Improvement of high-temperature oxidation resistance to water vapor by alumina coating on beta-sialon ceramic

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To improve oxidation resistance to water vapor in high-temperature environment, alumina (Al_2O_3) film is coated on β -sialon ($z=3$) ceramic. Aluminum alkoxide ($\text{Al}(\text{OBt})_3$) with diethanolamine and ethanol and Al_2O_3 sol with ethanol were used as precursor solutions. These precursors were coated on β -sialon substrate by dip coating method and the coated sample was heated at 600°C for 1 h (as-coated sample). The as-coated sample was heat-treated at 1300°C in Ar/O_2 (95/5 vol%) for 2 h and subsequently treated in Ar for 10 h (heat-treated sample). The samples were oxidized in $\text{Ar}/\text{O}_2/\text{H}_2\text{O}$ (8/2/90 vol%) at 1200°C for ~ 100 h. The heat-treated samples showed high oxidation resistance to water vapor comparing with as-coated sample.

Key words: sialon, alumina, oxidation, water vapor, coating

1. INTRODUCTION

Because of excellent mechanical properties, good oxidation resistance in high temperature condition and high thermal shock resistance, Si-Al-O-N (sialon) ceramics have been promising high-temperature structural materials for components of engines or gas turbines.¹ Generally high oxidation resistance of silicon based non-oxide ceramic to dry oxygen is achieved by the presence of protective surface layer based on amorphous SiO_2 .^{1, 2} In atmosphere containing water vapor, however, the silicon based non-oxide ceramics are easily oxidized, because a large amount of water comparing with oxygen is able to dissolve in amorphous SiO_2 and oxidizes the ceramics.³⁻⁶ Therefore, for the application in high-temperature and high $P_{\text{H}_2\text{O}}$ conditions, environmental barrier coating (EBC) to water vapor is needed. Alumina (Al_2O_3) and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) have been utilized as barrier coating materials because of high chemical stability and mechanical properties.⁷ In the mullite-coated ceramics, delamination between the coating and substrate due to poor adherence brings about an issue to overcome.⁷ To develop adhesivity of mullite coating, it is reported that alumina was coated on Si_3N_4 ceramic and was transformed to mullite by reaction between the coated alumina and SiO_2 , which is formed by oxidation of Si_3N_4 ceramic.⁸

It is known that β -sialon ($\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$, $z=0\sim 4.2$) ceramics produces mullite and silica by oxidation at high-temperature condition.^{1, 5, 9} In case of β -sialon with $z=3$, oxidation by O_2 is written as follows;

In the present study, alumina film was fabricated by dip-coating method of alumina precursors. To control crystallinity and to improve adhesivity of alumina coating, the coated samples were heat-treated in the

oxidative atmosphere to form mullite at the interface between β -sialon substrate and Al_2O_3 coating by a reaction between the coated alumina and silica

where SiO_2 is produced by oxidation of β -sialon in reaction (1).

2. EXPERIMENTAL PROCEDURE

Sintered β -sialon was fabricated by hot-pressing of β -sialon ($z=3$) powder without additive at 1900°C and at 24 MPa for 4 h in N_2 atmosphere. Relative density of the sintered compact was about 96%. The sintered β -sialon was cut to specimens of $15 \times 5 \times 2 \text{ mm}^3$ in size and the surface was polished. An aluminum alkoxide precursor solution (AK sol) was prepared by dissolving aluminum tri-sec-butoxide ($\text{Al}(\text{OBt})_3$, Kanto chemical) in a mixture of diethanolamine (DEA, Kanto chemical) and ethanol. The molar ratio of $\text{Al}(\text{OBt})_3$:DEA:EtOH was 1:1.5:10. Al_2O_3 sol precursor solution (CA sol) was prepared by dissolving commercially available Al_2O_3 sol (Nissan Chemical Industries, Ltd.) in ethanol. The molar ratio of Al_2O_3 :EtOH was 1:40. The β -sialon substrate was dipped into the precursor solutions and withdrawn at a speed of 60 mm min^{-1} . After the dip-coating, the sample was dried in air at room temperature for 1.5 h and heated in air at 600°C for 1 h. The process of dipping to the heating was 6 times repeated (as-coated sample). The as-coated sample was heated at 1300°C in Ar/O_2 (95/5 vol%) for 2 h and subsequently treated in Ar for 10 h (heat-treated sample). The samples was oxidized in $\text{Ar}/\text{O}_2/\text{H}_2\text{O}$ (8/2/90 vol%) at 1200°C for 24 ~ 100 h. Characterization of the samples was carried out by X-ray powder diffraction (XRD, RIGAKU RINT-2000), scanning electron microscope with energy dispersive analysis unit (SEM-EDS, JEOL JSM-6700F) and transmission electron microscope

(TEM JEOL, JEM-2000ES) with EDS analysis unit.

