journal

J. Am. Ceram. Soc., **82** [11] 3263–65 (1999)

Oxygen Content in β-Si_3N_4 Crystal Lattice

Mikito Kitayama*,†

Synergy Ceramics Laboratory, Fine Ceramics Research Association, Nagoya, Aichi 463-8687, Japan

Kiyoshi Hirao,* Akira Tsuge, Motohiro Toriyama, and Shuzo Kanzaki*

National Industrial Research Institute of Nagoya, Nagoya, Aichi 463-8687, Japan

β-Si_3N_4 crystals were obtained through the heat treatment of α-Si_3N_4 powder with additives, Y_2O_3:SiO_2 = 1:2 and 2:1, and subsequent acid treatments that removed the secondary phases. The lattice oxygen contents of these crystals were determined by the hot-gas extraction method to be 0.258 ± 0.006 and 0.158 ± 0.003 wt% for the additive compositions of Y_2O_3:SiO_2 = 1:2 and 2:1, respectively. The oxygen dissolved in the β-Si_3N_4 crystal lattice as much as in the α-Si_3N_4 crystral lattice prepared by the chemical vapor deposition process and in the AlN crystal lattice that exhibited high thermal conductivity.

I. Introduction

Silicon nitride (Si_3N_4) occurs in two modifications, designated α and β, which are considered to be the low- and high-temperature phases, respectively. Grieveson and coworkers[1–3] proposed that the α phase was, in fact, an oxynitride of the compositions $Si_{11.4}N_{15}O_{0.3}$ (0.90 wt% O) or $Si_{11.5}N_{15}O_{0.5}$ (1.48 wt% O). This hypothesis well explained the observed change of stable phases, β-Si_3N_4 → α-Si_3N_4 → Si_2N_2O → SiO_2, with increased oxygen partial pressure (P_{O_2}).[3] Mitomo[4] also confirmed that the α content increased with increased P_{O_2} during the nitridation of silicon. However, Edwards *et al.*[5] showed that the oxygen contents of mixed α- and β-Si_3N_4 samples were somewhat lower than required to meet the formula for the α phase. Priest *et al.*[6] prepared 100% α-Si_3N_4 through the chemical vapor deposition (CVD) process and reported that the oxygen content was 0.30 ± 0.005 wt%, which was much lower than the values shown above. Kijima *et al.*[7] successfully prepared α-Si_3N_4 single crystals with oxygen contents as low as 0.05 ± 0.03 and 0.09 ± 0.02 wt% by carefully adjusting P_{O_2} during the CVD process. Thus, it was demonstrated that oxygen was not necessary for the structural stabilization of α-Si_3N_4 and that the α phase was a polymorph of Si_3N_4. Table I summarizes oxygen contents of Si_3N_4 reported in previous works. Although it has not been strictly specified that the oxygen contents in these works were those dissolved in the α-Si_3N_4 lattice, we believe they are, because these data were taken from the bulk made from the nitridation of silicon metal or single crystals. Because previous works focused on α-Si_3N_4, the oxygen content in the β-Si_3N_4 crystal lattice has never been reported. From the observed change of stable phases with P_{O_2} during the nitridation of silicon, we might expect that the oxygen content would be lower in the β phase than in the α phase.

Haggerty and Lightfoot[8] reported that Si_3N_4 was also potentially a material with high thermal conductivity (200–320 W/(m·K)) at room temperature. Because of its excellent mechanical properties, β-Si_3N_4 ceramics are a candidate for electrical substrate application if their thermal conductivity can be improved to that of AlN ceramics. From experience with AlN ceramics,[9] it is highly possible that the oxygen content in the β-Si_3N_4 crystal lattice greatly influences its thermal conductivity. Thus, it is of great interest whether oxygen dissolves in the β-Si_3N_4 crystal lattice and, if so, how much.

