High Temperature Behavior of Si_3N_4 -bonded SiC Bricks in Blast Furnace Environment

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An extensive experimental study has been carried out to better understand the high temperature properties and behaviours, such as oxidation, alkali-erosion and thermal shock resistance of the Si_3N_4 -bonded SiC refractory. The mechanism of erosion damage of the Si_3N_4 -bonded SiC brick lining in the blast furnace environment was investigated by means of scanning electron microscope (SEM), electron probe micro-analysis (EPMA) and X-ray diffraction (XRD) techniques. The results show that the alkali erosion is mainly caused by potassium penetration into the brick lining. The alkali reactions with the oxidation product SiO_2 result in the formations of low melting point potassium silicates, such as $\text{K}_2\text{O} \cdot \text{SiO}_2$ and $\text{K}_2\text{O} \cdot 2\text{SiO}_2$. These silicates are then peeled off, from time to time, leading to continuous consumption of the SiO_2 layer formed by the oxidation of SiC. Abnormal temperature variations in the furnace wall due to blowing-on or unstable operation will create thermal shock damage to the brick lining and speed up the oxidation and alkali erosion process. As a result of the combined effect of the oxidation, alkali erosion and thermal shock, caves and cracks are generated at the working surface of the SiC brick lining. It is believed that these are the major factors that deteriorate the integrity and stability of the working surface of the SiC brick lining. Based on the current work, an erosion mechanism, namely, oxidation $\rightarrow$ alkali erosion $\rightarrow$ melting or peeling-off of silicates $\rightarrow$ new oxidation and so on, was proposed for the Si_3N_4 -bonded SiC brick lining used in the blast furnace.

KEY WORDS: SiC refractory; blast furnace; lining campaign life; wear mechanism; oxidation; alkali erosion; thermal shock.

1. Introduction

With the implementation of intensive smelting technology such as oxygen-enriched blast and pulverized coal injection in the blast furnace, there is an increasing need to use high quality refractory lining to extend the furnace campaign life. Industrial practices have demonstrated that SiC bricks are one of the best lining materials from tuyere band to mid-stack and stock line wear facing. Since late sixty, there has been increasing consumption of various types of SiC bricks as alternative lining materials in the blast furnace. Over 56% of the industrialized world blast furnaces have adopted this material.¹⁾

Compared with traditional oxide refractories, SiC bricks are characterised by low porosity, high mechanical strength, better alkali and thermal shock resistance and intermediate thermal conductivity.¹⁾ Si_3N_4 -bonded SiC bricks containing approximately 20–25% Si_3N_4 are major types of silicon carbides used in the blast furnace. Such SiC bricks are commonly installed in the most severely worn region, for example, in the lower stack of the blast furnace.²⁾ The wear mechanism of the brick lining in this region has been extensively studied for

various oxide refractories. The major wear factors include alkali attack, thermal shock and the abrasion/flushing from gas, burden and molten slag and hot metal.^{3–5)} A few researches indicate that, during service in the blast furnace, SiC bricks also suffer from the above wear factors. Among those wear factors, most important rated at 60% are alkali erosion (40%) and oxidation (20%) by carbon dioxide, carbon monoxide and water vapor. The remains are abrasions by the descending burden, slag adherence and thermal shock *etc.*¹⁾ Therefore, to understand the alkali erosion and oxidation behavior is of importance to achieve a longer service life of SiC bricks in the blast furnaces and to improve the quality of SiC bricks in manufacturing process.

The oxidations of SiC bricks by air, water vapor and CO/CO_2 gas mixture with different CO/CO_2 ratios at temperatures between 800 and 1300°C have been studied and reported previously.^{6,7)} Alkali erosion of SiC bricks has been investigated by Keran and Brown,¹⁾ Kaufman *et al.*⁸⁾ and Hirota *et al.*⁹⁾ for their specified products. Pareek and Shores¹⁰⁾ investigated oxidation of silicon carbide in environments containing potassium salt vapor. It is found that alkali salts in the gas phase react with and dissolve into the SiO_2 product layer and thereby

modify both the physical properties and transport properties of the product SiO_2 scale. The alkali metals drastically lower the oxidation resistance of SiC. McNallan *et al.*¹¹⁾ studied oxidation of SiC ceramics in the presence of alkali halide vapors including KCl and NaCl. It is reported that accelerated corrosion of SiC ceramics in the presence of alkali halide vapors is driven by the chemical potential of the alkali halide in the corrosive environment. The protective SiO_2 film is deteriorated by forming molten alkali silicates. The corrosion is accelerated by adding water vapor to the environment and inhibited by adding chlorine to the mixture.

