Control of Instability of Si_3N_4 during Pressureless Sintering

Shigetaka WADA

Toyota CRDL and Toyota Technological Institute, Nagakute, Aichi 480–1192

常圧焼結における窒化ケイ素不安定性制御

和田重孝

(株)豊田中央研究所兼豊田工業大学, 480–1192 愛知郡長久手町

The instabilities of Si_3N_4 and Si_3N_4 ceramics during sintering are investigated. As a result of the instabilities, Si_3N_4 and Si_3N_4 ceramics lose their mass or decompose. The major mass loss reaction of Si_3N_4 ceramics is shown as follows.

Regarding the mass loss, decreasing the sintering temperature by 30 K corresponds to an increase in N_2 pressure in the furnace by one order magnitude. By understanding well the mass loss phenomenon, Si_3N_4 ceramics will be produced commercially in 0.1 MPa N_2 gas or air.

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1. Introduction

IN 1955, Collins and Gerby reported that reaction-sintered Si_3N_4 has excellent mechanical properties.¹⁾ In 1961, Deeley consolidated Si_3N_4 ceramics from Si_3N_4 powder using a hot-press method.²⁾ Terwilliger³⁾ and Terwilliger and Lange⁴⁾ showed the possibility of consolidation of Si_3N_4 ceramics in 0.1 MPa N_2 gas in 1974 and 1975, respectively. However, the properties of the ceramics were not sufficient for practical applications. In 1976, Mitomo reported the advantage of sintering Si_3N_4 ceramics at high N_2 gas pressure.⁵⁾ However, the mechanical properties were still unsatisfactory.

Si_3N_4 powders with excellent sinterability and sintering additives to reduce sintering temperature were developed in the 1980s. Consequently, Si_3N_4 ceramics can now be sintered at 2000–2100 K.

High mechanical strength at elevated temperatures and large fracture toughness (K_{IC}) are the merits of Si_3N_4 ceramics. To improve those properties, sintering at temperatures above 2000 K is recommended to attain a morphology with a large aspect ratio and a small amount of the grain boundary phase. During sintering at elevated temperature, however, mass loss of Si_3N_4 ceramics occurs. Since an inhomogeneous surface layer or a porous layer is generated as a result of the mass loss, the loss should be decreased as small as possible.

The stability of Si_3N_4 and the Si–O–N system at elevated temperature has been studied thermodynamically.^{6)–12)} Mass loss of Si_3N_4 ceramics during sintering as a result of the instability has been investigated experimentally.^{13)–21)} Although various reactions involved in the instability and mass loss have been reported, no study that treats mass loss quantitatively has been carried out so far.

It is known that pressurized N_2 gas suppresses mass loss of Si_3N_4 ceramics during sintering. Thus, N_2 gas at around 1 MPa (10^6 Pa) has become the predominant sintering condition for Si_3N_4 ceramics in industry. Moreover, issues concerning mass loss and the formation of a heterogeneous surface layer during sintering have become closely guarded as an important “know how” of industry.

Non-pressurized N_2 gas sintering may be a feasible low-

cost fabrication method for Si_3N_4 ceramics. Therefore, we have been engaged in research to clarify the mechanism of the mass loss of Si_3N_4 ceramics during sintering over the past four years.^{22)–29)}

As a result of our research, we found that Si_3N_4 ceramics can be sintered without serious mass loss in air as well as in 0.1 MPa N_2 gas. The instability during heat treatment and sintering of Si_3N_4 and Si_3N_4 ceramics is summarized and the sintering of Si_3N_4 ceramics in 0.1 MPa N_2 gas and in air is reported.

2. Instability of Si_3N_4 and Si_3N_4 ceramics at elevated temperature2.1 Effect of temperature and pressure on the instability of Si_3N_4

Si_3N_4 ceramics are sintered in a N_2 gas atmosphere furnace. The furnace is usually kept in vacuum from room temperature to around 1300 K. This is followed by the introduction of N_2 gas, heating and sintering at a set temperature of 2000–2100 K. When the introduction of N_2 gas is forgotten for some reason, not Si_3N_4 but silicon metal is found in the position originally occupied by the Si_3N_4 specimen after sintering. A researcher of Si_3N_4 ceramics may have experienced this once or twice. This is the result of Reaction (1), namely, Si_3N_4 decomposes to Si(l) and $\text{N}_2(\text{g})$ at the sintering temperature in vacuum.

