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Short communication

# Investigation of shaped alumina based refractories used in slagging gasifiers

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## Abstract

Gasifiers are containment vessels used to react a carbon feedstock with oxygen and water in order to produce synthetic gas. During the gasification process the refractory liner protects the gasifier shell from high temperatures and pressures, corrosive slag, thermal shock and thermal cycling. However the performance of the currently used high chrome oxide materials does not meet the service requirements of industry, so there is a demand of new chrome oxide free materials. Compared to the sintering atmosphere the mechanical properties, phase formation as well as the resistance against thermal shock and alkali-corrosion of shaped alumina based refractories have been evaluated. According to the results potential candidates for further studies including reducing sintered β-alumina, spinel, hibonite and slag-stone.

*Keywords:* Alumina; Shaped refractories; Gasification

## 1. Introduction

Fossil fuels can be used mainly for power generation or as carbon source for the base mater industry. In the future coal as carbon source will come in the fore because petroleum gas and crude oil will not be available in such requested amounts. For using coke as carbon source the gasifier technology marks an essential process. A gasifier acts as a containment vessel to react carbon containing materials like lignite, water and oxygen at temperatures between about 1300 and 1600 °C, pressures between 20 and 40 bar and reducing atmosphere to produce synthetic gas [1]. However new technologies are necessary to improve the efficiency, flexibility, carbon dioxide emission and sustainability of the gasifiers in the future.

The development of innovative technologies for the material utilisation of brown coal demands in turn new durable refractories which resists the extreme conditions during the gasification process. Particularly the short durability of the state-of-the-art materials of about 3–24 months is one of the main reasons for the low dependability and efficiency of today's constructions [2]. In contrast to the energetic use of brown coal under oxidizing conditions the gasification takes place under reducing atmosphere. Therefore the materials should offer good thermal shock resistance as well as corrosion resistance against high temperatures and pressures in alkali-rich gas atmospheres.

In the 1970s and 80s numerous refractories for gasification process were evaluated including alumina–silicate, high alumina, chromia–alumina–magnesia spinels, alumina and magnesia, alumina and chrome and silicon carbide materials [3–11]. Liner materials with high chrome oxide content of today's gasifiers evolved from these materials as chrome oxide improves the resistance against acid slags. According to Bakker a minimum of 75% chromia is necessary for satisfactory performance [12]. Actual investigations deal with the improvement of the corrosion resistance of high chromia containing materials by adding phosphate compounds to decrease the penetration of the slag into the refractory stone [13].

In order to reduce production costs and increase the environmental compatibility other research trends deal with refractories that do not contain chrome oxide [14]. First results indicated good corrosion resistance of hafnium oxide, hafnium silicate and zirconia silicate under laboratory conditions [15]. Furthermore the corrosion mechanisms of silicon carbide refractory lining in waste incineration plants and in reactors of biomass gasification were investigated [16].

The wear of the refractory is basically caused by corrosion and spalling. Corrosion implies dissolution of the refractory material into the flowing slag or dissolution of the bond phase at

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the hot face followed by freeing coarse grains. Spalling occurs in stages and implies an irregular removal of large chunks of the refractory material [14]. However the ordinary guard of some materials by forming oxidic coatings is nearly not applicable under reduced conditions. Hence the refractories almost are unhindered exposed to the corrosion attack, which also ask for developing new materials.

In terms of this paper the potential of alumina based liner materials for gasification process under reduced conditions has been investigated by identifying mechanical specific values, the thermal shock resistance and the resistance against alkalis. The tested materials like alumina–magnesia–spinel, hibonite, β-alumina and a mixture of alumina with alkalis, the so called "slag-stone" had already proven their excellent resistance against alkalis and/or thermal shock like alumina–zirconia–titania [17–21].

## 2. Materials and methods

In order to investigate specific values like density, 3-point-bending strength or resistance against thermal shock alumina based materials according to Table 1 were pressed into bars with dimensions of 7 mm (width) × 7 mm (height) × 70 mm (length). The raw materials were alumina CT3000SG (Almatis GmbH, Frankfurt, Germany), brown coal ash (RWE AG, Essen, Germany) with composition displayed in Table 2, zirconia Mg-PSZ (Saint-Gobain, USA), titania Tronox TR (Kerr-McGee, Oklahoma City, USA), β-alumina Jargal (Horn & Co., Siegen, Germany), spinel AR78 (Almatis GmbH, Frankfurt, Germany) und $CA_6$ Bonite (Almatis GmbH, Frankfurt, Germany).

