Oxidation Resistance and Strength Retention of Silicon Nitride Coated with Lutetium Disilicate

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Lu₂Si₂O₇ コートした窒化ケイ素の耐酸化性及び強度保持性

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Silicon nitride (Si₃N₄) coated with lutetium disilicate (Lu₂Si₂O₇) layer through the intermediate silica (SiO₂)-rich phase was fabricated by reaction sintering after dip-coating. The Lu₂Si₂O₇ layer with a thickness of 3–29 μm was formed on Si₃N₄ substrate. It was relatively dense with several pores, and strongly jointed to the substrate through the intermediate phase. Oxidation resistance and strength retention of the coated Si₃N₄ were investigated and compared with those of the uncoated Si₃N₄. Apparent activation energy for oxidation at 1300–1500°C in air increased up to 523.1 kJ/mol with increasing thickness of the coating layer, which was about 1.7 times higher than that of the uncoated Si₃N₄ (310.3 kJ/mol). After long-term cycling oxidation at 1500°C for up to 1000 h in air, the total weight gain decreased by up to 51%, indicating that oxidation resistance improved by about 100%. The improvement was attributed to the protection of the substrate from an oxidative environment by the Lu₂Si₂O₇ layer and underlying SiO₂-rich phase. Flexural strength of the coated Si₃N₄ was not deteriorated before and after the cycling oxidation at 1500°C for up to 1000 h in comparison with that of the uncoated Si₃N₄. However, the high-temperature strength at 1400–1500°C in air was a little less than that of the uncoated Si₃N₄. The deterioration was attributed to the softening of amorphous SiO₂ phase, which existed in the intermediate phase (between the Lu₂Si₂O₇ layer and substrate) and inside the substrate.

[Received March 3, 2004; Accepted April 27, 2004]

Key-words : Lutetium disilicate, Silicon nitride, Dip-coating, Reaction sintering, Oxidation resistance, Strength retention

1. Introduction

Si₃N₄ has excellent thermomechanical properties: high strength at elevated temperatures, low thermal expansion coefficient, and high thermal shock resistance.^{(1)–(6)} Therefore it has a potential to replace conventional super alloy materials, which are currently used for high-temperature structural applications such as stator, rotor and combustor of gas turbine. To use it at higher temperatures (~1500°C) without cooling air as a component of gas turbine would increase thermal efficiency with a simultaneous decrease of emission of CO₂ and NO_x. Great efforts have been made to achieve this goal, and the mechanical properties have been improved remarkably. For example, Si₃N₄ doped with Lu₂O₃ system as additives, such as SN 281 and SN 282 (Kyocera Corp.), has achieved higher creep resistance^{(7), (8)} and higher strength at elevated temperatures⁽⁹⁾ than Si₃N₄ using other additives and provided comparable fracture toughness.⁽¹⁰⁾ These excellent mechanical properties are attributed to Lu₂SiO₅, Lu₂Si₂O₇ and Lu₄Si₂O₇N₂ phases with high melting points in the grain boundary regions.^{(7)–(11)}

However, one problem of Si₃N₄ is relatively low oxidation resistance at elevated temperatures.⁽¹²⁾ This low oxidation resistance is related to the grain boundary phases, which are produced from additives of Si₃N₄. Intrinsically, Si₃N₄ is difficult to sinter due to the low self-diffusivity, and additives such as Y₂O₃, Al₂O₃, MgO, and Yb₂O₃ are used to promote the densification through the liquid-phase sintering.^{(1), (4), (13)} These additives react with Si₃N₄ and SiO₂ (formed by oxidation of Si₃N₄), forming amorphous and crystalline phases in the grain boundary regions during the densification. The amorphous phases accelerate the oxidation of Si₃N₄ by the migration of additive cations.⁽¹⁴⁾ When the oxidation progresses, Si₃N₄ is damaged beneath the SiO₂ scale (produced by oxidation of Si₃N₄) with several pores, leading to the deterioration of mechanical properties.^{(15), (16)} Therefore, it is necessary to prevent the oxidation of Si₃N₄. Recently the oxidation resistance has been improved by crystallizing the grain boundary phases,⁽¹⁴⁾ by using additives with small cationic radius and high melting point in the system of SiO₂–RE₂O₃ (RE: rare earth cation),⁽¹⁷⁾ and by using nanoparticles such as SiC and MoSi₂ in the grain boundary regions.^{(18)–(20)} However, these improvements are insufficient for practical use in severe environments, and it is necessary to further improve the oxidation resistance.

