Possible Design of Chromeoxide-free Refractory Castables for Use in Slagging Gasifiers

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Gasifiers are containment vessels used to react carbon feedstocks with oxygen and water in order to produce synthetic gas. Raising the profitability by extending the service life of gasifiers on the one hand and the replacement of high chrome oxide materials by environmentally friendly, recyclable and economic refractories on the other hand, allows the reduction of CO_2 emission in more than one way. The development of a new gasification technique reduces the peak temperature at the liner wall from 1600 °C to about 1400 °C, which allows the development of new chrome oxide free materials. In these contribution three different approaches has been pursued to improve pure alumina refractory castable by enhancing the mechanical and chemical properties in order to reduce the wear by molten coal slag. Compared to pure alumina castable, the mechanical properties as well as corrosion resistance of $MgAl_2O_4$ (spinel) mixed with MA-spinel cement, alumina mixed with brown coal ash and alumina with titania and zirconia addition have been investigated. The resistance against an intermediate molten coal slag has been evaluated by applying the cup test at 1450 °C in gasification similar CO atmosphere. It has been shown that the developed environmentally friendly refractories are promising to replace chrome oxide based liner materials for gasification processes up to 1450 °C.

1 Introduction

Humanity is facing the problem of rising oil consumption and CO_2 emission. Gasification is a technology to reduce on the one hand the CO_2 emission of power generation by integrating a gasification process in combined-cycle plants (IGCC) and marks on the other hand an essential technology to replace petroleum gas and crude oil with domestic coal as carbon source for the base mater industry. A gasifier acts as a containment vessel, in which carbon containing materials like lignite or biomass react with water and oxygen at temperatures in the range between 1300 and 1600 °C and pressures of about 40 bar in reducing atmosphere in order to produce synthesis gas ($CO+H_2$), which is used for example as intermediate in creating synthetic natural gas and for producing methanol [1]. During the gasification process a refractory lining protects the gasifier shell from the high temperatures and has to withstand wear mechanism like thermal shock and cycling, erosion of solid carbon particles, creep and corrosion by molten coal slag composed of alkali and earth alkali elements [2, 3]. Research and industrial experiences in the 1970s and 1980s indicated that only liner materials with a minimum content of 75 % chromia provide satisfying performance as chromia shows very low solubility in brown coal slag at the high operating temperatures. In addition chromia reacts with the iron of the slag to form an iron-chromium spinel, which seals the chromium-brick surface and stops further slag penetration [4]. Unfortunately, the formation of iron-chromium spinel favours spalling [5]. 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 material [6]. However, because of the high costs of sintering and finishing chrome oxide refractories, future supply issues of the raw materials, the potential for the formation of toxic hexavalent chrome during service and the fact that high chrome oxide refractories have not met the performance requirements, several research trends deals with the development of low chrome or chrome oxide free refractories [7]. First results indicated good corrosion resistance of hafnium oxide, hafnium silicate and zirconia silicate under laboratory conditions [8]. Furthermore, the corrosion mechanisms of silicon carbide refractory linings in waste incineration plants and in reactors of biomass gasification were investigated [9].

The development of an innovative gasification technology has the side effect of reducing the peak temperature at the liner wall

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Tab. 1 Composition of alumina based refractory castables

Raw Materials [mass-%]	100A	MAC6	MAC18	11BCA	AT2.5	AZT	AZ5.0
Tabular alumina	88	25	25	83	85,5	78	83
Reactive alumina	9	8	–	12	9	9	9
Hydratable alumina	3	–	–	–	3	3	3
Spinel	–	61	57	–	–	–	–
MA-spinel cement	–	6	18	–	–	–	–
Brown coal ash	–	–	–	5	–	–	–
Titania	–	–	–	–	2,5	5	–
Zirconia	–	–	–	–	–	5	5
Additives	1	0,2	0,2	1,3	1	1	1
Water	5	4,9	5,4	4,7	4,7	4,6	4,9

during operation from 1600 °C to about 1400 °C [10]. This gives the opportunity to develop new chrome oxide free materials, which are produced with less energy input and CO_2-emission, enhance the operating lifetime of gasifiers and could easily be recycled or disposed. The new refractories should demand the mechanical requirements, offer good thermal shock resistance as well as corrosion resistance against high temperatures and high pressures in alkali-rich and reducing atmospheres.

