Prospects of Developing Self Glazing Al_2O_3–C Refractories for Monobloc Stopper Applications

V. Roungos, C.G. Aneziris

Since they were first used in the beginning of the last century, monobloc stoppers have seen many developments and improvements of their service life as functional components in steel casting applications. Due to their poor oxidation resistance, these components are coated with a protective glaze to inhibit carbon oxidation. An innovative improvement would be the development of Al_2O_3-C self glazing refractories. The prospects of this development were investigated at the present work. The samples were produced with both the uniaxial and the cold isostatic pressing route. Based on the fact that the critical temperature range affecting the glaze formation was 600 – 1300 °C, various oxidation tests in air atmosphere were carried out at the coked samples. A complete self glaze formation at the outer surface of the samples could be achieved only at the samples obtained from the uniaxial pressing route. The rather dense self glaze was a few hundred microns thick, while it had a high adhesion to the carbon bonded refractory substrate as well. As for the samples obtained by the isostatic pressing route, the self glaze formation was either only partial or it was porous, allowing the further oxidation of the samples. The reason for that was the higher binder amount needed for the granulation step. Thus, further investigations and modifications are needed for the samples obtained by the cold isostatic pressing route. Nevertheless, the mechanical and thermo-mechanical properties of the uniaxial pressed samples were very promising. These samples had overall very high strength values, both at room temperature as well as at 1400 °C. Moreover, they presented a negligible low strength loss even after 3 thermal shocks. In addition, the performance of a self glazed Al_2O_3-C bar sample during a severe dynamic corrosion test was very promising as well.

1 Introduction

Since they were first used in the beginning of the last century, monobloc stoppers have seen many developments and improvements of their service life as functional components in steel casting applications. However, next to the numerous advantages they exhibit, favoured from the carbon bonding, they have a significant drawback: very poor oxidation resistance. Even graphite, which presents the highest resistance against oxidation among carbons, it starts to burn out at around 550 °C. According to the state of the art, they are externally glazed with various methods [1] in order to protect them from oxidation. Additionally, fine powders of metallic antioxidants and especially silicon are being added. In this case and at the high temperatures during the refractories application, the phases with the highest partial pressure are the SiO- (at regions near the surface of the refractory body) and the CO-phase (in the refractory body) [2]. Taking this into account, adding fine metallic silicon could effectively lead to the in situ formation of SiC-phases, which reinforce these functional components [3–6]. These SiC-phases (in most cases in whisker or fibre form) are also stable at the high application temperatures of these refractories, on the contrary to Al_4C_3, which is the dominant product in the case of adding metallic aluminium. Often, both antioxidants are being used together, along with various other fine powders, like B_4C [7].

Materials which exhibit self glazing properties are well known and established in the ceramic industry, especially in flatware porcelain and sanitary ceramic tiles [8]. Some products, like refractory crucibles on SiC basis [9], include components with self glazing effects in their compositions. However, all of these products, as all of the carbon bonded refractories, are externally coated with a glaze to protect them from oxida-

Vasilios Roungos, Christos G. Aneziris
TU Bergakademie Freiberg, Institute for Ceramic, Glass and Construction Materials
09596 Freiberg, Germany

Corresponding authors:
V. Roungos, C.G. Aneziris
E-mail: vasileios.roungos@ikgb.tu-freiberg.de
aneziris@ikgb.tu-freiberg.de

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Tab. 1 Investigated Al_2O_3-C composition for both pressing routes

Raw materials	Composition [mass-%]	
	SBS	SBS–G
Al_2O_3	59,0	57,0
Graphite	25,0	23,0
Si	4,0	4,0
SiO_2	4,0	4,0
$Na_2B_4O_7$	2,0	2,0
Novolac resin	6,0	10,0
Hardener	0,6	1,0

tion [10]. The glazes for carbon bonded refractories need to fulfil many requirements. Having a very broad softening temperature range (between 500 – 1500 °C in the best situation), a slightly higher thermal expansion coefficient than the carbon bonded refractory substrate and a good adhesion to it, presenting no point defects like pinholes and being not permeable are the most important ones.

However, carbon bonded refractories without the need of an external glaze are not known or have not been established yet. The benefits from developing self glazing carbon bonded refractories would be many. First of all, the overall material costs for the production of these refractories would be reduced significantly. Moreover, the significant investment costs required for the glazing process could be avoided.

