Solid-Gas Reaction during Sintering of Si_3N_4 Ceramics (Part 1)—Stability of SiO_2 , Y_2O_3 and Al_2O_3 at High Temperature—

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 Si_3N_4 セラミックスの焼結時における固相-気相反応 (第1報)—高温下での SiO_2 , Y_2O_3 及び Al_2O_3 の安定性—

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The stability during sintering of SiO_2 , Y_2O_3 and Al_2O_3 , well known as sintering aids of Si_3N_4 ceramics, was examined from both thermodynamical and experimental aspects. Both the heat treatment of SiO_2 - Y_2O_3 - Al_2O_3 glass and the sintering of Si_3N_4 ceramics were carried out. In the thermodynamical considerations, the stability of the glass composition was discussed on the basis of known volatility diagrams for SiO_2 , Al_2O_3 and MgO and the thermodynamic data of Y_2O_3 available in the literature. The results suggest that Y_2O_3 is the most stable among all materials in the sintering temperature range usually selected for Si_3N_4 ceramics. SiO_2 - Y_2O_3 - Al_2O_3 (equi-mass%) glass was heat-treated in a BN sagger at 2023 K for 2 h in N_2 gas of 0.1 MPa. Si_3N_4 with addition of 5 mass% Y_2O_3 and 3 mass% Al_2O_3 was sintered in the BN sagger at 2023 K for 0 to 16 h in N_2 gas of 0.1 MPa. The elemental contents in the glass and ceramics before and after heat treatment and sintering were determined by chemical analysis. As a result, it was found that only SiO_2 in the glass and SiO_2 and Si_3N_4 in the Si_3N_4 ceramics vaporized. On the other hand, the Y_2O_3 and Al_2O_3 contents in both the glass and Si_3N_4 ceramics did not decrease under the selected temperature.

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Key-words : Si_3N_4 , Mass loss, Volatility diagram, SiO_2 - Y_2O_3 - Al_2O_3 glass

1. Introduction

During the sintering of Si_3N_4 ceramics, some amount of mass loss occurs.¹⁾⁻⁴⁾ The mass loss disturbs the consolidations, causes pores and hence degrades the mechanical properties of the ceramics. Therefore, the phenomena and the mechanism of mass loss during the sintering of Si_3N_4 ceramics have been studied.^{1),2),5),6)} Common well-known sintering aids of Si_3N_4 are Y_2O_3 - Al_2O_3 ^{7),8)} and MgO .⁹⁾⁻¹¹⁾ Actually, because a small amount of SiO_2 is formed on the Si_3N_4 grain, the net compositions of sintering aids are SiO_2 - Y_2O_3 - Al_2O_3 and SiO_2 - MgO , respectively. These sintering aids form a Si-Y-Al-O-N glass and a Si-Mg-Al-O-N glass during the sintering of Si_3N_4 ceramics.

It can be assumed that the vaporization of glass originates from the vaporization of each of its constituents, SiO_2 , Y_2O_3 , Al_2O_3 or MgO . The vaporization of SiO(g) in the Y-Si-Al-O-N glass has been reported for sintering in various Si_3N_4 powders with Y_2O_3 - Al_2O_3 ,¹²⁾⁻¹⁵⁾ but has not been discussed in detail. Although, the volatility diagrams for SiO_2 , Al_2O_3 and MgO have been reported,^{16),17)} that for Y_2O_3 has not yet been reported. In this work, the mass loss reaction of Si_3N_4 ceramics with Y_2O_3 and Al_2O_3 was considered from the viewpoint of thermodynamic data and was quantitatively investigated by the sintering of Si_3N_4 ceramics.

The volatility diagram of the Y-O system was drawn using the thermodynamic data compiled by Brain¹⁸⁾ and reported by Ackermann et al.^{19),20)} and Ames et al.²¹⁾ and its thermodynamical stability in the temperature range of 1800 to 2000 K was discussed in this investigation. The SiO_2 - Y_2O_3 - Al_2O_3 glass was prepared and was heat-treated at 2023 K to compare the stability of SiO_2 , Y_2O_3 and Al_2O_3 in the glass at this high temperature. Si_3N_4 ceramics with Y_2O_3 - Al_2O_3 additives were sintered at 2023 K. The con-

tents of SiO_2 , Y_2O_3 and Al_2O_3 in the glass and the ceramics were examined by chemical analysis.