Alumina is a widely available and cheap refractory, well known for its mechanical properties and good resistance against acidic and alkali corrosion. However, experiments have shown, that alumina reacts with brown coal ash to compounds with low melting point, which results in destruction of the microstructure and dissolution. The enhancement of alumina refractories with regard of corrosion resistance against coal slag is a rarely considered research field. In terms of these contribution three different approaches has been pursued to improve pure alumina refractory castable by enhancing the mechanical properties, structure and chemical character in order to reduce the wear by molten coal slag. On the one hand, the chemical composition of $MgAl_2O_4$ (spinel)-containing alumina castable has been modified by adding increasing content of special MA-spinel cement to increase the corrosion resistance [11]. On the other hand, an alumina castable mixed with brown coal ash was developed in order to reduce the driving force of corrosion caused by the similar chemistry of the refractory and corrosive medium [12]. Furthermore, titania and zirconia were added to alumina to investigate the interaction with the slag in order to prevent slag penetration.

Tab. 2 Composition of the intermediate brown coal ash

Element	Content in Ash [mass.-%]
O	40,34
Ca	22,19
Si	17,7
Fe	8,8
S	2,87
C	2,77
Mg	2,58
Al	1,38
Na	0,46
Mn	0,26
Ba	0,21
K	0,13
Trace elements	0,31

Referred to pure alumina and a currently used Cr_2O_3-Al_2O_3-ZrO_2 brick, the three different types of new developed alumina based refractory castables has been investigated by identifying mechanical properties as well as the performance against molten slag. The resistance against an intermediate molten coal slag has been evaluated by applying the cup test at 1450 °C in gasification similar 100 % CO-atmosphere.

2 Experimental

The investigated alumina based self-flowing masses with compositions given in Tab. 1 were designed corresponding to the grain size distribution model of *Funk* and *Dinger* with q = 0,28 [13]. As reference composition, sample 100A is composed of tabular and reactive alumina (T60/64 and CL370), bonded with hydratable alumina (AB300, all *Almatis GmbH/*DE) in order to contain very few impurities. The first approach of improving pure alumina deals with the development of alumina-spinel castables with cement addition. The alumina-spinel castables MAC6 and MAC18 are composed of tabular alumina (T60/64), reactive alumina (CTC50, CT3000SG) and spinel (AR78, all Almatis GmbH/DE) with the addition of 6 mass-% and 18 mass-% MA-spinel cement (CMA 72, *Kerneos SA/*FR) respectively. MAC6, MAC18 and 100A were compared in order to investigate the influence of the spinel and cement content. Another approach deals with the addition of brown coal filter ash to alumina to improve its corrosion resistance. Sample 11BCA, the so called slag containing refractory material, is composed of tabular and reactive alumina (T60/64 and CT9FG, CTC50, CT3000SG, Almatis GmbH/DE) with 11 mass-% intermediate brown coal filter ash (*RWE Power AG/*DE) with composition displayed in Tab 2. The samples AT2.5, AZT and AZ5.0 are composed of tabular and reactive alumina (T60/64 and CL370, Almatis GmbH/DE) with titania (TR-HP-2, *Crenox GmbH/DE*) and/or zirconia addition (CS02, *Saint-Gobain ZirPro/FR*), bonded with hydratable alumina (AB300, Almatis GmbH/DE).

The raw materials with a maximum grain size of 5 mm were mixed in an *Eirich* intensive mixer following the standard commercial practice, added with water and filled into metal forms. For the investigation of open porosity and cold modulus of rupture (CMOR) bars with dimension of 25 mm × 25 mm × 150 mm and for the alkali corrosion tests crucibles with edge length of 80 mm and a hole with a diameter of 45 mm were cast respectively. After demoulding and drying at 110 °C, the samples were sintered with 5 h dwell time. Composition 100A was sintered at 1500 °C, MAC6 and MAC18 were sintered at 1450 °C and the samples AT2.5, AZT and AZ5.0 were sintered at 1650 °C in order to reduce the open porosity. Because of degasing effects of the brown coal ash at 1240 °C in air, 11BCA was sintered at 1300 °C in coke (CO atmosphere) in order to prevent destructive elongation.

