Effect of Yb_2O_3 Addition on Si_3N_4 – Lu_2O_3 – SiO_2 Ceramics

Naoki KONDO, Hideki HYUGA, Katsumi YOSHIDA, Hideki KITA and Tatsuki OHJI

Advanced Manufacturing Research Institute, National Institute of Advanced Industrial Science and Technology (AIST),
2266–98, Shimo-shidami, Moriyama-ku, Nagoya-shi 463–8510, Japan

Small amount of Yb_2O_3 were added in Si_3N_4 – Lu_2O_3 – SiO_2 ceramics to improve their mechanical properties, and effect of the addition on gas-pressure sintering behavior and mechanical properties were investigated. The addition of small amount of Yb_2O_3 improved high temperature strength as well as fracture toughness, though the addition led to pore formation after gas-pressure sintering.

[Received July 10, 2006; Accepted September 21, 2006]

Key-words : Silicon nitride, Lu_2O_3 , Yb_2O_3 , Strength, Toughness

1. Introduction

Silicon nitride (Si_3N_4) is an important engineering ceramics because of its superior mechanical properties. In order to improve the high temperature mechanical properties, a number of research works have been conducted so far. Degradation of silicon nitrides at high temperatures has been considered in relation to softening of the glassy grain boundary phase and melting of secondary refractory phases. By choosing sintering additives and making a refractory grain boundary phase, high temperature strength can be improved.^{1),2)} Presently, the best additive for high temperature use is believed to be lutetia (Lu_2O_3).^{3)–8)}

Recently, some of the authors examined the gas-pressure sintering of silicon nitrides containing lutetia (Lu_2O_3) and silica (SiO_2) as sintering additives.^{9),10)} It was revealed that densification behavior, grain size and formation of secondary crystalline phases strongly depended on the initial composition with different $\text{Lu}_2\text{O}_3/\text{SiO}_2$ ratio. Mechanical properties of the sintered body also strongly depended on the composition. Furthermore, the ratio of lutetia and silica was variously changed to improve the mechanical properties. However, it was difficult to achieve the improvement only by changing the ratio.¹¹⁾

High temperature mechanical properties of silicon nitrides are strongly affected by softening of grain boundary glassy phase. Co-doping technique is one of the promising techniques to improve mechanical properties. In the case of Alumina, combination of sintering additives, even amounts of them are quite small, leads to considerable improvement of mechanical properties.¹²⁾ Though effect of co-doping on silicon nitrides is still unclear, the authors applied the concept on silicon nitrides to improve their mechanical properties. Small amount of ytterbia (Yb_2O_3), which is sometimes used as additive for high temperature use, was added in Si_3N_4 – Lu_2O_3 – SiO_2 system, and mechanical properties of the silicon nitrides were investigated.

2. Experimental

From our previous works,^{9)–11)} the composition where good high temperature mechanical properties are expected was Si_3N_4 – $8\text{Lu}_2\text{O}_3$ – 2SiO_2 (mass%). Here a small amount of lutetia was replaced by ytterbia, namely, three compositions, Si_3N_4 – $(8-x)\text{Lu}_2\text{O}_3$ – 2SiO_2 – $x\text{Yb}_2\text{O}_3$ (mass%, $x=0.1, 0.2$ and 0.3), were examined. For comparison, the silicon nitride without ytterbia additive ($x=0.0$) was also prepared.

α -silicon nitride powder (E10; Ube Industries, Ltd., Tokyo, Japan), Lu_2O_3 powder (Shin-Etsu Chemical Co., Ltd., Tokyo, Japan), Yb_2O_3 powder (High Purity Chemical Co.,

Ltd., Tokyo, Japan) and SiO_2 powder (Hokko Chemical Industry Co., Ltd., Tokyo, Japan) were used. The powder was ball milled for 72 h in ethanol, then dried and sieved. The powder was compacted using a steel die, followed by cold isostatic pressing (CIP) with a pressure of 400 MPa. The dimensions and relative density of the CIPed body were $53 \times 38 \times 7$ mm and $\sim 53\%$, respectively. Six CIPed bodies were covered by CIPed silicon nitride plates and silicon nitride powder. They were settled in a carbon crucible. The crucible was soaked for 1 h at 1700°C , 1 h at 1800°C and 6 h at 1950°C in 0.9 MPa N_2 atmosphere. The sintered bodies were heat-treated for 24 h at 1500°C to crystallize grain boundary glassy phase.

