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Corrosion of silicon carbide hot gas filter candles in gasification environment

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Abstract

Reliable cleaning of the fuel gas is required to meet the environmental regulations and to prevent corrosion and erosion of downstream components. The aggressive process environment in biomass-gasification power generation systems or in biofuels production systems can cause corrosion in ceramic hot gas filter candles used to clean the fuel gas. Therefore, to improve the reliability and durability of filters, the influence of steam, ash, and alkaline (earth) metals on the corrosion processes was studied for silicon carbide filter candles fabricated by Pall Schumacher. Exposures with biomass and lignite ashes caused a macroscopically expansion as well as microstructural effects that were analysed by X-ray diffraction (XRD) and energy dispersive X-ray (EDX) spectroscopy. All effects are discussed and it is shown that the employment of silicon carbide filter candles in water vapour containing, alkali-rich gasification environment at high temperature is problematic.

Keywords: Hot gas filters; Silicon carbide; Corrosion; Binder phases; Alkaline metals

1. Introduction

Already since the 1990s the usage of ceramic hot gas filters in advanced coal-fired power generation systems is established.[1,2] In addition, it is worthwhile to use hot gas filter candles in biomass-fired power generation systems. In these applications the ceramic filters operate at high temperature.[3] The fact that hot gas cleaning is a focal point of applied research in the gasification field is clear from the number of papers on it appearing in literature[4–6] and the number of nationally and internationally funded research projects, that deal with it in one way or another.

Cleaning the fuel gas is required to meet the environmental regulations and to prevent corrosion and erosion of turbine blades and other downstream components.[1,7] Hot gas filters need to operate reliably for more than 10,000 h, maintaining particulate removal efficiencies and high flow capacity. They should also possess durability and reliability against mechanical and thermal stresses.[2]

The composition of the gas and solid phases, which are released from the combustor or gasifier, is depending on the process operating temperature, pressure, fed fuel, and oxygen content. More specifically, in a reducing environment H_2, CO, CH_4, H_2O, N_2, and CO_2 are released from the gasifier. Sulfur is released as H_2S and COS, and chlorides are emitted as volatile HCl and alkali chlorides. The concentration of the gaseous sulfur, chlorine, and alkaline metal species, released from the gasifier, are both, feed and process operating parameter, dependent. Unlike combustion systems, alkali species are projected to remain as alkali chloride phases as the gas passes through the gasification system.[3] These aggressive process environments, containing steam, dust, gaseous sulfur and alkali,[7] cause microstructural changes in all common hot gas filter materials, including oxide, non-oxide, and mixed-oxide ceramics.[2]

Silicon carbide (SiC) is a commonly used filter candle material because of its high temperature stability, its thermal shock resistance, its low thermal expansion, its high fracture toughness and its creep resistance at high temperatures.[1,2,7] Furthermore, SiC has a very high oxidation resistance in certain environments. However, for high temperatures SiC is unstable in the presence of oxygen and exhibits either active or passive oxidation.[8] A low oxygen partial pressure causes an active oxidation to SiO gas.[9]

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A higher oxygen partial pressure results in a passive oxidation, the formation of SiO_2, that forms a thin layer on top of the SiC surface. This layer acts as a kind of protective face. Because of the lower oxygen diffusion rate in this layer, the oxidation rate in dry oxygen is decreased to a parabolic progress.[8,10]

On the contrary, the oxidation in water vapour containing atmospheres is a major disadvantage of SiC. The oxidation of SiC caused by wet oxygen or even pure water vapour is ten times higher than in dry oxygen.[11,12] Moreover, the oxidation rate increases with increasing water vapour content.[13–15] Furthermore, the existence of alkaline (earth) metals in atmosphere increases the oxidation rate of SiC. In this case, the oxidation rate is linear for all temperatures instead of the usual parabolic progress.[8]

To develop reliably working hot gas ceramic filter candles from SiC it is a matter of huge interest to understand the mechanisms of corrosion. Older researches show, that water vapour containing atmospheres cause oxidation of the SiC grains and crystallisation in the binder phase. The microstructural changes decrease the strength of filter markedly.[14] The results indicate that most of strength degradation occurs by degradation of the binder phase from hot corrosive gas.[16]

For a better understanding of the investigated effects silicon carbide filter candles fabricated by Pall Schumacher were exposed to a reducing, alkali-rich, gasifier-related atmosphere. Exposures, 250 h long, caused an effect of the chemical stability of the binder material and a macroscopic expansion of the filter candle pieces. These effects were studied for several biomass and lignite ashes at temperatures between 800 °C and 950 °C. Furthermore, the influence of several alkali species was observed. The effects were analysed by X-ray diffraction (XRD) and energy dispersive X-ray (EDX) spectroscopy. Investigations by XRD were done with Bragg–Bretano geometry and with a copper cathode (Cu_a). For EDX calibration the internal database was used.