Literature has also shown that high thermal stability of Si_3N_4 -bonded SiC bricks is a basic requirement to reduce the mechanical damage by the thermal shock and the chemical wear due to oxidation/alkali erosion in the blast furnaces. The stability is likely to be broken down when abnormal temperature variation and serious erosion reactions occurs in the SiC lining. As a result, the mechanical strength will significantly decrease and the original microstructure will be disintegrated. This will accelerate the oxidation/alkali erosion process. Therefore, it is also important to study the thermal shock resistance of the Si_3N_4 -bonded SiC bricks.

The present work reports the studies on high temperature behaviours, including thermal shock resistance and alkali erosion, of the Si_3N_4 -bonded SiC bricks used in a blast furnace environment.¹²⁾ The results are discussed in connection with industrial application of SiC bricks in the blast furnace.

2. Experimental Procedures

Table 1 shows the physical properties and chemical compositions of the Si_3N_4 -bonded SiC brick samples used in the present work.

2.1. Thermal Shock Resistance Test

The experiment was conducted in a MoSi_2 electric resistance tube furnace with inner diameter of 100 mm. Brick samples were approximately cut into $25 \times 25 \times 125$ mm in size. The test was divided into five groups with each group having 3 samples. The samples were heated in the electric furnace at a heating rate of $10^\circ\text{C}/\text{min}$ to 1350°C . For each test, the samples were kept at this temperature for about 20 min and subsequently quenched in water at room temperature for 15 min. After the samples were naturally dried in air for 5 min, the test was repeated by following the same procedure as above.

For each group, the samples were subjected to the thermal shock tests for different numbers of time. The maximum treatment numbers were $N=15$. Both of the original and tested samples were then used for the bend strength measurement at room temperature. The modulus of rupture, one of the most important indices to assess the mechanical properties of SiC bricks, was obtained by taking the average values from the measurements for each group of the samples. The cracks formed due to the thermal shock were examined by SEM.

Table 1. Physical and chemical properties of Si_3N_4 -bonded SiC bricks.

Mechanical properties:	
Density (kg/m^3)	≥ 2160
Porosity (%)	≤ 18
Strength pressure-resistance (MPa)	≥ 147
Strength breaking-resistance (MPa)	
a) At room temperature	≥ 29.4
b) At 1400°C	≥ 39.2
Thermal expansion coefficient ($1/^\circ\text{C}$)	4.9×10^{-6}
Thermal conductivity ($\text{W}/\text{m}\cdot^\circ\text{C}$)	20
Chemical composition (wt%):	
SiC	≥ 71
Si_3N_4	≥ 22
SiO_2	~ 2
Fe_2O_3	~ 1
Free Si	~ 0.5

2.2. Oxidation/Alkali Resistance Tests

The oxidation tests have been carried out in air, water vapor as well as CO/CO_2 gas mixture with different CO/CO_2 ratios to simulate the blast furnace conditions.^{6,7)} The increases in weight upon oxidation have been observed with all these oxidant agents. It has been shown that passive oxidation occurred and the oxidations are controlled by the mixed chemical reaction and the diffusion through product layer. Product SiO_2 layer prevents further oxidation under the given conditions.

However, both theoretical and experimental studies in the literature^{1,8-11,13)} clearly indicate that erosion of the protective SiO_2 layer is feasible due to the existence of the molten alkali or potassium vapour. Under the blast furnace conditions, the molten alkali and alkali vapour are generated by decomposition of the alkali containing compounds entering with the burden into the blast furnaces.¹⁴⁻¹⁶⁾ Therefore, the alkali resistance experiments on the pre-oxidised samples are of particular interest in investigating the wear behaviors of SiC brick lining.