Here, (s), (l) and (g) indicate solid, liquid and gas, respectively.

Si_3N_4 decomposes to Si(l) and $\text{N}_2(\text{g})$ at 2151 K in normal (10^5 Pa) N_2 gas atmosphere, as seen in the JANAF thermochemical table. Greskovich and Prochazka calculated the thermodynamic equilibrium among $\text{Si}_3\text{N}_4(\text{s})$, Si(l), $\text{N}_2(\text{g})$ and Si(g) for the reactions shown in Eqs. (1) and (2), and the result is shown in Fig. 1.¹³⁾

The following facts are understood from Fig. 1.

(1) The decomposition temperature of $\text{Si}_3\text{N}_4(\text{s})$ in Reaction (1) becomes high with increasing N_2 gas pressure. This relationship is shown by the line with a positive slope in the figure.

(2) $P_{\text{Si}(\text{g})}$ ((partial) pressure of Si gas) in Reaction (2)

Now with Chair Professor, Department of Material Science, Faculty of Science, Chulalongkorn University, Thailand

Fig. 1. Stability diagram for Si_3N_4 , where Si vapor is in equilibrium with Si_3N_4 as a function of N_2 pressure and temperature.

becomes high with increasing temperature and becomes low with increasing atmospheric N_2 gas pressure. This relationship is shown by line with a negative slope in the figure. The absolute value of $P_{\text{Si(g)}}$ is so low, being $P_{\text{Si(g)}} = 10$ Pa even at 2173 K and $P_{\text{N}_2} = 10^5$ Pa (10^5 Pa $\approx$ 1 atm).

The second fact is the reason why Si metal existed in the furnace when Si_3N_4 was sintered in vacuum, that is, Si(l) did not vaporize as Si(g) because $P_{\text{Si(g)}}$ is sufficiently low.

The hatched area in Fig. 1 is the recommended sintering conditions in the 80 th. The high sintering temperature above 2200 K might be due to the poor quality of the raw materials for sintering. Such high temperature required nitrogen gas pressures as high as $P_{\text{N}_2} > 10^6$ Pa. Today, Si_3N_4 powder for easy sintering and sintering additives having low melting temperature require approximately 1900 K to obtain dense Si_3N_4 ceramics.

Consequently, Reaction (1), is rather than Reaction (2), is responsible for the instability of Si_3N_4 at elevated temperature. Mass loss due to Reaction (2) was found to be negligible, because of the low gas pressure of Si.

2.2 Reaction between Si_3N_4 and CO gas

Si_3N_4 ceramics are usually sintered in a carbon heater furnace filled with N_2 gas. Carbon is also used as the material of a sagger. Si_3N_4 decomposes to SiC(s) and N_2 (g) when it contacts with carbon at elevated temperatures, as shown in Eq. (3).

This reaction is not the main reaction of Si_3N_4 with C, because specimens are prevented from direct contact with carbon during production as well as the experiment. One phenomenon that is usually observed is that SiC(s) layer is generated on the surface of the carbon sagger after using it many times. That is due to the following Reactions (4) and (5).

That is, SiO(g) generated by Reaction (4) reacts with carbon and regenerates CO(g) as shown in Eq. (5). From the material balance, Reaction (4) plus (5) is equal to Reaction (3). There are two sources of CO(g) for generating Reac-

Fig. 2. Mass loss of Si_3N_4 powder compacts heat-treated at 2023 K under 0.1 and 1 MPa N_2 in C and BN saggars as a function of soaking time. 0.1 MPa ($\square$) and 1 MPa ($\blacksquare$) with Si_3N_4 powder bed in BN sagger, 0.1 MPa ($\circ$) and 1 MPa ($\bullet$) without powder bed in BN sagger, 0.1 MPa ($\triangle$) and 1 MPa ($\blacktriangle$) with C powder bed in C sagger.

tion (4): one is oxygen impurity in the nitrogen gas used. Industrially pure nitrogen gas, grade B, contains 0.05 Pa oxygen. When $\text{O}_2(\text{g})$ reacts with C(s) in the furnace, 0.1 Pa CO(g) is generated in the furnace. The SiO(g) generated from Reaction (10), mentioned later in 2.3, also generates CO(g) via Reaction (5).

