# Ceramic Processing Research

# The Protective effect of The SiO<sub>2</sub> coating layer on the oxidation of Si<sub>3</sub>N<sub>4</sub>

#### Sea-Hoon Lee<sup>a</sup>, Keun-Ho Auh and Sung-Churl Choi\*

Department of Ceramic Engineering, Hanyang University, 17, Haengdang-dong, Sungdong-Gu, Seoul 133-791, Korea <sup>a</sup>Also affiliated to Max-Planck-Institut für Metallforschung

The microstructure of silicate layers formed by a spray coating technique was observed, and the oxidation behavior of  $Si_3N_4$ with and without the coating layer was investigated. Migration of the silicate phase into the sample was observed when the heat treatment temperature of the coating was higher than 1400°C. Many pores were observed below the silicate layer formed by oxidation of  $Si_3N_4$ , but the pore formation was inhibited in the coated and heat treated (in  $N_2$ ) layer. The oxidized layer contained cristobalite and Y-keivyite, while the formation of cristobalite was suppressed in the coated silicate layer. Oxygen is likely to play an important role for the crystallization of cristobalite in the silicate layer. The  $SiO_2$  coating inhibits the rapid oxidation of  $Si_3N_4$  at 1000°C effectively, and increases the oxidation resistance of  $Si_3N_4$  up to 1300°C.

Key words: Si<sub>3</sub>N<sub>4</sub>, Oxidation, Spray, Coating, SiO<sub>2</sub>.

### Introduction

Si<sub>3</sub>N<sub>4</sub> has excellent high temperature mechanical properties, but suffers at high temperature from poor oxidation resistance. Therefore, intensive research has been performed to clarify the oxidation mechanisms of  $Si_3N_4$ . Lamlik *et al.* reported [1] in their review paper the effect of sintering additives on the crystallization behavior of the silicate layer formed on Si<sub>3</sub>N<sub>4</sub> during oxidation. Alkali metal ions like Na<sup>+</sup> trigger the nucleation of tridymite, and alkaline-earth metal ions tend to promote the crystallization of cristobalite. Meara et al. observed [2] the microstructure of the silicate layer formed by oxidation using TEM. They reported that the oxidation reaction was not restricted to the SiO<sub>2</sub>/ matrix interface but occurred simultaneously in the sub-scale region which constituted a very large oxidation reaction zone. Oxygen can affect the crystallization behavior of silicate phases [3], but the effect on the oxidized layer of Si<sub>3</sub>N<sub>4</sub> has not been investigated so much.

Another problem which limits the application of  $Y_2O_3/Si_3N_4$  is its catastrophic failure caused by volume expansion due to the oxidation of secondary phases at intermediate temperature (~1000°C) [4]. A Hook's law estimation [5] shows that a total volume expansion of 1% generates a stress of about 1 GPa which is of the same order of magnitude as the strength of a fully dense silicon nitride ceramic. Flash oxidation has been proven to be a rather satisfactory solution to the

\*Corresponding author: Tel : +82-2-2290-0505 Fax: +82-2-291-6767

E-mail: choi0505@hanyang.ac.kr

problem [6]. This method consists of pre-oxidizing the specimens at a temperature above the catastrophic region so that the surface of  $Si_3N_4$  is covered with a silica-based protective layer. One of the disadvantages of this technique is pit or flaw formation during the oxidation, which can decrease the mechanical properties of the material.

Spray coating is used in classical ceramics to glaze porcelain. It has several advantages like ease of processing and low production costs. Buchanan *et al.* [7] used a spray coating technique to fabricate the oxidation protective layer on carbon-carbon composites. They mixed an oil-based binder, isopropyl alcohol, and boro-silicate glass powder to form a slurry which was sprayed onto the composite. During heat treatment, the sprayed layer formed a dense boro-silicate coating.