The monobloc stopper Al_2O_3-C refractories are widely used in steel casting applications. One of their common failure reasons during service life is their poor performance against oxidation, originating from cracks and point defects of the glaze, and leading to the deterioration of the refractory microstructure, and thus its properties. A self glaze formation would be advantageous in this case. The refractory body would act as a "smart refractory" by forming a self glaze and sealing the pores, performing a self healing process [3]. On the other hand, the use of low melting components in the refractory composition could deteriorate its high temperature properties, like hot modulus of rupture. As a consequence, care must be always taken when selecting these additives, especially after considering the severe application conditions of the monobloc stoppers.

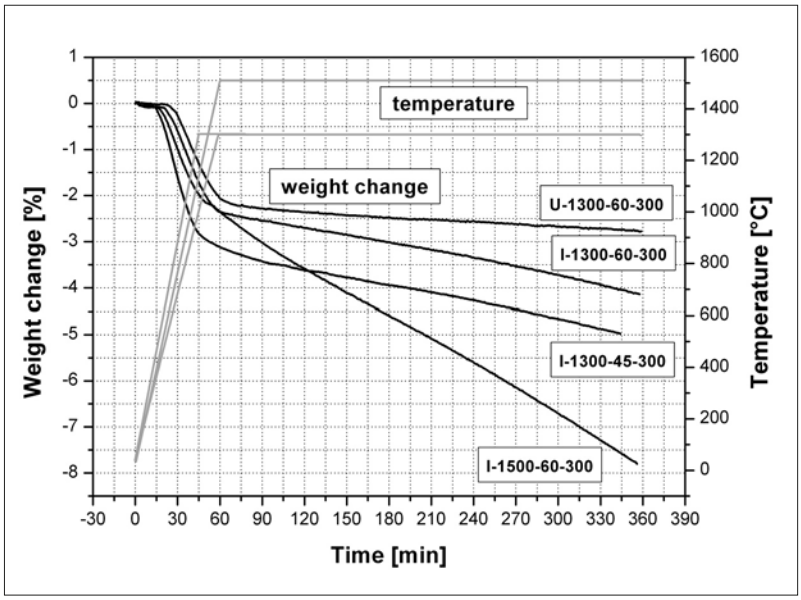

Fig. 1 Weight loss of the samples at different heating rates

2 Experimental

The investigated self glazing Al_2O_3-C composition is presented in Tab. 1. The selection of this composition is based on previous studies described elsewhere [11, 12]. The investigated samples in these studies were produced by uniaxial pressing. In their industrial production, monobloc stoppers are shaped with the use of the cold isostatic pressing (CIP) technology, due to their high length/diameter ratio and their high graphite content. The use of the above technology requires a production of a granulated material, which exhibits free flowing properties and allows the easy and homogeneous filling of the rubber moulds. Thus, a higher amount of binder is needed for the granulation. As a consequence, the finished product has differentiated properties (open porosity, porous structure and bulk density) compared to the uniaxial pressing route. For all the above reasons, both processing routes were used for the production of the Al_2O_3-C refractories.

Commercial grades of alumina and graphite were used for the preparation of the Al_2O_3-C samples. The alumina grades used were a fused alumina fine grade (99,70 mass-% Al_2O_3, 0,16 mass-% Na_2O) and a tabular alumina coarse grade (99,50 mass-% Al_2O_3, max. 0,40 mass-% Na_2O) with a maximal grain size of 0,60 mm. The natural graphite grades used were a finely ground natural graphite (96 – 97 mass-% carbon content) with 99,5 mass-% passing through 40 µm, and a normal flake graphite (94 – 96 mass-% carbon content) with 95,0 mass-% having a diameter higher than 71 µm. The binder used was a novolac type phenolic resin. Hexamethylenetetramine was used as hardener. All additives had a high purity and 99,5 mass-% of the grains were passing through 200 µm. The used additives on the investigated composition (Tab. 1) were metallic Si, SiO_2 and $Na_2B_4O_7$ (Borax).

