

Reaction sintering and mechanical properties of $\text{Si}_3\text{N}_4\text{-Si}_2\text{N}_2\text{O-MN}$ (M=B, Ti) composites densified by hot-pressing

H. Kiyono, Y. Noritake and S. Shimada

Graduate School of Engineering, Hokkaido University, Sapporo, 060-8628, JAPAN

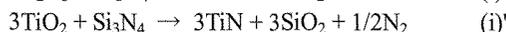
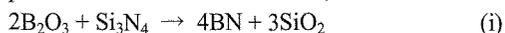
Fax: 81-11-706-6573, e-mail: kiyono@eng.hokudai.ac.jp

$\text{Si}_3\text{N}_4\text{-Si}_2\text{N}_2\text{O-MN}$ (M=B, Ti) composite ceramics were hot-pressed (HP) by using following reactions of $2\text{B}_2\text{O}_3 + \text{Si}_3\text{N}_4 \rightarrow 4\text{BN} + 3\text{SiO}_2$ (i), $3\text{TiO}_2 + \text{Si}_3\text{N}_4 \rightarrow 3\text{TiN} + 3\text{SiO}_2 + 1/2 \text{N}_2$ (i)', $\text{Si}_3\text{N}_4 + \text{SiO}_2 \rightarrow 2\text{Si}_2\text{N}_2\text{O}$ (ii). Reactions during sintering were followed by XRD and sintered composites were characterized by XRD, SEM, TEM, four-point bending test and Vickers indentation method. XRD results and TEM observations showed that *h*-BN and TiN were formed at about 1200°C by the reaction of (i) and (i)'. The $\text{Si}_2\text{N}_2\text{O}$ phase formed by reaction (ii) was found above 1800°C. $\text{Si}_3\text{N}_4\text{-Si}_2\text{N}_2\text{O-BN}$ composite consisted of $\text{Si}_2\text{N}_2\text{O}$ grains of 2-10 μm in size with Si_3N_4 and *h*-BN grains of about 0.5 μm in size. Strength of $\text{Si}_3\text{N}_4\text{-Si}_2\text{N}_2\text{O-BN}$ composite was lower than that of $\text{Si}_2\text{N}_2\text{O}$ ceramics but hardness and toughness were comparable to $\text{Si}_2\text{N}_2\text{O}$. $\text{Si}_3\text{N}_4\text{-Si}_2\text{N}_2\text{O-TiN}$ composites also consisted of 2-10 μm $\text{Si}_2\text{N}_2\text{O}$ grains with small TiN about 0.5 μm . Hardness and strength of $\text{Si}_3\text{N}_4\text{-Si}_2\text{N}_2\text{O-TiN}$ composites were comparable to those of $\text{Si}_2\text{N}_2\text{O}$ ceramics but toughness was greater than $\text{Si}_2\text{N}_2\text{O}$.

Key words: silicon nitride, silicon oxynitride, titanium nitride, boron nitride, composites

1. INTRODUCTION

Silicon nitride (Si_3N_4) based ceramics are promising high temperature structural materials because of its high chemical stability and mechanical properties in elevated temperature environments. To improve thermal shock resistance, corrosion resistance and mechanical properties, addition of secondary phases such as *h*-BN (graphite structure) or TiN has been reported.^{1,2} In the hot-pressing of *h*-BN containing composites, in situ formation of *h*-BN is favorable because orientation and agglomeration of *h*-BN particles resulting in anisotropy in mechanical properties often occur.³ In the fabrication of TiN- Si_3N_4 composites, the formation of small TiN particle in the composites is necessitated, but such fine powder is difficult to purchase and to handle in air without oxidation. B_2O_3 and TiO_2 react with Si_3N_4 to produce BN³ and TiN as follows,



SiO_2 produced in the reactions (i) and (i)' reacts with Si_3N_4 at higher temperatures to form $\text{Si}_2\text{N}_2\text{O}$,



