EVALUATING HIGH-TEMPERATURE CORROSION OF SiC REFRACTORIES BY COAL SLAG USING IMPROVED EXPERIMENTAL METHOD

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ABSTRACT

SiC refractories are currently utilized as lining materials for water-cooled gasifier at a service temperature lower than 1300°C. Very few researches have been reported on the corrosion of SiC materials at even higher temperature. In this paper, corrosion behavior of SSiC and Si_3N_4-SiC refractories interacted with coal slag was investigated at 1500°C under reducing atmosphere using improved rotary slag testing method. Moreover, interactions between refractory materials and molten slag were also predicted by thermodynamic calculations using modified model under the same conditions. The results showed that SSiC and Si_3N_4-SiC refractories presented the similar stability and corrosion behavior under simulated gasification conditions. SiC reacted with FeO to form Si-Fe-C alloy on the surface of the corroded materials. Meanwhile, SiO_2 phase was also formed by oxidation of SiC in the experimental atmosphere and then dissolved into the molten slag eventually.

INTRODUCTION

Coal gasification technology is a process that converts coal or the combustible part of the coal tar at high temperature and pressure into flammable gas mainly composed of carbon monoxide and hydrogen[1]. Coal water slurry gasification technology is one of the most widely used coal gasification technologies. It is typically operated between 1300 and 1600 ℃ at pressures of 2.0–6.9 MPa under a strongly reducing atmosphere[2,3]. Because of the complex working conditions in the coal gasifier, high chrome refractories are usually adopted as lining materials in the gasifier due to their excellent corrosion resistance. However, Cr^{+6} are formed by the reactions of CaO, Na_2O, and K_2O with Cr_2O_3,which is easily soluble in water[4]. As carcinogenic substance, Cr^{+6} pollutes the environment and endangers people's health seriously if the residual bricks are not disposed properly[5].Therefore, research on chrome-free materials as gasifier lining has great significance on environmental protection and occupational health.

SiC is utilized extensively as high-temperature structural material due to its excellent thermal shock stability, high-temperature strength, and low coefficient of thermal expansion[6,7], and it is used as lining material of gasifiers with water-cooled walls because of its excellent thermal conductivity. However, the working temperature of SiC is lower than 1300℃ in coal gasifiers with water-cooled walls. Few researches on the slag corrosion resistance of SiC materials at higher temperatures has been reported so far. In this paper, the dynamic corrosion of SSiC and Si_3N_4 bonded SiC interaction with coal slag has been investigated in an improved rotary drum furnace under simulated gasifier conditions at 1500℃. Moreover, the corrosion process has also been simulated by thermodynamic calculations based on an improved model. Finally, the mechanism of the slag-induced corrosion of SiC samples in a reducing atmosphere has been analyzed based on thermodynamic simulation and experimental results.

EXPERIMENTAL AND CALCULATION

Dynamic erosion experiment

To simulate the gasifier atmosphere for the following corrosion test, an atmosphere calibration experiment was conducted in the rotary drum furnace firstly. A mixture of C_2H_2 and O_2 was used as the fuel gas and the FeO content in the quenched slag was analyzed to determine the atmosphere.

Then the SSiC and Si_3N_4-SiC bricks were lined into the rotary drum furnace according to Fig.1. The furnace was heated up to 1500℃ at a rate of about 200℃/h by firing the C_2H_2 and O_2 gases at the flow ratio determined in the above calibration experiment. Coal slag was put into the furnace and kept the furnace temperature at 1500 ℃ for 2h. For deslagging, the furnace body was immediately inclined to an angle of 90° and the slag was poured into cold water. Subsequently, the furnace body was restored. This whole process was repeated for 20 h to complete the corrosion experiment. After the furnace was cooled down, the obtained corroded samples were collected and cut for further analysis. The polished samples were examined by EDS for morphological observation and compositional analysis.

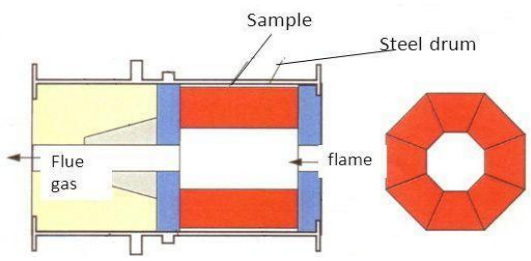

Fig.1: The diagram of the rotary drum furnace

Small quantities of the samples were pulverized and analyzed by XRD to examine the crystalline phases.

