Research on Oxidation Resistance of Silicon Carbide Refractories to High Temperature Steam

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Abstract: Refractory linings of waste incineration plants based on oxidation resistant SiC materials enable a long service life at suitable firing and operation conditions. Steam oxidation resistance of Si₃N₄-SiC, SiO₂-SiC, SiAlON-SiC material at 1000°C was tested according to ASTM-C863 after 50c, 100h, 200h, 250h and 300h respectively. The phase composition and microstructure before and after oxidation were analyzed by means of XRD and SEM. Results indicate that there is continuous increase of volume expansion and weight change on materials with the oxidation to the oxidation time. After 50h of oxidation, a small amount of cristobalite can be observed in these materials, which comes directly from the oxidation of SiC, Si₃N₄O and SiAlON or from the crystallization of glass phase. Oxidation weight gain occurs in the first 50h, but volume expansion takes place after 50h. Compared with the three materials, SiO₂-SiC material has a smaller weight change and volume expansion. Comparing the SEM these three materials, it is obvious that SiO₂-SiC material has a better density after 300h. Based on the above results, conclusions can be reached that: the sample of SiO₂-SiC has better oxidation resistance and is more suitable as lining material of waste incinerator.

1. Introduction
In waste incineration plants SiC refractories are widely used in different parts of the vessel. The combustion chamber consists of tubes with the function of heat exchange between the heat generated by the incineration of waste and circulating water to generate steam[1]. The tubes are covered by a refractory lining to protect the essential tubes from the steam environment[1][2]. For the incineration process the SiC refractory lining provides a high thermal conductivity for a good heat transfer and a good corrosion resistance[3]. Vessel and refractory surface temperatures, dust in the hot gases and slag formation of molten ashes influence the wear of the refractory lining[1][4]. Oxidation resistance is an important property of Silicon Carbide refractory materials[5]. Oxidation resistance is the basic valuation criterion for Silicon Carbide materials’ application in high temperature and oxidizing atmosphere. The Silicon Carbide materials were used as a high temperature material, the oxidation resistance property of Silicon Carbide materials was researched, and formed some accepted theory about Silicon Carbide material using in air atmosphere at high temperature[6]. With the extending of Silicon Carbide materials’ application fields, the new application fields such as the living garbage incinerators, whose working atmosphere with higher steam content[7]. The working temperature in the most seriously damaged area of the waste incinerators is generally 1000°C[6]. Therefore, it is necessary to understand the oxidation resistance of silicon carbide refractories in order to evaluate...
which silicon carbide refractories are more suitable for the working conditions with high steam content at 1000°C.

2. Experimental Procedures

2.1. Raw Materials and Experimental Formulations

The Si3N4-SiC, SiO2-SiC and SiAlON-SiC bricks were produced by following the production process of mixing, molding and nitriding sintering, by using silicon carbide grains, silicon carbide fine powder, silica powder and alumina micro powder as main raw materials. Table 1 shows the physical and chemical properties of Si3N4-SiC bricks. Table 2 shows the physical and chemical properties of SiO2-SiC bricks. Table 3 shows the physical and chemical properties of SiAlON-SiC bricks. The piece test specimens of dimension 30×30×30mm were cut from the Si3N4-SiC, SiO2-SiC and SiAlON-SiC bricks. Oxidation resistance of these three pieces of specimen to steam at 1000°C was tested according to ASTM-C863 after 50h, 100h, 150h, 200h, 250h and 300h respectively. The testing steam low rate is 32 kg H2O(g)/m3 per hour.

| Table 1. Physical and Chemical properties of Si3N4-SiC bricks. |
|---------------------------------------------------------------|
| Item | Si3N4-SiC bricks |
|----------------|----------------|
| Bulk Density/ g·cm⁻³ | 2.72 |
| Apparent Porosity/ % | 14.4 |
| Cold Crushing Strength/MPa | 205 |
| SiC Content/ % | 75.42 |
| β-Sialon Content/ % | 20.65 |
| Fe₂O₃ Content/ % | 0.45 |

| Table 2. Physical and Chemical properties of SiO2-SiC bricks. |
|---------------------------------------------------------------|
| Item | SiO2-SiC bricks |
|----------------|----------------|
| Bulk Density/ g·cm⁻³ | 2.72 |
| Apparent Porosity/ % | 12.8 |
| Cold Crushing Strength/ MPa | 203 |
| SiC Content/ % | 86.7 |
| β-Sialon Content/ % | 7.6 |
| Fe₂O₃ Content/ % | 0.21 |

| Table 3. Physical and Chemical properties of SiAlON-SiC bricks. |
|---------------------------------------------------------------|
| Item | SiAlON-SiC bricks |
|----------------|----------------|
| Bulk Density/ g·cm⁻³ | 2.73 |
| Apparent Porosity/ % | 13.9 |
| Cold Crushing Strength/ MPa | 246 |
| SiC Content/ % | 75.04 |
| β-Sialon Content/ % | 21.3 |
| Al₂O₃ Content/ % | 0.35 |
| Fe₂O₃ Content/ % | 0.33 |

