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Study on the erosion mechanism of acid coal slag interactions with silicon carbide materials in the simulated atmosphere of a coal gasifier

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ABSTRACT

In this paper, the dynamic erosion of silicon carbide interaction with acid coal slag was studied in an improved rotary drum furnace under the simulated conditions of a slagging gasifier at temperature of 1500 °C. Microstructures of corroded samples were observed by SEM, and the erosion mechanism was investigated by thermodynamic simulation based on SEM analysis. This revealed that SiC reacted with FeO to form a Si-Fe-C alloy on the sample surface, and the active oxidation of SiC was conducted in the experimental atmosphere. Furthermore, SiO_2(s), SiO(g), CO(g), and CO_2(g) were formed. Finally, SiO_2 dissolved in the molten slag, and SiO(g), CO(g), and CO_2(g) spread continuously. The pore structures on were altered by the oxidation reaction, which facilitated slag penetration into the samples through the pores to form a thin reaction layer.

1. 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. This gasification is typically operated between 1300 and 1600 °C at pressures of 2.0–6.9 MPa [2–4] under a strongly reducing atmosphere. In the gasifier, non-volatile mineral impurities in the carbon feedstock are liquefied at the elevated temperature to form a corrosive slag, which flows down along the inner furnace wall. Refractory linings are used to protect the steel vessel from attacks by corrosive gases, molten slag, and abrasive wear as well as to bear the tremendous thermal stress. Because of the harsh 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, the reactions of CaO, Na_2O, and K_2O with Cr_2O_3 form Cr^{+6}, which is easily soluble in water [5,6]. As carcinogenic substance, Cr^{+6} pollutes the environment and endangers people's health seriously if the residual bricks are not disposed properly [7]. Therefore, research on chrome-free materials as gasifier linings has great significance in 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 [8,9], 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 °C in coal gasifiers with water-cooled walls. Little research on the slag corrosion resistance of SiC materials at higher temperatures has been reported to date. In this paper, the dynamic corrosion of SiC interaction with acid coal slag has been investigated in an improved rotary drum furnace under simulated gasifier conditions at 1500 °C. Moreover, the corrosion process has also been simulated by thermodynamic calculations based on an established model. Finally, the mechanism of the acid slag-induced corrosion of SiC samples in a reducing atmosphere has been analyzed based on thermodynamic simulation and experimental results.

2. Materials and experimental process

2.1. Materials

Commercial SiC refractory brick with β–SiC as bonding phase bonded α–SiC aggregates was used in this paper. The properties is given in Table 1.

Industrial slag samples were collected in the gasifier of Huayi as the experimental slag. The chemical composition of the collected slag is

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Table 1
Properties of SiC refractory.

Property	SiC refractory
Chemical composition (wt%)	
SiC	95.46
Si_2N_2O	2.74
Free Si	0.86
Free C	0.61
FeO	0.33
Apparent porosity (%)	14.0
Average pore diameter (nm)	78.1
Bulk density ($g \cdot cm^{-3}$)	2.74
Compressive strength (MPa)	184
Bending strength (MPa)	52
Thermal conductivity(1000 ℃, $W \cdot m^{-1} \cdot K^{-1}$)	22.8

shown in Table 2, where FeO is the main phase as Fe oxides with FeO/Fe_2O_3 ration of 46.37 and $FeO/\Sigma(FeO_n)$ % of 97.89%. According to the definition of slag basicity $m(Fe_2O_3+FeO+CaO+MgO+Na_2O+K_2O)/m(SiO_2+Al_2O_3+TiO_2)$ [10], the calculated basicity of the experimental slag was 0.47, which is considered as acid slag.

2.2. Calibration of the experimental atmosphere

The gases composition in the Huayi gasifier is shown in Table 3. It show that the gases are mainly consisted of CO, H_2 and CO_2, which are also the main gas mixture as the combustion products of C_2H_2 and O_2 but has different compositional content. It was studied by us that with the C_2H_2/O_2 flow ratios increasing, the content of CO, H_2 in combustion gases increased and the partial pressures of O_2 and CO_2 decreased. Although there are some differences in the composition of combustion gases, the experimental O_2 partial pressures which are close to that in industrial gasifier can be obtained by adjusting the C_2H_2/O_2 flow ratios.

