1. Introduction

Silicon carbide ceramic matrix composites reinforced by continuous SiC fibers (SiC/SiC) have the advantages of low density, wear resistance, high specific strength, high-temperature resistance, non-brittle fracture etc. [1–3]. In high temperature, it is expected that dense oxidation layer (SiO₂) formed by the oxidation products of SiC can prevent the oxidizing medium from diffusion into the inner interphase and fibers [4]. However, despite the excellent anti-oxidation of SiC/SiC composites, the susceptibility to corrosion and volatilization of SiO₂ (Equation (1)) at high temperature (>1200°C) in water vapor environment decreases the service life of SiC/SiC composites [5,6]. To improve the service life of the composite in water vapor environments at high temperature and prevent or slowdown the diffusion of oxygen, the fabrication of an environmental barrier coating is an effective way to impede the oxygen attack [7–11]. However, the mismatch of the coefficient of thermal expansion between coating and substrate can weaken the interface bonding between coating and substrate and easily result in the debonding of coating from the substrate [12–14].

In order to improve the anti-oxidation, it was quite necessary to improve the stability of the SiO₂ by modification of the SiC matrix and thus to reduce the volatilization of SiO₂ in water vapor environments. Al₂O₃ is a glass network intermediate as well as an important ingredient of environment barrier coating [15] (e.g. Mullite, BSAS). It can effectively improve the high-temperature stability of silicate glass by repairing glass network structure [16]. Some research have found that Al₂O₃ could reduce volume shrinkage of SiO₂ [17,18], restraining the generation of cracks on the surface of oxidation layer during cyclic oxidation. In addition, when ceramics are corroded by water vapor, Kohn et al. [19,20] concluded that water dissolution lead to formation of bridging hydroxyl groups or protonated bridging oxygen (Al–O(H)–Si) (Equation (2)), which improve water vapor resistance, rather than disruption of the aluminosilicate network as it was in silica network.

\[
\text{Si} [\text{Q}^n] - \text{O} \rightarrow \text{Si} [\text{Q}^n] + \text{H}_2\text{O} \\
\rightarrow (\text{Si} [\text{Q}^n] - \text{OH})_2 (n \leq 4) \quad (1)
\]

\[
\text{Si} [\text{Q}_4^4(3\text{Si}, 1\text{Al})] - \text{O} \rightarrow \text{Al} [\text{Q}_4^4(4\text{Si}, 0\text{Al})] \\
\rightarrow \text{Si} [\text{Q}_4^4(3\text{Si}, 1\text{Al})] - \text{O} - \text{Al} [\text{Q}_4^4(4\text{Si}, 0\text{Al})] \quad (2)
\]

In view of the oxidation layer (SiO₂) of the SiC/SiC composites mainly from the SiC matrix oxidation, it is very important to study the modification of the SiC ceramic matrix. Previous studies mostly focused on AlN-modified SiC oxidation resistance under air environment [21–25]. However, few reports are about the oxidation resistance of Al₂O₃-modified SiC under O₂/\text{H}_2\text{O}. In this work, Al₂O₃ was introduced into SiC ceramics as an oxidation product modifier for the improvement of the corrosion resistance of the material in water vapor environment. The results show that
Al₂O₃ can effectively limit the volatilization of SiO₂ and improves the oxidation resistance of the material. The Al₂O₃-modified SiC is promising to be used as a kind of more corrosion-resistant matrix for ceramic matrix composite served in O₂/H₂O atmosphere.

2. Experimental procedure

2.1. Material preparation

SiC powder was ball milled together with different amounts of Al₂O₃ (wt% = 0, 5, 10, 15) for 24 h, with ethanol as solvent and polyvinyl butyl as binder. After oven drying, the mixed powders were die-pressed into cylinder-shaped samples (Φ 20 mm) at 30 MPa then debindered in a tubular furnace at 600 C for 1 h under the protection of Ar atmosphere. After that, the debindered sample was pre-sintered for 2 h at 1600 C in Ar to give it sufficient strength, then impregnated with phenolic resin, followed with pyrolysis at 900 C for 1.5 h under Ar atmosphere. Finally, the sample was infiltrated with melting silicon at 1500 C under vacuum in a carbon tube furnace. The residual silicon is about 30 wt%.