2. Volatility diagram

The well-known JANAF tables do not contain the data for Y and chemical compounds containing Y. The thermodynamic data compiled by Brain¹⁸⁾ lists Y(s, l) at 298.15 to 3607 K, Y(g) at 298.15 to 3700 K, Y_2O_3 (s) at 298.15 to 2000 K and YN(s) at 298.15 to 2200 K, and Ackermann et al.¹⁹⁾ reported YO(g) data, where s, l and g denote solid, liquid and gas, respectively. Although Si_3N_4 is commonly sintered at 1800 to 2100 K, the equilibrium states for Y(l), Y(g), YO(g) and Y_2O_3 (s) at 1800 to 2000 K were calculated because of the lack of data for Y_2O_3 (s) at >2000 K. The Gibbs free energy, ΔG and equilibrium constant, $\log K_p$ at 1800, 1900 and 2000 K for Reactions (1), (2), (3) and (4) are listed in Table 1. From the data of Table 1, the volatility diagram for the Y-O system can be drawn as shown in Fig. 1. In the condition on the lines in the figure, each reaction is in equilibrium state. The equilibrium partial vapor pressure of Y(g), p_Y , and YO(g), p_{YO} , increases with increasing temperature.

The lower limit of p_{O_2} in Fig. 1 was determined by the following reasoning. Nitrogen gas (grade: N_2 -B), commonly used for the sintering of Si_3N_4 ceramics, contains oxygen <0.5 ppm. When the nitrogen pressure, p_{N_2} , is 0.1 MPa, p_{O_2} is $<5 \times 10^{-2}$ Pa. The carbon activity (a_C) in the furnace consisting of a carbon heater is unity. Hence, the equilibrium conditions of O_2 (g), CO_2 (g) and CO(g) in the nitrogen gas are calculated from the following reactions;

These reactions require that the sum of the O_2 , CO_2 and CO

Table 1. Reactions in the Y–O System, and Gibbs Energy, ΔG , and $\log K_p$ at 1800, 1900 and 2000 K
Thermodynamic Data of Reactions (1) to (3) were Referred from Ref. 18 and That of Reaction (4) was Referred from Ref. 19

Reaction	T / K	ΔG / kJmol ⁻¹	$\log K_p$	Eq.
$Y(l) \rightarrow Y(g)$	1800	190.664	-5.58	(1)
	1900	179.414	-4.97	
	2000	168.276	-4.43	
$Y_2O_3(s) \rightarrow 2Y(g) + 3/2O_2(g)$	1800	1773.481	-51.88	(2)
	1900	1721.558	-47.71	
	2000	1669.804	-43.97	
$Y_2O_3(s) \rightarrow 2Y(l) + 3/2O_2(g)$	1800	1392.153	-40.73	(3)
	1900	1362.730	-37.77	
	2000	1333.252	-35.11	
$Y_2O_3(s) \rightarrow 2YO(g) + 1/2O_2(g)$	1800	1056.054	-30.64	(4)
	1900	1017.218	-27.96	
	2000	978.428	-25.55

Fig. 1. Volatility diagram at 1800, 1900 and 2000 K for the Y–O system. The number in parentheses corresponds to the equation number of Table 1.

Fig. 2. Volatility diagram at 2000 K for the Si–O, Mg–O, Al–O and Y–O systems.

————— Si–O system - - - - - Mg–O system
- - - - - Al–O system — — — — Y–O system

partial pressures is less than 5×10^{-2} Pa for $p_{N_2} = 0.1$ MPa.²²⁾ Although the calculation details are not shown here, the p_{O_2} in the N_2 gas at equilibrium state was calculated to lie in the range of 6.0×10^{-24} to 2.9×10^{-23} Pa at 1800 to 2000 K. Thus, in the following figures, the p_{O_2} range is 10^{-25} to 10^5 Pa (atmospheric pressure).

The volatility diagram at 2000 K for the Si–O, Al–O, Mg–O and Y–O systems is shown in Fig. 2. In this figure, the equilibrium lines of gas species with maximum equilibrium vapor pressure are shown for SiO_2 , Al_2O_3 and MgO . The data for the Y–O system is identified with that in Fig. 1. The equilibrium vapor pressure for each material is in the order, $p_{Mg} \approx p_{SiO} > p_{AlO_2(Al_2O_3, AlO, Al_2O_3)} > p_{YO}$ at $p_{O_2} > 10^{-9}$ Pa, while it is in the order, $p_{Mg} > p_{Al} > p_{Si} \approx p_Y$ at $p_{O_2} < 10^{-13}$ Pa.

On the basis of the thermodynamic relations in Fig. 2, it was concluded that Y_2O_3 is more stable than SiO_2 , Al_2O_3 and MgO . We performed a heat treatment of SiO_2 – Y_2O_3 – Al_2O_3 glass, as reported in Chapter 4, to confirm the stability of the Y–O system experimentally.

