Microstructural Observation of Silicon Nitride Ceramics Sintered with Addition of Titania

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チタニア添加窒化ケイ素の微構造観察

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Si_3N_4 sintered body was obtained by pressureless sintering and then post-HIPing with addition of small amount of TiO_2 (3 mass%). Sintering additives were 5 mass% Y_2O_3 , 3 mass% Al_2O_3 and 3 mass% AlN . It was found that round-shaped particles with diameter 0.2–0.5 μm were distributed within the grain-boundary phase. The particles contained high density crystalline imperfections. They contained Ti and N, and were identified as TiN by energy-dispersive-type X-ray microanalysis and X-ray diffractometry. The grain-boundary phase was mainly an amorphous phase containing Si, Y, Al and O, but it did not contain Ti. Formation of TiN from TiO_2 by reduction and nitridation was suggested based on thermodynamic calculations and crystal chemical considerations. High density crystalline imperfections may be introduced during reduction of TiO_2 particles. It is believed that the grain-boundary distribution of round-shaped TiN particles contributes to the improvement of wear resistance of Si_3N_4 ceramics.

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1. Introduction

Silicon nitride ceramics exhibit excellent strength, toughness and thermal shock resistance and has been highly developed for high-temperature structural applications such as gas turbine components and automobile engine parts such as turbo-charger rotor. It is also used as ceramic bearing parts and show excellent wear resistance under high-temperature or corrosive atmosphere. The mechanical properties of Si_3N_4 or SiAlON ceramics influenced significantly by its microstructure, so that many microstructural investigations have been carried out,^{1)–8)} particular attentions were paid on the development of β - Si_3N_4 grain morphology, phase transformation, seeds particle effect or characterization of secondary phases.

It has been reported that the wear resistance property of Si_3N_4 ceramics was improved by the addition of small amount of TiO_2 ,⁹⁾ but the mechanism of the improvement of wear resistance was not clear. Then, in this report, microstructure of Si_3N_4 sintered body with addition of TiO_2 is examined mainly by transmission electron microscopy to clarify the effect of TiO_2 addition, and then discuss the mechanism of wear resistance improvement. It is a merit for commercial production that a TiO_2 powder is cheaper than a TiN powder.

2. Experimental procedure

Silicon nitride observed in this study was sintered at 1800°C under 0.1 MPa N_2 gas atmosphere from the raw powder, SN-E10 of Ube with average particle size of 0.7 μm in diameter. The sintered body was further hot-isostatically pressed at 1700°C for 1 h under 100 MPa N_2 pressure. The following additives were mixed into the raw powder: 5 mass% of Y_2O_3 (RU, Shin-Etsu Chemical Co., Ltd.), 3 mass% Al_2O_3 (AKP-30, Sumitomo Chemical Co., Ltd.) and 3 mass% AlN (Grade-F, Tokuyama, Average particle size of 0.6 μm). Furthermore, 3 mass% of TiO_2 (Rutile type, R-11-P, Sakai Chemical, Average particle size of

0.2 μm) was added. These powders were wet ball-milled. The obtained sintered bodies showed almost full density (3.32 g/cm³).

Thin foils for transmission electron microscopy (TEM) were prepared by means of mechanical grinding, polishing, dimple-grinding and finally Ar ion-milling procedures. TEM used in the present study was an H-9000 (Hitachi) operating at 300 kV. A Kevex Delta-III energy-dispersive-type X-ray microanalyzer equipped with an ultra-thin window was also used. Powder X-ray diffraction analysis was carried out using $\text{Cu K}\alpha$ radiation (Philips, PW-1100).

3. Results

Microstructure of the sintered body showed general feature of liquid-phase sintered Si_3N_4 , i.e., Si_3N_4 grains with relatively large rod-like morphology (a few μm in long axis) and relatively small equi-axis grains (less than 0.5 μm in diameter) surrounded by glassy grain-boundary phase.^{1),5)} Grain-boundary glassy phase was recognized since they have sharp triangular edges with dark contrast, which was not changed by foil tilting. Relatively round-shaped particles with higher contrast were observed within the grain boundary phase throughout sintered body, as shown in Fig. 1. Slight higher magnification bright-field photograph, Fig. 1 (b), indicates that these particles contained very fine and high density irregular (not homogeneous) contrast. The size of these particles are 0.2 to 0.5 μm and relatively constant. Furthermore, around the outer boundary of the particle, thin layer was sometimes observed as indicated by an arrowhead.