All the raw materials and additives were mixed at room temperature in an Eirich intensive mixer following the standard commercial practice. After mixing, cylindrical samples (diameter of 50 mm, height of 45 mm) and bar samples (25 mm x 25 mm x 150 mm) were pressed with both shaping routes at 100 MPa. The pressed samples were cured at 180 °C and coked at 1400 °C (soaking time: 5 h) under reducing conditions. The

selection of the high coking temperature is affiliated with the in-situ formation of SiC structures, believed to play a key role for the performance of the self glazing Al_2O_3-C refractories [12].

The evaluation of the self glaze formation was performed with the use of oxidation tests. The cylindrical samples were placed in a special equipped furnace (LHT 04/16, Nabertherm), where both the weight of the samples and the temperature were registered as a function of time. The oxidation tests were carried out in air atmosphere at the temperatures of 1300 °C and 1500 °C with various heating rates and a soaking time of 5 h.

The phase compositions and the microstructure of the samples after the oxidation tests were evaluated with the aid of X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The mechanical and thermo-mechanical properties at bar samples after the oxidation tests at 1300 °C for 5 h were determined according to EN 993-6 for cold modulus of rupture (CMOR), EN 993-7 for hot modulus of rupture (HMOR) and ENV 993-11 for thermal shock resistance (with compressed air). The HMOR was measured at 1400 °C, with a previous soaking time of 30 min at this temperature for all tested samples. The residual CMOR was determined after the third thermal shock as well. The registered strength loss due to thermal shock provides important information about the thermo-mechanical performance of the self glazing refractory.

Furthermore, a severe dynamic corrosion test (finger test) was carried out at a self glazed Al_2O_3-C bar specimen: a refractory crucible was filled with 3 kg of a structural steel (grade: S235JR+AR) and placed into the special equipped furnace under the bar sample, which was fixed via corundum tube to the rotating mechanism of the furnace. After heating at 1600 °C in 4 h and soaking for 30 min, the bar sample was rotated with 24 rpm and dipped into the molten steel. The specimen was pulled out 10 min later and held at the ambient air of the furnace for another 10 min. The process of dipping and pulling out the bar sample was repeated twice and afterwards the furnace was cooled down to room temperature. Finally, X-ray micro-computed tomography investigations (CT ALPHA, ProCon X-ray) were carried out for the evaluation of the performance of the self glazed Al_2O_3-C bar specimen during the corrosion test.

3 Results and discussion

The weight loss of the samples, expressed in per cent, has been used for the evaluation of the oxidation resistance. Fig. 1 shows the results of the oxidation tests of cylindrical samples depending on their heat treatment. The heat treatment is based on the investigations presented in [12]. The weight change of the samples (left y-axis) and the temperature (right y-axis) are correlated as a function of time. About the nomenclature of the tested samples: the letters U and I provide information about the processing route (uniaxial or isostatic). The following three numbers give the maximum temperature (1300 °C or 1500 °C), the time in minutes till it was reached (45 or 60 min) and the soaking time, which was kept constant at 5 h for all oxidation tests.

Looking at the curves it can be readily seen that the major weight loss occurs in the temperature range between 600 °C and 1300 °C. The oxidation rate considerably decreases at around 1300 °C due to the formation of the self glaze. After that point, however, the weight loss of the samples is proceeding, with the oxidation rate highly depended on the extent and the permeability of the self glaze formation. The direct comparison between the uniaxial- and the isostatic-pressed sample, both heat treated at 1300 °C in 60 min (1300 – 60 – 300) reveals the significant difference in the microstructure of these two samples, originating from the different pressing routes. The higher amount of binder used in the isostatic pressing route ends up to higher porosity and lower density than the uniaxial route. This was also revealed by mercury porosimetry measurements. The sample from the uniaxial route had a weight loss of only 2,8 %, while the sample from the isostatic route exhibited a weight loss of 4,1 %. Regarding the above, an effort was made to improve the oxidation resistance of the isostatic pressed samples, by modifying the heat treatment. However, neither increasing the heating rate, nor increasing the maximum temperature brought any improvements.

Based on the above results, it was decided to use only the uniaxial pressed samples for the further investigations. As for the isostatic pressing route, it is obvious that the porosity generated by the binder content needs to be decreased. This could be realized by reducing the graphite content with a coeval addition of nanoscaled additives, and without influencing the thermo-mechanical performance of the Al_2O_3-C refractory. Another possibility would be the removal of the air prior to cold isostatic pressing, or pressing at higher pressures, in order to achieve a higher density of the refractory body.