Thermodynamic calculations

Thermodynamic calculations were performed using the FactPS and FToxid databases that are comprised in version 6.4 of the FactSage^{TM} software.

We calculated phase composition and gas partial pressures after SiC oxidation process under the atmosphere determined by the calibration experiment. Moreover, we simulated thermodynamic equilibrium phases after the interaction of SiC with slag according to the model illustrated in Fig.2. Therein, the left zone(S) is defined as slag and the right zone(R) as SiC sample, which are correlated according to the equation of (R)+(S)=100g. The percentage of SiC in the mixture is denoted by A (A=(R)/[(R)+(S)]*100%).

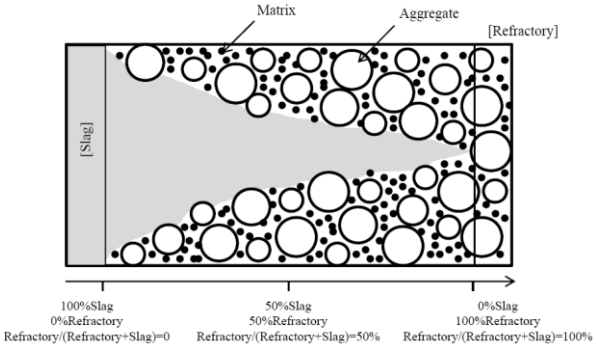

Fig.2: Thermodynamic calculation model

RESULTS AND DISCUSSION

Atmosphere calibration

The results of the atmosphere calibration are listed in Table1, which reveal that the FeO percentage in the Fe oxides increased gradually with the increase of the C_2H_2/O_2 flow ratio. At a flow ratio of C_2H_2/O_2 =45/55, the FeO percentage in the Fe oxides reached 96.15% after a soaking time of 15min and increased slightly to 98.55% after a prolonged soaking time of 1 h. At a flow ratio of C_2H_2/O_2=50/50, only a slightly larger FeO percentage of 98.76% was detected in the slag after 15min, which suggests that a further increase of the C_2H_2/O_2 flow ratio presumably causes no further increase of the FeO percentage.

At a C_2H_2/O_2 flow ratio of 45/55, only an amorphous phase was detected in the quenched slag by XRD analysis. This indicates that SiC materials can interact with molten amorphous slag under the experimental conditions. Kwong[2] and Font[8] also detected FeO mainly exist as Fe oxide species in amorphous silicate melt in coal gasifiers, which is in good agreement with the above experimental results. Therefore, a C_2H_2/O_2 flow ratio of 45/55, which can be realized in the simulated gasification atmosphere, was determined as the performing condition for corrosion testing and calculation procedures.

Tab. 1: Results of the atmosphere calibration

C_2H_2/O_2	Soaking time (mins)	Fe_2O_3 (%)	FeO (%)	FeO/Σ(FeO_n) (%)
40/60	15	6.54	3.02	31.59
45/55	15	0.35	8.74	96.15
45/55	60	0.13	8.86	98.55
50/50	15	0.11	8.79	98.76

Microstructure and phase analysis of corroded SiC bricks

Fig.3 shows the microstructure and phase analysis results of SSiC sample. It can be seen that small amount of slag and metal particles exist on the surface of corroded brick. The metal particles are detected as the composition of C, Fe and Si by SEM-EDS analysis. About 1mm reaction layer formed by the penetration of slag which led to unclear interfaces between matrix and aggregates. FeO and SiO_2 as the main phases exist in the reaction layer which is also detected by SEM-EDS. The XRD analysis of corroded SSiC brick shows that new phases of SiO_2 and $CaAl_2Si_2O_8$ were formed comparing to the original brick which only contains SiC and Si. The much lower peak intensity of new formed phases indicates a much thinner reaction layer formed on the surface. Moreover, no metal phases are detected by XRD which is due to the loss of formed metal during slag pouring process.