This reaction occurs at around 1800°C but progress of the reaction strongly depends on temperature, reaction time and compositions of eutectic liquid phase.^{4,5} Fracture toughness of monolithic $\text{Si}_2\text{N}_2\text{O}$ ceramic are similar or lower compared with typical Si_3N_4 ceramic,⁴ possibly because the fabrication of fully densified sintered body with low amount of residual glass phase is difficult. However, $\text{Si}_2\text{N}_2\text{O}$ grains tend to grow to needle or platelet shapes and is expected to toughen composites by virtue of crack wake bridging.³ There are a few studies on fabrication of $\text{Si}_3\text{N}_4\text{-Si}_2\text{N}_2\text{O-TiN/BN}$ composites,^{5,6} the mechanical properties of the composites have not been reported in detail. The present study describes the processing for fabrication of the $\text{Si}_3\text{N}_4\text{-Si}_2\text{N}_2\text{O-TiN/BN}$ ceramics by reaction sintering and characterization of the mechanical properties of the ceramics thus obtained.

2. EXPERIMENTAL PROCEDURE

The powders of $\alpha\text{-Si}_3\text{N}_4$ (Ube SN-E10), Al_2O_3 (Kanto chemical), Y_2O_3 (Koujyundokagaku), B_2O_3 (Kanto chemical) and TiO_2 (Kanto chemical, 30 nm) were used

Table I. Starting and expected compositions of composites.

Sample No.	Starting composition (wt%)				Expected composition of products (vol%)			
	Si_3N_4	B_2O_3	Al_2O_3	Y_2O_3	Si_3N_4	$\text{Si}_2\text{N}_2\text{O}$	BN or TiN	other oxide materials
	70	20	5	5	0	83	12 (BN)	5
TN-3	85	5	5	5	75	15	3 (TiN)	7
TN-5	80	10	5	5	58	30	5 (TiN)	7
TN-7	75	15	5	5	41	45	7 (TiN)	7
TN-10	70	20	5	5	28	58	10 (TiN)	5
TN-13	63	27	5	5	0	81	13 (TiN)	6

as starting materials. The mixture of powders was milled in ethanol for 24 h with plastic coated iron balls. The starting and expected compositions, on the assumption that the reactions of (i), (i') and (ii) completely proceed, are listed in Table 1. The mixed powders were hot-pressed by FVPHP-R-5 (Fuji Denpa Co.) at 1800-1900°C at a heating rate of 10°C/min and at 24 MPa for 1-4 h in N_2 atmosphere. Crystalline phases were identified by X-ray photoelectron spectroscopy (XPS, shimadzu ESCA3200), X-ray powder diffraction (XRD, RIGAKU, RINT-2000). Microstructure were investigated by scanning electron microscope (SEM, JEOL, JSM-6300F) and transmission electron microscope (TEM, JEOL, JEM-2000EX) with energy dispersive spectrum (EDS) analysis unit. Fracture strength was measured by four pointed bending test with cross head speed of 0.05 mm/min and hardness was measured by indentation method. Fracture toughness was obtained by Vickers-induced crack length at an applied pressure of 19.5 N.

3. RESULTS AND DISCUSSION

3-1 COMPOSITES OF $\text{Si}_3\text{N}_4\text{-Si}_2\text{N}_2\text{O-BN}$ CERAMICS

When the mixed powder was sintered at 1850°C for 1 h at a heating rate of 10°C/min, large $\alpha\text{-Si}_3\text{N}_4$ peaks with small $\text{Si}_2\text{N}_2\text{O}$ peaks were detected by XRD in the sintered ceramics, suggesting that the reactions (i) and (ii) didn't proceed completely during hot-pressing. To check whether the reaction (i) proceeds or not, TEM observation and XPS analysis were carried out for the samples hot-pressed at 1200° and 1300°C for 1 h. In both samples, rod-like grains about 0.1 μm in length with layered structure were observed by TEM. The grains were identified as $h\text{-BN}$ by measurements of interlayer distance. The signal of boron was also detected by XPS in both samples and was greater for the 1200°C sample than that for 1300°C sample. Therefore, the mixed powder was kept at 1200°C for 1 h and then was heated up to objective sintering temperatures.