In the present work, **a** protective  $SiO_2$  coating was fabricated by **a** spray coating method, and its effect on the oxidation of  $Si_3N_4$  was investigated. The processing conditions to get a dense coating layer on  $Si_3N_4$  was optimized. The effect of oxygen dissolved in the silicate layer was analyzed by comparing the microstructure and phase formation behavior of silicate layers formed by oxidation and by spray coating. Finally, the oxidation behavior of coated  $Si_3N_4$  at intermediate (1000°C) and at high temperature (1300~1400°C) was observed to investigate the protective effect of the spray coated layer against oxidation.

### **Experimental**

#### Sintering of Si<sub>3</sub>N<sub>4</sub>

Table 1 shows the compositions of the  $Si_3N_4$  materials prepared. To obtain a high sintered density in  $Y_2O_3/Si_3N_4$ , high pressure has to be applied during

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System	Si <sub>3</sub> N <sub>4</sub> (Wt %)	Y <sub>2</sub> O <sub>3</sub> (Wt %)	Al <sub>2</sub> O <sub>3</sub> (Wt %)	MgO (Wt %)	SiO <sub>2</sub> (coating)	BN (Wt %)
Manufacturer Powder type	UBE SN E10	H. C. Starck Grade C	Teimei Chem. Ultra Pure	Merck Extra Pure	Cerac Inc. S-1061	H. C. Stark Grade A01
Sys 1	88	10	_	2	×	_
Bed 1	45	10	_	5	×	40
Sys 2	91	6	3	—	×	_
Bed 2	49	6	5	_	×	40
Sys 3	88	10	_	2	0	_
Sys 4	91	6	3	_	О	-

Table 1. Compositions of the systems

sintering [8]. Alternatively, additional oxides like MgO can be included in the sintering additives. To Sys 1, 2 wt% MgO is added to increase the sintered density. Sys 2 is one of the most common compositions of commercial Si<sub>3</sub>N<sub>4</sub> ceramics. Sys 3 and Sys 4 are the sintered and spray coated Sys 1, and Sys 2 respectively. The powders were dried in a vacuum chamber at 250°C for 24 hours, and mixed for 4 hours by planetary milling with isopropyl alcohol, and additionally for 24 hours in a tumbling mixer using Si<sub>3</sub>N<sub>4</sub> balls. The resultant powder mixtures were dried at 70°C for 24 hours with stirring using a magnetic stirrer and were compacted at 600 MPa using cold isostatic pressing. The pressed samples were embedded in powder beds [9] (Sys 1: Bed 1, Sys 2 : Bed 2), and were sintered in 0.22 MPa  $N_2$  at 1700°C for 3 hours.

## Optimization of SiO<sub>2</sub> slurry and spray coating

A proper viscosity of the slurry is important to get a homogeneous coating layer by the spray coating method. If the viscosity of the slurry is too high, the sprayed droplet size tends to increase [10], and inhomogeneous coating layers are obtained. An organic binder (PVA, polyvinyl alcohol) is used to increase the adhesion and strength of the sprayed layer. In order to optimize the dispersion conditions, the iso-electric point (IEP) of aqueous SiO<sub>2</sub> slurries were measured using a Zetamaster instruments (Malvern). A 20 wt% SiO<sub>2</sub> slurry was fabricated using a planetary mill for 5 hours. The slurry was diluted with de-ionized and double distilled water, and was mixed by magnetic stirrer for 2 hours. The pH value of the diluted slurry was controlled using HCl and NH<sub>3</sub> solutions, and the resultant slurry was mixed for 2 hours before the zeta potential measurement. A 20 wt% SiO<sub>2</sub> slurry with 0.5 wt% PVA was used for the spray coating. The spray coated samples were dried in air for 24 hours and then in a dryer at 50°C for 24 hours.

# Heat treatment of the coating layer and oxidation measurement

The binder in the spray-coated layer was removed in air using the heating schedule shown in Fig. 1(a). Some cracks were observed in sprayed layers annealed with



Fig. 1. Heat treatment conditions (a) removal of binder (b) melting of  $SiO_2$  coating.

higher heating rates, which can be due to the fast thermal decomposition of PVA. After removing the binder, the samples were heat treated in 2.2 atm  $N_2$  atmosphere at temperatures between 1300°C and 1500 °C to form a dense layer on Si<sub>3</sub>N<sub>4</sub> (Fig. 1(b)).

