



High-temperature corrosion of silicon carbide ceramics by coal ashes

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Abstract

New high-efficiency gasification reactors with higher temperatures and pressures and with different temperature cycles than previously require new types of refractory linings. Besides the oxide materials currently in use, SiC ceramics show great promise as refractories in the reducing atmospheres found in gasifiers. The behaviour of RSiC and SSiC materials was investigated in a flowing CO/H₂-containing Ar atmosphere with three different ashes (from basic to strongly acidic) in the temperature range between 1000 °C and 1300 °C. After dwell times of up to 100 h the cross sections of the materials were analysed by SEM and EDS. The results showed the high stability of the materials in all ashes. The porous RSiC materials showed small amounts of infiltration depending on the ash composition, but no destruction of the necks between the SiC grains was observed. Thermodynamic calculations simulating the conditions prevailing in a gasification reactor yielded similar phases to those obtained in the corrosive conditions used in the experiments. Due to the strongly reducing conditions the sulphates in the starting ashes reduced to sulphides of much lower corrosion activity

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1. Introduction

Coal chemistry is gaining in importance due to the greater reserves of the fossil raw material coal and renewable biomass in comparison with those of natural oil and gas as starting materials for the petrochemical industry. The starting material in coal chemistry is a synthesis gas generated in gasification reactors. Higher gasifier efficiency can be achieved through a higher reaction temperature and a higher gas pressure. The reactor's service life is limited by the thermal shock resistance and the corrosion properties of the refractory lining [1–11]. Typical conditions for reactors are temperatures of around 1300 °C with a maximum temperature of 1600 °C and pressures of 25–40 bar as well as typical gas compositions of 55%–60% CO, 30%–35% H₂, 10%–15% CO₂ and 0.4%–1.5% H₂S [1,6,13]. The refractories of the reactor lining are subjected to a complex combination of stresses due to temperature, gas pressure, temperature fluctuations, abrasion by the solid fuel, the oxidising and reducing synthesis gas

components and especially by chemical reactions with ash and slag of widely varying composition resulting from the variations in sources used [1,2,3–10]. Different corrosion mechanisms responsible for the failure of refractories have been observed [1,4–9]:

- Chemical dissolution of the refractory by molten slags resulting in a continuous but low wear rate. The reaction of the melt with the binder phase of the refractory can weaken the bonds inside the refractory until pullout of grains or parts of grains occurs. In the case of the widely used high chrome oxide refractories this rate of chemical attack can reach 3–5 mm/1000 h [1].
- Spalling [1] leading to a sudden loss of material (spalled surface layers can reach thicknesses of greater than 2 cm). This results from different damage mechanisms caused by slag infiltration and stresses caused by thermal shock or creep [1,6]. To avoid these processes a non-wetting surface and strong and chemically resistant bonds between the refractory grains are useful.
- Interaction with components of the gas phase (e.g. H₂S, H₂O or Cl-containing components).

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- Thermal shock, insufficient creep resistance and abrasion can also limit the service life of the refractory.

The corrosion resistance of the refractory strongly depends on the ash composition which in turn strongly depends on the coal deposit or the biomass used. With respect to corrosive attack, a distinction can roughly be made between acidic, alkaline and (nearly) neutral ashes. Basic ashes are particularly harmful because they present a high corrosion risk even at relatively low temperatures due to the strong reduction of the viscosity of the slag and the high reactivity with oxide refractories. Acidic ashes with high SiO₂ contents strongly react with basic refractories such as MgO or spinel. However, the corrosive effects of the other ash components (e.g. sulphates and chlorine) must also be taken into consideration [9,12].