XRD patterns of the composites hot-pressed at 1800°-1900°C are shown in Fig. 1. The peaks of $h\text{-BN}$ were hardly detected in the samples, due to overlapping with $\alpha\text{-}$, $\beta\text{-Si}_3\text{N}_4$ and $\text{Si}_2\text{N}_2\text{O}$ peaks.⁷ Strong peaks of $\alpha\text{-Si}_3\text{N}_4$ with small peaks of $\text{Si}_2\text{N}_2\text{O}$ were observed in the sample sintered at 1800°C for 1 h. The peaks of the $\text{Si}_2\text{N}_2\text{O}$ became stronger with increasing sintering temperature (1850° and 1900°C for 1 h), but the $\alpha\text{-Si}_3\text{N}_4$ still remained and the peaks of $\beta\text{-Si}_3\text{N}_4$, which is transformed from $\alpha\text{-Si}_3\text{N}_4$, were intensified at 1900°C. The presence of $\alpha\text{-}$ and $\beta\text{-Si}_3\text{N}_4$ denoted that the reaction (ii) did not proceed completely. In sintering at 1850°C, the $\text{Si}_2\text{N}_2\text{O}$ increased and the $\alpha\text{-}$ and $\beta\text{-Si}_3\text{N}_4$ decreased with increasing time from 1 to 4 h, suggesting that prolonging the sintering time was effective to proceed in the reaction (ii) compared with increasing the sintering temperature.

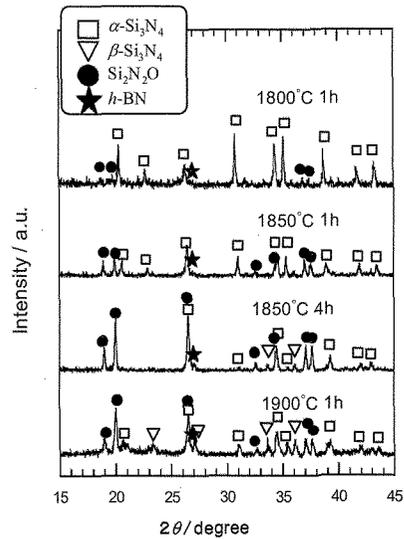


Fig. 1 XRD patterns of $\text{Si}_3\text{N}_4\text{-Si}_2\text{N}_2\text{O-BN}$ composites.

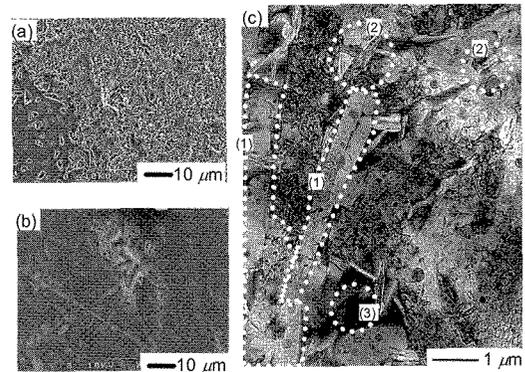


Fig. 2 SEM images of etched ($\text{HF}:\text{H}_2\text{O}=1:1, 1\text{h}$) surface of the composites sintered at 1850°C for (a) 1 and (b) 4 h. (c) TEM image of a bulk microstructure of sample (b). Areas surrounded by dashed lines of (1), (2) and (3) in photograph (c) denotes $\text{Si}_2\text{N}_2\text{O}$, $h\text{-BN}$ and SiO_2 amorphous phases, respectively.

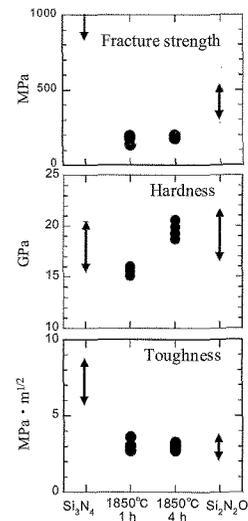


Fig. 3 Fracture strength, Vickers hardness and fracture toughness of $\text{Si}_3\text{N}_4\text{-Si}_2\text{N}_2\text{O-BN}$ composites with typical values of Si_3N_4 and $\text{Si}_2\text{N}_2\text{O}$ ceramics.