The open porosity of the samples was measured by *Archimedes* principle according to

EN 993-1. Furthermore, the shrinkage as well as CMOR of the samples has been carried out according to EN 993-6. In addition, phase identification of milled powders with a d_{50} of 20 µm based on the bars of the compositions was performed by X-ray diffractometry (XRD) using a *PHILIPS* diffractometer with Cu Kα radiation. The milling of the bars was carried out using a vibration grinding mill (MSL 2, BHK-type, Freiberg/DE). In order to determine the corrosion with molten slag, the cup test was performed based on CEN/TS 15418 by filling 30 g intermediate brown coal ash in the crucible and heating it at 1450 °C for 3 h in 100 % CO atmosphere. After cooling, the crucibles were cutted, the corrosion evaluated and the corrosion mechanism analysed.

Tab. 3 **OP, shrinkage and CMOR of the developed castables compared with pure alumina (100A) and Cr_2O_3-Al_2O_3-ZrO_2 brick (CAZ)**

Property	100A	MAC6	MAC18	11BCA	AT2.5	AZT	AZ5.0	CAZ
OP [%]	16,6	16,7	15,2	17,1	14,9	15,1	14,7	10,7
CMOR [MPa]	16,8	38,8	26,1	40,8	30,6	10,6	22,9	29,9
Shrinkage [%]	0,3	0,6	0,1	0,1	1,5	1,5	0,9	unk.

Tab. 4 Main phases of pure alumina and the developed castables after sintering

Sample	Existing Main Phases [%]
100A	α-Al_2O_3 (99), β-Al_2O_3 (1)
MAC6	$MgAl_2O_4$ (75), α-Al_2O_3 (15), $CaAl_{12}O_{19}$ [CA_6] (10)
MAC18	$MgAl_2O4$ (80), $CaAl_{12}O_{19}$ [CA6] (10),α-Al_2O_3 (7), $CaAl_4O_7$ [CA_2] (3)
11BCA	α-Al_2O_3 (88), $CaAl_4O_7$ [CA_2] (4), $CaAl_2Si_2O_8$ [CAS_2] (3), $Ca_2Al[AlSiO_7]$ [C_2A_2S] (3)
AT2.5	α-Al_2O_3 (97), Al_2TiO_5 (2), TiO_2 (1)
AZT	α-Al_2O_3 (90), $ZrTiO_4$ (3), ZrO_2 (2), TiO_2 (2)
AZ5.0	α-Al_2O_3 (94), ZrO_2 (5)

3 Results and discussion

3.1 Investigation of alumina-spinel castables with MA-spinel cement addition

In Tab. 3 the open porosity (OP), shrinkage and CMOR of the developed alumina based refractory castables compared with pure alumina (100A) and a currently used Cr_2O_3-Al_2O_3-ZrO_2 (CAZ) brick (62 mass-% Cr_2O_3, 17 mass-% Al_2O_3, 12 mass-% ZrO_2) are listed. In order to minimize slag infiltration, the currently used CAZ brick has an open porosity of about 11 %. However, with respect to the resistance against thermal shock, chrome free refractories for gasifiers should provide a higher open porosity in a range between 15 and 18 % and CMOR of more than 15 MPa to withstand the self-weight of the lining [7].

Alumina bonded with hydratable alumina provides a critically low CMOR after sintering at 1500 °C. Even if spinel generally reduces the strength of alumina based castables, with the addition of MA-spinel cement sample MAC6 shows CMOR of about 39 MPa and hence meet the required demands for application in gasifiers. Furthermore, by adding MA-spinel cement to spinel containing alumina castables, not only the total amount of spinel rises in order to improve corrosion resistance, but also the structure could be improved by optimizing the open porosity to prevent slag infiltration and damaging by thermal shock. With further increasing cement content, the open porosity of sample MAC18 could be further reduced but the strength decreases. Hence, with regard to mechanical and chemical properties, there is an ideal content of about 6 mass-% MA-spinel cement, which should be added to spinel-containing alumina castable.

