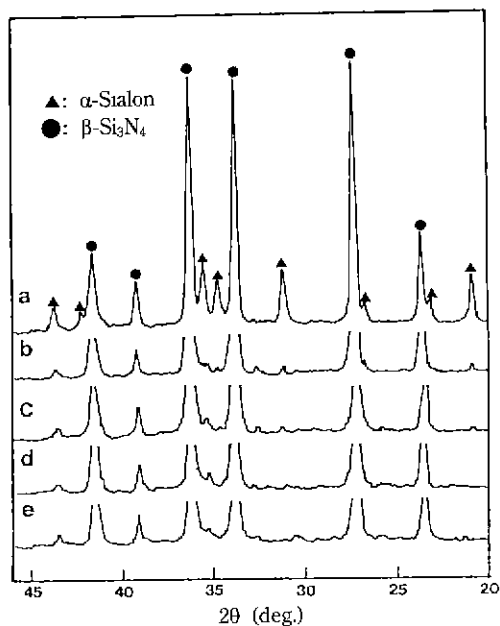


Fig. 8. X-ray diffraction pattern of specimen sintered at 1900°C as a function of time. (a) 0 min (b) 15 min (c) 30 min (d) 60 min (e) 90 min

Table 2. EDS Analysis Results in Specimens Sintered at 1900°C as a Function of Soaking Time

Soaking Time (min)	Chemical Composition (wt%)		
	Si_3N_4	AlN	Y_2O_3
15	95.55	3.80	0.65
30	95.73	3.78	0.49
90	95.83	3.69	0.48

(All Specimens were Etched in NaOH Solution)

specimens (Table 2), which shows that the amount of yttria remaining after etching away the grain boundary phase decreased with increasing sintering time. It is assumed that alpha-sialon was converted into beta- Si_3N_4 through the solution-reprecipitation process and the yttrium from alpha-sialon lattice interstitial site segregated to the grain boundaries and changed the composition of the glass phase. Fig. 9 shows that flexural strength at room temperature increases as sintering time increases to 60 min, at which time maximum strength of 825 MPa was obtained. With knowledge of density changes depending on sintering time in Fig. 6 the strength was increased to the 30 min with the increasing of sintering time because the sintered body which has

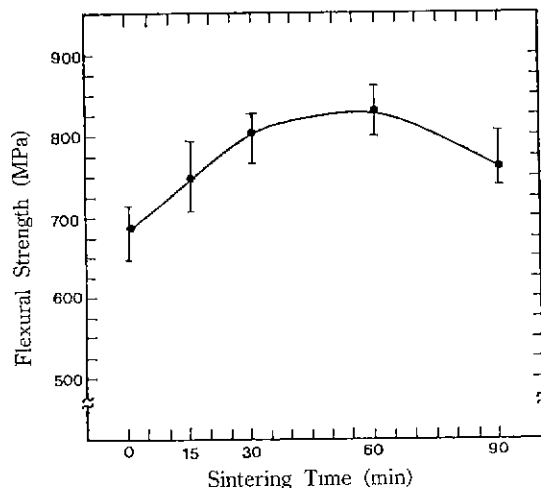


Fig. 9. Flexural strength of specimen sintered at 1900°C as a function of time.

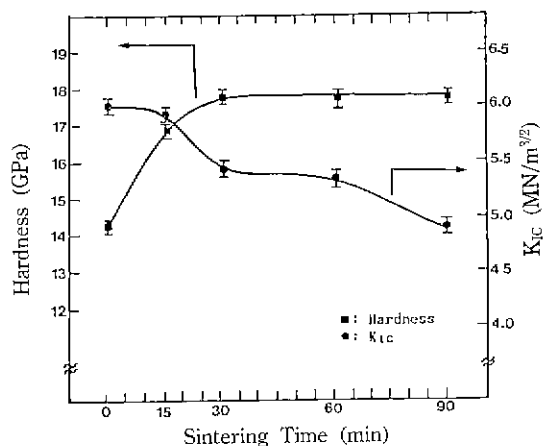


Fig. 10. Hardness and K_{1C} of specimen sintered at 1900°C as a function of time.

above 99% of relative density was acquired. And when the strength of 30 min-sintered body was compared with that of 60 min-sintered body, it had little higher strength that 60 min-sintered body got more grown particles. As the body was sintered 90 min, it was thought that the strength was decreased because the excess growth of particles was occurred. Fracture toughness and hardness curves with sintering time at 1900°C are in Fig. 10. As sintering time passes, fracture toughness decreases gradually and hardness increases to 17.6 GPa at 30 min and remains constant at that value up to 90 min. Fig. 11 provides more understand-