The phase compositions of the samples after the oxidation tests, identified by X-ray dif-

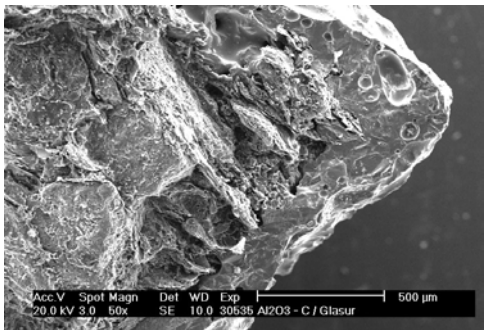

Fig. 2 SEM micrograph of the self glaze formation in cross section

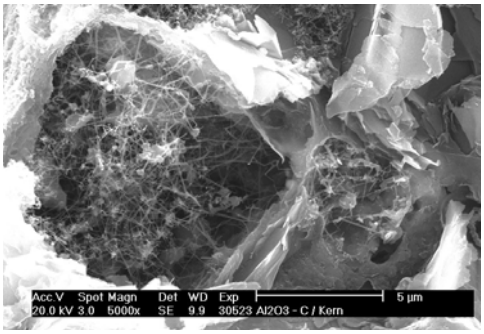

Fig. 3 SEM micrograph of the in situ formation of a dense SiC whisker network

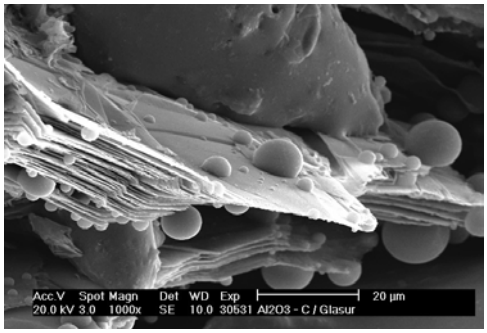

Fig. 4 SEM micrograph of the interface between carbon layer and self glaze after the oxidation test at 1300 °C for 5 h

Tab. 2 Mechanical and thermo-mechanical properties of the uniaxial pressed samples after oxidation tests at 1300 °C for 5 h (heat treatment: 1300–60–300)

CMOR [N/mm²]	HMOR [N/mm²]	CMOR after 3 thermal shocks [N/mm²]	Strength loss [%]
14,4 ± 1,6	11,7 ± 0,7	13,8 ± 0,9	4,2

fraction (XRD), came to good agreement with the results presented in [11] and [12]. The investigated samples were taken from both layers i.e. the self glaze layer and the carbon layer. The crystalline phases present in the self glaze layer were corundum, mullite and an aluminium borate phase ($Al_4B_2O_9$), complying with the investigations presented in [13]. This self glaze could be considered rather dense, had a thickness of a few hundred micrometer and presented a good adhesion to the carbon bonded substrate (Fig. 2). As for the carbon layer, the identified phases were corundum, graphite, traces of free silicon and two modifications of SiC, a cubic and a trigonal one. The in situ formation of a dense SiC whisker network is shown in Fig. 3. These whiskers had a diameter of 20 – 30 nm and were several micrometer long.

The self glaze microstructure was investigated via scanning electron microscopy, supported by energy dispersive X-ray spectroscopy (SEM-EDS). The general mechanism of the self glaze formation is pointed out in Fig. 4. Numerous boron containing spheres, presumably sodium tetraborate, are in contact with graphite flakes in the interface between self glaze and carbon layer. As soon as carbon starts to burn out at the outer surface, new pores i.e. new surfaces are being generated, permitting the further oxygen diffusion. The highly reactive sodium tetraborate is melting at around 880 °C and forms with the components of Al_2O_3 and SiO_2 (either as raw material or after oxidation of metallic silicon) a highly viscous glass at the outer surface of the Al_2O_3-C refractory.

The results of the mechanical and thermo-mechanical properties of the uniaxial pressed samples after oxidation tests at 1300 °C for 5 h are shown in Tab. 2. These samples had overall very high strength values, both at room temperature as well as at 1400 °C. Moreover, they presented a negligible low strength loss even after 3 thermal shocks.