Tab. 4 gives an overview of all main phases of pure alumina and the developed materials, which were analysed with the aid of XRD-method, whereat the concentrations were approximated with the *Rietvel* method. Sample 100A, which contain hydratable alumina, mainly consist of corundum phase and some traces of β-alumina. If some fractions of coarse and fine tabular alumina are replaced by spinel and 6 mass-% CMA 72 were added (MAC6), a total amount of about 75 % spinel phase are detectable. Furthermore, the calcium aluminates (CA and CA_2) containing in CMA 72 react with alumina to form CA_6, which reduces the amount of corundum phase in the material. With further increasing CMA 72 content (sample MAC18), the total amount of spinel increases to about 80 % and again, CA_6 and also the formation of some CA_2 are detectable. Thus, the addition of spinel and especially the addition of MA-spinel cement to pure alumina castable increase the spinel content but cause the formation of CA-phases in turn.

The most decisive property for the application in a gasifier is the resistance against molten slag. A coal slag predominantly consists of SiO_2 and CaO and contains also Al_2O_3, Fe_2O_3, alkali and earth alkali elements. In order to investigate the corrosion resistance of the developed materials, the cup test was applied. During the cup test, the crucibles were filled with 30 g intermediate brown coal ash with composition displayed in Tab. 2 and were heated in a furnace at 1450 °C for 3 h. For applying gasification-similar conditions, the crucibles were at first heated in N_2. Afterwards, at testing tempera-

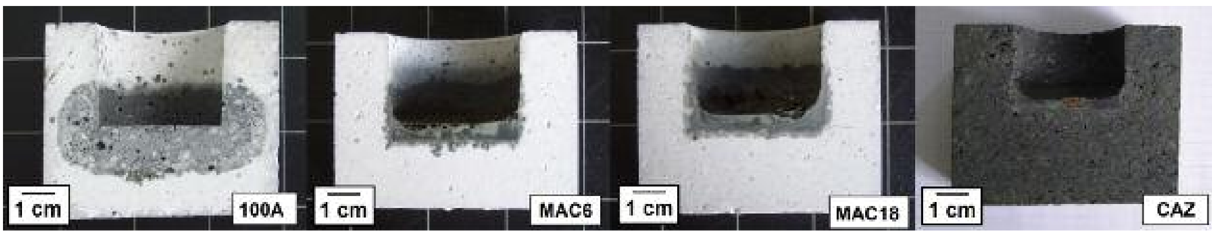

Fig. 1 **The interaction of the samples and intermediate slag after cup test at 1450 °C for 3 h in CO**

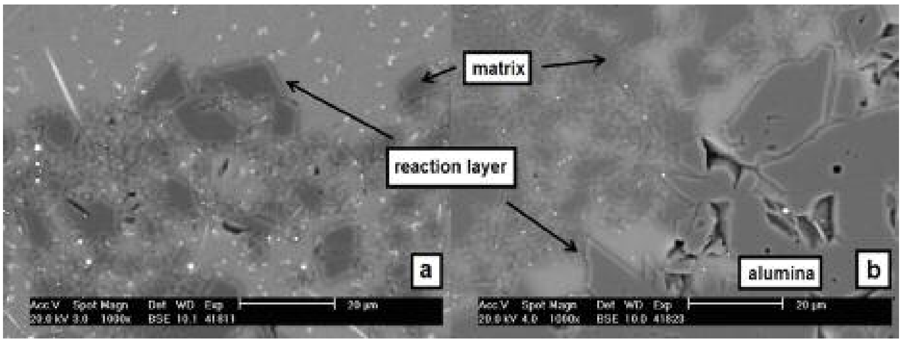

Fig. 2 SEM image of reaction layer surrounding the spinel matrix (a) as well as porous alumina grain (b)