A furnace (L5/S, Nabertherm) and a thermogravimetric analyzer (STA 409, Netzsch) were used to measure the oxidation behavior of the samples. Prior to the studies, the samples were cleaned, in sequence with de-ionized water, isopropyl alcohol and acetone [11]. Four different kinds of samples were prepared, namely: sintered Sys 1 and Sys 2, flash oxidized (at 1300°C) Sys 1 and Sys 2, flash oxidized and etched Sys 1 and Sys 2, etched Sys 3 and Sys 4. In order to examine the

**Table 2.** Sintering properties of Sys 1 and Sys 2

	Weight loss after sintering (%)	Sintering shrinkage (%)	Relative density (%)
Sys 1	0.12	18.1	94.5
Sys 2	1.32	17.9	95.8

effect of the protective silicate layer, the samples were etched in diluted HF solution (20%). To observe the oxidation behavior at intermediate and high temperature, the samples were heated in air at 1000°C (10°C/min) for 24 hours and 72 hours or at 1400°C for 1 hour, and the weight gain of the samples by oxidation was measured. A slower heating rate (5°C/min) was applied using TGA at 1300°C. The microstructure of the oxidized samples was observed by SEM (Stereoscan 200, Cambridge instruments) and XRD (D 5000, Siemens).

# **Results and Discussion**

### Sintering of Si<sub>3</sub>N<sub>4</sub>

Open porosity must be completely eliminated during sintering in order to obtain meaningful oxidation results. The weight loss and shrinkage of Sys 1 and Sys 2 during sintering and the density of the sintered sample are shown in Table 2. Both the samples shows low weight loss and high sintering shrinkage.

#### Fabrication of the SiO<sub>2</sub> slurry for spray coating

The rheological behavior of aqueous slurries can be controlled by changing the pH of the system [12]. The particles in the slurry loose their repulsive electrostatic interaction as the pH of the system approaches the isoelectric point (IEP). As a result, agglomeration of the particles occurs and the viscosity of the slurry increases. The IEP of Quartz and silica fume are known to be pH 2 [13] and pH 3.45, respectively. The different IEP values of quartz and silica fume are due to the different degree of hydration of their surfaces



Fig. 2. Zeta potential of  $SiO_2$  slurries with and without 0.5 w/o PVA

[14]. The surface of silica is covered by silanol groups, whereas the surface of quartz is relatively inert, being covered mostly by siloxane groups. The number of these groups can be changed by ball milling, which affects the IEP of the  $SiO_2$  slurry.

Figure 2 shows the zeta potential values of the  $SiO_2$  slurry versus pH. The IEP of the slurry is at pH 2.8. The absolute value of the zeta potential is decreased by adding PVA, but the IEP is not much affected by the addition of that binder [15]. The zeta potential value changes through the region of pH 2.5~pH 4. Therefore, the slurry was adjusted to pH 5 for the spray coating.

# Heat treatment of the coating and microstructure examination

The silicate layer which was heat treated at 1300°C peeled off from the substrate, while a dense layer was formed when the heat treatment temperature was at 1400°C. The lowest ternary eutectic point of the SiO<sub>2</sub>-MgO-Y<sub>2</sub>O<sub>3</sub> system is 1385°C [16], and the heat treatment temperature of Sys 3 should be higher than this to form a liquid phase on the surface of Si<sub>3</sub>N<sub>4</sub>.

Figure 3 shows the microstructure of oxidized Sys 1 and heat treated Sys 3. Many pores are formed near the silicate layer of Sys 1, while pore formation is suppressed in Sys 3 after the heat treatment in  $N_2$  at the same temperature. Two gas formation reactions during the oxidation of  $Si_3N_4$  are possible:

$$Si_3N_{4(s)} + 3SiO_{2(s)} \rightarrow 6SiO_{(g)} + N_{2(g)}$$
 [17] (1)

$$2Si_{3}N_{4(s)} + 3O_{2(g)} \to 6SiO_{(g)} + 4N_{2(g)}$$
(2)

The results show that the pore formation during the oxidation mainly follows formula (2).