In the present research, Si₃N₄ was coated with Lu₂Si₂O₇ layer through the intermediate SiO₂-rich phase. Lu₂Si₂O₇

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has extremely high chemical stability at high temperatures and a thermal expansion coefficient close to that of Si_3N_4 .²¹⁾ The coated Si_3N_4 was fabricated by reaction sintering after dip-coating. This coating process is simple, easy, cost-effective, and applicable even to complex-shaped components. Therefore it is much more suitable for industrial applications than are other processes such as chemical vapor deposition, spray coating, sputtering and hot-pressing. Three kinds of coated specimens were prepared to examine the oxidation resistance: single-, triple-, and 5-times-coated ones. Apparent activation energy for oxidation was examined at 1300–1500°C in air. Long-term cycling oxidation behavior was investigated at 1500°C for up to 1000 h in air. The flexural strength after the long-term cycling oxidation was examined, and so was high-temperature strength.

2. Experimental procedure

2.1 Materials

The raw materials used for the present research were α -rich Si_3N_4 (SN-E10, UBE Industries, Ltd.; >99.5% purity), Lu_2O_3 (Shin-Etsu Chemical Co., Ltd.; 99.9% purity), and SiO_2 (quartz, Kojundo Chemical Laboratory Co., Ltd.; 99.9% purity, 0.8 μm particle size) powders. Si_3N_4 was mixed with 8 mass% of Lu_2O_3 and 2 mass% of SiO_2 in ethanol for 48 h by using ball mill, and cold isostatic pressed (CIPed) at 392 MPa before pressure sintering. It was pressure-sintered in 1 MPa- N_2 atmosphere at 2000°C for 4 h in graphite resistance furnace (FVPHP-R-10, FRET-40, Fujidempa Kogyo Co., Ltd.). The specimens with dimensions of 3 × 4 × 37 mm were cut and ground (R_a : <0.2 μm), and their edges were chamfered at 45°.

The coated specimens were prepared by the reaction sintering method after dip-coating. The slurry for dip-coating was composed of Lu_2O_3 and SiO_2 powder with dispersant (A-6114, Toagosei Co., Ltd.), polyvinyl alcohol aqueous solution (163-03045, Wako Pure Chemical Industries, Ltd.; about 500 average polymerization degrees), deformer (RA-20A, Matsumoto Yushi-Seiyaku Co., Ltd.), and distilled water. The detailed composition is summarized in Table 1. It was ball-milled for 48 h. The composition of $\text{SiO}_2/\text{Lu}_2\text{O}_3$ in the slurry for the 1st coating was 1.0 (molar ratio), which was less than the stoichiometric composition of $\text{Lu}_2\text{Si}_2\text{O}_7$ ($\text{SiO}_2/\text{Lu}_2\text{O}_3 = 2.0$), because SiO_2 was generated by oxidation of Si_3N_4 in the sintering process of the coating layer. The specimens dipped in the slurry were CIPed at 392 MPa before reaction sintering. This CIP treatment was performed in order to densify the $\text{Lu}_2\text{Si}_2\text{O}_7$ coating layer by increasing the initial density before sintering. Reaction sintering was conducted in air at 1550°C for 20 h. The heating rate was 2.6°C/min, and the cooling rate was 3.1°C/min down to 1000°C followed by natural cooling. Triple- and 5-times-coated specimens were also prepared by repeating the above-mentioned method 3 times and 5 times, respectively. (In the 2nd–5th coating, the composition of $\text{SiO}_2/\text{Lu}_2\text{O}_3$ in the slurry was 2.0 (molar ratio), because the formation of SiO_2 during the sintering was suppressed by the 1st coating layer.)

