Wear of Monolithic Al$_2$O$_3$–SiC–C Refractories in the Slag Runner of a Cupola Furnace

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The cupola furnace is the most important melting device in the foundry industry. Currently, the availability of the cupola, i.e. the possible iron output as a function of time, is particularly restricted by the lifetime of the refractories used in the slag runner. In order to understand the mechanism decisive for the wear of slag runner refractories in more detail, a commercially available and frequently applied Al$_2$O$_3$–SiC–C ramming mix was investigated in the initial condition and post mortem. The results show that during application in the slag runner the graphite of the ramming mix is not subjected to oxidation. Therefore, the cupola slag does not infiltrate the matrix of the ramming mix. Unlike graphite, both alumina and silicon carbide are significantly corroded during application. Alumina is transformed and dissolved by silicate cupola slag, whereas silicon carbide is atmospherically degraded to secondary carbon and silicate melt. The findings are considered fundamental for the development of monolithic refractories with improved durability for application in the slag runner.

1 Introduction

The world production of cast iron amounts to about 70 Mt per year. In Germany alone, the output of cast iron is about 3,7 Mt per year [1]. The majority of cast iron is melted in cupolas, which are the most important melting devices in the foundry industry [2].

The cupola belongs to the group of shaft furnaces and can be designed for short-term or long-term operation. Only the latter is of interest for the present paper. A sketch of a long-term cupola with a pressure siphon is shown in Fig. 1. The melting process can be described as follows: At the beginning of the campaign the coke, which is situated at the bottom of the shaft, is heated and the shaft is loaded with the charge (pig iron, scrap, etc.). Owing to the combustion of the ignited coke with hot wind, the temperature increases (up to 2000 °C in the coke bed [3]), the charge melts, and molten iron and slag run into the siphon. In the siphon, iron and slag are separated by means of density separation with the aid of two drains, the iron and the slag runner, which are located at different heights. The most demanding areas of the cupola (hearth, bottom, siphon, slag runner) are currently lined with monolithic Al$_2$O$_3$–SiC–C re-

fractories [4]. Tab. 1 gives an overview of common compositions. In terms of quantity, the main component in monolithic Al$_2$O$_3$–SiC–C refractories for cupola application are alumina-rich raw materials, e.g. white fused alumina, tabular alumina, brown fused alumina (BFA), bauxite, andalusite, alumina-rich chamotte, calcined and reactive alumina [5], whereby bauxite-based raw materials are most frequently used. After alumina-rich raw materials, SiC is the second largest component of Al$_2$O$_3$–SiC–C refractories. Most common are SiC contents ranging from 10 to 30 %. The optimum amount of SiC is a constant subject of discussion between manufacturers and operators. The recommendations on this matter published in the literature are mixed. According to investigations on Al$_2$O$_3$–SiC–C castables with varying SiC content conducted by Inomata et al. [6], the optimum SiC content should be 28,25 %. In contrast, *Holland et al.* [4] state that the optimum SiC content is dependent on the slag composition. For low-basicity slags (basicity of 0,6–0,8) a SiC content ranging from 15–25 % is recommended, whereas a SiC content ≤15 % is favourable when the basicity of the slag is high (basicity of 1,0–1,2). In order to decrease the wettability of cupola refractories,

carbon raw materials (e.g. graphite, distilled pitches with reduced benzo(a)pyrene content etc.) are commonly used.

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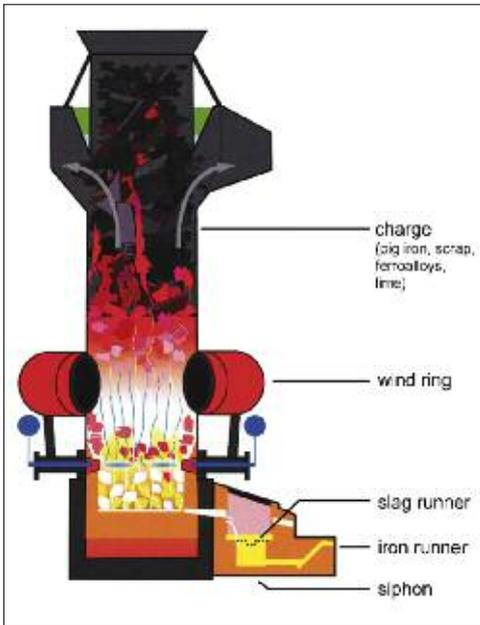E-mail: zimmermann@fg-feuerfest.de