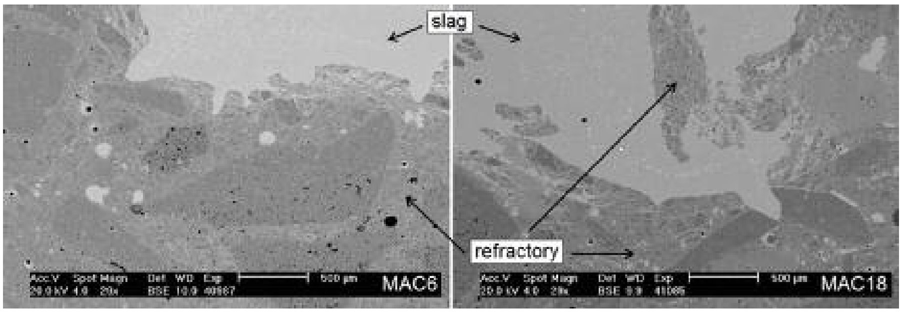

Fig. 3 SEM image of the slag-refractory boundary of sample MAC6 and MAC18

ture of 1450 °C, the furnace chamber was filled with a constant CO-gas flow of 150 l/h for 3 h. Hence, after about 5 min, the atmosphere in which the corrosion tests have been done is composed of 100 % CO. The coal ash melts and the slag infiltrates the crucible or reacts with the refractory material. After cooling, the crucibles were cut and the corrosion was evaluated.

Fig. 1 shows the crucibles of pure alumina, the developed MA-spinel cement containing castables and CAZ brick after cup test. Pure alumina (100A) is completely infiltrated by the slag, which will result in crack formation and damaging by corrosion. As the addition of MA-spinel cement improves the mechanical properties of spinel-containing alumina castable, less slag penetration (MAC6) with an infiltration depth of about 1 mm is visible. Even though further increasing cement content lowers the open porosity and improves the refractories structure, sample MAC18 shows a slightly higher slag penetration of 3 mm and furthermore, no more sharp changeover from slag to refractory is visible. As expected, the chromia brick (CAZ) shows no slag infiltration or corrosion. Hence, the sample MAC6 shows nearly the same results like a currently used high chromia brick after corrosion tests at 1450 °C and atmospheric pressure in testing CO atmosphere.

SEM and EDX investigations of the spinel matrix-slag interface have shown that there are two different corrosion mechanisms detectable. On the one hand, the slag surrounds the spinel matrix and a reaction layer is formed, which is composed of spinel and the major slag components CaO and SiO_2 (Fig. 2a). However, this reaction layer in not stable and gets solved in slag because of the presence of S, Na and K, which forms compounds with low melting point. On the other hand slag infiltrates also coarse alumina grains, which offers a porous structure after sintering. At the edge of the alumina grains and the slag-infiltrated pores another reaction layer is visible (Fig. 2b). In the first step, CaO reacts with alumina to form CA-phases (CA, CA_2 and CA_6). These phases are not stable and react in the next step with SiO_2 to form compounds of the Al_2O_3-SiO_2-CaO system.

Again, because of the presence of Na and K, this layer also gets solved in the slag. However, because of the dense structure of the spinel grains and matrix and the fact that alumina is faster infiltrated by slag, alumina dissolution is the predominantly corrosion mechanism.

Compared to MAC6, MAC18 exhibits a higher CaO content after sintering, which originates from the MA-spinel cement. This leads to the formation of more CaO-Al_2O_3 phases in the refractory resulting in a more distinctive interaction of refractory and slag. The SEM-images of the slag-refractory boundary of sample MAC6 and MAC18 in Fig. 3 demonstrates the different dimension of matrix dissolution. Hence, with the addition of 6 mass-% MA-spinel cement, the corrosion resistance of spinel-containing alumina castables against molten coal slag can be improved remarkable, but the dissolution process cannot be stopped.

3.2 Development of slag containing refractory material

The usage of a refractory castable composed of great amounts of flue ash in high temperature applications is a promising approach. Especially the chemically similarity of a slag containing refractory material composed of brown coal ash and the corrosion medium brown coal slag decreases the corrosive reaction and hence the refractory wear during the gasification process. However, this theoretical consideration must be confirmed under testing conditions. Especially the ash contents like SiO_2 or Na_2O may critically reduce the materials melting point and hence limit the operating temperature. In order to examine this topic, a slag containing refractory material composed of alumina mixed with brown coal ash was developed. Investigations have shown that brown coal ash compounds containing sulphur dioxide degas at about 1240 °C in air. In turn, this effect causes large elongation, micro-sized defects and high open porosity of slag containing materials sintered in air [14]. In order to prevent this destructive degasing effect, a reducing sintering atmosphere (coke) has been applied.