The bricks received were cut into two different shapes, approximately $25 \times 25 \times 25$ mm cubic and $25 \times 25 \times 1$ mm plate, respectively. The samples were divided into two groups for different test arrangements. The group one was oxidised at temperature of 1200°C with air flow rate of about $5 \text{ cm}^3/\text{min}$ for 12 h and then naturally cooled down to room temperature, creating a number of pre-oxidised samples. These pre-oxidised samples were then used for the alkali resistance test as described in the following. The group two, *i.e.* the original SiC brick samples, were directly applied to alkali resistance test.

The alkali resistance test was conducted in an electric resistance furnace by the following procedure. The as-cut original and pre-oxidised samples were immersed in a stainless steel crucibles filled with a mixture of fine coke and K_2CO_3 with weight ratio of 1:1. The crucibles were sealed up and heated to 900°C at a heating rate of $10^\circ\text{C}/\text{min}$ and then kept at this temperature for about 36 h. Under the given condition, the SiC brick samples were eroded by both molten K_2CO_3 (with melting temperature of about 891°C) and K vapour which is produced by the reaction:

After alkali treatment, the samples were examined by SEM and XRD techniques to investigate the changes in microstructure and mineralogical composition of the samples.

3. Results and Discussion

3.1. Mechanical and Chemical Behaviors at High Temperature

Figure 1 shows a typical structure of the original Si_3N_4 -bonded SiC sample used in the current work. It is seen that the dispersed granular SiC is enveloped by Si_3N_4 network with a uniform texture. Under normal conditions, such a network structure provides the SiC brick with a high mechanical strength and ability against the chemical attack. However, it is likely that stability of the structure is destroyed by strong thermal shock. As shown in Fig. 2, the thermal shock treatment has significantly reduced the rupture modulus of the Si_3N_4 -bonded SiC bricks under the given experimental

Fig. 1. Typical structure of the original Si_3N_4 -bonded SiC brick.

conditions. The bricks decrease in bend strength strongly after first three treatments, and then gradually with further thermal treatment.

The reason for this is that thermal shock leads to the formation of cracks both on the sample surface and inside the sample. Figure 3 is the images taken from the cross-section of the bended SiC samples after thermal shock test. It clearly shows that these cracks have two typical characteristics. One can be defined as interface crack, *i.e.* the long cracks formed on the interface between SiC grains and bonding phase Si_3N_4 , as marked with 'L' in Fig. 3. The formation and extension of these cracks destabilised the SiC brick structure and deteriorated the overall strength of the bricks. Another characteristic is the formation of massive and short cracks within the SiC grains, so called internal grain crack, as shown with mark 'M' in Fig. 3. The strength of the SiC bricks is then lowered since the SiC grains are broken down into smaller ones due to these cracks. Therefore it is considered that the microscopic cracks have been initiated in the samples

Fig. 2. Variation of rupture modulus after thermal shock treatment.

Fig. 3. Typical SEM images of the cracks formed during thermal shock (N means the number of thermal shock, L interface crack and M internal grain crack).

Fig. 4. XRD patterns for the Si_3N_4 -bonded SiC samples: 0 Si; 1 SiO_2 ; 2 $\alpha\text{-SiC}$; 3 $\beta\text{-Si}_3\text{N}_4$; 4 $\text{K}_2\text{O}\cdot\text{SiO}_2$; 5 $\text{K}_2\text{O}\cdot 2\text{SiO}_2$ and 6 KFeSi_3O_8 .

by the initial three thermal shock treatments, then cracks have gradually propagated by further treatments, resulting in gradual decrease in the bend strength.

Figure 4 gives the XRD ($\text{CuK}\alpha$, 40 kV $\times$ 100 mA) patterns of the original SiC sample and those treated by oxidation, alkali erosion and pre-oxidation/alkali erosion, respectively. Significant changes have been found among these patterns. The free Si in the bricks [Fig. 4a)] was almost completely transformed to SiO_2 [Fig. 4b)]. SiC and Si_3N_4 were also partially oxidised to SiO_2 as indicated by reduction in peak intensity of SiC and Si_3N_4 . The SiO_2 product layer then reacted with molten alkali or/and vapour K to form low melting point silicate, $\text{K}_2\text{O}\cdot 2\text{SiO}_2$ [Fig. 4d)]. Compound KFeSi_3O_8 was also found in the eroded sample [Fig. 4d)].