Figure 2 shows another particles in the sintered specimen. The contrast of round-shaped particles was resemble with those shown in Fig. 1. It is noted that one of the particles showed wavy contrast around outer part of the particle. Only the core part showed darker contrast. The outer part is more transparent than inner part and then looked as shadow of inner part.

Fig. 1. (a) Bright-field micrograph of the specimen showing dark contrast particles. (b) An enlarged micrograph of a portion in (a). Outer layer-like contrast is indicated by an arrowhead.

Fig. 2. Bright-field micrograph of the specimen. One of the particle showed wavy contrast around darker core.

Fig. 3. High-resolution micrograph of darker-contrasted particle. Electron diffraction pattern of the particle is inserted.

Figure 3 is a high-resolution micrograph of darker-contrasted particle, of which diffraction pattern is inserted. The lattice fringes of the particle showed the array of dots crossing 90° . Distribution of darker contrast means the presence of some lattice irregularity such as dense dislocations. Shallow look of these array of dots clarifies that the arrays of dots are frequently curved or waved and presence of extra half-planes (dislocations). Analysis of the diffraction pattern indicated that it was consistent with the $\{100\}$ reciprocal plane of TiN.

EDX analysis was carried out for elongated grains, round-shaped grains and grain-boundary phase. The typical example of the results is shown in Fig. 4. Figure 4(a) is a profile taken from an elongated grain, indicating that main constituents are Si and N (It is noted that intensity of light weight elements such as O, N, C is relatively very weak due to low detection efficiency of low energy characteristic X-rays), and a small amount of Al is also detected. This grain corresponds Si_3N_4 or SiAlON . It is well known that Si_3N_4 is able to include Al and O which replace Si and N, respectively, and making β -SiAlON phase.^{10),11)} The typical profile from small round-shaped particles with darker contrast is shown in Fig. 4(b). It is clear that the main constituents are Ti and N. It is not clear that the trace amount of Si is the signal from the round-shaped grain or surrounding phases, but the latter case is more probable based on our experiences. The results strongly suggest that these particles are Ti-N phase. Grain-boundary was filled with almost glassy phase containing Si, Al, Y, O and N, as shown in Fig. 4(c). Ti was not contained in this phase. It was reported that the grain boundary phase was oxynitride glass when Si_3N_4 was sintered with oxides such as Al_2O_3 and nitride such as AlN un-

Fig. 4. EDX profiles of (a) elongated grains, (b) round-shaped grains and (c) grain-boundary phase.

der N₂ atmosphere.^{1),2),11),12)} In the present specimen, it was concluded that the grain-boundary phase was mainly oxynitride glass.

Powder XRD profile indicated the presence of TiN as a minor phase with dominant β -Si₃N₄ phase, as shown in Fig. 5. Very small unknown X-ray peaks with $d=0.3142$ and 0.2538 nm were detected, probably crystallized phase (s) in grain-boundary.

Round-shaped particles were observed for the same specimen before HIPing, and also confirmed as TiN by EDX analysis. These particles also contained high density crystalline imperfections, as shown in Fig. 6.

4. Discussion

Above mentioned experimental results clearly indicate that the round-shaped particles are TiN grains, and they distributed in grain-boundary phase throughout the sintered bodies. The size of these grains is almost corresponded to the size of raw TiO₂ grains. TiN grains contained large amount of lattice strain and many crystalline imperfections. Sometimes the grains show a core-outer part double structure.

Hiraga et al. reported that TiN crystals in the Si₃N₄-TiN composites prepared by chemical vapor deposition were very thin fiber-shaped and distributed in the matrix Si₃N₄ crystal with specific crystallographic orientations.¹³⁾ The size and morphology of TiN particles in that report is quite different with those of the present study, because of different synthesis procedures. Iwamoto et al. recently reported that the synthesis of Si₃N₄-TiN mixed powder by pyrolysis of polymer precursors.¹⁴⁾ TiN particles obtained by this method was smaller than 100 nm. There were several reports on Si₃N₄-TiN system concerning mechanical properties,¹⁵⁾⁻¹⁷⁾ mechanical and electrical properties for electrical discharge machining,¹⁸⁾⁻²²⁾ or porous sensor properties,²³⁾ but these cases TiN powders were used as a raw material.

It is supposed that TiN grains in the present study were formed from TiO₂. Possible reactions to form TiN are deduced based on the thermodynamic calculations,²⁴⁾ as follows.

It is estimated that this reaction can proceed if the oxygen partial pressure is lower such as 5.9×10^{-4} (atm) at 1700 K, 0.024 (atm) at 2000 K or 0.066 (atm) at 2100 K. Another possible reaction is as follows.

