

A new process to grow β - Si_3N_4 whiskers using thermal decomposition and closed pores

Chang-Sam Kim^{a,*} and Shin-Woo Kim^b

^aBattery Research Center, KIST, P.O.Box 131, Seoul 130-650, Korea

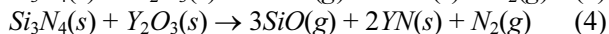
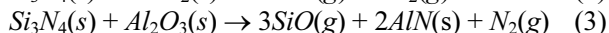
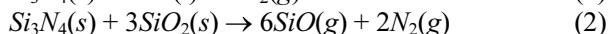
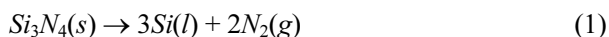
^bDepartment of Materials Engineering, Hoseo University, Asan, Chungnam 336-795, Korea

In this study, a novel and interesting method to grow β - Si_3N_4 whiskers was developed using thermal decomposition of Si_3N_4 and large pores introduced intentionally during liquid phase sintering. The pore size, pore vol%, pore morphology and nitrogen pressure were chosen as experimental variables to find proper conditions for growing whiskers. In this experiment, commercial α - Si_3N_4 , Al_2O_3 and Y_2O_3 were selected as starting materials, and polymer beads with average diameters of 100 and 200 μm were used as pore formers to make intentional pores in the sintered sample. A polyvinyl film was also used to make a film type of pore. β - Si_3N_4 whiskers grew well on the inside of pores in the case of a low vol% of pores, 14 and 27 vol% or closed pores of a film shape, but not for a high vol% of pore, 39 and 50 vol% or open pores of a film shape. The variation of pore size, pore morphology and nitrogen pressure did not have any influence on whisker growth.

Key words: Si_3N_4 whiskers, Thermal decomposition, Sintering, Open pores, Closed pores.

Introduction

Si_3N_4 is a promising ceramic material having excellent mechanical, chemical, and thermal properties at high temperatures and has been widely used for structural applications such as cutting tools, mechanical seals, ball bearings, and engine components. It has a better thermal expansion coefficient, fracture toughness, and thermal shock resistance than another good ceramic material, silicon carbide, even if it has less thermal stability and corrosion resistance. Si_3N_4 products are usually sintered with liquid sintering additives such as Al_2O_3 , Y_2O_3 , MgO and SiO_2 but have a main problem with the following thermal decompositions and densification at the sintering temperature [1]. Therefore, high N_2 pressures or powder bed techniques are often used to suppress the thermal decompositions:



On the other hand, Si_3N_4 whiskers have some more advantages of high mechanical strength, melting point and elastic modulus due to less defects and have been used as one of the important reinforcing materials in composites [2]. Therefore, many studies on the various synthesis methods of Si_3N_4 whiskers using chemical systems such as SiO_2 - Si - N_2 - H_2 , SiO_2 - C - N_2 , SiO_2 - N_2 - Na_3AlF_6 , and

SiO_2 - Al_2O_3 - Y_2O_3 have been reported [3-14]. But in this study a novel and interesting method to grow Si_3N_4 whiskers using the thermal decomposition of Si_3N_4 and large pores formed intentionally during liquid sintering was developed. The pore size, pore vol%, pore morphology and nitrogen pressure were chosen as experimental variables to find a proper condition to grow whiskers.

Experimental

In this experiment, commercial α - Si_3N_4 ($\alpha > 90\%$, M11, H.C.Stark, Germany) was selected as a starting material, and Al_2O_3 (AKP-30, Sumitomo Chemical Co., Japan) and Y_2O_3 (Grand Chemical Co., Korea) were used as sintering additives. In order to make large intentional pores in a sintered sample, polymer beads of two different sizes with average diameters of 100 and 200 μm were used as pore formers. In addition, a polyvinyl film was also used for making a film type of pore. First of all, Si_3N_4 powders were well mixed with 5 wt% Al_2O_3 , 10 wt% Y_2O_3 and distilled water in a polyethylene bottle through wet ball milling for 24 h. After that, the polymer binder and polymer beads were added to the Si_3N_4 mixture and mixed again for 24 h to make a uniform slurry. Four different amounts of beads, 14, 27, 39 and 50 vol% were added to make different volume fractions of pores in the sample. The mixed slurry was poured into a steel mold and dried in an oven at 80 $^\circ\text{C}$ for 24 h. In case of the film type of pore, the slurry without any polymer beads was prepared and a thin polyvinyl film was inserted in the middle of the poured slurry. In order to make an open film pore, the dried sample was cut in half and thus the inserted polyvinyl film was revealed to the air. The dried Si_3N_4 sheet (15 $\times$ 15 $\times$ 3 mm)

