Available online at www.sciencedirect.com
SciVerse ScienceDirect
Journal of the European Ceramic Society 33 (2013) 3301–3312
www.elsevier.com/locate/jeurceramsoc

Corrosion of alumina and mullite hot gas filter candles in gasification environment

Sarah Schaafhausen[a,*], Elena Yazhenskikh[a], Astrid Walch[b], Steffen Heidenreich[b], Michael Müller[a]

[a] *Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research (IEK-2): Microstructure and Properties of Materials, 52425 Jülich, Germany*
[b] *Pall Filtersysteme GmbH, Werk Schumacher, 74564 Crailsheim, Germany*

Received 22 January 2013; received in revised form 22 May 2013; accepted 27 May 2013
Available online 24 June 2013

Abstract

Reliable fuel gas cleaning is required to meet environmental regulations as well as to prevent corrosion and erosion of downstream components. The aggressive process environment in biomass-gasification power generation systems or in biofuels production systems causes corrosion in the ceramic hot gas filter candles used to clean the fuel gas. Therefore, in order to improve the reliability and durability of filters, the influence of steam, ash, hydrogen sulfide, and alkaline metals on the corrosion processes was studied for alumina and mullite filter candles fabricated by Pall Schumacher. Exposure to these contaminants effects the chemical composition of the binder phases resulting in exchange of alkaline metals and alkaline earth metals. Analyses by energy dispersive X-ray spectroscopy demonstrate the negative effect of silicon containing binder phases. These effects are discussed and it is shown that the usage of silicon-free binder phases in hot gas filter candles for gasification processes is promising.

Keywords: Hot gas filter; Alumina; Mullite; Corrosion; Alkaline metal

1. Introduction

Since the 1990s the use of ceramic hot gas filters in advanced coal-fired power generation systems has been reported.[1,2] Ceramic filters are widely used in processes where hot gas cleaning is crucial particularly coal combustion. In addition, hot gas filter candles may be used in biomass-gasification systems, where the ceramic filters must operate at high temperature.[3] The “dirty” gases emitted require adequate filtration to minimize particulate entrainment to a gas stream, the atmosphere and surrounding environments.[4] Hot gas cleaning solves the tar problem that is well known for conventional filtration systems. Furthermore, an increase of efficiency is achieved by hot gas filtration compared to “cold” filtration. By way of example hot gas filter candles can be installed in a fluid-bed gasification reactor as tested by Westinghouse.[5] Hot gas cleaning is clearly a focal point of applied research in the gasification field due to the number of related papers appearing in literature[6–8] and the number of nationally and internationally funded research projects, dealing with the subject.

Fuel gas cleaning is required to meet environmental regulations and to prevent corrosion and erosion of turbine blades and other downstream components.[1,9] Hot gas filters need to operate reliably for more than 10,000 h, maintaining particulate removal efficiencies and high flow capacity. They should also be durable and reliable under conditions where mechanical and thermal stresses are present.[2]

The composition of the gas and solid phases, released from the combuster or gasifier depend on the process operating temperature, pressure, 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 dependent on both feed and process operating parameters. Unlike combustion systems, alkali species are predicted 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 species,[9] cause microstructural

* Corresponding author. Tel.: +49 2461 61 4504.
E-mail address: s.schaafhausen@fz-juelich.de (S. Schaafhausen).

0955-2219/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jeurceramsoc.2013.05.024

changes in all common hot gas filter materials, including oxide, non-oxide, and mixed-oxide ceramics.[2]

Silicon carbide is a commonly used filter candle material because of its stability at high temperatures and its thermal shock resistance. However, a major disadvantage is its oxidation to silica at high temperatures in the presence of water vapour.[10,11] A promising alternative for dependable filter candles is the use of mullite or alumina materials. Mullite ($3Al_2O_3$–$2SiO_2$) is one of the most extensively studied crystalline phases in the Al_2O_3–SiO_2 system.[12] It is a promising candidate for use in hot gas filter applications as it can be processed economically. It also possesses several beneficial properties that are crucial to fuel gas cleaning namely low thermal expansion, good thermal shock and corrosion resistance, and high temperature mechanical stability.[13,14]

The use of alumina for high temperature filter candles is not get common practice despite its good performance in high-alkali environments.[15] Alumina and mullite are appropriate for the fuel gas cleaning applications, the problem is to find a binder phase which is capable of withstanding the harsh conditions found in these environments.