2.2 Evaluation of the coated Si_3N_4

To obtain apparent activation energies for oxidation, the coated and uncoated specimens were exposed to air at 1300, 1350, 1400, 1450, and 1500°C for up to 100 h. Long-term cycling oxidation tests were conducted at 1500°C in a static air atmosphere. It took 100 h for each cycle, and 10 cycles were carried out (total oxidation time was 1000 h). All the specimens were set on the triangular poles of Si_3N_4 (same as the uncoated specimen) during the oxidation test, in order to

Table 1. Composition of the Slurry for Coating

Composition	mass%
Lu_2O_3 and SiO_2 powder	59.6
PVA 5mass% aqueous solution	11.9
Dispersant	3.0
Deformer	0.6
Distilled water	24.9

Fig. 1. Schematic of the specimen setting in the furnace.

prevent the direct diffusion of impurities such as Na from Al_2O_3 plate to specimens. Schematic of the specimen setting in the furnace was shown in Fig. 1. Before and after the cycling oxidation at 1500°C for 100, 500, and 1000 h, the four-point bending tests (inner and outer spans were 10 mm and 30 mm, respectively) were conducted at room temperature at a cross-head speed of 0.5 mm/min (Sintech 10/GL, MTS Systems Corp., U.S.A.). High-temperature flexural strength before oxidation was also measured at 1200, 1300, 1400, and 1500°C in air using a system (Model 1186 and 4500, Instron Corp., U.S.A.). Four specimens were used for the measurements. The microstructures and compositions were examined by scanning electron microscopy (SEM; JSM-5600 and JSM-6330F, JEOL) and energy dispersive spectroscopy (EDS; JED-2140, JEOL), respectively. Crystalline phases were identified by X-ray diffractometry (XRD; RINT 2000, Rigaku Corp.), using $\text{Cu K}\alpha$ radiation at 40 kV and 100 mA. The surface roughness of the specimens was defined by arithmetic mean roughness value (R_a) using a test machine (SV-624-3D, Mitutoyo Corp.).

3. Results and discussion

3.1 Characterization of the coated Si_3N_4

The density of the uncoated Si_3N_4 specimen was 3.35–3.37 g/cm³, and almost 100% of the theoretical density. Figure 2 shows the XRD pattern. The β - Si_3N_4 phase with $\text{Lu}_2\text{Si}_2\text{O}_7$ in the grain boundary regions was observed. The $\text{Lu}_2\text{Si}_2\text{O}_7$ phase in the grain boundary regions was the same with that of coating layer, leading to the chemical compatibility between the layer and Si_3N_4 substrate.

Using the reaction sintering method after dip-coating, Si_3N_4 was coated with $\text{Lu}_2\text{Si}_2\text{O}_7$ layer through the intermediate SiO_2 -rich phase. Figure 3 shows SEM micrographs of surface and cross section of the coated specimens (Fig. 3(3) for the single-coated one, and Figs. 3(1), (2), and (4) for the triple-coated one). The composition and crystalline phases of the coating layer were characterized by EDS (Fig. 4) and XRD (Fig. 5) analyses, respectively. From these analyses, it was found that $\text{Lu}_2\text{Si}_2\text{O}_7$ layer was coated on the Si_3N_4 substrate through the intermediate SiO_2 -rich phase. The layer was relatively dense

Fig. 2. XRD pattern of the uncoated Si_3N_4 (■ $\beta\text{-Si}_3\text{N}_4$ (33-1160), ● $\text{Lu}_2\text{Si}_2\text{O}_7$ (34-0509)).

Fig. 3. SEM micrographs of the coated Si_3N_4 ((1) surface of the triple-coated one, (2) magnified surface of the triple-coated one, (3) cross section of the single-coated one, (4) cross section of the triple-coated one).