According to Tab. 3, sample 11BCA provides an open porosity of about 17 % and a remarkable improvement of CMOR to about 41 MPa. In order to identify the maximum operating temperature, the refractoriness under load (RuL) has been analysed according to EN 993-8 in argon atmosphere. As 11BCA provides a T05-value of 1407 °C, the slag containing castable can be applied in gasifiers up to 1400 °C. However, refractory for gasifiers not only has to withstand the self-weight but also erosion caused by high-

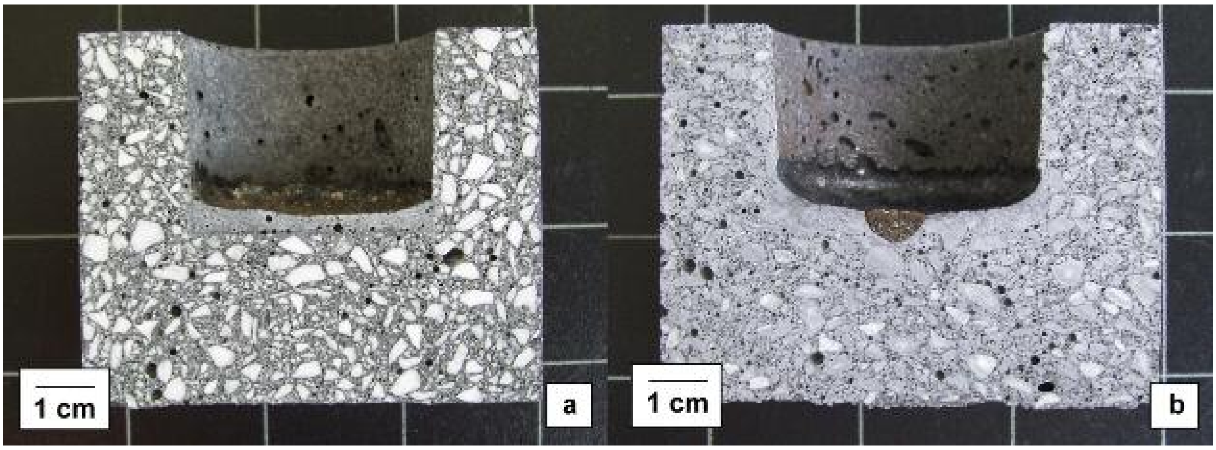

Fig. 4 **The interaction of samples 11BCA and intermediate slag after cup test at 1300 °C (a) and 1450 °C (b) for 3 h in CO atmosphere**

speed gases at high temperatures. The resistance against erosion at high temperatures could be identified by the measurement of hot modulus of rupture (HMOR) according EN 993-7. 11BCA provides a HMOR of 8,5 MPa at 1300 °C in Argon atmosphere. Compared to HMOR of 5 MPa of high chromia brick (CAZ) at application temperature of 1500 °C, the HMOR of the slag containing castable is high enough to withstand erosion caused by high-speed gases at an operating temperature of 1300 °C. Of course, HMOR of the slag containing refractory material at 1500 °C will be lower than HMOR of high chromia brick. Hence, 11BCA cannot be applied in slagging gasifiers but is a promising material for low temperature gasifiers with fluidised bed (e.g. *HTW*) and fixed bed principle (e.g. *Lurgi*).

XRD and SEM analyses has been shown that the low open porosity and the high CMOR after sintering in CO atmosphere are predominantly caused by formation of CA_2 (Tab. 4) and by an distinctive microsized sintering effect due to the presence of ash components [14]. In contrast, sintering in air causes degasing effects and the formation of CA_6, which results in open porosity of about 22 % and favours slag infiltration and corrosion in turn.

Fig. 4 shows the crucible of the slag containing refractory material after cup test at intended operating temperature of 1300 °C (Fig. 4a) and at 1450 °C for comparison with the other developed materials (Fig. 4b). At 1300 °C, there is no slag infiltration visible. Furthermore, even though 11BCA exhibits a higher open porosity than pure alumina, at 1450 °C no slag infiltration but a small flux line is detectable. This performance shows that the idea behind the addition of brown coal ash to alumina, the reduction of the corrosion by similar chemistry of the refractory and the corrosion medium, is a promising approach. With exception of the flux line, sample 11BCA shows nearly the same corrosion resistance like CAZ after corrosion tests at 1450 °C and atmospheric pressure in testing CO atmosphere.