2.2. Oxidation test and microstructure characterization

Specimens of 5 mm × 5 mm × 5 mm in size were cut from the sintered plates with a diamond saw. Oxidation tests were performed using a tube furnace (GSL-1700X, Hefei Crystal Materials Technology Co., Ltd., Hefei, China) under normal pressure with flowing O₂/H₂O atmosphere at 1300 C for 100 h. During the test, the specimens were supported on an Al₂O₃ crucible, and the flow rate of O₂/H₂O was kept constant at 500 ml/min (200 ml O₂ + 300 ml H₂O) by a liquid phase vaporization system (LVD-F1, Hefei Crystal Materials Technology Co., Ltd., Hefei, China). The heating and cooling rates were 8 and 5 C/min, respectively. The specimens were weighed before and after the oxidation test, using an analytical balance (MT5, Mettler Toledo Co., Ltd., Switzerland) with an accuracy of ±0.01 mg. The surfaces and cross-sections of the oxidized specimens were characterized using a S4800 field emission scanning electron microscope (Hitachi, Tokyo, Japan) along with energy-dispersive spectroscopy (EDS, Inca energy) for elemental analysis. Micro zone-Raman spectroscopy was applied to investigate the internal vibration modes and analyze how Al₂O₃ improves the water vapor oxidation resistance ability of samples.

3 Results

3.1. Microstructure of the as-processed samples

Figure 1 shows the XRD patterns of the reaction-sintered SiC ceramics doped with 10% Al₂O₃. The distinctive peaks of SiC, Si and Al₂O₃ are shown.

Figure 2 shows the Optical micrograph of the as-prepared samples. It can be seen that all the phases, including SiC, Si and Al₂O₃, are well distributed.

3.2. Oxidation curves under O₂/H₂O oxidation atmosphere

The weight gain of the reaction sintered SiC ceramics after oxidation in O₂/H₂O atmosphere at 1300 C is shown in Figure 3. The addition of Al₂O₃ plays an important role in affecting the weight gain. The samples with Al₂O₃ always show more weight gain compared with the samples without Al₂O₃, and the weight gain difference becomes increasingly large with the prolongation of oxidation time. For the sample without Al₂O₃, its oxidation curve first slowly rises and then slowly decreases after 50 h, explaining that after this moment (50 h), the quality lost has exceeded the quality obtained. With increasing the content of Al₂O₃, the weight gain curve slope continually increases but still be parabolas-like, which illustrates
that the oxidation reaction is still dominated by diffusion control \[26,27\]. Such a phenomenon also indicates that the addition of \( \text{Al}_2\text{O}_3 \) seems to improve the anti-oxidation ability of reaction-sintered SiC ceramics in \( \text{O}_2/\text{H}_2\text{O} \) atmosphere.

However, it’s necessary to point out that the specific weight gain curve is the result of two simultaneous processes that are oxidation weight gain and volatilization weight loss. Therefore, weight gain curves alone are not enough to completely reflect the anti-oxidation behavior of the material. The whole chemical and physics reactions involved in the oxidation process are as follows \[28,29\]:

Oxidation weight gain:
\[
\text{Si} (s)+\text{O}_2 (g) \rightarrow \text{SiO}_2 (l) \quad (3)
\]
\[
\text{SiC} (s)+\text{O}_2 (g) \rightarrow \text{SiO}_2 (l)+\text{CO}_2 (g) \quad (4)
\]

Volatilization weight loss:
\[
\text{SiO}_2 (l)+\text{H}_2\text{O} (g) \rightarrow \text{SiO(OH)}_2 (g) \quad (5)
\]
\[
\text{SiO}_2 (l)+\text{H}_2\text{O} (g) \rightarrow \text{Si(OH)}_4 (g) \quad (6)
\]
\[
\text{SiO}_2 (l)+\text{H}_2\text{O} (g) \rightarrow \text{Si}_2\text{O(OH)}_6 (g) \quad (7)
\]

To further testify the oxidation process, surface morphology and cross-sectional morphology of the oxidized material and phase composition of the oxidation should be studied.

