Microstructure and Mechanical Properties of Sintered Bodies of Fine Powders in Si_3N_4 -TiN System

Junichi Hojo^{☆1}, Koji Eto^{☆1}, Motohiro Umezū^{☆1}, Kazushi Kishi^{☆2} and Seiki Umebayashi^{☆2}

^{☆1}Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812. ^{☆2}Kyushu National Industrial Research Institute, Shuku-machi, Tosu 841.

Received September 8, 1997

SYNOPSIS

Fine Si_3N_4 powder and Si_3N_4 -TiN composite powder were prepared by vapor phase reaction method, and hot-pressed to investigate the effects of sintering condition and TiN inclusion on the microstructure and mechanical properties of sintered bodies. The prepared powders were fine with the size below $0.05\mu\text{m}$. Hot-pressing was conducted at 1800 – 1850°C in N_2 (1 atm) with 6wt% Y_2O_3 and 2wt% Al_2O_3 as sintering aid. When fine Si_3N_4 powder was sintered at 1800°C , the sintered body had a fine-grained microstructure. By increase in temperature to 1850°C , rod-like grains grew in the fine matrix, resulting in an increase in fracture toughness. Fine TiN particles were dispersed in Si_3N_4 matrix by sintering of Si_3N_4 -TiN composite powder, indicating the formation of nanocomposite. In the composite system, the growth of rod-like grains was observed even at 1800°C . This suggests the acceleration of Si_3N_4 grain growth by TiN inclusion. The composite had a high fracture toughness.

KEY WORDS

fine powder, composite powder, silicon nitride, titanium nitride, nanocomposite

1 INTRODUCTION

Refractory ceramics have been developed as high-temperature engineering materials. However, the low fracture toughness and the low thermal-shock resistance limit the applications. There are two ways to improve the mechanical properties of ceramics: one is the control of microstructure and another is the fabrication of composite. Recently, the excellent mechanical properties of ceramic nanocomposites have been receiving a great attention¹⁾. Hojo et al. have studied on the preparation of fine powders and composite powders of silicon carbide (SiC) and silicon nitride (Si_3N_4) by vapor phase reaction method²⁻⁴⁾. The fine powder had a high sinterability⁵⁾. The composite powders were useful for fabrication of nanocomposites^{4,6,7)}.

In the present work, fine Si_3N_4 powder and Si_3N_4 -TiN composite powder prepared by vapor phase reaction method were hot-pressed and the effects of sintering condition and TiN inclusion on the microstructure and mechanical properties of sintered bodies were investigated. Si_3N_4 -TiN composites have been investigated with emphasis on the improvement of mechanical properties and the increase of electrical conductivity of Si_3N_4 because TiN is a metallic conductor⁸⁻¹⁰⁾. They were fabricated by pressureless-sintering of mixed powder, or reaction sintering. On the

other hand, the use of Si_3N_4 -TiN composite powder will make it possible to achieve fine dispersion of TiN particles in Si_3N_4 matrix.

2 EXPERIMENTAL

2.1 Preparation of powders

Si_3N_4 powder was prepared in SiCl_4 - NH_3 - H_2 system and Si_3N_4 -TiN composite powder in SiCl_4 - TiCl_4 - NH_3 - H_2 system. The vapor phase reaction was conducted by using a flow-type reactor consisting of an alumina reaction tube and an electric furnace as previously described²⁻⁴⁾. Vapors of SiCl_4 and TiCl_4 were carried by H_2 . The metal chloride and ammonia were separately introduced into the reactor and mixed in the hot zone at about 1000°C . Reaction temperature was 1400 – 1500°C at the center of furnace. The powder product included NH_4Cl . It was removed by sublimation at 400°C in N_2 stream. In some experiments, the synthesized powders were heat-treated at 1000 – 1350°C for 1–2h in N_2 . Commercial α - Si_3N_4 powder (Ube Ind. Ltd., SN-E10: particle diameter $<0.5\mu\text{m}$) was also used for comparison.