3.3 Alumina castables with titania and zirconia addition

Adding titania and zirconia to alumina has several improving effects. On the one hand, because of the different thermal expansion coefficient of zirconia, titania and alumina, a special micro crack designed structure is formed after sintering, which leads to superior thermal shock performance [15]. Thermal shock resistant refractories allow a faster starting or shutdown and withstand abrupt temperature drop during breakdown of a gasifier. However, the microcrack structure reduces the mechanical properties of such materials at sintering temperatures above 1500 °C. On the other hand, the titania and zirconia of the refractory may interact with the slag components during service by forming compositions like $CaTiO_3$ or $CaZrO_3$, leading to a more viscous slag, which will prevent slag infiltration.

Because of the high sintering temperature and sintering effects of titania and zirconia, AT2.5, AZT and AZ5.0 provide very low open porosity (Tab. 3). However, depending on the content of titania and zirconia, the CMOR differs from 10 to 30 MPa. Sample AZT with a distinctive microstructure provides a very low CMOR and hence does not meet the required demands for application in gasifiers. In contrast, the addition of titania to alumina remarkably improves the strength. Hence, the presence of both, zirconia and titania, in the alumina matrix reduces the CMOR, whereas titania or zirconia improves the strength of alumina based castables.

According to Tab. 4, Al_2O_3 predominantly reacts with TiO_2 to form Al_2TiO_5. If zirconia is additionally present, ZrO_2 reacts with TiO_2 to form $ZrTiO_4$. However, there is no reaction between alumina and zirconia detectable. Fig. 5 shows the crucibles of AT2.5, AZ5.0 and AZT after cup test. The AZ5.0 and AZT crucibles are totally infiltrated by slag, which leads to crack formation. In contrast, AT2.5 with containing Al_2TiO_5 shows a low slag infiltration depth of about 4 mm. Hence Al_2TiO_5 seems to be a corrosion resistance improving compound. Because of the presence of ZrO_2 in AZ5.0 and AZT, TiO_2 predominantly react with ZrO_2 and no Al_2TiO_5 is formed. The effectiveness of Al_2TiO_5 on the slag resulting in lower infiltration depth will be investigated more precisely.

Hence, compared with pure alumina, the developed environmentally friendly refractories exhibit an improved structure, which prevent slag infiltration and provide higher resistance against molten slag. However, during gasification the refractories are affected by slag attack and corrosion by the characteristic gasifier atmosphere containing CO, H_2, CO_2 and also water vapor.

In order to evaluating the stability and performance of the developed castables in gasification atmosphere and high pressure, further corrosion tests in real gasifiers will be performed to clarify their potential to replace high chromia bricks as economic and ecological lining material.

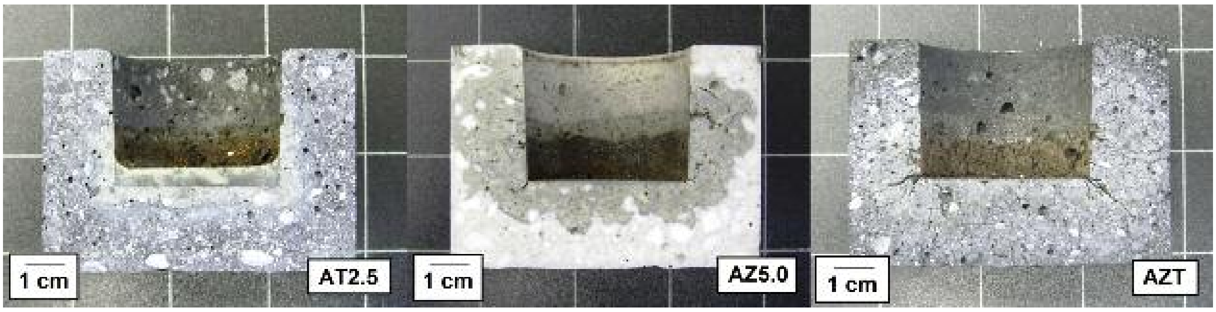

Fig. 5 **Crucibles of alumina with titania and zirconia addition after cup test at 1450 °C for 3 h in CO**