3. Experimental procedure

Two experiments were carried out to confirm that the Y and Al ions in the oxynitride glass are stable during sintering. The first involved the preparation of the SiO_2 – Y_2O_3 – Al_2O_3 glass and the second, analysis of the Si, Y and Al contents after heat treatment.

The SiO_2 (Nacalai Tesque, Inc., Guaranteed Reagent), Y_2O_3 (Shin-Etsu Chemical Co., Ltd., RU) and Al_2O_3 (Taimei Chemical Co., Ltd., TM-D) powders were mixed in a dry condition. The powder was melted in a Pt crucible at 1600°C in air. The glass was composed equimolecular amounts of SiO_2 , Y_2O_3 and Al_2O_3 . The melting point of the equimolar mixture is about 1803 K.²³⁾ The melted glass was quenched by pouring it into water and was ground manually using a Si_3N_4 mortar. The glass obtained was amorphous, as revealed by X-ray diffraction (XRD; Rigaku, RINT-2200) analysis. The powder was compacted by uniaxial pressing at 20 MPa in a die of 18 mm in diameter, followed by cold isostatic pressing at 300 MPa. The compact was heat-treated at 2023 K for 2 h under N_2 pressure of 0.1 MPa. The Si, Y and Al contents before and after heat treatment were measured by chemical analysis.

The Si_3N_4 ceramics were fabricated according to the following procedure. Commercial Si_3N_4 powder (Ube Ind., Ltd., E-10) plus 5 mass% Y_2O_3 and 3 mass% Al_2O_3 were processed by ball-milling with a Si_3N_4 pot and ball for 24 h in ethanol. The mixed powder was compacted by the same method used for the SiO_2 – Y_2O_3 – Al_2O_3 glass. The compacts were sintered at 2023 K (1750°C) for 0 to 16 h under N_2 pressure of 0.1 and 1 MPa in a BN sagger. The Y, Al and O contents before and after sintering were measured by chemical analysis. The quantitative analysis of Si, Y and Al was performed by inductively coupled plasma emission spectroscopy using an ICP spectrometer (Shimadzu, ICPS-2000) and that of O was performed by inert gas fusion method using an EMGA-650 instrument (Horiba).

4. Results and discussion

The SiO_2 – Y_2O_3 – Al_2O_3 glass pellet became an opaline, pore-free glassy block which adhered to the BN sagger. XRD analysis revealed a quartz phase in the glass. The quartz phase was assumed to be precipitated on cooling. After eliminating the adhered part of BN sagger by grinding, chemical analysis of the glass was carried out. The Si, Y and Al contents before and after the heat treatment are shown in Table 2. The values before the heat treatment corresponded to the calculated values of the Si, Y and Al contents; 15.6, 26.2 and 17.6 mass%, respectively, based on

Table 2. Mass Loss and Si, Y and Al Content of the Y-Si-Al-O Glass before and after Heat Treatment at 2023 K in a BN Sagger under N_2 Pressure of 0.1 MPa

Specimen	(mass%)		
	Si	Y	Al
Before heat treatment	15.8	25.8	17.6
After heat treatment	14.4	25.8	17.7

Fig. 3. Relationships between p_{N_2} p_{O_2} at 2000 K for the Si-O-N, Al-O-N and Y-O-N systems.

the mixing ratio of the raw powder. According to the table, the Y and Al contents did not change after the heat treatment, while the Si content decreased from 15.8 to 14.4 mass%. This result suggested that SiO_2 in the glass was vaporized according to Reaction (8) due to the higher SiO vapor pressure, as shown in Fig. 2.

If the value of p_{O_2} around the glass is approximately 10^{-23} Pa, corresponding to the calculated atmospheric condition within the furnace at 2023 K, the stable phases in the Si-O, Y-O and Al-O systems are Si(l), Y(l) and Al(l), respectively. Under a N_2 pressure of 10^5 Pa, Si_3N_4 is stable at p_{O_2} of $< 10^{-9}$ Pa, as shown in Fig. 3. However, neither the metal Si phase nor the Si_3N_4 phase was detected by XRD analysis in the glass. Therefore, it is speculated that the vaporization of $\text{SiO}(\text{g})$ and $\text{O}_2(\text{g})$, followed by Reaction (8) gave rise to a p_{O_2} in the BN sagger, especially near the surface of the glass block and a p_{O_2} was maintained at more than 10^{-10} Pa even though the p_{O_2} in the furnace was approximately 10^{-23} Pa.