2.2 Sintering of powders

As sintering aid, Y_2O_3 (6wt%) and Al_2O_3 (2wt%) were added to the powders. A mixed sol of Y_2O_3 and Al_2O_3 was prepared by addition of NH_4OH to an ethanol solution of

$Y(NO_3)_3$ and $Al(NO_3)_3$. The sol particles were washed with ethanol to eliminate water because fine amorphous Si_3N_4 powder was partially hydrolyzed with water. Si_3N_4 powder and Si_3N_4 -TiN composite powder were mixed with the sol particles in ethanol, dried with a rotary evaporator, and then heat-treated at 550°C in N_2 .

Powder samples were hot-pressed into disks of 10mm in diameter and about 2mm thick. Hot-pressing was performed using a graphite mold painted with BN lubricant in N_2 (1 atm). A rf-induction furnace was used for heating, in which the heating rate was controlled at 20°C/min or 100°C/min in the temperature range above 1000°C. The temperature was kept for 2h at 1800°C and 1850°C. The loading pressure was 64MPa. The surface of sintered disk was polished with SiC and diamond abrasives.

2.3 Characterization of powders and sintered bodies

Particle morphology was observed with a transmission electron microscope (TEM) or a scanning electron microscope (SEM). Crystalline phases were analyzed by X-ray diffraction (XRD). In Si_3N_4 -TiN composite powder, the Si/Ti atomic ratio was determined by energy dispersive X-ray analysis (EDX) with SEM and the compositions were calculated on the assumption of stoichiometric formulas of Si_3N_4 and TiN.

Sintered specimens were analyzed by the Archimedes density measurement, X-ray diffraction, and SEM observation. Hardness and fracture toughness were measured by the Vickers indentation technique (load: 10kg). The fracture toughness was calculated by using Niihara's equation¹¹⁾. Thermal shock resistance was evaluated by quenching method with water at room temperature, in which cracks on the disk surface were observed with an optical microscope. The test was repeated for each sample with increasing temperature at about 30°C interval.

3 RESULTS AND DISCUSSION

3.1 Properties of synthesized powders

Fine powders of Si_3N_4 -TiN system were formed by the vapor phase reaction method. The particle diameter was below 0.05 μm . TiN content was controlled in the range of 0–20vol% by the concentration ratio of $TiCl_4$ to $SiCl_4$ in the vapor phase. XRD patterns of the synthesized powders are shown in Fig.1. The crystalline phase of Si_3N_4 was not detected. Although XRD peaks of TiN were observed in Si_3N_4 -TiN composite powder, the peaks were very weak. These results mean that Si_3N_4 was in an amorphous state and TiN had very small particle size or low crystallinity.

It has been already reported that fine powders of Si_3N_4 and TiN were formed by vapor phase reactions of $SiCl_4$ -

Fig.1 X-ray diffraction patterns of synthesized powders and sintered bodies. (A) Si_3N_4 powder, (B) Si_3N_4 -TiN composite powder, (C) Si_3N_4 sintered body, (D) Si_3N_4 -TiN sintered composite.

NH_3 - H_2 system¹²⁾ and $TiCl_4$ - NH_3 - H_2 system¹³⁾, respectively. Since the metal chlorides are highly reactive with ammonia, it is possible to form Si_3N_4 -TiN composite particles by codeposition of Si_3N_4 and TiN. It is known that the nitride powders prepared by the vapor phase reaction method contained excess nitrogen and hydrogen. Therefore, the synthesized powders were heat-treated for degassing. Si_3N_4 was not crystallized at 1000–1350°C. XRD peaks of TiN became somewhat strong after the heat treatment but were still small. Figure 1 shows a TEM photograph of Si_3N_4 -TiN composite powder. It was confirmed by EDX analysis that Si_3N_4 and TiN were mixed in very small range. Black spots observed in each particle may be assigned to TiN.