### 3.3. Morphology of oxidized samples

Figure 4 shows the natural surface of samples oxidized at 1300°C under \( \text{O}_2/\text{H}_2\text{O} \). The surface of the sample without \( \text{Al}_2\text{O}_3 \) (Figure 4(a)) is smooth and no grain is precipitated. By contrast, the sample surface becomes frothy with the addition of \( \text{Al}_2\text{O}_3 \). It is believed that high viscosity of the oxidation products melt makes it difficult for bubbles to generate and discharge, resulting in bubbling phenomenon \[30,31\]. As to the cross-section, since the role of gravity and the rate of volatilization vary from place to place, the oxidation layer thickness is different at different locations. The cross-section of samples with different content of \( \text{Al}_2\text{O}_3 \) at different positions is shown in Figure 5. In the same samples, the thickness of oxide layers increases from ~6, ~15 to ~40 µm as the position moves from top surface toward bottom of side (shown in Figure 5(a,e,i)). This can also be seen in sample with 15% \( \text{Al}_2\text{O}_3 \) (shown in Figure 5(d,h,l)), the oxide layers thickness of which increases from ~10, ~28 to ~60 µm. Moreover, in the same position of sample with different \( \text{Al}_2\text{O}_3 \) content, the thickness of oxidation layers increases gradually as the content of \( \text{Al}_2\text{O}_3 \) rises. EDS results (Figure 5(l)) show that Al is enriched in the oxidation layer.

The above analysis seems to indicate that the addition of \( \text{Al}_2\text{O}_3 \) does not improve the oxidation resistance of the material. As already mentioned above, weight gain and thickness changes of oxide layer are general results of two different simultaneous processes. It is necessary to measure the macroscopic size changes of the sample before and after oxidation.

Figure 6 shows the width changes of the upper and lower surfaces of samples with 0% and 15% \( \text{Al}_2\text{O}_3 \) before and after oxidation for 100 h under \( \text{O}_2/\text{H}_2\text{O} \) environment. The width of upper surface of samples with 0% and 15% \( \text{Al}_2\text{O}_3 \) is reduced by 29.15 and 4.55 µm, respectively, while the width of lower surface is increased by 5.57 and 15.6 µm, respectively. The above results indicate that \( \text{Al}_2\text{O}_3 \) additive can effectively prevent the reduction of macroscopic size and reduce the volatilization of the oxide layer, leading to thicker oxidation layer both in upper and lower surface. These are consistent with the results of the oxidation curve.

### 4. Discussion

In order to better explain the corrosion resistance effect of \( \text{Al}_2\text{O}_3 \) in water vapor, the surface of oxidation layer after oxidized under \( \text{O}_2/\text{H}_2\text{O} \) atmosphere was analyzed by micro-zone Raman spectra. Although the glass phase at room temperature does not completely represent its true state at high temperatures, it can reflect the difference of bonded structure at high temperatures to some extent. There are some different vibrational modes originated from the relative arrangement of atomic or molecular units in the glass network. Apart from the amorphous glass phase, well-crystallized Si, SiC and C phases are also present in Figure 7. The appearance of Si, SiC and C is quite unexpected. It is probably resulted from Raman laser penetrating the oxide layer. Broad bands and protuberant are
Figure 4. SEM images of the samples’ surface under O\(_2\)/H\(_2\)O: (a) 0% Al\(_2\)O\(_3\), (b) 5% Al\(_2\)O\(_3\), (c) 10% Al\(_2\)O\(_3\), (d) 15% Al\(_2\)O\(_3\).