The experimental results of the Reaction between Si_3N_4 (s) and CO(g) are shown in Fig. 2.²⁴ When Si_3N_4 compacts are heat-treated in the presence of carbon powder, about 20 mass% of the mass loss occurs at 2023 K and 2h ($\triangle$). The mass loss is due to Reactions (4) and (5). Then, the same specimens are set in a BN sagger so that the reaction of SiO(g) generated by Eq. (4) with carbon (Reaction (5)) will be controlled. Mass loss decreased to 4.4 mass% even after heat treatment for 8h ($\circ$). Mass loss decreased to 2.5 mass% at 8h when the same specimens were packed in a mixed powder of Si_3N_4 and BN ($\square$). These heat treatments were performed under 0.1 MPa ($\approx$ 1 atm) N_2 gas. Mass loss decreased noticeably when $P_{\text{N}_2(\text{g})}$ was increased to 1 MPa independent of the kind of sagger and the packing powder conditions. The following facts are concluded from the chemical analysis of oxygen and carbon and the X-ray diffraction data of the heat-treated specimens.

(1) Si_3N_4 (s) reacts with CO(g) very rapidly.

(2) By disturbing the reaction of SiO(g) with C(s), the regeneration of CO(g) is controlled. However, CO(g) diffuses into the sagger through the gap of the sagger and reacts with Si_3N_4 (s).

(3) The packing powder, which is the mixture of silicon nitride and BN, controls the diffusion of SiO(g) to the outside of the sagger and stops the access of CO(g) to the specimen by pre-reacting with CO(g) diffusing into the sagger.

Consequently, though Si_3N_4 (s) reacts easily with CO(g), the reaction is controlled practically by means of the sagger and packing powders.

2.3 Reaction between Si_3N_4 and oxygen

Silicon nitride and Si_3N_4 ceramics are easily oxidized in air at elevated temperatures above 1300 K. The oxidation mechanisms are passive oxidation in the atmosphere of $P_{\text{O}_2} \geq 10^2$ Pa and active oxidation at less than 10^2 Pa, as shown in Eqs. (6) and (7).

Fig. 3. Mass loss of Si_3N_4 ceramics sintered at 1923 K for 2 h as a function of oxygen partial pressure, P_{O_2} under N_2 gas flow of 0.1 MPa. Δ mass loss in the region of passive oxidation, $\square$ mass loss in the transition region from passive to active oxidation, $\circ$ mass loss in the region of active oxidation, $\bullet$ mass loss in the region of vaporization.

In the sintering of Si_3N_4 ceramics in a carbon furnace, the oxidation of Si_3N_4 ceramics scarcely occurs because P_{O_2} is as low as 10^{-24} Pa.²²⁾ When Si_3N_4 is sintered using a Mo- or W-heater continuous furnace, however, much amount of oxygen than that in pure nitrogen gas used will exist in the furnace. Then, sintering in flowing N_2 gas with various oxygen partial pressures was performed.²⁶⁾ In this experiment, N_2 gas had to be introduced to control P_{O_2} . Otherwise, P_{O_2} less than 1 Pa could not be attained by the diffusion of air from the outside.

The relationship between P_{O_2} in N_2 gas and mass loss is shown in Fig. 3. When $P_{\text{O}_2} > 10^3$ Pa, passive oxidation obviously occurs because the mass increases. When P_{O_2} is between 10^2 Pa and 10^3 Pa, oxidations both passive and active occur, based on the appearance of the specimens and X-ray diffraction data, though mass loss increased. Though porous bubbles of SiO_2 was on the surface, the inside of the specimens was sintered without porosity. Mass loss decreased quickly when P_{O_2} was reduced to less than 10^2 Pa. However, the mass loss does not decrease to less than about 5 mass% even when P_{O_2} is less than 10^0 Pa. That is, there must be some other mass loss reactions from the active oxidation in flowing N_2 gas atmosphere of $P_{\text{O}_2} < 10^0$ Pa.

