Lutetium Disilicate Coating on Silicon Nitride for High Temperature Oxidation Resistance

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Lu₂Si₂O₇ コーティングによる窒化ケイ素の高温酸化抑制効果

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Lutetium disilicate (Lu₂Si₂O₇) layer of 4–12 μm in thickness with a small amount of silica (SiO₂) phase was coated on silicon nitride (Si₃N₄) by reaction sintering after dip coating. The oxidation resistance and flexural strength of the coated sample were investigated and compared with those of the uncoated one. After cycling oxidation at 1500°C for up to 100 h in air, the total weight gain of the coated sample was almost half that of the uncoated one, indicating that oxidation resistance of Si₃N₄ was improved by about 100%. The flexural strength of the coated sample was not deteriorated in comparison with that of the uncoated one, and it was also maintained after the cycling oxidation at 1500°C for 100 h in air. Those physical and chemical stabilities can be attributed to the presence of Lu₂Si₂O₇ layer, which effectively prevents oxidation of Si₃N₄ at high temperature.

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1. Introduction

Si₃N₄ has excellent thermo-mechanical properties; high strength at elevated temperatures, low coefficient of thermal expansion, and high thermal shock resistance.^{1)–3)} Therefore, it is one of the most promising materials for high temperature structural applications such as stator, rotor, and combustor of gas turbine engines. For example, the use of it for components of gas turbine engines would effectively improve the thermal efficiency by realizing higher operating temperature than that achieved by the conventional super-alloy materials.

However, one problem is that its oxidation resistance is relatively low at elevated temperatures (–1500°C).⁴⁾ When it is oxidized in air, SiO₂ scale with silicate glassy and/or crystalline phases (by reacting SiO₂ with grain boundary phase of Si₃N₄) is formed with a cracked surface, leading to the deterioration of mechanical properties. It has been known that the oxidation resistance of Si₃N₄ is improved by using nanoparticles such as SiC and MoSi₂ in the grain boundary region,^{5),6)} or by crystallizing the grain boundary phase.⁷⁾ However, these improvements are not sufficient, and it is necessary to further improve the oxidation resistance.

In the present research, in order to realize better oxidation resistance, Si₃N₄ was coated with Lu₂Si₂O₇, which had extremely high chemical stability and close coefficient of thermal expansion to that of Si₃N₄. The sample coated with Lu₂Si₂O₇ was fabricated by reaction sintering after dipping Si₃N₄ substrate into Lu₂O₃–SiO₂ slurry. This coating process is easy and applicable even to complex-shaped components. It is also more cost-effective than other methods such as the chemical vapor deposition and plasma spray, and therefore suitable for industrial applications. Two kinds of coated samples were prepared for investigating the influence of thickness of coating layer on preventing the oxidation; one is single coated sample,

and the other is triple coated sample. These samples were exposed to cycling oxidation test at 1500°C for up to 100 h in air, and the weight changes and flexural strength at room temperature after the oxidation were examined.

2. Experimental procedure

Prior to fabricating the samples coated with Lu₂Si₂O₇, the coefficients of thermal expansion of pure Lu₂Si₂O₇ and β-Si₃N₄ (same as the substrate for coating) were examined at temperatures from 30 to 1400°C in Ar atmosphere. The samples with dimensions of 3 × 4 × 20 mm were cut and ground (R_a : < 0.2 μm). The heating rate was 5°C/min, and sapphire (Al₂O₃ single crystal) was used as a reference sample.

The Si₃N₄ used in the present research was prepared by gas pressure sintering (2000°C, 4 h, under 1 MPa–N₂ atmosphere) of Si₃N₄ with additive system of Lu₂O₃–SiO₂. The samples with dimensions of 3 × 4 × 37 mm were cut and ground (R_a : < 0.2 μm), and the edges of the samples were chamfered at 45°. The coated samples were prepared by the reaction sintering method after dipping Si₃N₄ substrate into the slurry of Lu₂O₃–SiO₂ (SiO₂/Lu₂O₃ = 1.0; molar ratio) with dispersant, binder, deformer, and water. The concentration of Lu₂O₃–SiO₂ into the slurry was 60 mass%. The dipped samples were cold isostatic pressed at 392 MPa before reaction sintering. The reaction sintering was conducted at 1550°C for 20 h in air. The triple coated sample was prepared by repeating the above-mentioned process; in the second and third coating, the mole ratio of SiO₂/Lu₂O₃ in the slurry was 2.0.