This reaction also can proceed if $P_{\text{O}_2} < 6.6 \times 10^{-7}$ (atm) at 1700 K, $< 9.9 \times 10^{-6}$ (atm) at 2000 K or $< 3.85 \times 10^{-4}$ (atm) at 2100 K. Sintering of the present specimen was carried out at 2073 K (1800°C) under 0.1 MPa N₂ atmosphere using carbon crucible and carbon heater furnace, therefore oxygen partial pressure should be much lower than these values required for both reactions, however, Reaction (1) occurs more easily. The amount of AlN (3 mass%) to TiO₂ (3 mass%) is almost 2 : 1 in molar ratio in the present case, so sufficient amount of AlN is present. Thus, the rest of AlN may be dissolved into the glassy phase, which contains nitrogen as shown in Fig. 4(c).

Miyata et al. synthesized the Si₃N₄-TiN composites with improved mechanical properties by nitridation of powder mixture of Si, TiC and TiO₂ and subsequent hot-pressing. They mentioned that TiN was formed from TiC and TiO₂ by decomposition and nitridation during sintering, but trace of TiC particles was maintained in the composite.²⁵⁾ Ueno et al. surveyed the "in-situ" formation of TiN grains into Si₃N₄

Fig. 5. XRD profile of the sintered specimen.

Fig. 6. Bright-field micrograph of the specimen before HIPing showing dark-contrasted particle.

matrix from the powder mixture of TiO₂ and AlN.²⁶⁾ They confirmed the formation reaction of TiN through the Reaction (1) was progressed between 1150 to 1450°C, before the Si₃N₄ matrix sintering. Furthermore, if large particles ($> 1 \mu\text{m}$) of TiO₂ were used as a raw material, it crumbled into fragments and underwent nitridation to TiN with a smaller size than that of the original particle. TiN/Si₃N₄ or TiN/Si₂N₂O composites were also fabricated from powder mixture of Si, TiO₂ and additives after nitridation under N₂ atmosphere.^{27),28)} The former one case suggested that TiN was formed by nitridation of mainly TiC and the latter two cases from nitridation of TiO₂ particles. Yoshimura et al.,²⁹⁾ Umezū³⁰⁾ and Licko et al.³¹⁾ also reported TiN particles formation from TiO₂ and C mixture under N₂ atmosphere. Since present system of the raw mixture is the same as that of Ueno et al., and based on the many reports mentioned above, it is certain that TiN is produced from TiO₂, but further microstructural and crystallo-chemical analyses are seemed to be important. These round-shaped particles were observed for the same specimen before HIPing, and also confirmed as TiN by EDX analysis. It is indicated that TiN

was formed during the first heat treatment.

TiN belongs NaCl type crystal structure with $a = 0.4239$ nm and Z (number of atoms in unit cell) = 4, V (unit cell volume) = 0.07617 nm^3 . Density of the crystal is 5.43 g/cm^3 .³²⁾ On the other hand, TiO_2 of the present study belongs rutile type crystal structure with $a = 0.4592$ nm, $c = 0.2959$ nm and $Z = 2$, $V = 0.0624 \text{ nm}^3$. Density of TiO_2 is 4.26 g/cm^3 .³²⁾ There are oxygen-deficient structures (sheared structure) based on rutile structure with chemical composition of $\text{Ti}_n\text{O}_{2n-1}$ ($n = 4 - 10$).³³⁾ High temperature phase of TiO is a defected NaCl type structure with $a = 0.4180$ nm and $Z = 4$, $V = 0.0730 \text{ nm}^3$. Density is 4.93 g/cm^3 . Between Ti_4O_7 and TiO, Ti_3O_4 with pseudobrookite structure and Ti_2O_3 with corundum type structure are existed.^{33), 34)} Umezu³⁰⁾ and Licko et al.³¹⁾ indicated that the transition from TiO_2 to TiN happened via "lower oxides" such as Ti_4O_7 , Ti_2O_3 or TiO. Based on these reports and these crystal chemical data of crystals, the following changes in crystal structure was expected. First, TiO_2 with rutile type structure gradually changes its composition due to pull out of oxygen with keeping basically rutile-type structure (sheared structures (and pseudobrookite structure)). Further reduction of oxygen necessitates reconstructive structural changes into corundum type or NaCl type structures, if the composition changed gradually and there is sufficient time to reconstruct these structures. It is supposed that reduction and nitridation reaction from the phase of basically rutile type structures will simultaneously happen,³¹⁾ instead of the formation of NaCl type TiO and subsequent nitridation to TiN, if the reaction happened very quickly under higher temperature-increasing rate. As a result, crystalline imperfections originally induced into the sheared structures are

possibly included into TiN crystals. This seems to be the reason of high defect density in TiN particles, resulting darker contrast due to lattice strain, as shown in Figs. 1–3 and 5. Change from TiO_2 to TiN induces volume shrinkage of about 40% and corresponding density increase of 27% for the same number of Ti atom.