Fig. 1 Sketch of a long-term cupola with attached pressure siphon based on [10]

The composition of the matrix is strongly dependent on the desired installation method. Ramming mixes usually contain clay as a primary bonding agent and to achieve suitable plasticity, whereas the bonding of castables is most often based on calcium aluminate cement. A recently developed alternative to cement-bonded castables are cement-free castables, which do not form any hydrates during setting. Owing to the absence of hydrates, the heat-up of those castables can be accelerated and the addition of hydrogen-emitting additives is no longer necessary [7]. Currently, the availability of the cupola, i.e. the possible iron output as a function of time, is particularly restricted by the lifetime of the refractories applied in the slag runner. The reason is that the lining of the slag runner has to be repaired or relined at one- or two-week intervals owing to wear, whereas in other areas of the cupola (e.g. the shaft) the lifetime of the refractories can easily ex-

ceed half a year [4]. As a consequence, the comparatively short lifetime of the slag runner refractories causes a significant loss of possible production because the frequently required repairs necessitate a shutdown of the cupola for at least one or two days. This is a problem especially in times of a booming economy when production is required throughout the weekend. Besides the loss of production a significant amount of energy and resources is consumed for every repair because the cupola has to be almost completely cooled down before the repair and has to be reheated afterwards.

The reason for the premature wear of the refractories used in the slag runner is not well understood. In general, concerning the wear of refractories used in the cupola, the combination of temperature load (T ≈ 1550 °C [8]), corrosion induced by interfacial reactions between refractories and slag as well as hot erosion induced by flowing melts is regarded as crucial [6, 9]. However, more detailed insights, e.g. microscopic investigations of post-mortem samples, cannot be found in the literature. Considering this, the aim of this work was to establish more detailed knowledge of the wear of slag runner refractories. For this purpose, a commercially available Al_2O_3–SiC–C ramming mix (hereafter named reference ramming mix) was investigated in the initial condition and after 14 days of application in a long-campaign cupola (hereafter named reference cupola).

2 Materials and techniques

The reference cupola is a water-cooled, liningless long-term cupola with a pressure siphon and a melting capacity of up to 80 t/h. In the siphon, the melt temperature amounts to about 1550 °C. According to XFA, the slag features a calcium silicate composition with a basicity (CaO + MgO) / SiO_2) of about 0,5. Depending on the furnace area, the reference cupola is lined

with different kinds of refractory materials. Despite the use of the state-of-the-art Al_2O_3–SiC–C reference ramming mix in the slag runner, the slag runner has to be repaired or relined at one- or two-week intervals owing to wear.

In order to determine the mechanisms decisive for wear, the reference ramming mix was investigated prior to and after 14 days of application. Specimens of the reference ramming mix in initial state were prepared by means of ramming. Following manufacturing, the samples were dried at 110 °C for 24 h. In order to simulate the state at the hot face during cupola application, a certain amount of the prepared samples was subjected to firing at 1550 °C for 5 h in coke. As opposed to the samples prepared in the laboratory, the post-mortem samples were merely cut into samples with suitable sizes or milled to obtain powdered samples.

Chemical analyses were carried out with X-ray fluorescence analysis (XFA, *Bruker* Tiger S8) and a carbon analyzer (Leco CS200). Mineralogical investigations were conducted with X-ray-diffraction (X XRD, *Siemens* D5000) as well as optical (*Zeiss* AxioScop 40) and scanning electron microscopy *(Jeol* 6360/Röntec energy-dispersive X-ray spectroscopy (EDS) detection unit). As far as thermomechanical properties are concerned, refractoriness under load (RUL, *Netzsch* RUL/CIC 421) as well as hot modulus of rupture (HMOR, Netzsch HMOR 422 D/3) and hot crushing strength were determined. The hot crushing strength (HCS) measurements were conducted in a self-built device at 1550 °C with a loading speed of 1 MPa/s. The thermomechanical properties measurements were conducted according to the currently valid standards but with argon purging in order to avoid oxidation reactions. Furthermore, computer-aided thermochemical calculations using Factsage™ software were conducted.