The bars were pressed by using a uniaxial press (RUCKS engine building GmbH, Glauchau, Germany) with an applied pressure of 150 MPa. Afterwards the bars were sintered at 1300 °C under oxidizing conditions and under reducing conditions by using coke. The density of the bars was measured by Archimedes principle according to EN 993-1. In addition, the shrinkage after sintering was detected. Three-point bending strength tests of ten bar samples have been carried out at a 200 kN servohydraulic universal testing machine type TIRA (Rauenstein, Germany) with a support distance of 40 mm and 0.15 $N/mm^2$ s traverse speed according to EN 843. The modulus of elasticity was measured by analyzing the sonic runtime.

In order to analyze the resistance against thermal shock, the residual three-point bending strengths were measured after quenching samples from 950 °C in water (25 °C) once or after five quenching cycles. In case of the reducing sintered samples, the heating for the quenching tests has been carried out in coke. For each value five samples have been quenched. In addition, phase identification of milled powders with a $d_{50}$ of 20 μm based on the bars of the six compositions (sintered under reducing or oxidizing conditions) was performed by X-ray diffractometry (XRD) using a PHILIPS diffractometer with Cu$K\alpha$ radiation. The milling of the bars was carried out using a vibration grinding mill (MSL 2, BHK-type, Freiberg, Germany).

Table 1
Investigated alumina based materials.

| Sample | Chemical composition |
|---|---|
| $Al_2O_3$ + ash A1 | 50 wt.% $Al_2O_3$ + 50 wt.% intermediate brown coal ash |
| $Al_2O_3$ + ash A2 | 50 wt.% $Al_2O_3$ + 50 wt.% alkaline brown coal ash |
| AZT | 95 wt.% $Al_2O_3$ + 2.5 wt.% $ZrO_2$ + 2.5 wt.% $TiO_2$ |
| β-Alumina | 38 wt.% $Al_2O_3$ + 62 wt.% ($Na_2O\cdot 11Al_2O_3$) |
| Spinel | 78 wt.% $Al_2O_3$ + 22 wt.% MgO |
| $CA_6$ | $CaO\cdot 6Al_2O_3$ |

Table 2
Composition of brown coal ash A1 (intermediate) und A2 (alkaline).

| Contents | Proportion in ash A1 [%] | Proportion in ash A2 [%] |
|---|---|---|
| $SiO_2$ | 37.2 | 26.1 |
| $Fe_2O_3$ | 12.3 | 8.9 |
| $Al_2O_3$ | 2.3 | 1.9 |
| CaO | 32.5 | 36.0 |
| MgO | 7.2 | 8.3 |
| $Na_2O$ | 1.0 | 3.3 |
| $K_2O$ | 0.3 | 0.5 |
| $SO_3$ | 6.4 | 14.4 |
| MnO | 0.2 | 0.1 |
| BaO | 0.2 | 0.1 |
| $TiO_2$ | 0.2 | 0.2 |
| $P_2O_5$ | 0.2 | 0.2 |

In order to determine the alkali-corrosion behaviour the "disc test" has been performed [22]. Thereto the sintered and milled raw materials according to Table 1 were mixed with intermediate brown coal ash (A1) in a ratio 70:30. The mixture was pressed with a forming pressure of 100 MPa to discs with a diameter of 50 mm and 10 mm thickness. The samples were heated at 1300 °C for 3 h and the change of diameter was determined.

## 3. Results and discussion

### 3.1. Mechanical and thermal shock properties

Table 3 shows the shrinkage, density, Young's modulus of elasticity (MOE), average three-point bending strength (CMOR) and the residual three-point bending strengths after one and five thermal shock cycles respectively of the samples. A low shrinkage involves low stresses inside the materials during sintering. Overall the shrinkage values of the reducing sintered samples are lower compared to the materials sintered under oxidizing atmosphere.

The oxidizing sintered AZT, both slag-stones and hibonite exhibits good bending strengths. After sintering under reducing conditions the bending strength of AZT, spinel and hibonite decreases remarkable and the strength values of both slag-stones and β-alumina substantially increase. Analogue to this effect the modulus of elasticity of the materials differs subjected to the sintering atmosphere. According to Hasselman a low Young's modulus of elasticity improve the thermal shock performance [23,24].