A silicate layer which has >3  $\mu$ m thickness is formed on the surface of Sys 3 when the heat treatment temperature is 1400°C. A migration of this silicate layer into the Si<sub>3</sub>N<sub>4</sub> material is already observed at 1400°C (Fig. 3(b)), and little silicate layer survives on the surface of Si<sub>3</sub>N<sub>4</sub> when the heat treatment temperature is 1500°C (Fig. 3(c)). Backhaus-Ricoult *et al.* investigated [18] the oxidation behavior of Si<sub>3</sub>N<sub>4</sub>. Silicate phases that were formed by the oxidation of Si<sub>3</sub>N<sub>4</sub> migrated into the inner part of the samples, and the amount of silicate phase under the surface of oxidized Si<sub>3</sub>N<sub>4</sub> was increased by the migration.

By oxidation at 1400°C, pores begin to form below the surface of Sys 2, while the pore formation is suppressed in Sys 4. A silicate layer with >2  $\mu$ m thickness is formed after the heat treatment of Sys 4 at 1400°C (Fig. 4(b)), but the layer vanishes with increas-



Fig. 3. Microstructure of (a) Sys 1 oxidized at 1400°C and Sys 3 heat treated at (b) 1400°C (c) 1500°C ( $\Box$ ): migration of silicate phase and dissolution of Si<sub>3</sub>N<sub>4</sub> grains,  $\blacktriangle$ : pore formation).



Fig. 4. Microstructure of (a) Sys 2 oxidized at 1400°C and Sys 4 heat treated at (b) 1400°C (c) 1450°C (d) 1500°C ( $\blacktriangle$  : pore formation,  $\Rightarrow$ : silicate phase from the coating layer).



**Fig. 5.** XRD data after the heat treatment (a) Sys 1, after sintering (b) Sys 1, after oxidation at 1400°C (c) Sys 3, after heat treatment in N<sub>2</sub> at 1400°C (d) Sys 3, after heat treatment in N<sub>2</sub> at 1500°C ( $\mathbf{\bullet}$  :  $\beta$ -Si<sub>3</sub>N<sub>4</sub>,  $\mathbf{\bullet}$  : Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>,  $\mathbf{\bullet}$  : Y<sub>2</sub>Si<sub>3</sub>O<sub>3</sub>N<sub>4</sub>,  $\mathbf{\nabla}$  : MgSiO<sub>3</sub>,  $\mathbf{+}$ : SiO<sub>2</sub> (cristobalite)).

ing heat treatment temperature. Part of the silicate layer survives after the heat treatment at 1450°C (Fig. 4(c)), and the migration of the silicate phase can be clearly seen below the surface of the sample. Only a small fraction of the silicate layer remains on the surface of Sys 4 when the heat treatment temperature is 1500°C. The migrated silicate is not clearly seen in Fig. 4(d), which is likely to be due to a more homogeneous distribution of the phase in the samples at 1500°C.

The phases formed in the silicate layer change with oxidation temperature. The Crystallization temperature of amorphous silicate to cristobalite is known as 1000°C to 1200°C, and Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> crystallizes at 1200°C. Babini et al. report [19] on the phase formation of Si<sub>3</sub>N<sub>4</sub> during oxidation using MgO and Y<sub>2</sub>O<sub>3</sub> as sintering additives. In their report, the amount of the  $Y_2Si_2O_7$ phase increases rapidly at 1385°C. Over 1400°C, Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> peaks decrease, and cristobalite was the main phase up to 1500°C. Figure 5 shows the XRD data of Sys 1 and Sys 3 before and after the surface treatment. Y-keivyite  $(Y_2Si_2O_7)$  and cristobalite  $(SiO_2)$  are formed in the silicate layer of Sys 1 after oxidation. By contrast, the cristobalite phase is not detected in the layer formed by the spray coating method. The crystallization of the silicate layer is affected by the oxidation temperature