The purpose of this work was to analyze the oxygen content in the β-Si_3N_4 crystal lattice. Because Hirao *et al.*[10] developed a method for fabricating high-quality β-Si_3N_4 single crystals, it was used for sample preparation in this work. The hot-gas extraction method was applied for oxygen analysis of β-Si_3N_4 because it was shown to be capable to distinguish the surface, grain-boundary, and lattice oxygen of AlN.[11]

II. Experimental Procedure

Powder mixtures of α-Si_3N_4 (SN-E05 Grade, aluminum content of <50 ppm, UBE Industries, Ltd., Yamaguchi, Japan), Y_2O_3, and SiO_2 (Hokko Chemicals, Ltd., Tokyo, Japan) with the molar ratios of 20:1:2 and 20:2:1, which are called 1:2 and 2:1, respectively, later in this work, were planetary milled for 3 h in a Si_3N_4 jar with Si_3N_4 balls using methanol as a mixing medium. The resulting slurries were dried and passed through a 60 mesh nylon sieve. The powder mixtures were then charged into BN crucibles in a loose powder state and heat-treated at 1850°C for 2 h under a nitrogen pressure of 1 MPa. The aggregated porous bodies were lightly crushed using a mortar and pestle, passed through a 100 mesh nylon sieve, and rinsed using 50% HF and then concentrated H_2SO_4 to remove the glassy phase and possible yttrium compounds. The Si_3N_4 powders thus obtained were phase identified using X-ray diffractometry (XRD).

A commercial hot-gas extraction analyzer (Model TC-436, LECO Co., St. Joseph, MI) was used for oxygen and nitrogen determinations. About 20 mg of powder sample was weighed into a graphite crucible (10 mm diameter × 16 mm high), and ~300 mg of graphite powder (No. 501-073, LECO Co.) was added to the sample to accelerate the carbothermal reduction of the oxide phases. A crucible was heated to 2500°C in 5 min in a flowing argon atmosphere. The release of oxygen and nitrogen as a function of temperature and total concentrations of oxygen and nitrogen were recorded. Three measurements were performed for both samples.

III. Results and Discussion

XRD identified that both powders contained only β-Si_3N_4. Figures 1 and 2 show the release counts (arbitrary unit) of oxygen and nitrogen as a function of temperature for the 1:2 and 2:1 powders, respectively. Because it was found that oxygen was extracted in two or three fractions, deconvolution was performed assuming a gaussian distribution. In Fig. 1, a small peak around 1500°C and a large peak around 1800°C were

---

F. Aldinger—contributing editor

Manuscript No. 189336. Received May 12, 1999; approved August 24, 1999.

*Member, American Ceramic Society.

†Author to whom correspondence should be addressed.

Table I. Oxygen Contents in the Si_3N_4 Crystal Lattice Prepared by Various Methods[†]

Fabrication method	Phase composition (%) α	Phase composition (%) β	Oxygen content (wt%)	Reference
Unknown	90	10	2	2
Unknown	10	90	0.2	2
Silicon-metal nitridation	87	13	0.53 ± 0.05	5
Silicon-metal nitridation	81	19	0.48 ± 0.02	5
Silicon-metal nitridation	58	26	0.26 ± 0.03	5
Silicon-metal nitridation	6	83	0.31 ± 0.03	5
CVD	100	0	0.30 ± 0.005	6
CVD	100	0	0.05 ± 0.02	7
CVD	100	0	0.09 ± 0.02	7
LPS[‡] (1:2)	0	100	0.258 ± 0.006	This work
LPS[‡] (2:1)	0	100	0.158 ± 0.003	This work
AlN[§]			0.29	12
AlN[¶]			0.16	12

[†] Also includes some representative values in the AlN crystal lattic. [‡] Liquid-phase sintering of α-Si_3N_4 powder with additives (ratios in the parenthesis indicate Y_2O_3:SiO_2 additive ratios). [§] AlN ceramics that exhibited thermal conductivity of 150 W/(m·K). [¶] AlN ceramics that exhibited thermal conductivity of 200 W/(m·K).

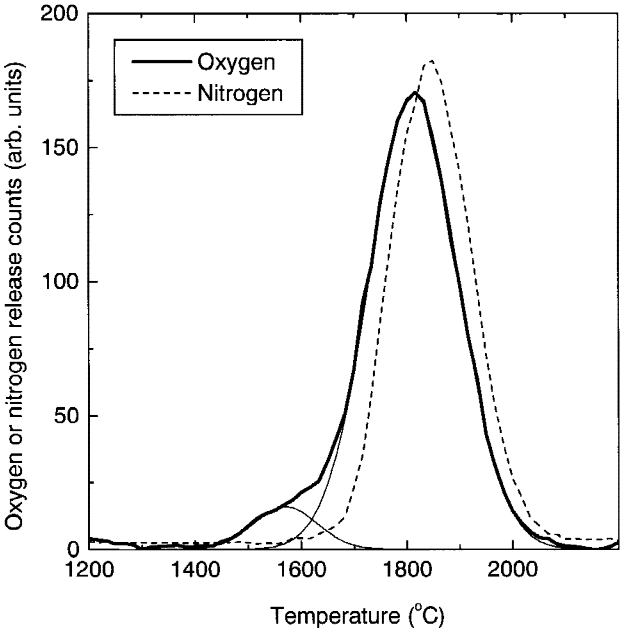

Fig. 1. Result of the hot-gas extraction analysis for the 1:2 powder showing the release counts (arbitrary unit) of (—) oxygen and (---) nitrogen as a function of temperature. A result of the gaussian peak separation for (—) oxygen release is also shown. The second peak coincides with the nitrogen release.