2.2. Characterization

The phase compositions of samples were characterized by X-ray diffractometry (XRD, XPert Pro, Philips, Netherlands) in a 2θ range from 10° to 80° with a scanning speed of 2°/minute, using Cu-Kα radiation (λ =1.542 Å), operating at 40 kV and 40 mA. The microstructures of samples were observed by a scanning electron microscope (SEM, JSM-6610, ZESS, BRUKER Company, Germany) equipped with energy dispersive X-ray spectroscopy (EDS, QUANTAX200-3, BRUKER Company, Germany).
The volume, weight, bulk density and apparent porosity of specimens before and after oxidation were tested respectively. And the volume changes before and after oxidation was used to evaluate the oxidation resistance performance of Silicon Carbide materials.

3. Results and Discussion

3.1. Thermodynamic calculation

When Si₃N₄-SiC, SiO₂-SiC and SiAlON-SiC specimen was exposed in steam environment, the possible reaction between steam and Silicon Carbide refractories are listed as follows[8-12]:

\[
\begin{align*}
\text{SiC(s)} + 3\text{H}_2\text{O(g)} & \rightarrow \text{SiO}_2\text{(s)} + \text{CO(g)} + 3\text{H}_2\text{(g)} \quad (1) \\
\text{Si}_3\text{N}_4\text{(s)} + 6\text{H}_2\text{O(g)} & \rightarrow 3\text{SiO}_2\text{(s)} + 4\text{NH}_3\text{(g)} \quad (2) \\
\text{Si}_2\text{N}_2\text{O(s)} + 3\text{H}_2\text{O(g)} & \rightarrow 3\text{SiO}_2\text{(s)} + 3\text{H}_2\text{(g)} + \text{N}_2 \quad (3) \\
\beta\text{-Sialon(s)} + \text{H}_2\text{O(g)} & \rightarrow \text{SiO}_2\text{(s)} + \alpha\text{Al}_2\text{O}_3\text{(s)} + 3\text{H}_2\text{(g)} + \text{N}_2\text{(g)} \quad (4) \\
\text{SiO}_2\text{(s)} + 2\text{H}_2\text{O(s)} & \rightarrow \text{Si(OH)}_4\text{(g)} \quad (5) \\
3\text{Al}_2\text{O}_3\text{(s)} + 2\text{SiO}_2\text{(s)} & \rightarrow 3\alpha\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\text{(s)} \quad (6)
\end{align*}
\]

The reaction Gibbs energy has been calculated using the thermodynamic computer modeling package FactSage. The function of the reaction Gibbs energy with temperature for the reactions (1-6) is shown in figure 1.

It can be seen that the reaction Gibbs energy of these reactions is negative, meaning these reaction could occur from thermodynamic viewpoint. By comparison, the reaction of SiAlON with H₂O reaction (4) shows the most favorable tendency to occur even at lower temperatures. Moreover the value of the Gibbs energy of reaction (2) is more negative than that of reaction (3), indicating that Si₃N₄ is more likely to react with water vapor in the temperature range investigated. From above thermodynamic calculations, the specimen of SiAlON-SiC shows a most favorable to occur in the steam environment, but the specimen of SiO₂-SiC material is the least likely to react in water vapor environment.

Figure 1. The reaction Gibbs energy of the possible reactions in steam environments.
3.2. Oxidation result

The weight change, volume expansion, apparent porosity and bulk density of specimens as a function of oxidation time are shown from figure 2 to figure 5.

As can be seen from figure 2 and figure 3, the weight changes and volume expansion of specimen gain constantly with the increase of oxidation time. It is shown that the specimens undergo a significant oxidation reaction with steam during the first 50h oxidation, and the degree of oxidation reaction is more than 50h-300h. The volume of the specimens increases with the slowly increase of the oxidation time in the 100h oxidation process, but the volume of the sample is rapidly increased after 100h-300h. The increase of mass and volume in the oxidation process of the specimen is not synchronous. Figure 4 shows that the apparent porosity of the sample decreased obviously at the stage of 0h-100h, and then decreased slowly. The decrease of the apparent porosity of the specimens corresponds to the increase of the mass, which indicates that the oxidation product can fill the porosity of the sample, thus reducing the apparent porosity. As can be seen from Figure 5, the bulk density of specimens changed little with the increase of oxidation time.