Figure 2 shows SEM images of the etched surface by a HF solution of the composites sintered at 1850°C for 1 and 4 h and TEM image of microstructures of the bulk sintered at this temperature for 4 h. It was found that the surface of the composites sintered for 1 h (a) was severely etched but not so much in the sample sintered for 4 h (b). Because amorphous SiO₂ is readily etched by HF solution, it was suggesting that the amount of SiO₂ glass phase was decreased by reaction (ii) with sintering time. The microstructure of the bulk, observed by TEM (Fig. 2 (c)), shows that large Si₂N₂O with 2 - 10 μm long denoted at position (1) were composed of small tabulated grains, *h*-BN grains were less than 1 μm at position (2) and amorphous gassy phase at position (3) was present. EDS analysis showed that the amorphous phase was composed of SiO₂ containing small amount of Al and Y and formed eutectic liquid phase at the sintering temperature. The presence of the amorphous phase denoted the reaction (ii) did not proceed completely. The *h*-BN grains were distributed randomly in the composites and some of the grains were included in Si₂N₂O grains.

Fracture strength and toughness and Vickers hardness were indicated in Fig. 3 with the reported values of Si₃N₄ and Si₂N₂O⁴ ceramics. Fracture strength of BN containing composites smaller because of the intrinsic small strength of *h*-BN, as reported in the previous study.¹ On the other hand, the values of hardness and fracture toughness of the composites did not change significantly with sintering time (1 and 4 h) similarly to the reported value of Si₂N₂O monolithic ceramic.⁴

3-2 COMPOSITES OF Si₃N₄-Si₂N₂O-TiN CERAMICS

Production of TiN phase by reaction (i)' was confirmed by XRD in the samples hot-pressed at ≥ 1250°C with a heating rate of 10°C/min. TEM observation of the sample hot-pressed at 1250°C for 1 h showed that the TiN particles were about 30 nm in size and the size was comparable to that of the starting TiO₂ particles. XRD patterns of TN-5 composites sintered at 1850° and 1900°C are shown in Fig. 4. The Si₂N₂O, TiN, α- and β-Si₃N₄ were observed in the samples sintered at 1850°C for 1 h. The peaks of Si₂N₂O were increased with sintering time of 1 to 4 h at 1850°C and sintering temperature to 1900°C. More β-Si₃N₄ was formed in the sample sintered at 1900°C compared with the sample sintered at 1850°C for 4 h.

Figure 5 shows SEM photographs of etched surface of the TN-5 composites sintered at 1850°C for 1 and 4 h and TEM photograph of bulk sample obtained at this temperature for 1 h. Similarly to the BN-composites, the composites sintered for 1 h were more etched than the composites sintered for 4 h. From TEM observation with EDS analysis, the composites obtained at 1850°C for 1 h had large Si₂N₂O grains of 2 - 10 μm long with ≤ 0.5 μm TiN grains and amorphous phase. The TiN

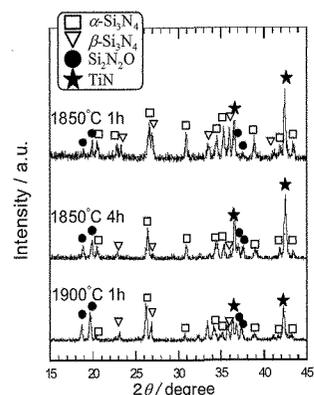


Fig. 4 XRD patterns of Si₃N₄-Si₂N₂O-TiN composites with TN-5 composition..

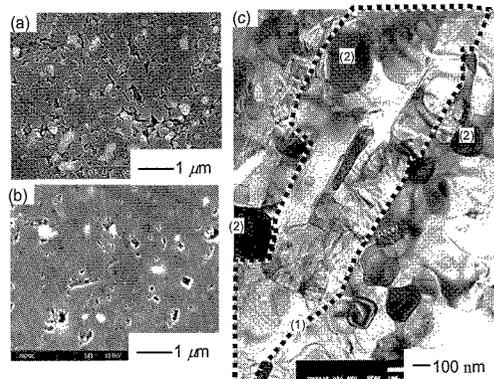


Fig. 5 SEM images of etched (HF:H₂O=1:1, 1h) surface of the composites sintered at 1850°C for (a) 1 and (b) 4 h. (c) TEM image of a bulk microstructure of sample (b). An area surrounded by dashed line (1) is assemblage of Si₂N₂O grains and dark areas shown by (2) are TiN grains.