with several pores, and strongly jointed to the substrate. The amorphous and crystalline (cristobalite) SiO_2 -rich phase was formed by the oxidation of the substrate through several pores in the $\text{Lu}_2\text{Si}_2\text{O}_7$ layer during the sintering process. The SiO_2 -rich phase increased with increasing thickness of the coating layer. It was because the total sintering time of the coating layer was longer in the specimen with thicker layer, to progress further oxidation of Si_3N_4 . **Table 2** shows the thickness of the layer, average grain size in the layer, aspect ratio, and surface roughness (R_a) of each of the coated specimens (with data after long-term cycling oxidation at 1500°C for 1000 h in air). The thickness of the layer was 3–6 μm for the single-coated specimen, 12–16 μm for the triple-coated one, and 26–29 μm for the 5-times-coated one, respectively. It indicates that simply repeating coating process could control the thickness of the layer. The average grain sizes in the layer were 2.10–2.76 μm , and average aspect ratios were 1.51–1.59. There was no distinct difference in the grain size and aspect ratio among all the coated specimens. R_a of the coated ones before oxidation was relatively small (0.20–0.24 μm), indicating that the coating layer was very homogeneous although the coating method

Fig. 5. XRD pattern of the triple-coated Si_3N_4 (● $\text{Lu}_2\text{Si}_2\text{O}_7$ (34-0509), ▼ SiO_2 (cristobalite: 39-1425)).

Fig. 4. SEM-EDS analyses of the coating layer ((1) SEM micrograph of the cross section of the triple-coated Si_3N_4 . Element mapping of (2) Lu, (3) Si, and (4) O, indicated by white color).

Table 2. Thickness of the Coating Layer, Average Grain Size in the Layer Aspect Ratio, and Surface Roughness (R_a) of Each of the Single-, Triple-, and 5-Times-Coated Si_3N_4 Before and After Long-Term Cycling Oxidation Test at 1500°C for 1000 h in Air

	Thickness / μm		Average grain size / μm		Average aspect ratio		Roughness: R_a / μm	
	before	after	before	after	before	after	before	after
Single-coated	3-6	2-4	2.76 ± 1.26	4.69 ± 2.10	1.52 ± 0.49	1.53 ± 0.38	0.22 ± 0.03	1.43 ± 0.40
Triple-coated	12-16	10-14	2.10 ± 0.95	7.12 ± 3.00	1.51 ± 0.47	1.55 ± 0.47	0.24 ± 0.03	0.88 ± 0.29
5-times-coated	26-29	23-29	2.31 ± 1.01	8.69 ± 4.41	1.59 ± 0.50	1.56 ± 0.42	0.20 ± 0.04	0.47 ± 0.08

was quite simple.

3.2 Oxidation resistance

In general, when Si_3N_4 is oxidized, SiO_2 scale is generated by the following Reaction (1).

In the case of the oxidation of Si_3N_4 with additives, silicate phases are also generated by the migration of additive cations from the grain boundary regions to the surface. Therefore, oxygen or cation diffusion is rate controlling in oxidation of Si_3N_4 , and oxidation behavior obeys a parabolic law as follows:

$$\Delta m^2 = k_p t \quad (2)$$

where Δm is the weight gain per unit surface area, k_p is the parabolic oxidation rate constant, and t is the oxidation time. The oxidation rate constant at each temperature of 1300 to 1500°C was examined to obtain Arrhenius plots, as shown in Fig. 6. The calculated apparent activation energy was 310.3 kJ/mol, 455.6 kJ/mol, and 523.1 kJ/mol for the uncoated, single-coated, and triple-coated specimens, respectively. They increased with increasing the thickness of the coating layer.

Long-term cycling oxidation behaviors were investigated at 1500°C for up to 1000 h in air for the uncoated, single-coated, triple-coated, and 5-times-coated specimens. The weight gains were described as a function of square root of time, as shown in Fig. 7. The plot of the uncoated specimen showed linearity, indicating that oxidation behavior obeyed a parabolic law (Eq. (2)). However, in the case of the coated ones, small deviations from linearity were observed. The deviations were

attributed mainly to the diffusion of SiO_2 phase to the measured specimens from the triangular pole of Si_3N_4 during oxidation, which was used for setting the specimens. In fact, the area of the coated specimens contacted with the triangular pole contained more SiO_2 phase than the un-contacted area. The total weight gain was 0.336 mg/cm², 0.248 mg/cm², and 0.225 mg/cm² for single-coated, triple-coated and 5-times-coated specimens, respectively; they were all less than that of the uncoated one, 0.444 mg/cm². It decreased with increasing the thickness of the coating layer and underlying SiO_2 -rich phase. However, the difference of weight gains between triple- and 5-times-coated specimens was small. The total weight gain decreased by up to 51%, indicating that oxidation resistance improved by about 100%. The improvement was attributed to the protection of the substrate from an oxidative environment by the $\text{Lu}_2\text{Si}_2\text{O}_7$ layer and underlying SiO_2 -rich phase.