3.2 Sintering behavior of powders

Si_3N_4 powder was sintered in different heating schedules as follows:

- (A) the temperature was raised at 100°C/min and kept for 2h at 1800°C,
 - (B) the temperature was raised at 20°C/min and kept for 2h at 1800°C,
 - (C) after the sintering for 2h at 1800°C, the sintering was repeated for 2h at 1850°C (heating rate: 100°C/min).
- The sintering data are summarized in Table 1. The relative densities of sintered bodies of monolithic Si_3N_4 were 96–98%. Si_3N_4 -TiN composite powders were all sintered with

Fig.2 Particle morphology of Si_3N_4 -TiN composite powder (after heat treatment for 1h at 1000°C in N_2).

heating schedule (A). The relative densities of sintered composites were 94–98%. The density tended to decrease with an increase in TiN content. In both monolithic and composite systems, the heat-treated powders gave slightly lower density than the as-synthesized ones. The polished surface of sintered body was analyzed by XRD. The XRD patterns are added to Fig.1. Amorphous Si_3N_4 was crystallized into β - Si_3N_4 during sintering. The peaks of TiN became strong, indicating the increase of crystallite size or crystallinity.

The microstructures of sintered bodies of as-synthesized powders are shown in Figs.3, 4 and 5. Figure 3 shows the fracture surfaces of Si_3N_4 sintered with heating schedule (A). The sintered body of synthesized Si_3N_4 powder had a fine-grained microstructure (Fig.3a). On the other hand, when commercial Si_3N_4 powder was sintered under the

Fig.3 Fracture surfaces of Si_3N_4 sintered with heating schedule (A). (a) synthesized Si_3N_4 powder, (b) commercial Si_3N_4 powder.

same condition, the grain growth was remarkable (Fig.3b), leading to growth of rod-like grains which are typically observed in Si_3N_4 ceramics. The retardation of grain growth in synthesized Si_3N_4 powder may be due to the small particle size and the narrow size distribution. The sintered body of synthesized Si_3N_4 powder with heating schedule (B) also exhibited a fine-grained microstructure although small acicular grains were rarely observed. This indicates that

Table 1 Sintering data and mechanical properties of monolithic Si_3N_4 and Si_3N_4 -TiN composites.

Sample		TiN (vol%)	Heating schedule for sintering	Properties of sintered body			
				dr (%)	Hv (GPa)	K _{IC} (MPa·m ^{1/2})	ΔT (°C)
Si_3N_4	As-synthesized	0	(A) 100°C/min, 1800°C (2h)	97.8	18.2	6.0	600
		0	(B) 20°C/min, 1800°C (2h)	98.0	—	—	—
		0	(C) 1800°C (2h)+1850°C (2h)	97.5	17.0	6.4	—
	Heat-treated	0	(A) 100°C/min, 1800°C (2h)	96.9	17.4	6.0	650
Si_3N_4 -TiN	As-synthesized	8	(A) 100°C/min, 1800°C (2h)	98.1	17.7	6.5	490
		18	(A) 100°C/min, 1800°C (2h)	95.1	17.1	6.5	460
	Heat-treated	10	(A) 100°C/min, 1800°C (2h)	96.7	16.7	6.1	530
		18	(A) 100°C/min, 1800°C (2h)	94.6	15.9	6.0	460

Heat-treatment : 1350°C, 2h in N_2 . dr : relative density. Hv : Vickers hardness. K_{IC} : fracture toughness.
ΔT : critical temperature difference for crack initiation.

Fig.4 Fracture and polished surfaces of sintered body of synthesized Si_3N_4 powder with heating schedule (C). The crack was propagated by the Vickers indentation.

Fig.5 Fracture and polished surfaces of sintered body of Si_3N_4 -TiN composite powder (heating schedule (A)). The crack was propagated by the Vickers indentation.

the effect of heating rate was small. Figure 4a shows the microstructure of sintered body of synthesized Si_3N_4 powder with heating schedule (C). In this specimen, rod-like grains were observed in fine-grained matrix. This was caused by repeated sintering at higher temperature (1850°C). When the synthesized powders were directly heated up to 1850°C , Si_3N_4 partially decomposed. Fine amorphous Si_3N_4 powder seemed to be unstable under the present sintering atmosphere (1 atm N_2). Therefore, the preliminary sintering was useful to sinter the fine amorphous powder at the high temperature. Figure 5a shows the microstructure of Si_3N_4 -TiN composite sintered with heating schedule (A). In this composite system, rod-like grains were observed even at 1800°C . It has been suggested that fine TiN inclusions worked as nuclei accelerating the growth of Si_3N_4 rod-like grains in liquid phase sintering¹⁴⁾. In the present work also, Si_3N_4 seemed to grow in the same mechanism.