3. RESULTS AND DISCUSSION

3-1 As-coated sample

Figure 1 shows SEM images of as-coated samples by using AK and CA precursors. Many cracks were observed at surface of the sample by using AK precursor (Fig. 1(a)). In contrast, few cracks were observed at surface by using CA precursor (Fig. 1(b)). Thickness of the Al_2O_3 films for both as-coated samples was about $1.5\ \mu\text{m}$, confirmed by cross-sectional images obtained by SEM observations. By XRD analysis, both samples gave no observable peak except for those of β -sialon, possibly due to a small amount and low crystallinity of coated Al_2O_3 . However, the powders obtained by heating AK and CK precursors at 600°C for 1 h gave broad peaks corresponding to γ - Al_2O_3 (Fig. 2), showing that the coated alumina must be γ -phase.

3-2 Heat-treated sample

Figure 3 shows the XRD patterns of heat-treated samples by using AK precursor. The heat-treatment was carried out for as-coated samples at 1300°C in Ar/O_2 (95/5 vol%) for 2 h and subsequently in Ar for 10 h. In XRD pattern of the sample heated in Ar/O_2 for 2 h (Fig. 3 (a)), small peaks of cristobalite were observed in addition to the peaks of β -sialon substrate and α - Al_2O_3 . The observed cristobalite was formed by oxidation (eq. (1)). In the sample heated in Ar/O_2 atmosphere for 2 h and subsequently in Ar for 10 h (Fig. 3 (b)), peak intensity of cristobalite and α - Al_2O_3 was decreased, whereas peaks of mullite were observed, suggesting that the cristobalite was reacted with coated alumina and was transformed to mullite. In the samples by using CA precursor, almost same patterns were observed by the heat-treatment at the corresponding conditions.

Figure 4 shows surface SEM images of the heat-treated samples using AK and CA precursors. No remarkable change was caused by the heat-treatment in the surface microstructure from that of corresponding as-coated samples shown in Fig. 1. However, small grains about $0.3\ \mu\text{m}$ long were observed in high-magnification images. These grains were not observed in as-coated samples. Figure 5 shows the cross-sectional TEM image of the heat-treated sample using CA precursor. At the surface, a dense layer was observed on the β -sialon substrate. Between the surface layer and β -sialon substrate, a white contrasted interlayer with about $200\ \text{nm}$ thick was observed. From EDS analysis and XRD results (Fig. 3), the surface and the interlayer were mainly composed of α - Al_2O_3 and mullite,

Fig. 1 Surface SEM images of as-coated samples by using (a) AK and (b) CA precursors.

Fig. 2 XRD patterns of powders obtained by heating (a) AK and (b) CA precursors at 600°C for 1 h.

Fig. 3 XRD patterns of the Al_2O_3 coated sample by using AK precursor heated (a) at 1300°C in Ar/O_2 (95/5 vol%) for 2 h and (b) subsequently treated in Ar for 10 h.

Fig. 4 Surface SEM images of samples by using (a) AK and (b) CA precursors. Inserts are the magnified images.

respectively.

3-3 Oxidation in high $P_{\text{H}_2\text{O}}$ atmosphere

Figure 6 shows the plot of weight gain of the samples due to oxidation with time at 1200°C in Ar/O₂/H₂O (8/2/90 vol%) atmosphere. The weight gain of non-coated β -sialon ceramic at 100 h was 1.1 mg cm⁻². This value is greater than the value (about 0.07 mg cm⁻²) reported in low $P_{\text{H}_2\text{O}}$ atmosphere (Ar/O₂/H₂O = 80/10/10 vol%) at higher temperature of 1300°C.⁵ The large weight gain in the present work demonstrated that the water vapor with high partial pressure significantly accelerate oxidation of β -sialon. The all Al₂O₃ coated samples decreased weight gains compared with non-coated β -sialon. The decrease of weight gain showed that Al₂O₃ coating improves oxidation resistance, irrespective of the crystallinity of the coating. The weight gain of heat-treated samples by using AK and CA precursors were similar to each other and were slightly smaller than those of as-coated samples.

