Solid–Gas Reaction during Sintering of Si₃N₄ Ceramics (Part 7)
—Temperature Dependence of Mass Loss of Sintered Si₃N₄ Ceramics during Heat Treatment—

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Si₃N₄ セラミックスの焼結過程における固相–気相反応（第7報）
—Si₃N₄ セラミックス焼結体熱処理時の質量損失の温度依存性—

The objectives of the present work are to elucidate the rate-determining factor of mass loss. Sintered Si₃N₄ ceramics were heat-treated at 1823–2098 K under 0.1 MPa N₂ and mass loss during heat treatment was measured. The mass loss increased with increasing temperature and the slope of the Arrhenius plot of the mass loss rate was similar to that of the equilibrium gas pressure of SiO generated from the mass loss reaction of Si₃N₄ ceramics. This finding suggests that the rate-determining factor of mass loss is the diffusion rate of SiO to the outside of the sagger.

Key-words: Si₃N₄ ceramics, Si₃N₄, Sintering, Mass loss, Temperature, SiO(g)

1. Introduction

During the sintering of Si₃N₄ ceramics, some mass loss occurs. The mass loss disturbs the consolidation of Si₃N₄ ceramics and induces the formation of pores and color spots. These phenomena degrade the mechanical properties of Si₃N₄ ceramics. As for Si₃N₄ ceramics with Y₂O₃ and Al₂O₃ as sintering additives, two of the authors previously reported that the mass loss occurs according to Reaction (1).

Si₃N₄(s) + 3SiO₂(l) → 6SiO(g) + 2N₂(g) (1)

In order to suppress the occurrence of this reaction and to obtain dense Si₃N₄ ceramics, gas pressure sintering (GPS), in which high pressure (1–10 MPa) N₂ gas is loaded during sintering, is a well known method. Two of the authors succeeded in sintering Si₃N₄ ceramics with no mass loss even under 0.1 MPa N₂ gas pressure by means of sintering in the mixed powder of Si₃N₄, BN and SiO₂.

An other way to suppress mass loss is to lower the sintering temperature. However, the relationship between mass loss and sintering temperature has not been quantitatively studied yet.

The objectives of the present work are to elucidate the relationship between mass loss of Si₃N₄ ceramics and temperature, and the rate-determining factor of mass loss of Si₃N₄ ceramics.

2. Experimental procedure

Si₃N₄ ceramics were fabricated using the following procedure. Commercial Si₃N₄ powder (UBE Ind., Ltd., E–10), 5 mass% Y₂O₃ (Shin-Etsu Chemical Co., Ltd., RU), and 3 mass% Al₂O₃ (Taihei Chemical Co., Ltd., TM–D) were mixed by ball milling with a Si₃N₄ pot and balls in ethanol for 24 h. The mixed powder was compacted by uniaxial pressing at 20 MPa using a 22 mm diameter die, followed by cold isostatic pressing at 300 MPa. The compact was sintered at 2023 K for 2 h under 1 MPa N₂ in 50 mass%–Si₃N₄ and 50 mass%–BN mixed powder. The density of the sintered samples was from 3.17 to 3.19 g/cm³. After the surface of the sintered sample (0.3 mm) was removed by grinding with a diamond wheel (#800), X-ray diffraction analysis of the sample was carried out to reveal that the crystal phase was only β-Si₃N₄. The sample measured 15.8 by 3.8 mm.

The sample was heat-treated at 1823–2098 K for 20 and 120 min under 0.1 MPa N₂ in a BN sagger with or without BN powder. Figure 1 shows the schematic diagram of the BN sagger. The BN sagger was set in a larger carbon sagger. The three samples were put together under one heat treatment condition.

The mass loss percentage, mass%, of each sample during heat treatment was measured. The mass loss percentage of 20-min-soaked sample was subtracted from that of the 120-min-soaked one, and the obtained value was converted into mass loss percentage per unit time, s⁻¹ (here after referred to as k). The value of k was used for the analysis. The effects of the process of increasing the temperature and cooling on mass loss were eliminated by this operation.

3. Results and discussion

Figure 2 shows the relationship between mass loss percentage per unit time, k/s⁻¹, and heat treatment temperature. Figure 3 shows the Arrhenius plot of k. Each plot of the heat-treated sample with or without BN powder forms a straight line. The slope of the line is −4.1 × 10⁴ for the sample with BN powder, −3.8 × 10⁴ for that without BN powder.