Two reactions were observed in flowing $\text{N}_2(\text{g})$ with $P_{\text{O}_2} < 10^0$ Pa. One is Reaction (10), which will be explained in 2.4. The other is Reaction (2), which was mentioned in 2.1 as the reaction of little importance from the standpoint of mass loss. The contribution of Reaction (2) to mass loss in flowing N_2 gas will be explained in 2.5.

Therefore, oxidation is not the direct cause of mass loss of Si_3N_4 ceramics under the condition of $P_{\text{O}_2} < 10^0$ Pa in this experiment.

2.4 Reaction between Si_3N_4 with glass phase component

Silicon nitride ceramics are consolidated by liquid-phase sintering with the addition of Al_2O_3 and Y_2O_3 or MgO as sintering additives. A glass phase composed of SiO_2 , which covers the surface of Si_3N_4 particle, and the additives mentioned above fill grain boundaries at elevated temperature. The free energy of the glass phase, which is composed of several components, can be calculated in general, though it

Fig. 4. Relationship between experimental values of mass loss and calculated ones on the basis of an assumption that all of the oxygen loss occurred via Reaction (10), for the samples sintered at 2023 K under 0.1 and 1 MPa N_2 in BN sagger without powder bed.

is difficult to determine the free energy of the grain-boundary glass phase because its composition changes with the heating process. Then, the stability of the grain-boundary glass phase was evaluated from the stability of each component. Magnesium oxide and $\text{SiO}_2(\text{l})$ easily decompose to $\text{Mg}(\text{g})$, $\text{SiO}(\text{g})$ and $\text{O}_2(\text{g})$ via the reactions shown in Eqs. (8) and (9). On the other hand, $\text{Al}_2\text{O}_3(\text{s})$ and $\text{Y}_2\text{O}_3(\text{s})$ are stable, based on thermodynamic calculations.²²⁾

When SiO_2 - Al_2O_3 - Y_2O_3 glass was heat-treated in N_2 atmosphere at 2023 K, only the quantity of Si ion decreased. The Si ion was thought to be vaporized as $\text{SiO}(\text{g})$.²²⁾

The reaction between $\text{Si}_3\text{N}_4(\text{s})$ and the glass phase is important in the sintering of Si_3N_4 ceramics. Reactions (10)–(13) are considered to be the causes of the mass loss of Si_3N_4 ceramics when Al_2O_3 and Y_2O_3 are used as sintering additives.

$P_{\text{SiO}(\text{g})}$ calculated from the thermodynamic equilibrium in Reaction (10) is the highest among those in Reactions (10)–(13) at the same N_2 gas pressure at 2000–2100 K. When Reaction (10) occurs, oxygen content in the specimen decreases. Mass loss corresponding to the decrease in oxygen content can be calculated from Eq. (10). On the other hand, the mass of specimens is measured precisely before and after sintering.^{24),25)} Comparison of both values showed very good coincidence, as shown in Fig. 4. The major mass loss reaction is, therefore, concluded to be Reaction (10) from the experiment.^{24),25)}

In Reaction (10), $P_{\text{SiO}(\text{g})}$ at thermodynamic equilibrium is related to $P_{\text{N}_2(\text{g})}$ as shown in Eq. (14).^{24),25)}

$$P_{\text{SiO}(\text{g})} \propto (P_{\text{N}_2(\text{g})})^{-1/3} \quad (14)$$

That is, $P_{\text{SiO}(\text{g})}$ is related to $P_{\text{N}_2(\text{g})}$ by the slope of $-1/3$ in the

Fig. 5. Relationship between $\log \Delta M$ and $\log P_{\text{N}_2}$ for samples sintered at 2023 K for 2 h under 0.1 to 100 MPa N_2 in BN sagger.