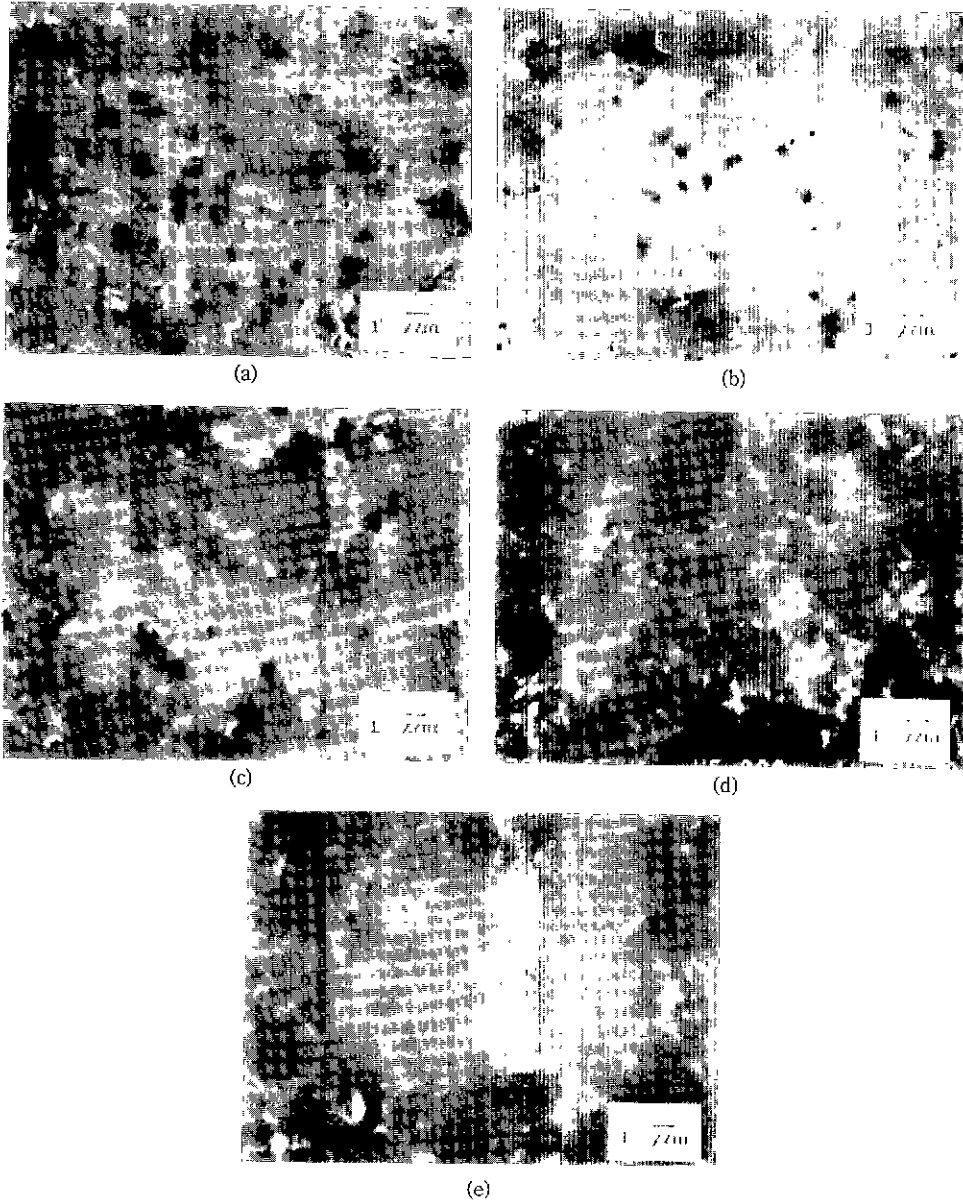


Fig. 11-1. SEM micrographs of polished specimen surfaces sintered at 1900°C as a function of time (before etching).
 (a) 0 min (b) 15 min (c) 30 min (d) 60 min (e) 90 min

ding for the flexural strength trends. Many pores of 1~2 μm can be seen on the unetched surfaces of the specimens sintered for 0, 15 and 30 min at 1900°C, but few pores are present at the sintering time of 60 and 90 min. These pores could act as flaws resulting in a decreased strength. The specimens hot-pressed for 90 min also have few pores on the unetched surfaces but they had experienced the large grain growth up

to about 10~15 μm (Fig. 11-2), which was thought to be responsible for lower flexural strength of the specimen sintered for 90 min than that sintered for 60 min.