Figure 5. SEM images of the samples’ cross-sections under O\(_2\)/H\(_2\)O. The top surface: (a) 0% Al\(_2\)O\(_3\), (b) 5% Al\(_2\)O\(_3\), (c) 10% Al\(_2\)O\(_3\), (d) 15% Al\(_2\)O\(_3\); the upper half of the side: (e) 0% Al\(_2\)O\(_3\), (f) 5% Al\(_2\)O\(_3\), (g) 10% Al\(_2\)O\(_3\), (h) 15% Al\(_2\)O\(_3\); the lower half of the side: (i) 0% Al\(_2\)O\(_3\), (j) 5% Al\(_2\)O\(_3\), (k) 10% Al\(_2\)O\(_3\), (l) 15% Al\(_2\)O\(_3\).
attributed to superposition of small adjacent peaks. According to the location of broad bands, the Raman spectra were divided into three regions for convenience, low-frequency region (LF) 450–750 cm\(^{-1}\), medium frequency region (MF) 1100–1500 cm\(^{-1}\) and high frequency region (HF) 2500–3400 cm\(^{-1}\). Compared to that of sample without Al\(_2\)O\(_3\), the broad bands of samples with Al\(_2\)O\(_3\) have more obvious protuberant in LF region, less obvious protuberant in MF region and less broad bands in HF region.

To get detailed and precise information, the spectra were deconvoluted by Gaussian curves fits as shown in Figure 8. The high absorption peak at ~520 cm\(^{-1}\) is assigned to free silicon under oxidation layer. Peak at about ~1350 cm\(^{-1}\) can be assigned to the graphite D-band. Important Raman absorption bands in these
The enhanced intensity of peaks at ~558 and 618 cm\(^{-1}\) (comparing Figure 8 (b), (c), (d) with (a)) denotes that the addition of Al\(_2\)O\(_3\) can significantly improve the stability of glass structure in high temperature under water vapor environment. In addition, the rapid decreases of the hydrogen-bonded molecules (~2960 and ~3265 cm\(^{-1}\)) with addition of Al\(_2\)O\(_3\) suggest a decrease of water concentration in the oxidation layer [40]. Furthermore, the significant decrease of peaks at ~1220–1280 denotes that the addition of Al\(_2\)O\(_3\) pronoucnedly affects the Si–O–Si linkages in high-temperature water vapor environment. The interconnection degree of structural units is enhanced, and the tendency of the bridged oxygen atoms (Si–O–Si, Si–O–Al) to become non-bridged oxygen atoms (Si–O–H) is weakened. Therefore, Al\(_2\)O\(_3\) can significantly inhibit the volatilization of SiO\(_2\) and improve the high-temperature water vapor oxidation resistance of the materials.

The above analysis strongly infers that the easily broken bond Si–O–Si under the O\(_2\)/H\(_2\)O environment makes the oxidation layer constantly volatile at high temperature and results in decrease in sub- strate size (Figure 9). However, the addition of Al\(_2\)O\(_3\) impedes the breakage of Si–O–Si bond (Figure 8(e-h)) and inhibits the volatilization of the oxide layer. Consequently, the overall size of the substrate is substantially unchanged (Figure 9).

**Figure 8.** Deconvoluted Raman spectra in LF region (450–750 cm\(^{-1}\)): (a) 0% Al\(_2\)O\(_3\), (b) 5% Al\(_2\)O\(_3\), (c) 10% Al\(_2\)O\(_3\), (d) 15% Al\(_2\)O\(_3\); MF region (1100–1500 cm\(^{-1}\)): (e) 0% Al\(_2\)O\(_3\), (f) 5% Al\(_2\)O\(_3\), (g) 10% Al\(_2\)O\(_3\), (h) 15% Al\(_2\)O\(_3\); HF region (2500–3400 cm\(^{-1}\)): (i) 0% Al\(_2\)O\(_3\), (j) 5% Al\(_2\)O\(_3\), (k) 10% Al\(_2\)O\(_3\), (l) 15% Al\(_2\)O\(_3\).
Conclusion