The high residual bending strength of the oxidizing sintered slag-stones and AZT denote a good thermal shock resistance of these materials. On the contrary β-alumina, spinel and hibonite

Table 3
Shrinkage, density, average three-point bending strength (CMOR), Young's modulus of elasticity (MOE) and residual three-point bending strengths after quenching from 950 °C in water one or 5 times respectively of the samples sintered under reducing or oxidizing conditions.

| Raw material | | Shrinkage [%] | Density [g/cm$^3$] | CMOR [MPa] | MOE [GPa] | Residual CMOR [MPa] after | |
|---|---|---|---|---|---|---|---|
| | | | | | | 1 thermal shocks | 5 thermal shocks |
| Oxidizing conditions | Alumina + ash A1 | −6.8 | 1.93 | 21.9 ± 2.3 | 32.3 | 5.3 ± 1.1 | 2.5 ± 1.0 |
| | Alumina + ash A2 | 0.0 | 2.08 | 32.4 ± 4.4 | 42.2 | 5.0 ± 1.2 | 1.5 ± 0.6 |
| | AZT | 8.5 | 3.28 | 95.8 ± 9.4 | 167.7 | 10.4 ± 1.6 | 4.1 ± 1.6 |
| | β-Alumina | −0.1 | 2.56 | 2.2 ± 0.4 | 5.4 | 1.1 ± 0.2 | Busted |
| | Spinel "AR 78" | 0.3 | 2.43 | 12.7 ± 1.7 | 19.7 | 2.1 ± 0.5 | Busted |
| | $CA_6$ "Bonite" | 1.0 | 2.37 | 19.9 ± 2.0 | 27.1 | 2.1 ± 0.2 | Busted |
| Reducing conditions | Alumina + ash A1 | −3.4 | 2.07 | 44.3 ± 3.8 | 43.8 | 9.4 ± 1.4 | 2.8 ± 0.9 |
| | Alumina + ash A2 | −0.3 | 2.29 | 36.0 ± 3.7 | 46.9 | 3.0 ± 0.7 | 1.5 ± 0.3 |
| | AZT | 2.5 | 2.79 | 37.0 ± 7.1 | 73.1 | 4.4 ± 1.6 | 0.9 ± 0.4 |
| | β-Alumina | 0.4 | 2.54 | 7.9 ± 1.1 | 16.7 | 4.1 ± 0.8 | 4.1 ± 1.2 |
| | Spinel "AR 78" | 0.4 | 2.42 | 8.5 ± 2.5 | 15.6 | Busted | Busted |
| | $CA_6$ "Bonite" | 0.5 | 2.32 | 12.2 ± 6.2 | 16.5 | Busted | Busted |

Table 4
Shrinkage of the material-brown coal ash-mixture after sintering at 1300 °C subjected to the pre-sintering atmosphere of the materials.

| Raw material | Shrinkage [%] | |
|---|---|---|
| | Oxidizing pre-sintered | Reducing pre-sintered |
| Alumina + A1 | 8.3 | 3.3 |
| Alumina + A2 | 6.7 | −1.1 |
| AZT | −15.0 | −13.0 |
| β-Alumina | −4.2 | 1.1 |
| Spinel AR78 | 1.3 | 0.5 |
| $CA_6$ Bonite | −1.8 | −0.7 |

getting busted after three thermal shock cycles. The thermal shock resistance of the slag-stones and particularly of β-alumina increases by sintering the samples under reducing atmosphere.

### 3.2. Alkali-corrosion resistance – "disc test"

Mixing, pressing and sintering the raw materials with the corrodent brown coal ash simulate the impingement of slag into the refractory material which is the worst corrosion effect during gasification. The solid alkaline particles of the ash enclose the solid raw materials and lead to alkali reactions on the complete aggregate surface area. Therefore the "disc test" is a strong test method for characterizing alkali-corrosion. It delivers insight into the expected corrosion mechanism and offers a fast characterization of the material in regard to its alkali-corrosion resistance. The alkali reaction with the liner material leads to new phase formation having different density compared to the initial raw material. In turn this involves volume changes. In the majority of cases a volumetric expansion takes place and causes the removal of large chunks of the refractory material ("spalling"). One can divide the tested compounds in suitable and unsuitable materials on the basis of at most ±2% elongation. Because of forming less new phases or phases with minor changes in density, the suitable materials will show less corrosion or aftermath after corrosion.