The sintered body of heat-treated Si_3N_4 powder also had a fine-grained microstructure although several rod-like grains were observed even at 1800°C . On the other hand, rod-like grains scarcely formed in the heat-treated powder of Si_3N_4 -TiN system. The reason for the difference in sintered texture between as-synthesized and heat-treated

powders was obscure. Although the fine particles slightly grew by heat treatment at 1350°C , the powders were still fine. The heat treatment might have increased the oxygen content by accumulation of impurity oxygen in N_2 stream.

3.3 Mechanical properties of sintered bodies

The data of mechanical properties are added to Table 1. In the sintered bodies of as-synthesized Si_3N_4 powder, the hardness was 17–18 GPa, the fracture toughness was $6.0\text{--}6.4\text{MPa} \cdot \text{m}^{1/2}$ and the critical temperature difference for crack initiation was about 600°C . It should be noted that the fracture toughness was increased by repeated sintering at 1850°C . Figure 4b shows the polished surface with a crack propagated by the Vickers indentation. The zigzagged crack means the crack deflection by rod-like grains contained in this specimen. This is the reason for the increase in fracture toughness.

The mechanical properties of sintered bodies of as-synthesized Si_3N_4 -TiN composite powders are illustrated as a function of TiN content in Fig.6. The hardness slightly decreased with increasing TiN content because of the decrease in sintered density. On the other hand, the fracture toughness was increased by TiN addition. Figure 5b shows the polished surface with a Vickers indentation crack.

Fig.6 Variation of hardness (H_v), fracture toughness (K_{IC}) and critical temperature difference for crack initiation (ΔT) with TiN content in Si_3N_4 -TiN system.

Whitish particles were assigned to TiN. Although TiN particles grew maximally up to $2\mu\text{m}$, the composite included many fine TiN particles with the size below $1\mu\text{m}$. This suggests that Si_3N_4 -TiN composite powder may be useful for fabricating Si_3N_4 -TiN nanocomposites. The high fracture toughness of the composite may be due to crack deflection as seen in Fig.5b. The crack deflection may be caused by rod-like grains formed by inclusion of fine TiN particles, and residual stresses evolved from the difference in thermal expansion coefficient between Si_3N_4 ($2.8 \times 10^{-6}/^\circ\text{C}$) and TiN ($9.3 \times 10^{-6}/^\circ\text{C}$)¹⁵. As described above, the addition of TiN was effective to improve the fracture toughness. However, the thermal shock resistance was lowered by TiN addition because the gap in thermal expansion coefficient also brings an opposite effect, that is, rupture by thermal stress during quenching.

The mechanical properties of some specimens in Table 1 could not be evaluated because many pores remained on the surface. This may be due to gas evolution during sintering. Although the synthesized powders were heat-treated to improve the sinterability, the sintered density was decreased. The sintered bodies of heat-treated Si_3N_4 -TiN powders had low hardness and fracture toughness because of the low density. On the other hand, the thermal shock resistance was somewhat high in the heat-treated powders when TiN content was zero or small. This may be due to the absorption of thermal stress by small pores.

4 CONCLUSION

Fine powders of Si_3N_4 -TiN system can be prepared by the vapor phase reaction method, in which Si_3N_4 is in the

amorphous state and TiN has very small particle size or low crystallinity. β - Si_3N_4 and TiN clearly appear during sintering. The sintered bodies have fine-grained microstructures. The increase of sintering temperature stimulates the growth of rod-like Si_3N_4 grains, leading to increase in the fracture toughness. It is possible to fabricate Si_3N_4 -TiN nanocomposites by sintering of the composite powders. The TiN addition stimulates the rod-like grain growth even at a low temperature. The Si_3N_4 -TiN composites have a high fracture toughness although the thermal shock resistance is decreased. The problem in use of the fine powders is that the sintered bodies are not densified up to the full density. The improvement of sinterability is required for achieving more excellent mechanical properties.