Figure 8 shows XRD patterns of the surface of the uncoated and triple-coated specimens after the oxidation at 1500°C for 1000 h in air. In the case of the uncoated specimen, large amount of SiO_2 (cristobalite) phase was generated and $\text{Lu}_2\text{Si}_2\text{O}_7$ phase increased remarkably after the oxidation. The cristobalite phase was formed by the oxidation of Si_3N_4 , and $\text{Lu}_2\text{Si}_2\text{O}_7$ phase was formed by reaction between SiO_2 and remaining Lu_2O_3 or related elements in grain boundary regions of Si_3N_4 . The XRD pattern of $\text{Lu}_2\text{Si}_2\text{O}_7$ phase in the uncoated specimen showed strong preferred orientation of (h k 0) plane. The peaks related to (110) and (220) planes drastically increased after the oxidation. It indicates that

Fig. 6. Arrhenius plots of the uncoated (◆), single-coated (■), and triple-coated (▲) Si_3N_4 at 1300–1500°C in air.

Fig. 7. Long-term oxidation behaviors of the uncoated (◆), single-coated (■), triple-coated (▲), 5-times-coated (●) Si_3N_4 at 1500°C for up to 1000 h in air.

Fig. 8. XRD patterns of the uncoated (1) and triple-coated (2) Si_3N_4 after long-term oxidation at 1500°C for 1000 h in air (■ β - Si_3N_4 (33–1160), ● $\text{Lu}_2\text{Si}_2\text{O}_7$ (34–0509), ▼ SiO_2 (cristobalite: 39–1425)).

Fig. 9. SEM micrographs of the surface (i) and cross section (ii) of the uncoated (1) and triple-coated (2) Si_3N_4 after long-term oxidation at 1500°C for up to 1000 h in air.

$\text{Lu}_2\text{Si}_2\text{O}_7$ was crystallized anisotropically during the oxidation. Such anisotropic crystallization of oxidation product was also observed in the case of $\text{RE}_2\text{Si}_2\text{O}_7$ by other researchers.^{14),19)} In the case of the triple-coated specimen, the cristobalite phase also increased a little. It indicates that Si_3N_4 was somewhat oxidized to form cristobalite, and/or that the pre-existed SiO_2 -rich phase was further crystallized to generate large amount of cristobalite with small amount of amorphous SiO_2 . The $\text{Lu}_2\text{Si}_2\text{O}_7$ phase in the coating layer was maintained without phase transition.

Figure 9 shows SEM micrographs of the surface and cross section of the uncoated and coated specimens after the oxidation at 1500°C for 1000 h in air. In the case of the uncoated one, SiO_2 scale with a thickness of 6–10 μm was generated with $\text{Lu}_2\text{Si}_2\text{O}_7$ particles. The surface was drastically cracked, because of the large mismatch of thermal expansion coefficients between SiO_2 scale and Si_3N_4 substrate. In the case of the triple-coated one, $\text{Lu}_2\text{Si}_2\text{O}_7$ layer did not completely protect the substrate. SiO_2 scale also existed between the layer and substrate, and some cracks were observed in the scale. It was due to the oxidation of the substrate, and due to the further crystallization of the pre-existed intermediate SiO_2 -rich phase (amorphous and crystalline SiO_2 phase before the oxidation). The oxidation presumably occurred through several pores of the $\text{Lu}_2\text{Si}_2\text{O}_7$ layer, which permitted oxygen to approach the substrate and intermediate SiO_2 -rich phase, and in fact small weight gains of the coated specimens occurred. The SiO_2 scale beneath the $\text{Lu}_2\text{Si}_2\text{O}_7$ layer in the coated specimens influenced the surface roughness. Figure 10 shows the surface roughness (R_a) of the specimens as a function of oxidation time. R_a increased with increasing the oxidation time. It also increased with decreasing the thickness of the coating layer, probably because the SiO_2 scale lifted the thinner layer up relatively easily when the scale increased between the layer and substrate. However, it should be noted that no delamination was observed in all the coated specimens even after the oxidation. It indicates that the coating layer with SiO_2 scale was strongly jointed to the substrate. The thickness of the coating layer after the oxidation became smaller than that before (Figs. 3, 9 and Table 2), indicating further densification of the layer progressed. This densification also progressed with grain growth. Figure 11 shows the average grain size of the coating layer and aspect ratio as a function of oxidation time. The grain size increased with increasing oxidation time and