The coated and uncoated samples were exposed to cycling oxidation at 1500°C in air, and the samples were weighed before and after cycling. The heating rate was 2.5°C/min, and the cooling rate was 2.8°C/min down to 1000°C followed by natural cooling. It took 25 h for one cycle, and weight changes

were measured in each cycle. In total, four cycles were carried out (the total oxidation time was 100 h). The samples were set on the triangle pole of Si_3N_4 . The four-point flexural strength test (inner and outer spans were 10 and 30 mm long, respectively) was performed at a cross-head speed of 0.5 mm/min at room temperature before and after the cycling oxidation. Four samples were used for each measurement. The microstructures and compositions of the samples were examined by scanning electron microscopy (SEM), energy dispersive spectroscopy, and X-ray diffractometry (XRD).

3. Results and discussion

Figure 1 shows the coefficients of thermal expansion of pure $\text{Lu}_2\text{Si}_2\text{O}_7$ and $\beta\text{-Si}_3\text{N}_4$ at temperatures from 30 to 1400°C in Ar atmosphere. In this temperature range their coefficients were very close and the maximum difference was $0.6 \times 10^{-6} ^\circ\text{C}^{-1}$ at 300°C , indicating very small mismatch of thermal expansion between $\text{Lu}_2\text{Si}_2\text{O}_7$ and $\beta\text{-Si}_3\text{N}_4$. Therefore, $\text{Lu}_2\text{Si}_2\text{O}_7$ is considered to be suitable for coating $\beta\text{-Si}_3\text{N}_4$ without delamination.

The slurry composition of $\text{SiO}_2/\text{Lu}_2\text{O}_3$ for the first 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 formed by the oxidation of Si_3N_4 in sintering process of the coating layer. After reaction sintering, single coated and triple coated samples had $\text{Lu}_2\text{Si}_2\text{O}_7$ layers with a thickness of about $4\text{ }\mu\text{m}$ and $12\text{ }\mu\text{m}$ on the Si_3N_4 substrate, respectively (**Fig. 2**). These layers were relatively dense with a few pores

and jointed to the substrate, containing a small amount of SiO_2 phase. This phase was formed between the coating layer and substrate by the oxidation of the substrate during the sintering of $\text{Lu}_2\text{Si}_2\text{O}_7$.

The weight gains of the uncoated and coated samples are shown as a function of square root of time in **Fig. 3**. The plots of all the samples deviated somewhat from the linearity, the deviation being more pronounced in the case of the coated samples, indicating the weight gain did not obey a pure parabolic law ($\Delta m^2 = kt$; Δm : weight change, k : parabolic oxidation rate constant, t : time), which is most often used for describing oxidation behavior. This deviation can be presumably attributed mainly to the diffusion of SiO_2 phase to the samples from the triangle pole of Si_3N_4 during oxidation, which was used for setting the samples. The total weight gains of the coated samples (single coating: 0.11 mg/cm^2 , triple coating: 0.099 mg/cm^2) were almost half that of the uncoated sample (0.18 mg/cm^2), indicating that oxidation resistance of Si_3N_4 was improved by about 100%. The small weight gains of the coated samples were caused by the diffusion of oxygen through a few pores in the $\text{Lu}_2\text{Si}_2\text{O}_7$ layer. The total weight gain of the triple coated sample was less than that of the single coated one. However, the difference in the total weight gains between the single and triple coated samples was relatively small, indicating small influence of the thickness of the coating layer on preventing the oxidation. **Figure 4** shows the XRD patterns of the surface of the uncoated and triple coated samples before and after the oxidation test at 1500°C for 100 h in air. In the case of the uncoated sample, SiO_2 and $\text{Lu}_2\text{Si}_2\text{O}_7$

Fig. 1. Coefficients of thermal expansion of $\beta\text{-Si}_3\text{N}_4$ (○) and $\text{Lu}_2\text{Si}_2\text{O}_7$ (■).

Fig. 3. Cycling oxidation behaviors of the uncoated sample (◆), single coated sample (■), and triple coated sample (▲) (at 1500°C for up to 100 h in air).