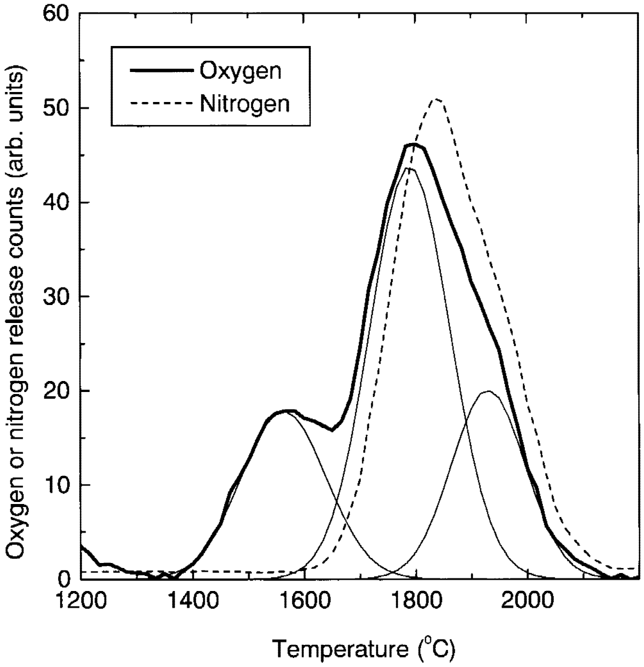

Fig. 2. Result of the hot-gas extraction analysis for the 2:1 powder showing the release counts (arbitrary unit) of (—) oxygen and (---) nitrogen as a function of temperature. A result of the gaussian peak separation for (—) oxygen release is also shown. The second and third peaks coincide with the nitrogen release.

observed. The second peak of oxygen release coincides with that of nitrogen release. (There is a slight delay of detection for nitrogen because of the order of detectors. Also, the detector for oxygen is much more sensitive than that for nitrogen.) This means that the second peak of oxygen release occurred when β-Si_3N_4 crystals decomposed, and this further implies that it was the oxygen content dissolved in the β-Si_3N_4 crystal lattice. In Fig. 2, three peaks were observed, and the latter two peaks were found to coincide with the nitrogen release. Each peak area was integrated, and each total oxygen content was divided into these peak areas. Table I also shows the results of oxygen contents thus obtained for the 1:2 and 2:1 samples averaged from three measurements. The lattice oxygen contents of the 1:2 and 2:1 samples were determined to be 0.258 ± 0.006 and 0.158 ± 0.003 wt%, respectively. The heat treatment was done using a furnace with graphite heating elements that had never been used for materials containing aluminum, and we confirmed semiquantitatively using X-ray fluoresence that the aluminum content in the β-Si_3N_4 crystals was as low as the raw material (UBE SN E05). Therefore, we could negate the possibility of the formation of SiAlON. Thus, we could conclude that oxygen dissolved in the β-Si_3N_4 crystal lattice as much as in the α-Si_3N_4 crystal lattice prepared by CVD and in the AlN crystal lattice that exhibited high thermal conductivity ranging from 150 to 200 W/(m·K)[12] (Table I).

It is expected from these results that the SiO_2:Y_2O_3 ratio and, hence, the grain-boundary phases strongly influence oxygen content in the β-Si_3N_4 crystal lattice. In both cases, the first peak would correspond to the decomposition of the residual secondary phases. The reason why two peaks were observed for the 2:1 samples is unknown, but probably was due to the 2:1 powder containing crystals with much larger sizes than the 1:2 powder, and its size distribution was bimodal.[13] Peak separation was not as clear as that observed in the case for AlN ceramics.[11] This would be due to the difference of the decomposition temperature between Si_3N_4 (~1850°C) and AlN (~2000°C). However, the hot-gas extraction method has been shown to be applicable to Si_3N_4 with the aid of gaussian peak separation in this work. The application of this method to the liquid-phase-sintered Si_3N_4 ceramics and the relationship between the lattice oxygen content and termal conductivity will be reported elsewhere.[14]

IV. Conclusion

The oxygen content in the β-Si_3N_4 crystal lattice has been measured by the hot-gas extraction method, and it has been determined to be 0.258 ± 0.006 and 0.158 ± 0.003 wt%. Oxygen dissolves in the β-Si_3N_4 crystal lattice as much as in the α-Si_3N_4 crystal lattice prepared by CVD and in AlN crystal lattice that exhibits high thermal conductivity.