Further interest feature of TiN grains observed in Figs. 1 (b) and 2 is shadow-like contrast surrounding a round-shaped core part of some particles. Core part of the shadow-like contrast was TiN in the present study, and this feature seemed to be formed by the effects of surrounding liquidus phase during phase transition, since TiN formed from TiO_2 without liquidus phase maintained its original irregular shape²⁸⁾ and TiN formed from TiO_2 was covered with carbon layer maintaining original particle shape.³¹⁾ If TiN phase is obtained from the center core of the particles, this is an experimental result, it will be formed into relatively round-shape morphology and an excess volume is rest around particles due to large volume shrinkage, consequently further filling up of glassy phase is expected. Since it is a non-crystalline phase, it looks more homogeneous without crystalline defects. It may lead shadow-like contrast. Ueno et al. reported that the nitridation reaction of TiO_2 was completed as low temperature as 1450°C .²⁶⁾ But under actual sintering condition, reduction-nitridation process and glassy phase formation may overlapped during increasing specimen temperature. From microstructure observation, voids or pores were not observed around TiN particles. It is considered that the evolved O_2 gas due to the Reaction (1) was used as oxidant of AlN or Si_3N_4 , or dissolved into grain-boundary phase. Schematic illustration of a sequence of reaction is presented in Fig. 7.

Fig. 7. Schematic illustration of a sequence of reactions.

It has been reported that the wear resistance property has been improved by the addition of small amount of TiO_2 . Hayashi et al.⁹⁾ reported that the bending strength of the Si_3N_4 specimen containing TiN after 10^5 cyclic indentation test using WC/Co ball did not change, comparing large decrease of bending strength in the specimen without TiN. Improvement of wear resistance can be partly explained by the formation of TiN grains, since Vickers hardness of TiN (25 GPa) is higher than that of a liquid-phase sintered Si_3N_4 (15–18 GPa). Furthermore, Reaction of (1) produces Al_2O_3 , which is a constituent of a liquid phase, therefore increase in sinterability may be attained due to increase in Al_2O_3 . From the view point of wear resistance, distribution of round-shaped TiN within grain-boundary phase has some merits such as difficulty to grain falling-out. Formation of TiN grains from TiO_2 grains does not induces internal tensile strain into surrounding matrix, since large volume shrinkage is expected.

5. Conclusions

Si_3N_4 sintered body was obtained by pressureless sintering and then HIPping with addition of small amount of TiO_2 (3 mass%). Sintering additives were 5 mass% Y_2O_3 , 3 mass% Al_2O_3 and 3 mass% AlN. It was found that round-shaped particles with 0.2–0.5 μm in diameter distributed in grain-boundary phase throughout sintered body. These particles showed dark contrast during electron microscopy due to the presence of high density crystalline imperfections. Furthermore, sometimes they showed shadow-like contrast surrounding a core part. This particle contained Ti and N, and was identified as TiN based on EDX analysis and XRD. Formation of TiN from TiO_2 by reduction and nitridation was suggested based on thermodynamic calculations and crystal chemical considerations. High density crystalline imperfections may be introduced during reduction of TiO_2 particles into the lower oxides. It is believed that the distribution of round-shaped TiN particles contributes the improvement of the wear resistance of Si_3N_4 ceramics.