Fig. 2. SEM micrographs of cross section of the single coated (A) and triple coated (B) samples fabricated by reaction sintering after dip coating.

Fig. 4. XRD patterns of the uncoated (A) and triple coated (B) samples before (i) and after (ii) cycling oxidation at 1500°C for 100 h in air ($\text{Lu}_2\text{Si}_2\text{O}_7$ (● 34-0509), SiO_2 (▼ 39-1425), $\beta\text{-Si}_3\text{N}_4$ (■ 33-1160)).

Fig. 5. SEM micrographs of the uncoated (A) and triple coated (B) samples after cycling oxidation at 1500°C for 100 h in air ((i) surface, (ii) cross section).

phases increased remarkably after the cycling oxidation. It is considered that SiO_2 phase was formed by oxidation of Si_3N_4 substrate and reacted with remaining Lu_2O_3 or related elements at grain boundary of the substrate to produce $\text{Lu}_2\text{Si}_2\text{O}_7$. On the other hand, in the case of the triple coated sample, SiO_2 phase increased little, indicating that $\text{Lu}_2\text{Si}_2\text{O}_7$ layer protected the Si_3N_4 substrate from oxidation. The good oxidation resistance of the coated samples was also confirmed by SEM observation for the surface and cross section of the triple coated sample after the oxidation as shown in Fig. 5. In the case of

the uncoated sample, SiO_2 scale with a thickness of about 3 μm formed with $\text{Lu}_2\text{Si}_2\text{O}_7$ particles, and the surface was cracked. This is because of large mismatch in coefficients of thermal expansion between the scale and substrate. In contrast, it is noticed that the $\text{Lu}_2\text{Si}_2\text{O}_7$ layer protected well the Si_3N_4 substrate in the case of the triple coated sample. The layer was densified with a thickness of about 10 μm , which was less than that before the oxidation test. This indicates that further sintering of $\text{Lu}_2\text{Si}_2\text{O}_7$ progressed during oxidation, and that oxidation resistance of Si_3N_4 would improve further by

Fig. 6. Flexural strengths of the uncoated, single coated, and triple coated samples before (□) and after (■) cycling oxidation at 1500°C for 100 h in air. Error bars stand for ± 1 standard deviations.

fabricating more densified $\text{Lu}_2\text{Si}_2\text{O}_7$ layer in the future.

Figure 6 shows the flexural strength of the uncoated, single coated, and triple coated samples before and after the cycling oxidation test at 1500°C for 100 h in air. The flexural strength of the coated sample was not deteriorated before the oxidation in comparison with that of the uncoated one, although that of single coated one was relatively low with a large standard deviation. It was also maintained after the oxidation, whereas the strength of the uncoated sample was deteriorated a little because of the cracked surface by the formation of SiO_2 scale. The small improvements of the strengths of the coated samples after the oxidation were probably because of the healing of the defects inside the substrate during the oxidation. These results indicate that the coating layer of $\text{Lu}_2\text{Si}_2\text{O}_7$ protected Si_3N_4 from oxidation.

4. Conclusion

$\text{Lu}_2\text{Si}_2\text{O}_7$ layer of 4–12 μm in thickness with a small amount of SiO_2 phase was coated by reaction sintering after dip coating. The oxidation resistance and flexural strength of the coated samples were investigated and compared with those of the

uncoated sample.

Although the fabricated layer was somewhat porous, the total weight gain of the coated sample was almost half that of the uncoated sample after the cycling oxidation test at 1500°C for up to 100 h in air, indicating that oxidation resistance of Si_3N_4 was improved by about 100%. The improvement of the oxidation resistance can be attributed to the $\text{Lu}_2\text{Si}_2\text{O}_7$ layer, which protected Si_3N_4 substrate from oxidation. The weight gain became less when the coating layer was thicker, but the effect of thickness on preventing the oxidation was relatively small. The flexural strength of the coated sample was not deteriorated in comparison with that of the uncoated one. It was also maintained after the cycling oxidation at 1500°C for 100 h in air. Those physical and chemical stabilities can be attributed to the presence of $\text{Lu}_2\text{Si}_2\text{O}_7$ layer, which effectively prevents oxidation of Si_3N_4 .

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