Acknowledgment: This work has been conducted as part of the Synergy Ceramics Project under the Industrial Science and Technology Frontier (ISTF) Program promoted by AIST, MITI, Japan. Under this program, part of the work has been funded through the New Energy and Industrial Technology Development Organization (NEDO). The authors are members of the Joint Research Consortium of Synergy Ceramics.

References

[1] S. Wild, P. Grieveson, and K. H. Jack, "The Thermodynamics and Kinetics of Formation of Phases in the Ge-N-O and Si-N-O Systems"; pp. 271–81 in *Special Ceramics*, Vol. 5. Edited by P. Popper. British Ceramic Research Association, Stoke-on-Trent, U.K., 1972.

[2] S. Wild, P. Grieveson, and K. H. Jack, "The Crystal Structures of Alpha and Beta Silicon and Germanium Nitrides"; see Ref. 1, pp. 385–93.

[3] I. Colquhoun, S. Wild, P. Grieveson, and K. H. Jack, "Thermodynamics of the Silicon-Nitrogen-Oxygen System," *Proc. Br. Ceram. Soc.*, [22] 207–27 (1973).

[4] M. Mitomo, "Effect of Oxygen Partial Pressure on Nitridation of Silicon," *J. Am. Ceram. Soc.*, **58** [11–12] 527 (1975).

[5] A. J. Edwards, D. P. Elias, M. W. Lindley, A. Atkinson, and A. J. Moulson, "Oxygen Content of Reaction-Bonded α-Silicon Nitride," *J. Mater. Sci.*, **9**, 516–17 (1974).

[6] H. F. Priest, F. C. Burns, G. L. Priest, and E. C. Skaar, "Oxygen Content of Alpha Silicon Nitride," *J. Am. Ceram. Soc.*, **56** [7] 395 (1973).

[7] K. Kijima, K. Kato, Z. Inoue, and H. Tanaka, "Oxygen Content of α-Si_3N_4 Single Crystals," *J. Mater. Sci.*, **10**, 362–63 (1975).

[8] J. S. Haggerty and A. Lightfoot, "Opportunities for Enhancing the Thermal Conductivities of SiC and Si_3N_4 Ceramics through Improved Processing," *Ceram. Eng. Sci. Proc.*, **16** [4] 475–87 (1995).

[9] G. A. Slack, "Non-Metallic Crystals with High Thermal Conductivity," *Phys. Chem. Solids*, **34**, 321–35 (1973).

[10] K. Hirao, A. Tsuge, M. E. Brito, and S. Kanzaki, "Preparation of Rodlike β-Si_3N_4 Single-Crystal Particles," *J. Ceram. Soc. Jpn.*, **101** [9] 1078–80 (1993).

[11] A. Thomas and G. Müller, "Determination of the Concentration of Oxygen Dissolved in the AlN Lattice by Hot Gas Extraction from AlN Ceramics," *J. Eur. Ceram. Soc.*, **8**, 11–19 (1991).

[12] H. Buhr, G. Müller, H. Wigge, F. Aldinger, P. Foley, and A. Roosen, "Phase Composition, Oxygen Content, and Thermal Conductivity of AlN[Y_2O_3] Ceramic," *J. Am. Ceram. Soc.*, **74** [4] 718–23 (1991).

[13] M. Kitayama, K. Hirao, M. Toriyama, and S. Kanzaki, "Control of β-Si_3N_4 Crystal Morphology and Its Mechanism: I. Effect of SiO_2 and Y_2O_3 Ratio," *J. Ceram. Soc. Jpn.*, (1999), in press.

[14] M. Kitayama, K. Hirao, A. Tsuge, M. Toriyama, and S. Kanzaki, "Thermal Conductivity of β-Si_3N_4: II, Effect of Lattice Oxygen," *J. Am. Ceram. Soc.*, in review. □