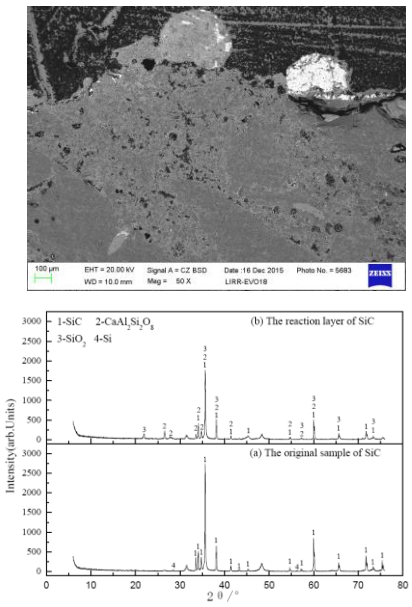

Fig. 3: Microstructure and XRD analysis of corroded SSiC

Fig.4 presents the microstructure and phase analysis results of Si_3N_4-SiC sample. It can also be seen that small amount of remained slag and metal particles exist on the surface of the

brick. The penetration depth of slag is slightly thinner than that of SSiC. The main phases in the reaction layer are also detected as FeO and SiO_2. The XRD analysis shows that new phase of SiO_2 and Si_2N_2O formed during the corrosion process, which may be caused by oxidation of SiC and Si_3N_4. No $CaAl_2Si_2O_8$ phase is found in the XRD pattern which is also due to the less slag penetration. Moreover, no metal phases are found either.

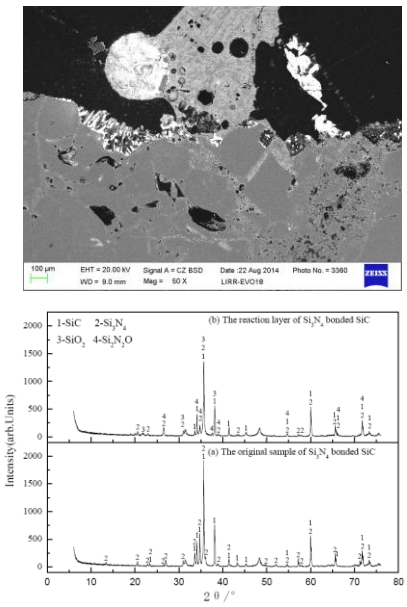

Fig. 4: Microstructure and XRD analysis of corroded Si_3N_4-SiC

Corrosion mechanism-Atmosphere oxidation

In the simulated atmosphere, the O_2 partial pressure is much higher than that SiC and Si_3N_4 could exist stably. Therefore, the SiC and Si_3N_4 will be oxidized to form SiO_2 in the present atmosphere. The calculated phase composition and gas partial pressure after oxidation are shown in Fig. 5. When SiC brick interacted with experimental gases, solid phase of SiO_2 and gas phases of SiO and CO will be formed accordingly. The O_2 partial pressure decreases and then becomes to a table value. However, when the gases interacted with Si_3N_4, both the O_2 and CO partial pressures decrease and become to a table value but the N_2 partial pressure increases accordingly. The solid phases of SiC, SiO_2 and Si_2N_2O and gas phases of SiO, CO, N_2 and NO are formed after oxidation process.

It is well known that SiC and Si_3N_4 will be oxidized when interacted with gases containing O_2 at high temperature. If the O_2 partial pressure is higher, solid SiO_2 layer will be formed on the surface of SiC and Si_3N_4 and inhibit the further oxidation process, which is named passive oxidation. If the O_2 partial pressure is lower, no solid SiO_2 layer exist and the oxidation process will be continued, the process of which is named as active oxidation.

It is reported by Yamaguchi[9] that the critical condition of passive oxidation and active oxidation of SiC is $P(O_2)=P(SiO+CO)$. When $P(O_2) < P(SiO+CO)$, the active oxidation will proceed. Accordingly, the critical condition of passive oxidation and active oxidation of Si_3N_4 is $P(O_2)=P(SiO+N_2)$. When $P(O_2) < P(SiO+N_2)$, the active oxidation will proceed. It can be seen from Fig. 5 that when the gas-solid reaction between SiC/Si_3N_4 and the gas mixture reached equilibrium state, $P(O_2)$ is lower than $P(SiO+CO)$ and $P(SiO+N_2)$ where the active oxidation proceeded and solid SiO_2 and gases formed accordingly.