In the directly alkali eroded sample, both compounds $\text{K}_2\text{O}\cdot\text{SiO}_2$ and $\text{K}_2\text{O}\cdot 2\text{SiO}_2$ were found. The reduction in intensity of SiC and particular of Si_3N_4 was also observed. This indicates that SiC and Si_3N_4 were both first oxidised by $\text{CO}_{(g)}$ gas produced by reaction between K_2CO_3 and C at 900°C in the experimental work, and then SiO_2 was reacted with alkali to form $\text{K}_2\text{O}\cdot\text{SiO}_2$ and $\text{K}_2\text{O}\cdot 2\text{SiO}_2$.

Figures 5a) and 5b) are the SEM images of the Si_3N_4 -bonded SiC samples after the alkali erosion test. Compared with the original structure as shown in Fig. 1, all the samples obtained after alkali or pre-oxidation/alkali erosion have a rough surface and loose structure. The corrosion on the surface of the eroded SiC samples resulted in formation of a number of caves. The first type of caves, as shown in Fig. 5a), was generated within the SiC grains as a skeletal material. This was mainly caused by the erosion of the SiC grains. The

Fig. 5. SEM images of the sample surface after alkali resistance tests: a) direct alkali erosion; b) direct alkali erosion and c) pre-oxidation/alkali erosion.

second type was formed in the adhesive region surrounding the SiC grains [Fig. 5b)], which was formed by the erosion of the bonding phase Si_3N_4 in SiC bricks.

It is interesting to note that the formation of caves was simultaneously accompanied by the cracks, as shown in Fig. 5c). This is mainly caused by the thermal stress due to alkali erosion at high temperatures. It should be mentioned that some slight cracks were also observed in both the pre-oxidised sample and the as-cut original samples. These initial cracks also affect on the formation and/or extension of cracks during alkali erosion. It is believed, for the pre-oxidised sample, that the erosion resistance against alkali metals is proportional to the thickness of oxide layer, but the thickness was not measured at this stage.

The EPMA analysis further indicates that the K content in the treated SiC samples is usually high, and particularly high in the regions where the caves were formed. It is interesting to note that Fe and K are enriched in the caves and the nearby regions. Small amount of impurity such as Fe has accelerated the alkali

Fig. 6. Characteristics of the cracks formed under blast furnace conditions.

Fig. 7. Potassium enrichment in the eroded SiC brick measured by EPMA.

erosion of the bricks by destroying SiO_2 protection layer and forming KFeSi_3O_8 as indicated by XRD analysis. The alkali metals and Fe are the major components to cause “caves” phenomena.

3.2. Wear of SiC Bricks in the Blast Furnace Environment

Some investigations during the campaign of commercial blast furnaces have been reported in open literature. It is suggested that the wearing damage of SiC brick lining is closely related to its behaviors at high temperature. Hirota *et al.*,⁹⁾ for instance, have observed the same mechanical phenomena as found in the present thermal shock test, for their Si_3N_4 -bonded SiC bricks used in the Mizushima Blast Furnace. In order to investigate the high temperature behavior of SiC bricks under the actual blast furnace environment, a plant test was also carried out by means of core drilled sample from a blast furnace after about 8 months campaign. The procedure of the field test has been reported in details elsewhere.¹⁷⁾ The following only focus on the analysis of microscopic structure and the reaction product of the eroded SiC brick, which can be compared with the experimental measurements under laboratory conditions as mentioned above. Based on all these results, the wearing mechanism of SiC brick lining in the blast furnace is then highlighted.