![Figure 2](image1.png)

**Figure 2.** The weight change as a function of oxidation time.

![Figure 3](image2.png)

**Figure 3.** The volume expansion as a function of oxidation time.
For Si$_3$N$_4$-SiCa obvious increase in weight and volume can be observed due to the corrosive conditions by steam. The weight maximum increase is about 0.04727%, and the volume maximum increase is about 0.04499%. Under the condition of steam corrosion, the weight and volume of SiO$_2$-SiC sample have a small increase. The weight maximum increase is about 0.02321%, and the weight maximum increase is about 0.0095%. The mass of the sample changes after SiO$_2$-SiC oxidation, and the effect of filling pores on reducing the apparent porosity are more obvious[13]. The sample of SiAlON-SiC increase in weight and volume can be observed due to the corrosive conditions by steam. The weight maximum increase is about 0.03948% and the volume maximum increase is about 0.03789%. The apparent porosity of SiO$_2$-SiC exhibits decreased continuously with the increase of oxidation time, but the he apparent porosity of Si$_3$N$_4$-SiC and SiAlON-SiC exhibits an obvious upward trend after 250h. By comparison weight change, volume expansion, volume expansion, apparent porosity and bulk density of specimens, the SiO$_2$-SiC materials maintains the better performance after oxidation in water vapor for 300 hours.

Figure 6 shows the XRD patterns of the original brick, specimen after 50h of oxidation and specimen after 300h of oxidation. And the phase composition analysis of the sample with different oxidation time is carried out. From XRD patterns, the content of Si$_3$N$_4$ which is the primary
combination phase of material decline, and a small amount of cristobalite and quartz appears after 50h of oxidation. After 300h of oxidation, the content of Si$_3$N$_4$ continues decline, the content of cristobalite and quartz increase constantly. The Si$_3$N$_4$-SiC brick has a large amount of well-developed Si$_3$N$_4$ whisker in the matrix. For microscopic observation of the morphologies of the Si$_3$N$_4$-SiC after 50h of oxidation, we find that Si$_3$N$_4$ whiskers significantly decrease under the steam environments. After 500 h of oxidation, Si$_3$N$_4$ whisker is completely converted to quartz and cristobalite.

![Figure 6. XRD patterns of specimens before and after oxidation and SEM images of the surface morphology of after Si$_3$N$_4$-SiC oxidation at 1000°C for 0h (a), 50h (b) and 300h (c) in steam environments.](image)

Exposure of Si$_3$N$_4$-SiC to steam at 1000°C resulted in the formation protective SiO$_2$ layer on the specimen surface. With the reaction of protective SiO$_2$ layer with steam to form Si(OH)$_4$ and the volatile gaseous, the structure of dense protective layer is destroyed and becomes thick and porous SiO$_2$ layer, which can not hinder the further oxidation of Si$_3$N$_4$-SiC, resulting in the continuous oxidation of Si$_3$N$_4$-SiC in the sample.

Figure 7 shows the XRD patterns of the original brick, specimen after 50h of oxidation and specimen after 300h of oxidation. The XRD patterns shows that the content of Si$_2$N$_2$O as primary combination phase of material decline, cristobalite and quartz appeared after 50h of oxidation. After 300h of oxidation, the content of Si$_2$N$_2$O continues decline, the content of cristobalite and quartz increase constantly. For microscopic observation of the morphologies, the SiO$_2$-SiC original brick has a dense structure and a large amount of well-developed Si$_2$N$_2$O phase in the matrix. From the XRD patterns, it can be know there is nitrogen element in specimen, which means Si$_2$N$_2$O phase exists under the steam environments.
Figure 7. XRD patterns of specimens before and after oxidation and SEM images of the surface morphology of after SiO$_2$-SiC oxidation at 1000°C for 0h (a), 50h (b) and 300h (c) in steam environments.

The exposure of SiO$_2$-SiC in steam at 1000°C resulted in the formation of a thick porous SiO$_2$ layer on the surface of the sample. The reaction of protective SiO$_2$ layer to form Si(OH)$_4$ and the volatile gaseous under the steam environments. For microscopic observation of the morphologies of the SiO$_2$-SiC, the sample of SiO$_2$-SiC maintains a dense structure after oxidation in steam for 300 hours.

Figure 8 shows the XRD patterns of the original brick, specimen after 50h of oxidation and specimen after 300 h of oxidation. And the phase composition analysis of the sample with different oxidation time is carried out. From XRD patterns, we can indicate that the content of β-Sialon decline, and a small amount of cristobalite and α-Al$_2$O$_3$ appears. After 300hs of oxidation, the content of β-Sialon continues decline, the content of cristobalite and α-Al$_2$O$_3$ increase constantly. It can be seen from figure 7, the SiAlON-SiC brick has a dense structure and a large amount of columnar Sialon phase in the matrix. From the EDS specimen after 50h of oxidation, it can be know there is no nitrogen element in specimen, which means Sialon phase completely transformed into SiO$_2$ and Al$_2$O$_3$.