Fig. 10. Surface roughness of the uncoated ($\diamond$), single-coated ($\blacksquare$), triple-coated ($\blacktriangle$), 5-times-coated ($\bullet$) Si_3N_4 as a function of oxidation time at 1500°C in air.

Fig. 11. Average grain size and aspect ratio in each coating layer of single-coated ($\blacksquare$, $\square$), triple-coated ($\blacktriangle$, $\triangle$), 5-times-coated ($\bullet$, $\circ$) Si_3N_4 as a function of oxidation time at 1500°C in air. Black colored marker indicates average grain size and white colored one indicates aspect ratio.

increasing the thickness of the coating layer. It indicates that grains in the thicker layers have less constraint from the substrate than those in the thinner ones, leading to the further progress of grain growth. The aspect ratio was maintained during the oxidation in all the coated specimens.

The densification of the coating layer with grain growth means that the fabricated layer was not perfectly dense but had several pores. $\text{Lu}_2\text{Si}_2\text{O}_7$ layer would be densified by longer oxidation time at higher temperatures (although the substrate would be also oxidized to form more SiO_2 phase in this case) and by making more SiO_2 -rich composition of the slurry for coating (the accelerated densification would occur through the liquid phase sintering of SiO_2 – Lu_2O_3 system in this case). However, the excessive SiO_2 phase would cause the delamination of the coating layer through the volatilization of SiO_2 in more severe corrosive environment containing water vapor.^{22),23)} Therefore, it is necessary to further develop a coating layer, which is perfectly dense with neither pores nor SiO_2 phase.

3.3 Strength retention after oxidation

Figure 12 shows the flexural strengths of the uncoated, and coated specimens at room temperature before and after long-term cycling oxidation at 1500°C for up to 1000 h in air. Before the oxidation, the strength of the uncoated specimen was smaller (~ 470 MPa) than that of commercial Si_3N_4

Fig. 12. Flexural strengths of the uncoated, single-coated, triple-coated, 5-times-coated Si_3N_4 before and after long-term oxidation at 1500°C for up to 1000 h in air. Error bars stand for ± 1 standard deviations.

Fig. 13. Retentions of flexural strengths of the uncoated, single-coated, triple-coated Si_3N_4 from room temperature to 1500°C in air. Error bars stand for ± 1 standard deviations.

perhaps due to the grain growth. The strengths of the coated specimens, except that of the single-coated one, were a little higher than that of the uncoated one before the oxidation. It was attributed mainly to the healing of defects inside and on the substrate by heat treatment during the sintering process of the coating layer. This healing phenomenon in Si_3N_4 ceramics was observed by other researchers.²⁴⁾ After the oxidation, the strengths of the triple-coated and 5-times-coated specimens were maintained, while the uncoated and single-coated ones showed the strength increase. The strength increase of the uncoated one after the oxidation was presumably due to oxidation-induced strengthening effects including healing of defects as well as compressive stress by the formed SiO_2 scale.^{24),25)} This result, however, was different from the results by other researchers,^{15),16)} where the damage of the substrate beneath the scale with several pores degraded the strength. The observed strength increase after the oxidation was probably because the effect of the damage of substrate was less than the effect of the oxidation-induced strengthening in the range of relatively low strength (400–600 MPa).

3.4 Strength retention at high temperatures

The high-temperature bending tests of the uncoated and coated specimens were conducted at 1200 – 1500°C in air, and the strength retentions were examined, as shown in Fig. 13.