3 Results and discussion

3.1 Al_2O_3–SiC–C reference ramming mix prior to cupola application

The chemical composition of the reference ramming mix according to XFA and carbon analysis is shown in Tab. 2. With an Al_2O_3 content of 72 %, a SiC content of 16 % and a free carbon content of 7 % the compos-

Tab. 1 Typical composition of Al_2O_3–SiC–C refractories for the application in the cupola

	Al_2O_3	SiC	$C_{(free\ carbon)}$	SiO_2
Amount in the refractory [mass-%]	>50 %	≤30 %	≤10 %	<3 % or <20 %*
Applied raw materials	White fused alumina, tabular alumina calcined alumina, reactive alumina brown fused alumina, bauxite andalusite, alumina rich chamotte	Synthetic silicon carbide (SiC-content ≤98 %)	I.a. graphite, carbon black pitch, resin	Silica fume, clay

*When applying SiO_2-containing alumina-rich raw materials, e.g. andalusite or alumina-rich chamotte

ition is typical for Al_2O_3–SiC–C refractories for cupola applications. Concerning the mineralogical composition after drying, the reference ramming mix consists of corundum, silicon carbide, silicon, graphite and kaolinite, as indicated by XRD analysis (Tab. 2). As can be derived from microscopic investigation, the formulation is based on brown fused alumina (BFA) with a grain size up to 10 mm. Besides BFA the microstructure consists of SiC with a grain size up to 1 mm and flake graphite. According to the data sheet, the bonding is based on clay, which coincides with the detection of kaolinite by means of XRD.

The mineralogical composition after firing for 5 h at 1550 °C in coke differs from the state after drying. Compared to the state after drying, silicon and kaolinite are no longer detectable after firing and mullite has been formed. Concerning the microstructural evolution, after firing secondary mullite and corundum crystals can be identified from their idiomorphic shape (Fig. 2). Furthermore, a glassy phase containing alkaline and alkaline earth metal oxides concentrations of up to 10 % in total was detected. An increased amount of glassy phase is visible in the close vicinity of BFA grains. This glassy phase is a reaction product between BFA impurities, which migrated into the matrix during firing, and the matrix of the ramming mix.

As far as the thermo-mechanical behaviour of the reference ramming mix is concerned, the RUL after drying (curve R1) and after pre-firing at 1550 °C in coke for 5 h (curve R2) is shown in Fig. 3. Up to 1200 °C the curve shapes of R1 and R2 are almost congruent. However, beyond 1200 °C the expansion of R1 declines until in the temperature range between 1400 °C and 1600 °C a contraction can be determined. This behaviour is believed to be caused by the earlier mentioned conversion of clay to secondary corundum, mullite and glassy phase. After this conversion is completed, the stability of the microstructure is re-established, which can be derived from the end of contraction at T ≥1600 °C. Since for R2 the conversion of clay already proceeded before the RUL measurement, due to pre-firing, the curve differs significantly from R1. In contrast to R1, the curve shape of R2 shows no negative expansion up to almost 1700 °C. Nevertheless, a decrease in expansion is clearly visible

Tab. 2 Chemical and mineralogical composition of the reference ramming mix after drying at 110 °C for 24 h and firing at 1550 °C for 5 h respectively

Reference Mix after Drying	[110 °C/24 h]	[1550 °C/5 h]
Chemical composition [mass-%]		
Al_2O_3	72,4	n.d.
SiC	16,2	n.d.
C_{free}	6,7	n.d.
TiO_2	1,7	n.d.
Σ alkaline metal oxides	0,4	n.d.
Σ alkaline earth metal oxides	0,6	n.d.
Mineralogical composition		
Corrundum	++++	++++
Silicon carbide	++	++
Graphite	+	+
Silicon	traces	none
Kaolinite	traces	none
Mullite	none	traces

at about 1400 °C, which indicates a softening of the structure. This finding is in accordance with the results of HMOR and HCS conducted at 1550 °C, because the hot strength of the ramming mix at 1550 °C was below the detection limit of both testing devices.

3.2 Al_2O_3–SiC–C reference ramming post-mortem

Fig. 4 shows a sample of the reference ramming mix after 14 days of application in the slag runner of the reference cupola. As can be seen in the illustrated picture, the ramming mix was eroded by the ochre-coloured slag in a channel-like way.

Macroscopically, neither a significant chemical interaction between reference ramming mix and slag nor the formation of cracks or an oxidation of the refractory material can be derived.