4 Conclusions

Raising the profitability by extending the service life of gasifiers on the one hand and the replacement of high chrome oxide materials by environmentally friendly, recyclable and economic refractories on the other hand, allows the reduction of CO_2 emission in more than one way. In terms of these contribution three different approaches has been pursued to improve pure alumina refractory castable in order to reduce the wear by molten coal slag. Self-flowing masses of spinel-alumina with MA-spinel cement addition, alumina mixed with brown coal ash and alumina with titania and zirconia addition have been investigated by identify the open porosity and CMOR and tested according their resistance against molten intermediate coal slag in gasification similar CO atmosphere at 1450 °C. Compared with pure alumina, the developed castables shows improved structure with lower open porosity as well as much higher CMOR to meet the required mechanical demands. The addition of 6 mass-% MA-spinel cement to spinel-containing alumina castables improves the corrosion resistance by preventing slag penetration and major matrix dissolution. Mixing alumina with 11 mass-% brown coal ash sintered in CO atmosphere results in a recycled material with excellent mechanical properties and no visible slag infiltration but a small flux line after corrosion test, caused by the reduction of the driving force of corrosion by providing similar chemistry of refractory and corrosive medium. Because of the interaction of Al_2TiO_5 with slag, alumina castable with 2,5 mass-% titania addition shows enhanced resistance against wear by molten slag. It has been shown, that the different approaches allows the development of promising liner materials for gasification processes up to 1450 °C. However, in order to investigate the stability in gasification atmosphere and high pressure, further corrosion tests in real gasifiers will be performed to clarify the potential to replace high chromia bricks as lining material.

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References

[1] Mahgagaokar, U.; Krewinghaus, A.B.: Coal conversion processes (gasification). In: Kirk-Othmer encyclopedia of chemical technology. Ed. by Kroschwitz, J.P.; Howe-Grant, M. New Jersey 1992, 541–568

[2] Dogan, C.P.; et al.: Refractory loss in slagging gasifiers. Proc. of UNITECR (2001) [1] 270–275

[3] Fahrion, M.E.: Materials testing at cool water coal gasification plant. Mater. at High Temperatures **11** (1993) [1–4] 107–112

[4] Bakker, W.T.: Refractories for present and future electric power plants. Key Engin. Mater. **88** (1993) [5] 41–70

[5] Kwong, K.-S. et al.: Wear mechanisms of chromia refractories in slagging gasifiers. Int. J. of Appl. Ceram. Technol. **6** (2007) [4] 503–513

[6] Dogan, C.P.; et al.: A new refractory for slagging coal gasifiers. Proc. of the 28th Int. Conf. on Coal Utilization and Fuel Systems (2003) 9–14 March 2003, Clearwater, USA

[7] Bennett, J.P. et al.: Low chrome/chrome free refractories for slagging gasifiers. USDOE/NETL-IR-2006-119

[8] Müller, M.; Hilpert, K.; Singheiser, L.: Corrosion behaviour of chromium-free ceramics for liquid slag removal in pressurized pulverized coal combustion. J. of the Europ. Ceram. Soc. **29** (2009) [13] 2721–2726

[9] Poirier, J.; Colombel, L.; Prigent, P.: The corrosion mechanisms of SiC refractory lining in waste incineration plants and in reactors of biomass gasification. Proc. of the 52th Int. Coll. of Refractories (2009), 23–24 September 2009, Aachen, Germany

[10] Patent DE 10 2007 006 981 A1

[11] Wöhrmeyer, C.; et al.: New spinel containing calcium aluminate cement for corrosion resistant castables. Proc. of UNITECR (2011) 30 October–2 November 2011, Kyoto, Japan, CD-ROM

[12] Routschka, G.: Taschenbuch Feuerfeste Werkstoffe. Essen 1997

[13] Funk, J.E.; Dinger, D.R.: Particle Packing VI – Applications of particle size distribution concepts. Interceram **43** (1994) [5] 350–353

[14] Gehre, P.; Aneziris, C.G.: Investigation of slag containing refractory materials for gasification processes. J. of the Europ. Ceram. Soc. **32** (2012) [16] 4051-4062

[15] Aneziris, C.G. et al.: Thermal shock performance of fine grained Al_2O_3 ceramics with TiO_2 and ZrO_2 additions for refractory applications. Advanced Engineering Materials 1**2** (2010) [6] 478–485