*Corresponding author:
Tel : +82 2 958 5483
Fax: +82 2 958 5479
E-mail: cskim@kist.re.kr

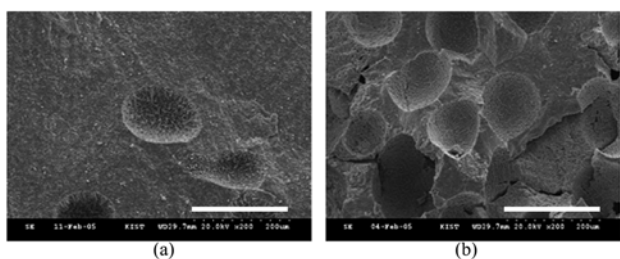


Fig. 1. SEM micrographs of sintered Si_3N_4 with (a) 14 and (b) 39 vol% of 200 μm pores.

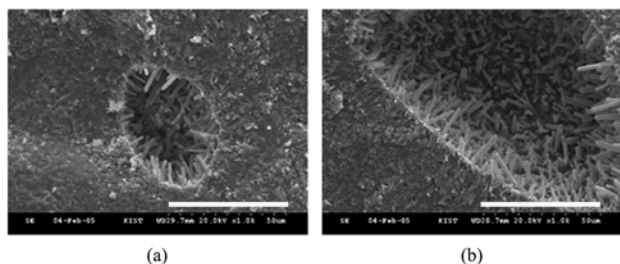


Fig. 2. SEM micrographs of sintered Si_3N_4 with 14 vol% of (a) 100 and (b) 200 μm pores.

was heated up to 500 $^{\circ}\text{C}$ at a rate of 0.3 $^{\circ}\text{C}$ minute $^{-1}$ to evaporate and eliminate the polymer binder, beads or polyvinyl film. Finally the samples were sintered at 1,850 $^{\circ}\text{C}$ for 2 h under three different N_2 pressures of 3, 5, and 10 atm in a graphite furnace. After sintering, the phase analysis and microstructures of samples were investigated with X-Ray Diffraction (XRD) and a Scanning Electron Microscope (SEM).

Results and Discussion

Fig. 1 are cross-sectional SEM micrographs of sintered Si_3N_4 with 14 and 39 vol% of 200 μm pores. They show that artificially large pores were well formed and distributed inside the sample after the evaporation of the beads as expected. Pores were isolated at low vol%, 14 and 27 vol% but interconnected with neighboring pores and the sample surface at high vol%, 39 and 50 vol%.

On the other hand, the XRD results of sintered Si_3N_4 showed that the initial β - Si_3N_4 was almost transformed into β - Si_3N_4 after sintering. Fig. 2 are SEM micrographs of the inside of 100 and 200 μm pores in Si_3N_4 sintered under 10 atm N_2 with 14 vol% of pores. β - Si_3N_4 whiskers grew well on the inside of pores. They have a diameter of 0.2–1 μm and a length of 10–20 μm . Fig. 3 are SEM micrographs of the inside of 100 and 200 μm pores in Si_3N_4 sintered under 10 atm N_2 with 39 vol% of pores. But in this case Si_3N_4 whiskers were not grown at all on the inside of pores. This trend was found equally irrespective of size of pore. That is, the vol% of pores is thought to be a more important factor in growing Si_3N_4 whiskers than the size of pores. In order to find the effect of nitrogen pressure on whisker growth, three different pressures, 3, 5 and 10 atm, were used for sintering. But the variation of nitrogen pressure did not

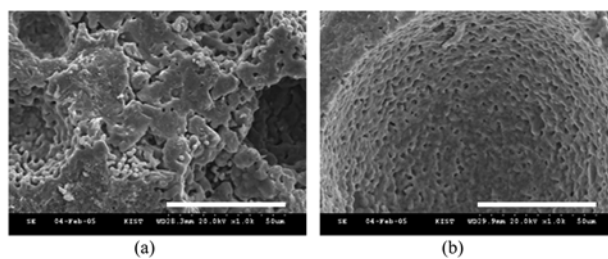


Fig. 3. SEM micrographs of sintered Si_3N_4 with 39 vol% of (a) 100 and (b) 200 μm pores.