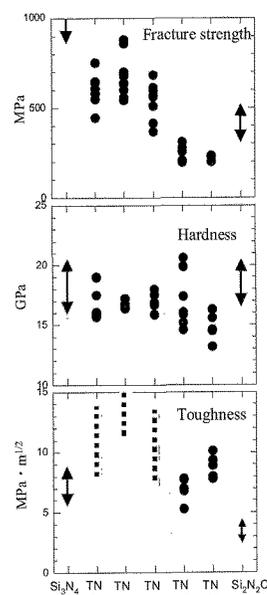


Fig.6 Fracture strength, Vickers Hardness and fracture toughness of Si₃N₄-Si₂N₂O-TiN composites with reported values of Si₃N₄ and Si₂N₂O ceramics.

grains were distributed whole in the sample, being included in $\text{Si}_2\text{N}_2\text{O}$ grains. EDS analysis showed that the amorphous phase was silicate glass with small amount of Al and Y.

Figure 6 shows the changes in fracture strength and toughness and Vickers hardness of the composites sintered at 1850°C for 4 h. Since crack length induced by Vickers indenter was too short to give fracture strength with accuracy for the TN-3, -5 and -7 samples, the obtained fracture toughness were shown by dashed lines. The fracture strength increased with increasing TiN content (TN-3 to TN-5) but decreased from TN-7 to TN-13. The strength of the TN-5 sample was about 1.5 times greater than that of monolithic $\text{Si}_2\text{N}_2\text{O}$ ceramic. Vickers hardness did not change with the sample composition. Fracture toughness increased to $10 \text{ MPa m}^{1/2}$ with increasing TiN content (TN-3 to TN-5) and was decreased for TN-10 and -13 samples. The values of fracture toughness for TN-3, -5 and -7 were comparable to the reported values in Si_3N_4 composites with the high TiN content (30vol.%), probably because of the presence of the $\text{Si}_2\text{N}_2\text{O}$ phase in addition to TiN also contributing to toughening of the composites, as reported in $\text{Si}_2\text{N}_2\text{O-Si}_3\text{N}_4$ composites.⁵

4. SUMMARY

$\text{Si}_3\text{N}_4\text{-Si}_2\text{N}_2\text{O-BN}$ and -TiN composites were fabricated by reaction sintering. The $\text{Si}_2\text{N}_2\text{O-Si}_3\text{N}_4\text{-BN}$ composites sintered at 1850°C for 4 h was composed of $\text{Si}_2\text{N}_2\text{O}$ grains of 2-10 μm in size with Si_3N_4 and *h*-BN grains of about 0.5 μm in size. Strength of the composite was lower than that of $\text{Si}_2\text{N}_2\text{O}$ ceramics but hardness and toughness were comparable to $\text{Si}_2\text{N}_2\text{O}$. The composites sintered at 1850°C for 4 h was composed of $\text{Si}_2\text{N}_2\text{O}$ grains of 2-10 μm in size with Si_3N_4 and TiN grains of about 0.5 μm in size. Strength of the composite was increased at 3-5 vol.% TiN composites and then decreased with increasing of TiN fractions. Hardness of the composites was comparable to Si_3N_4 and $\text{Si}_2\text{N}_2\text{O}$, but fracture toughness was changed in the similar way of strength changes. Fracture toughness of the TiN-composites were comparable to or greater than those of typical Si_3N_4 value.

REFERENCES

1. E. H. Lutz and M. V. Swain, *J. Am. Ceram. Soc.*, 75(1992) 67-70
2. A. Bellosi, S. Guicciardi and A. Tampieri, *J. Eur. Ceram. Soc.*, 9 (1992) 89-93
3. W. S. Coblenz and D. Lewis III, *J. Am. Ceram. Soc.*, 71 (1988) 1080-85
4. R. Larker, *J. Am. Ceram. Soc.*, 75(1992)92-66
5. R. Xie, M. Mitomo, F. Xu, G. Zhan, Y. Bando and Y. Akimune, *J. Eur. Ceram. Soc.*, 22 (2002) 963-971
6. R. Duan, G. Roebben, J. Vlegels and O.V. Biest, *J.*

Eur. Ceram. Soc., 22(2002) 2527-2535

7. A-K. Wetman, S. Forsberg and H. T. Larker, *J. Eur. Ceram. Soc.*, 18(1998)633-640

(Received December 10, 2006; Accepted January 31, 2007)