The strengths at 1200 and 1300°C were all higher than those at room temperature with small standard deviations. It was attributed to the healing effect inside and on the substrate. The uncoated specimen showed very good strength retention at high temperatures, which was attributed to the formation of $\text{Lu}_2\text{Si}_2\text{O}_7$ in the grain boundary regions with high melting point and to its crystallization during the sintering process of Si_3N_4 (Fig. 2). In addition, Lu^{3+} has a small ionic radius, and produces a stronger grain boundary phase.³⁾ The single-coated and triple-coated specimens also showed good high-temperature strength; however, the strength retentions at 1400 – 1500°C were not as good as that of the uncoated specimen. This was presumably because the coated specimens contained amorphous SiO_2 phase in the intermediate SiO_2 -rich phase (between the $\text{Lu}_2\text{Si}_2\text{O}_7$ layer and substrate) and inside the substrate, which was softened at 1400 – 1500°C . This speculation was supported by the fractured surface observations (Fig. 14). The fractured surface of the coated specimen was macroscopically flatter than that of the uncoated one. Therefore, it is very important to fabricate the coating layer without SiO_2 phase for high-temperature strength retention as well as for high oxidation resistance in severe environment.

Fig. 14. Typical fractured surfaces of the uncoated (1) and triple-coated (2) Si_3N_4 at 1500°C in air.

4. Conclusions

Si_3N_4 coated with $\text{Lu}_2\text{Si}_2\text{O}_7$ layer through the intermediate SiO_2 -rich phase was successfully fabricated by reaction sintering after dip-coating. The layer with a thickness of $3\text{--}29\ \mu\text{m}$ was relatively dense with several pores and strongly jointed to the substrate through the intermediate phase. Simply repeating the coating process could control the thickness of the layer. The surface roughness was relatively small ($0.20\text{--}0.24\ \mu\text{m}$), indicating that the coating layer was very homogeneous although the coating method was quite simple.

The apparent activation energy of the coated Si_3N_4 ($523.1\ \text{kJ/mol}$) for oxidation at $1300\text{--}1500^\circ\text{C}$ in air was up to about 1.7 times higher than that of the uncoated one ($310.3\ \text{kJ/mol}$). After long-term cycling oxidation at 1500°C for up to 1000 h in air, the oxidation resistance was improved up to about 100% by increasing the thickness of coating layer. The improvement was attributed to the protection of the substrate from an oxidative environment by $\text{Lu}_2\text{Si}_2\text{O}_7$ layer and underlying SiO_2 -rich phase.

Flexural strength of the coated Si_3N_4 at room temperature was not deteriorated before and after the oxidation in comparison with that of the uncoated Si_3N_4 . However, the strength at 1400 and 1500°C in air was a little less than that of the uncoated Si_3N_4 . This deterioration was probably because the coated Si_3N_4 contained amorphous SiO_2 phase in the intermediate phase (between the $\text{Lu}_2\text{Si}_2\text{O}_7$ layer and substrate) and inside the substrate, and it was softened at $1400\text{--}1500^\circ\text{C}$.

The coating process used for the present research was simple, easy, and cost-effective. It was also applicable to complex-shaped components, and quite suitable for industrial applications. However, it is necessary to further develop a process in order to fabricate completely dense coating layer with neither pores nor SiO_2 phase for higher oxidation and corrosion resistance as well as for higher strength retention at high temperatures.

Acknowledgements This work has been supported by the Ministry of Economy, Trade and Industry (METI) of Japan as part of the Synergy Ceramics Project. Part of the work has

been supported by the New Energy and Industrial Technology Development Organization (NEDO). The authors are members of the Joint Research Consortium of Synergy Ceramics. They wish to express their gratitude to Masahiro Asayama, Seiichi Suenaga and Takayuki Fukasawa of Toshiba Corp. and to Shunkichi Ueno of the National Institute of Advanced Industrial Science and Technology (AIST), for assistance received in the course of this work.