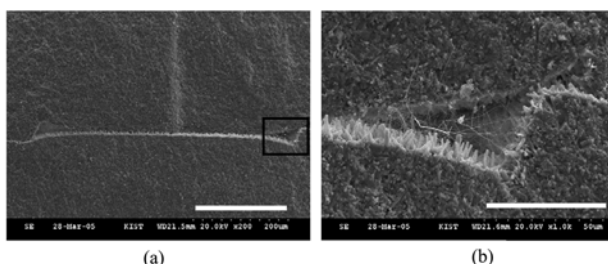


Fig. 4. SEM micrographs of sintered Si_3N_4 with a closed pore of film shape; (a) low magnification and (b) high magnification.

have any influence on Si_3N_4 whisker growth and so, only in the case of a low vol%, 14 and 27 vol% of pores, β - Si_3N_4 whiskers were well developed on the inside of pores. Fig. 4 are cross-sectional SEM micrographs of sintered Si_3N_4 with a closed pore of film shape to show the growth of Si_3N_4 whiskers inside. On the other hand, Fig. 5 are cross-sectional SEM micrographs of sintered Si_3N_4 with an open pore of film shape which do not show any Si_3N_4 whiskers inside.

From the above experimental results, the most critical factor in growing Si_3N_4 whiskers on the inside of pores during sintering is thought to be the pore vol%. The proper conditions to grow them was on the surface of closed pores in the sintered sample with a low vol% such as 14 and 27 vol% or a closed pore of film shape. But they did not grow at all on the surface of open pores which were interconnected with each other and up to the sample surface. That is, Si_3N_4 whiskers are very difficult to nucleate and grow on open pores because the gas phases equilibrated with the Si_3N_4 - Al_2O_3 - Y_2O_3 liquid due to the thermal decomposition at the sintering temperature and diffused out to the surface through the connected path. On the other hand,

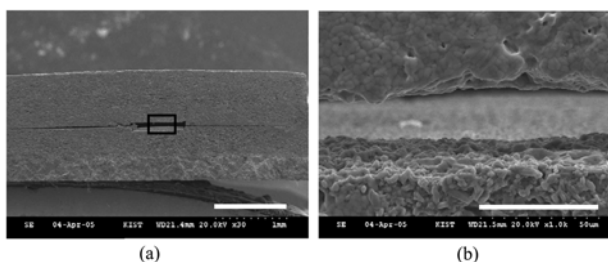


Fig. 5. SEM micrographs of sintered Si_3N_4 with an open pore of film shape; (a) low and (b) high magnification.

they are well confined in closed pores and so whiskers can nucleate and grow easily by precipitation during cooling. Therefore, it is very important to maintain the closed pores to grow Si_3N_4 whiskers during sintering.

Summary

A novel method to grow Si_3N_4 whiskers on the inside of large pores formed intentionally during liquid sintering was developed. Si_3N_4 whiskers grew well at a low vol% of pores such as 14 and 27 vol% or on a closed pore of film shape but not at a high vol% of pores such as 39 and 50 vol% or on an open pore of film shape. The variation of pore size, pore morphology and nitrogen pressure did not have any influence on the trend of whisker growth. The most important factor to grow Si_3N_4 whiskers on the inside of large pores during sintering was to maintain a low vol% of pores, that is, closed pores which were thought to confine the volatile species due to thermal decomposition and condense them into whiskers during cooling.

References

1. P. Sajgalik and M. Haviar, *Ceram. Int.* 18 (1992) 279-283.
2. M. Wang and H. Wada, *J. of Mat. Sci.* 25 (1990) 1690-1698.
3. Y. Luo, Z. Zheng, Z. Xie and Z. Zhang, *Mat. Lett.* 58 (2004) 2114-2117.
4. T. Hashishin, Y. Kaneko, H. Iwanaga and Y. Yamamoto, *J. of Mat. Sci.* 34 (1999) 2193-2197.
5. P.C. Silva and J.L. Figueiredo, *Mat. Chem. and Phys.* 72 (2001) 326-331.
6. C. Kawai and A. Yamakawa, *Ceram. Int.* 24 (1998) 135-138.
7. V.N. Gribkov, V.A. Silaev, B.V. Shchetanov, E.L. Umantsev and A.S. Isaikin, *Sov. Phys. Cryst.* 16[5] (1972) 852-854.
8. A. Markwitz, H. Baumann and E.F. Krimmel, *Physica E* 11 (2001) 110-113.
9. H. Iwanaga and C. Kawai, *J. Am. Ceram. Soc.* 81[3] (1998) 773-776.
10. C. Kawai and A. Yamakawa, *J. of Mater. Sci. Lett.* 14 (1995) 192-193.
11. Y. Mizuhara, M. Noguchi, T. Ishihara, Y. Takita, T. Shiomitsu and H. Arai, *J. of Euro. Ceram. Soc.* 12 (1993) 111-116.
12. Y. Bi, Z. Yu and P. Zhang, *Sci. of Sintering* 23[1] (1991) 33-40.
13. D. Chen, B. Zhang, H. Zhuang and W. Li, *Ceram. Inter.* 29 (2003) 326-331.
14. K.J. Hüttinger and T.W. Pieschnick, *J. of Mater. Sci.* 29 (1994) 2879-2883.