Fig. 6. Arrhenius plot of mass loss per unit time (k) for the sample sintered under 0.1 MPa N_2 in BN sagger.

$\log/\log$ scale plot. The relationship between mass loss and $P_{\text{N}_2(\text{g})}$ of same specimens as those in Fig. 4 and sintered at 0.1–100 MPa of $P_{\text{N}_2(\text{g})}$ is shown in Fig. 5. Figure 5 shows that the logarithmic value of the mass loss rate of Si_3N_4 ceramics is proportional to $-1/3$ of the logarithmic value of $P_{\text{SiO}(\text{g})}$. As a result, mass loss rate is proportional to $P_{\text{SiO}(\text{g})}$. Specimens were set in a BN sagger and there was no big gap between the lid and the belly of the sagger in the experiment.^{24),25)} The evaporation rate of $\text{SiO}(\text{g})$ from Si_3N_4 ceramics will be controlled by the rates of diffusion of Si and O ions in the grain boundaries, $\text{SiO}(\text{g})$ vaporization from the surface of specimen and $\text{SiO}(\text{g})$ diffusion through the gap of the sagger. Figure 5 suggests that the rate-controlling step is the diffusion rate of $\text{SiO}(\text{g})$ through the gap of the sagger. High N_2 gas pressure in the furnace effectively suppresses the mass loss rate during sintering.

Figure 6 shows the relationship between mass loss and heat-treatment temperature of Si_3N_4 ceramics under almost the same experimental conditions as Fig. 4.²⁸⁾ The mass loss mechanism was confirmed to be the same as that shown

Fig. 7. Mass loss as a function of soaking time for the sample sintered at 1923 K in oxygen pressure of 5.0×10^{-2} Pa under flowing N_2 gas (A) without a covering, (B) with Si_3N_4 packing powder in an Mo crucible.

● Experimental mass loss value, ▲ calculated mass loss value on the basis of the assumption that all of the mass loss occurred via Reaction (10).

in Reaction (10). The slope of the Arrhenius plot of the mass loss is almost the same as that of $P_{\text{SiO}(\text{g})}$. It is seen from the figure that the mass loss rate decreases by one order of magnitude when the heat-treatment temperature decreases by 30 K.

The dependence of $P_{\text{SiO}(\text{g})}$ upon the temperature in Reaction (11) is larger than that in Reaction (10), though the details of the thermodynamic calculation are not shown here. Therefore, Reaction (11) may become the main mass loss reaction at temperatures above 2146 K. When Reaction (11) occurs, Si metal will precipitates in Si_3N_4 ceramics and $\text{SiO}(\text{g})$ will vaporize. This is evidenced by the observation that Si metal is sometimes observed in Si_3N_4 ceramics sintered at very high temperatures.

Consequently, the following are summarized;

- (1) The major mass loss reaction of Si_3N_4 ceramics during sintering is Reaction (10).
- (2) The mass loss rate depends on N_2 gas pressure, as shown by Eq. (14).
- (3) The mass loss rate decreases with decreasing heat-treatment temperature, as shown in Fig. 6.

It should be noted that the mass loss reaction of Si_3N_4 ceramics using MgO or MgAl_2O_4 as sintering additives should be performed hereafter, because $\text{Mg}(\text{g})$ has high vapor pressure, as mentioned in 2.4.

2.5 Effect of gas flow

Figure 7 shows mass loss as a function of soaking time for the sample sintered at 1923 K in $P_{\text{O}_2(\text{g})} = 5.0 \times 10^{-2}$ Pa under flowing N_2 gas (A) without a covering, (B) with Si_3N_4 packing powder in a Mo crucible. Gas flow strongly influences mass loss whether it flows directly on the surface of the specimen or the surface of the specimen is covered from the flowing gas.

It was mentioned in 2.1 that Reaction (2) is not im-

portant. However, as shown in Fig. 7, Reaction (2) cannot be neglected when N_2 gas flows directly on the surface of the specimen; that is, since $Si(g)$ on the surface of the specimen is removed from the surface by the flowing N_2 gas, $P_{Si(g)}$ decreases to a value below the equilibrium value and the reaction proceeds from left to right.