ACKNOWLEDGEMENT

This work has been entrusted by NEDO as part of the Synergy Ceramics Project under the Industrial Science and Technology Frontier (ISTF) Program promoted by AIST, MITI, Japan.

REFERENCES

- 1) K.Niihara: "New Design Concept of Structural Ceramics-Ceramic Nanocomposites", J. Ceram. Soc. Japan, 99(1991)974-982.
- 2) J.Hojo, H.Maeda and A.Kato: "Preparation of Composite Particles of SiC- Si_3N_4 System by Vapor Reaction Method", Yogyo-Kyokai-Shi, 95(1987)45-49.
- 3) J.Hojo, M.Aratani and A.Kato: "Vapor Phase Synthesis and Sintering of SiC-BN Composite Particles", Ceramic Transactions Vol.22, S.Hirano, G.L.Messing and H. Hausner ed., American Ceramic Society, (1991)121-126.
- 4) J.Hojo: "Fabrication of Nanocomposite Particles by Vapor Phase Reaction and Its Applications", Proc. Fourth Nisshin Engineering Particle Technology International Seminar, K.Niihara ed., Osaka, Nisshin Engineering Co. Ltd., (1995)9-17.
- 5) J.Hojo: "Sintering Behavior of Ultrafine Silicon Carbide Powder", Silicon Carbide Ceramics-1, S.Somiya and Y.Inomata ed., Elsevier, (1991)149-168.
- 6) J.Hojo, M.Aratani and A.Kato: "Preparation of SiC-BN Ceramics Using Fine Composite Particles", Euro-Ceramics II, G.Ziegler and H.Hausner ed., Deutsche Keramische Gesellschaft e.V.(1991)1505-1509.
- 7) J.Hojo, K.Kishi and S.Umeybayashi: "Nanocomposites Obtained from Ultrafine Composite Particles", Ceramic Transactions Vol.51, H.Hausner, G.L.Messing and

- S.Hirano ed., American Ceramic Society, (1995)597-601.
- 8) Y.Yasutomi, K.Nakamura, M.Sobue and Y.Kubo: "Development and Characterization of Electro-Conductive Si_3N_4 Bonded TiN Ceramics", J. Ceram. Soc. Japan, 97(1989)148-154.
- 9) T.Nagaoka, M.Yasuoka, K.Hirao and S.Kanzaki: "Effects of TiN Particle Size on Mechanical Properties of Si_3N_4 /TiN Particulate Composites", J. Ceram. Soc. Japan, 100(1992)617-620.
- 10) K.Ueno, T.Inoue, S.Sodeoka, M.Suzuki, H.Ishikawa, K.Uchiyama and T.Inui: " Si_3N_4 -Matrix Composite with TiN Particles Formed by In-situ Reaction", J. Ceram. Soc. Japan, 105(1997)304-307.
- 11) K.Niihara, R.Morena and D.P.H.Hasselman: "Evaluation of K_{IC} of Brittle Solids by the Indentation Method with Low Crack-to-Indent Ratios", J. Mater. Sci. Letters, 1(1982)13-16.
- 12) A.Kato, Y.Ono, S.Kawazoe and I.Mochida: "Finely Divided Silicon Nitride by Vapor Phase Reaction between Silicon Tetrachloride and Ammonia", Yogyo-Kyokai-Shi, 80(1972)114-120.
- 13) A.Kato, M.Iwata, J.Hojo and M.Nagano: "Fine Titanium Nitride Powders by the Vapor Phase Reaction of $\text{TiCl}_4\text{-NH}_3\text{-H}_2\text{-N}_2$ System", Yogyo-Kyokai-Shi, 83(1975)453-459.
- 14) Joint Research Consortium of Synergy Ceramics: Research and Development of Synergy Ceramics, Fine Ceramics Research Association, (1996)325.
- 15) Y.Sakurai, M.Koizumi and C.Matsumoto: New Ceramics (Materials and Its Applications), Nikkan Kogyo, (1977)251.