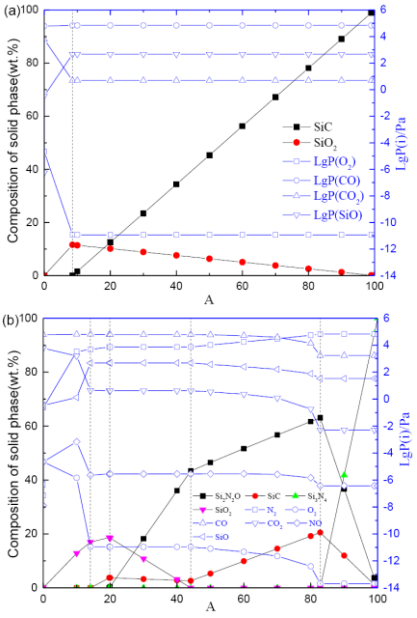

Fig.5: Calculated results of solid phases and gas pressure under simulated atmosphere

Corrosion mechanism-Slag corrosion

In the present experimental atmosphere, the oxidation of SiC and Si_3N_4 will decrease the O_2 partial pressure. The FeO in molten slag will be reduced to Fe which will then reacted with SiC to form FeSi and C. The reaction products of Fe, FeSi, and C interact to form liquid alloys and precipitate into the slag. The largest amount of the liquid alloys was poured into water with the slag, and the remaining liquid alloys adhered to the surface upon cooling.

Fig. 6 shows the calculated results when SiC and Si_3N_4 interacted with molten slag at experimental atmosphere. Solid phase of SiO_2 will be formed when the molten slag interacted with SiC while Si_2N_2O formed when with Si_3N_4. The formed SiO_2 dissolves into the molten slag to cause an increase of SiO_2 content and decrease of CaO and Al_2O_3 in slag.

In the experimental process, the O_2 partial pressure in the furnace was always higher than the O_2 partial pressure when SiC and Si_3N_4 existed stably. Thus, SiC and Si_3N_4 were continuously oxidized and dissolved in the molten slag. Furthermore, the SiO_2

dissolution in the slag became gradually saturated and excessive SiO_2 precipitated on the pore surface, leading to continuous slag penetration. The process comprising dissolution, precipitation of SiO_2 and slag penetration increased the SiO_2 content in the molten slag and the slag viscosity which would weaken further infiltration. Therefore, the molten slag exhibited a much thinner penetration depth into the sample during the present corrosion testing process.

Additionally, SiC could be easily oxidized at present experimental atmosphere but Si_3N_4 will only be oxidized to form Si_2N_2O at relatively lower O_2 partial pressure. Therefore, the molten slag infiltrated deeper in SSiC sample comparing to that in Si_3N_4-SiC sample.

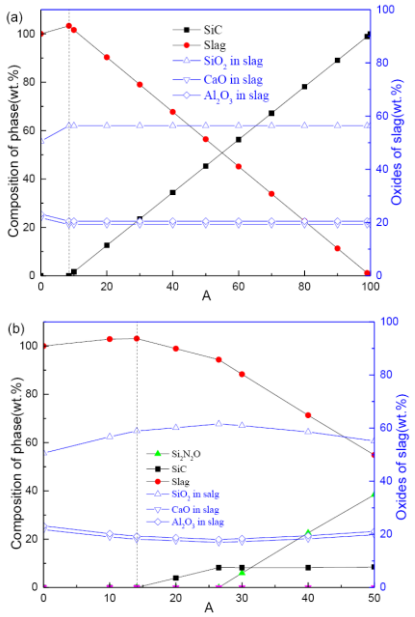

Fig.6: Calculated results of interactions of SiC brick and molten slag

CONCLUSION

In the present experimental atmosphere, the corrosion processes of SSiC and Si_3N_4-SiC by molten slag are much similar. The solid phase of SiO_2 formed by active oxidation of SiC and Si_3N_4 will dissolve into the molten slag. The oxidation process changed the pore structure on the surface and the molten slag infiltrated into the pores to form a thinner reaction layer.

In the gasification atmosphere, SSiC and Si_3N_4-SiC bricks will be oxidized by active oxidation process of gases. Moreover, the molten slag could also react with the SiC bricks. Because of the poor wettability of SiC bricks, no remained slag existed on the surface which could not inhibit the active oxidation process and dissolution of SiO_2. Thus, SSiC and Si_3N_4-SiC refractories will not be applicable for the water coal slurry gasification.

ACKNOWLEDGMENT

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