ARTICLE IN PRESS

Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Corrosion of high chromia refractory materials by basic coal slag under simulated coal gasification atmosphere

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ARTICLE INFO

Keywords:
Coal gasifier
Reducing atmosphere
High chromia refractory
Thermodynamic simulation
Corrosion mechanism

ABSTRACT

In this paper, dynamic corrosion experiment of a high chromia refractory interaction with basic coal slag under slagging gasifier conditions was conducted by using rotary drum corrosion test with the FactSage thermodynamic analysis. The microstructures and chemical compositions of the corroded samples were analyzed by scanning electron microscopy (BEI and EDS), and the corrosion mechanism was investigated by combining thermodynamic simulation and SEM analysis. The results show that the simulation results were consistent with the results of corrosion test. Reaction layer and penetration layer are formed from the surface to the interior of the sample after corrosion. The (Mg, Fe) (Al, Cr)$_2$O$_4$ spinel solution was formed in the reaction layer, which make the matrix structure become dense and change the overall structure of the particles' uniformity. Corrosion of Cr_2O_3 aggregate is relatively weak by slag. The Cr_2O_3 dissolves into the slag through the formed spinel solution layer on the surface of aggregates. While, Cr_2O_3 and Al_2O_3 dissolve into molten slag through the spinel solution layer formed in the matrix. ZrO_2 in the matrix directly dissolved into molten slag and penetrates inner the matrix with the penetration of the slag to form a ZrO_2-free region. The liquid sintering of the matrix has happened in the melt, causes the structure of the penetration layer become dense, which is different from that of the original sample.

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. At 1500 °C, the oxygen partial pressure in the gasifier was $10^{-4.8} \sim 10^{-3.5}$ Pa, and the oxygen partial pressure in the gasifier was from $10^{-3.9}$ to $10^{-2.7}$ Pa at 1600 °C [5]. In the gasifier, non-volatile mineral impurities in the carbon feedstock are liquified 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, the refractories with excellent corrosion resistance are needed as lining materials in gasifer. High chromia refractory is made of Cr_2O_3 as the main raw material, and the content of Cr_2O_3 is more than 86 wt%. Since the solubility of Cr_2O_3 in the slag is very low [6], so that high chromia refractory has excellent resistance, it is widely used as a coal water slurry gasifier lining material.

The corrosion behavior of high chromia refractories by coal slag changes with slag basicity [7]. However, the refractory failures are mainly caused by chemical corrosion, erosion, penetration and spalling caused by the temperature fluctuations [8,9]. The service life of the refractory lining is between 3 and 36 months [10], which is dependent on the ash chemistry and quantity, the operating temperature, gasifier maintenance, and the frequency of gasifier cycling. Low rank coal is abundant in XinJiang but has not been used for gasification production. One of the main reasons is that the high content of Na, K and other alkali metal in the raw coal, which leads to high basicity and low viscosity of molten slag under the condition of high temperature [11]. High chromia refractory could be seriously corroded in the gasifier which reduce the service life of the gasifier. Moreover, the research on

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https://doi.org/10.1016/j.ceramint.2017.11.023
Received 19 April 2017; Received in revised form 19 October 2017; Accepted 5 November 2017
0272-8842/

Please cite this article as: Cai, B., Ceramics International (2017), https://doi.org/10.1016/j.ceramint.2017.11.023

the corrosion mechanism of high chromia refractory by high basicity slag has not yet reported in the literature.

At present, research on the corrosion mechanism of high chromia refractory was mostly based on a static test in air atmosphere or CO and CO_2 atmosphere [3,12–16], which has great difference with the real gasification conditions. In the present work, dynamic corrosion experiments of high chromia refractory interacted with high basicity coal slag were conducted in the rotary drum furnace using C_2H_2 and O_2 mixed gas as fuel at 1600 °C to simulate the gasifier conditions. Moreover, the corrosion process of the interaction between high chromia refractory (aggregate and matrix, separately) and slag was also calculated using Factsage 6.4 thermodynamic software based on the established calculation model. Finally, the corrosion mechanism of high chromia refractory by high basicity slag in the experimental atmosphere was analyzed by combining thermodynamic simulation and experimental results.

2. Materials and experimental process

2.1. Materials

Commercial high chromia refractory with (Al, Cr)$_2$O$_3$ solution as bonding phase was used in this study. The properties of the refractory are given in Table 1.

Because the XinJiang coal has not been used for gasification production, there was no slag available at present. Thus, coal ashes formed by direct combustion of Xinjiang coal were collected as the experimental slag. The chemical composition of the collected slag was analyzed by the wet chemistry analyses, and the results are shown in Table 2. 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) [17], the calculated basicity of the experimental slag was 1.13, which is considered as high basicity slag.