References

- 1) Tsuge, A. and Nishida, K., *Am. Ceram. Soc. Bull.*, Vol. 57, pp. 424–426 (1978).
- 2) Komeya, K., *Am. Ceram. Soc. Bull.*, Vol. 63, pp. 1158–1159 (1984).
- 3) Sanders, W. A. and Mieskowski, D. M., *Am. Ceram. Soc. Bull.*, Vol. 64, pp. 304–309 (1985).
- 4) Knickerbocker, S. H., Zangvil, A. and Brown, S. D., *J. Am. Ceram. Soc.*, Vol. 68, pp. C99–C101 (1985).
- 5) Cinibulk, M. K., Thomas, G. and Johnson, S. M., *J. Am. Ceram. Soc.*, Vol. 75, pp. 2050–2055 (1992).
- 6) Anzai, K. and Hashimoto, H., *J. Mater. Sci.*, Vol. 12, pp. 2351–2353 (1977).
- 7) Wiederhorn, S. M. and Ferber, M. K., *Current Opinion in Solid State and Materials Science*, Vol. 5, pp. 311–316 (2001).
- 8) Lofaj, F., Wiederhorn, S. M., Long, G. G., Hockey, B. J., Jemian, P. R., Browder, L., Andreason, J. and Taffner, U., *J. Eur. Ceram. Soc.*, Vol. 22, pp. 2479–2487 (2002).
- 9) Guo, S., Hirosaki, N., Yamamoto, Y., Nishimura, T. and Mitomo, M., *Scripta Materialia*, Vol. 45, pp. 867–874 (2001).
- 10) Guo, S., Hirosaki, N., Yamamoto, Y., Nishimura, T. and Mitomo, M., *J. Eur. Ceram. Soc.*, Vol. 23, pp. 537–545 (2003).
- 11) Hirosaki, N., Yamamoto, Y., Nishimura, T., Mitomo, M., Takahashi, J., Yamane, H. and Shimada, M., *J. Am. Ceram. Soc.*, Vol. 85, pp. 2861–2863 (2002).
- 12) Mieskowski, D. M. and Sanders, W. A., *J. Am. Ceram. Soc.*, Vol. 68, pp. C160–C163 (1985).
- 13) Park, H., Kim, H.-E. and Niihara, K., *J. Am. Ceram. Soc.*, Vol. 80, pp. 750–756 (1997).
- 14) Cinibulk, M. K., Thomas, G. and Johnson, S. M., *J. Am. Ceram. Soc.*, Vol. 75, pp. 2044–2049 (1992).
- 15) Guo, S., Hirosaki, N., Yamamoto, Y., Nishimura, T. and Mitomo, M., *J. Am. Ceram. Soc.*, Vol. 85, pp. 1607–1609 (2002).
- 16) Klemm, H., Taut, C. and Wötting, G., *J. Eur. Ceram. Soc.*, Vol. 23, pp. 619–627 (2003).
- 17) Choi, H.-J., Lee, J.-G. and Kim, Y.-W., *J. Mater. Sci.*, Vol. 32, pp. 1937–1942 (1997).
- 18) Park, H., Kim, H.-W. and Kim, H.-E., *J. Am. Ceram. Soc.*, Vol. 81, pp. 2130–2134 (1998).
- 19) Kim, H.-W., Koh, Y.-H. and Kim, H.-E., *J. Mater. Res.*, Vol. 15, pp. 1478–1482 (2000).
- 20) Klemm, H. and Schubert, C., *J. Am. Ceram. Soc.*, Vol. 84, pp. 2430–2432 (2001).
- 21) Suetsuna, T., Ishizaki, M., Ando, M., Kondo, N., Ohji, T. and Kanzaki, S., *J. Ceram. Soc. Japan*, Vol. 112, pp. 301–304 (2004).
- 22) Jacobson, N. S., Opila, E. J. and Lee, K. N., *Current Opinion in Solid State and Materials Science*, Vol. 5, pp. 301–309 (2001).
- 23) Klemm, H., *J. Eur. Ceram. Soc.*, Vol. 22, pp. 2735–2740 (2002).
- 24) Choi, S. R. and Tikare, V., *Scripta Metall. Mater.*, Vol. 26, pp. 1263–1268 (1992).
- 25) Lange, F. F., *J. Am. Ceram. Soc.*, Vol. 63, pp. 38–40 (1980).