The addition of Al$_2$O$_3$ greatly improves the oxidation resistance of SiC ceramics in O$_2$/H$_2$O atmosphere. The specific weight gain curve with Al$_2$O$_3$ has been parabolas-like and no downward trend. Although the thickness of oxidation layer at different locations increases with the increases of Al$_2$O$_3$. The macro size is increased by $-29.15$ and $5.57$, but $-4.55$ and $15.6$ µm with the addition of 15 wt% Al$_2$O$_3$, at upper surface and lower surface, respectively. Raman spectra results reveal that Al$_2$O$_3$ significantly improves the stability of glass structure and weakens the tendency of the bridged oxygen atoms (Si–O–Si, Si–O–Al) to become non-bridged oxygen atoms (Si–O–H). It is believed that this leads to lower reaction activity of the aluminosilicate with steam melt in comparison with silicate one, thereby significantly inhibits the volatilization of SiO$_2$ and improves the high-temperature water vapor oxidation resistance of the materials. The Al$_2$O$_3$-modified SiC is promising to be used as a kind of more corrosion-resistant matrix for ceramic matrix composite served in O$_2$/H$_2$O atmosphere.

Disclosure statement

No potential conflict of interest was reported by the authors.

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References

[1] Naslain R. Ceramic matrix composites. Phil Trans R Soc Lond A. 1995;485–496.
[2] Morscher GN, DiCarlo JA, Kiser JD. Int J Appl Ceram Technol. 2010;7(3):276–290.
[3] Belmonte M. Adv Eng Mater. 2010;8(8):693–703.
[4] Nasiri NA, Patra N, Ni N, et al. J Eur Ceram Soc. 2016;36:3293–3302.
[5] Jacobson NS. J Am Ceram Soc. 1993;76:3–28.
[6] Opila EJ. Oxidation kinetics of chemically vapor-deposited silicon carbide in wet oxygen. J Am Ceram Soc. 1994;77(3):730–736.
[7] Zhang YL, Fei T, Zeng WY, et al. Microstructure and oxidation behavior of C/C–zrB$_2$ –SiC composites coated with SiC coating at high temperature. Corros Sci. 2015;100:421–427.
[8] Fan XM, Yin XW, Ma YZ, et al. Oxidation behavior of C/SiC-Ti 3 SiC 2 at 800–1300 °C in air. J Eur Ceram Soc. 2016;36:2427–2433.
[9] Zuo XZ, Zhang LT, Liu YS, et al. Oxidation behaviour of two-dimensional C/SiC modified with self-healing Si–B–C coating in static air. Corros Sci. 2012;65:87–93.
[10] Wang YG, Liu JL. Corrosion of barium aluminosilicates by water-vapour: an investigation from first principles. Corros Sci. 2009;51:2126–2129.
[11] Wang YG, Wu YH, Cheng LF, et al. Hot corrosion behavior of barium aluminosilicate-coated C/SiC composites at 900Å°C. J Am Ceram Soc. 2010;93:204–208.
[12] Zou BL, Khan ZS, Gu LJ, et al. Microstructure, oxidation protection and failure mechanism of Yb2Si5O9/LaMgAl11O19 coating deposited on C/SiC composites by atmospheric plasma spraying. Corros Sci. 2012;62:192–200.
[13] Lu Y, Luo L, Liu J, et al. Failure mechanism associated with the thermally grown silica scale in environmental barrier coated C/SiC composites. J Am Ceram Soc. 2016;99:2713–2719.
[14] Li L. Appl Compos Mater. 2016;4:1–21.
[15] Ferraris M, Salvo M, Smeacetto F. Cordierite–mullite coating for SiCf/SiC composites. J Eur Ceram Soc. 2002;22:2343–2347.
[16] Wuhan Institute of Building Materials, East China Institute of Chemical Technology, Zhejiang University. Glass process principle. China Building Industry Press; 1981. p. 71–76.
[17] Feng JP, Yan YY, Chen DP. Study of thermal stability of fumed silica based thermal insulating composites at high temperatures. J Compos Part B. 2011;42:1821–1825.