2.6 Packing powder

Si_3N_4 specimens are sometimes sintered in a packing powder. The objective of using the packing powder is to prevent the formation of a surface layer that differs in morphology and properties from the inside part of the specimen. The formation mechanism of the surface layer has not yet been reported in detail. Yokoyama and Wada reported that the surface layer is generated by Reaction (10).^{24),25)}

The vaporization of $SiO(g)$ from specimens is controlled by burying specimens in packing powder. One of the effects of the packing powder is to disturb the diffusion of $SiO(g)$ to outside of the sagger, as mentioned in 2.2. This effect is produced regardless of the kind of powder used.

Another more effective process is to create an $SiO(g)$ atmosphere when Si_3N_4 powder with SiO_2 layer is used as the packing powder. For example, the mass of the specimen increases in the early stage of sintering when Si_3N_4 is used as the packing powder (Fig. 6 of Ref. 24). However, since the amount of SiO_2 on the surface of Si_3N_4 powder is small, the effect is not sustained for a long time.²⁴⁾

The third effect of the Si_3N_4 packing powder is to prevent the reaction of $CO(g)$ with the specimen; that is, the Si_3N_4 packing powder reacts beforehand with $CO(g)$ that diffuses into the sagger through the gap.²⁴⁾

It was reported that AlN sucked out SiO_2 from the grain boundary of Si_3N_4 ceramics.³⁰⁾ The mechanism may be that AlN reacts with $SiO(g)$, thus decreasing the $P_{Si(g)}$ around specimen.²⁹⁾

Such operations as burying and taking off specimens in and from the packing powder are not welcome from the operation time and the dusty environment. Therefore, N_2 gas pressure sintering to suppress Reaction (10) has been used in industry.

3. Sintering of Si_3N_4 ceramics in 0.1 MPa N_2 gas

The science of Si_3N_4 ceramics, especially the sintering technology, has progressed greatly in the 1980s. The morphology in which Si_3N_4 grains have a large aspect ratio has been investigated to attain a large K_{IC} and a high mechanical strength. To attain such properties, sintering temperatures above 2000 K, preferably above 2100 K, have been recommended. Sintering has been performed at 1 MPa N_2 gas to suppress Reaction (10). From the standpoint of sintering cost, normal gas pressure sintering is preferable in the future. To this end, decreasing the sintering temperature and using packing powder are efficient ways, as discussed in 2.5 and 2.6. When the mixed powder of Si_3N_4 and SiO_2 is used as packing powder, $SiO(g)$ atmosphere is sustained for a long time.²⁷⁾ In this case, specimens are not essentially packed in the powder. The role of the mixed powder is to create a $SiO(g)$ atmosphere in the sagger. Then, when some amount of the mixed powder is present in the sagger in the form of pellets, mass loss of specimens as a result of Reaction (10) is controlled.²⁷⁾ Thus, the operation time is shortened and dusty environment problem is solved.

Only a few papers have reported the sintering of Si_3N_4 ceramics with excellent mechanical properties at low temperature and in normal N_2 pressure in the 1980s and the 1990s. Regarding mass loss, decreasing the sintering temperature by 30 K (Fig. 6) is comparable to increasing the N_2 pressure by one order of magnitude (Fig. 5). As far as the mass loss is concerned, it will be negligible even if the Si_3N_4 ceramics are sintered without packing powder when

the sintering temperature is as low as 1900 K. Detailed research on the sintering of Si_3N_4 ceramics at low temperature should be performed hereafter.