The boundary layer between the reference ramming mix and adhering slag is shown in

Fig. 5a. Three distinct areas are discernible, which were optically separated with the aid of dashed lines. Adjacent to the apparently
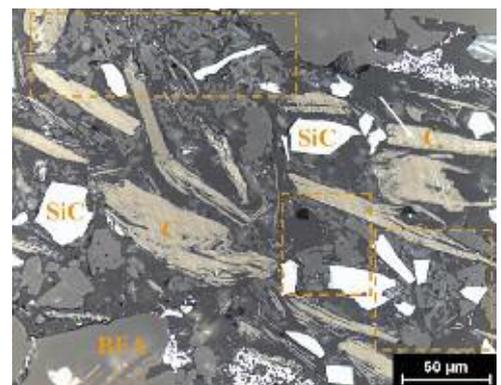

Fig. 2 Reference ramming mix after firing at 1550 °C for 5 h (BFA = brown fused alumina, SiC = silicon carbide, C = graphite). The dashed rectangles highlight the areas which contain secondary idiomorphic corundum and mullite crystals (reflected light image, 500× magnified)
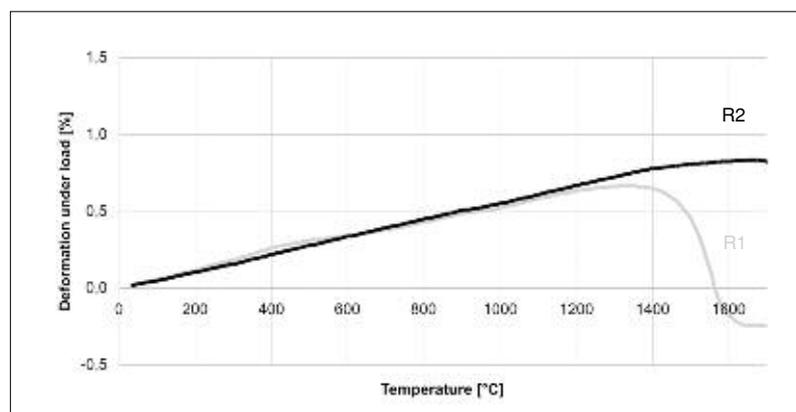

Fig. 3 RUL of the reference ramming mix after drying at 110 °C for 24 h (curve R1) and after pre-firing at 1550 °C for 5 h (curve R2)

Fig. 4 Post-mortem sample of the reference ramming mix after 14 days of application in the slag runner

unaltered microstructure of the reference ramming mix, a reaction zone with a thickness of 1 mm is visible. The reaction zone consists of glassy phase, idiomorphic anorthite ($CaAlSi_2O_8$) and hibonite ($CaAl_6O_{19}$) crystals as well as coarse BFA grains. The latter are partially or completely detached from

the ramming mix due to premature matrix corrosion that occurred earlier.

The BFA grains are significantly corroded by the calcium silicate slag. This can be derived from the altered grain shape and transformation to hibonite (H) as well as from the glassy phase (G) (Fig. 5b). The glassy phase (G) documents the significant dissolution of alumina because according to EDS the amount of dissolved alumina in the glassy phase (up to 30 % Al_2O_3) exceeds the initial alumina content of the slag (6 % Al_2O_3) by the factor of 5, even though the precipitated Al_2O_3-rich hibonite crystals (H) are not considered. These findings comply with the results of thermochemical calculations, according to which significant amounts of alumina are soluble in the cupola slag. In fact, about 66 g alumina can be dissolved in 100 g slag at 1550 °C.

Owing to the low wettability of the ramming mix, caused by the intact primary carbon (Fig. 5b (C)), the matrix of the ramming mix

is only negligibly infiltrated by slag. It is assumed that the stability of carbon is attributed to the CO-rich atmosphere in the pressure siphon, which is caused by the combustion of coke in the cupola shaft. Besides primary carbon (flake graphite), secondary carbon is formed during the application in the slag runner. The formation of secondary carbon attributed to an atmospheric degradation of SiC to carbon according to (1):

$$SiC(s) + 2\ CO(g) \rightarrow SiO_2(l) + 3\ C(s) \qquad (1)$$

On the one hand, this can be derived from the shape of the secondary carbon, which resembles SiC grains (Fig. 5b (S)). On the other hand, the formation of secondary carbon cannot only be detected at the boundary layer between the refractory material and slag but also a few centimetres into the microstructure (Fig. 6a–b). This indicates atmospheric-induced degradation because, since the ramming mix is not infiltrated by slag, a degradation induced by the interaction between SiC and slag can be excluded for SiC grains situated a few centimetres away from the hot face. The degradation of SiC according to (1) can be divided in (2) and (3):