[18] Han L, Yuan L, Liu JZ. Effect of Al2O3 powder on properties of fumed silica thermal insulating composites using mechanofusion technique. Appl Mech Mater. 2012;148–149:1011–1015.
[19] Kohn SC, Dupree R, Smith ME. A multinuclear magnetic resonance study of the structure of hydrous albite glasses. Geochimica et. Cosmochimica Acta. 1989;53:2925–2935.
[20] Kohn SC, Dupree R, Mortuza MG. The interaction between water and aluminosilicate magmas. Chemical Geology. 1992;96:399–409.
[21] Sciti D, Winterhalter F, Bellosi A. Oxidation behaviour of a pressureless sintered AlN–SiC composite. J Mater Sci. 2004;39(23):6965–6973.
[22] Guo S, Hirotsuki N, Tanaka H, et al. Oxidation behavior of liquid-phase sintered SiC with AlN and Er2O3 additives between 1200°C and 1400°C. J Eur Ceram Soc. 2003;23(12):2023–2029.
[23] Magnani G, Antolini F, Beaulardi L, et al. Sintering, high temperature strength and oxidation resistance of liquid-phase-pressureless-sintered SiC–AlN ceramics with addition of rare-earth oxides. J Eur Ceram Soc. 2009;29(11):2411–2417.
[24] Lavrenko VA, Desmaison-Brut M, Panasyuk AD, et al. Features of corrosion resistance of AlN–SiC ceramics in air up to 1600°C. J Eur Ceram Soc. 1998;18(16):2339–2343.
[25] Magnani G, Antolini F, Beaulardi L, et al. Oxidation resistance of SiC–AlN ceramics coated by oxidation-assisted-pack cementation process. J Eur Ceram Soc. 2011;31(3):369–376.
[26] Deal B, Grove A. General relationship for the thermal oxidation of silicon. J Appl Phys. 1965;36(12):3770–3778.
[27] Jacobson NS, Kang NL, Fox DS. Reactions of silicon carbide and silicon(IV) oxide at elevated temperatures. J Am Ceram Soc. 1992;75(6):1603–1611.
[28] Opila EJ, Smialek JL, Robinson RC. J Am Ceram Soc. 1999;82(7):1826–1834.
[29] Bunker BC. Molecular mechanisms for corrosion of silica and silicate glasses. J Non-Cryst Solids. 1994;179:300–308.
[30] Wuhan Institute of Building Materials, East China Institute of Chemical Technology, Zhejiang University. Glass process principle. China Building Industry Press; 1981. p. 86–92.
[31] Kamitsos EI, Kapoutsis JA, Jain H. Vibrational study of the role of trivalent ions in sodium trisilicate glass. J Non-Cryst Solids. 1994;171:31–45.
[32] Buixaderas E, Anghel EM, Petrescu S. Structural investigation in the TiB2–(Na2O·B2O3·Al2O3) system. J Solid State Chem. 2010;183:2227–2235.
[33] Sciti D, Winterhalter F, Bellosi A. Oxidation behaviour of a pressureless sintered AlN–SiC composite. J Mater Sci. 2004;39(23):6965–6973.
[34] Guo S, Hirotsuki N, Tanaka H, et al. Oxidation behavior of liquid-phase sintered SiC with AlN and Er2O3 additives between 1200°C and 1400°C. J Eur Ceram Soc. 2003;23(12):2023–2029.
[35] Magnani G, Antolini F, Beaulardi L, et al. Sintering, high temperature strength and oxidation resistance of liquid-phase-pressureless-sintered SiC–AlN ceramics with addition of rare-earth oxides. J Eur Ceram Soc. 2009;29(11):2411–2417.
[36] Lavrenko VA, Desmaison-Brut M, Panasyuk AD, et al. Features of corrosion resistance of AlN–SiC ceramics in air up to 1600°C. J Eur Ceram Soc. 1998;18(16):2339–2343.
[37] Magnani G, Antolini F, Beaulardi L, et al. Oxidation resistance of SiC–AlN ceramics coated by oxidation-assisted-pack cementation process. J Eur Ceram Soc. 2011;31(3):369–376.
[38] Deal B, Grove A. General relationship for the thermal oxidation of silicon. J Appl Phys. 1965;36(12):3770–3778.