4. Sintering of Si_3N_4 ceramics in air furnace

Sintering of Si_3N_4 ceramics in an air furnace has never been attempted so far. The authors have noted that Si_3N_4 ceramics must be sintered in an air after the research which are reviewed in 2.²¹⁾⁻²⁹⁾ Air is composed of 80% N_2 gas and 20% O_2 gas ($P_{O_2} = 2 \times 10^4$ Pa). The important fact is that $P_{N_2} \approx 8 \times 10^4$ Pa; that is, Si_3N_4 does not decompose via Reaction (1) up to 2100 K, as long as $P_{N_2} = 8 \times 10^4$ Pa. The problem is the oxygen content in air, i.e., $P_{O_2} = 2 \times 10^4$ Pa. Silicon nitride ceramics change to SiO_2 by passive oxidation, as shown in Reaction (6), when it is sintered in air. Therefore, the Si_3N_4 specimen must be isolated from air as much as possible.

Then, Si_3N_4 ceramics are sintered in a sagger. Considering the anti-oxidation property and high temperature resistance, Al_2O_3 ceramics are considered to be one of the candidate materials for the sagger. When Si_3N_4 ceramics are sintered in the sagger, there are two different sources of oxygen: one is the oxygen in the sagger, the other is the oxygen diffusing into the sagger through a gap. The amount of oxygen calculated from the volume of the sagger is not so large.¹⁾ When the sagger is filled with Si_3N_4 powder, the powder consumes oxygen in the sagger via Reaction (6) and then, when P_{O_2} in the sagger decreases to below 10^2 Pa, Reaction (7) occurs. Once Reaction (7) occurs, three moles of $O_2(g)$ changes to 6 mol of $SiO(g)$ and 4 mol of $N_2(g)$. Therefore, once active oxidation occurs, the generated gas increases in volume and flows out through the gap of the sagger, thereby decreasing the oxygen partial pressure in the sagger and disturbing the diffusion of air from outside of the sagger. After most of the oxygen in the sagger has reacted with Si_3N_4 , the generated gas flow stops and air will again diffuse into the sagger. However, since the sagger is filled with Si_3N_4 powder, oxygen diffusing into the sagger reacts with Si_3N_4 powder near the gap of the sagger and these will not reach the Si_3N_4 specimen.

Experiments based on the above consideration demonstrated that homogeneous Si_3N_4 ceramics can be sintered without much mass loss.³¹⁾

5. Future work

The science and technology of Si_3N_4 and $SiAlON$ ceramics have progressed rapidly over the past 30 years. However, we have not yet gotten sufficient harvest from the standpoint of the industrial applications. Most of the research performed by academic organizations has been aimed at attaining ultra high strength and ultra large K_{IC} , neglecting process cost in the last 15 years. Those researches have worth in the investigation of the frontier. Materials having excellent properties based on the advanced technologies such as hot-pressing, hot-isostatic-pressing and complicated processes, however, have not found many applications.

Considering these facts, the research to produce Si_3N_4 ceramics with moderate properties and at a cheap cost, for example, sintering at normal N_2 pressure or sintering in air, must be one of the research themes conducted. Research to reduce the cost of Si_3N_4 ceramics on the whole, and not only the sintering cost, should be performed in the future.

6. Summary

The instabilities of Si_3N_4 and Si_3N_4 ceramics during sintering were reviewed. As a result of the instabilities, Si_3N_4 and Si_3N_4 ceramics lose their masses or decompose. The major mass loss reaction of Si_3N_4 ceramics is as follows.

Regarding mass loss, decreasing the sintering temperature by 30 K corresponds to increasing N_2 pressure in the furnace by one order of magnitude. By being well acquired with the mass loss phenomena, sintering of Si_3N_4 ceramics in N_2 gas at 0.1 MPa or air will become the candidate conditions for the mass production of Si_3N_4 ceramics. The research to reduce the total cost of Si_3N_4 ceramics was discussed.