Figure 4 shows the Y, Al and O contents in the Si_3N_4 samples before and after sintering at 2023 K. Each value in the figure was corrected to the percentage in the green compact considering the mass losses. In Si_3N_4 ceramics, because Si belongs to either Si_3N_4 or SiO_2 , the behavior of SiO_2 during sintering cannot be discussed based on the Si content. The O content before sintering was 3.8 mass%. This corresponds to the sum of the amount of oxygen in the Si_3N_4 , Y_2O_3 and Al_2O_3 raw powders and the amount of oxygen increased during the processing of mixed Si_3N_4 powder.²⁴⁾ As seen in Fig. 4, the Y and Al contents showed little change even after 16 h of soaking, while the O content decreased with the increase in soaking time. This result suggests that Y_2O_3 and Al_2O_3 are more stable during the sintering of Si_3N_4 ceramics, as mentioned in Section 2, although

Fig. 4. Y, Al and O contents in the Si_3N_4 samples before and after sintering at 2023 K in a BN sagger with Si_3N_4 /BN powder bed under N_2 pressure of 0.1 MPa.

Fig. 5. Mass loss of Si_3N_4 sample sintered at 2023 K under N_2 pressure of 0.1 MPa with Si_3N_4 /BN powder bed as a function of soaking time. Lines A, B, C and D denote the calculated mass losses based on an assumption that the decrease of oxygen resulted from Reactions (8), (9), (10) and (11), respectively.

there is no thermodynamic data for $\text{Y}_2\text{O}(\text{g})$ and $\text{YO}(\text{g})$. Figure 5 shows the relationships between the mass loss and soaking time. The calculated mass loss based on an assumption that the decrease of O is followed by Reaction (8) is represented as line A. A higher $\text{SiO}(\text{g})$ pressure is also attributed to Reactions (9),^{1),13)} (10)^{6),14)} and (11).^{6),14)}

The mass losses calculated using Reactions (9), (10) and (11) are also shown as lines B, C and D, respectively. As seen in this figure, the experimental data (○) were in good agreement with lines B and C. Reaction (10) promotes the dissolution of nitrogen into the oxynitride glass or the formation of AlN in the Si_3N_4 grain boundary, and hence α - or β -SiAlON should be formed when Reaction (10) proceeded. However, α - and β -SiAlON were not detected by XRD analysis in this work. Moreover, the p_{SiO} pressure according

to Reaction (9) is higher than that according to Reaction (10). On the basis of these findings, we concluded that the mass loss of Si_3N_4 ceramics during sintering mainly occurred according to Reaction (9).

Si_3N_4 ceramics is a composite consisting of Si_3N_4 grains and grain boundary glass phase. In this investigation, the grain boundary glass phase was the Si-Y-Al oxynitride glass. It was thought that, although SiO_2 was mainly vaporized from the glass phase in the Si_3N_4 ceramics, the loss reaction was attributed to Reaction (9) rather than to the vaporization of only SiO_2 . The mass loss reaction during the sintering of Si_3N_4 ceramics will be described in detail in our following papers.

From these results, it is concluded that Y_2O_3 and Al_2O_3 are stable at 2023 K in the SiO_2 - Y_2O_3 - Al_2O_3 glass and in the Si_3N_4 ceramics including Si-Y-Al oxynitride glass.

5. Conclusion

The stabilities of SiO_2 , Y_2O_3 and Al_2O_3 , known as sintering aids of the Si_3N_4 ceramics, during sintering were examined from the thermodynamical and the experimental aspects.

(1) Based on the thermodynamical consideration, it is suggested that Y_2O_3 and Al_2O_3 are more stable than SiO_2 in Si-Y-Al oxynitride glass.

(2) SiO_2 - Y_2O_3 - Al_2O_3 (equi-mass%) glass prepared was heat-treated in the BN sagger at 2023 K for 2 h in N_2 gas of 0.1 MPa. The mass loss of the glass during heat treatment was attributed to the vaporization of SiO_2 .

(3) Si_3N_4 with the addition of 5 mass% Y_2O_3 and 3 mass% Al_2O_3 was sintered in a BN sagger at 2023 K for 0 to 16 h in N_2 gas of 0.1 MPa. The Y ion and Al ion contents in the Si_3N_4 ceramics did not decrease even after sintering at 2023 K for 16 h, while the O content decreased with the increase in soaking time. The experimentally measured mass loss was in good agreement with the mass loss calculated using Reactions (9) and (10). The p_{SiO} pressure according to Reaction (9) is higher than that according to Reaction (10). On the basis of these findings, we concluded that the mass loss of Si_3N_4 ceramics during sintering mainly occurred according to the following reaction;

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