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References

- 1) Kleebe, H. J., *J. Ceram. Soc. Japan*, **105**, 453–75 (1997).
- 2) Hwang, S.-L. and Chen, I. W., *J. Am. Ceram. Soc.*, **77**, 1719–28 (1994).
- 3) Lee, W. E. and Hilmas, G. E., *J. Am. Ceram. Soc.*, **72**, 1931–37 (1989).
- 4) Hirosaki, N., Tanimura, M., Okamoto, Y., Akimune, Y. and Mitomo, M., *J. Ceram. Soc. Japan*, **102**, 875–79 (1994) [in Japanese].
- 5) Hirosaki, N., Okamoto, Y., Akimune, Y. and Mitomo, M., *J. Ceram. Soc. Japan*, **102**, 790–94 (1994) [in Japanese].
- 6) Hirosaki, N. and Matsubara, H., *J. Ceram. Soc. Japan*, **105**, 218–22 (1997) [in Japanese].
- 7) Imamura, H., Hirao, K., Brito, M. E., Toriyama, M. and Kanzaki, S., *J. Ceram. Soc. Japan*, **104**, 748–51 (1996) [in Japanese].
- 8) Akimune, Y., Munakata, F., Matsuo, K., Okamoto, Y., Hirosaki, N. and Sato, C., *J. Ceram. Soc. Japan*, **107**, 1180–82 (1999).
- 9) Hayashi, T., Tatami, J., Komeya, K., Meguro, T. and Kim, D.-K., Proc. 19th Forum on Basic Science for High-Temperature Ceramics (2000) pp. 25–27 [in Japanese].
- 10) Oyama, Y. and Kamigaito, O., *Japan. J. Appl. Phys.*, **10**, 1637 (1971).
- 11) Jack, K. H., *J. Mater. Sci.*, **11**, 1135–58 (1976).
- 12) Ukyo, Y. and Suda, A., *J. Ceram. Soc. Japan*, **104**, 371–76 (1996).
- 13) Hiraga, K., Hirabayashi, M., Hayashi, S. and Hirai, T., *J. Am. Ceram. Soc.*, **66**, 539–42 (1983).
- 14) Iwamoto, Y., Kikuta, K. and Hirano, S., *J. Ceram. Soc. Japan*, **108**, 350–56 (2000).
- 15) Nagaoka, T., Yasuoka, M., Hirao, K. and Kanzaki, S., *J. Ceram. Soc. Japan*, **100**, 617–20 (1992).
- 16) Sato, Y. and Ueki, M., *J. Ceram. Soc. Japan*, **101**, 365–68 (1993) [in Japanese].
- 17) Herrmann, M., Balzer, B., Schubert, C. and Hermel, W., *J. Eur. Ceram.*, **12**, 287–96 (1993).
- 18) Akimune, Y., Munakata, F., Ando, M., Okamoto, Y. and Hirosaki, N., *J. Ceram. Soc. Japan*, **105**, 122–25 (1997) [in Japanese].
- 19) Akimune, Y., Munakata, F., Hirosaki, N. and Okamoto, Y., *J. Ceram. Soc. Japan*, **106**, 75–78 (1998) [in Japanese].
- 20) Sinha, S. N. and Tiegs, T. N., *Ceram. Eng. Sci. Proc.*, **16**, 489–96 (1995).
- 21) Yasutomi, Y. and Sobue, M., *Ceram. Eng. Sci. Proc.*, **11**, 857–67 (1990).
- 22) Bellosi, A., Guicciardi, S. and Tampieri, A., *J. Eur. Ceram.*, **9**, 83–93 (1992).
- 23) Nakayama, S. and Kuroshima, H., *J. Ceram. Soc. Japan*, **100**, 758–62 (1992) [in Japanese].
- 24) JANAF Thermodynamic Tables, 3rd ed., J. Phys. Chem., Ref. Data, **14** [Suppl. 1] (1985).
- 25) Miyata, M., Yasutomi, Y., Sawai, Y. and Kanai, T., *J. Ceram. Soc. Japan*, **105**, 761–67 (1997) [in Japanese].
- 26) Ueno, K., Inoue, T., Sodeoka, S., Suzuki, M., Ishikawa, H., Uchiyama, K. and Inui, T., *J. Ceram. Soc. Japan*, **105**, 304–07 (1997).
- 27) Shih, C. J., Yang, J.-M. and Ezis, A., *Scripta Metal. Mater.*, **24**, 2419–24 (1990).
- 28) Liu, W., Yang, J.-M., Ting, S.-J., Ezis, A. and Shih, C. J., *J. Am. Ceram. Soc.*, **75**, 2945–52 (1992).
- 29) Yoshimura, M., Nishioka, M. and Sōmiya, S., *J. Mater. Sci. Lett.*, **6**, 1463–65 (1987).
- 30) Umezu, S., *Proc. Imperial Acad.*, **7**, 353–56 (1931).
- 31) Licko, T., Figusch, V. and Puchyova, J., *J. Eur. Ceram.*, **5**, 257–65 (1989).
- 32) Pearson's Handbook of Crystallographic Data for Intermetallic Phases, Ed by Villars, P. and Calvert, L. D., American Metal Society Press, Metal Park, OH (1985).
- 33) Fueki, K. and Yamauchi, S., "Kagaku-Sousetsu," Vol. 9, Ed by Chemical Society of Japan, University of Tokyo Press (1975) pp. 7–30 [in Japanese].
- 34) Kiriya, R. and Kiriya, H., "Kouzou-Muki-Kagaku, I," Kyoritsu Shuppan, Tokyo (1964) [in Japanese].