4. Conclusions

An alpha-sialon composition with 94.78 wt% Si_3N_4 , 3.24 wt% AlN and 1.98 wt% Y_2O_3 , could be hot-pressed

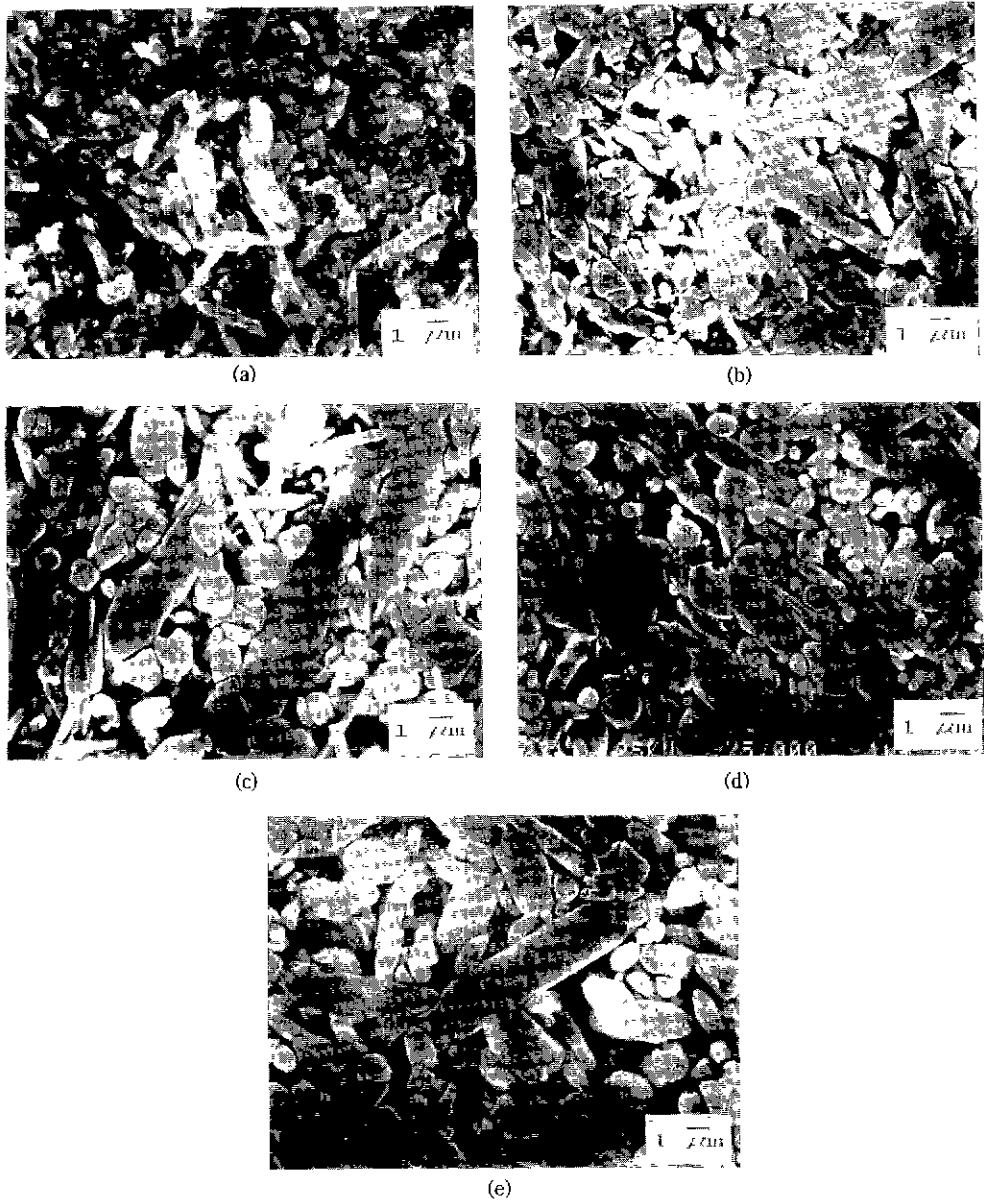


Fig. 11-2. SEM micrographs of polished specimen surfaces sintered at 1900°C as a function of time (after etching).
 (a) 0 min (b) 15 min (c) 30 min (d) 60 min (e) 90 min

to 99% of theoretical density at 1900°C for 60 min at 30 MPa. As the sintering temperature increased from 1800 to 1900°C, the content of alpha-sialon decreased because alpha-sialon transformed to beta-Si₃N₄ through the solution-reprecipitation process. In the case of hot-pressing at 1900°C, densification proceeded with sintering time and a density above 99% of theoretical was attained after 30 min. The content of alpha-phase dec-

reased with sintering time. It is thought from SEM photographs and EDS analysis of the specimens after etching that alpha-sialon was converted to beta-Si₃N₄ and Y-Si-Al-O-N glass. The maximum strength of 825 MPa was obtained by hot-pressing at 1900°C for 60 min. Fracture toughness and hardness of this sample were 5.4 MN/m^{3/2} and 17.6 GPa, respectively.

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