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References

- 1) Collins, J. F. and Gerby, R. W., *J. Metals*, 7, 612 (1955).
- 2) Deeley, G. G., Herbert, J. M. and Moore, N. C., *Powd. Metall.*, No. 8, 145–51 (1961).
- 3) Terwilliger, G. R., *J. Am. Ceram. Soc.*, 57, C48–49 (1974).
- 4) Terwilliger, G. R. and Lange, F. F., *J. Mater. Sci.*, 10, 1169–74 (1975).
- 5) Mitomo, M., *J. Mater. Sci.*, 11, 1103–07 (1976).
- 6) Lou, V. L. K., Mitchell, T. E. and Heuer, A. H., *J. Am. Ceram. Soc.*, 68, 49–58 (1985).
- 7) Wada, H., Wang, M.-J. and Tien, T.-Y., *J. Am. Ceram. Soc.*, 71, 837–40 (1988).
- 8) Heuer, A. H. and Lou, V. L. H., *J. Am. Ceram. Soc.*, 73, 2785–803 (1990).
- 9) Wada, H., *J. Mater. Sci.*, 26, 2590–94 (1991).
- 10) Panek, Z., *J. Am. Ceram. Soc.*, 78, 1087–88 (1995).
- 11) Isomaki, I., NTIS-Report PB96–169735, U. S. Dept. Comm. (1995).
- 12) Rocabois, P., Chatillen, C. and Bernard, C., *J. Am. Ceram. Soc.*, 79, 1351–60, 1361–65 (1996).
- 13) Greskovich, C. and Prochazka, S., *J. Am. Ceram. Soc.*, 64, C96–97 (1981).
- 14) Pompe, R., Eklund, L. and Hermansson L., *Proc. Brit. Ceram. Soc.*, No. 31, 97–105 (1981).
- 15) Lange, F. F., *J. Am. Ceram. Soc.*, 65, C120–21 (1982).
- 16) Messier, D. R. and Deguire, E. J., *J. Am. Ceram. Soc.*, 67, 602–05 (1984).
- 17) Baik, S. and Raj, R., *J. Am. Ceram. Soc.*, 68, C124–26 (1985).
- 18) Heidhardt, U., Schubert, H., Bischoff, E. and Petzow, G., *Key Eng. Mater.*, Vol. 89–91, 187–92 (1994).
- 19) Hwang, S.-L., Becher, P. E. and Lin, H.-T., *J. Am. Ceram. Soc.*, 80, 329–35 (1997).
- 20) Lee, W.-H., Kim, H.-E. and Cho, S.-J., *J. Am. Ceram. Soc.*, 80, 2737–40 (1997).
- 21) Arato, P. and Weber, F., *Key Eng. Mater.*, Vol. 161–163, 221–24 (1999).
- 22) Yokoyama, K. and Wada, S., *J. Ceram. Soc. Japan*, 108, 6–9 (2000).
- 23) Yokoyama, K. and Wada, S., *J. Ceram. Soc. Japan*, 108, 138–43 (2000).
- 24) Yokoyama, K. and Wada, S., *J. Ceram. Soc. Japan*, 108, 230–35 (2000).
- 25) Yokoyama, K. and Wada, S., *J. Ceram. Soc. Japan*, 108, 357–43 (2000).
- 26) Yokoyama, K. and Wada, S., *J. Ceram. Soc. Japan*, 108, 627–32 (2000).
- 27) Yokoyama, K. and Wada, S., *J. Ceram. Soc. Japan*, 109, 238–43 (2001).
- 28) Hattori, T., Wada, S. and Yokoyama, K., *J. Ceram. Soc. Japan*, 109 (2001) in press.
- 29) Hattori, T. and Wada, S., submitted to *J. Ceram. Soc. Japan*.
- 30) Tsuge, A., Inoue, H. and Komeya, K., *J. Am. Ceram. Soc.*, 72, 2014–16 (1989).
- 31) Wada, S., Hattori, T. and Yokoyama, K., *J. Ceram. Soc. Japan*, 109, 281–83 (2001).

Shigetaka Wada was born in Nagano, Japan, on Dec. 7, 1938. He received B. S. Degree from Department of Physics, Nagoya University in 1961 and D. Eng. Degree from Osaka University in 1990. He worked for NGK Insulators, Ltd. from 1961 to 1982 and for Toyota Central R&D Labs. Inc. from 1982 to 2001. He was a Guest Professor for Nagasaki University and Toyota Technological Institute from 1994 to 2001. His research interests now are sintering of Si_3N_4 ceramics and thermal conductivity of ceramic materials.