All the specimens provided for investigation were taken from inner four sintered bodies. X-ray diffraction analysis was conducted to identify phases. Microstructures of the specimens were examined by scanning electron microscopy (SEM). Specimens ($3 \times 4 \times 40$ mm) for measuring bending strength were cut from the sintered bodies. Three-point bending strength was measured following ISO 14704–2000 or JIS R 1601 with a span of 30 mm and a displacement rate of $0.5 \text{ mm} \cdot \text{min}^{-1}$ in air at room temperature ($R.T.$) and elevated temperatures. Measurement at elevated temperatures was done in air and after 20 min. soaking at the temperature. Fracture toughness was measured by Vickers Indentation-Fracture (IF) method (JIS R 1607). Indentation load and time were 196 N and 15 sec, respectively.

3. Results and discussion

Densities of the sintered specimens were 3.33, 3.35, 3.34, 3.32 for $x=0.0, 0.1, 0.2$ and 0.3 , respectively. By adding ytterbia, density of the specimen first increased and then decreased. Weight loss of the specimens were 2.8, 2.3, 2.3 and 2.4% for $x=0.0, 0.1, 0.2$ and 0.3 . Thus the addition of ytterbia suppressed the weight loss during sintering. The addition of ytterbia seemed to enhance densification at the early stage of sintering, which leads to suppression of the weight loss. However, the effect of Yb on densification and on vaporization of each element is still somewhat vague. Detailed observation is needed to clarify the effect.

Figure 1 shows SEM micrographs of the specimens. Rod-like silicon nitride grains were observed in all the specimens. No significant differences were found in sizes and aspect ratios of grains among four specimens. Amount of residual pores increased as the amount of ytterbia increased. Therefore, addition of small amount of ytterbia leads to the formation of residual pores. Here melting and boiling temperatures of lutetium and ytterbium are compared. As vapor pressure and melting/boiling temperatures are correlated, these tempera-

Fig. 1. Microstructures of the sintered specimens.

Fig. 2. Results of X-ray diffraction analysis.

tures were used for discussion here. Vapor pressures of these elements in the grain boundary glassy phase must be compared for accurate discussion. Melting and boiling temperatures are 1652°C and 3402°C for lutetium and 824°C and 1194°C for ytterbium. Thus ytterbium should easily vaporize compared to lutetium. Vaporization of ytterbium at the late stage of sintering is the plausible reason why the residual pores formed.

Figure 2 shows the result of an X-ray diffraction analysis. Detected crystalline phases were β -silicon nitride and lutetium disilicate ($\text{Lu}_2\text{Si}_2\text{O}_7$) in all the specimens. Neither lutetium monosilicate (Lu_2SiO_5) nor other crystalline phases were found. As the amount of ytterbia is small compared to lutetia, the addition of ytterbium did not affect the formation of secondary crystalline phases.

Strength the specimens are shown in Fig. 3. At *R.T.*, specimens with $x=0.0$, 0.1 and 0.2 showed almost the same strength of about 550 MPa. Only a specimen with $x=0.3$ showed lower strength of about 460 MPa. As known from SEM observations, the specimen with $x=0.3$ had the largest

Fig. 3. Strength of the specimens at room temperature (*R.T.*) as well as elevated temperatures.

Fig. 4. Fracture toughness of the specimens.

amount of pores, which led to the lowered strength. At elevated temperatures, strength degradation occurred. They became smaller as increasing the amount of ytterbia addition. The effect of oxidation should be negligible small,^{(13), (14)} thus, oxidation was not considered in this paper. The strength decrement of the specimen with $x=0.0$ was large, and it was about 150 MPa at 1500°C compared to that at *R.T.* Strength of the specimen with $x=0.2$ was about 480 MPa at 1500°C and decrement of it was about 70 MPa, therefore, strength decrement was half of that without ytterbia. It is not appropriate to compare the strength at *R.T.* and 1500°C of the specimen with $x=0.3$, since the strength at *R.T.* was lowered due to the residual pores. Thus, the addition of small amount of ytterbia is concluded to be effective to improve the high temperature strength.

Fracture toughness also improved by adding the small amount of ytterbia as shown in Fig. 4. Fracture toughnesses of the specimens with $x=0.1$, 0.2 and 0.3 were about 6 $\text{MPa}\cdot\text{m}^{1/2}$, which were higher than that with $x=0.0$ of less than 6 $\text{MPa}\cdot\text{m}^{1/2}$. Crack wakes introduced by the Vickers indentation were observed by SEM. The crack in $x=0.0$ ran almost straight. By adding ytterbia, crack wake changed to the shape with deflection and pull-out of grains, which are the major toughening mechanisms of silicon nitride.