**Fig. 6.** XRD data after the heat treatment (a) Sys 2, after sintering (b) Sys 2, after oxidation at 1400°C (c) Sys 4, after heat treatment in N<sub>2</sub> at 1400°C (d) Sys 4, after heat treatment in N<sub>2</sub> at 1500°C ( $\bullet$  : β-Si<sub>3</sub>N<sub>4</sub>,  $\bullet$  : Y<sub>10</sub>Si<sub>3</sub>Al<sub>2</sub>O<sub>18</sub>N<sub>4</sub>,  $\blacksquare$  : Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, ♥ : Y<sub>5</sub>Si<sub>3</sub>O<sub>12</sub>N,  $\frac{1}{2}$ : SiO<sub>2</sub> (cristobalite)).

and the presence of metallic ions. Boganov *et. al.* reported [20] that cristobalite can be crystallized in oxygen-deficient vitreous silica only when oxygen is contained in the atmosphere during the heat treatment. It is reasonable to think that the silicate layer of Sys 3 which is formed by the heat treatment in N<sub>2</sub> contains less oxygen than the native oxide layer of Sys 1. The difference in the oxygen content of the silicate layers can be one of the reasons for the different crystallization behavior of Sys 1 and Sys 3, although the difference in metal ion content can also affect the crystallization behavior of cristobalite [21].

Sys 2 shows similar crystallization behavior as Sys 1 after oxidation (Fig. 6). A small amount of cristobalite, together with  $Y_8Si_4N_4O_{14}$ , is detected in Sys 4, but the cristobalite formation is still suppressed as in Sys 3.

# Oxidation behavior with and without the protective coating

Table 3 shows the weight gain of samples after 24 hours and 72 hours of oxidation at 1000°C. In the case of Sys 2, the weight gain by oxidation is not much affected by the further treatment. In contrast, flash oxidation and the spray coating technique do affect the 1000°C oxidation behaviors of Sys 1. The microstructure of oxidized samples (Fig. 7) gives a hint as to

Table 3. The weight gains of samples after 24 hours and 72 hours of oxidation at 1000°C

System		Sys 1	Sys 1 (Flash Oxidized)	Sys 1 (F. O. & etched)	Sys 3 (etched)
Weight Gain	24 hr	0.20	0	0.11	0
(%)	72 hr	0.41	0.19	0.22	0
System		Sys 2	Sys 2 (Flash Oxidized)	Sys 2 (F. O. & etched)	Sys 4 (etched)
Weight Gain	24 hr	0	0	0	0
(%)	72 hr	0.12	0.12	0.12	0.12

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**Fig. 7.** Microstructure of samples after 72 hours of oxidation at 1000°C: (a) flash oxidized and etched (40 minutes) Sys 1 (b) etched (20 minutes) Sys 4 (  $\triangleright$  : Silicate phase formed under the coating layer by oxidation).

the different weight gain behavior of Sys 1 and Sys 2. A silicate layer is not formed on the surface of flash oxidized and etched Sys 1 after 72 hours of oxidation even if the weight of the sample increases by 0.22%. Looking at Sys 4, a new silicate layer is formed under the coating layer, which can clearly explain the 0.12% weight gain. The results suggest that the weight gain of Sys 1 originates from the oxidation of the  $Y_2Si_2O_3N_4$  phase which is located in the grain boundaries, while the oxidation of Sys 2 and Sys 4 follows the ordinary passive oxidation mechanism of Si<sub>3</sub>N<sub>4</sub>.

During the heat treatment of spray coated samples in  $N_2$  at 1400°C, the pore formation is suppressed, because oxygen, which causes the pore formation reaction according to formula (1), can not be supplied. During the heat treatment, the metal ion content under the surface of  $Si_3N_4$  decreases due to diffusion into the silicate layer [22]. Since the diffusion rate of metal ions increases with temperature, the heat treatment temperature will affect the metal ion content in grain boundaries under the silicate layer, and thus the resistance of the samples against oxidation [23].