The useful tool of X-ray micro-computed tomography (Fig. 5) enabled the non-destructive three-dimensional characterization of the self glazed bar sample after the corrosion test. The homogeneous structure of the tested specimen can be readily seen. Differences regarding the self glaze formation on the outer surface of the sample can be observed as well. Thus, a clear distinction between areas with a rather dense self glaze and areas with a less dense self glaze can be made (for example areas 1 and 2, respectively). The dark colour in the latter areas is suggesting the existence of pores. Interesting information is also given by the distribution of the in-situ formed SiC structures shown in area 3 (Fig. 5), which have a grain size of up to 2 mm. The performance of the self glazed specimen during the corrosion test can be regarded overall as positive. Of course, further efforts shall be made concerning the improvement of the refractoriness of the self glazing Al_2O_3-C refractories, by adding for instance zirconia into the composition.

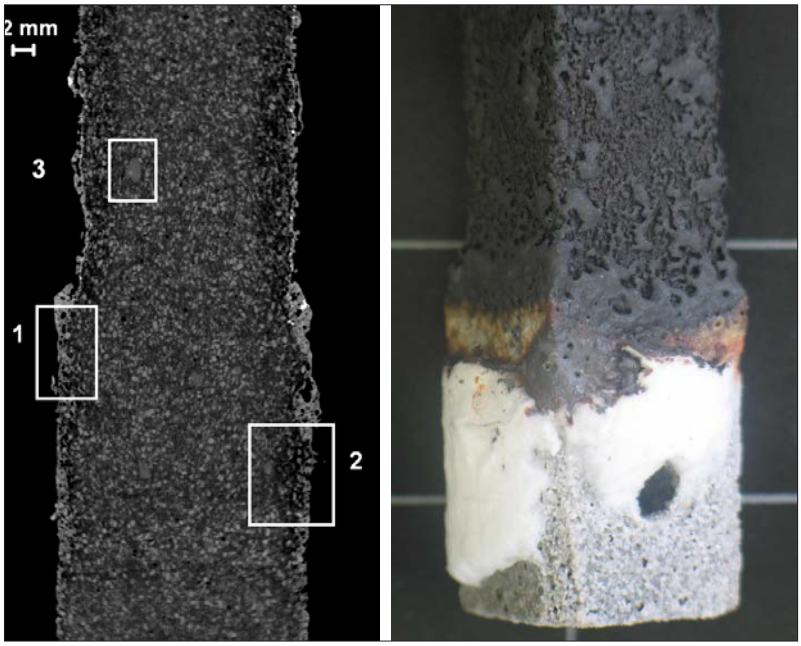

Fig. 5 X-ray micro-computed tomography image (left) and digital picture (right) of a self glazed Al_2O_3-C bar sample after a dynamic corrosion test (finger test)

4 Conclusions

The present work investigated the prospects of developing self glazing Al_2O_3-C refractories for monobloc stopper applications. The investigated samples were produced with both the uniaxial and the cold isostatic pressing route. The oxidation tests revealed that the critical temperature range affecting the self glaze formation was 600 – 1300 °C. Moreover, a clear correlation between the pressing route and the effectiveness of the self glaze formation at the outer surface of the refractory could be observed. The reason for the poor oxidation resistance of the samples obtained via the isostatic pressing technology lies on the binder content, and consequently its microstructure. Further investigations are needed here in order to further improve the oxidation resistance of these refractories. Nevertheless, a complete, homogeneous and relatively dense self glaze formation was achieved at the uniaxial pressed samples.

The identified crystalline phases of the highly viscous aluminium boron silicate glass formation (self glaze) were corundum, mullite and a modification of aluminium borate. Moreover, the in situ formation of various SiC polytypes is giving an indication of the complexity of the system under a kinetic point of view.

The uniaxial pressed samples exhibited very high CMOR and HMOR values after oxidation tests at 1300 °C for 5 h, while the

strength loss after 3 thermal shocks in compressed air was negligible low.

Finally, the performance of the self glazed Al_2O_3-C bar sample during the dynamic corrosion test was regarded as positive. However, further modifications in order to improve the refractoriness of the self glazing Al_2O_3-C refractories shall be certainly made.

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