Figure 6 shows the cracks formed in the Si_3N_4 -bonded SiC brick which has been undergone through the erosion for about 8 months campaign in the blast furnace. Figure 7 gives the representative EPMA results of the same SiC sample. The sample was sliced along the direction normal

Fig. 8. XRD pattern for the eroded SiC sample in a commercial blast furnace.

to and at about 20 mm distance from the working surface of the eroded SiC brick. The results indicated that the brick structure was obviously deteriorated by thermal shock and alkali erosion. Like the findings under current laboratory conditions, the cracks indicate the breaking down of both SiC and Si_3N_4 bonding in a wide range because of the different thermal expandability of the phases SiC and Si_3N_4 or the porous structure defect after erosion. The penetrations of potassium vapor and CO/CO_2 , the alkali erosion and the carbon deposition are all accelerated by such cracks. EPMA result as shown in Fig. 7 indicates the potassium enrichment of about 6.41% nearby these cracks compared with the original Si_3N_4 -bonded SiC brick in which there is almost no alkali metals. The concentration of Fe nearby the cracks is about 1.964%, obviously higher than the chemical analysis of Fe_2O_3 (<1%) in original bricks (refer to Table 1). Carbon deposition was not measured, but a distinct boundary between the eroded and un-eroded parts of the sample brick was observed. Compared with the un-eroded region, eroded part has a deep black where carbon deposition clearly has occurred.

Figure 8 shows the XRD pattern of the SiC sample taken from the surface layer (about 1.5 mm depth) of the eroded Si_3N_4 -bonded SiC brick after taking away the adhered slag layer. The result also indicates the existence of $\text{K}_2\text{O} \cdot \text{SiO}_2$, $\text{K}_2\text{O} \cdot 2\text{SiO}_2$ and KFeSi_3O_8 , being closely consistent with the results obtained for the laboratory samples (see Fig. 4). This implies that the alkali erosion of Si_3N_4 -bonded SiC brick lining in the blast furnace environment follows the same mechanism as in the present laboratory study, *i.e.* by forming various potassium silicates.

Because of the lower melting point of these silicates, the brick layer eroded will be further dissolved to form “slag shell” on working surface. The shell is then peeled off by either descending burden or thermal shock due to abnormal local temperature variation in the blast furnace. The new working surface is then formed to stand the corrosive environment of the blast furnace. Therefore, oxidation → alkali erosion → melting or/and peeling off are the three basic steps to damage the Si_3N_4 -bonded SiC brick lining in the blast furnace. Oxidation promotes the alkali erosion which, together with the thermal shock, breaks down the original structure of SiC bricks. In other

words, alkali erosion transforms the protective (passive) oxidation at normal conditions to a continuous (active) oxidation in the blast furnace environment. Thermal shock creates cracks and increases the reaction area for alkali erosion and oxidation, thus accelerates the chemical corrosion. Therefore, stable operations are essential to minimise the thermal shock. As discussed elsewhere,¹⁸⁾ controlling the heat transfer of furnace wall can control alkali erosion and reduce thermal shock, and improve the performance of the Si₃N₄-bonded SiC brick lining in the blast furnace.

4. Conclusions

It has been realised from extensive industrial practices that the blast furnace campaign is strongly dependent on the high temperature behavior of lining materials. To better understand this issue, a combined experimental work in laboratory and plant has been carried out on the SiC brick lining by studying the physico-chemical and mechanical behavior of the brick such as oxidation, alkali-erosion and thermal shock at high temperature under the blast furnace conditions. The eroded SiC samples from both laboratory and a plant furnace were analysed by means of SEM, EPMA and XRD techniques. The results show that the alkali erosion is mainly caused by potassium penetration and subsequent formation of potassium silicates, such as K₂O·SiO₂ and K₂O·2SiO₂ etc. within a certain range from the working surface of brick lining. Such alkali erosion transforms the oxidation process from a protective to a continuous reaction. Thermal shock damage caused by abnormal local temperature variations due to blowing-on or unstable operation will enhance the oxidation and alkali erosion process. As results of the combined effect of the oxidation, alkali erosion and thermal shock, "cavernous corrosion" and cracks are generated at the working

surface of the SiC brick lining. This is regarded as the direct reason deteriorating integrity and stability of the working surface of the SiC brick lining. Therefore, the Si₃N₄-bonded SiC brick lining during the campaign of blast furnace suffers from the physical attack and chemical erosion in a periodical way, i.e. oxidation→alkali erosion→melting or peeling-off.

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