$$SiC(s) + CO(g) \rightarrow SiO(g) + 2\ C(s) \qquad (2)$$
$$SiO(g) + CO(g) \rightarrow SiO_2(l) + C(s) \qquad (3)$$
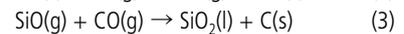
As mentioned earlier, (2) proceeds at the hot face as well as up to a few centimetres into the microstructure, whereas the condensation of gaseous SiO (3) can be detected particularly in colder regions, evidenced by glassy phase formation (Fig. 6a). The glassy phase contains idiomorphic mullite and induces the dissolution of BFA grains (Fig. 6b). Owing to the lack of CaO in the glassy phase, an involvement of the cupola slag in the glassy phase formation can be excluded.

4 Conclusion and outlook

The attained results indicate that alumina as well as SiC are not stable during the application in the slag runner. Alumina is corroded by silicate cupola slag, whereas SiC is atmospherically degraded to carbon and silica. As opposed to carbon, silica is not stable in the matrix of the ramming mix but reacts with alumina, forming significant amounts of silica-rich alumosilicate melt. Owing to
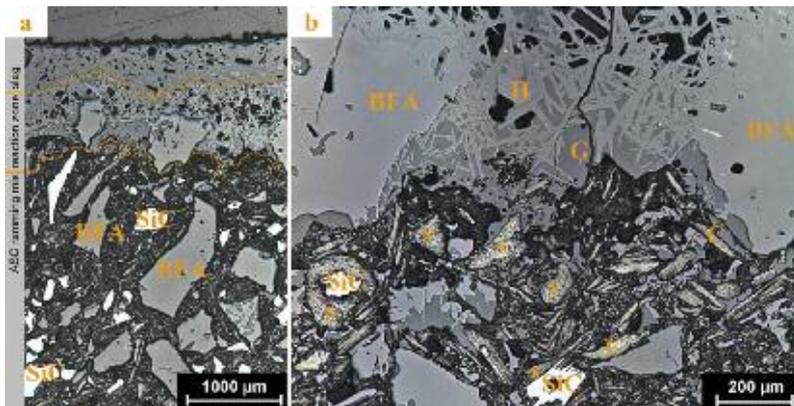

Fig. 5a–b Overview (l., 25× magnified) and more detailed micrograph (r., 100× magnified) of the boundary layer between reference ramming mix and slag after 14 days of application in the slag runner (reflected light images, BFA = brown fused alumina, SiC = silicon carbide, C = graphite, G = glassy phase, H = hibonite, S = secondary carbon)
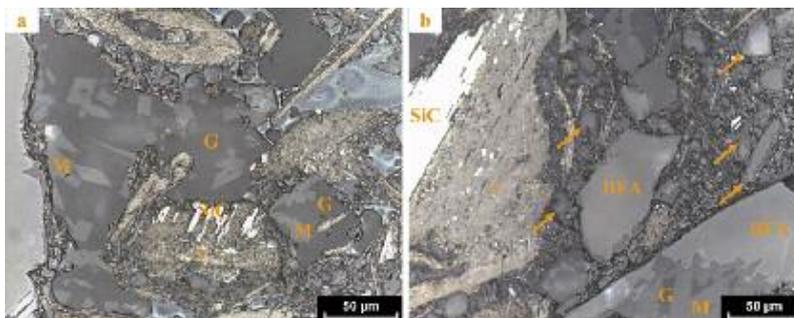

Fig. 6a–b Matrix of the reference ramming mix after 14 days of application in the slag runner (reflected light images, 500× magnified, BFA = brown fused alumina, SiC = silicon carbide, G = glassy phase, M = mullite, S = secondary carbon, arrows = alumina dissolution)

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the melt formation, a deterioration of the thermomechanical properties of the ramming mix can be expected. However, despite the melt formation and the fact that HMOR as well as HCS investigations indicate optimization potential concerning the thermomechanical properties of the ramming mix even in the initial state, significant wear owing to erosion cannot be derived from the microscopic investigation of the post-mortem samples. In fact, the significant dissolution of alumina in the slag as well as almost completely detached BFA grains protruding from the refractory into the slag indicate premature wear of the refractory material induced by slag corrosion.

Consequently, the corrosion resistance of the matrix and the oxidic aggregates has to be improved in order to enhance the durability of the refractory lining in the slag runner.

Furthermore, to avoid melt formation in the matrix of the refractory, SiC has to be substituted with stable raw materials or the chemical composition of the matrix has to be adjusted to the SiC degradation.

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