A detailed mechanism why strength and toughness are improved by adding ytterbia is still uncertain. It is the interest where ytterbia exists, *i.e.*, in $\text{Lu}_2\text{Si}_2\text{O}_7$ or at grain boundaries, and what the effect is. To solve the problem, further observations including TEM observation of their grain boundaries are

in progress.

4. Summary

To improve the mechanical properties of $\text{Si}_3\text{N}_4\text{-Lu}_2\text{O}_3\text{-SiO}_2$ ceramics, small amount of ytterbia was added, and sintering behavior and mechanical properties were investigated. For specimens with different compositions, $\text{Si}_3\text{N}_4\text{-(8-x)Lu}_2\text{O}_3\text{-2SiO}_2\text{-xYb}_2\text{O}_3$ (mass%, $x=0.0, 0.1, 0.2$ and 0.3), were gas pressure sintered. The addition of small amount of ytterbia in the system can improve high temperature strength as well as fracture toughness. The addition of 0.1 to 0.2 mass% is enough for the improvement. However, the addition of 0.3 mass% lead to the formation of pores, results in strength degradation.

References

- 1) Cinibulk, M. K., Thomas, G. and Johnson, S. M., *J. Am. Ceram. Soc.*, Vol. 75[8], pp. 2050–2055 (1992).
- 2) Cinibulk, M. K., Kleebe, H. J., Schneider, G. A. and Ruhle, M., *J. Am. Ceram. Soc.*, Vol. 76[11], pp. 2801–2808 (1993).
- 3) Tanaka, K., Tsuruzono, S. and Terazono, H., Proc. of 6th International Symposium on Ceramic Materials and Components for Engines (Oct. 19–23, 1997, Arita, Japan), Ed. by Niihara, K., Hirano, S., Kanzaki, S., Komeya, K. and Morinaga, K. (1997) pp. 248–252.
- 4) Nakashima, T., Tatsumi, T., Takehara, I., Ichikawa, Y. and Kobayashi, H., Proc. of 6th International Symposium on Ceramic Materials and Components for Engines (Oct. 19–23, 1997, Arita, Japan), Ed. by Niihara, K., Hirano, S., Kanzaki, S., Komeya, K. and Morinaga, K. (1997) pp. 233–236.
- 5) Ohji, T., *Ceram. Eng. Sci. Proc.*, Vol. 22[3], pp. 159–166 (2001).
- 6) Lofaj, F., Wiederhorn, S. M., Long, G. G. and Jemian, P. R., *Ceram. Eng. Sci. Proc.*, Vol. 22[3], pp. 167–174 (2001).
- 7) Lofaj, F., Wiederhorn, S. M., Long, G. G., Hockey, B. J., Jemian, P. R., Browder, L., Andreason, J. and Taefner, U., *J. Eur. Ceram. Soc.*, Vol. 22(14–15), pp. 2479–2487 (2002).
- 8) Guo, S.-Q., Hirotsaki, N., Yamamoto, Y., Nishimura, T. and Mitomo, M., *Scripta Mater.*, Vol. 45(7), pp. 867–874 (2001).
- 9) Kondo, N., Ishizaki, M. and Ohji, T., *Silicate Industries*, Vol. 69(7–8), pp. 183–186 (2004).
- 10) Kondo, N., Ishizaki, M. and Ohji, T., *Ceram. Eng. Sci. Proc.*, Vol. 25(3), pp. 153–158 (2005).
- 11) Kondo, N., Hyuga, H., Yoshida, K., Kita, H. and Ohji, T., *Ceram. Int.*, in preparation.
- 12) Yasuda, S., Yoshida, H., Yamamoto, T. and Sakuma, T., *Mater. Trans.*, Vol. 45(7), pp. 2078–2082 (2004).
- 13) Suetsuna, T., Ishizaki, M., Ando, M., Kondo, N., Ohji, T. and Kanzaki, S., *J. Ceram. Soc. Japan*, Vol. 112, pp. 301–304 (2004).
- 14) Suetsuna, T., Ishizaki, M., Ando, M., Kondo, N., Ohji, T. and Kanzaki, S., *J. Ceram. Soc. Japan*, Vol. 112, pp. 388–394 (2004).