To develop reliable hot gas filter candles from mullite or alumina it is important to understand the mechanisms of corrosion of the prospective binder materials. Therefore, different alumina and mullite filter candles fabricated by Pall Schumacher were exposed to a reducing, alkali-rich atmosphere to simulate conditions found inside a commercial gasifier. Exposures for 250 h had a corrosive effect on the binder material. These effects were studied for several compositions of binder materials in mullite and alumina hot gas filter candles to determine the most reliable binder composition.

2. Materials and methods

In order to understand the corrosion processes in alumina and mullite hot gas filter candle binders several samples fabricated by Pall Schumacher were studied. Each filter was produced by pressing a pourable mixture of solid particles into a mold. After hardening, the samples were sintered under oxidizing conditions. The alumina-based candles produced by this method have an overall porosity of 42% and a pore diameter range of 40–50 μm. The mullite-based candles have an overall porosity of about 35% and a pore diameter of about 55 μm. The candle filter composition is shown in Table 1.

To study the influence of steam, ash, hydrogen sulfide, and alkali on the binder corrosion processes, the samples were exposed in a furnace to temperatures of 800 °C and 950 °C under various atmospheres at atmospheric pressure. The duration of exposure was 250 h with cooling-down to <50 °C and heating-up again after 100 h. The atmosphere was similar to that of the allotherm fluidized bed gasifier in Güssing (Austria). At a temperature of 850 °C the equilibrium gas composition was 36 vol.% H_2, 25 vol.% CO, 17 vol.% H_2O (g), 11 vol.% CO_2, and 11% Ar (balance).[16] Experiments to analyze the influence of 120 ppm H_2S or 1630 ppm HCl in the atmosphere were also conducted. To study the influence of several gasified fuels, the exposure tests were performed with real gasifier wood ash from Güssing and four laboratory ashes of straw, miscanthus, DDGS (dried distillers grains with solubles) and sulfur-rich lignite. The composition of these ashes is shown in Table 2. A high alkali concentration was ensured by adding alkali sources, adjusted to the ash used for each test. The desired concentration of gaseous alkali species was achieved by evaporating alkaline salts inside the furnace. To compare the influence of alkali metals an experiment with straw ash, ashed with Kao SM (Kaolin from Salzmünde, Germany), without alkaline salts was added. The experimental details are shown in Table 3, and the setup is illustrated in Fig. 1. Two different types of samples were used. First, the filter candles were ground to <100 μm, mixed with an equal mass of ash, and pressed into homogenous tablets. Secondly, about 2 cm long pieces of the filter candles were embedded in the respective ashes. Both samples were exposed under the same conditions.

After exposure, the tablets were ground in a mortar and a qualitative phase characterization was done by X-Ray Diffraction (XRD). Cross-sections of filter candle pieces were analyzed by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) in order to detect microstructural details and estimate the composition of the filters' binder phases.

3. Results

The main difference between the unexposed filters is the composition of the binder phase. Filters K51-15 and K49a-15 only contain alumina as the binder phase, with a small amount of SiO_2-free additive added to improve sintering. Filters K54-15 and K54-17 are bonded with aluminosilicate fibers, which were determined to be $Al_{4.6}Si_{1.4}O_{9.7}$ by XRD. Moreover, these filters contain a low amount of sodium. The difference between both filters is the quantitative amount of sodium, which is less in the K54-15 filter. Filter K55-17 is bonded with calciumaluminate, determined to be $CaO(Al_2O_3)_6$. The mullite filter M8-15 is bonded with alumina and a small amount of illit.

Table 1
Composition of candle filter material, binder phase and sintering additives.

K49a-15:	corundum	+ alumina 1		+ SiO_2-free additive
K51-15:	corundum	+ alumina 2		+ SiO_2-free additive
K54-15:	corundum	+ alumina 1	+ aluminosilicate fibers	+ SiO_2-free additive
K54-17:	corundum	+ alumina 1	+ aluminosilicate fibers	+ SiO_2-free additive
K55-17:	corundum		+ calciumaluminate	
M8-15:	mullite	+ alumina 1	+ illite	