Figure 7 shows XRD patterns of samples oxidized for 50 h. The pattern of oxidized non-coated sample brings about broad and small peaks of mullite and β -sialon. The decreasing of peak intensity is due to a formation of oxidation products mainly amorphous SiO₂ on the β -sialon substrate. The as-coated samples by using AK precursor give peaks of mullite and cristobalite in addition to peaks of β -sialon, showing that the β -sialon is oxidized following the equation (1). Compared with the pattern of non-coated sample, the peaks of β -sialon and mullite were larger and clearly seen in the pattern of as-coated sample. This indicates that the amount of oxidation products formed on sample was smaller than that on non-coated sample. The samples with heat-treatment ((Fig. 7 (c)) gave smaller peaks of mullite and cristobalite than those of as-coated samples. Decrease of peak intensity of mullite and cristobalite showed that the oxidation resistance is improved by the heat-treatment. Similar patterns were obtained in the samples by using CA precursor.

Figure 8 shows the surface and cross sectional images of oxidized samples. The samples were as-coated and heat-treated ones by using AK sol. In as-coated sample, surface became rough and some pores shown by arrow were appeared, compared with the sample before oxidation (shown in Fig. 1 (a)). The surface consisted of grains, which are clearly seen in high magnification images. Although no obvious difference was observed between areas of (i) and (ii), they were corresponding to the Al₂O₃ and mullite, respectively, confirmed by EDS analysis. The former is remnant of the alumina coating and the latter is formed by oxidation of β -sialon or the reaction

Fig. 5 Cross-sectional TEM image at the interface between alumina coating and β -sialon substrate. The sample is heat-treated one by using CA precursor.

Fig. 6 Plots of weight gains due to oxidation in H₂O/O₂/Ar (90/2/8 kPa) atmosphere at 1200 °C. Marks of square and circle denote the sample by using AK and CA precursors, respectively.

Fig. 7 Surface XRD patterns of the oxidized samples. (a) no-coat β -sialon, (b) as-coated and (c) heat-treated samples by using AK precursor.

between coated Al₂O₃ and SiO₂ formed by oxidation of β -sialon. In the heat-treated sample (Fig. 8 (b)), the microstructure of the surface was similar to that of the sample before oxidation (Fig. 4 (a)). From the EDS analysis, the surface layer was composed of alumina.

However, from the cross sectional observation (Fig. 8 (c)), the thickness of the alumina coating was decreased to $0.5\ \mu\text{m}$ from that of non-oxidized sample ($1.5\ \mu\text{m}$) and an interlayer about $3\ \mu\text{m}$ thick possibly due to oxidation products was observed between surface layer and β -sialon substrate. The formation of the interlayer suggests that water and/or oxygen diffuse through the alumina coating and oxidize β -sialon substrate. The mullite layer, which was observed in the sample before oxidation, was disappeared in the oxidized sample.

Since the alumina coating remained at surface in the heat-treated sample, the heat-treatment is effective to improve oxidation resistance possibly due to the high chemical stability of α - Al_2O_3 comparing with γ - Al_2O_3 . Because almost same results were obtained in the sample by using CA precursor, oxidation resistance is influenced not by the microstructure but by the crystalline phase of the alumina coating.

4 SUMMARY

Al_2O_3 thin film was formed as EBC on the surface of β -sialon ceramics by dip-coating method of alkoxide (AK) and alumina sol (CA) precursors and heating at 600°C for 1 h in air (as-coated sample). The thickness of the coated film was about $1.5\ \mu\text{m}$. Cracks were formed in the film fabricated by using AK precursor but the formation of cracks was restrained by using CA precursor. As-coated samples were heat-treated at 1300°C in Ar/O_2 (95/5 vol.%) for 2 h subsequently in Ar for 10 h (heat-treated sample). By the heat-treatment, crystalline phase of coated Al_2O_3 was changed from γ - to α -phase and thin mullite layer was formed between Al_2O_3 coating and β -sialon substrate. From the oxidation test in $\text{Ar}/\text{O}_2/\text{H}_2\text{O}$ (8/2/90 vol.%) at 1200°C , Al_2O_3 coated samples showed high oxidation resistance comparing with no-coated samples. Among the Al_2O_3 coated samples, the heat-treated samples showed highest oxidation resistance. After the oxidation test for 50 h, alumina coating was left on the surface of the β -sialon substrate, showing that the coating of α - Al_2O_3 effectively acts as an EBC to the high $P_{\text{H}_2\text{O}}$ atmosphere.

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Fig. 8 Surface and cross-sectional SEM images of oxidized samples by using AK sol. Surface of (a) as-coated and (b) heat-treated samples and (c) cross section of (b). The samples were oxidized for 50 h in $\text{Ar}/\text{O}_2/\text{H}_2\text{O}$ (8/2/90 vol.%) atmosphere. Inserts are high magnification images.

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