2. Materials and methods

To understand corrosion processes in SiC hot gas filter candles samples fabricated by Pall Schumacher were studied. Fig. 1 shows a SEM picture of the SiC filter candle as delivered. The SiC based filter candle was bonded with clay based silicate binder and covered with a Mullite protective layer. The filters were produced in the following way. At first, a pourable mixture was fabricated. Following, the mixture was stamped into a mould. After hardening the samples were sintered under oxidising conditions. Produced by this way, the SiC candles have an overall porosity of 35% and a pore diameter of nearly 75 μm.

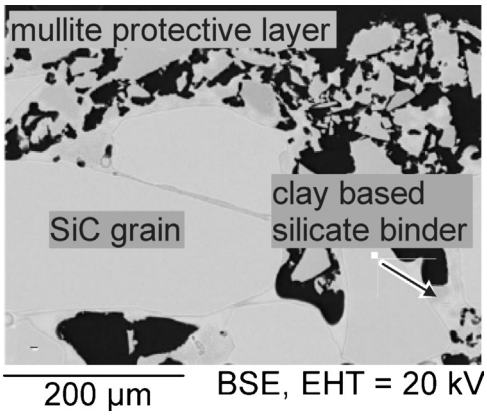

Fig. 1. SEM image of the SiC hot gas filter candle.

To study the influence of steam, ash, hydrogen sulfide, and alkali on the corrosion processes the samples were exposed in a furnace at temperatures of 800–950 °C and in various atmospheres at atmospheric pressure. The duration was 250 h with a cool-down and heat-up again after 100 h. The atmosphere was set up similar to the allotherm fluidised bed gasifier in Güssing (Austria). At a temperature of 850 °C the gas consists under equilibrium of 36 vol.% H_2, 25 vol.% CO, 17 vol.% H_2O (g), 11 vol.% CO_2, and 11% Ar (replacing all inert gases and hydrocarbons).[17] An exposure to analyse the influence of 120 ppm H_2S or 1630 ppm HCl in atmosphere was added. To study the influence of several gasified fuels the exposures were operated with a real gasifier wood ash from Güssing and four laboratory ashes of straw, miscanthus, DDGS (dried distilled grains with soluble) and sulfur-rich lignite (HKN-S+). The composition of these ashes is shown in Table 1. A high alkali concentration was ensured by adding alkali sources, adjusted to the used ash. The desired concentration of gaseous alkali species in atmosphere was achieved by evaporating alkaline salts inside the furnace. To compare the influence of alkali metals a experiment with straw ash, ashed with Kao SM (Kaolin from Salzmünde, Germany), without alkaline salts was added. The experimental details are shown in Table 2, and the experimental set up is illustrated in Fig. 2. Two different experimental setups were done. First, the filter candles were ground to <100 μm, mixed in an equal percentage of mass with ash, and pressed into homogenous tablets. Secondly, about 2 cm long pieces of the filter candles were bedded in the several ashes. Both setups were exposed under same conditions. After exposure the tablets were ground in a morter again and a

Table 1
Composition of the employed ashes (in mass.-%).

	Al_2O	CaO	Fe_2O_3	K_2O	MgO	Na_2O	P_2O_5	SiO_2	SO_3	Cl
Straw 1997	0.81	4.3	0.51	15.3	0.92	0.24	1.15	61.2	1.0	7.50
Miscanthus	2.08	5.9	1.72	23.7	4.18	1.13	6.18	34.7	2.3	3.95
Wood chips	1.36	31.8	0.49	21.9	6.72	0.32	8.66	7.8	2.7	0.17
DDGS	0.05	2.9	0.26	38.1	8.87	10.00	38.70	1.9	10.0	0.02
lignite	1.42	33.0	9.44	1.2	10.50	8.51	–	1.4	29.3	0.01