Numerous refractories for gasification reactors including high alumina, chromia alumina and silicon carbide materials have been evaluated [1–9,11,12]. Cr₂O₃-based and ZrO₂-based materials used in reactors have proven to be the most stable [1], but they also undergo corrosion which limits their lifetime [1–3,5,8]. SiC materials have also been investigated as refractories in gasification reactors [7,10]. However, the materials investigated were silicate-bonded or nitride-bonded materials in which corrosion mainly takes place in the binder phase. RSiC materials have not yet been tested, despite the fact that they have shown good stability as refractories in furnaces and refractory linings in waste incineration plants [11,14–18]. In contrast to silicate- or nitride-bonded materials in which the bond is formed by a secondary phase, recrystallised silicon carbide (RSiC) consists of SiC grains bonded directly to one another, allowing the high chemical stability of silicon carbide to be fully utilised. The result of this bonding is not only a fairly high strength, but also a relatively high thermal conductivity and hence a high thermal shock resistance. However, this material is produced at higher temperatures (up to 2400 °C) than is the case for clay- or nitride-bonded materials and is therefore slightly more expensive. Nevertheless, RSiC could be an interesting candidate for use in gasifiers due to its expected excellent corrosion resistance particularly under the reducing conditions prevailing in such applications and its high thermal shock resistance. The aim of this paper was to evaluate the stability of recrystallised SiC in coal ashes under reducing atmospheres. A solid state-sintered SiC was investigated for comparison purposes.

2. Experimental

Two commercial SiC materials were used for the investigations: a recrystallised silicon carbide with a porosity of 17% (mainly open porosity) and a dense sintered silicon carbide material with carbon and boron sintering additives. The properties of the materials are given in Table 1.

The corrosion experiments were carried out in a reactor tube furnace (Fig. 1) at temperatures of 1000 °C to 1300 °C with dwell times of 50 h and 100 h. The corrosive media were an acidic coal ash (S1), a basic coal ash (B1) and a mixed ash (BS) with a

Table 1
Properties of the used SiC materials.

Material	Density (g/cm ³)	Open porosity (%)	Strength (MPa)	Strength after 8 thermo shocks from 950 °C to water (MPa)
RSiC	2.65	15	90 ± 8	14
SSiC	3.18	0.6	412 ± 46	Not measured

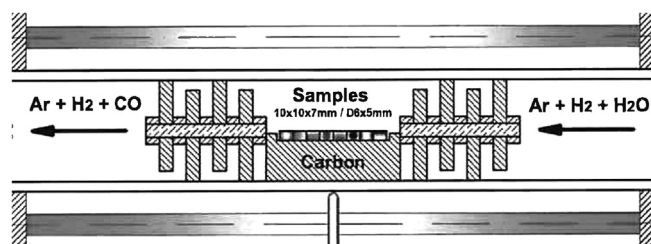


Fig. 1. Set up for the corrosion experiments.

slightly acidic character. The chemical compositions and the phase compositions of the ashes are shown in Table 2. The different ashes were chosen because they were expected to exhibit strong differences in behaviour in acidic and basic ashes.

A gas mixture consisting of 95% argon and 5% hydrogen with a dew point of 23 °C was guided over graphite moderators inside the reactor tube at a rate of 30 l/h. This was expected to result in the formation of a synthesis gas corresponding to the given reaction temperature according to the equilibrium reaction:



Thermodynamic calculations carried out in Factsage 6.3 [19] yielded a composition of the resulting gas atmosphere at 1300 °C of 7.4 vol% hydrogen, 2.5 vol% carbon monoxide and 91.1 vol% argon as the main components. The argon content was selected to limit the explosion potential of hydrogen and the poisoning potential of carbon monoxide based on the lengthy period of operation of the laboratory system and to ensure that sufficient carbon would be available for gas synthesis.

For the corrosion experiments cuboids with dimensions of 10 × 10 × 7 mm³ and brick-shaped material samples of the same geometry, but with a blind hole 6 mm in diameter × 5 mm in depth, were used for the RSiC materials. The SSiC samples were plates with dimensions of 8 × 8 × 7 mm³. For investigating the corrosion resistance of the materials, the cuboid samples were placed in graphite crucibles containing the various ashes, or ash was inserted into the brick openings. This allowed the effects of the sintered ash or the slag formed through melting of the ash, the temperature and the dwell time to be investigated on multiple materials under the same conditions in a single test.

Following high-temperature corrosion, the samples were investigated using light and electron microscopy. Cross sections were prepared through the SiC samples and the ashes/slag and the reaction layers formed during high-temperature corrosion were examined using an FESEM (field emission scanning electron microscope) and energy dispersive X-ray spectroscopy.

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