To simulate the gasifier atmosphere for the following corrosion test, an atmosphere calibration experiment was conducted in the rotary drum furnace lined with corundum bricks. In this experiment, a mixture of C_2H_2 and O_2 was used as the fuel gas. Temperature and atmosphere inside the furnace were adjusted by controlling flow and flow ratio of the gas mixture. The furnace temperature was continuously measured by an optical pyrometer. To ensure the accuracy, the measured temperature was also calibrated with a standard W-Mo thermocouple which is inserted into the furnace chamber.

The calibration experiment was performed as follows: first, the furnace was heated up to 1500 °C, and the gas flow was controlled using a high precision flowmeter. Then, 500 g slag was put into the furnace, and the furnace temperature was maintained at 1500 °C for a certain time while the gas flow was adjusted to various precalculated gas flow ratios before pouring the molten slag immediately into cold water. The quenched slag samples were dried for 10 h at 80 °C, and their Fe_2O_3 and FeO contents were determined by wet chemical analysis. Finally, the atmosphere conditions in the rotary drum furnace at 1500 °C were calibrated with respect to the FeO content in the slag. Based on the above results, the C_2H_2/O_2 flow ratios were determined to obtain the required experimental atmosphere conditions with the oxygen partial pressure close to calculated result($10^{-4.57}$ Pa) according to the gases composition in the Huayi gasifier and reported result ($10^{-5.4}$–$10^{-2.4}$ Pa) [11] at 1500 °C.

Table 3
Chemical composition of gases.

Chemical composition	CO	H_2	N_2	H_2S	CO_2	CH_4	Ar	COS
Content, mol.%	35.23	46.01	0.12	0.06	18.32	0.10	0.03	0.13

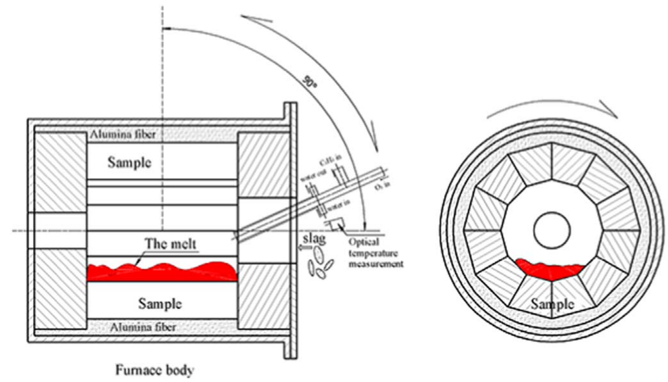

Fig. 1. Schematic of the rotary slag test.

2.3. Dynamic erosion experiment

The isosceles trapezoid SiC bricks with the dimensions of 230×65×40.2/75 (mm) were lined into the rotary drum furnace according to Fig. 1. The furnace body with outer size of Φ340×390(mm) and inner size of Φ150×230 (mm) was oriented horizontally and could rotate at a rate of about 5 r/min. The furnace was heated up to 1500 °C at a rate of about 200 °C/h by firing the C_2H_2 and O_2 gases at the flow ratio determined in the above calibration experiment. 500 g slag was put into the furnace and kept the furnace temperature at 1500 °C for 2 h. 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, and this whole process of putting 500 g slag, kept the furnace temperature for 2 h, and deslagging was repeated for 20 h to complete the corrosion experiment. After the furnace was cooled down, the obtained corroded SiC samples were collected and cut for further analysis. The samples were cross-sectioned to expose the infiltration into the sample and progressively polished. The polished samples were examined by EDS for morphological observation and compositional analysis. Small quantities of the samples were pulverized and analyzed by XRD to examine the crystalline phases. The pore size distributions of original and corroded SiC refractories were measured using a mercury injection instrument (AutoPore IV 9500) with injection pressure from 0.1 to 3300 psia.

2.4. Thermodynamic calculations

Thermodynamic calculations were performed at 1500 °C and 1 atm using the FactPS and FToxid databases that are comprised in version 6.4 of the FactSage™ software.

The predominance area diagram of SiC in the C-Si-O system was calculated for a temperature of 1500 °C using the Predom module. The partial pressures of CO and O_2, which were produced by the combustion of C_2H_2/O_2 mixtures at various flow ratios, were calculated using the Equilib module. Furthermore, we calculated phase composition and

Table 2
Chemical composition of coal slags.

Chemical composition	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	TiO_2	K_2O	Na_2O	basicity
Content, wt%	46.02	21.08	0.19	8.81	19.82	0.90	0.78	1.07	1.33	0.47