2.2. Dynamic corrosion experiment

The isosceles trapezoid high chromia samples 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 1600 °C at a rate of about 200 °C/h by firing the C_2H_2 and O_2 gases at the flow ratio of 45/55, making the majority of the iron is present as Fe^{2+} in amorphous slag [18]. 500 g slag was put into the furnace and kept the furnace temperature at 1600 °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 was repeated for 20 h to complete the corrosion experiment. After the furnace was cooled down, the obtained corroded high chromia 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 backscattered electron imaging (BEI) and EDS analysis was performed for morphological observation and compositional analysis. The quenching slag in the experiment was pulverized and analyzed by XRD to examine the crystalline phases. XRD data were collected using a Philips X'Pert diffractometer fitted with a Cu LFF tube operated at 40 kV and 40 mA. Electrons that emitted by cathode tungsten wire hit the target material (Cu) at high speed to produce X-ray beam.

Table 1
Properties of high chromia refractories used in this study.

Property	High chromium refractory
Chemical composition (wt%)	
Cr_2O_3	86.49
Al_2O_3	7.96
ZrO_2	4.75
Apparent porosity (%)	16.5
Bulk density (g cm^{-3})	4.23
Compressive strength (MPa)	156
Bending strength (MPa)(1400 °C × 0.5 h)	38

2.3. Thermodynamic simulation

The reaction of high chromia refractory with coal slag is a complex reaction of multi systems. The Factsage™ 6.4 software was used to simulate the interaction of high chromia refractory with slag based on the established calculation model and predict the phase formation when thermodynamic equilibrium was reached.

Thermodynamic calculations were performed at 1600 °C, 1 atm and the molar ratio of C_2H_2 and O_2 gases is 45/55($P_{O2} = 10^{-3.8}$ Pa) using the FactPS and FToxid databases that are comprised in version 6.4 of the FactSage™ software. All the solutions in the FToxid databases were selected in this simulation. The solid solution of corundum is mainly composed of Al_2O_3, Cr_2O_3, Fe_2O_3 and Ti_2O_3. The solution of spinel compound is mainly composed of $FeCr_2O_4$, $MgCr_2O_4$, $FeAl_2O_4$ and $MgAl_2O_4$. The liquid phase is composed of Na_2O, K_2O, Al_2O_3, SiO_2, $NaAlO_2$, CaO, FeO, Fe_2O_3, MgO, CrO, Cr_2O_3, Ti_2O_3 and TiO_2, in which $NaAlO_2$ was considered as a part of the slag model, and Cr_2O_3 in the slag was represented in the form of CrO and Cr_2O_3. Thermodynamical equilibrium phases after the interaction of high chromia refractory with slag were simulated using Equilib module under experimental condition according to the calculation model in Fig. 2. Where the left zone (S) is defined as slag and the right (R) as high chromia refractory with the equation of (R) + (S) = 100 g. A represents the percentage of high chromia refractory in the mixture (A = (R) / [(R) + (S)] * 100%).

3. Results

3.1. Phase of the molten slag

Only amorphous phase was observed in the quenched slag by XRD analysis as shown in Fig. 3. This result revealed that high chromia refractory would interact with molten slag under experimental conditions.

3.2. Phase and microstructure analysis of the original sample

Fig. 4 shows the XRD pattern of original high chromia refractory. It can be observed that besides the diffraction peaks of Cr_2O_3 and monoclinic ZrO_2, there is also a small diffraction peak near the Cr_2O_3 diffraction peak. The chemical composition of high chromia sample is Cr_2O_3, Al_2O_3, ZrO_2. Cr_2O_3 and Al_2O_3 cannot react with ZrO_2 to form compounds or corundum solutions, only Cr_2O_3 and Al_2O_3 can form (Al, Cr)$_2$O$_3$ solution [20]. It is concluded that the diffraction peak with small intensity is the diffraction peak of (Al, Cr)$_2$O$_3$ solution. The diffraction peak of (Al, Cr)$_2$O$_3$ solution is between Cr_2O_3 and Al_2O_3, close to the peaks of high content components [21]. With the increase of the diffraction angle, the diffraction peak of (Al, Cr)$_2$O$_3$ solution becomes gradually obvious. This is due to the lattice parameter of (Al, Cr)$_2$O$_3$ solution is different from that of Cr_2O_3, which is more obvious when the angle is large [15]. The diffraction peaks of Al_2O_3 were not found in the samples, indicating that Al_2O_3 was completely dissolved into Cr_2O_3. Thus, the phases of the sample contain Cr_2O_3, (Al, Cr)$_2$O$_3$ solution and monoclinic ZrO_2.

The samples used in the experiment were high chromia bricks with a Cr_2O_3 content of about 86%. The microstructure of the brick is shown in Fig. 5(a). It reveals that the particles with different shapes, different chemical compositions and different density constitute the high chromia brick with uneven microstructure. The matrix is well combined with the