The oxidation behavior of Sys 1 at 1000°C is im-

proved by the flash oxidation technique. However, flash oxidized samples are reported to suffer from the 1000°C oxidation problem if the protective silicate layer is damaged [1]. To investigate the effect of surface damage on the oxidation at 1000°C, the coating layers were etched by an HF solution, and the weight gain behavior of samples prepared by different methods (sintered Sys 1 and Sys 2, flash oxidized Sys 1 and Sys 2, flash oxidized and etched Sys 1 and Sys 2, etched Sys 3 and Sys 4) was observed. The silicate layer remains after 20 minutes of etching (Fig. 7(b)), but most of it is removed after 40 minutes (Fig. 7(a)). An over-etched microstructure is observed when the etching time is longer than 40 minutes. Based on these results, the etching time of the silicate layer was fixed at 40 minutes.

No weight gain is observed in Sys 3 even after the etching, which implies that the protective effect of Sys 3 is more reliable than that of flash oxidized Sys 1. One possible explanation for this observation is the difference of the heat treatment temperature. Intensive pore formation is observed in Sys 1 and Sys 2 flash oxidized at 1400°C (Fig. 3(a), Fig. 4(a)). The pore formation, which can decrease the mechanical properties of samples, limited the maximum temperature for flash oxidation up to 1300°C.

Figure 8 shows the weight gain of Sys 2 and Sys 4 during oxidation at 1300°C. The weight gain of Sys 2 begins at 1000°C and increases linearly with temperature. By contrast, weight gain is not detected in Sys 4 until the temperature reaches approximately 1200°C, and the slope above 1200°C is still flatter for Sys 4 than that for Sys 2. This result suggests that the silicate layer formed by spray coating inhibits the oxidation of Si<sub>3</sub>N<sub>4</sub> up to this temperature effectively. The metal ion content in the silicate layer of Sys 4 is likely to be lower than that of Sys 2, because the pure SiO<sub>2</sub> sprayed on the surface of Si<sub>3</sub>N<sub>4</sub> dilutes the metal ion content during the heat treatment. The thickness of the silicate layer will also affect the oxidation behavior, because



Fig. 8. Weight gain of samples by oxidation (a) Sys 2 and (b) Sys 4.

more time is needed for the inward diffusion of oxygen or outward diffusion of metal ions if the thickness of the layer increases. At the maximum oxidation temperature (1300°C), the slopes of Sys 2 and Sys 4 becomes similar after a holding time of about 250 minutes. This result suggests that the protective effect of the coating layer decreases with increasing oxidation time. During the long-term oxidation, metal ions have enough time to diffuse into the silicate layer, and can reach a saturation level. After an oxidation time of 500 minutes, the weight gains of Sys 2 and Sys 4 are 0.75% and 0.4% respectively, and the oxidation behavior of Si<sub>3</sub>N<sub>4</sub> at 1300°C is improved by the spray coating method.

## Conclusions

From the results outlined above, the following conclusions can be drawn:

- Dense silicate layers on Si<sub>3</sub>N<sub>4</sub> were obtained by the spray coating method.
- Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and the silicate coating layer disappear after a heat treatment in N<sub>2</sub> at 1500°C, which is likely to be due to the migration of silicate melt into the samples.
- Many pores are observed below the silicate layer formed by the oxidation of  $Si_3N_4$ , while the pore formation is suppressed in the silicate layer formed by spray coating of  $SiO_2$  on  $Si_3N_4$  and a subsequent heat treatment in  $N_2$ . Pore formation during the oxidation mainly results from the reaction between  $Si_3N_4$  and oxygen which diffuses through the silicate layer.
- Y-keivyite (Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>) and cristobalite are formed in the native silicate layer, while cristobalite formation is suppressed in the coated silicate layer. The difference of oxygen content can be the reason of the different crystallization behavior of the silicate layers.
- The spray coating technique decreases the oxidation rate of  $Si_3N_4$  at 1000°C, and the protective effect is sustained even after etching the protective silicate layer with HF.
- Oxidation is strongly inhibited by the coating layer up to 1200°C. After the oxidation at 1300°C for 500 minutes, the weight gains of the unprotected and protected  $Si_3N_4$  are 0.75% and 0.4% respectively, which means the oxidation behavior of  $Si_3N_4$  at 1300°C is improved by the spray coating method.

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