Comprehensive analysis shows that in the early stage of the oxidation, there is continuous volume expansion and weight change of SiAlON-SiC with the increase of oxidation time, the main reason is the steam oxidation of SiC and β-Sialon. During the later stage of oxidation; with the decreasing of apparent porosity, the weight gain of specimens became slowly, which indicates the oxidation rate be came slowly, but the volume expansion increase constantly, especially when the weight gain changed little after 250h of oxidation. The main cause for the continuous volume expansion is the crystal transformation of SiO$_2$ which released out by SiAlON-SiC during oxidation and oxidation products of SiC.
Figure 8. XRD patterns of specimens before and after oxidation and SEM images of the surface morphology of after SiAlON-SiC oxidation at 1000°C for 0h (a), 50h (b) and 300 h (c) in steam environments.

By comparing the phase compositions and morphological analysis, the surface of Si₃N₄-SiC material and SiAlON-SiC material is completely porous structure, but there are obvious protective layer on the surface of SiO₂-SiC material after 300h of oxidation. The size of pores in the matrix is small due to well-development of Si₂N₂O, the oxidation products are more likely to fill the surface pores and form protective oxidation. Based on the above results, the sample of SiO₂-SiC has better oxidation resistance and is more suitable as lining material of waste incinerator.

4. Conclusions
In this chapter, the changes of physical properties and microstructure parameters of Si₃N₄-SiC, SiO₂-SiC, SiAlON-SiC material before and after steam corrosion were studied. The water vapor corrosion mechanism of different refractories is investigated, and the following conclusions can be drawn.

1) There is continuous volume expansion and weight change of Si₃N₄-SiC, SiO₂-SiC, SiAlON-SiC material with the increase of oxidation time. The SiO₂-SiC material has a small weight gain, and the weight maximum increase is only about 0.0095%.

2) After 300h of oxidation, protective SiO₂ layer can be observed in the surface materials from SEM images, and the sample of SiO₂-SiC maintains a dense structure after oxidation in steam for 300 hours.

3) The working temperature in the most seriously damaged area of the waste incinerators is generally 1000°C. The SiO₂-SiC refractories are more suitable lining material for waste incinerator.

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References

[1] Tonnesen T, Telle R 2011 Quality control management of refractory SiC for waste incineration plants 12th Biennial Worldwide Conference on Refractories. UNITECR, Japan, Kyoto, 10.30-11.2: 1-E-4.

[2] Yun S N, Jiang M X and Feng X F 2012 Research status on gas corrosion resistance of SiC refractories Refractories 6 459

[3] Brossard J M, Prigent P and Poirier J 2013 High temperature corrosion of oxide bonded silicon carbide refractory lining in WTE facilities J Eur Ceram Soc. 33 2065

[4] Hartman M L, King J A 2010 Silicon-carbide refractories for water-gas generators J Am Ceram Soc. 9 758

[5] Spiegel M 2001 Corrosion mechanisms and failure cases in caste incineration plants Mater Sci Forum. 369-372 971

[6] Li C B, Dong S J 2011 Properties of refractory for waste Incineration Plant Refractories 45 477

[7] Pan M, Nan C W 2000 High temperature oxidation and corrosion of SiC-based materials Corros Sci Prot Technol. 12 109

[8] Opila E J 1999 Variation of the oxidation rate of silicon carbide with water-vapor pressure J Am Ceram Soc. 82 625

[9] Opila E J, Fox D S and Jacobson N S 1997 Mass spectrometric identification of Si-O-H(g) species from the reaction of silicawith water vapor at atmospheric pressure J Am Ceram Soc. 80 1009

[10] Plyasunov A V 2012 Thermodynamic properties of H4SiO4 in the ideal gas state as evaluated from experimental dataGeochim Cosmochim Acta 75 3853

[11] Deal B E, Grove A S 1965 General relationship for the thermal oxidation of silicon Journal of Applied Physics. 36 3770

[12] Zhang X H, Wang J P, Huang Z G, Liu Y, Wen B and Chang C 2016 Research on oxidation resistance of SiAlON bonded silicon carbide. The 7th International Symposium on Refractories. China , Xi an, September, 20-22

[13] Liu C X, Zhao J G, Zhang Z P andWang W W 2005 Study on oxidation resistance of nitride bonded silicon carbide kiln utensils Ceramic. 5 18