The authors[10,11,12] reported that the mass loss reaction of Si₃N₄ ceramics during sintering is as follows.
Therefore, the atmosphere near the Si₃N₄ samples is composed practically of SiO and N₂, and the sum of the partial pressures of SiO and N₂ is 0.1 MPa. Figure 4 shows the Arrhenius plot of the equilibrium gas pressure of SiO by reaction (1) under the condition of \( P_{\text{SiO}} + P_{\text{N}_2} = 0.1 \text{ MPa} \) obtained by thermodynamical calculation. The slope of this line is \(-5.8 \times 10^4\), which is in fair agreement with that of \( k \).

Since the outer sagger and the furnace are made of carbon, the partial pressure of SiO \( (P_{\text{SiO}}) \) outside the BN sagger is practically zero because of the following Reaction (2).

\[
\text{Si}_3\text{N}_4(s) + 3\text{SiO}_2(l) \rightarrow 6\text{SiO}(g) + 2\text{N}_2(g) \quad (2)
\]

Therefore, the difference in \( P_{\text{SiO}} \) inside and outside the BN sagger is equal to \( P_{\text{SiO}} \) inside BN sagger.

We apply the Fick's law to the diffusion of SiO.

\[
J = -D(\frac{dc}{dx}) \quad (4)
\]

where \( J \), \( D \), and \( c \) are flux, diffusion coefficient, concentration, and position of SiO \( (g) \), respectively. As aforementioned, the gradient of \( P_{\text{SiO}} \) inside and outside the BN sagger is equal to \( P_{\text{SiO}} \) inside the BN sagger. Flux \( J \)/mol·m⁻²·s⁻¹ is,
assuming that the gap of the sagger is the same in all experiments, proportional to $k$. Consequently, $k$ is proportional to the product of $D/m^2 \cdot s^{-1}$ and $p_{SiO}$ inside BN sagger. It is known that the temperature dependence of the diffusion coefficient of a gas, $D$, is determined by the following equation.\(^{13}\)

\[ D_T = D_0 (T/T_0)^n \]  \hspace{1cm} (5)

where $T(T_0)$, $D_T(D_0)$, and $n$ are temperature, diffusion coefficient at $T(T_0)$, and the constant that is characteristic of each gas, respectively.

It is known that the value of $n$ ranges from 1.75 to 2.\(^{13}\) According to this formula, the ratio of $D$ at 2098 K and at 1823 K ($D_{2098}/D_{1823}$) ranges from 1.28 to 1.32, and this value is negligible because the ratio of the equilibrium $SiO$ pressure at 2098 K and at 1823 K is much larger. In other words, the diffusion coefficient $D$ can be treated as a constant. Consequently, $k$ is proportional to the difference in $p_{SiO}$ inside and outside the BN sagger. As aforementioned, according to the experimental results, the slope of the Arrhenius plot of $k$ is near that of the equilibrium gas pressure of $SiO(g)$ via Reaction (2); that is, within the temperature range of this series of experiments, $k$ is proportional to the equilibrium gas pressure of $SiO(g)$ via Reaction (2). Consequently, under the condition that the gap of the BN sagger is sufficiently narrow, $SiO(g)$ reaches the equilibrium gas pressure via Reaction (2) in the BN sagger at the early phase of heat treatment, and the diffusion of $SiO(g)$ out of the sagger determines the mass loss of $Si_2N_4$ samples.

4. Conclusions

Sintered $\beta$-$Si_2N_4$ ceramics were heat-treated at 1823–2098 K under 0.1 MPa $N_2$ gas in the BN sagger with or without BN powder. Mass loss percentage of sample was increased with increasing temperature and the Arrhenius plots of the mass loss percentage per unit time, $k$, were formed a line under the condition of heat treatment both with and without BN powder. The slope of the Arrhenius plot of the equilibrium pressure of $SiO(g)$ via the mass loss reaction:

\[ Si_3N_4(s) + 3SiO_2(l) \rightarrow 6SiO(g) + 2N_2(g) \]  \hspace{1cm} (6)

is similar to those of $k$ both with and without BN powder. This finding suggests that the diffusion of $SiO(g)$ out of the BN sagger determines the rate of mass loss of $Si_2N_4$ samples.

References