Table 4 shows the shrinkage of mixtures of brown coal ash with the materials sintered at 1300 °C under oxidizing and reducing conditions. Spinel and hibonite sintered under oxidizing conditions show low shrinkage and hence could be described as resistant against alkali-corrosion. Generally the materials sintered under reducing atmosphere show better alkali-corrosion resistance against brown coal ash. The alkali slag-stone and β-alumina show remarkable improvements of the shrinkage and again also spinel and hibonite exhibit very low values.

Table 5
Main phases of the bars sintered at 1300 °C under reducing and oxidizing conditions analyzed with the aid of XRD-method.

| Sample | | Existing main phases |
|---|---|---|
| Oxidizing conditions | Alumina + ash A1 | $Ca_2Al[AlSiO_7]$, $CaAl_2Si_2O_8$, $MgAl_2O_4$, $\alpha$-$Al_2O_3$ |
| | Alumina + ash A2 | $Ca_2Al[AlSiO_7]$, $\alpha$-$Al_2O_3$, $CaAl_2Si_2O_8$, $MgAl_2O_4$ |
| | AZT | $\alpha$-$Al_2O_3$, $ZrTiO_4$, $TiO_2$, $ZrO_2$ |
| | β-Alumina | $Na_2O(Al_2O_3)_{11}$, $\alpha$-$Al_2O_3$ |
| | Spinel "AR 78" | $MgAl_2O_4$ |
| | Hibonite | $CaAl_{12}O_{19}$ |
| Reducing conditions | Alumina + ash A1 | $CaAl_2Si_2O_8$, $Ca_2Al[AlSiO_7]$, $\alpha$-$Al_2O_3$, $MgAl_2O_4$ |
| | Alumina + ash A2 | $\alpha$-$Al_2O_3$, $Ca_2Al[AlSiO_7]$, $CaAl_2Si_2O_8$, $MgAl_2O_4$ |
| | AZT | $\alpha$-$Al_2O_3$, $TiO_2$, $ZrO_2$ |
| | β-Alumina | $Na_2O(Al_2O_3)_{11}$, $\alpha$-$Al_2O_3$ |
| | Spinel "AR 78" | $MgAl_2O_4$ |
| | Hibonite | $CaAl_{12}O_{19}$, $\alpha$-$Al_2O_3$ |

According to the results of the ''disc test'' spinel and hibonite seem to be the most promising materials in terms of alkali-corrosion resistance and corrosion aftermath independent of the sintering atmosphere.

### *3.3. XRD-analysis for investigation of the phase evolution after sintering*

In Table 5 all main phases of the bars sintered at 1300 °C under oxidizing and reducing conditions are listed, which were analyzed with the aid of XRD-method. The slag-stones predominantly consist of the silicates gehlenite and anorthite and corundum and spinel. Depending on the sintering atmosphere only the concentration of the phases varies. AZT consists of corundum and some minor zirconia and titania phases and also some minor zirconia titanate under oxidizing atmosphere. β-Alumina, spinel and hibonite predominantly consists of their eponymous phases and some corundum. Subjected to the sintering atmosphere the phase concentrations vary only marginal.

## 4. Conclusions

Sintering oxide ceramics in reducing atmosphere leads to changes of the concentration of the existing phases and to formation of defects. Compared to materials sintered in oxidizing atmosphere this effect causes a change of the mechanical properties and to the resistance against thermal shock and alkali-corrosion.

Different shaped chrome oxide free alumina based refractories were investigated regarding their qualification as liner material of gasifiers. The tested materials which mostly consist of alumina and alkalis were sintered under oxidizing and reducing conditions. Depending on the sintering atmosphere the mechanical properties, the phase evolution as well as the alkali-corrosion resistance and thermal shock properties were investigated.

In general compared to the materials sintered in oxidizing atmosphere a sintering under reducing conditions leads to a degradation of the mechanical properties but improves the resistance against thermal shock and alkali-corrosion.

Overall the slag-stones, spinel, hibonite and β-alumina sintered in reducing atmosphere show the best results and are potential basic materials which could be further developed to refractory liner materials for the gasification process.

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